



# CHEMISTRY

## STUDENT TEXTBOOK

### GRADE 11

1	1.01																	2	4.003																
H	Hydrogen																	He	Helium																
3	6.94	4	9.01															10	20.18																
Li	Lithium	Be	Beryllium															Ne	Neon																
11	22.99	12	24.31															18	39.95																
Na	Sodium	Mg	Magnesium															Ar	Argon																
19	39.10	20	40.08	21	44.96	22	47.90	23	50.94	24	51.996	25	54.94	26	55.85	27	58.93	28	58.70	29	63.55	30	65.37	31	69.72	32	72.59	33	74.92	34	78.96	35	79.90	36	83.80
K	Potassium	Ca	Calcium	Sc	Scandium	Ti	Titanium	V	Vanadium	Cr	Chromium	Mn	Manganese	Fe	Iron	Co	Cobalt	Ni	Nickel	Cu	Copper	Zn	Zinc	Ga	Gallium	Ge	Germanium	As	Arsenic	Se	Selenium	Br	Bromine	Kr	Krypton
37	85.47	38	87.62	39	88.91	40	91.22	41	92.91	42	95.94	43	(98)	44	(101.07)	45	102.91	46	106.40	47	107.87	48	112.41	49	114.82	50	118.69	51	121.75	52	127.60	53	126.90	54	131.30
Rb	Rubidium	Sr	Strontium	Y	Yttrium	Zr	Zirconium	Nb	Niobium	Mo	Molybdenum	Tc	Technetium	Ru	Ruthenium	Rh	Rhodium	Pd	Palladium	Ag	Silver	Cd	Cadmium	In	Indium	Sn	Tin	Sb	Antimony	Te	Tellurium	I	Iodine	Xe	Xenon
55	132.91	56	137.33	57	138.91	72	178.49	73	180.95	74	183.85	75	(186.2)	76	190.20	77	192.22	78	195.09	79	196.97	80	200.59	81	204.37	82	207.19	83	208.98	84	(209)	85	(210)	86	(222)
Cs	Cesium	Ba	Barium	La	Lanthanum	Hf	Hafnium	Ta	Tantalum	W	Tungsten	Re	Rhenium	Os	Osmium	Ir	Iridium	Pt	Platinum	Au	Gold	Hg	Mercury	Tl	Thallium	Pb	Lead	Bi	Bismuth	Po	Polonium	At	Astatine	Rn	Radon
87	(223)	88	226.03	89	227.03	104	(261)	105	(262)	106	(266)	107	(262)	108	(255)	109	(266)	110	(271)	111	(272)	112	(277)	(113)	(114)	(115)	116	(289)	(117)	(118)	(293)				
Fr	Francium	Ra	Radium	Ac	Actinium	Rf	Rutherfordium	Db	Dubnium	Sg	Seaborgium	Bh	Berkelium	Hs	Hassium	Mt	Moscovium																		

58	140.12	59	140.91	60	144.24	61	(145)	62	150.4	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.04	71	174.97
Ce	Cerium	Pr	Praseodymium	Nd	Niodymium	Pm	Promethium	Sm	Samarium	Eu	Europium	Gd	Gadolinium	Tb	Terbium	Dy	Dysprosium	Ho	Holmium	Er	Erbium	Tm	Thulium	Yb	Lutetium	Lu	Lutetium
90	232.04	91	231.04	92	238.03	93	(237.04)	94	(244)	95	(243)	96	(247)	97	(247)	98	(251)	99	(252)	100	(257)	101	(258)	102	(259)	103	(262)
Th	Thorium	Pa	Protactinium	U	Uranium	Np	Neptunium	Pu	Plutonium	Am	Americium	Cm	Curium	Bk	Berkelium	Cf	Californium	Es	Einsteinium	Fm	Fermium	Md	Mendelevium	No	Nobelium	Lr	Lanthanum

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CHEMISTRY STUDENT TEXTBOOK GRADE 11

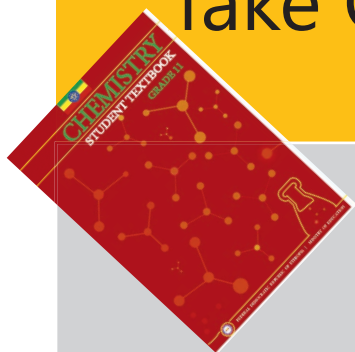
# CHEMISTRY

## STUDENT TEXTBOOK

### GRADE 11



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# CHEMISTRY

## TEXTBOOK

### GRADE 11

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## Foreword

Education and development are closely related endeavors. This is the main reason why it is said that education is the key instrument in Ethiopia's development and social transformation. The fast and globalized world we now live in requires new knowledge, skill and attitude on the part of each individual. It is with this objective in view that the curriculum, which is not only the Blueprint but also a reflection of a country's education system, must be responsive to changing conditions.

It has been almost three decades since Ethiopia launched and implemented new Education and Training Policy. Since the 1994 Education and Training Policy our country has recorded remarkable progress in terms of access, equity and relevance. Vigorous efforts also have been made, and continue to be made, to improve the quality of education.

To continue this progress, the Ministry of Education has developed a new General Education Curriculum Framework in 2021. The Framework covers all pre-primary, primary, Middle level and secondary level grades and subjects. It aims to reinforce the basic tenets and principles outlined in the Education and Training Policy, and provides guidance on the preparation of all subsequent curriculum materials – including this Teacher Guide and the Student Textbook that come with it – to be based on active-learning methods and a competency-based approach.

In the development of this new curriculum, recommendations of the education Road Map studies conducted in 2018 are used as milestones. The new curriculum materials balance the content with students' age, incorporate indigenous knowledge where necessary, use technology for learning and teaching, integrate vocational contents, incorporate the moral education as a subject and incorporate career and technical education as a subject in order to accommodate the diverse needs of learners.

Publication of a new framework, textbooks and teacher guides are by no means the sole solution to improving the quality of education in any country. Continued improvement calls for the efforts of all stakeholders. The teacher's role must become more flexible ranging from lecturer to motivator, guider and facilitator. To assist this, teachers have been given, and will continue to receive, training on the strategies suggested in the Framework and in this teacher guide.

Teachers are urged to read this Guide carefully and to support their students by putting into action the strategies and activities suggested in it.

For systemic reform and continuous improvement in the quality of curriculum materials, the Ministry of Education welcomes comments and suggestions which will enable us to undertake further review and refinement.

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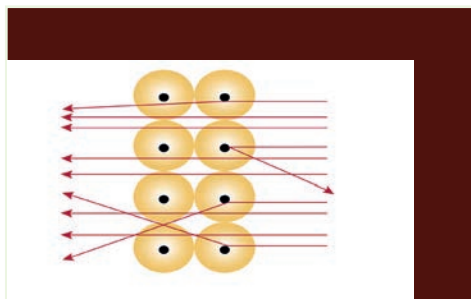
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# UNIT 1



## ATOMIC STRUCTURE AND PERIODIC PROPERTIES OF THE ELEMENTS

### Unit Outcomes

*At the end of this unit, you will be able to:*

- ☞ discuss the historical development of atomic structure*
- ☞ explain the experimental observations and inferences made by some famous scientists to characterize the atom*
- ☞ list the subatomic particles*
- ☞ identify atomic mass and isotope terms*
- ☞ explain electromagnetic radiation, atomic spectra and Bohr models of the atom*
- ☞ compute the calculations involving atomic structure*
- ☞ describe the quantum mechanical model of the atom and the related postulates and principles*
- ☞ demonstrate periodic law and how electronic configurations of atoms are related to the orbital diagrams and can explain periodic trends*
- ☞ describe scientific enquiry skills along this unit: inferring, predicting, classifying, comparing and contrasting, communicating, asking questions and making generalizations.*




## Start-up Activity

Discuss the following questions in groups, and present your ideas to the whole class.

- What are the basic building blocks of the following substances?
  - water
  - chalk
  - sugar
  - table salt
 Are the basic building blocks of these substances the same or different?
- Why do different materials show different properties? For example, materials such as woods can burn; an iron nail can rust; table salt dissolves in water, etc.

## 1.1 Introduction

*At the end of this section, you will be able to:*

-  compare the views of different philosophers on the nature of matter.

In Grade 9, you learned about the historical development of the atomic theories of matter. In this unit, we will briefly revise it and discuss in detail about early experiments to characterize an atom, the atomic spectra, different models of an atom, etc.



### Activity 1.1

Form a group and discuss the following questions, then present your views to the whole class.

- How do the beliefs about the structure of matter evolve?
- Describe the early developments leading to the modern concept of the atom.
- Can we see atoms with our naked eyes?

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? Although most philosophers, including **Plato** and **Aristotle**, believed that matter is continuous, **Democritus** disagreed.

The Greek philosopher **Democritus** (460–370 BC) suggested that if you divided matter into smaller and smaller pieces, you would eventually end up with tiny, indestructible particles called **atomos**, or “**atoms**”, meaning “indivisible”.

His ideas were based on philosophical speculation rather than experimental evidence. The ideas of **Democritus** were not widely accepted until 1808. After nearly 2000 years, **John Dalton**, developed an atomic theory that had gained broad acceptance.

### 1.2 Dalton's Atomic Theory and the Modern Atomic Theory

*At the end of this section, you will be able to:*

- ☞ state postulates of Dalton's atomic theory*
- ☞ state postulates of the modern atomic theory*
- ☞ state the laws of conservation of mass, definite proportions, multiple proportions and the basis of each of these laws*
- ☞ use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions*
- ☞ evaluate postulates of Dalton's and the modern atomic theories.*

#### 1.2.1 Postulates of Dalton's Atomic Theory



#### Activity 1.2

Recall your Grade 9 knowledge in order to answer the following questions in groups, and share your responses with the whole class.

1. Describe the five postulates of Dalton's atomic theory.
2. How do the scientific ideas develop based on previous scientific findings?

Scientific laws usually develop based on previous scientific findings. The laws that are the basis for Dalton's atomic theory are the law of conservation of mass and the law of definite proportions.

What is the law that Dalton formulated based on the law of conservation of mass and the law of definite proportions? Write its statement in your notebook.



### Activity 1.3

In your Grade 9 chemistry lesson, you learned about the law of conservation of mass and the law of definite proportion. Form a group and discuss the following questions, then present your responses to the whole class.

1. The mass of a piece of wood before and after it is burnt to ashes is not the same. Does this show that mass is created or destroyed?
2. What would be the mass of products if the burning of wood was carried out in a closed container?
3. Sugar consists of C, H, and O atoms. When a certain amount of sugar is burned in a crucible, it changes from white sugar to black carbon. Where has the hydrogen and oxygen gone?

### Example 1.1

1. What mass of hydrogen and oxygen can be obtained from
  - a. 18.0 g of water
  - b. 1.00 g of water

#### Solutions:

Water is always 11.2% hydrogen and 88.8% oxygen by mass, so:

- a. mass of hydrogen in 18.0 g water =  $0.112 \times 18.0 \text{ g} = 2.02 \text{ g}$   
 mass of oxygen in 18.0 g water =  $0.888 \times 18.0 \text{ g} = 15.98 \text{ g}$ ; or  
 $= 18.0 \text{ g} - 2.02 \text{ g} = 15.98 \text{ g}$
- b. mass of hydrogen in 1.00 g water =  $0.112 \times 1.00 \text{ g} = 0.112 \text{ g}$   
 mass of oxygen in 1.0 g water =  $0.888 \times 1.0 \text{ g} = 0.888 \text{ g}$ ; or  
 $= 1.0 \text{ g} - 0.112 \text{ g} = 0.888 \text{ g}$

2. The following data were collected for several compounds of nitrogen and oxygen:

	Compound A	Compound B	Compound C
<b>Mass of nitrogen that combines with 1 g of oxygen</b>	1.750 g	0.8750 g	0.4375 g

Show how these data illustrate the law of multiple proportions.

**Solution:**

For the law of multiple proportions to hold, the ratios of the masses of nitrogen combining with 1 gram of oxygen in each pair of compounds should be small whole numbers.

We therefore compute the ratios as follows:

$$\frac{A}{C} = \frac{1.750}{0.4375} = \frac{4}{1} \qquad \frac{B}{C} = \frac{0.875}{0.4375} = \frac{2}{1} \qquad \frac{C}{C} = \frac{0.4375}{0.4375} = \frac{1}{1}$$

These results support the law of multiple proportions.

**Exercise 1.1**

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?

**1.2.2 Postulates of Modern Atomic Theory****Activity 1.4**

Remember what you have learned in Grade 9 and discuss the following questions in a group of three or four, then present your responses to the whole class.

1. Which of Dalton's postulates about atoms are inconsistent with later observations? Do these inconsistencies mean that Dalton was wrong?
2. Is Dalton's model still useful?

Most of the experiments conducted during the development of the modern atomic theory will be discussed in Sections 1.3-1.6. In this section, generalizations derived from the experiments are presented as postulates of the modern atomic theory. The 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.

**Exercise 1.2**

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?

**1.3 Early Experiments to Characterize the Atom**

*At the end of this section, you will be able to:*

- ☞ *discuss the discovery of the electron*
- ☞ *describe the properties of cathode rays*
- ☞ *define the terms: radioactivity, radioactive decay and radio-isotope*
- ☞ *describe the common types of radioactive emissions*
- ☞ *illustrate the alpha scattering experiment, and summarize and interpret the major contribution of experiments of Thomson, Millikan and Rutherford concerning atomic structure.*

**1.3.1 The Discovery of the Electron****Activity 1.5**

Think back to Grade 9 and reflect on the following questions in a group of four. Then, present your responses to the whole class.

- a. How were electrons discovered?
- b. Are cathode rays visible to the naked eye?





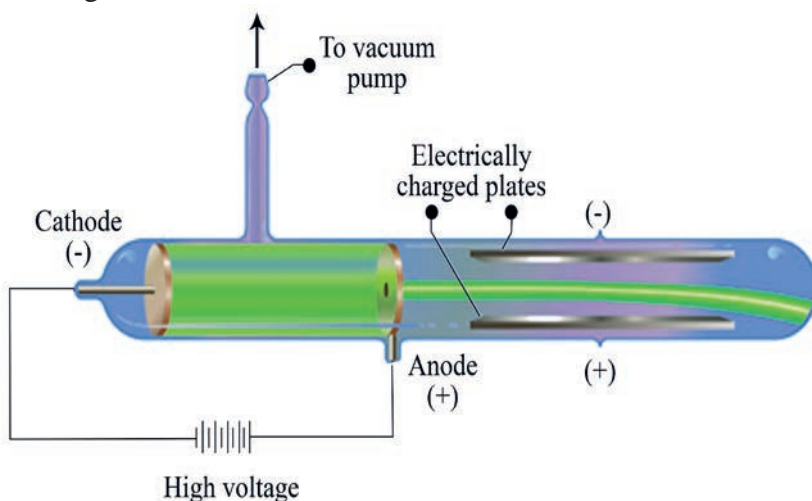
**Sir Joseph Thomson**

**Historical note:** J.J. Thomson (1856-1940) was a British physicist and Nobel laureate. Sir Joseph John Thomson was born near Manchester, England, and educated at Owens College (now part of Victoria University of Manchester) and Trinity College, University of Cambridge. At Cambridge he taught mathematics and physics, served as Cavendish Professor of Experimental Physics, and was (1918-40) master of Trinity College.

Thomson's work on cathode rays led to the discovery of the electron in 1897. His later work with positive ion beams led to a method of separating atoms and molecules by mass and the discovery of neon. Thomson was awarded the Nobel Prize in Physics in 1906 and was knighted in 1908.

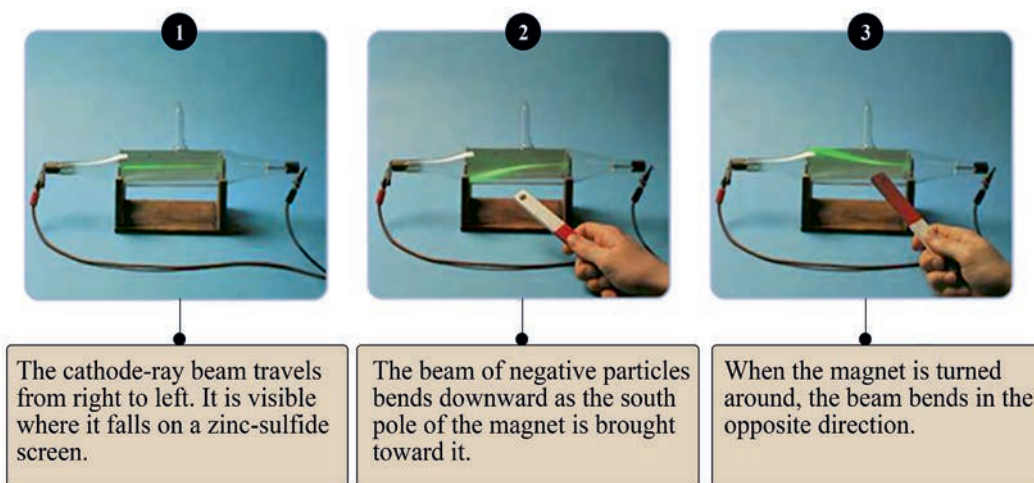
## Cathode Rays

One of the first experiments on subatomic particles was carried out by the English physicist **J.J. Thomson** in 1897. **Figure 1.1** shows an experimental apparatus similar to the one used by Thomson. 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 1.1: 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 (**Figure 1.1**). This beam bends away from the negatively charged plate and toward the positively charged plate. **What did Thomson conclude from this observation?** **Figure 1.2** shows a similar experiment, in which cathode rays are seen to bend when a magnet is brought toward them. **Thomson** showed that the characteristics of cathode rays are independent of the material making up the cathode. From such evidence, he concluded that a cathode ray consists of a beam of negatively charged particles (or **electrons**) and that electrons are constituents of all matter.



**Figure 1.2: 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,  $e$ . The number he came up with is  $-5.686 \times 10^{-12} \text{ kg C}^{-1}$  (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  $9.109 \times 10^{-31} \text{ kg}$ .

$$\begin{aligned} m_e &= \frac{m_e}{e} \times e = -5.686 \times 10^{-12} \text{ kg C}^{-1} \times -1.602 \times 10^{-19} \text{ C} \\ &= 9.109 \times 10^{-31} \text{ kg} \end{aligned}$$

## 1.3.2 Radioactivity and the Discovery of the Nucleus



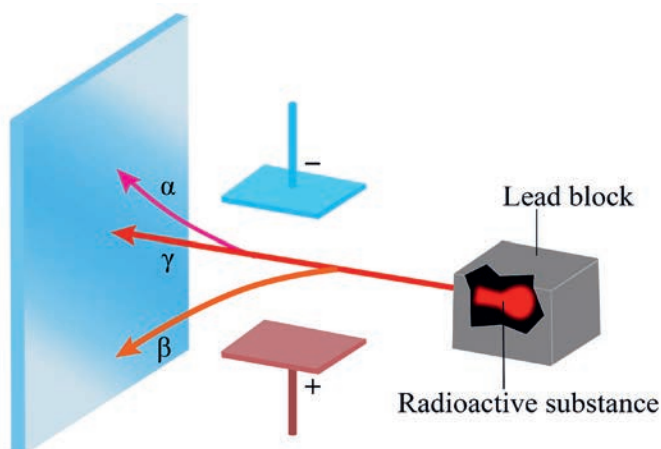
## Activity 1.6

Answer the following questions individually, then share your answers with the whole class.

1. Describe the properties of cathode rays.
2. Which rays are used to see whether bones are broken or not?

## Radioactivity

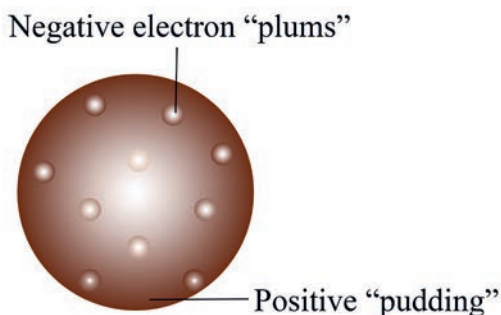
Radioactivity or radioactive decay is the spontaneous emission of particles and/or radiation from the unstable nuclei of certain atoms such as uranium, radium, etc. Does radioactivity support Dalton's idea of atoms? Shortly after the discovery of radioactivity, three types of rays were identified in the emissions from radioactive substances. Two are deflected by oppositely charged metal plates (**Figure 1.3**). Alpha ( $\alpha$ ) rays consist of positively charged particles, called  $\alpha$  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 ( $\beta$ ) rays, or  $\beta$  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 ( $\gamma$ ) rays. They have no charge and are not affected by an external electric or magnetic field.



**Figure 1.3: Three types of ray emitted by radioactive elements**

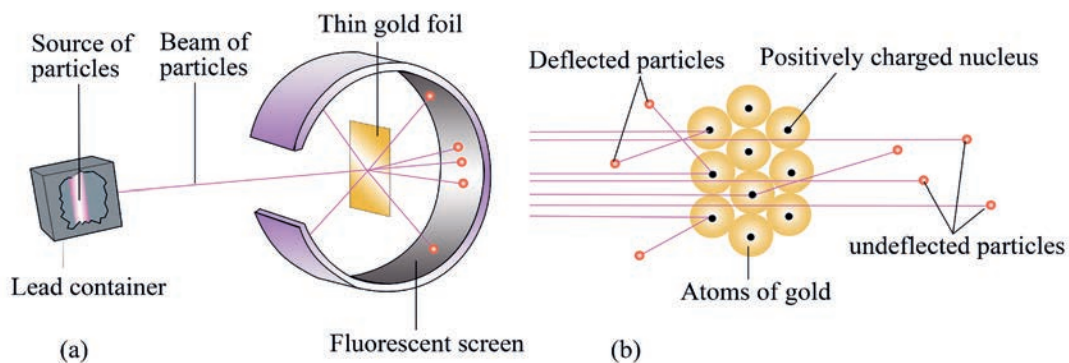
## The Discovery of the Nucleus

Thomson proposed a “plum-pudding” model (Figure 1.4) for the atom in which the electrons and protons were randomly distributed in a positively charged cloud like plums in a pudding.



**Figure 1.4: 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 aimed 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.



**Figure 1.5: (a)  $\alpha$ -particles aimed at a piece of gold foil, (b) Magnified view of  $\alpha$ -particles passing through and being deflected by nuclei**



### Activity 1.7

Form a group and discuss Rutherford's experiment as shown in **Figure 1.5 (a)** and **(b)** and answer the following questions:

1. Why did most of the  $\alpha$ -particles pass through the foil undeflected?
2. Why did only a small fraction of the  $\alpha$ -particles show a slight deflection?
3. Why didn't all  $\alpha$ -particles bounce at an angle of  $180^\circ$ ?
4. Based on the findings of Rutherford's experiment, what is your conclusion about an atom?
5. When Rutherford's co-workers bombarded gold foil with  $\alpha$ -particles, they obtained results that overturned the existing (Thomson) model of the atom. Explain. Report your responses to the whole class.

### 1.3.3 Discovery of the Neutron

The neutron was also 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.



### Activity 1.8

Discuss the following questions in groups, and present your responses to the whole class.

1. A sample of a radioactive element is found to be losing mass gradually. Explain what is happening to the sample.
2. Describe the experimental basis for believing that the nucleus occupies a very small fraction of the volume of the atom.

## 1.4 Make-up of the Nucleus

*At the end of this section, you will be able to:*

- ☞ describe the make-up of the nucleus
- ☞ define atomic mass
- ☞ define isotope, and calculate the relative atomic mass (atomic mass) of naturally occurring isotopic elements.

### 1.4.1 Subatomic Particles

In 1919, Rutherford discovered that hydrogen nuclei, or what 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** compares the relative masses and charges of the three subatomic particles (note that "amu" stands for "atomic mass unit", which is equal to  $\frac{1}{12}$  the mass of an atom of carbon-12).

Table 1.1: Properties of subatomic particles

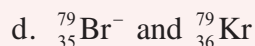
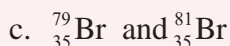
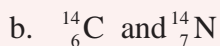
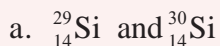
Particle	Actual mass (kg)	Relative mass (amu)	Actual charge (C)	Relative charge
<b>Proton (p)</b>	$1.672622 \times 10^{-27}$	1.007276	$1.602 \times 10^{-19}$	+1
<b>Neutron (n)</b>	$1.674927 \times 10^{-27}$	1.008665	0	0
<b>Electron (e<sup>-</sup>)</b>	$9.109383 \times 10^{-31}$	$5.485799 \times 10^{-4}$	$-1.602 \times 10^{-19}$	-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 total number of protons and neutrons in the nucleus of an atom is its **mass number (A)**. The mass number and atomic number of an element X are often written with the symbol,



### Activity 1.9

Based on your previous knowledge, write the similarities and differences between the pairs of atomic notations and present your responses to the whole class.



### 1.4.2 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. For example, all carbon atoms have six protons in the nucleus ( $Z = 6$ ) but only 98.89 % of naturally occurring carbon atoms have six neutrons in the nucleus ( $A = 12$ ). A small percentage (1.11 %) have seven neutrons in the nucleus ( $A = 13$ ), and even fewer (less than 0.01 %) have eight ( $A = 14$ ). Hence, carbon has three naturally occurring isotopes:  ${}^{12}\text{C}$ ,  ${}^{13}\text{C}$ , and  ${}^{14}\text{C}$ .

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:  $A = A_1 f_1 + A_2 f_2 + \dots + A_n f_n$ .

### Example 1.2

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

#### Solution:

Find the portion of the atomic mass from each isotope:

$$\begin{aligned} \text{Portion of atomic mass from } ^{107}\text{Ag} &= \text{isotopic mass} \times \text{fractional abundance} \\ &= 106.90509 \text{ amu} \times 0.5184 = 55.42 \text{ amu} \end{aligned}$$

$$\text{Portion of atomic mass from } ^{109}\text{Ag} = 108.90476 \text{ amu} \times 0.4816 = 52.45 \text{ amu}$$

Find the atomic mass of silver:

$$\text{Atomic mass of Ag} = 55.42 \text{ amu} + 52.45 \text{ amu} = 107.87 \text{ amu}$$

### Exercise 1.3

- How many protons and neutrons are in the nucleus of each of the following atoms?
  - $^{27}_{13}\text{Al}$
  - $^{32}_{16}\text{S}$
  - $^{64}_{30}\text{Zn}$
  - $^{207}_{82}\text{Pb}$
- 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.
- Naturally occurring boron consists of two isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ , 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
- 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?



## 1.5 Electromagnetic Radiation and Atomic Spectra

*At the end of this section, you will be able to:*

- ☞ characterize electromagnetic radiation (EMR) in terms of wavelength, frequency and speed*
- ☞ calculate the wavelength and frequency of EMR*
- ☞ explain the dual nature of light*
- ☞ describe emission spectra of atoms as consisting a series of lines*
- ☞ define a photon as a unit of light energy*
- ☞ distinguish how the photon theory explains the photoelectric effect*
- ☞ identify the relationship between a photon absorbed and an electron released*
- ☞ state Bohr's assumption of energy of the electron in an hydrogen atom*
- ☞ calculate the radius of electron orbit, the electron velocity and the energy of an electron using Bohr's model*
- ☞ explain that the line spectrum of hydrogen atom demonstrates the quantized nature of the energy of its electron*
- ☞ explain that atoms emit or absorb energy when they undergo transitions from one state to another*
- ☞ compose the limitations of Bohr's theory.*

### 1.5.1 Electromagnetic Radiation

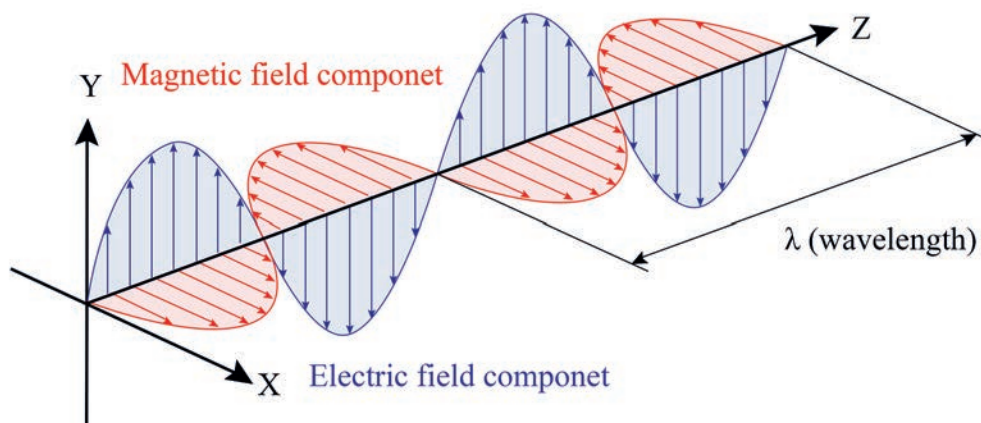


#### Activity 1.10

Form a group and discuss the following questions, then present your responses to the whole class.

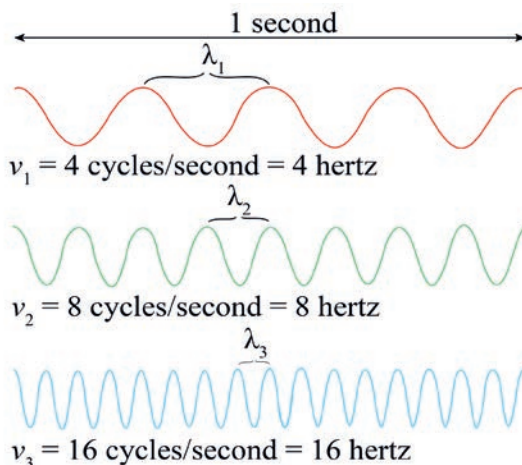
1. Explain how energy travels in space.
2. What is the importance of electromagnetic radiation (EMR) in chemistry?
3. What are the common features of different energy sources?

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 1.6: The electric field and magnetic field components of an electromagnetic waves**

Electromagnetic waves have three primary characteristics: **wavelength**, **frequency** and **speed**. **Wavelength** ( $\lambda$ , *Greek lambda*), is the distance the wave travels during one cycle (**Figure 1.7**). It is expressed in meters (m) and often, for very short wavelengths, in nanometers (nm), picometers (pm), or angstrom ( $\text{\AA}$ ). **Frequency** ( $\nu$ , *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).



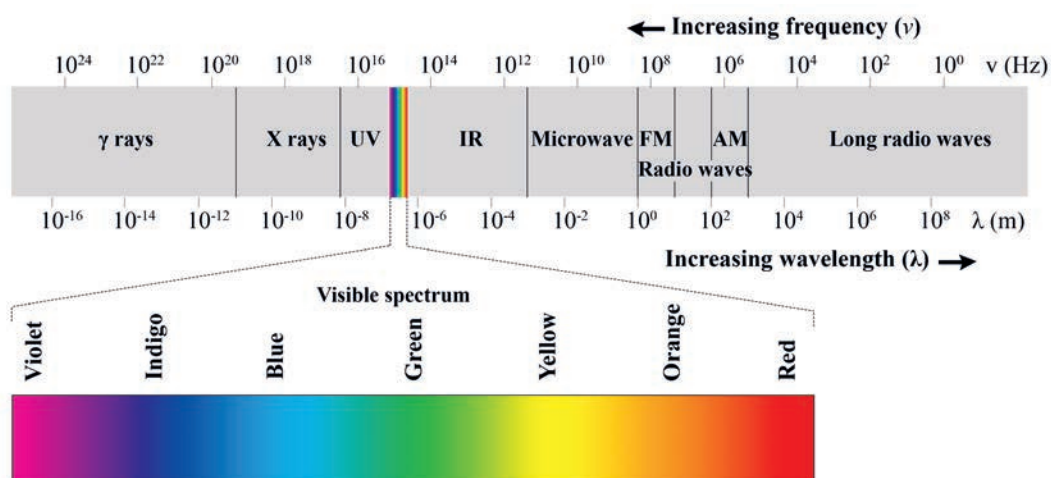
**Figure 1.7: Frequency of waves**

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:

$$c = v\lambda \quad (1.1)$$

In a vacuum, electromagnetic waves travel at  $3 \times 10^8$  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 ( $\lambda = 750$  nm) to violet ( $\lambda = 380$  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 1.8: The electromagnetic spectrum**

### Example 1.3

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**

$$\text{so, } \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{2.4 \times 10^6 \text{ s}^{-1}} = 125.0 \text{ m}$$

### Exercise 1.4

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?

## 1.5.2 The Quantum Theory and Photon

### Why are waves treated as particles?

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:

$$E = h\nu \quad (1.2)$$

Where  $h$  is called Planck’s constant and  $\nu$  is the frequency of radiation. The value of Planck’s constant is  $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ .

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

$$E = \frac{hc}{\lambda} \quad (1.3)$$

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**. Thus, energy seems to have particulate properties.

### Example 1.4

The blue color in fireworks is often achieved by heating copper (I) chloride (CuCl) to about 1200 °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 ( $\nu$ ) for this case can be calculated as follows:

$$\begin{aligned} \nu &= \frac{c}{\lambda} \\ &= \frac{3.0 \times 10^8 \text{ ms}^{-1}}{6.0 \times 10^{-7} \text{ m}} \\ &= 0.5 \times 10^{15} \text{ s}^{-1} \end{aligned}$$

$$\text{So, } E = h\nu$$

$$\begin{aligned} &= 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 0.50 \times 10^{15} \text{ s}^{-1} \\ &= 3.315 \times 10^{-19} \text{ J} = 3.32 \times 10^{-19} \text{ J} \end{aligned}$$

## 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**,  $\nu_0$ .

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:

$$E_o = h\nu_o \quad (1.4)$$

Where  $E_o$  is the minimum energy (of the photon), and  $\nu_o$ , 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  $\nu_o$  produces no electrons. On the other hand, if a light has  $\nu > \nu_o$ , the energy in excess of that required to remove the electron is given to the electron as kinetic energy (KE):

$$\text{KE}_e = \frac{1}{2} m\nu^2 = h\nu - h\nu_o \quad (1.5)$$

Where  $\text{KE}_e$  is the kinetic energy of an electron,  $m$  is mass of an electron,  $\nu$  is the velocity of an electron,  $h\nu$ , is the energy of an incident photon, and  $h\nu_o$  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  $\nu > \nu_o$  for the radiation). In his theory of relativity in 1905, Einstein derived the famous equation:

$$E = mc^2 \quad (1.6)$$

Rearranging this equation, we have

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

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

The main significance of **Equation 1.7** is that **energy has mass**. Using this equation, we can calculate the mass associated with a given quantity of energy or the *apparent* mass of a photon. For electromagnetic radiation of wavelength,  $\lambda$ , the energy of each photon is given by the expression:

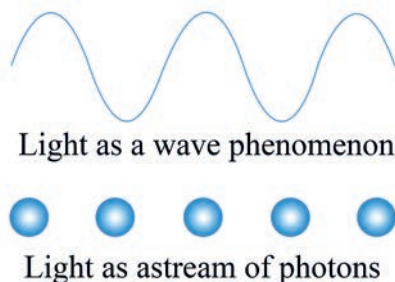
$$E_{\text{photon}} = \frac{hc}{\lambda} \quad (1.8)$$

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

$$m = \frac{E}{c^2} = \frac{\left(\frac{hc}{\lambda}\right)}{c^2} = \frac{h}{c\lambda} \quad (1.9)$$

We can summarize the important conclusions from the work of Planck and Einstein as follows:

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 1.9**.



**Figure 1.9: The dual nature of light**

### Example 1.5

- Compare the wavelength for an electron (mass =  $9.11 \times 10^{-31}$  kg) traveling at a speed of  $1.00 \times 10^7$  m/s with that for a ball (mass = 0.10 kg) traveling at 35 m/s.

#### Solution:

We use the equation  $m = h/c\lambda$ ,

Where  $h = 6.63 \times 10^{-34}$  J.s =  $6.63 \times 10^{-34}$  kg. m<sup>2</sup>.s Since 1 J = 1 kg. m<sup>2</sup>/s<sup>2</sup>

For the electron:

$$\begin{aligned} \lambda &= \frac{6.63 \times 10^{-34} \text{ kg.m}^2.\text{s}}{9.11 \times 10^{-31} \text{ kg} \times 1.00 \times 10^7 \text{ m/s}} \\ &= 7.28 \times 10^{-11} \text{ m} = 7.28 \text{ nm} \end{aligned}$$

For the ball:

$$\lambda = \frac{6.63 \times 10^{-34} \text{ kg.m}^2.\text{s}}{0.10 \text{ kg} \times 35 \text{ m/s}} = 1.89 \times 10^{-34} \text{ m} = 189 \times 10^{-25} \text{ nm}$$

2. The maximum kinetic energy of the photoelectrons emitted from a give metal is  $1.5 \times 10^{-20}$  J when a light that has a 750 nm wavelength shines on the surface. Determine the threshold frequency,  $\nu_0$ , for this metal. Calculate the corresponding wavelength,  $\lambda_0$ .

**Solution:**

- a) Determination of the threshold frequency,  $\nu_0$

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

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

Similarly, rearrange **Equation 1.5** and solve  $\nu_0$

$$\begin{aligned}\nu_0 &= \frac{h\nu - KE}{h} \\ &= \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s} \times 4.0 \times 10^{14} \text{ s}^{-1} - 1.5 \times 10^{-20} \text{ J}}{6.63 \times 10^{-34} \text{ J}\cdot\text{s}} \\ &= \frac{26.52 \times 10^{-20} \text{ J} - 1.5 \times 10^{-20} \text{ J}}{6.63 \times 10^{-34} \text{ J}\cdot\text{s}} = \frac{24.02 \times 10^{-20} \text{ J}}{6.63 \times 10^{-34} \text{ J}\cdot\text{s}} \\ &= 3.77 \times 10^{14} \text{ s}^{-1}\end{aligned}$$

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

- b) Calculate the corresponding wavelength  $\lambda_0$ :

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



## Exercise 1.5

- The following are representative wavelengths in the infrared, ultraviolet, and X-ray regions of the electromagnetic spectrum, respectively:  $1.0 \times 10^{-6}$  m,  $1.0 \times 10^{-8}$  m, and  $1.0 \times 10^{-10}$  m.
  - What is the energy of a photon of each radiation?
  - Which has the greatest amount of energy per photon?
  - Which has the least?
- A clean metal surface is irradiated with light of three different wavelengths  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ . The kinetic energies of the ejected electrons are as follows:  $\lambda_1$ :  $7.2 \times 10^{-20}$  J;  $\lambda_2$ : approximately zero;  $\lambda_3$ :  $5.8 \times 10^{-19}$  J. Which light has the shortest wavelength and which has the longest wavelength? Determine the threshold frequency,  $\nu_0$ , for this metal.
- The minimum energy required to cause the photoelectric effect in potassium metal is  $3.69 \times 10^{-19}$  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?

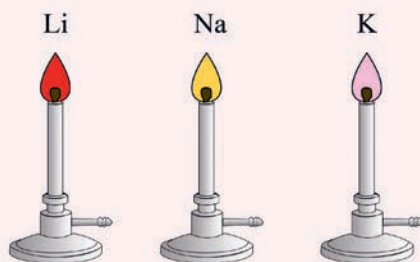
## 1.5.3 Atomic Spectra



## Activity 1.11

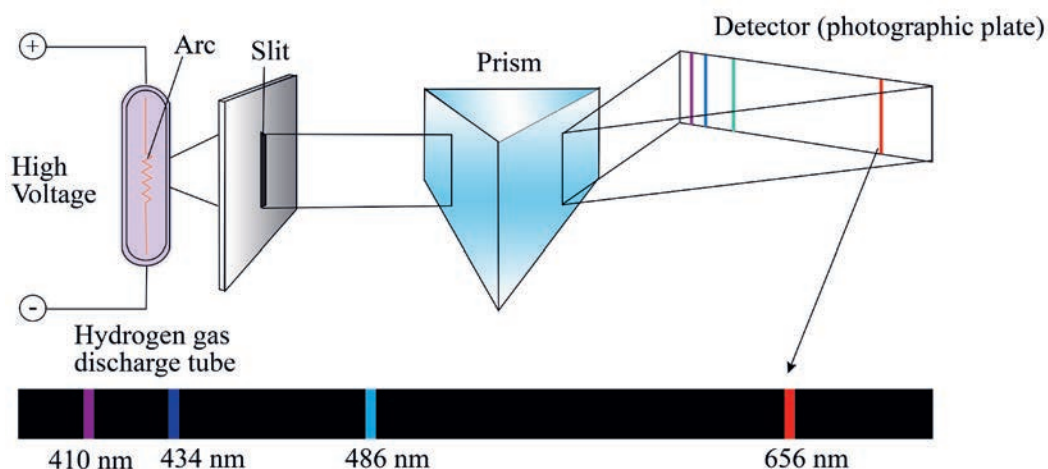
Discuss the following ideas in pairs and share with the rest of the class.

- Why do you observe different colors when you are watching fireworks?
- As it is shown in the **Figure 1.10**, when compounds of the alkali metals: lithium, sodium, and potassium are excited in the gas flames they give different colored flames. Why do they emit different colors?



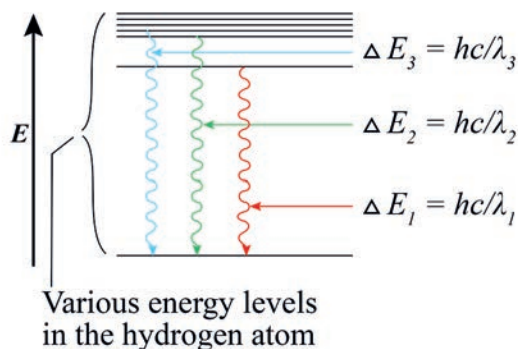
**Figure 1.10: Flame colors of lithium, sodium, and potassium compounds**

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 1.11**.



**Figure 1.11: 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 1.12**. 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 1.12: A change between two discrete energy levels emits a photon of light**

### 1.5.4 The Bohr Model of the Hydrogen Atom



#### Activity 1.12

Form a group and discuss the following questions. Share your ideas with the rest of the class.

The nature of the nucleus of the atom was explained by Rutherford. However, he was not able to explain the position and velocity of electrons in the atom.

1. Is it possible to know the exact location of an electron in the atom?  
Defend your suggestion.
2. Explain why an electron does not enter the nucleus, even though they are oppositely charged.

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:

1. The electron in an hydrogen atom travels around the nucleus in a circular orbit.
2. 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.
3. Only limited number of orbits with certain energies are allowed. This means, the orbits are quantized.
4. The only orbits that are allowed are those for which the angular momentum of the electron is an integral multiple of  $h/2\pi$ .
5. 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.
6. 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,  $h$ , 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):

$$E = \frac{1}{2}mv^2 + \frac{e^2}{r} \quad (1.10)$$

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:

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \quad (1.11)$$

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

$$mvr = \frac{nh}{2\pi} \quad (1.12)$$

Solving **Equation 1.12** for  $v$  gives:

$$v = \frac{nh}{2\pi mr} \quad (1.13)$$

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

$$r = \frac{n^2 h^2}{4\pi m e^2} = n^2 \left( \frac{h^2}{4\pi m e^2} \right) \quad (1.14)$$

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

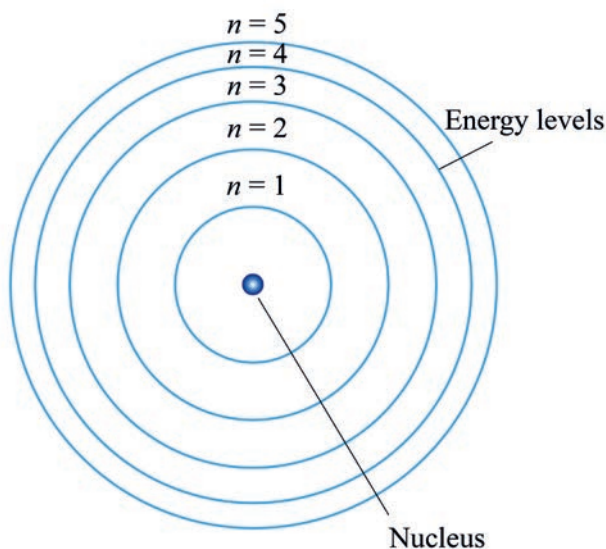
$$r = n^2 a_0 \quad (1.15)$$

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  $a_0$  is  $0.53 \text{ \AA}$ . 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 1.13: Bohr's energy levels of a hydrogen atom**

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

$$E_n = -\frac{R_H}{n^2} \quad (1.16)$$

Where  $R_H$ , the Rydberg constant for the hydrogen atom and has the value  $2.18 \times 10^{-18}$  J. Thus, **Equation 1.15** can be written as:

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

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),  $E_n$  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 1.6

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**:

$$\begin{aligned} v &= \frac{nh}{2\pi mr} \\ &= \frac{5(6.63 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})}{2 \times 3.14 \times 9.11 \times 10^{-31} \text{ kg} \times 1.524 \times 10^{-9} \text{ m}} \\ &= 3.8 \times 10^5 \text{ m/s} \end{aligned}$$

**Equation 1.16** is used to solve  $E_5$

$$E_5 = -\frac{2.18 \times 10^{-18} \text{ J}}{5^2} = 8.72 \times 10^{-20} \text{ J}$$

Calculate the energies of the hydrogen electron in  $n = 1$ ,  $n = 2$  and  $n = 3$

#### Solution: Using Equation 1.16:

$$\text{For } n = 1, E_1 = -\frac{2.18 \times 10^{-18} \text{ J}}{1^2} = -2.18 \times 10^{-18} \text{ J}$$

$$n = 2, E_2 = -\frac{2.18 \times 10^{-18} \text{ J}}{2^2} = -5.45 \times 10^{-19} \text{ J}$$

$$n = 3, E_3 = -\frac{2.18 \times 10^{-18} \text{ J}}{3^2} = -2.42 \times 10^{-19} \text{ J}$$

Bohr's model also quantitatively explained the line spectra of hydrogen atom. He proposed that the **absorptions and emissions** in line spectra correspond to the transfer of the electron from one orbit to another. Energy must be absorbed for the electron to move from one orbit to another one having a bigger radius. Whereas, energy is emitted when an electron moves from the higher orbital energy level,  $n_i$ , to the lower orbital,  $n_f$ , energy level. Thus, the change in energy,  $E$ , is the difference in the energy between the final and the initial state electron:

$$\Delta E = E_f - E_i \quad (1.17)$$

This equation is similar to:

$$\begin{aligned} \Delta E &= -R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \end{aligned} \quad (1.18)$$

Where  $n_i$  and  $n_f$  represent quantum numbers for initial and final states respectively.

But,  $\Delta E = h\nu$ , thus we have:

$$\Delta E = h\nu = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (1.19)$$

Notice that when  $n_f > n_i$ ,  $\Delta E$  is positive, indicating that the system has absorbed energy. But,  $n_i > n_f$ ,  $\Delta E$  is negative and this corresponds to emission of energy.

### Example 1.7

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:**

**Equation 1.19** is used, to determine the emitted energy:

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

To obtain  $\lambda$ , **Equation 1.19**:

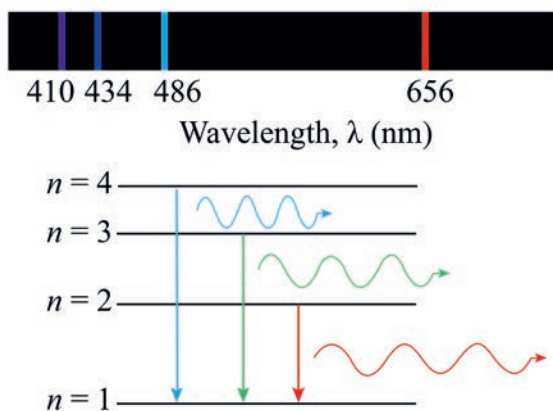
$$\begin{aligned} \Delta E &= h\nu = \frac{hc}{\lambda} \\ \text{Thus, } \frac{hc}{\Delta E} &= \frac{6.63 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \frac{\text{m}}{\text{s}}}{3.03 \times 10^{-19} \text{ J}} \\ &= 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm} \end{aligned}$$



## Exercise 1.6

1. 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?
2. Calculate the frequency of the green line arising from the electron moving from  $n = 4$  to  $n = 2$  in the visible spectrum of the hydrogen atom using Bohr's theory.

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 1.14: 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	$n_f$	$n_i$	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  $\nu$ , shorter  $\lambda$ ) of the emitted photon.

### Exercise 1.7

1. 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.
2. 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?

## 1.5.5 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<sup>+</sup> and Li<sup>2+</sup>. 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.

### 1.5.6 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 ( $E = hv = hc/\lambda$ ), de Broglie derived an equation for the wavelength of any particle of mass,  $m$ , whether a planet, ball, or electron-moving at speed,  $v$ .

$$\lambda = \frac{h}{mv} \quad (1.20)$$

According to this **Equation 1.20**, matter and energy show both wave and particulate properties. The distinction between a particle and a wave is only meaningful in the macroscopic world, it disappears at the atomic level. This dual character of matter and energy is known as the **wave-particle duality**.

#### Example 1.8

Calculate the de Broglie wavelength of an electron that has a velocity of  $1.00 \times 10^6$  m/s. (electron mass,  $m_e = 9.11 \times 10^{-31}$  kg;  $h = 6.63 \times 10^{-34}$  J.s).

**Solution:**

$$\lambda = \frac{h}{m_e v} = \frac{6.63 \times 10^{-34} \text{ kg} \frac{\text{m}^2}{\text{s}}}{1.00 \times 10^6 \frac{\text{m}}{\text{s}} \times 9.11 \times 10^{-31} \text{ kg}}$$

$$= 0.73 \times 10^{-9} \text{ m} = 0.728 \text{ nm}$$

What is the speed of an electron that has a de Broglie wavelength of 1.00 nm

**Solution:**

$$v = \frac{h}{m_e \lambda} = \frac{6.63 \times 10^{-34} \text{ kg} \frac{\text{m}^2}{\text{s}}}{1.00 \times 10^{-9} \text{ m} \times 9.11 \times 10^{-31} \text{ kg}}$$

$$= 0.728 \times 10^6 \frac{\text{m}}{\text{s}} = 7.28 \times 10^5 \frac{\text{m}}{\text{s}}$$

### Exercise 1.8

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

## 1.6 The Quantum Mechanical Model of the Atom

*At the end of this section, you will be able to:*

- ☞ *state Heisenberg's uncertainty principle*
- ☞ *describe the significance of electron probability distribution.*
- ☞ *explain the quantum numbers  $n$ ,  $l$ ,  $m_l$ ,  $m_s$*
- ☞ *write all possible sets of quantum numbers of electrons in an atom.*
- ☞ *describe the shapes of orbitals designated by  $s$ ,  $p$  and  $d$ .*



### Activity 1.13

Form a group and discuss the following questions, then present your responses to the rest of the class.

1. If particles have wavelike motion, why can't we observe its motion in the macroscopic world?
2. If electrons possess particle nature it should be possible to locate electrons. How can an electron be located?
3. Is there any wave associated with a moving elephant?

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.

Scientists have developed **quantum mechanics**, which presents a different view of how electrons are arranged about the nucleus in the atom. This view depends on two central concepts: the wave behavior of matter and the uncertainty principle. The combination of these two ideas leads to a mathematical description of electronic structure.

### 1.6.1 The Heisenberg's 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 1827, 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  $\Delta p$  is the uncertainty in the momentum and  $\Delta x$  is the uncertainty of the position of the electron, then:

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi} \quad \text{or} \quad (\Delta x) \Delta(mv) \geq \frac{h}{4\pi}$$

This equation shows that if we measure the momentum of a particle precisely (i.e., if  $\Delta p$  is very small), then the position will be correspondingly less precise (i.e.,  $\Delta x$  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 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 letter psi,  $\psi$ ). 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,  $\psi^2$ , 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 place in spaces. The fourth one is used to describe the spin (magnetic property) of the electrons that occupy the orbitals. The four quantum numbers are:

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 in which the orbital resides and it is analogous to the energy levels in Bohr’s model.
2. **The angular momentum quantum number ( $\ell$ )** 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  $\ell$  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  $n = 4$ ,  $\ell$  has values of 0, 1, 2, and 3. Each value of  $\ell$  corresponds to an orbital label and an orbital shape.

The following letters are usually used to denote the values of  $\ell$ :

Value of $\ell$	Corresponding subshell
0	s
1	p
2	d
3	f

### Example 1.9

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** ( $m_\ell$ ) is also called the **orbital-orientation quantum number**. It has integral values between  $-\ell$  and  $\ell$ , 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  $\ell$  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  $n$ ,  $\ell$ , 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 1.9

- What are the values of  $n$  and  $\ell$  for the following subshells?
  - 1s
  - 3p
  - 4s
  - 3d
  - 4f
- Write the subshell notations that correspond to
  - $n = 3$  and  $\ell = 0$
  - $n = 3$  and  $\ell = 1$
  - $n = 7$  and  $\ell = 0$
  - $n = 3$  and  $\ell = 2$

## Example 1.10

- What are the allowed values of the quantum numbers through  $n = 2$ ?

**Solution:** The allowed quantum number values in  $n = 2$  are:

$n$	$\ell$	$m_\ell$	$m_s$	Electron capacity of subshell $4\ell + 2$	Electron capacity of shell $2n^2$
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
2	1(2p)	-1, 0, 1	$\pm\frac{1}{2}$ for each value of $m_\ell$	6	8

- What values of the angular momentum quantum number ( $\ell$ ) 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  $\ell$  values:

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

Determining  $m_\ell$  for each  $\ell$  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



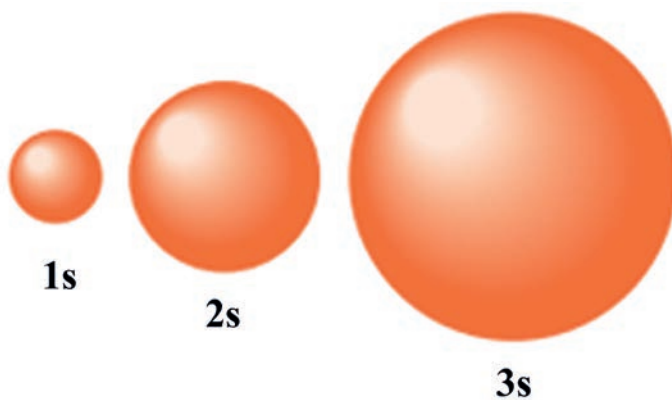
## Exercise 1.10

1. What are the allowed values of the quantum numbers through  $n = 4$ ?
2. Write an orbital designation corresponding to the quantum numbers:
  - a.  $n = 4, \ell = 2, m_\ell = 0$
  - b.  $n = 3, \ell = 1, m_\ell = 1$
  - c.  $n = 5, \ell = 1, m_\ell = -1$
  - d.  $n = 4, \ell = 3, m_\ell = -3$
3. What values  $\ell$  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)  $\ell$ ?
6. Which of the following orbitals do not exist: 1p, 2s, 2d, 3p, 3d, and 3f?

## 1.6.3 Shapes of Atomic Orbitals

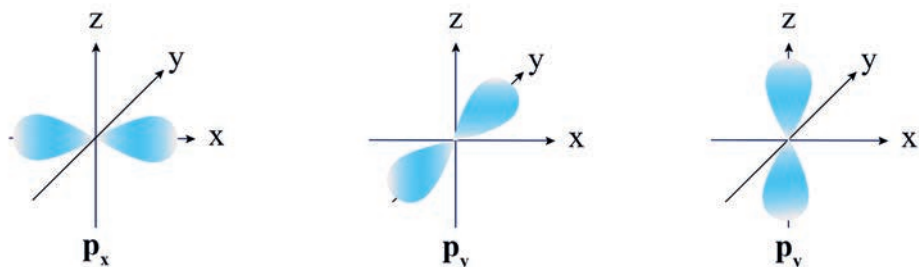
The three-dimensional aspects of the orientation of the atomic orbitals are usually represented by drawing a **boundary surface diagram** that encloses the highest probability (about 90%) of the total electron density in an orbital.

**Figure 1.15**, 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 1. 15: The three s-orbitals**

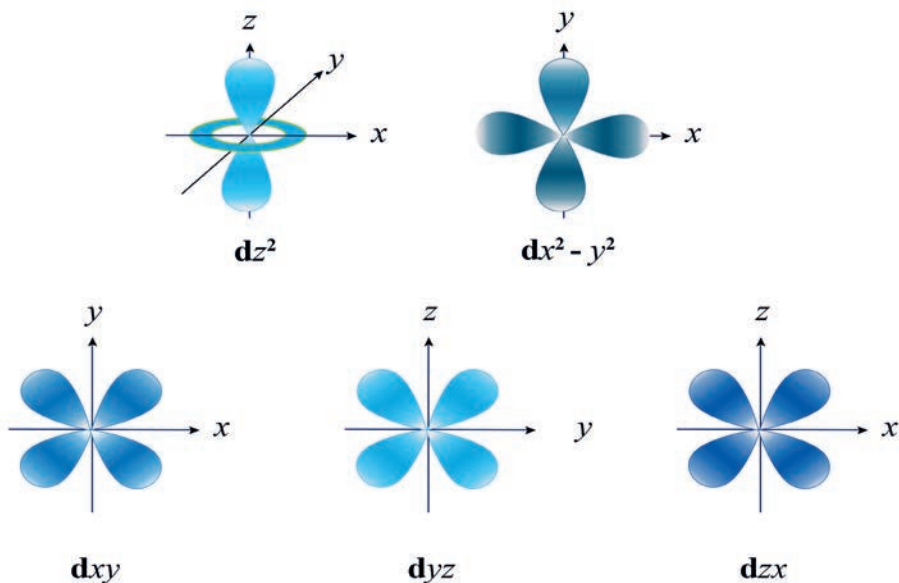
The p orbitals of any principal quantum number are arranged along three mutually perpendicular axes,  $x$ ,  $y$ , and  $z$ , so that the region of the highest electron density are in dumb bell-shaped boundary surface (**Figure 1.16**). The three p orbitals are designated as  $p_x$ ,  $p_y$  and  $p_z$ .



**Figure 1.16: 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  $2p_x$ ,  $2p_y$  and  $2p_z$ .

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 1.17** shows the different distribution of the five d atomic orbitals.







**Figure 1.17: 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 Electronic Configurations and Orbital Diagrams

*At the end of this section, you will be able to:*

-  explain the Aufbau Principle
-  explain Pauli's Exclusion Principle
-  explain Hund's Rule
-  write ground state electron configurations of multi-electron atoms.



### Activity 1.14

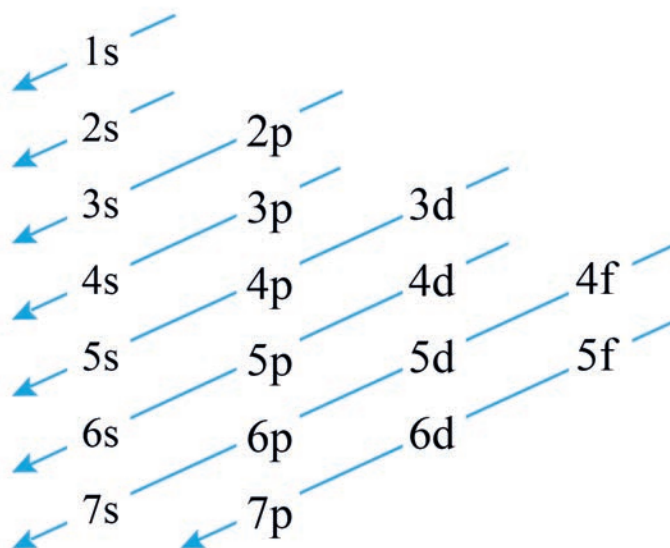
Form a group and discuss the given questions. Then, share your ideas with the rest of the class.

1. Why doesn't an atomic orbital hold more than two electrons?
2. Why do you think that electrons in an atom could not occupy the spaces between the main energy levels?

Several questions arise when you look carefully at the electron configuration of an atom. To answer these questions, it is necessary to know the basic principles governing the distribution of electrons among atomic orbitals. The electron configuration for any atom is governed by the following three principles:

#### 1. Aufbau (building up) Principle:

This is a scheme used to reproduce the electron configurations of the ground state of atoms by successively filling with electrons in a specific order (the building up order). 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, as indicated in **Figure 1.18**.



**Figure 1.18: The order of filling orbitals**

### 2. 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 ( $2p_x$ ,  $2p_y$  and  $2p_z$ ) will hold a single electron before any of them receives a second electron.

### 3. 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 Electronic Configuration of the Elements

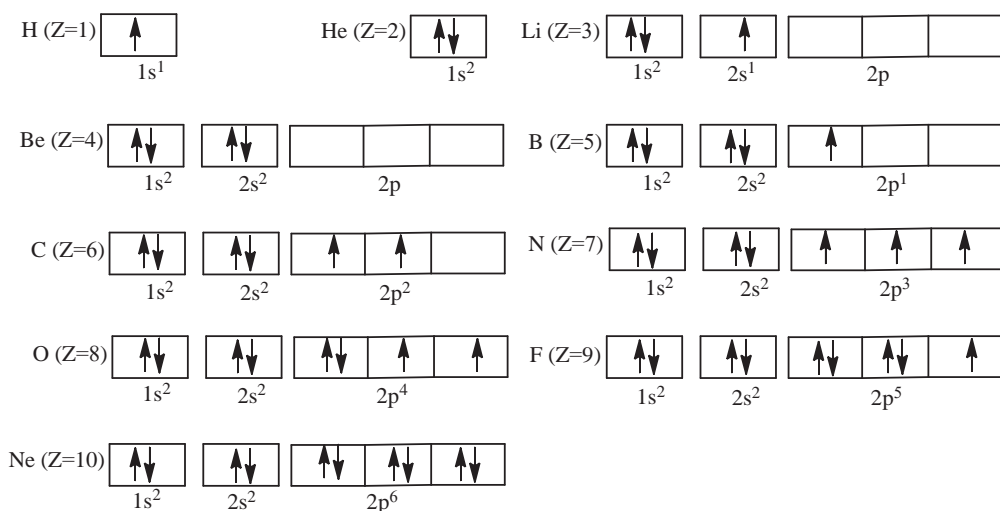
The electronic configuration of an atom describes the distribution of the electrons among atomic orbitals in the atom. Two general methods are used to denote electron configurations. The subshell (sublevel) notation uses numbers to designate the principal energy levels and the letters s, p, d and f to 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  $1s^1$ .



## Activity 1.15

Form a group and discuss the reason why the notation  $n\ell^e$  does not include electron spin quantum numbers. (Where  $n$ ,  $\ell$  and  $e$  are principal quantum number, azimuthal quantum number and number of electrons, respectively).

The other way to present this information is through an orbital diagram, which consists of a rectangular box (or circle, or just a line) for each orbital available in a given energy level, with an arrow indicating the electron's presence and its direction of spin. Traditionally,  $\uparrow$  represents,  $m_s = +\frac{1}{2}$  whereas  $\downarrow$  designates  $m_s = -\frac{1}{2}$ . The orbital diagrams for the first ten elements are:



The three orbitals in the 2p sublevel are degenerate (have equal energy) and have the same  $n$  and  $\ell$  values), thus, the fifth electron of boron can go into any one of the 2p orbitals. Since a  $p$  sublevel has  $\ell = 1$ , the  $m_\ell$  (orientation) values can be  $-1$ ,  $0$ , or  $+1$ . For convenience, the boxes are labeled from left to right,  $-1$ ,  $0$ ,  $+1$ , and assume it enters the  $m_\ell = -1$  orbital:  $n = 2$ ,  $\ell = 1$ ,  $m_\ell = -1$ , and  $m_s = +\frac{1}{2}$ .

The three 2p orbitals have equal energy, but they can be along the  $x$ ,  $y$ , or  $z$  axes.



### Activity 1.16

Discuss the following questions in groups, and share your ideas with the rest of the class.

1. What does each box in an orbital diagram represent?
2. What are the similarities and differences between a 1s and a 2s orbital?
3. What is the difference between a  $2p_x$  and a  $2p_y$  orbital?
4. What is the meaning of the symbol  $4d^6$ ?

### Exercise 1.11

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. $(3, 2, 1, 1)$	

For Li, the first 2 electrons occupy the 1s orbital, and the third electron must occupy the first orbital with  $n = 2$ , the 2s orbital. Thus, the electron configuration for Li is  $1s^2 2s^1$ . To avoid writing the inner-level electrons, this configuration is often abbreviated as  $[\text{He}] 2s^1$ , where  $[\text{He}]$  represents the electron configuration of He,  $1s^2$ . Similarly, Mg ( $Z = 12$ ), has the configuration  $1s^2 2s^2 2p^6 3s^2$ , or  $[\text{Ne}] 3s^2$ . Then the next six elements, *aluminium to argon*, have configurations obtained by filling the 3p orbitals one electron at a time. Table 1.3 shows the ground state electron configurations of some atoms.

Table 1.3: 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 $[\text{He}]2s^2$
O	8	$1s^2 2s^2 2p^4$ or $[\text{He}]2s^2 2p^4$
Ne	10	$1s^2 2s^2 2p^6$ or $[\text{He}]2s^2 2p^6$
Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$ or $[\text{Ne}] 3s^2 3p^5$
Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$ or $[\text{Ne}] 3s^2 3p^6$
Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or $[\text{Ar}] 4s^2$
Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ or $[\text{Ar}] 4s^2 3d^1$
Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ or $[\text{Ar}] 4s^1 3d^5$

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 electrons are the electrons in the  $2s$  and  $2p$  electrons. Valence electrons are the most important electrons to chemists since they are involved in bonding, as you will learn in the next chapter. 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)	$[\text{Ar}]4s^2 3d^4$	$[\text{Ar}]4s^1 3d^5$
Cu (Z = 29)	$[\text{Ar}]4s^2 3d^9$	$[\text{Ar}]4s^1 3d^{10}$

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.

Because there is little difference between the 4s and 3d orbital energies, expected and observed electron configurations are quite close in energy. At higher principal quantum numbers, the energy difference between certain subshell is even smaller than that between the 3d and 4s subshells. As a result, there are still more exceptions to the Aufbau principle among the heavier transition elements.



### Activity 1.17

Form a group and complete the following table for the first-row transition metals on your note book:

Element	Atomic number	Ground state electron configuration	Condensed electron configuration
Sc	21		
Ti	22		
V	23		
Cr	24		
Mn	25		
Fe	26		
Co	27		
Ni	28		
Cu	29		
Zn	30		



## 1.8 Electronic Configurations and the Periodic Table of the Elements

*At the end of this section, you will be able to:*

- ☞ correlate the electron configurations of elements with their positions in the periodic table*
- ☞ give a reasonable explanation for the shape of the periodic table*
- ☞ classify elements as representative, transition and inner-transition elements*
- ☞ explain the general trends in atomic radius, ionization energy, electron affinity, electronegativity, and metallic character of elements within a period and group of the periodic table*
- ☞ write the advantages of the periodic classification of elements.*

### 1.8.1 The Modern Periodic Table



#### Activity 1.18

In your Grade 9 chemistry lessons, you have learned about the development of the modern periodic table. Form a group and discuss the following questions, then present your responses to the whole class.

1. How is today's periodic table different from the one that Mendeleev published?
2. What is a "period?" What does it represent?
3. What is a "group?" What does it represent?
4. How does the electron configuration of an element give information about the period and group it is in?
5. Why are some elements placed out of the main body of the 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



#### Activity 1.19

Answer the following questions in groups and present your responses to the whole class.

1. What is the importance of classifying elements in groups and periods?
2. What could be the basis of classifying elements?
3. Why are there two different numbering systems for groups?
4. Which sublevel is being filled in period 1?

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.

## Project 1.1

Form a group of five and do the following activities and submit a report both in word and PDF formats.

The elements can be divided into representative, transition, and inner transition elements based on the type of subshell being filled. Discuss these different classes of elements by searching information from the internet or any other sources. Also, identify each block in the blank periodic table.

### 1.8.3 Periodic Properties



#### Activity 1.20

Discuss the following questions in groups and, present your responses to the whole class.

1. How does size of elements vary across a period?
2. Why are elements of Groups 1 (IA) and 2 (IIA) called metals, while those of Group 17 (VIIA) non-metals?
3. Why are elements of Group 18 (VIII A) least reactive?

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)



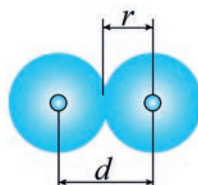
## Activity 1.21

Answer the following questions in groups, then present your responses to the whole class.

1. Why don't the sizes of atoms increase uniformly with increasing atomic number?
2. In which location in the periodic table would you expect to find the elements having the largest atoms? Explain.
3. How do the sizes of atoms change:
  - a. from left to right in a row in the periodic table?
  - b. from top to bottom in a group in the periodic table? Explain.

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 1.19**).



**Figure 1.19: 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 ( $Z_{\text{eff}}$ ) **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.



### Activity 1.22

Discuss the following questions in groups, and present your responses to the whole class.

Compare the effect of  $Z_{\text{eff}}$  and  $n$  on atomic size. Which one dominates?

- down a group?
- across a period? Explain the reason.

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  $Z_{\text{eff}}$ . 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 1.12

- What are the factors affecting the size of an atom of an element? Explain your answer using examples.
- Using the periodic table, rank each set of main-group elements in order of decreasing atomic size:
  - Ca, Mg, Sr
  - K, Ga, Ca
  - Br, Rb, Kr
  - Sr, Ca, Rb
- 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.).

## Ionization Energy (IE)

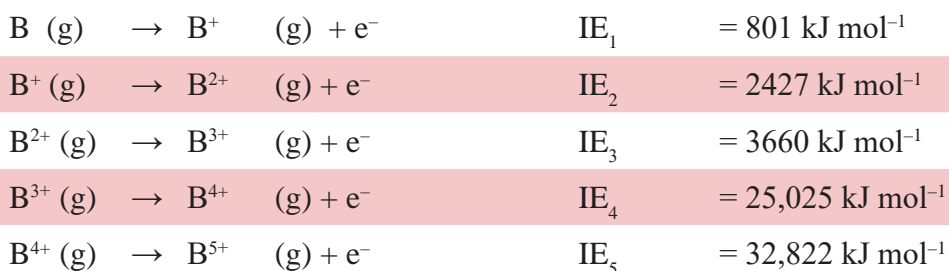


### Activity 1.23

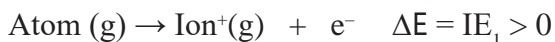
Form a group and discuss the following, then present your responses to the whole class.

- Write the electron configuration of the following pairs of atoms of an element and compare their stability. Explain your answer.
  - oxygen and nitrogen
  - magnesium and aluminum
  - fluorine and neon
- From which atom in each pair (question number 1) will it be easier to remove an electron from the outer most shell? Explain your answer based on their electron configurations.

The **ionization energy (IE)** is the energy (in kJ) required for the complete removal of 1 mol 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 ( $2s^2 2p^1$ ). The five ionization steps and their ionization energies,  $IE_1$  through  $IE_5$ , are:



The **first ionization energy** ( $IE_1$ ) 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.

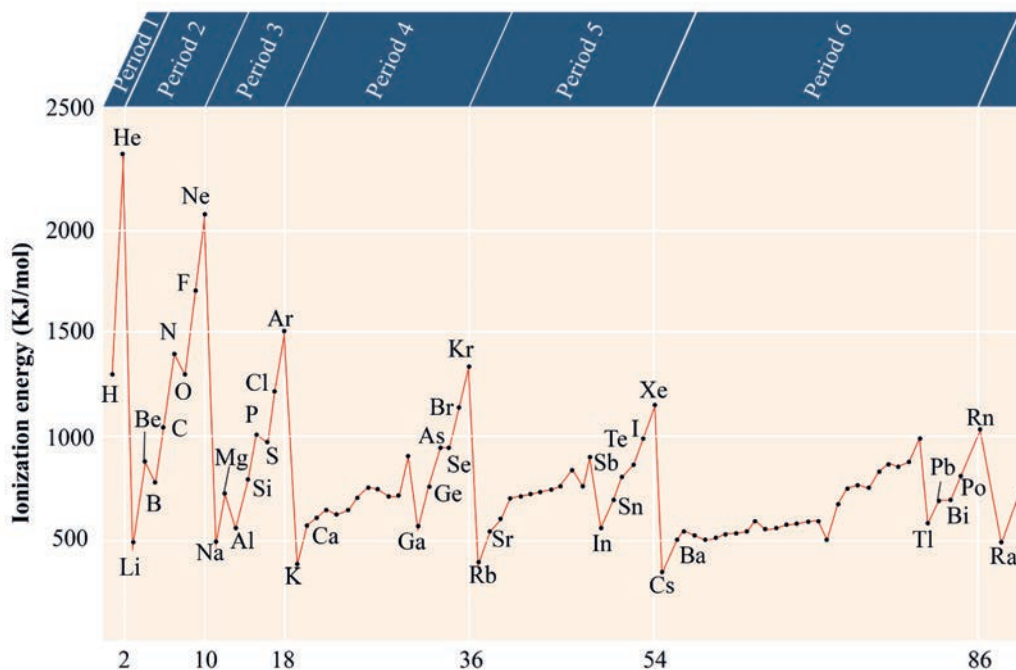


The **second ionization energy** ( $IE_2$ ) removes the second electron. Since the electron is being pulled away from a positively charged ion,  $IE_2$  is always larger than  $IE_1$ :



The first ionization energy is a key factor in an element's chemical reactivity because, atoms with a low  $IE_1$  tend to form **cations** during reactions, whereas those with a high  $IE_1$ , (except the noble gases) often form **anions**.

Ionization energies display a periodic variation when plotted against atomic number, as **Figure 1.20** shows. 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,  $Z_{\text{eff}}$  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.



**Figure 1.20: Ionization energy versus atomic number**

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.

### Group Assignment 1.1



Form a group and discuss on the following questions. Write your reflections and submit it to your teacher.

- The first ionization energy in general increases across a period, however, large drops occur when a new period begins. Why?
- Explain the irregularities in the trends across periods:
  - Boron has a smaller first ionization energy than beryllium.
  - The first ionization energy of nitrogen is higher than oxygen.

### Exercise 1.13

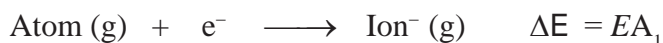
- Choose the element with the higher ionization energy from each pair:
  - As or Bi
  - As or Br
  - Al or In
  - K or Ge
- The first and second ionization energies of potassium, K, are  $419 \text{ kJ mol}^{-1}$  and  $3052 \text{ kJ mol}^{-1}$  and those of calcium, Ca, are  $590 \text{ kJ mol}^{-1}$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

$IE_1$	$IE_2$	$IE_3$	$IE_4$	$IE_5$	$IE_6$
1012	1903	2910	4956	6278	22,330



## 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** ( $EA_1$ ) is usually negative. The **second electron affinity** ( $EA_2$ ), however, is always positive because energy must be absorbed to overcome electrostatic repulsions and add another electron to a negative ion.

For example, the  $EA_1$  and  $EA_2$  of an oxygen atom can be written as:



**Figure 1.21** 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 VIIIA (18), indicate that energy is absorbed to form the **anion**; in fact, these anions are unstable and the values are estimated.

<b>IA</b> (1)						<b>VIIIA</b> (18)	
<b>H</b> -72.8	<b>IIA</b> (2)	<b>IIIA</b> (13)	<b>IVA</b> (14)	<b>VA</b> (15)	<b>VIA</b> (16)	<b>VIIA</b> (17)	<b>He</b> (0.0)
<b>Li</b> -59.6	<b>Be</b> ≤0	<b>B</b> -26.7	<b>C</b> -122	<b>N</b> +7	<b>O</b> -144	<b>F</b> -328	<b>Ne</b> (+29)
<b>Na</b> -52.9	<b>Mg</b> ≤0	<b>Al</b> -42.5	<b>Si</b> -134	<b>P</b> -72	<b>S</b> -200	<b>Cl</b> -349	<b>Ar</b> (+35)
<b>K</b> -48.4	<b>Ca</b> -2.37	<b>Ga</b> -28.9	<b>Ge</b> -119	<b>As</b> -78.2	<b>Se</b> -195	<b>Br</b> -325	<b>Kr</b> (+39)
<b>Rb</b> -46.9	<b>Sr</b> -5.03	<b>In</b> -28.9	<b>Sn</b> -107	<b>Sb</b> -103	<b>Te</b> -190	<b>I</b> -295	<b>Xe</b> (+41)
<b>Cs</b> -45.5	<b>Ba</b> -13.95	<b>Tl</b> -19.3	<b>Pb</b> -35.1	<b>Bi</b> -91.3	<b>Po</b> -183	<b>At</b> -270	<b>Rn</b> (+41)

**Figure 1.21: Electron affinities of the main-group elements (in kJ/mol)**



### Activity 1.24

Discuss the following questions in groups, then present your answers to the whole class.

1. Which group in the periodic table has elements with high (endothermic)  $IE_1$  and very negative (exothermic) first electron affinities ( $EA_1$ )? Give the charge on the ions these atoms form.
2. Silicon has an electron affinity of  $-134$  kJ/mol. The electron affinity of phosphorus is  $-72$  kJ/mol. Give a reason for this difference.
3. Why are the electron affinities of the alkaline earth metals either negative or small positive values?

Electron affinities,  $EA$ , have a periodic variation, just as atomic radii and ionization energies do. Broadly speaking, the general trend is toward more negative electron affinities from left to right in any period.

*What could be the reason the IIA element and the VA element tend to have smaller electron affinities (Figure 1.21) than the preceding element?*

Note that the Group VIA and Group VIIA elements have the largest negative electron affinities of any of the main-group elements. The trend in going across a period is rather clear but there is no simple trend in going down a column of elements.

In most cases, the added electron goes into an energy sublevel that is already partly filled. For Group IIA and VIIIA atoms, however, the added electron would be required to enter a significantly higher energy level, the  $np$  level for the Group IIA atoms and the  $s$  level for the next principal level for the Group VIIIA atoms. In these cases, a stable anion does not form.

## 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 1.4.

Table 1.4: (a) Electronegativity values (on Pauling scale) across the periods

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

Table 1.4: (b) Electronegativity values (on Pauling scale) down a group

<b>Atom (Group IA)</b>	<b>Electronegativity value</b>	<b>Atom (Group VIIA)</b>	<b>Electronegativity value</b>
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	At	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.



### Activity 1.25

Discuss the following questions in groups, and present your answers to the whole class.

1. What is the electronegativity of an atom? How is it different from electron affinity?
2. In a given family of the periodic table, what is the general relationship between electronegativity and size?

## Metallic Character



### Activity 1.26

Form a group and summarize the trend in metallic character in the periodic table. Is it the same as the trend observed for atomic size and ionization energy? Present your responses to the whole the class.

**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



### Activity 1.27












Form a group and discuss the following questions, then share your answers with the whole class.















1. In which region of the periodic table are metals located?
2. In which region are the elements with general electronic configuration of  $ns^2p^5$  located? Give the group number.
3. Write the group number and period of an element with atomic number 26.
4. Is an element with the electronic configuration  $1s^2 2s^2 2p^6 3s^1$  a metal or a non- metal? Will it form a cation or an anion readily? Explain your answer.



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.




































-  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 ( $\lambda$ ), frequency ( $\nu$ ), and speed ( $c = 3.0 \times 10^8$  m/s), which are related by the formula:
$$c = \lambda\nu$$
-  Electromagnetic radiation can be viewed as a stream of “particles” called photons, each with energy  $h\nu$ , where  $h$  is Planck's constant ( $6.63 \times 10^{-34}$  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  $\ell$ ; the magnetic quantum number,  $m_\ell$ ; and the spin quantum number,  $m_s$ .
-  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  $\ell$  are in the same sublevel.
-  The shape of orbitals depend on the values of  $\ell$ . Thus, the s orbital ( $\ell = 0$ ) is spherical and the p orbital ( $\ell = 1$ ) is dumbbell-shaped.
-  The  $n$ ,  $\ell$  and  $m_\ell$  quantum numbers define an orbital, but a fourth quantum number,  $m_s$ , 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.

## CHECKLIST

## KEY TERMS

- |  |  |
|--|--|
|  <i>Amplitude</i>                   |  <i>Mass number</i>                 |
|  <i>Atomic mass</i>                 |  <i>Non-metal</i>                   |
|  <i>Atomic mass unit (amu)</i>      |  <i>Pauli's Exclusion Principle</i> |
|  <i>Atomic number</i>               |  <i>Period</i>                      |
|  <i>Aufbau Principle</i>            |  <i>Periodic law</i>                |
|  <i>Cathode</i>                     |  <i>Periodic table</i>              |
|  <i>Cathode rays</i>                |  <i>Photon</i>                      |
|  <i>Charge/mass ratio</i>           |  <i>Proton</i>                      |
|  <i>Dalton's atomic theory</i>     |  <i>Quantum numbers</i>            |
|  <i>Effective nuclear charge</i>  |  <i>Representative element</i>    |
|  <i>Electromagnetic radiation</i> |  <i>s-block elements</i>          |
|  <i>Electronic configuration</i>  |  <i>Schrödinger equation</i>      |
|  <i>Excited state</i>             |  <i>Transition metal</i>          |
|  <i>Frequency</i>                 |  <i>Uncertainty principle</i>     |
|  <i>Ground state</i>              |  <i>Wavelength</i>                |
|  <i>Hund's Rule</i>               |  |
|  <i>Inner-transition metal</i>    |  |
|  <i>Isotope</i>                   |  |



## REVIEW EXERCISE

## Part I: Multiple Choice Questions:

Choose the correct answer from the given alternatives.

- Which of the following scientists did not contribute to determining the structure of the atom?
  - Thomson
  - Rutherford
  - Becquerel
  - Dalton
- What is the frequency in Hz of the gamma radiation from a radioactive cobalt-60 source if its wave length is  $1.0 \times 10^{-9}$  nm?
  - $3.3 \times 10^{-27}$  Hz
  - $3.3 \times 10^{-8}$  Hz
  - $3.0 \times 10^{18}$  Hz
  - $3.0 \times 10^{-26}$  Hz
- What is the energy of the electronic transition associated with the sodium-D line having a wavelength of 589 nm?
  - $6.63 \times 10^{-34}$  J
  - $1.13 \times 10^{-27}$  J
  - $3.38 \times 10^{-19}$  J
  - $5.82 \times 10^2$  J
- Among the following, which colour corresponds to light of the highest frequency?
  - Green
  - Red
  - Yellow
  - Blue
- Which of the following orbital designations does not exist?
  - 1s
  - 2d
  - 3p
  - 4f
- Which of the following sets of quantum numbers are not allowed in the hydrogen atom?
  - $n = 3, \ell = 2, m_\ell = 2$
  - $n = 4, \ell = 3, m_\ell = 4$
  - $n = 1, \ell = 0, m_\ell = 0$
  - $n = 2, \ell = 1, m_\ell = -1$
- The species that has the same number of electrons as  $^{32}\text{S}$  is:
  - $^{32}\text{Cl}$
  - $^{33}\text{P}^+$
  - $^{34}\text{S}^+$
  - $^{28}\text{Si}^{2-}$
- Which of the following has the lowest electronegativity?
  - Carbon
  - Magnesium
  - Beryllium
  - Boron
- How many unpaired electrons are there in the  $\text{Cr}^{3+}$  ion?
  - 0
  - 1
  - 2
  - 3
- Which of the following species would require the highest energy for the removal of one electron?
  - $\text{Mg}^{2+}$
  - $\text{Na}^+$
  - Ne
  - $\text{F}^-$

**Part II: Complete the following statements.**

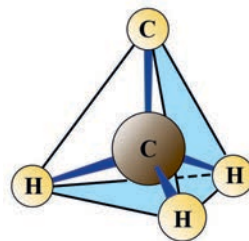
11. The atomic number gives the number of \_\_\_\_\_ in the nucleus.
12. In an atom, the number of electrons is equal to the number of \_\_\_\_\_.
13. When  $n = 2$ , the values of  $\ell$  could be \_\_\_\_\_ and \_\_\_\_\_.
14. When  $\ell = 1$ , the values of  $m_\ell$  could be \_\_\_\_\_, \_\_\_\_\_ 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:
  - a.  ${}^{114}_{48}\text{Cd}$
  - b.  ${}^{98}_{43}\text{Tc}$
  - c.  ${}^{199}_{79}\text{Au}$
  - d.  ${}^{222}_{86}\text{Rn}$
19. Iridium has two naturally occurring isotopes.  ${}^{191}\text{Ir}$  and  ${}^{193}\text{Ir}$  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,  $1.0 \times 10^{-6}$  m,  $1.0 \times 10^{-8}$  m and  $1.0 \times 10^{-10}$  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  $1.38 \times 10^7$  cm/s? The mass of a proton is  $1.76 \times 10^{-24}$  kg.
22. The photon emitted by a cyclotron has a velocity of  $1.50 \times 10^3$  m/s. What is the wavelength of this photon? The mass of photon =  $1.676 \times 10^{-27}$  kg and Planck's constant =  $6.62 \times 10^{-34}$  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. $n = 3, l = 1$ | c. $n = 3, l = 2$ |
| b. $n = 4, l = 0$ | d. $n = 5, l = 3$ |
25. What type of orbital (i.e. 3s, 4p, ...) is designated by these quantum numbers?
- |                                   |                                   |
|-----------------------------------|-----------------------------------|
| a. $n = 5, \ell = 1, m_\ell = 0$  | c. $n = 2, \ell = 0, m_\ell = 0$  |
| b. $n = 4, \ell = 2, m_\ell = -2$ | d. $n = 4, \ell = 3, m_\ell = -3$ |
26. Write the ground-state electron configurations for the following elements:
- |                    |                   |
|--------------------|-------------------|
| a. Br ( $Z = 35$ ) | c. W ( $Z = 74$ ) |
| b. Mo ( $Z = 42$ ) |                   |
27. Write the period number for each of the following and state if they are metal, non-metal or metalloid:
- |       |      |
|-------|------|
| a. P  | c. F |
| b. Ge | d. W |

# UNIT 2



## CHEMICAL BONDING

### Unit Outcomes

*At the end of this unit, you will be able to:*

- ☞ *explain that a chemical bond is an attractive force between particles*
- ☞ *demonstrate an understanding of the formation and general properties of substances containing ionic, covalent and metallic bonds*
- ☞ *draw Lewis structure for simple ionic and covalent compounds*
- ☞ *identify the origin of polarity within molecules*
- ☞ *describe the formation and nature of hydrogen bonds, dipole-dipole forces and London forces*
- ☞ *explain the bonding models (Lewis model, valence bond model and molecular orbital model) and show the usefulness of the bonding theories in explaining and predicting molecular properties (bond angle, bond length, bond energy, etc...)*
- ☞ *explain how the properties of a substance (solid or liquid) depends on the nature of the particles present and the type of intermolecular forces*
- ☞ *discuss the importance of intermolecular forces in plant and animal life*
- ☞ *explain how the Valence Shell Electron Pair Repulsion (VSEPR) model can be used to predict molecular shape*
- ☞ *conduct experiments to observe and analyze the physical properties of different substance to determine the type of bonding present*
- ☞ *describe scientific enquiry skills along this unit: observing, inferring, predicting, classifying, comparing and contrasting, making models, communicating, asking questions, applying concepts, relating cause and effect and making generalization.*



## Start-up Activity

Discuss the following issues in a group and present your ideas to the class.

Why do the substances around us behave differently? For instance, table salt is a hard, brittle, high-melting solid that conducts electricity only when molten or dissolved in water. Candle wax melts at a low temperature, is soft, and non-conducting. Copper (and most other metallic substances) is shiny, malleable, and able to conduct electricity whether it is molten or solid.

## 2.1 Introduction

*At the end of this section, you will be able to:*

- ☞ *define chemical bonding*
- ☞ *explain why atoms form chemical bonds*
- ☞ *illustrate chemical bonding using the octet rule*
- ☞ *describe the types of chemical bonding and the mechanisms of the bonding process.*

In Grade 9, you learned about chemical bonding and its types, such as ionic, covalent and metallic bonding. In this unit, we will discuss some new concepts about chemical bonding, like intermolecular forces, molecular geometry, theories of chemical bonding, etc.



### Activity 2.1

Discuss the following issues in groups, then present your ideas to the whole class.

1. Why do atoms combine?
2. Why are molecules more stable than free atoms?
3. What forces act on two atoms as they come together?
4. Explain how the potential energy changes when two hydrogen atoms form a bond.

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



#### Activity 2.2

From your knowledge of Grade 9 chemistry discuss the following questions in a group of four, then present your responses to the whole class.

1. Why do some atoms combine while others do not? Give some examples in your answer.
2. Why do different atoms form different types of bonding?

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).

Do you know any compound whose central atom does not obey the octet rule?

### 2.1.2 Types of Chemical Bonding



#### Activity 2.3

Discuss the following questions in pairs and share your ideas with the whole class.

1. Why do metals tend to form cations and why do non-metals tend to form anions?
2. Why do two non-metals combine to form compounds while no similar process exists for two metals to form a compound?

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

*At the end of this section, you will be able to:*

- ☞ define ionic bonding*
- ☞ use Lewis electron dot symbols for main group elements*
- ☞ describe ionic bonding using Lewis electron dot symbols*
- ☞ list the favourable conditions for the formation of ionic bonds*
- ☞ explain the formation of ionic bonding*
- ☞ give examples of ionic compounds*
- ☞ define lattice energy*
- ☞ calculate lattice energy of ionic crystals from given data using the Born-Haber cycle*
- ☞ discuss the exceptions to the octet rule*
- ☞ describe the properties of ionic bonding*
- ☞ carry out an activity to demonstrate the effect of electricity on ionic compounds ( $PbI_2$  and  $NaCl$ )*
- ☞ carry out an investigation into the melting point and solubility of some ionic compounds ( $NaCl$  and  $CuCl_2$ ).*



### Activity 2.4

Form a group of four and discuss the following questions, then present your responses to the whole class.

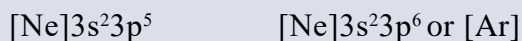
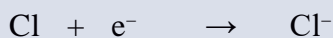
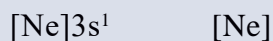
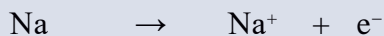
1. Why do elements form ions in certain chemical reactions?
2. Which of the following pairs of elements are likely to form an ionic compound?
  - a. sodium and chlorine
  - b. nitrogen and fluorine
  - c. lithium and oxygen

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 2.1

The formation of NaCl from sodium and chlorine can be explained as:



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. [What about an ionic compound containing an ammonium ion?](#)

### Exercise 2.1

- Explain the formation of bonds in the following pairs of elements:
  - potassium and chlorine
  - magnesium and oxygen
  - sodium and oxygen
- Which of the following elements will form an ionic bond with chlorine, why?
  - calcium
  - carbon
  - oxygen
  - silicon
- Identify the species found in the following ionic compounds:  $\text{CaCl}_2$ ,  $\text{MgO}$ , and  $\text{Al}_2\text{O}_3$ . From this what can you conclude about the formation of these compounds?
- Why do elements located on the opposite sides of the periodic table tend to form ionic bonds?



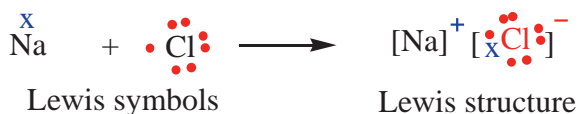
### 2.2.1 Lewis Electron-Dot Symbols

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,  $[\text{Ne}]3s^23p^5$ , is



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:



### Activity 2.5

Discuss the following questions in pairs and present your responses to the whole class.

1. Sodium atom is highly reactive, but sodium ion is not. Explain.
2. Write the Lewis symbols of  $\text{K}^+$ ,  $\text{S}^{2-}$ ,  $\text{Al}^{3+}$ , and  $\text{F}^-$  ions.

### 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

### 2.2.2 Formation of Ionic Bonds

You may be surprised to learn that the electron-transfer process actually absorbs energy! So why does it occur? As you will see, the reason ionic substances exist at all is because of the enormous release of energy when the ions come together and form a solid.

Consider just the electron-transfer process for the formation of lithium fluoride, which involves two steps:

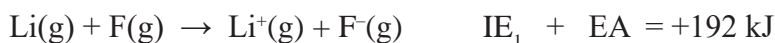
1. A gaseous Li atom loses an electron ( $IE_1$ ):



2. A gaseous F atom gains an electron lost by Li atom (EA):

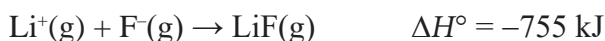


Note that the two-step electron-transfer process by itself requires energy:

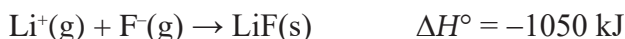


The total energy needed for ion formation is even greater than this because metallic lithium and diatomic fluorine must first be converted to separate gaseous atoms, which also requires energy. Despite this, the standard heat of formation ( $\Delta H_f^\circ$ ) of solid LiF is  $-617 \text{ kJ/mol}$ ; that is,  $617 \text{ kJ}$  is released when  $1 \text{ mol}$  of LiF(s) forms from its elements. That is, there must be some exothermic energy component large enough to overcome the endothermic steps. These are:

- When  $1 \text{ mol}$  of  $\text{Li}^+(\text{g})$  and  $1 \text{ mol}$  of  $\text{F}^-(\text{g})$  form  $1 \text{ mol}$  of LiF (g):



- When the gaseous ions coalesce into a crystalline solid. That occurs because each ion attracts others of opposite charge:



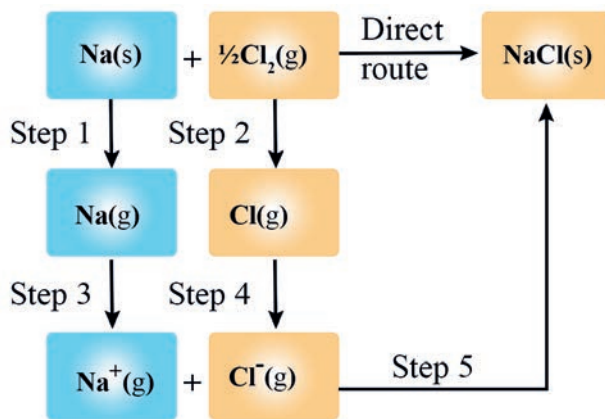
The negative of this value,  $1050 \text{ kJ}$ , is the lattice energy of LiF. The **lattice energy (U)** is the enthalpy change that occurs when  $1 \text{ mol}$  of ionic solid separates into gaseous ions. It indicates the strength of ionic interactions, which influence melting point, hardness, solubility, and other properties.

## Lattice Energies from the Born–Haber Cycle

So we need to know the lattice energy of solid lithium fluoride. Finding the lattice energy of an ionic solid by experiment is difficult. However, this quantity can be found indirectly using the Born–Haber cycle. The reasoning is based on **Hess's law**, which states that an overall reaction's enthalpy change is the sum of the enthalpy changes for the individual reactions that make it up:

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

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  $\frac{1}{2}\text{Cl}_2(\text{g})$ ;  $\Delta_f H^\circ -411 \text{ kJ mol}^{-1}$



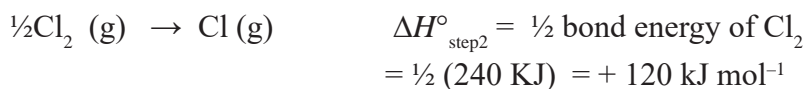
**Figure 2.1:** Born–Haber cycle for NaCl

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:



**Step 2:** Chlorine molecules are dissociated to atoms:



**Step 3:** Sodium atoms are ionized to  $\text{Na}^+$  ions:



**Step 4:** Formation of chloride ion:



**Step 5:** Formation of NaCl(s) from ions. The ions  $\text{Na}^+$  and  $\text{Cl}^-$  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  $-411 \text{ kJ mol}^{-1}$ . Therefore, we can calculate the lattice energy using *Hess's law*: Solving for  $U_{\text{NaCl}}$  gives:

$$\begin{aligned} U_{\text{NaCl}} &= \Delta_f H^\circ - (\Delta H^\circ_{\text{step1}} + \Delta H^\circ_{\text{step2}} + \Delta H^\circ_{\text{step3}} + \Delta H^\circ_{\text{step4}}) \\ &= -411 \text{ kJ mol}^{-1} - [108 \text{ kJ mol}^{-1} + 120 \text{ kJ mol}^{-1} + 496 \text{ kJ mol}^{-1} + (-349 \text{ kJ mol}^{-1})] \\ &= -786 \text{ kJ mol}^{-1} \end{aligned}$$

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

### Exercise 2.3

- Draw a Lewis electron-dot symbol for each atom:
  - Rb
  - As
  - I
- Give the group number and general electron configuration of an element with each electron-dot symbol:
  - $\cdot \ddot{\text{X}}$
  - $\cdot \ddot{\text{X}} \cdot$
- How does the lattice energy of an ionic compound depend on the charges and sizes of the ions?
- 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.
  - Ba and Cl
  - Sr and O
  - Al and F
  - Rb and O
- Identify the main group to which X belongs to in each ionic compound formula:
  - $\text{X}_2\text{O}_3$
  - $\text{XCO}_3$
  - $\text{Na}_2\text{X}$
- For each pair, choose the compound with the lower lattice energy, and explain your choice:
  - CaS or BaS
  - NaF or MgO
  - LiCl or CsCl
  - BaS or CsCl

## Factors Affecting the Formation of Ionic Bonds



### Activity 2.6

Discuss each of the following questions and forward your responses to the whole class.

1. In general, how does the lattice energy of an ionic compound depend on the charges and sizes of the ions?
2. Why is an ionic compound unlikely to consist of ions of noble gases?
3. What characteristic charges do atoms in Groups 13 (IIIA) up to 17 (VIIA) of the periodic table have when they form ions?

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 favours the formation of an ionic bond.

**Electron affinity (EA):** A higher electron affinity favours the formation of an anion. Generally, the elements having higher electron affinity such as halogens favour 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 (coulombic) 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 coulombic attraction forces are stronger, then more energy gets released and a more stable or a stronger ionic bond is formed. Larger lattice energy would favour the formation of an ionic bond. 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 a higher ionic charge will have a larger lattice energy. If the total energy released is more than that which is absorbed, then the formation of an ionic compound is favoured.



### Activity 2.7

Answer the following questions in groups, then present your answers to the whole class.

1. Given that the ions in LiF and in MgO are of similar size, which compound has the stronger ionic bonding?
2. The radii of the sodium and potassium ions are 102 pm and 138 pm, respectively. Which compound has stronger ionic attractions, sodium chloride or potassium chloride?

## 2.2.3 Exceptions to the Octet Rule in Ionic Compounds



### Activity 2.8

Discuss the following issues in a group of four and share your responses with the whole class.

1. Comment on the possible formation of the  $K^{2+}$  ion. Why is its formation unlikely?
2. How many electrons does a Se atom have to gain to have a complete octet in its valence shell?
3. Identify the cations that obey the octet rule in the following compounds:
  - a. LiF
  - b. NaCl
  - c. CuO
  - d.  $FeCl_3$

Why does the octet rule work well only for the representative metals (Groups IA, IIA) and the non-metals, but not for the transition elements?

There are certain exceptions to the octet rule. We will discuss it here with ionic compounds.

## 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 ( $\text{H}^-$ ), lithium ion ( $\text{Li}^+$ ), beryllium ion ( $\text{Be}^{2+}$ ) and boron ion ( $\text{B}^{3+}$ ) are isoelectronic with He.

Can you give some compounds that contain less than eight electrons around the central atom?

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  $\text{BF}_3$  is stable, but it will form  $\text{BF}_4^-$  when possible.

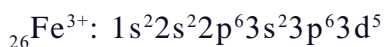
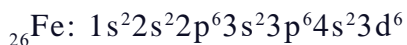
## More than Octet (18-Electron Rule)

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.

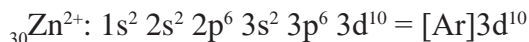
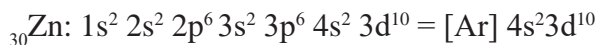
Why don't the atoms of these elements lose electrons to achieve the noble-gas configurations of  $ns^2np^6$ ?

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:



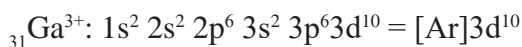
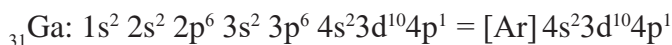
A stable ion of iron with valence shell electron configuration is  $3s^2 3p^6 3d^5$  which is not isoelectronic with a noble gas.  $\text{Fe}^{2+}$  is a well-known stable ion with a valence shell electron configuration  $3s^2 3p^6 3d^6$  which is not isoelectronic with any of the noble gases.

**Electron configurations of zinc:**

$\text{Zn}^{2+}$  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  $\text{Ga}^{3+}$  ion as



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

**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,  $\text{Sn}^{2+}$ , and  $\text{Sn}^{4+}$ ? Check if any of these tin ions are isoelectronic with any of the noble gases.
3. Which group of ions of elements, in general, show more than the octet (18-electron rule)?



## 2.2.4 Properties of Ionic Compounds

### Experiment 2.1

#### Investigation of Solubility of Ionic Compounds

**Objective:** To investigate the solubility of NaCl and  $\text{CuCl}_2$  in polar and non-polar solvents

**Apparatus and Chemicals:** Test tube, Bunsen burner, NaCl,  $\text{CuCl}_2$ , water, ethanol, cyclohexane, and petroleum ether

#### Procedure:

1. Place about 0.5 g each of NaCl and  $\text{CuCl}_2$  in to two separate test tubes and add about 2.5 mL of water and shake both test tubes quickly.
2. If some residue is left in the test tubes, heat the solutions with a Bunsen burner.

**SAFETY:** Turn off the Bunsen burners as these chemicals are HIGHLY FLAMMABLE!

3. Repeat Step 1 using fresh ethanol, cyclohexane, and petroleum ether solvents, separately. (SAFETY: Do not heat these, as they are highly flammable!)

#### Observations and analysis:

Prepare an observation table in your notebook for the solubility of NaCl and  $\text{CuCl}_2$  in all the four solvents at room temperature and on heating (SAFETY: only heat when water is the solvent) and record the observations.

Solvent	NaCl	$\text{CuCl}_2$
Water		
Ethanol		
Petroleum ether		
Cyclohexane		

#### Inference/Conclusion

Interpret the observation table and give results.

Make a generalized statement about the solubility of ionic compounds in polar and non-polar solvents.

## Experiment 2.2

### Thermal behavior of ionic compounds

**Objective:** To study the effect of heat on ionic compounds

**Apparatus and chemicals:** Test tubes, Bunsen burner, test tubes holders, sodium chloride, and copper (II) chloride.

#### Procedure:

1. Take two hard glass test tubes and label them as A and B.
2. Add 0.5 g each of dry sodium chloride crystals and copper (II) chloride in test tubes A and B, respectively.
3. Hold these test tubes with the help of test tube holders.
4. Heat the tubes at the same time in the Bunsen burner flame, first slowly and then strongly. Shake them a little when heating.

**Caution:** Chlorine gas is produced, this would be best carried out in a fume cupboard.

#### Observations and analysis:

- A. Do the crystals melt?
- B. Do they have high or low melting points?

## Experiment 2.3

### Electrical Conductivity of Ionic Compounds

**Objective:** To test the electrical conductivity of molten compounds

**Apparatus and chemicals:** 9-volt battery, 6-watt bulb with a bulb holder, conducting wires include: beaker, tripod, wire gauze, clamp and stand, two carbon rods, lead (II) iodide or lead (II) bromide, copper (II), sulphate or sodium chloride. Caution: Lead compounds are harmful. Copper sulphate is corrosive and an irritant.

#### Procedure A:

1. Connect the circuit as shown in **Figure 2.2** in which a 9 volt DC is connected via a bulb.

- Using about 2 cm depth of lead (II) iodide or lead (II) bromide in a small beaker, test the conductivity of the crystals. Do not throw the crystal away and be careful not to contaminate the sample because you will reuse it later. (Note: A fairer test of the solid compound would be to use a lump of the compound rather than its powder).
- Test the conductivity of large crystals of copper (II) sulphate and sodium chloride if any of them are available in your laboratory.

### Procedure B:

- Now heat the same lead (II) iodide or lead (II) bromide (used in the above experiment) in a beaker on a tripod and wire gauze or in a boiling tube supported by a clamp and stand until it melts.
- Test the conductivity of the molten compound by dipping the carbon electrodes (carbon rods) into the molten compound as shown in the **Figure 2.2**.
- Repeat for the other compounds.

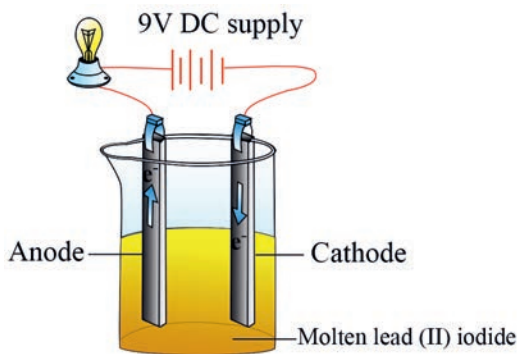


Figure 2.2: Conductivity in the molten state

### Observations and analysis:

- What did you observe?
- Which of the compounds (molten or solid) conduct electricity? Why?
- All compounds contain at least two elements. Examine the names of those compounds which conduct electricity when in the molten state and decide which groups of the components of these compounds belong. Name the type of bonding that exists in the compounds used.

## Experiment 2.4

### Electrical Conductivity of Ionic Compounds

**Objective:** To test the electrical conductivity of the aqueous solutions of some common ionic compounds

**Apparatus and chemicals:** 9-volt battery, 6-watt bulb with a bulb holder, conducting wires, two carbon rods,  $\text{H}_2\text{O}$ , lead (II) iodide,  $\text{NaCl}$ . Caution: Lead compounds are harmful.

#### Procedure:

1. Dissolve the compound in 50 mL of water in two separate beakers.
2. Connect the same circuit you used in Experiment 2.3 and test the conductivity of each aqueous solution (Figure 2.3).

#### Observations and analysis:

- A. Predict what happens at the electrodes based on the type of the compound used for the experiment.
- B. Do you expect the same product(s) at the electrodes when electricity passes through molten and aqueous solutions of the compounds?

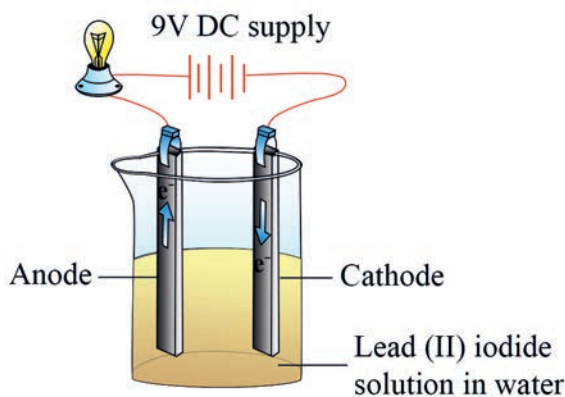


Figure 2.3: Electrochemical cell showing the conductivity of an aqueous solution

## Group Assignment 2.1



Based on the observations and results of **Experiments 2.1** to **Experiment 2.4**, give a summary of the properties of ionic compounds.

## 2.3 Covalent Bonds and Molecular Geometry

*At the end of this section, you will be able to:*

- ☞ define covalent bonding*
- ☞ explain the formation of covalent bonding using examples*
- ☞ draw Lewis structures or electron dot formulas of some covalent molecules*
- ☞ illustrate the formation of coordinate covalent bonding using examples*
- ☞ draw resonance structures of some covalent molecules and polyatomic ions*
- ☞ discuss the exceptions to the octet rule in covalent bonding*
- ☞ distinguish between polar and non-polar covalent molecules*
- ☞ describe the properties of covalent molecules*
- ☞ carryout an activity to investigate the effects of heat, electricity and some solvents on covalent compounds (naphthalene, graphite, iodine and ethanol)*
- ☞ describe the valence shell electron pair repulsion theory (VSEPR)*
- ☞ distinguish between the bonding pairs and nonbonding pairs of electrons*
- ☞ describe how electron pair arrangements and shapes of molecules can be predicted from the number of electron pairs*
- ☞ explain why double bonds and lone pairs cause deviations from ideal bond angles*
- ☞ explain the term dipole moment with the help of a diagram*
- ☞ describe the relationship between dipole moment and molecular geometry*
- ☞ describe how bond polarities and molecular shapes combine to give molecular polarity*

- ☞ *predict the geometrical shapes of some simple molecules on the bases of hybridization and the nature of electron pairs*
- ☞ *construct models to represent shapes of some simple molecules*
- ☞ *define intermolecular forces*
- ☞ *name the different types of intermolecular forces*
- ☞ *explain dipole-dipole interactions*
- ☞ *give examples of dipole-dipole interaction*
- ☞ *define hydrogen bonding*
- ☞ *explain the effect of hydrogen bond on the properties of substances*
- ☞ *give reasons why hydrogen bonding is stronger than ordinary dipole-dipole interactions*
- ☞ *explain dispersion (London) forces*
- ☞ *give examples of dispersion forces*
- ☞ *predict the strength of intermolecular forces for a given pair of molecules.*

## Formation of Covalent Bonding



### Activity 2.9

Discuss each of the following in your group and present your ideas to the whole class.

1. Can two non-metal atoms combine together? How?
2. Why doesn't a hydrogen atom lose an electron and form an ionic bond?
3. Give one main difference between ionic and covalent bonds.
4. Explain the formation of polar covalent and coordinate covalent bonds.

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 2.4). If the attractive forces are stronger than the repulsive forces, a covalent bond is formed, with the two atoms held together and the two shared electrons occupying the region between the nuclei.

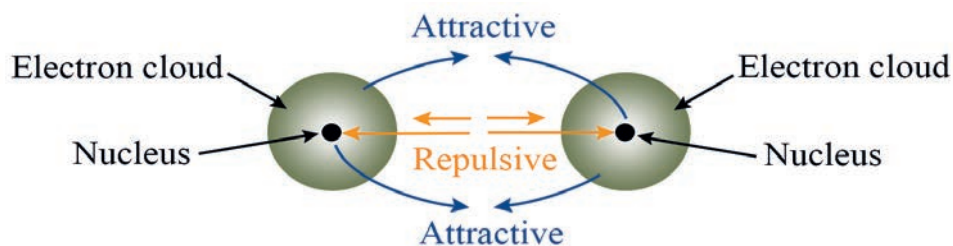


Figure 2.4: Attractive and repulsive forces in a covalent H-H bond formation

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.

What happens if the hydrogen atoms are too far apart? What if the hydrogen atoms are too close together?

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 H<sub>2</sub> molecule, the bond length is 74 pm. On a graph of energy versus internuclear distance, the bond length is the H-H distance in the minimum energy. This is the most stable arrangement (Figure 2.5).

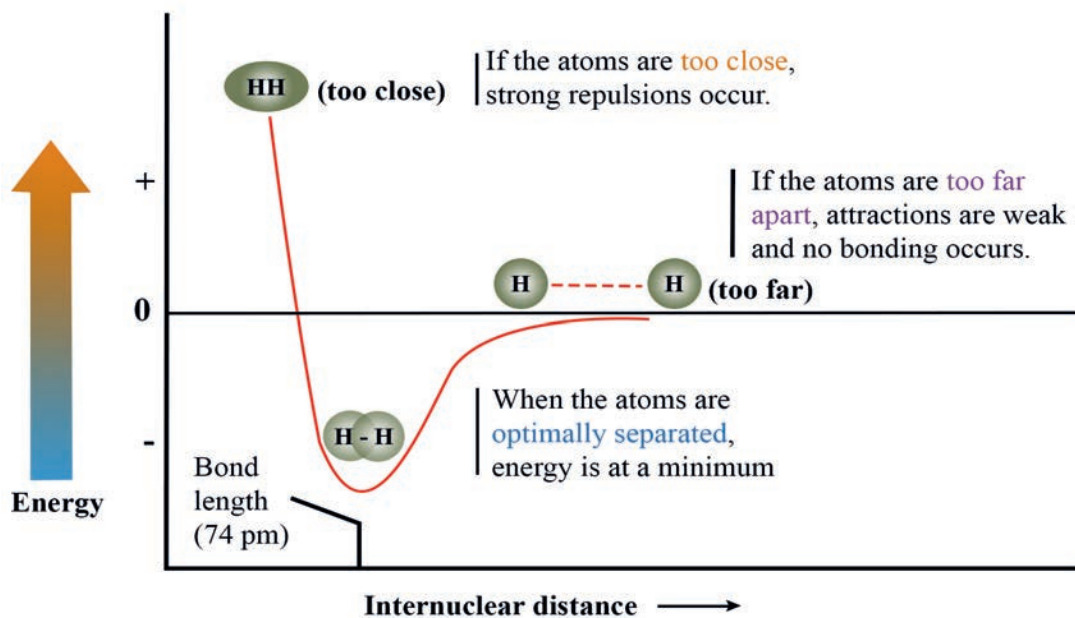
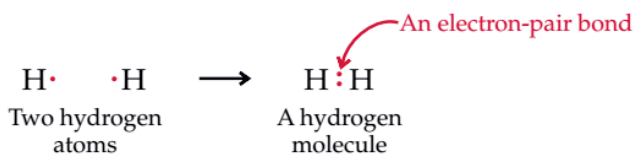


Figure 2.5: Covalent bond formation in H<sub>2</sub>

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, H<sub>2</sub>S, C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>, CCl<sub>4</sub>, BCl<sub>3</sub>, H<sub>2</sub>O, NH<sub>3</sub>, SO<sub>2</sub>, PCl<sub>5</sub>, O<sub>3</sub>, etc. Generally, substances that contain covalent bonds are called **molecules**.

### Representation of Covalent Bonds (Drawing Lewis Structures)

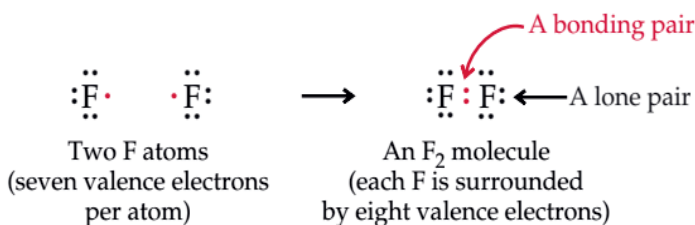
The representation of covalent bonding through Lewis symbols and shared electron pairs is called a **Lewis structure**. The Lewis structure for a hydrogen molecule formed from hydrogen atoms is:



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



Similarly, fluorine has seven valence electrons, and an electron-dot structure for the F<sub>2</sub> 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**.

Do the fluorine atoms in a fluorine molecule (F<sub>2</sub>) obey the octet rule?

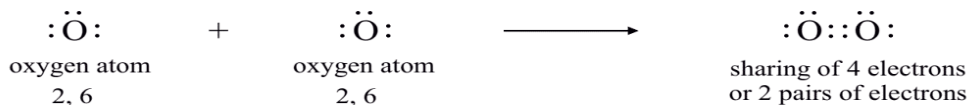
Note that in molecules such as O<sub>2</sub>, N<sub>2</sub>, and many others, the atoms share more than one pair of electrons, leading to the formation of multiple covalent bonds.



For example, consider the formation of oxygen molecule (O<sub>2</sub>) from the oxygen atoms.

Can you give the atomic number, number of protons and electrons of an oxygen atom?

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 follows:  $:\ddot{\text{O}}=\ddot{\text{O}}:$

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 2.2

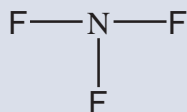
Write the Lewis structure for nitrogen trifluoride ( $\text{NF}_3$ ) in which all three F atoms are bonded to the N atom.

**Solution:**

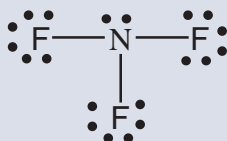
We follow the steps for writing Lewis structures.

**Step 1:** The outer-shell electron configurations of N and F are  $2s^2 2p^3$  and  $2s^2 2p^5$ , respectively. Thus, there are  $5 + (3 \times 7)$ , or 26, valence electrons to account for in  $\text{NF}_3$ .

**Step 2:** The N atom is less electronegative than F, so in the skeletal structure of  $\text{NF}_3$ , 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.

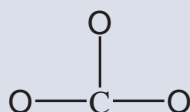
**Example 2.3**

Write the Lewis structure for the carbonate ion ( $\text{CO}_3^{2-}$ ).

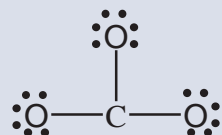
**Solution:** We follow the steps for writing Lewis structures and note that this is an anion with two negative charges.

**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:

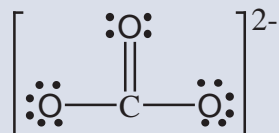


**Step 3:** We draw a single covalent bond between C and each O and comply with the octet rule for the O atoms:



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

- Determine the total number of valence electrons for the following:
  - $\text{CO}_2$
  - $\text{SO}_4^{2-}$
  - $\text{NH}_4^+$
  - $\text{N}_2\text{O}_4$
- Write a Lewis structure of
  - nitrogen trichloride,  $\text{NCl}_3$
  - chlorate ion,  $\text{ClO}_3^-$
  - phosphonium ion,  $\text{PH}_4^+$
- Draw a Lewis structure for  $\text{SF}_4$  and  $\text{HCOOH}$  (formic acid).
- Which of the following atoms O, He, F, H, and P cannot be used as a central atom in a Lewis structure? Explain.
- Write a Lewis structure for carbonyl sulphide,  $\text{COS}$ .

## Coordinate-Covalent Bonding

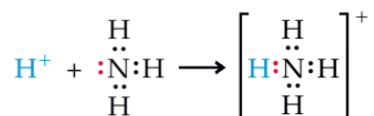


## Activity 2.10

Form a group and discuss the following issues, then present your responses to the whole class.

- Consider ammonia and boron trifluoride molecules; identify which has an incomplete octet and which one has lone pair electrons on the central atom of the molecule.
- Can these two molecules react with each other to complete the octet of an atom with an incomplete octet? How?

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 ( $\text{NH}_4^+$ ), for example, forms when the lone-pair electrons from the nitrogen atom of ammonia,  $\text{NH}_3$ , bond to  $\text{H}^+$ . Such kind of bonds is called **coordinate covalent bonds or dative bonds**.



Some examples of molecules which contain coordinate-covalent bonds include  $\text{NH}_3$ ,  $\text{BCl}_3$ ,  $\text{H}_3\text{O}^+$  and  $\text{AlCl}_4^-$ .

## Resonance Structures

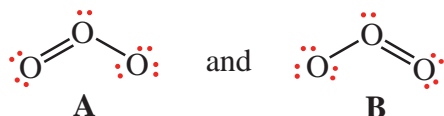


## Activity 2.11

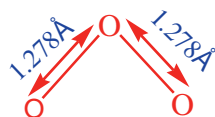
Form a group and discuss the following questions and present your responses to the whole class.

- How many structural formulas can you write for each of the following?
  - $\text{H}_2\text{O}$
  - $\text{NH}_4^+$
  - $\text{CO}_3^{2-}$
  - $\text{C}_6\text{H}_6$  (Benzene)
- What is the difference between a resonance structure and a resonance hybrid?

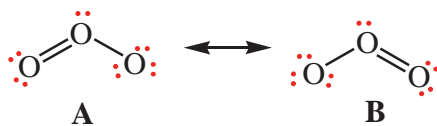
Sometimes more than one valid Lewis structure is possible for a given molecule. For example, two Lewis structures are possible for ozone ( $\text{O}_3$ ):



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  $\text{O}_3$  molecules, just different Lewis structures for the same molecule. However, neither one of these two Lewis structures accounts for the known bond lengths in  $\text{O}_3$  (1.278 Å).

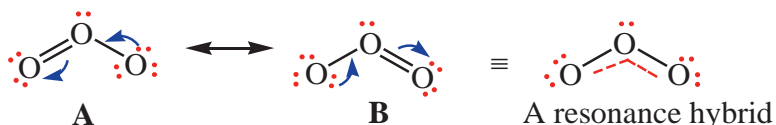


Since both the bonds are identical, which one is a double bond? Bond length and bond energy measurements indicate that the two oxygen-oxygen bonds in  $\text{O}_3$  are identical, with properties that lie between those of an  $\text{O}-\text{O}$  bond and an  $\text{O}=\text{O}$  bond, something like 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 ( $\leftrightarrow$ ) between them.



Unfortunately, this notation can be misinterpreted. It does not mean that the ozone molecule flips back and forth between two forms. There is only one ozone molecule. The double-headed arrow means that you should form a mental picture of the molecule by joining the various resonance formulas.

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 ion are called **resonance forms or resonance contributors or resonance structures**.

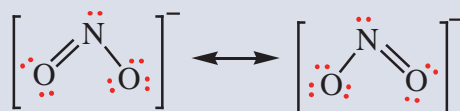
### Example 2.4

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  $N\text{---}O$  bonds, each one intermediate between a single and a double bond.

**Exercise 2.6**

- Write three equivalent structures for the  $\text{SO}_3$  molecule that obey the octet rule.
- Draw Lewis structures of all the important resonance forms of each of the following:
  - $\text{NO}_2\text{F}$  (N central)
  - $\text{HNO}_3$
  - $\text{NO}_2^-$

**Exceptions to the Octet rule in Covalent Bonding**

**Activity 2.12**

Discuss the following issues in groups and present your answers to the whole class.

- What requirements are needed for an atom to expand its valence shell?
- Which of the following atoms can expand its valence shell: F, S, H, Al?
- Identify the atoms in  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{OF}_2$ ,  $\text{BF}_3$ , and  $\text{SiF}_4$  which do not obey octet rule.

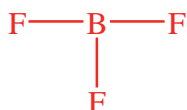
Although many Lewis structures follow the octet rule, there are exceptions. There can be categorized into three groups:

**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,  $\text{BeCl}_2$ ,  $\text{BF}_3$  and  $\text{AlCl}_3$ , whose Lewis formulas are shown:



4 electrons around Be



6 electrons around B



6 electrons around Al

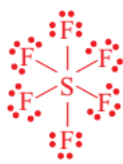
**ii. More than octet (central atom has excess of electrons):**

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

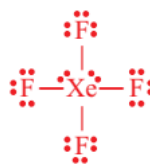
empty d orbitals in the valence shell. For example  $\text{PF}_5$ ,  $\text{SF}_6$  and  $\text{XeF}_4$  :



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  $\text{ClO}_2$ ,  $\text{NO}$  and  $\text{NO}_2$  having 19, 11 and 17 valence electrons, respectively. For example, the best way to suggest the Lewis-like structure for the  $\text{NO}$  molecules is:



#### Exercise 2.7

- Suggest the Lewis-like structure for  $\text{NO}_2$  and  $\text{ClO}_2$  molecules.
- The following do not obey the octet rule. Draw a Lewis structure for each one and state the type of octet rule exception:
  - $\text{BH}_3$
  - $\text{AsF}_4^-$
  - $\text{SeCl}_4$
  - $\text{PF}_6^-$

### Polar and Non-Polar Covalent Molecules



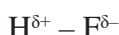
#### Activity 2.13

Discuss the following questions in groups and present your responses to the whole class.

- Describe the trend in electronegativity as “increases” or “decreases” for each of the following:
  - from B to F
  - from Mg to Ba
  - from F to I
- What does the word “dipole” refer to?
- How does electronegativity relate to bond polarity?



When the atoms are alike in a covalent bond, as in the case of the H–H bond of H<sub>2</sub>, 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  $\delta+$  and  $\delta-$  (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 ( $\mu$ ) is defined as the product of the magnitude of the charge ( $\delta$ ) 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  $1\text{D} = 3.33564 \times 10^{-30} \text{Cm}$ . 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

- Both  $\text{CO}_2$  and  $\text{BCl}_3$  have zero dipole moments, but the  $\text{C} = \text{O}$  and  $\text{B} - \text{Cl}$  bond moments are not zero. Explain.
- Compare the dipoles in the covalent molecules  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$ . Explain your answer.
- For each of the following bonds, indicate the positive end with  $\delta^+$  and the negative end with  $\delta^-$ . Draw an arrow to show the dipole for each.
  - N and F
  - Si and Br
  - C and O
  - P and Br
  - N and P

### Properties of Covalent Compounds

Carbon tetrachloride is a covalent compound. Would you expect it to conduct electricity?

### Experiment 2.5

#### Investigating the melting point of covalent compounds

**Objective:** To investigate the melting point of naphthalene.

**Apparatus and chemicals:** Thermometer, stirrer, beaker, melting point tube, naphthalene, glycerine, Bunsen burner.

#### Procedure:

- Set up the apparatus shown in **Figure 2.6**.
- Place a small amount of naphthalene in the melting point tube.
- Attach the tube to the side of the thermometer (the liquid in the beaker will hold the tube in position).
- Heat the beaker slowly. When the naphthalene melts, record the reading on the thermometer.

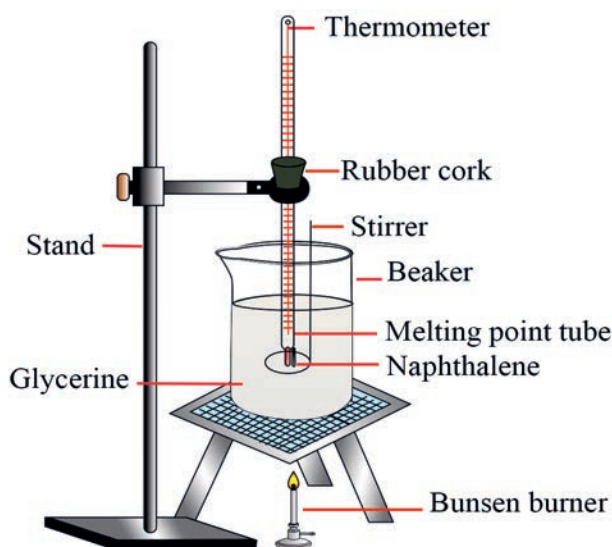


Figure 2.6: Determination of melting point of naphthalene

### Observations and analysis:

Check your result by referring to standard melting point values. Discuss possible reasons for the differences in melting point compared to the standard melting point.

## Experiment 2.6

### The effects of electricity and some solvents on covalent compounds

**Objective:** To test the effects of electricity and some solvents on covalent compounds.

**Apparatus and chemicals:** Beakers, stirrer, test tubes, table sugar, cyclohexane, petroleum ether, water, alcohol, naphthalene.

#### Procedure A: Solubility test

1. Place about 0.5 g or 5 drops each of naphthalene, table sugar, and ethanol in three separate test tubes and add about 2.5 mL of distilled water and shake the test tubes vigorously.
2. See a change in the amount of naphthalene, and table sugar added in each case; if some residue remains in the test tube/s, heat it on a Bunsen burner.

- Observe if a separating layer is formed between the ethanol and water, it indicates ethanol is not soluble in water.
- Repeat the experiment using cyclohexane and petroleum ether solvents, separately (Caution: do not heat it.)

### Procedure B: Conductivity test

- Connect the circuit as shown in **Figure 2.2**, (**Experiment 2.3**) in which a 9-volt DC is connected via a bulb.
- Test the conductivity of table sugar.
- Dissolve a spoonful of table sugar in 50 mL of distilled water in a beaker. Test the resulting solution for electrical conductivity using the setup of **Figure 2.3**, in **Experiment 2.4**.

### Observations and analysis:

Record your observations on your notebook. Copy and complete the table below.

Property			
Substance	Solubility in water	Solubility in non-polar solvent	Effect of electricity
Naphthalene			
Table sugar			
Ethanol			

### Results and Discussion:

- Draw your conclusion from the above observations.
- Do these substances conduct electricity either in the solid state or in the molten (liquid) state?
- Is there any chemical reaction that takes place at the electrodes?



### Activity 2.14

Form a group of four and discuss the following questions. Then, present your responses to the whole class.

1. Why does ammonia,  $\text{NH}_3$ , dissolve in water but methane,  $\text{CH}_4$ , does not?
2. Distilled water is very poor electrical conductor, whereas rain water can conduct electricity. Explain why.
3. Unlike ionic compounds, covalent compounds do not conduct electricity in molten state. Why is that so?

Unlike any ionic compound, many of the covalent compounds are found in gaseous state at room temperature. Consider methane ( $\text{CH}_4$ ), the simplest compound between carbon and hydrogen, which have comparable, intermediate electronegativity. It is a gas at room temperature. Cooling methane to a low temperature condenses it first to a liquid and then to a solid. 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:  $\text{H}_2\text{O}$ ,  $\text{Br}_2$

Gas:  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{NH}_3$

- 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. 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/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, trigonalbipyramidal 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 2.7) by their ball and stick models.

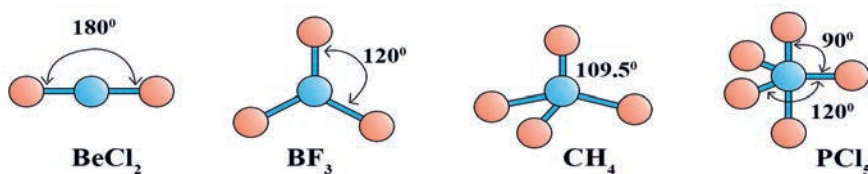


Figure 2.7: The shapes of molecules in which the central atom has no lone pair

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.

### ii. 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**

Why is that repulsions exerted by lone pair is greater than that of bonding pair?

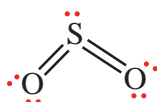
To keep track of the total number of bonding pairs and lone pairs, we show molecules with lone pairs as  $AB_xE_y$ , where A is the central atom, B is a surrounding atom, and E is a lone pair on A. Both  $x$  and  $y$  are integers;  $x = 2, 3, \dots$ , and  $y = 1, 2, \dots$ . Thus, the values of  $x$  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<sub>2</sub>E: Sulfur Dioxide (SO<sub>2</sub>)**

The Lewis structure of sulfur dioxide is:



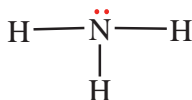
Because VSEPR treats double bonds as though they were single, the SO<sub>2</sub> molecule can be viewed as consisting of three electron pairs on the central S atom. Of these, two are bonding pairs and one is a lone pair. Thus, the overall arrangement of three electron pairs is **trigonal planar**. But because one of the electron pairs is a lone pair, the SO<sub>2</sub> molecule has a “bent” shape.



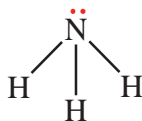
Because the lone-pair versus bonding-pair repulsion is greater than the bonding-pair versus bonding-pair repulsion, the two sulfur-to-oxygen bonds are pushed together slightly and the OSO angle is less than 120°.

**AB<sub>3</sub>E: Ammonia (NH<sub>3</sub>)**

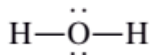
The ammonia molecule contains of three bonding pairs and one lone pair:



The overall arrangement of four electron pairs is **tetrahedral**. But in NH<sub>3</sub> one of the electron pairs is a lone pair, so the geometry of NH<sub>3</sub> is **trigonal pyramidal**. Because the lone pair repels the bonding pairs more strongly, the three NH bonding pairs are pushed closer together:

**AB<sub>2</sub>E<sub>2</sub>: Water (H<sub>2</sub>O)**

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<sub>2</sub>O is bent.

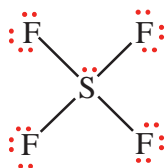
Why do you think this is?



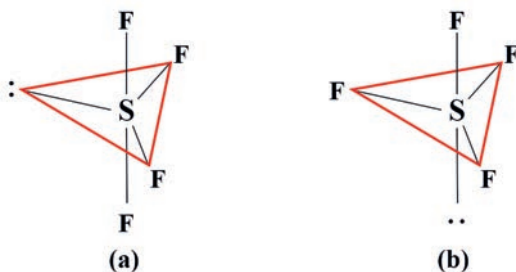


### AB<sub>4</sub>E: Sulfur Tetrafluoride (SF<sub>4</sub>)

The Lewis structure of SF<sub>4</sub> is:



The central sulfur atom has five electron pairs whose arrangement is **trigonal bipyramidal**. In the SF<sub>4</sub> 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:

1. Write the Lewis structure of the molecule, considering only the electron pairs around the central atom (that is, the atom that is bonded to more than one other atom).
2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double and triple bonds as though they were single bonds. If there is more than one central atom, treat each central atom separately.
3. Use the VSEPR geometry to predict the shape of the molecule.
4. In predicting bond angles, note that a lone pair repels another lone pair or a bonding pair more strongly than a bonding pair repels another bonding pair.

## Molecular Shape and Molecular Polarity



### Activity 2.15

Discuss the following questions in a group of four and present your answers to the whole class.

1. Why is it useful to know the polarities of molecules?
2. Are all dissymmetric molecules polar?
3. Under what conditions do bonds of a compound become non-polar?

Many aspects of molecule's chemical behaviour can be understood if we know the geometry (*shape*) of a substance. Molecular shape affects many properties of the molecule like molecular polarity, which in turn influence melting and boiling points, solubility, and even reactivity. Molecular polarity is created by molecules with a net imbalance of charge. In molecules with more than two atoms, both shape and bond polarity determine the molecular polarity.

## Bond Polarity and Dipole Moment



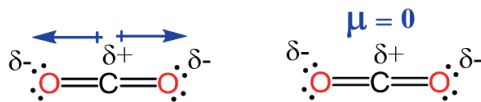
### Activity 2.16

Discuss the following concepts in groups, and share your ideas with the rest of the class.

1. How do we indicate a bond dipole when we draw the structure of a molecule?
2. Use a drawing to show why the  $\text{SO}_2$  molecule is polar.
3. Water has a resultant dipole moment of  $6.23 \times 10^{-30} \text{ C m}$  (1.87D). Explain why this fact proves that the  $\text{H}_2\text{O}$  molecule must have a bent shape.

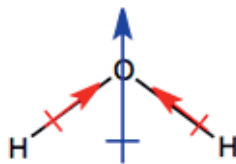
Diatomic molecules containing atoms of different elements (for example,  $\text{HCl}$ ,  $\text{CO}$ , and  $\text{NO}$ ) have dipole moments and are called **polar molecules**. Diatomic molecules containing atoms of the same element (for example,  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{F}_2$ ) are examples of non-polar molecules because they do not have dipole moments. 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 ( $\text{CO}_2$ ) has a linear shape, and its bonds are directed  $180^\circ$  from each other, there is no net dipole moment ( $\mu$ );  $\mu = 0 \text{ D}$ .



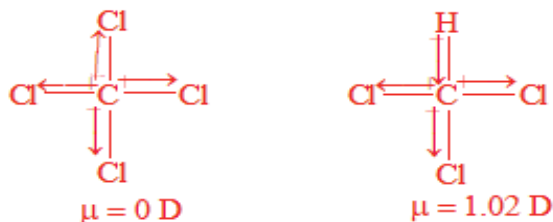
Equal dipole moments with opposite direction  
cancel each other.

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.

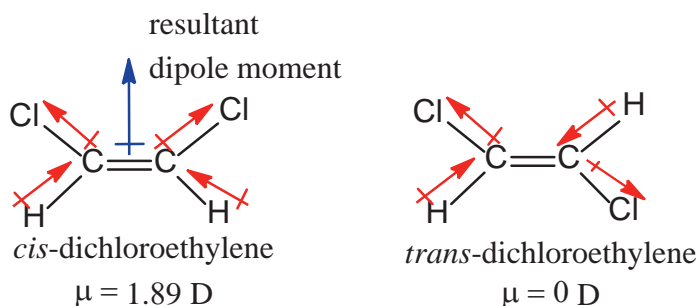


Predict whether ammonia molecule is polar or non-polar and show the direction of bond dipoles and the overall molecular dipole.

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 tetrachloromethane ( $\text{CCl}_4$ ) and trichloromethane ( $\text{CHCl}_3$ ), two  $\text{AB}_4$  type molecules: tetrahedral shape with different polarities. In  $\text{CCl}_4$ , 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  $\text{CHCl}_3$ , 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.



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

- Determine the molecular shape and ideal bond angles in:
  - $\text{COCl}_2$
  - $\text{PCl}_3$
  - $\text{SF}_2$
  - $\text{SO}_4^{2-}$
  - $\text{CS}_2$
- When is the molecular shape and the electron-set arrangement the same?
- Arrange the following  $\text{AF}_n$  species in order of increasing F–A–F bond angles.  $\text{BF}_3$ ,  $\text{BeF}_2$ ,  $\text{CF}_4$ ,  $\text{NF}_3$ ,  $\text{OF}_2$
- In the gas phase, phosphorus pentachloride exists as separate molecules. In the solid phase, however, the compound is composed of alternating  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$  ions. How does the molecular shape change as  $\text{PCl}_5$  solidifies? How does the angle change?
- For molecules of general formula  $\text{AB}_n$  (where  $n > 2$ ), how do you determine if a molecule is polar?

### 2.3.2 Intermolecular Forces in Covalent Compounds



#### Activity 2.17

Form a group of four and discuss the following questions. Then, present your responses to the whole class.

1. Why does a polar liquid generally have a higher normal boiling point than a non-polar liquid of the same molecular mass?
2. State the reason why  $\text{CH}_4$  is a gas at room temperature whereas  $\text{H}_2\text{O}$  is a liquid.
3. Only one of these substances is a solid at standard temperature and pressure (STP):  $\text{C}_6\text{H}_5\text{COOH}$ ,  $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ ,  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3\text{CH}_2)_2\text{O}$ . Which do you think it is and why?
4. Only one of these substances is a gas at STP:  $\text{NI}_3$ ,  $\text{BF}_3$ ,  $\text{PCl}_3$ , and  $\text{CH}_3\text{COOH}$ . Which do you think it is and why?

There are two types of force that hold matter together. These are intramolecular and intermolecular forces. Intramolecular 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 force are those bonds that hold particles (ions or molecules) together. A glass of water for example, contains many molecules of water. These molecules are held together by intermolecular forces, whereas the intramolecular forces hold the two hydrogen atoms to the oxygen atom in each molecule of water. Intermolecular forces are relatively weak as compared to intramolecular 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.



## Activity 2.18

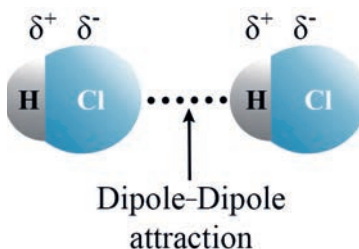
Discuss the following in a group of four, and share your answers with the rest of the class.

1. Name some intermolecular forces.
2. Explain why *cis*-1,2-dichloroethene has a higher boiling point than *trans*-1,2-dichloroethene.
3. Which type of compound exhibit hydrogen bonding?
4. Name the factors on which the strength of dispersion forces of the particles depends.
5. Ice is lighter than water. Why?

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  $\text{Cl}_2$ , and  $\text{Br}_2$ .

### 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 ( $\delta$ ).



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.

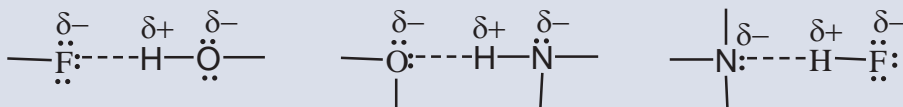
## Hydrogen Bonding

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. The atom sequence that leads to an H bond (*dotted line*) is indicated below. Hydrogen bonds are the strongest type of attractive forces between polar covalent molecules.

What is the difference between hydrogen bonds and chemical bonds?

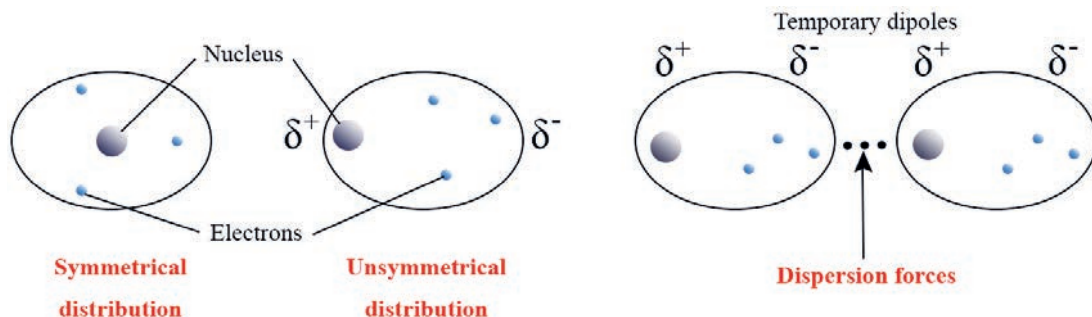
### Example 2.5

Some examples of H-bonding are given below.



## 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 momentary dipoles align the molecules so that the positive end of one molecule is attracted to the negative end of another molecule.



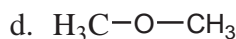
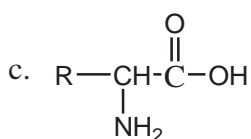
These weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei are called **London forces or dispersion forces**. They are present between all particles (atoms, ions, and molecules). Although dispersion forces are very weak, they make it possible for non-polar molecules like  $\text{CO}_2$ ,  $\text{Cl}_2$ , noble gases, etc., to form liquids and solids.

London forces tend to increase with molecular weight, why do you think this is?

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 ( $36^\circ\text{C}$ ) than its isomers 2-methylbutane ( $28^\circ\text{C}$ ), and 2, 2-dimethylpropane ( $9.5^\circ\text{C}$ ).

### Exercise 2.10

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



- What kinds of intermolecular forces (London, dipole–dipole, hydrogen bonding) would you expect in the following substances?
  - $\text{CHCl}_3$
  - $\text{H}_2\text{O}$
  - $\text{F}_2$
  - $\text{HBr}$
- 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:
  - $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{CH}_2\text{OH}$
  - Hexane or cyclohexane
  - $\text{MgCl}_2$  or  $\text{PCl}_3$
  - $\text{CH}_3\text{NH}_2$  or  $\text{CH}_3\text{F}$
- Compare intermolecular forces with intramolecular bonding.
- Compare the strength and polarity of intermolecular forces.



## 2.4 Metallic Bonding

*At the end of this section, you will be able to:*

- ☞ explain how a metallic bond is formed*
- ☞ explain the properties of metals related to the concept of bonding, and investigate the conductivity, malleability and ductility of some metals and non-metals (Al, Cu, Fe, Sn, Zn, S, C charcoal, C graphite and Si).*

### 2.4.1 Formation of Metallic Bonding



#### Activity 2.19

Form a group and discuss the following questions. Then, share your responses to the whole class.

1. What are the two characteristics that lead to an element being classified as a metal?
2. Which types of bond exist in solid copper?
3. What is delocalization of electrons?

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.

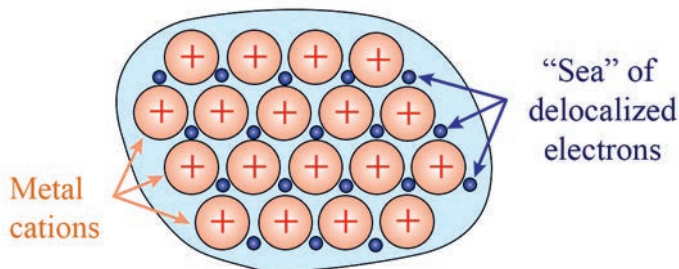
**How is a metallic bond different from that of covalent and ionic bonds?**

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.
2. 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 2.8**. 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 2.8:** 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 Metals and Bonding



#### Activity 2.20

Perform the following activity in groups, and share your results to the rest of the class.

1. Take a piece of metal and a piece of wood of the same size.
2. Let these remain on a table so that both reach room temperature.
3. Place your left hand on the metal and right one on the wood. Which hand feels colder? Why?

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.

**To what do properties of metals like malleability and ductility refer?**

The regularity, but not rigidity, of the metal-ion array and the mobility of the valence electrons account for the physical properties of metals.

We can explain a lot of the properties of metals by thinking about this model of metallic bonding. 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.

**Why do not ionic compounds conduct electricity when they are in solid form? But conductor when they are dissolved in water?**

The electrostatic bonds between the metal ions and the delocalized electrons are hard to break, so metals are strong. Why do metals bend or dent, rather than crack or shatter as ionic solids do when they struck by a hammer? 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. This makes them extremely useful for making things.

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 °C) but doesn't boil until 2403 °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.



### Activity 2.21

Form a group and discuss the following questions, then present your responses to the whole class.

1. List four physical characteristics of a solid metal.
2. Briefly account for the following relative values:
  - a. Lithium boils at 1317 °C and melts at 179 °C. The boiling point is about 1138 °C higher than its melting point.
  - b. The melting point of Li and Be are 180 °C and 1287 °C, respectively.
  - c. The melting point of sodium is 89 °C, whereas that of potassium is 63 °C.

## 2.5 Chemical Bonding Theories

*At the end of this section, you will be able to:*

- ☞ name two chemical bond theories
- ☞ explain the valence bond theory
- ☞ distinguish the Lewis model and the valence bond model
- ☞ discuss the overlapping of orbitals in covalent bond formation
- ☞ explain hybridization
- ☞ show the process of hybridization involved in some covalent molecules
- ☞ draw hybridization diagrams for the formation of  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$  and  $sp^3d^2$  hybrids
- ☞ suggest the kind of hybrid orbitals on the basis of the electron structure of the central atom
- ☞ predict the geometrical shapes of some simple molecules on the basis of hybridization and the nature of electron pairs
- ☞ discuss the hybridization involved in compounds containing multiple bonds
- ☞ explain bond length and bond strength
- ☞ explain molecular orbital theory
- ☞ describe molecular orbital using atomic orbitals
- ☞ describe bonding and anti-bonding molecular orbitals

- ☞ *draw molecular orbital energy level diagrams for homonuclear diatomic molecules*
- ☞ *write the electron configuration of simple molecules using the molecular orbital model*
- ☞ *define bond order and determine the bond order of some simple molecules and molecule-ions*
- ☞ *determine the stability of a molecule or an ion using its bond order; and predict magnetic properties of molecules.*

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.

Which theory explains all aspects of bonding?

### 2.5.1 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  $\text{H}_2$  molecule from two hydrogen atoms. Each atom has the electron configuration  $1s^1$ . As the H atoms approach each other, their  $1s$  orbitals begin to overlap and a covalent bond forms (Figure 2.9). 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 2.9: Atomic orbital overlap and bonding in  $\text{H}_2$

How is the strength of the bond between any two atoms affected by the extent of the overlap between the two orbitals?

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 internuclear 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. Thus, whenever possible, a bond involving  $p$  or  $d$  orbitals will be oriented in the direction that maximizes overlap.

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 2.10). Any other direction would result in less overlap and, thus, a weaker bond.

Note that a single bond consists of two electrons of opposite spin: hence, the two atomic orbitals that give rise to a single bond can have no more than two electrons in total.

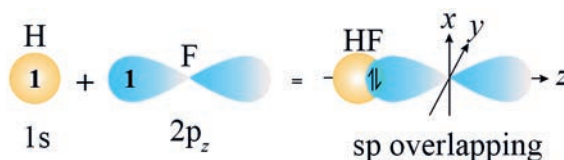


Figure 2.10: Orbital and spin pairing in the formation of a HF molecule

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 2.11).

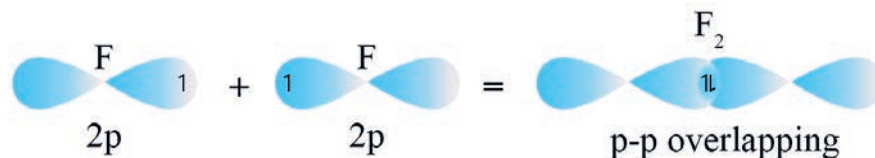


Figure 2.11: Orbital and spin pairing in the formation of a  $F_2$  molecule

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 ( $\sigma$ )**. Such an overlap is sometimes referred to as a **head on, end-to-end, end on or linear overlap**. In Figures 2.9, 2.10 and 2.11, 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.

So far we have considered only sigma bonds, 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 2.12. A bond formed in this way is called  **$\pi$ -bond ( $\pi$ )**.

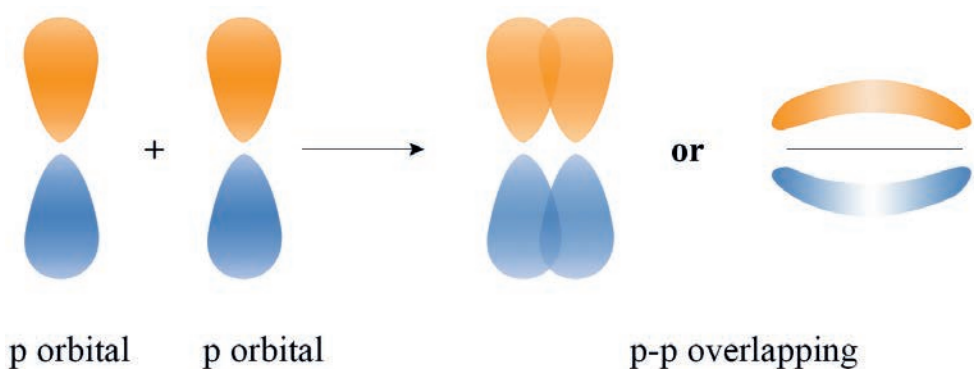


Figure 2.12: Formation of a pi bond ( $\pi$  bond) by the overlap of two half-filled p orbitals that are perpendicular to the internuclear axis

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** ( $\sigma$ ) and **pi** ( $\pi$ ) 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.

Can you give examples of compounds contain multiple bonds?

All of the electron density in a  $\pi$  bond is found in lobes above and below the line connecting the atomic centers: one above and one below the sigma bond axis. One  $\pi$  bond holds two electrons that occupy both regions of the bond. A double bond always consists of one  $\sigma$  and one  $\pi$  bond. The double bond increases electron density between the nuclei. A triple bond consists of one  $\sigma$  and two  $\pi$  bonds.



### Activity 2.22

Answer the following questions in groups, and share your answers with the rest of the class.

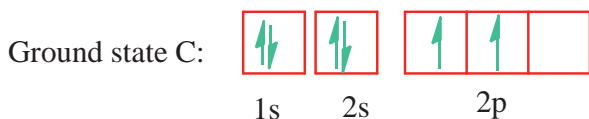
1. Which bond is stronger: sigma ( $\sigma$ ) or pi ( $\pi$ )? Why?
2. Compare the bond strength and length of single, double, and triple bonds.



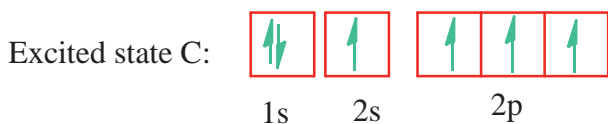
## Hybridization of Orbitals

How many covalent bonds is a carbon atom supposed to form? How many covalent bonds does carbon actually form? This discrepancy and molecular structure, specifically bond angle, can be explained using the idea of **hybridization**. It 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.



One can predict the simplest hydrocarbon molecule to be  $\text{CH}_2$ , by overlapping the two unpaired electrons from two H atoms with the two unpaired electrons of carbon. However, experiment shows that  $\text{CH}_2$  is not a stable molecule. The simplest stable hydrocarbon is **methane**,  $\text{CH}_4$ . 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 H–C–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  $\sigma$  bonds comprise a double bond.
2. A triple bond consists of one  $\pi$  bond and two  $\sigma$  bonds.
3. Bonds formed from atomic s orbitals are always  $\sigma$  bonds.
4. A  $\pi$  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.

### 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 orbital 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  $\text{BeCl}_2$  molecule has an sp hybridization.

$\text{BeCl}_2$ : The ground state electronic configuration of Be is  $1s^2 2s^2$ . In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its bivalency **Figure 2.13**. One 2s and one 2p-orbital gets hybridized to form two sp hybridized orbitals as shown in **Figure 2.14**.

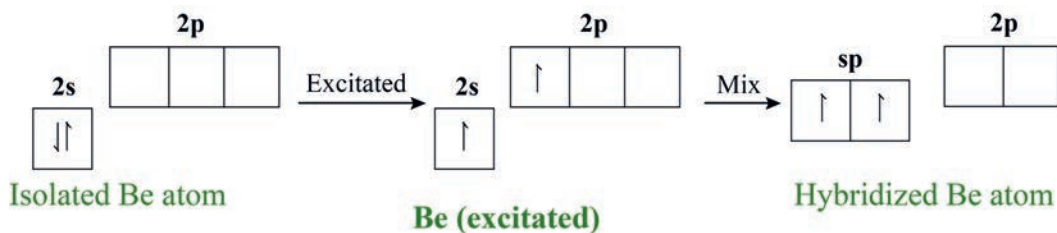


Figure 2.13: Excitation of Be 2s electrons and sp hybrid orbitals formation

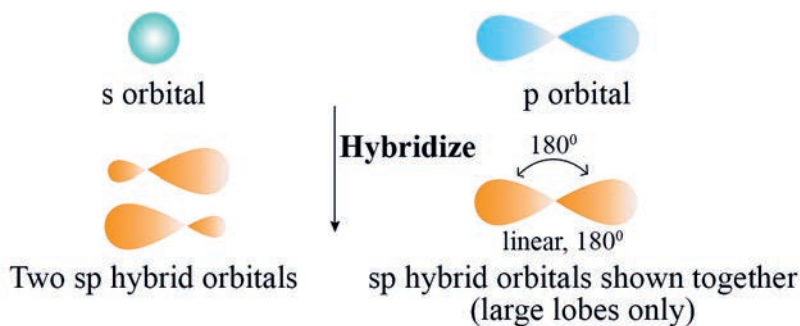


Figure 2.14: The formation of two equivalent  $sp$  hybrid orbitals in Be

These two  $sp$  hybrid orbitals face opposite directions, forming an angle of  $180^\circ$ . Each of the  $sp$  hybridized orbitals overlaps with the  $2p$ -orbital of chlorine axially and forms two  $\text{BeCl}$  sigma bonds. This is shown in Figure 2.15.

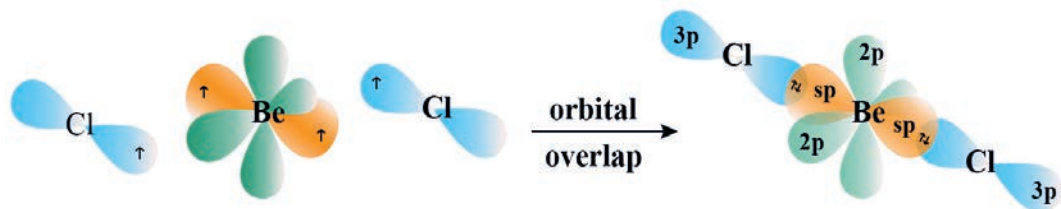


Figure 2.15: The  $sp$  hybrid orbitals in gaseous  $\text{BeCl}_2$ ,  $sp^2$  hybrid orbitals

### $sp^2$ hybridization

In this hybridization there is involvement of one  $s$  and two  $p$ -orbitals in order to form three equivalent  $sp^2$  hybridized orbitals. For example, in  $\text{BCl}_3$  molecule, the ground state electronic configuration of central boron atom is  $1s^2 2s^2 2p^1$ . In the excited state, one of the  $2s$  electrons is promoted to vacant  $2p$  orbital (Figure 2.16) as a result boron has three unpaired electrons. These three orbitals (one  $2s$  and two  $2p$ ) hybridize to form three  $sp^2$  hybrid orbitals as shown in Figure 2.16.

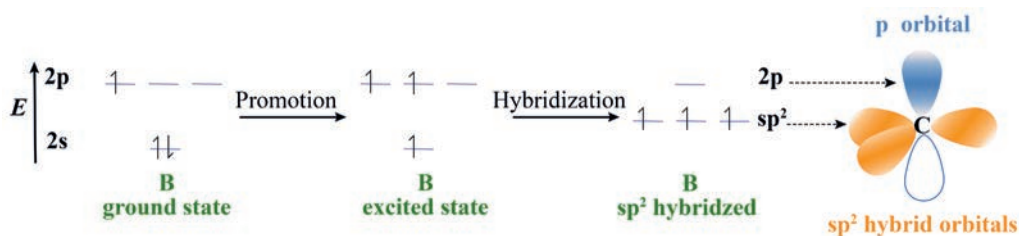


Figure 2.16: Excitation of boron  $2s$  electrons and  $sp^2$  hybrid orbitals formation

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  $\text{BCl}_3$  (Figure 2.17), the geometry is *trigonal planar* with ClBCl bond angle of  $120^\circ$ .

What is the percent of s-character and p-character in each  $sp^2$  hybrid orbital?

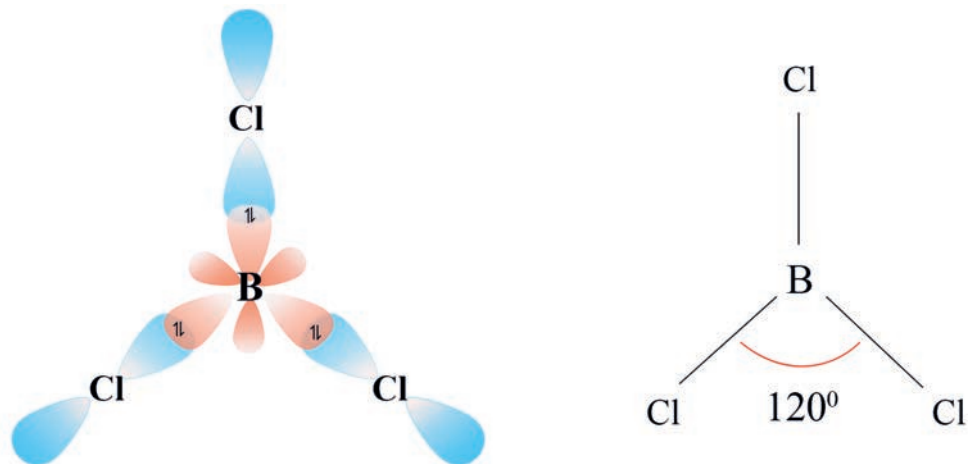


Figure 2.17:  $sp^2$  hybrid orbitals and bonding in  $\text{BCl}_3$

### $sp^3$ hybridization

$sp^3$  type of hybridization can be explained by taking the example of  $\text{CH}_4$  molecule in which there is mixing of one s-orbital and three p-orbitals (Figure 2.18) of the valence shell to form four  $sp^3$  hybrid orbital of equivalent energies and shape.

Can you determine the percent of s-character and p-character in each  $sp^3$  hybrid orbital?

The four  $sp^3$  hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between  $sp^3$  hybrid orbital is  $109.5^\circ$  as shown in Figure 2.19.

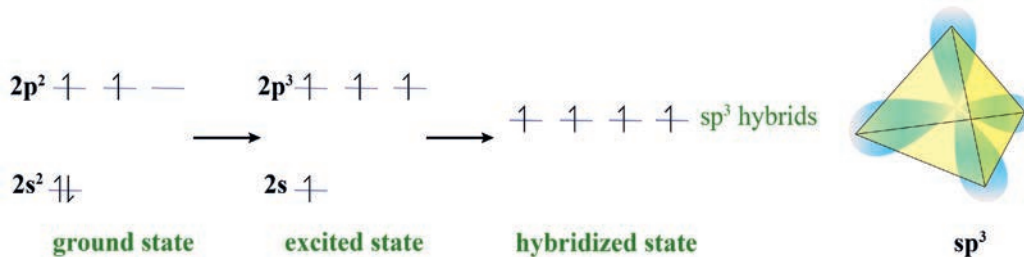


Figure 2.18: Excitation of carbon  $2s$  electrons and  $sp^3$  hybrid orbitals formation

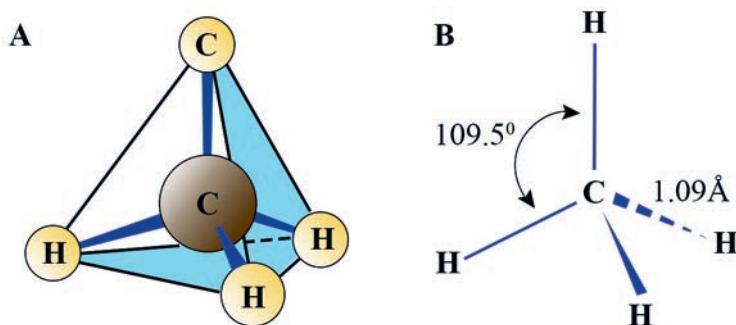


Figure 2.19:  $sp^3$  hybrid orbitals and bonding in methane

The structure of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules can also be explained with the help of  $sp^3$  hybridization. In  $\text{NH}_3$ , the valence shell (outer) electronic configuration of nitrogen in the ground state is  $2s^2 2p_x 2p_y 2p_z$ . In the formation of  $\text{NH}_3$ , one  $2s$  orbital and three  $2p$  orbitals of nitrogen are mixed up forming four hybrid orbitals ( $sp^3$ ) of equivalent energy. One of the  $sp^3$  hybrid orbitals has a lone pair of electrons and the other three  $sp^3$  orbitals are half-filled. These three half-filled hybrid orbitals overlap with  $1s$  orbitals of hydrogen atoms to form three N–H sigma ( $\sigma$ ) 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  $107^\circ$  from  $109.5^\circ$ . The geometry of such a molecule will be pyramidal as shown in Figure 2.20.

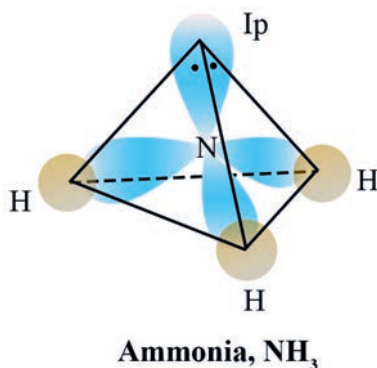


Figure 2.20:  $sp^3$  hybrid orbitals and bonding in  $\text{NH}_3$

In the case of  $\text{H}_2\text{O}$  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  $104.5^\circ$  from  $109.5^\circ$  (Figure 2.21) and the molecule thus acquires a *V-shape* or *angular geometry*.

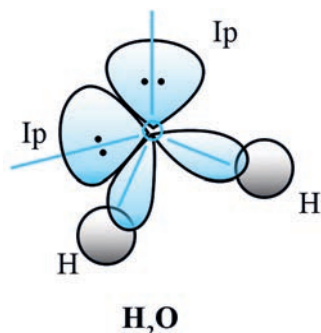


Figure 2.21:  $sp^3$  hybrid orbitals and bonding in  $H_2O$

Why is the HOH bond angle in water less than the HNH bond angle in  $NH_3$ ?

### 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.

Do you expect hybrid orbitals formation by mixing 3p, 3d and 4s orbitals? Explain it.



### Group Assignment 2.2

Summarize in a table the shapes of molecules and ions, types of hybridization involving s, p and d orbitals, the number of atomic orbitals engaged in the hybridization, and give examples.

#### 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 2.22a.

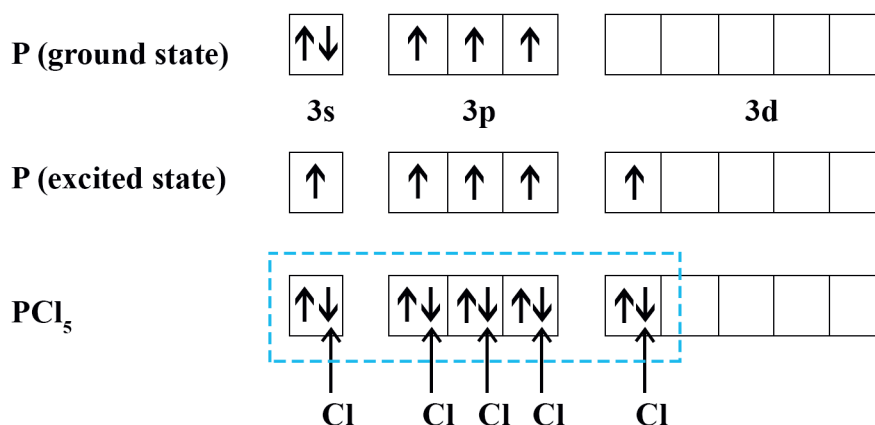


Figure 2.22 ( a ):  $sp^3d$  hybrid orbitals filled by electron pairs donated by five Cl atoms

Now the five orbitals (i.e., one s, three p and one d orbitals) are available for hybridization to yield a set of five  $sp^3d$  hybrid orbitals which are directed towards the five corners of a **trigonal bipyramidal** as in Figure 2.22b.

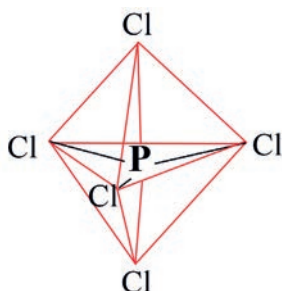


Figure 2.22 ( b ): Trigonal bipyramidal geometry of PCl<sub>5</sub> molecule

Note that all the bond angles in **trigonal bipyramidal** geometry are not equivalent. In PCl<sub>5</sub>, the five  $sp^3d$  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  $120^\circ$  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  $90^\circ$  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 PCl<sub>5</sub> molecule more reactive.

ii. Formation of SF<sub>6</sub> (sp<sup>3</sup>d<sup>2</sup> hybridization):

In SF<sub>6</sub> the central sulphur atom has the ground state outer electronic configuration 3s<sup>2</sup>3p<sup>4</sup>. In the excited state the available six orbitals i.e., one s, three p and two d orbitals are singly occupied by electrons (Figure 2.23a). These orbitals hybridize to form six new sp<sup>3</sup>d<sup>2</sup> hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF<sub>6</sub>. These six sp<sup>3</sup>d<sup>2</sup> hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus, SF<sub>6</sub> molecule has a regular octahedral geometry as shown in Figure 2.23b.

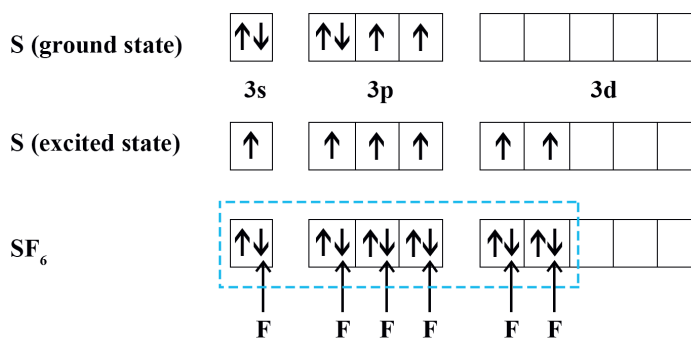


Figure 2.23 ( a ): sp<sup>3</sup>d<sup>2</sup> hybridization

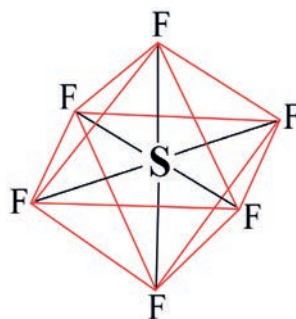


Figure 2.23 ( b ): Octahedral geometry of SF<sub>6</sub> molecule



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:

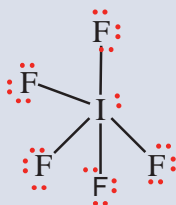
1. Write a reasonable Lewis structure for the chemical.
2. Use VSEPR theory to predict the electron-set arrangement of the central atom.
3. Select the hybridization scheme that corresponds to the VSEPR prediction.
4. Describe the orbital overlap.

### Example 2.6

Describe a hybridization scheme for the central atom of iodine pentafluoride,  $\text{IF}_5$ .

**Solution:**

- a. The reasonable Lewis structure for  $\text{IF}_5$  is



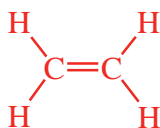
- VSEPR predicts an octahedral electron-set arrangement for six electron pairs ( $\text{AB}_5\text{E}$  type)
- The hybridization scheme corresponding to **octahedral** electron arrangement is  $\text{sp}^3\text{d}^2$
- The six  $\text{sp}^3\text{d}^2$  hybrid orbitals are directed to the corners of 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  $90^\circ$ .

## Exercise 2.13

1. 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.
2. Describe a hybridization scheme for the central atom and molecular geometry of the triiodide ion,  $I_3^-$ .

## 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 have already discussed that multiple bonds consist of  $\sigma$  and  $\pi$  bonds. Now, we will consider how we visualize these components and how they relate to hybrid orbitals. We will discuss here the *ethene*,  $C_2H_4$ , and *acetylene*,  $C_2H_2$  molecules, however *pi* bonds are also present in other molecules such as  $N_2$ ,  $SO_2$ ,  $NO_3$ , etc. 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  $\sigma$  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 2.24). These orbitals form the C–H single bonds and the  $\sigma$  bond in the C = C double bond (Figure 2.25). The  $\pi$  bond in the C = C double bond results from the overlap of the third (remaining) 2p orbital on each carbon atom that is not involved in hybridization. This unhybridized *p* orbital (lobes shown in red and blue in Figure 2.25 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 internuclear axis and form a  $\pi$  bond.

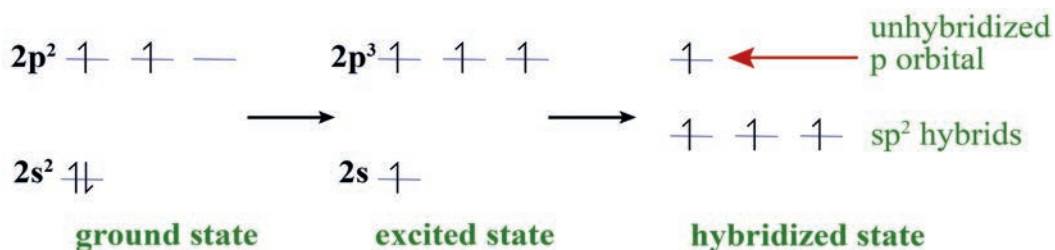


Figure 2.24:  $sp^2$  hybridization of each carbon atom in ethene

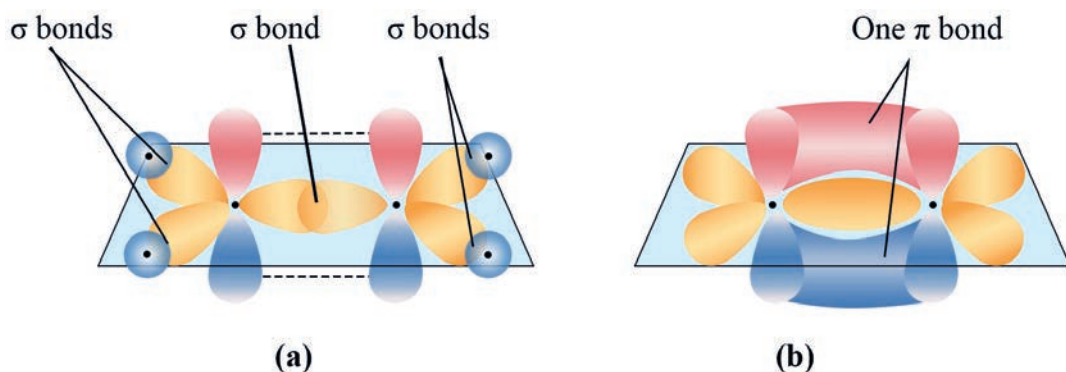


Figure 2.25: Bond formation in the ethene molecule,  $C_2H_4$ : (a) five  $\sigma$  bonds and (b) one  $\pi$  bond

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  $\pi$  bond.

Why does rotation around single ( $\sigma$ ) bond occur easily, but is much more difficult for multiple bonds?

In molecules with  $sp$  hybrid orbitals, two unhybridized p orbitals remain on the atom (Figure 2.26). 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 unhybridized p orbitals at perpendicular angles (Figure 2.26). The  $sp$  hybrid orbitals of the two carbon atoms overlap end to end to form a  $\sigma$  bond between the carbon atoms (Figure 2.27). The remaining  $sp$  orbitals form  $\sigma$  bonds with two hydrogen atoms. The two unhybridized p orbitals per carbon are positioned such that they overlap side by side and, hence, form two  $\pi$  bonds. The two carbon atoms of acetylene are bound together by one  $\sigma$  bond and two  $\pi$  bonds, giving a ***triple bond***.

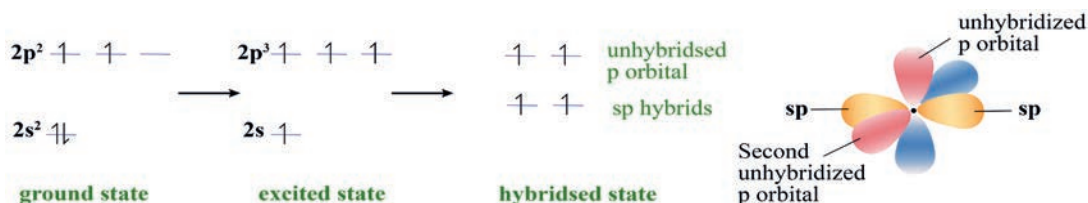


Figure 2.26:  $sp$  hybridization of each carbon atom and the two linear  $sp$  hybrid orbitals of a carbon atom in acetylene

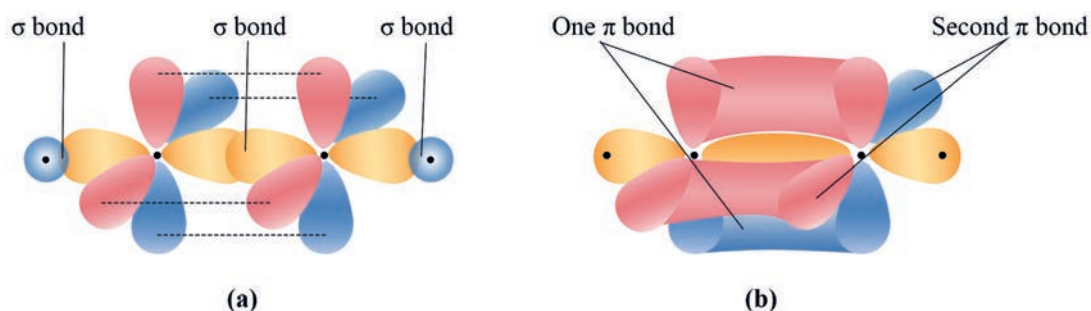


Figure 2.27: (a) The formation of  $\sigma$  bonds in an acetylene molecule,  $C_2H_2$ , and (b)  $\pi$  bonds

### Exercise 2.14

- Describe the hybridization of the central atoms N and S in molecules and the molecular geometry of:
  - $NO_2$
  - $SO_3$
- Discuss the bonding in ammonium and sulphate ions: predict the ideal bond angles, bond length, shape of the ions, and the number of  $\sigma$  and  $\pi$  bonds.
- 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).

## 2.5.2 Molecular Orbital Theory (MOT)

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).

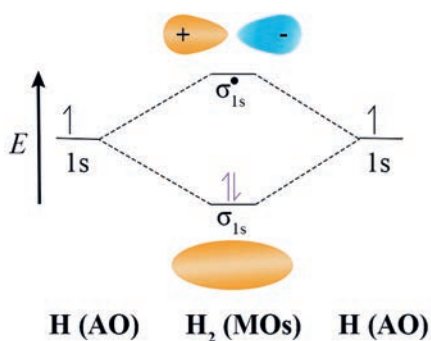
Which theory (VBT or MOT) perfectly explains all aspects of bonding?

### 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 **antibonding molecular orbital**. In antibonding 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 antibonding orbital is increased compared with that of the two isolated atomic orbitals. When two atomic orbitals overlap end-to-end, they form two  $\sigma$  MOs. Consider the  $H_2$  molecule, which has two H atoms and therefore two  $1s$  AOs. The two  $1s$  atomic orbitals combine (Figure 2.28) to produce two  $\sigma$  MOs, which differ in energy and location. One of the  $\sigma$  MOs is a bonding orbital, denoted  $\sigma_{1s}$ , the other is an anti-bonding orbital denoted  $\sigma_{1s}^*$ . 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  $\sigma_{1s}^*$  MO has a higher energy. **What is the advantage of VBT compared with that of MOT?**

## 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  $\text{H}_2$  will go into the lower energy orbital denoted by  $(\sigma_{1s})^2$ . There are no more electrons in  $\text{H}_2$  so the  $\sigma_{1s}^*$  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 2.28** is the molecular orbital diagram for  $\text{H}_2$ .



**Figure 2.28: Molecular orbital diagram and bonding in the  $\text{H}_2$  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 antibonding MOs, divided by two:

$$\text{Bond order} = \frac{1}{2} \left[ \left( \begin{array}{c} \text{Number of } e^- \text{ in} \\ \text{bonding MOs} \end{array} \right) - \left( \begin{array}{c} \text{Number of } e^- \text{ in} \\ \text{anti-bonding MOs} \end{array} \right) \right]$$

Thus, for  $\text{H}_2$ , 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.

**Why is MOT better than VBT in explaining covalent bond formation?**

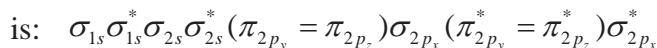
**Exercise 2.15**

1. Draw molecular orbital energy diagrams for:

- a.  $C_2^-$       b.  $C_2$       c.  $C_2^+$

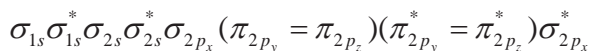
The order of energy of molecular orbitals has been determined mainly from spectroscopic data.

a. In simple homonuclear diatomic molecules (total electrons = 14 or less) the order is:



b. For simple homonuclear diatomic molecules (total electrons greater than 14) the

$(\pi_{2p_y} = \pi_{2p_z})$  comes after  $\sigma_{2p_x}$  and the order is:



Note that the  $2p_y$  atomic orbital give  $\pi$  bonding and  $\pi$  antibonding ( $\pi^*$ ) MOs of the same energy as those produced from  $2p_z$  orbitals. The  $\pi_{2p_y}$  and  $\pi_{2p_z}$  orbitals are said to be double degenerate, and similarly  $\pi_{2p_y}^*$  and  $\pi_{2p_z}^*$  are double degenerate. A similar arrangement of MOs exists from  $\sigma_{3s}$  to  $\sigma_{3p_x}^*$ , but energies are known with less certainty.

**Example 2.7**

Use the molecular orbital theory to derive the electron configuration of:

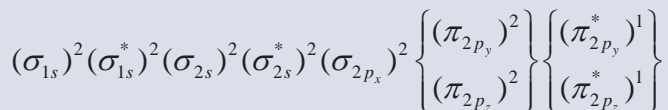
- a.  $H_2^+$       b.  $Li_2$       c.  $He_2^+$       d.  $O_2$

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  $\sigma_{1s}^1$ .
- b.  $Li_2$  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.

- c.  $\text{He}_2^+$  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  $\text{He}_2^+$  should exist, and it has been observed spectroscopically.
- d.  $\text{O}_2$  molecule. Each oxygen has eight electrons, making a total of sixteen for the molecule. These are arranged:



The antibonding  $\pi_{2p_y}^*$  and  $\pi_{2p_z}^*$  orbitals are singly occupied in accordance with **Hund's rule**. As in previous examples, the inner shell does not participate in bonding and the  $\pi_{2p_y}$  and  $\pi_{2p_z}$  bonding and antibonding 2s orbitals cancel each other. A  $\sigma$  bond results from the filling of  $(\sigma_{2p_x})^2$ . Two half  $\pi$  bonds arise from bonding and antibonding.

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

### Exercise 2.16

- 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.  $\text{He}_2$  b.  $\text{Be}_2$  c.  $\text{B}_2$  d.  $\text{C}_2$  e.  $\text{N}_2$
- Use the MO theory to predict the bond order and the number of unpaired electrons in  $\text{O}_2^{2-}$ ,  $\text{O}_2^-$ ,  $\text{O}_2^+$ , NO and CO.

### 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.

Can you predict magnetic properties of diatomic molecules by employing VBT?



The antibonding  $\pi_{2py}$  and  $\pi_{2pz}$  orbitals for  $O_2$  are singly occupied in accordance with Hund's rule. Unpaired electrons give rise to **paramagnetism**. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic. The MO theory successfully predicts the **paramagnetism** of  $O_2$ , a fact not even thought of with the VB representation of the oxygen molecule ( $O = O$ ).

### Exercise 2.17

1. What is the bond order for  $CN^-$ ,  $CN$  and  $CN^+$ ?
2. Which homonuclear diatomic molecules from the second period elements, besides  $O_2$ , should be paramagnetic?

## 2.6 Types of Crystal

*At the end of this section, you will be able to:*

- ☞ *define a crystal*
- ☞ *name the four types of crystalline solid and give examples*
- ☞ *mention the types of attractive force that exist within each type of crystalline solid*
- ☞ *describe the properties of each type of crystalline solid*
- ☞ *build a model of sodium chloride crystal structure.*

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. **Are metals crystalline or amorphous solids?**

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.

**Do you expect similar repetitive pattern also in amorphous solids?**

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 (Figure 2.29).

Does an ionic bonding have intermolecular or intramolecular bonding?

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 inter-ionic forces, which create a high lattice energy. Ionic solids have high melting points, an indication of the strong attraction force holding the ions together.

Why don't ionic solids conduct electricity? How can ionic compounds conduct electricity when they are in a molten state or dissolved in water? Can you give some examples of ionic solids we use in everyday life?

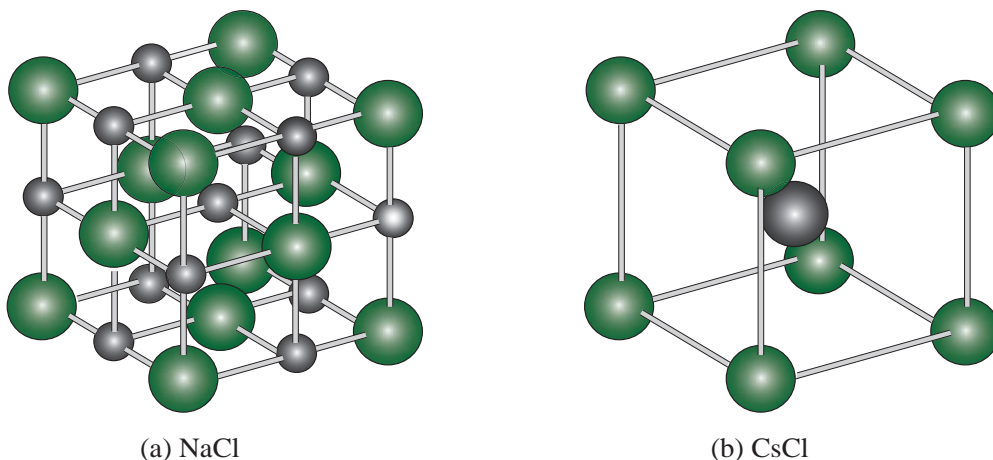


Figure 2.29: Ball-and stick diagrams of the unit cells of (a) NaCl(s) and (b) CsCl(s)



### Group Assignment 2.3

1. Using balls and sticks of any material or any other modelling material, build a model of crystal sodium chloride.
2. Explain why ice, which is a crystalline solid, has a melting temperature of  $0^{\circ}\text{C}$ , whereas butter, which is an amorphous solid, softens over a range of temperatures.

## 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. Compare the strength of intermolecular forces with covalent and ionic bonds.

Why do molecular crystals have much lower melting points than ionic, metallic and network covalent solids?

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.

Can you give some examples of molecular crystals we use in everyday life?

## 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 (Figure 2.30).

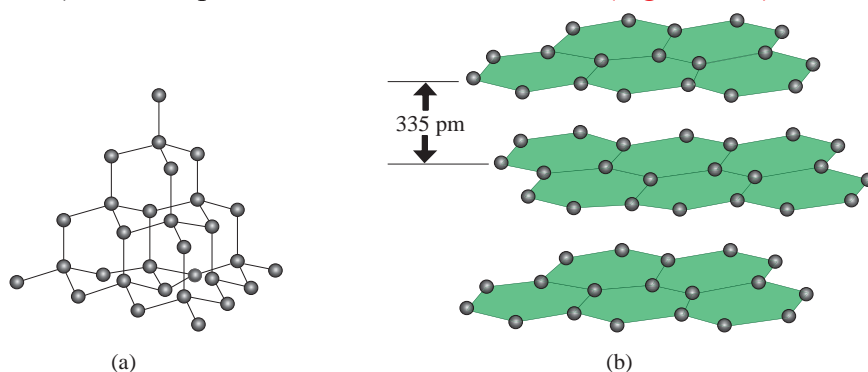


Figure 2.30: The structures of (a) diamond and (b) graphite

Describe the basic differences in properties of graphite and diamond.

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 neighbours. These crystals are usually hard, non-conductors 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

- Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:
  - $\text{SiO}_2$
  - KCl
  - Cu
  - $\text{CO}_2$
  - C (diamond)
- 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



## 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.

## CHECKLIST

## KEY TERMS

- ⌘ *Anion*
- ⌘ *Atomic orbital*
- ⌘ *Covalent bond*
- ⌘ *Crystal*
- ⌘ *Delocalization of electrons*
- ⌘ *Dipole*
- ⌘ *Dipole moment*
- ⌘ *Double bond*
- ⌘ *Electric charge*
- ⌘ *Ionic bond*
- ⌘ *Ionization*
- ⌘ *Kinetic energy*
- ⌘ *Lattice energy*
- ⌘ *London dispersion forces*
- ⌘ *Molecule*
- ⌘ *Molecular orbital*
- ⌘ *Noble gases*
- ⌘ *Potential energy*
- ⌘ *Single bond*
- ⌘ *Substance*
- ⌘ *Triple bond*
- ⌘ *Valence bond theory*
- ⌘ *Valence electron*
- ⌘ *Van der Waals force*

## REVIEW EXERCISE

## Part I: Multiple Choice Questions:

Choose the correct answer from the given alternatives.

- Which of the following is not a property of ionic bonds?
  - loss of electrons
  - gain of electrons
  - sharing of electrons
  - transferring of electrons
- Which one of the following does not comply with the octet rule?
  - $\text{PCl}_3$
  - $\text{CBr}_4$
  - $\text{NF}_3$
  - $\text{AsF}_5$
- A  $\pi$ (pi) bond is the result of the:
  - overlap of two s orbitals
  - overlap of an s and a p orbital
  - overlap of two p orbitals along their axes
  - sidewise overlap of two parallel p orbitals
- The maximum number of hydrogen bonds that a molecule of water can have is:
  - 1
  - 2
  - 3
  - 4
- Which of the following is planar?
  - $\text{NO}_3^-$
  - $\text{H}_3\text{O}^+$
  - $\text{SO}_3^{2-}$
  - $\text{PF}_3$
- Among the following mixtures dipole–dipole as the major interaction is present in:
  - benzene and ethanol
  - acetonitrile and acetone
  - KCl and water
  - benzene and carbon tetrachloride
- The main axis of a diatomic molecule is Z. Atomic orbitals  $p_x$  and  $p_y$  overlap to form which of the following orbital?
  - $\pi$ -molecular orbital
  - $\sigma$ -molecular orbital
  - $\delta$ -molecular orbital
  - no bond will form
- The structure of  $\text{IF}_7$  is:
  - pentagonal bipyramid
  - square pyramid
  - trigonal bipyramid
  - octahedral
- In which of the following molecule is a co-ordinate covalent bond present?
  - $\text{F}_2$
  - $\text{O}_3$
  - $\text{NH}_3$
  - $\text{CCl}_4$

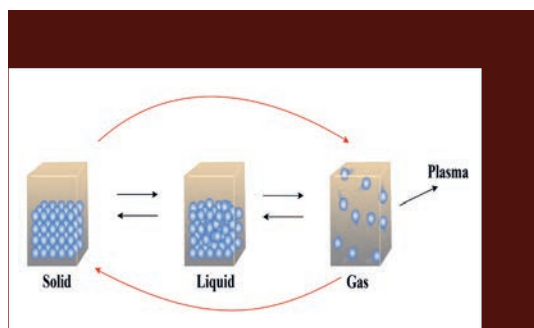


10. In which of the following compounds are 8 valence electrons present in every atom?
- a.  $\text{IF}_7$                       b.  $\text{C}_2\text{H}_4$                       c.  $\text{SiF}_4$                       d. KH
11. Molecules are held together in a crystal by:
- a. hydrogen bonds                      c. Van der Waal's attraction  
b. electrostatic attraction                      d. dipole-dipole attraction
12. Find the molecule with the maximum dipole moment:
- a.  $\text{CH}_4$                       b.  $\text{NH}_3$                       c.  $\text{CO}_2$                       d.  $\text{NF}_3$
13. Which of the molecules does not have a permanent dipole moment?
- a.  $\text{SO}_3$                       b.  $\text{SO}_2$                       c.  $\text{H}_2\text{S}$                       d.  $\text{CS}_2$
14. The F-S-F bond angles in  $\text{SF}_6$  are \_\_\_\_\_.
- a.  $109^\circ 28'$                       b.  $120^\circ$  only                      c.  $90^\circ$  and  $120^\circ$                       d.  $90^\circ$  and  $180^\circ$
15. A neutral molecule having the general formula  $\text{AB}_3$  has two unshared pair of electrons on A. What is the hybridization of A?
- a. sp                      b.  $\text{sp}^2$                       c.  $\text{sp}^3$                       d.  $\text{sp}^3\text{d}$

### Part II: Answer the following questions

16. Write Lewis dot symbols for the following atoms and ions: Mg, Na, B, N, Br, Be,  $\text{Li}^+$ ,  $\text{Cl}^-$ ,  $\text{O}^{2-}$ ,  $\text{Mg}^{2+}$  and  $\text{N}^{3-}$
17. List four major difference between sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds.
18. Which one is stronger:  $\sigma$ -bond or  $\pi$ -bond? Why?
19. Explain why a  $\text{BeH}_2$  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  $\text{CH}_4$  is square planar with the four H atoms at the corners of the square and C atom at its center. Explain why  $\text{CH}_4$  is not square planar?
23. Sketch the bond moments and resultant dipole moments in the following molecules:  $\text{H}_2\text{O}$ ,  $\text{PCl}_3$ ,  $\text{NH}_3$ ,  $\text{NF}_3$
24. Write the resonance structures for  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{NO}_3^-$ . S

# UNIT 3



## PHYSICAL STATES OF MATTER

### Unit Outcomes

*At the end of this unit, you will be able to:*

- ☞ *discuss the kinetic molecular theory and properties of the three physical states of matter*
- ☞ *explain the behavior of gases by using the variables volume, temperature, pressure and number of moles*
- ☞ *distinguish these terms: ideal gas, diffusion, evaporation, boiling, condensation, vapour pressure, boiling point, molar heat of vaporization, molar heat of condensation, melting, fusion, sublimation, melting point, freezing point, molar heat of fusion, and molar heat of solidification*
- ☞ *analyse the gas laws*
- ☞ *develop skills in solving problems to which the gas laws apply*
- ☞ *perform activities to illustrate gas laws*
- ☞ *carryout experiments to determine the boiling points of liquids*
- ☞ *demonstrate an experiment to show phase changes.*
- ☞ *describe scientific enquiry skills along this unit: inferring, predicting, classifying, comparing and contrasting, communicating, asking questions, and making generalizations.*






## Start-up Activity

Form groups and discuss the following questions. Share your ideas with the rest of the class.

1. During rainy season sometimes we observe ice rain. What is the source of this ice rain (precipitation)? What makes it different from water?
2. If you put some water in an evaporating dish and gently heat for some time, what kind of change do you observe?

## 3.1 Introduction

*At the end of this section, you will be able to:*

-  describe the physical states of matter
-  give examples for each of the three physical states of matter
-  compare and contrast the three physical states of matter.



### Activity 3.1

Discuss the following questions in pairs and present your discussion to the class.

1. Why do substances exist in different physical states; for example, water (liquid), sugar (solid), and  $\text{CO}_2$  (gaseous) states at room temperature?
2. What happens to ice if you place it in the open air for some time? Why?

From your previous lessons you will remember that all objects around us are called **matter**. 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**.

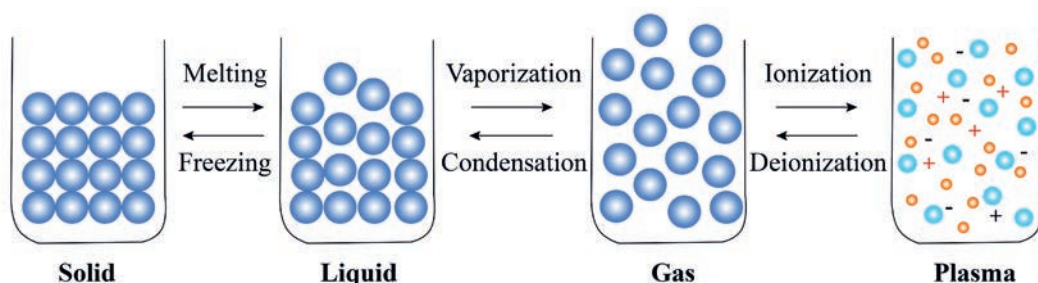


Figure 3.1: A particle diagram of a solid, liquid, gas and plasma

### 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?

## 3.2 Kinetic Theory and Properties of Matter

*At the end of this section, you will be able to:*

- ☞ state the kinetic theory of matter
- ☞ explain the properties of matter in terms of the kinetic theory.



### Activity 3.2

Form a group and perform the following tasks. Present your findings to the class.

1. Select any three different substances; one existing in the solid state, the second in the liquid state, and the third in the gaseous state at room temperature. Use the following table to explain the motion, distance, and attraction between particles.

Substance	Motion of particles	Distance between particles	Attraction between particles
1			
2			
3			

2. In which state of matter do the particles possess the highest kinetic energy?

### 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



#### Activity 3.3

Attempt to answer the following question independently, and share your ideas with a friend who sits next to you.

Compare and contrast the density and compressibility of a solid, liquid, and gaseous forms of a substance using particle model diagrams.

As it has been earlier discussed, matter can exist as a solid, liquid, and gas. The properties of these 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 interparticle 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. |

## 3.3 The Gaseous State

*At the end of this section, you will be able to:*

-  explain the assumptions of the kinetic molecular theory of gases
-  describe the properties of gases using the kinetic molecular theory
-  describe the behavior of gases by using the variables  $V$  (volume),  $T$  (temperature),  $P$  (pressure) and  $n$  (number of moles)
-  state Boyle's law
-  perform an activity to show changes in volume and pressure of gases to illustrates Boyle's law
-  apply Boyle's law in solving problems



- ☞ *state Charles' law*
- ☞ *conduct an activity to show changes in volume and temperature of gases to illustrate Charles' law*
- ☞ *apply Charles' law in solving problems*
- ☞ *state Gay-Lussac's law*
- ☞ *use Gay-Lussac's law in solving problems*
- ☞ *derive the combined gas law equation from Boyle's law, Charles' law, and Gay-Lussac's law*
- ☞ *use the combined gas law to calculate changes in volume, pressure or temperature*
- ☞ *define an ideal gas*
- ☞ *derive an ideal gas equation from Boyle's law, Charles' law and Avogadro's law*
- ☞ *compare the nature of real gases with ideal gases*
- ☞ *solve problems related to the ideal gas equation*
- ☞ *define diffusion*
- ☞ *state Graham's law of diffusion*
- ☞ *carry out an activity to compare the rate of diffusion of two different gases*
- ☞ *apply Graham's law of diffusion in solving problems.*



### Activity 3.4

In pairs, discuss the following points and share your ideas to the whole class

Consider three water samples that are taken in containers: A, B, and C. The three water samples are kept at different temperatures:  $120\text{ }^{\circ}\text{C}$ ,  $20\text{ }^{\circ}\text{C}$ , and  $-10\text{ }^{\circ}\text{C}$ , respectively, and under constant atmospheric pressure.

- a. Which sample molecule has the highest kinetic energy?
- b. Which sample has the greatest density?
- c. Which sample has the most regular arrangement of molecules?

### 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.
4. The average kinetic energy of gas particles is proportional to the temperature of the gas in kelvins. This means that as the temperature increases, the particles move faster and therefore have more energy. The mathematically expressed as:

$$KE = \frac{1}{2}mv^2 \quad (3.1)$$

Where **KE** is kinetic energy, *m* is mass and *v* is velocity of gas molecules. According to this formula different molecules have different velocities and, therefore, have different kinetic energies.

Generally, the gaseous state is characterized by the following physical properties:

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than solids and liquids.
- The volume and the shape of gases are not fixed. These take the volume and shape of the container.
- Gases mix evenly and completely.

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behavior is governed by similar general laws, which were discovered as a result of their experimental studies. These laws have relationships between measurable properties of gases. Some of these properties such as pressure, volume, temperature and mass are very important. Interdependence of these variables leads to the gas laws.

### 3.3.2 The Gas Laws



#### Activity 3.5

Discuss the following in terms of the gas laws with a partner who sits next to you. Present your conclusion to the class.

- The increase in pressure in a car tire on a hot day.
- The loud noise heard when a light bulb shatters.

The gas laws are the result of various research conducted for several centuries on the physical properties of gases. The first reliable measurement on the properties of gases was made by Robert Boyle in 1662 (an Anglo-Irish scientist). The observation of Boyle's and other scientists led to the development of the gas laws. The gas laws express mathematical relationships between the volume, temperature, pressure, and quantity of a gas.

**Pressure:** The pressure exerted by a gas sample is defined as the force per unit area that results from the collisions of gas particles with surrounding surfaces.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \quad (3.2)$$

Pressure is one of the measurable properties of gases. Thus, the pressure of a gas can be expressed in unit of atmosphere, Pascal, torr, millimeter of mercury. The SI unit of pressure is Pascal (Pa).

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

$$1 \text{ atm} = 760 \text{ mmHg} = 76 \text{ cmHg} = 760 \text{ torr} = 101,325 \text{ Pa} = 101.325 \text{ kPa}$$

**Volume:** Volume is the space occupied by a substance. The SI unit of volume is the cubic meter ( $\text{m}^3$ ). Volume is also expressed in cubic centimeter ( $\text{cm}^3$ ) and cubic decimeter ( $\text{dm}^3$ ). Other common units of volume are milliliter (mL) and liter (L).

$$1 \text{ cm}^3 = (1 \times 10^{-2} \text{ m})^3 = 1 \times 10^{-6} \text{ m}^3$$

$$1 \text{ dm}^3 = (1 \times 10^{-1} \text{ m})^3 = 1 \times 10^{-3} \text{ m}^3 = 1 \text{ L}$$

A liter is equivalent to one cubic decimeter, as follows:

$$1 \text{ L} = 1000 \text{ mL} = 1000 \text{ cm}^3 = 1 \text{ dm}^3$$

**Temperature:** Temperature is the degree of hotness or coldness of a body. Three temperature scales are commonly used. These are  $^{\circ}\text{F}$  (degrees Fahrenheit),  $^{\circ}\text{C}$  (degrees Celsius) and **K** (Kelvin). In calculations, the Kelvin scale is usually used. The three units are inter-converted by Equations 3.3 and 3.4:

$$\text{K} = ^{\circ}\text{C} + 273 \quad (3.3)$$

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) \frac{5}{9} \quad (3.4)$$

### Exercise 3.3

Convert the following:

- 500 mmHg into atm, torr, and cmHg
- 100  $\text{dm}^3$  into mL,  $\text{cm}^3$ , L,  $\text{m}^3$
- 54  $^{\circ}\text{C}$  into K and  $^{\circ}\text{F}$ .

**Molar Volume and Standard Conditions:** The conditions of a pressure of 1 atmosphere and a temperature of 0  $^{\circ}\text{C}$  (273 K) are called **standard temperature and pressure** (STP) for gases. At STP the volume of one mole of any gas is 22.4 liters. This volume is known as **the molar volume of gases**.

### i. Boyle's Law

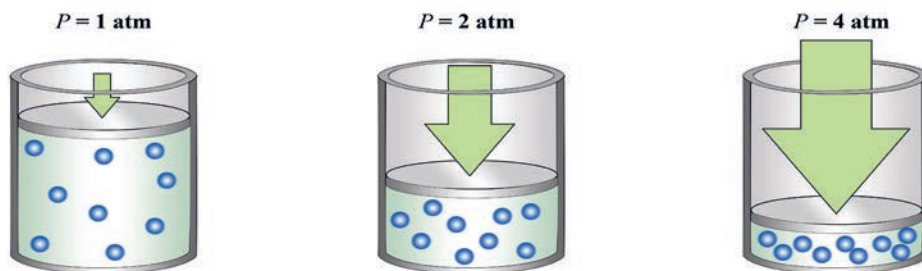


### Activity 3.6

Independently, attempt to answer the following phenomenon, and share your ideas with a friend who sits next to you.

Explain why a hydrogen gas weather balloon expands as it rises more in the air. (Assume the temperature remains constant.)

The first quantitative experiments on gases were performed by Robert Boyle (1662). His experiment helped to understand the relationship between the volume and pressure of a fixed amount of a gas at constant temperature. On the basis of his experiments, Robert Boyle concluded that, at constant temperature, the pressure of a fixed amount of gas varies inversely with its volume. This is shown in **Figure 3.2**.



**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. Values of volume-pressure relationships are given in **Table 3.1**.

**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

Figure 3.3 (a and b) shows the graphical representation of the relationship between  $p$  and  $v$ , using the data of **Table 3.1**

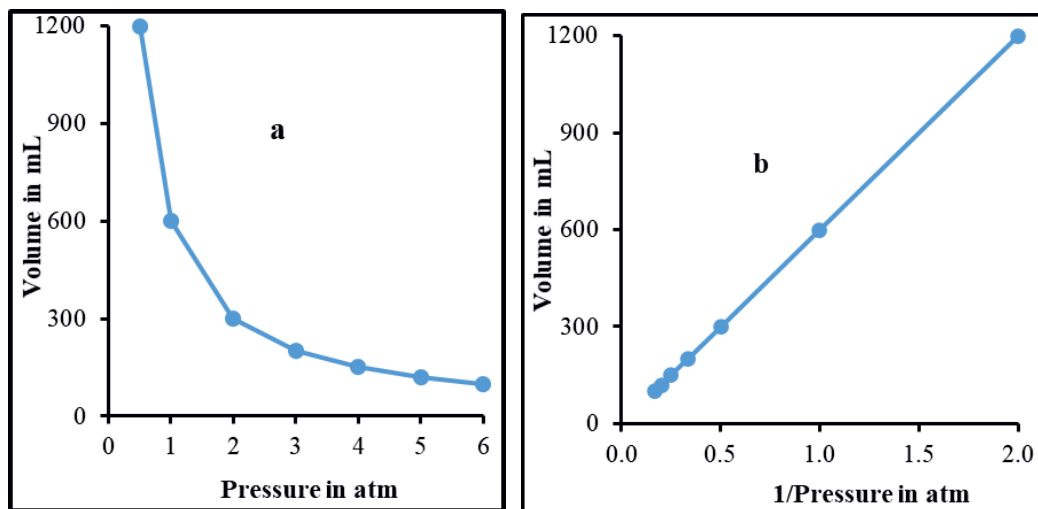


Figure 3.3: Graphs of Boyle's law, using Table 3.1 data: (a)  $V$  versus  $P$  and (b)  $V$  versus  $1/P$

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:

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

$$V = k \left( \frac{1}{P} \right) \text{ or } PV = k \quad (3.5)$$

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:

$$P_1 V_1 = k = P_2 V_2 \quad (3.6)$$

$$P_1 V_1 = P_2 V_2 \quad (3.7)$$

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.

### Experiment 3.1

#### The effect of pressure on the volume of gas

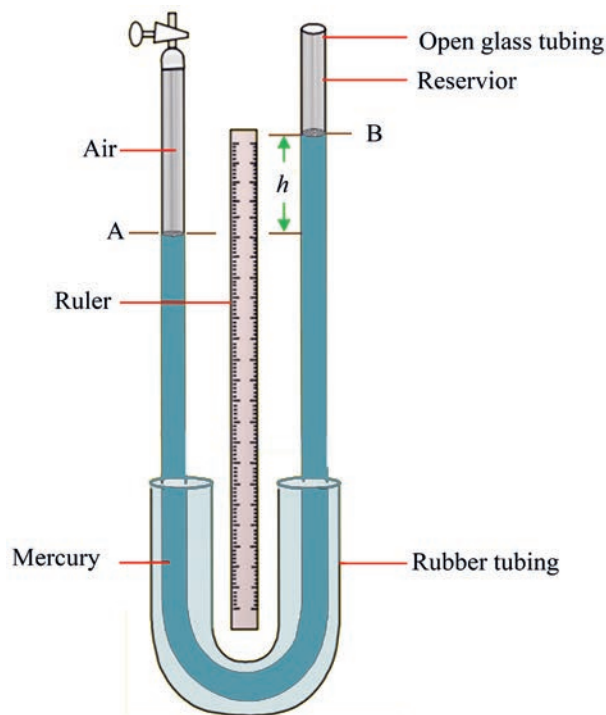
**Objective:** To observe the relationships between the volume and pressure of a gas at constant temperature.

**Apparatus:** U-tubes, ruler, rubber tube, burette, glass tube.

**Chemicals:** Mercury

#### Procedure:

1. Join two tubes by a rubber tubing to give a U-arrangement as shown in **Figure 3.4**, and then partially fill these two tubes with mercury.
2. Put a ruler in the middle of the tube.
3. The first arm of the tube (A) contains air and is sealed by a tap.
4. By moving the second arm of the tube (B) up and down, the volume of air in the first tube can be varied.
5. The pressure exerted on the air is obtained from the difference in height of mercury in the two arms of the tube.



**Figure 3.4:** The effect of pressure on the volume of a gas at constant temperature

**Observations and analysis:**

1. Plot a graph taking pressure on the vertical axis versus volume on the horizontal axis and comment on the shape of the graph.
2. What can you conclude from this experiment?

**Activity 3.7**

Discuss the following activity in your group and present your discussion to the class. Plot a graph of pressure,  $P$ , versus  $1/V$ , using the following data. Note: Calculate  $1/V$  values from the given volume by yourself, and add the values to a new row in your table.

<b>Pressure (atm)</b>	0.5	1	2	3	4	5	6
<b>Volume (mL)</b>	40	20	10	6.7	5	4	3.3

- a. What does the graph look like?
- b. What does the graph shows?
- c. What can you conclude from the graph?

**Example 3.1**

Sulfur dioxide ( $\text{SO}_2$ ), 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  $\text{SO}_2$  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:  $P_1 = 5.6 \text{ kPa}$  and  $V_1 = 1.5 \text{ L}$

Final conditions:  $P_2 = 15.0 \text{ kPa}$  and  $V_2 = ?$

Use Boyles' law equation:  $P_1 V_1 = P_2 V_2$

Thus,

$$\begin{aligned}
 V_2 &= \frac{P_1 V_1}{P_2} \\
 &= \frac{5.6 \text{ kPa} \times 1.5 \text{ L}}{15.0 \text{ kPa}} = 0.56 \text{ L}
 \end{aligned}$$



### Exercise 3.4

1. A certain gas occupies a volume of  $10.0 \text{ m}^3$  at a pressure of  $100.0 \text{ kPa}$ . If its volume is increased to  $20 \text{ m}^3$ , 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  $4.0 \text{ atm}$  and a volume of  $6.0 \text{ L}$ . What is the volume of the cylinder if the applied pressure is decreased to  $1.0 \text{ atm}$ ?

### ii. Charles' Law



### Activity 3.8

Form a group and discuss the following activity. Present your discussion to the class.

- Have you ever wondered what makes popcorn 'pop'?

Following Boyle's findings, other scientists continued to study the properties of gases. One of these scientists was Jacques Charles (a French physicist), who was the first person to fill a balloon with hydrogen gas and who made the first balloon flight. In 1787, Charles found that the volume of a gas at constant pressure increases linearly with the temperature of the gas. That is, a plot of the volume of a gas versus its temperature (K) gives a straight line. This behavior is shown for samples of several gases in **Figure 3.5**.

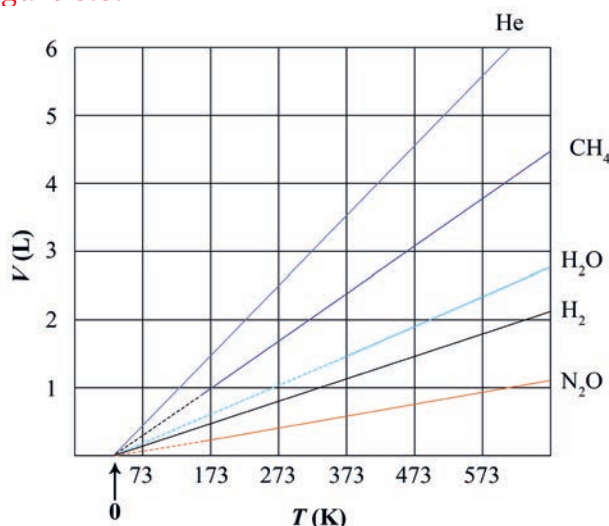


Figure 3.5: Plots of  $V$  versus  $T$  (K) for several gases

The slopes of the lines in this graph are different because the samples contain different numbers of moles of gas. But, the volumes of all the gases extrapolate to zero at the same temperature,  $-273\text{ }^{\circ}\text{C}$ .

On the Kelvin temperature scale this point, i.e.,  $-273\text{ }^{\circ}\text{C}$ , is defined as  $0\text{ K}$ , which leads to the following relationship between the Kelvin and Celsius scales:

$$\text{K} = ^{\circ}\text{C} + 273 \quad (3.7)$$

At temperatures below  $0\text{ K}$ , the extrapolated volumes of gases would become negative. However, in reality a gas cannot have a negative volume, this implies that  $0\text{ K}$  has a special significance.  $0\text{ K}$  ( $-273\text{ }^{\circ}\text{C}$ ) is considered as absolute zero, which is theoretically the lowest attainable temperature, but practically cannot be attainable.

The average kinetic energy of gas molecules is closely related to the Kelvin temperature. The volume of a gas and Kelvin temperature are directly proportional to each other. For example, doubling the Kelvin temperature causes the volume of a gas to double, and reducing the Kelvin temperature by half causes the volume of a gas to decrease by half. This relationship between Kelvin temperature and the volume of a gas is known as Charles' law.

**Charles' law** states that the volume of a fixed mass of gas at constant pressure varies directly with the Kelvin temperature.

This means,

$$\begin{aligned} V &\propto T \\ k &= VT \end{aligned} \quad (3.8)$$

The value of  $T$  is the Kelvin temperature, and  $k$  is a constant. The value of  $k$  depends only on the quantity of gas and the pressure. The ratio  $V$  to  $T$  for any set of volume-temperature values always equals the same  $k$ . Charles' law can be applied directly to volume-temperature problems using the relationship:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (3.9)$$

### Example 3.2

1. A sample of gas at 15 °C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38 °C and 1 atm?

**Solution:**

**Given:** Initial conditions:  $T_1 = 15\text{ °C} = 15 + 273 = 288\text{ K}$ ,  $V_1 = 2.58\text{ L}$

Final Conditions:  $T_2 = 38\text{ °C} = 311\text{ K}$ ,  $V_2 = ?$

By rearranging Charles' equation (Equation 3.9),  $V_2$  can be calculated as:

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{2.58\text{ L} \times 311\text{ K}}{288\text{ K}} = 2.78\text{ L}$$

2. A sample of gas has a volume of 2.80 L at an unknown temperature. When the sample is submerged in ice water at 0 °C, its volume decreases to 2.57 L. What was its initial temperature (in kelvins and in Celsius)?

**Solution:**

**Given:** Initial conditions:  $T_1?$ ,  $V_1 = 2.80\text{ L}$

Final conditions:  $T_2 = 0\text{ °C} = 273\text{ K}$ ,  $V_2 = 2.57\text{ L}$

$$T_1 = \frac{T_2 V_1}{V_2} = \frac{273\text{ K} \times 2.80\text{ L}}{2.57\text{ L}} = 297.43\text{ K}$$

in °C,  $297.43 - 273 = 24.43\text{ °C}$

### Experiment 3.2

#### The effect of temperature on the volume of a gas

**Objective:** To observe the changes in volume of a gas as temperature changes.

**Apparatus:** Round bottomed flask, beaker, delivery tube and burner.

**Procedure:**

1. Set up the apparatus as shown in **Figure 3.6**.
2. Warm the flask gently with a low Bunsen flame.
3. Cool the flask and note what happens.
4. Record your observation.

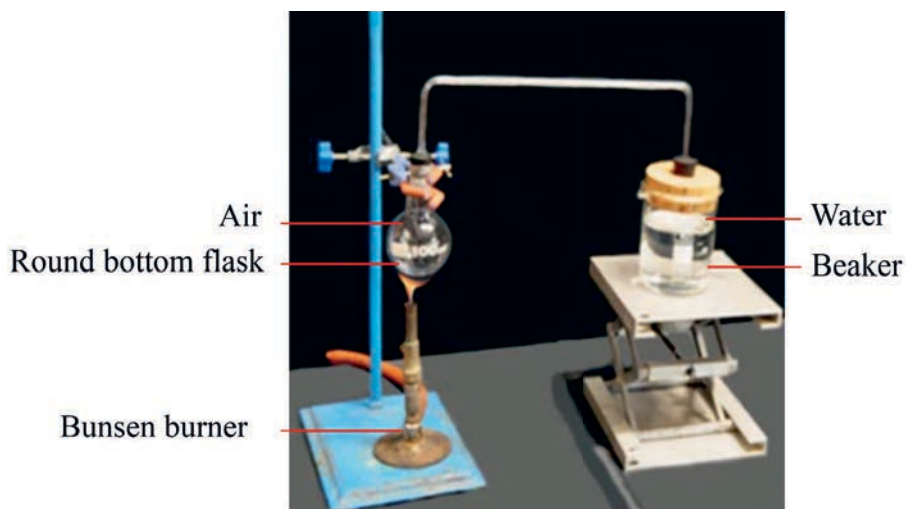


Figure 3.6: Relationship between temperature and volume of a gas

**Observations and analysis:**

1. What do you observe from the experiment?
2. What is your conclusion from this activity?



### Activity 3.9

Form a group and perform the following activity and present to the class.

Given the following data at a constant pressure:

Volume of nitrogen gas (L)	Temperature (K)
4.28 L	303
5.79 L	410
7.77 L	550

- a. Draw a graph to show the relationship between volume and temperature.
- b. Calculate the expected volume of the gas when the temperature reaches 700 K.
- c. Explain the relationship between temperature and volume.

### Exercise 3.5

- At constant pressure, by what fraction of its volume will a quantity of gas change if the temperature changes from  $-173\text{ }^{\circ}\text{C}$  to  $27\text{ }^{\circ}\text{C}$ ?
- At what temperature will the volume of a gas be
  - halved,
  - doubled, and
  - tripled at constant pressure if the original temperature is  $17\text{ }^{\circ}\text{C}$ ?
- At  $25\text{ }^{\circ}\text{C}$  and  $1\text{ atm}$  a gas occupies a volume of  $1.5\text{ dm}^3$ . What volume will it occupy at  $100\text{ }^{\circ}\text{C}$  and  $1\text{ atm}$ ?

### iii. Gay Lussac's Law



#### Activity 3.10

Form a group and discuss the following phenomena in terms of the gas laws. Present your conclusion to the class.

- Why does the pressure of car tires increase on a hot day, but decrease on a cold morning?
- Why do pressurized containers, such as deodorant cans or spray-paint cans, have warning labels stating that the container must be kept away from fire and stored in a cool environment?

Joseph Louis Gay-Lussac (a French scientist) studied how the pressure and temperature of a fixed amount of gas at constant volume are related. The relationship that he established is called **Gay-Lussac's law** or the **pressure-temperature law**. It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature. Mathematically:

$$P \propto T$$

$$k = \frac{P}{T} \quad (3.10)$$

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

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (3.11)$$

### Example 3.3

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:  $T_1 = 25\text{ °C} = 25 + 273 = 298\text{ K}$ ,  $P_1 = 3.0\text{ atm}$

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

By rearranging, Equation 3.11,  $P_2$  can be calculated:

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{3.0\text{ atm} \times 1,118\text{ K}}{298\text{ K}} = 11.23\text{ atm}$$

### 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.

## iv. The Combined Gas Law

A sample of a gas can undergo simultaneous changes in temperature, pressure, and volume. In such cases, the three variables should be considered at the same time.

The three gas laws we have learned can be brought together into a single equation known as the **combined gas law**. The combined gas law expresses the relationship between pressure, volume, and temperature of a fixed amount of gas. Mathematically:

$$PV \propto T$$

$$\frac{PV}{T} = k \quad (3.12)$$

Where **k** is a proportionality constant,

The ratio **PV to T** for any set of pressure, volume and temperature values always equals the same **k**. Thus,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (3.13)$$

Where  $P_1$ ,  $V_1$  and  $T_1$  are the initial pressure, volume and temperature;  $P_2$ ,  $V_2$  and  $T_2$  are the final pressure, volume and temperature of the gas respectively.

### Example 3.4

A sample of gas occupies 12.0 L at 240.0 °C under a pressure of 80.0 kPa. At what temperature would the gas occupy 15.0 L if the pressure were increased to 107.0 kPa?

#### Solution:

**Given:** Initial conditions:  $T_1 = 240\text{ °C} = 513\text{ K}$ ,  $P_1 = 80.0\text{ kPa}$ , and  $V_1 = 12.0\text{ L}$

Final conditions:  $T_2 = ?$ ,  $V_2 = 15.0\text{ L}$  and  $P_2 = 107.0\text{ kPa}$

By rearranging Equation (3.13) we solve for  $T_2$

$$T_2 = \frac{P_2 V_2 T_1}{P_1 V_1} = \frac{107\text{ kPa} \times 15\text{ L} \times 513\text{ K}}{80.0\text{ kPa} \times 12\text{ L}} = 857.67\text{ K} \approx 858\text{ K} = 585\text{ °C}$$

### Exercise 3.7

1. If a 50 cm<sup>3</sup> sample of gas exerts a pressure of 60.0 kPa at 35 °C, what volume will it occupy at STP (0 °C and 1 atm)?
2. A 280 mL sample of neon exerts a pressure of 660 torr at 26 °C. At what temperature in °C would it exert a pressure of 940 torr in a volume of 440 mL?

## v. Avogadro's law



### Activity 3.11

Form a group and discuss the following phenomena. Present your discussion to the class. Suppose while you are playing a football in your school football team, the ball becomes flat. Then, you fill the ball with air using a pump.

1. Why did the ball become strong enough?
2. What happened to the number of particles in the ball?
3. Which gas law can be obeyed? Explain.

In 1811, **Amedeo Avogadro** (an Italian scientist) suggested that at the same temperature and pressure, equal volumes of gases contain equal numbers of moles. This observation is called **Avogadro's law**, shown as:

$$V \propto n$$

$$\frac{V}{n} = k \quad (3.14)$$

Where  $V$  is the volume of the gas,  $n$  is the number of moles of gas particles, and  $k$  is the proportionality constant.

This equation states that for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles (molecules) of gas. In other words, equal numbers of molecules of different gases compared at the same temperature and pressure occupy equal volumes.

For two samples of gas at the same temperature and pressure, the relation between volumes and numbers of moles can be represented as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (3.15)$$

The volume occupied by a mole of gas at STP, is called the standard molar volume. It is nearly constant for all gases. The **standard molar volume** of an ideal gas is equal to 22.4 L per mole at STP. For an ideal gas: 1 mol gas = 22.4 L gas

### Example 3.5

Suppose we have a 12.2 L sample containing 0.50 moles oxygen gas ( $O_2$ ) at a pressure of 1 atm and a temperature of 25 °C. If all this  $O_2$  were converted to ozone ( $O_3$ ) at the same temperature and pressure, what would be the volume of the ozone?

**Solution:** The balanced equation for the reaction is:



To calculate the moles of  $O_3$  produced, we must use the appropriate mole

$$\text{ratio: Mol of } O_3(g) = 0.5 \cancel{\text{mol } O_2} \times \frac{2 \text{ mol } O_3}{3 \cancel{\text{mol } O_2}} = 0.33 \text{ mol}$$



Then, to determine the volume of 0.33 mol O<sub>3</sub>, use Equation 3.15.

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

Where  $V_1$  is the volume of  $n_1$  moles of O<sub>2</sub> gas and  $V_2$  is the volume of  $n_2$  moles of O<sub>3</sub> gas. In this case we have

$$n_1 = 0.5 \text{ mol}$$

$$n_2 = 0.33 \text{ mol}$$

$$V_1 = 12.2 \text{ L}$$

$$V_2 = ?$$

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

### 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?

## vi. The Ideal Gas Equation



### Activity 3.12

Form a group and discuss the following.

A balloon was inflated and finally burst when too much air was pumped into it.

1. Why did it burst when too much air is pumped into it?
2. What happens to the pressure, volume, temperature, number of moles, and the balloon itself as it is inflated and finally bursts?
3. Can you derive an equation which describes these relationships?

Present your discussion to the class.

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.

$$V \propto n \frac{T}{P}$$

$$V = Rn \frac{T}{P} \quad (3.16)$$

Where  $R$ , is proportionality constant called the gas constant. By rearranging Equation 3.16, we obtain the ideal gas equation:

$$VP = nRT \quad (3.17)$$

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 ( $n = 1$  mol,  $V = 22.4$  L,  $T = 273$  K ( $0^\circ\text{C}$ ) and  $P = 1$  atm), the values of  $R$  can be calculated from the ideal gas equation:

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}} = 0.082 \text{ atm}\cdot\text{L}/\text{mol}\cdot\text{K}$$

### Example 3.6

What pressure, in atm, is exerted by 54.0 g of Xe in a 1.00 L flask at  $20.0^\circ\text{C}$ ? (Molar mass of Xe = 131.3 g/mol)

**Solution:** By rearranging Equation 3.16

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

But  $n = m/M$ , Where  $m$  is given mass and  $M$  is molar mass of a substance Thus,

$$P = R \frac{mT}{MV}$$

$$V = \frac{0.082 \text{ atm}\cdot\text{L}/\text{mol}\cdot\text{K} \times 54 \text{ g} \times 293 \text{ K}}{131.3 \frac{\text{g}}{\text{mol}} \times 1 \text{ L}} = 9.88 \text{ atm}$$

At STP, 0.280 L of a gas weighs 0.400 g. Calculate the molar mass of the gas.

**Solution:**

**Given:**  $V = 0.280 \text{ L}$ ,  $m = 0.400 \text{ g}$ ,  $T = 273 \text{ K}$  and  $P = 1 \text{ atm}$

So to solve the molar mass of the gas, we use the following formula:

$$M = R \frac{mT}{VP}$$

$$0.082 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times \frac{0.400 \text{ g} \times 273 \text{ K}}{0.280 \text{ L} \times 1 \text{ atm}} = 31.98 \frac{\text{g}}{\text{mol}}$$

### Exercise 3.9

1. The density of a gas at a pressure of 1.34 atm and a temperature of 303 K 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 ft<sup>3</sup>. How many grams of helium would be required to inflate this balloon to a pressure of 745 torr at 21°C? (1 ft<sup>3</sup> = 28.3 L)

## vii. Graham's Law of Diffusion



### Activity 3.13

Form a group and discuss the following phenomenon. Present your discussion to the class.

Why do helium-filled balloons deflate over time faster than air-filled balloons? (Hint: A balloon has many invisible tiny holes.)

We have discussed that the 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**.

Thomas Graham (1805–869), a Scottish chemist, studied the rate of diffusion of different gases. He found that gases having low densities diffuse faster than gases that have higher densities. Based on his observations, in 1829, he postulated the relationship between the density of a gas and its rate of diffusion, which is known as **Graham's law of diffusion**.

Graham's law of diffusion states that, 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,  $M$ .

Mathematically it is expressed as:

$$r \propto \sqrt{\frac{1}{d}} \quad \text{Or} \quad r \propto \sqrt{\frac{1}{M}} \quad (3.18)$$

Where  $r$  is the rate of diffusion,  $d$  is the density and  $M$  is the molecular mass of the gas. For two gases (Gas 1 and Gas 2), their rates of diffusion can be given as:

$$r \propto \sqrt{\frac{1}{d_1}} \quad \text{Or} \quad r \propto \sqrt{\frac{1}{M_1}} \quad (3.19)$$

$$r \propto \sqrt{\frac{1}{d_2}} \quad \text{Or} \quad r \propto \sqrt{\frac{1}{M_2}} \quad (3.20)$$

By rearranging Equations 3.19 and 3.20 we obtain equation 3.21:

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{Or} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad (3.21)$$

Where  $r_1$ ,  $d_1$  and  $M_1$  represent the rate of diffusion, density and molecular mass of gas 1.  $r_2$ ,  $d_2$  and  $M_2$  represent the rate of diffusion, density and molecular mass of gas 2.

### Experiment 3.3

#### Determination of diffusion of gases

**Objective:** To compare the rate of diffusion of two different gases.

**Apparatus:** Porous pot, cork, delivery tube, U-tube, and beaker

**Chemicals:** Colored water, hydrogen and CO<sub>2</sub>.

#### Procedure:

1. Set up the apparatus as shown in **Figure 3.7**.
2. Fit the porous pot with a cork and delivery tube.
3. Attach the delivery tube to a U-tube containing colored water.
4. Place the porous pot in a beaker of hydrogen gas.
5. Watch the change in the level of the colored water in the U-tube

- The pressure in pot increases as hydrogen diffuses in quicker than the air diffuses out
- Repeat the experiment by putting the porous pot in beaker of carbon dioxide

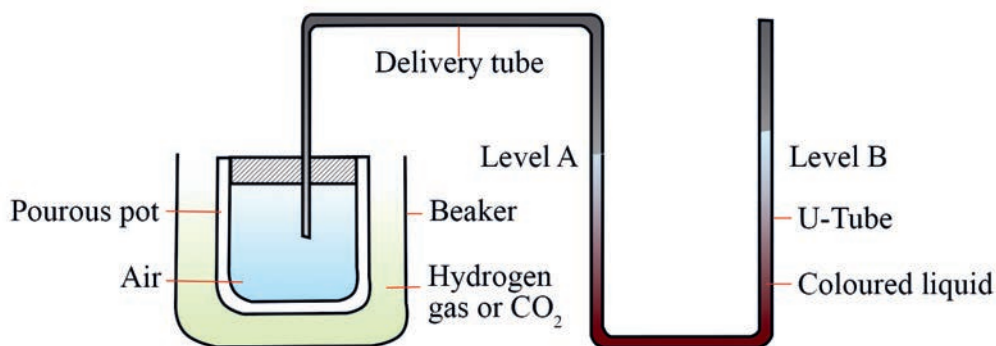


Figure 3.7: The determination of diffusion of gases

#### Observations and analysis:

- In which case did the pressure in the pot decrease?
- How did you observe the changes in pressure?
- Write your conclusions about the experiment.

### Example 3.7

- Which gas will diffuse faster, oxygen or carbon dioxide? What is the relative rate of diffusion?

#### Solution:

The molecular weight of  $\text{CO}_2$  is 44 g/mol and that of  $\text{O}_2$  is 32 g/mol. Therefore,  $\text{NH}_3$  diffuses faster than  $\text{CO}_2$ .

- Let the rate of diffusion of  $\text{O}_2$  be  $r_{\text{O}_2}$
- Let the rate of diffusion of  $\text{CO}_2$  be  $r_{\text{CO}_2}$

We can calculate the rate of diffusion using Equation 3.21

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_{\text{O}_2}}{r_{\text{CO}_2}} = \sqrt{\frac{M_{\text{CO}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{44 \text{ g/mol}}{32 \text{ g/mol}}} = 1.17$$

This means, rate of diffusion of  $\text{O}_2$  is 1.17 times that of  $\text{CO}_2$ .

- The rate of diffusion of methane ( $\text{CH}_4$ ) is twice that of an unknown gas. What is the molecular mass of the gas?

**Solution:**

Let  $r_{CH_4}$  and  $r_x$  be the rates of diffusion of  $CH_4$  and the unknown gas as well as  $M_{CH_4}$  and  $M_x$  be the molecular masses of  $CH_4$  and the unknown gas, respectively. The rate of diffusion of  $CH_4$  is two times faster than the unknown gas. This can be written mathematically as  $r_{CH_4} = 2r_x$ .

Now, substitute  $2r_x$  in place of  $r_{CH_4}$  and solve for  $M_x$  using Graham's law (Equation 3.15)

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_{CH_4}}{r_x} = \sqrt{\frac{M_x}{M_{CH_4}}}$$

By substituting  $2r_x$  in place of  $r_{CH_4}$  we obtain

$$\frac{2r_x}{r_x} = \sqrt{\frac{M_x}{M_{CH_4}}}$$

$$\text{thus, } 2 = \sqrt{\frac{M_x}{M_{CH_4}}}$$

By rearranging this equation we obtain the value of  $M_x$

$$M_x = 2^2 M_{CH_4} = 4 \times 16 \frac{\text{g}}{\text{mol}} = 64 \text{ g / mol}$$

Therefore, the molecular mass of the unknown gas is 64.

The rate at which a gas diffuses is also inversely proportional to the time it takes to move a certain distance. Mathematically:

$$r \propto \frac{1}{t} \quad (3.16)$$

If two different gases (gas 1 and gas 2) under the same conditions of temperature and pressure diffuse through a porous container, then the time required to diffuse for the two gases can be given by the following formula:

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

Where  $t_1$  and  $t_2$  are the time taken,  $r_1$  and  $r_2$  are the rates,  $M_1$  and  $M_2$  are the molecular masses of gas 1 and gas 2, respectively.

## Exercise 3.10

1. A sample of ethane,  $C_2H_6$ , diffuses at a rate of  $3.6 \times 10^{-6}$  mol/h. An unknown gas, under the same diffuses at a rate of  $1.3 \times 10^{-6}$  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  $O_2$
  - b.  $N_2$  and acetylene ( $C_2H_2$ )

## 3.4 The Liquid State

*At the end of this section, you will be able to:*

- ☞ *explain the terms: evaporation, boiling, condensation, vapor pressure; boiling point, molar heat of vaporization and molar heat of condensation*
- ☞ *carry out an activity to demonstrate the concept of vapor pressure*
- ☞ *carry out an activity to determine the boiling points of water and ethanol.*



## Activity 3.14

Discuss the following activities in your group and present to the class.

1. Why are some liquids volatile and others are not?
2. What is the relationship between altitude and boiling point of a liquid?

From your previous lessons you have learned that liquids have a definite volume, but an indefinite shape. They take the shape of their containers to the level they fill. Liquids are denser than gases, but less dense than solids.

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



#### Activity 3.16

Form a group and discuss the following and present your discussion to the class:

Why does a mirror (or glass window) get foggy (misty) when hot air is breathed on it?

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 3.8**). 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.

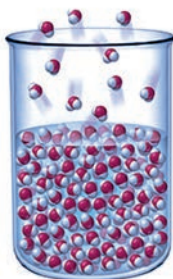


Figure 3.8: Evaporation of liquid

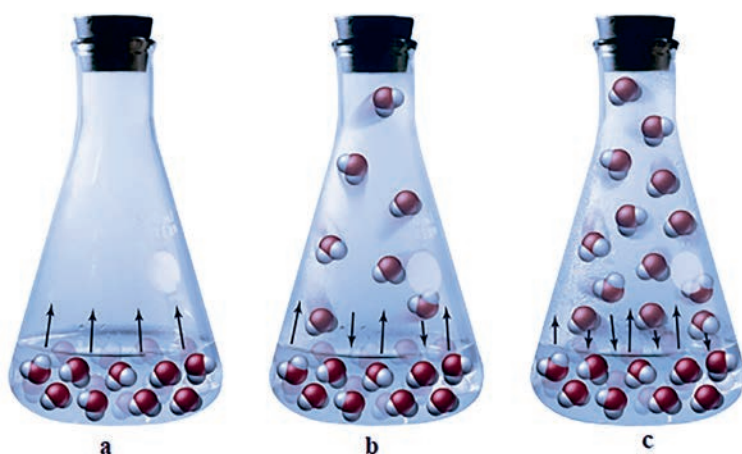
Evaporation is explained in terms of the energy that the molecules on the surface of the liquid have. In an open container, evaporation continues until all of the liquid enters the gas (vapor) phase (Figure 3.8). Most of the molecules that escape into the vapor phase do *not* collide with the surface 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 3.9a**). However, as the number of gaseous water molecules increases, the rate of condensation also increases (**Figure 3.9b**). At the point where the rates of condensation and evaporation become equal (**Figure 3.9c**), 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 3.9: Evaporation and condensation: (a) when water is first put into a closed container, water molecules begin to evaporate; (b) Evaporation continues, but condensation also begins to occur; and (c) Dynamic equilibrium: 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).

As we previously discussed, liquids have no definite shape; instead, they take the shape of containers in which they are contained. So, 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



### Activity 3.17

Discuss the following questions in a group and report your responses to the whole class

1. Atmospheric pressure is usually higher at a lower altitude than at a higher altitude. How does the kinetic-molecular theory explain this fact?
2. Ice melts normally at  $0\text{ }^{\circ}\text{C}$ . What happens to the melting point of ice in the presence of impurities? Does it melt below  $0\text{ }^{\circ}\text{C}$ , above  $0\text{ }^{\circ}\text{C}$  or exactly at  $0\text{ }^{\circ}\text{C}$ ? Explain.

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.

### Experiment 3.4

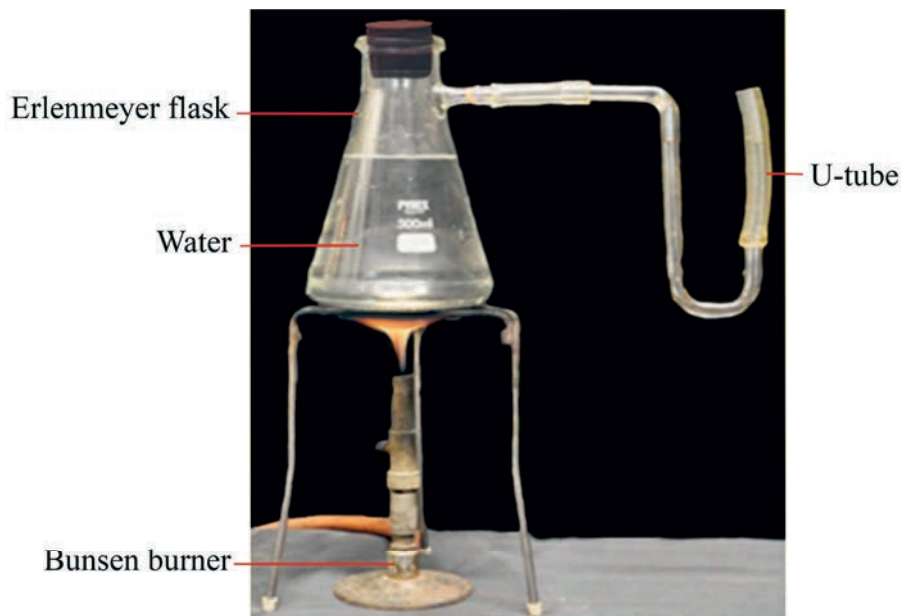
#### Observing the vapor pressure of a liquid

**Objective:** To observe the vapor pressure of a liquid.

**Apparatus:** Erlenmeyer flask, rubber bung, U-tube and burner.

#### Procedure:

1. Set up the apparatus as shown in **Figure 3.10**.
2. Add about 100 mL of water into the Erlenmeyer flask and put a stopper. Heat the flask to expel the air above the water in the flask.
3. Half fill the U-tube with water.
4. Connect the U-tube to Erlenmeyer flask and note the water level in the two arms of the U-tube.
5. Heat the flask gently and observe the water level changes in the arms of the U-tube.



**Figure 3.10:** Determination of vapor pressure

#### Observations and analysis:

What do you observe? Give an explanation for the observation.

## Experiment 3.5

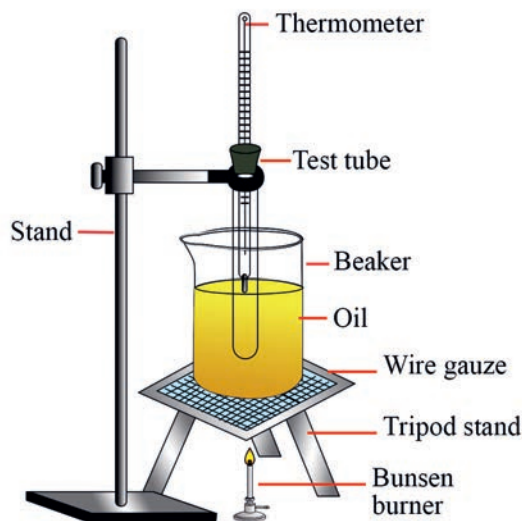
### Determining of boiling points

**Objectives:** To determine the boiling point of water and ethanol.

**Apparatus:** Test tube, stopper, thermometer, beaker, burner, clamp, stand and base.

### Procedure:

1. Half fill the test tube with a sample of pure water and add some porcelain chips.
2. Take a rubber stopper and pierce a thin opening on the side of the rubber stopper to allow the vapor to escape.
3. Fit the thermometer with the rubber stopper and insert it in the test tube.
4. Put the test tube in a beaker containing oil as shown in **Figure 3.11**.
5. Heat the oil in beaker gently and record the temperature at which the water boils.
6. Repeat the experiment by replacing the water sample by ethanol.



**Figure 3.11: Determination of boiling point**

### Observations and analysis:

1. What is the boiling point of water and ethanol that you obtained from these experiments?
2. Does the temperature from the thermometer reading increase after the water and ethanol started to boils?
3. Explain why the thermometer was not put into the liquid.
4. What is the purpose of adding porcelain chips?

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** ( $\Delta H_{\text{vap}}$ ) 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 vapour condenses to liquid at the condensing point of a vapour. 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 realised when 1 mole of a gas is converted to a liquid at its condensation point is called **the molar heat of condensation** ( $\Delta H_{\text{cond}}$ ).

Molar heat of vaporization ( $\Delta H_{\text{vap}}$ ) and molar heat of condensation ( $\Delta H_{\text{cond}}$ ) 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?

## 3.5 The Solid State

*At the end of this section, you will be able to:*

- ☞ describe phase changes
- ☞ explain the terms melting, fusion, sublimation, melting point, freezing point, molar heat of solidification
- ☞ explain temperature changes associated with phase changes
- ☞ determine melting point of ice
- ☞ demonstrate an experiment to show the phase changes from ice to liquid water and then to water vapor.



### Activity 3.18

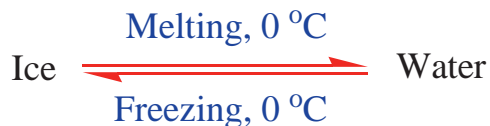
Form a group and discuss the following points. Present your discussion to the class.

1. When the crystals of iodine are warmed, they disappear into vapors without being changed into liquid.
2. When ethyl alcohol is taken in an open container it disappears after sometime.

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) take 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  $0\text{ }^{\circ}\text{C}$  and water freezes at  $0\text{ }^{\circ}\text{C}$ . Ice and water coexist in equilibrium at  $0\text{ }^{\circ}\text{C}$  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 ( $\Delta H_{\text{fus}}$ ) 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  $6.01\text{ kJ}$  at  $0\text{ }^{\circ}\text{C}$ . This is the



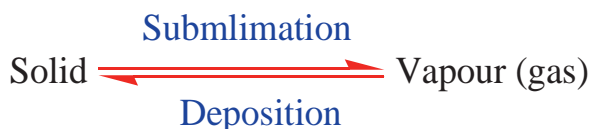
amount of energy needed to break the attractive forces in the solid, ice, at its melting point. Melting requires the supply of energy; therefore, it is an **endothermic process**.

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 ( $\Delta H_{\text{cryst}}$ ) 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**,  $\Delta H_{\text{sub}}$ , 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, bypassing the liquid state. Whereas, during deposition heat energy ( $\Delta H_{\text{dep}}$ ) is released. The enthalpy change during deposition is equal in magnitude but opposite in sign to sublimation. The enthalpy of deposition,  $\Delta H_{\text{dep}}$ , 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?

**Heating curve**

A **heating curve** is a plot of the temperature versus the amount of heat added (**Figure 3.12**). 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.

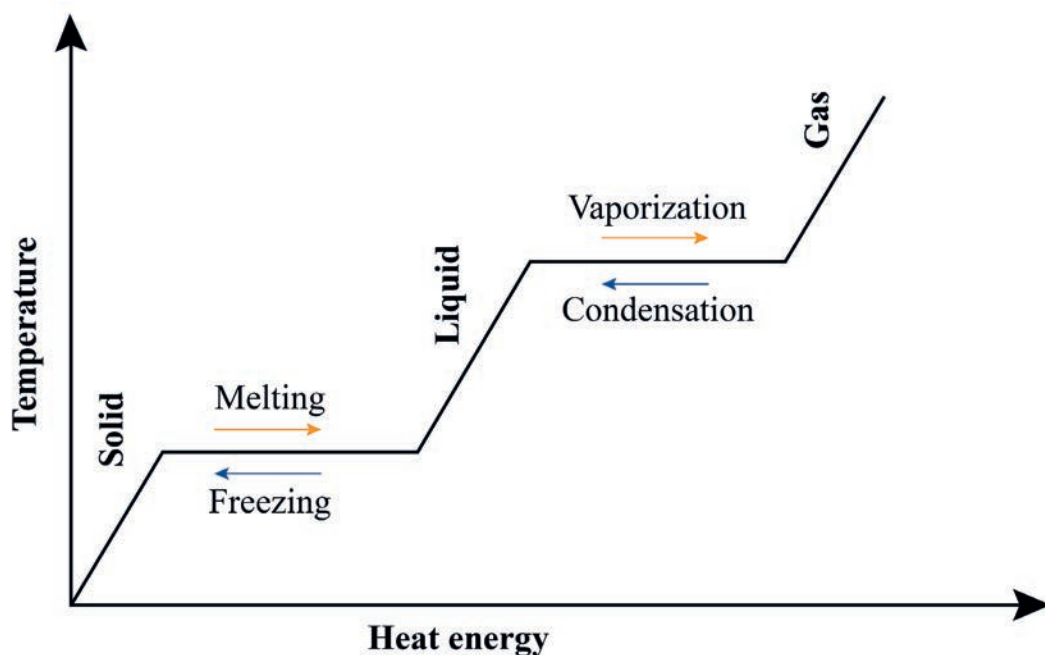


Figure 3.12: A heating curve

## Experiment 3.6

### Demonstration of phase changes

**Objective:** To show the phase changes from ice to water and then to water vapour

**Apparatus:** Beakers, thermometer, glass rod, burner, clamp stand, tripod stand and wire gauze.

### Procedure:

1. Take a 250 mL beaker and half-filled with the dry crushed ice given by your teacher.
2. Place the beaker on a wire gauze, which is placed on a tripod stand.
3. Suspend a thermometer from the clamp stand such that the bulb of the thermometer is completely surrounded by ice as shown in **Figure 3.13**.
4. Heat the ice cubes and stir continuously for uniform heating.
5. Record the temperature ( $T_1$ ) when ice starts melting.
6. Heat continuously till ice melts completely. Record this temperature ( $T_2$ ).
7. Continue heating, record at the temperature ( $T_3$ ) when water begins to boil.
8. Continue to heat the water for at least 3 minutes after the water begins to boil, record the temperature ( $T_4$ ) after 3 minutes

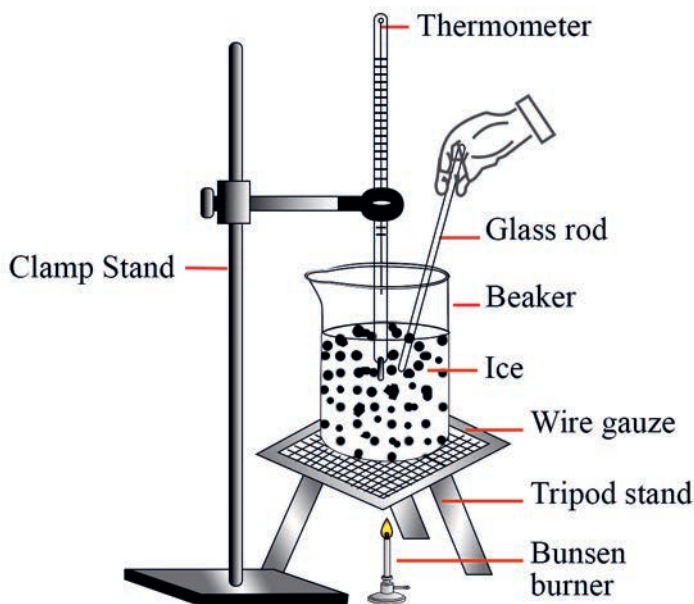


Figure 3.13: Phase changes from ice to water and then to water vapour

**Observations and analysis:**

1. At any time did the temperature seem to rise at or near a constant rate?
2. When is the temperature change slow?
3. When is the temperature change fast?
4. Is there difference between  $T_1$  and  $T_2$  as well as between  $T_3$  and  $T_4$ ?

**Exercise 3.13**

1. Draw a cooling curve.
2. What is the relationship and difference between a heating curve and a cooling curve?


















## CHECKLIST

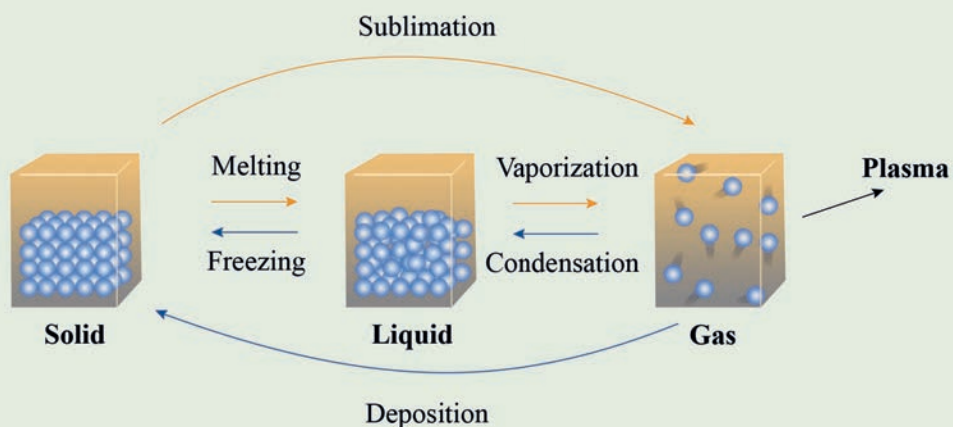
## KEY TERMS

- *Absolute zero*
- *Atmospheric pressure*
- *Avogadro's law*
- *Boiling*
- *Boiling point*
- *Boyle's law*
- *Charles' law*
- *Collision*
- *Combined gas law*
- *Condensation*
- *Evaporation*
- *Fluid*
- *Freezing*
- *Freezing point*
- *Gas constant*
- *Gas laws*
- *Gases*
- *Graham's law*
- *Heat of condensation*
- *Heat of vaporization*
- *Heating curve*
- *Ideal gas equation*
- *Kelvin temperature*
- *Kinetic molecular theory of gases*
- *Liquids*
- *Melting*
- *Melting point*
- *Molar heat of condensation*
- *Molar heat of fusion*
- *Molar heat of sublimation*
- *Non-volatile liquid*
- *Normal boiling point*
- *Properties of gases*
- *Solidification*
- *Standard temperature and pressure (STP)*
- *Sublimation*
- *Vapor pressure*
- *Volatile liquid*



## 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 $\rightarrow$ Liquid	Energy is absorbed.
Vaporization	Liquid $\rightarrow$ Gas	Energy is absorbed.
Sublimation	Solid $\rightarrow$ Gas	Energy is absorbed.
Freezing	Liquid $\rightarrow$ Solid	Energy is released.
Condensation	Gas $\rightarrow$ Liquid	Energy is released.
Deposition	Gas $\rightarrow$ 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



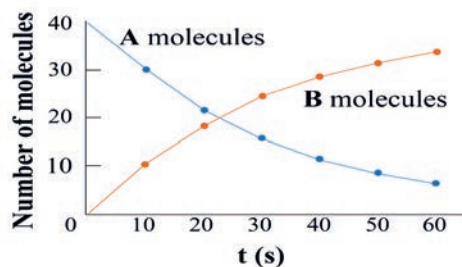
18. A sample of oxygen occupies 47.2 L under a pressure of 1240 torr at 25 °C. What volume would it occupy at 25 °C if the pressure were decreased to 730 torr?
- a. 27.8 L                      b. 32.3 L                      c. 29.3 L                      d. 80.2 L
19. A sample of nitrogen occupies 5.50 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 ( O<sub>2</sub> ) 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                      c. It evaporates  
b. It freezes                      d. It condenses

**Part IV: Solve the following problems**

26. What will be the minimum pressure required to compress 500 dm<sup>3</sup> of air at 1 bar to 200 dm<sup>3</sup> 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 cm<sup>3</sup> of methane diffuse into air in 72 seconds, how long will it take 210 cm<sup>3</sup> 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:



# UNIT 4



## CHEMICAL KINETICS

### Unit Outcomes

*At the end of this unit, you will be able to:*

- ☞ explain rate of reaction
- ☞ describe the pre-conditions for a chemical reaction to occur
- ☞ discuss factors that affect rate of chemical reaction, and
- ☞ demonstrate scientific enquiry skills, including observing, predicting, comparing and contrasting, communicating, asking questions, drawing conclusions, applying concepts, relating cause and effect, making generalizations and problem solving.



### Start-up Activity

Discuss the following phenomena in groups and present your conclusion to the class.

- Determine the approximate time taken for completion of the following chemical changes:
  - burning of a piece of paper
  - conversion of milk to yogurt
  - formation of soils
  - ripening of banana
  - charring of sugar
- Why do some reactions take place rapidly and others slowly?

## 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. Can you add more examples from your experience?

To be useful reactions must occur at a reasonable rate. 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 times in the concentration of a reactant or a product.

## 4.2 The Rate of a Reaction

*At the end of this section, you will be able to:*

- ☞ define rate of reaction
- ☞ describe rate of reaction using graphs
- ☞ conduct an experiment to illustrate the relative rate of reactions
- ☞ list the pre-conditions for a chemical reaction to occur, and
- ☞ explain how collision, activation energy and proper orientation of reactants cause a chemical reaction to occur.



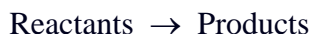
### Activity 4.1

Discuss each of the following questions in a group and present your responses to the whole class.

1. What does "rate" mean?
2. Does sugar dissolve faster in hot or in cold tea? Why?
3. How can we measure the rate of reaction?
4. What is the importance of knowing the rate of reaction?

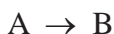
The rate of a chemical reaction measures the change in concentration of a reactant or a product per unit time. This means that the rate of a reaction determines how fast the concentration of a reactant or product changes with time.

For example, for a general reaction:



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:



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  $\Delta$  denotes the difference between the final and initial state.

Thus, for the preceding reaction we can express the rate as:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

in which,  $\Delta[A]$  and  $\Delta[B]$  are the changes in concentration ( $\text{mol L}^{-1}$ ) over a period  $\Delta t$ . 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).

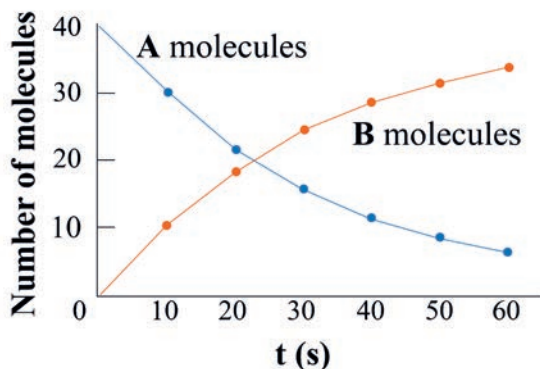


Figure 4.1: The rate of reaction  $A \rightarrow B$ , represented as the decrease of A molecules with time and the increase of B molecules with time

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:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

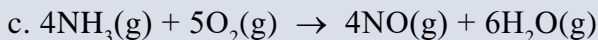
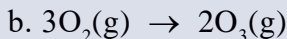
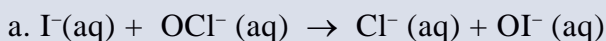
Similarly, for the reaction:



the rate is given by  $\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$

## 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:**

- a. Because each of the stoichiometric coefficients equals 1,

$$\text{Rate} = -\frac{\Delta[\text{I}^-]}{\Delta t} = -\frac{\Delta[\text{OCl}^-]}{\Delta t} = \frac{\Delta[\text{Cl}^-]}{\Delta t} = \frac{\Delta[\text{OI}^-]}{\Delta t}$$

- b. Here the coefficients are 3 and 2, so

$$\text{Rate} = -\frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t}$$

- c. 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  $\text{N}_2$ ?

**Solution:**

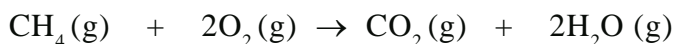
The rate of reaction for the formation of  $\text{N}_2$

$$\text{Rate} = \frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{1}{2} (-5.0 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1})$$

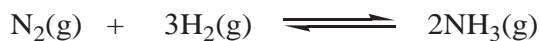
$$\text{Rate} = 2.5 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

## Exercise 4.1

1. Write the rate expression for the following reaction:

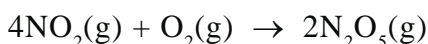


- the formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$
  - the disappearance of  $\text{CH}_4$  and  $\text{O}_2$
2. The reaction for the formation of ammonia is given as



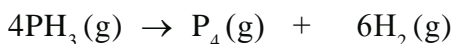
Write the rate reaction for:

- the formation of  $\text{NH}_3$
  - the disappearance of  $\text{N}_2$  and  $\text{H}_2$
3. Consider the reaction of:



Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of  $0.037 \text{ mol L}^{-1}\text{s}^{-1}$ .

- At what rate is  $\text{N}_2\text{O}_5$  being formed?
  - At what rate is  $\text{NO}_2$  reacting?
4. Consider the reaction of:



Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of  $0.078 \text{ mol L}^{-1}\text{s}^{-1}$ .

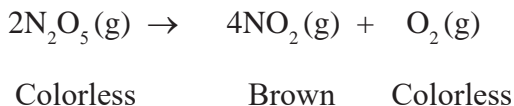
- At what rate is  $\text{P}_4$  being formed?
- At what rate is  $\text{PH}_3$  reacting?

## 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 colour 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 dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , to give the brown gas nitrogen dioxide:



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  $\text{NO}_2$  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:

$$\text{Rate of reaction} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

**Table 4.1: Concentrations (mol L<sup>-1</sup>s<sup>-1</sup>) as a function of time at 55 °C for the thermal decomposition of gaseous dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ )**

Time (s)	$\text{N}_2\text{O}_5$	$\text{NO}_2$	$\text{O}_2$
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  $\text{NO}_2$  and  $\text{O}_2$  increase as the concentration of  $\text{N}_2\text{O}_5$  decreases. In the decomposition of  $\text{N}_2\text{O}_5$ , the rate of formation of  $\text{O}_2$  is given by the equation:

$$\text{Rate of formation of } \text{O}_2 = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\text{Conc. of } \text{O}_2 \text{ at time } t_2 - \text{Conc. of } \text{O}_2 \text{ at time } t_1}{t_2 - t_1}$$

During the time period 300 to 400 s, for example, the average rate of formation of  $\text{O}_2$  is  $9 \times 10^{-6} \text{ mol L}^{-1}\text{s}^{-1}$ :

$$\text{Rate of formation of O}_2 = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{0.0049 \text{ M} - 0.0040 \text{ M}}{400 \text{ s} - 300 \text{ s}} = 9 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

The average rate of formation of  $\text{NO}_2$  during the time period 300–400 s is  $3.7 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ , which is four times the rate of formation of  $\text{O}_2$ , as with the 4:1 ratio of the coefficients of  $\text{NO}_2$  and  $\text{O}_2$  in the chemical equation for the decomposition of  $\text{N}_2\text{O}_5$ .

$$\text{Rate of formation of NO}_2 = \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{0.0197 \text{ M} - 0.0160 \text{ M}}{400 \text{ s} - 300 \text{ s}} = 3.7 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

Similarly, during the time period 300–400 s, the average rate of decomposition of  $\text{N}_2\text{O}_5$  is  $1.9 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ ;

$$\begin{aligned} \text{Rate of formation of N}_2\text{O}_5 &= -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{-(0.0101 \text{ M} - 0.0120 \text{ M})}{400 \text{ s} - 300 \text{ s}} \\ &= 1.9 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

It's also important to specify the time when quoting a rate because the rate changes as the reaction proceeds. For example, the average rate of formation of  $\text{NO}_2$  is  $3.7 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$  during the time period 300 – 400 s, but it is only  $2.2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$  during the period 600 – 700 s.

In general, the rate of reaction at the beginning is fast and it decreases as the reaction proceeds.

**What could be the possible reason for this decrease in the rate of reaction with time?**

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  $\text{O}_2$  curve,  $\Delta[\text{O}_2]$  and  $\Delta t$  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  $\Delta[\text{O}_2]/\Delta t$ , the average rate of  $\text{O}_2$  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  $\Delta[\text{NO}_2]$  and  $\Delta t$  during the time period 300 – 400 s and 600 – 700 s.

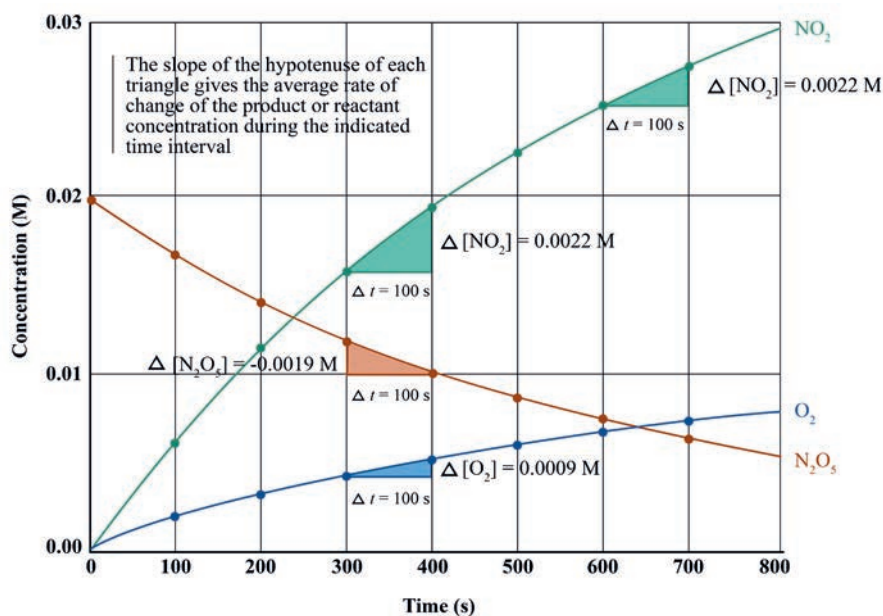


Figure 4.2: Concentration as a function of time when gaseous  $\text{N}_2\text{O}_5$  decomposes to gaseous  $\text{NO}_2$  and  $\text{O}_2$  at  $55^\circ\text{C}$

It is important to realize that, given the initial concentrations in **Table 4.1** the concentrations of  $\text{NO}_2(\text{g})$  and  $\text{O}_2(\text{g})$  can be calculated from the concentration of  $\text{N}_2\text{O}_5(\text{g})$  at any time. The following example illustrates such a calculation.

### Example 4.2

Using the data in **Table 4.1**, if  $[\text{N}_2\text{O}_5] = 1.20 \times 10^{-2} \text{ mol L}^{-1}$  at 300 s, calculate  $[\text{NO}_2]$  and  $[\text{O}_2]$  at  $t = 300 \text{ s}$ .

#### Solution:

The chemical equation is:  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ . The number of moles per liter of  $\text{N}_2\text{O}_5(\text{g})$  that have reacted in 300 s is the difference between the initial concentration and the concentration at 300 s  $[\text{N}_2\text{O}_5]$ . From **Table 4.1**,  $[\text{N}_2\text{O}_5]_0 = 2.00 \times 10^{-2} \text{ mol L}^{-1}$ .

$$\begin{aligned} \text{Molarity of } \text{N}_2\text{O}_5(\text{g}) \text{ reacted} &= [\text{N}_2\text{O}_5]_0 - [\text{N}_2\text{O}_5] \\ &= 2.00 \times 10^{-2} \text{ mol L}^{-1} - 1.20 \times 10^{-2} \text{ mol L}^{-1} \\ &= 0.8 \times 10^{-2} \text{ mol L}^{-1}. \end{aligned}$$

According to the chemical equation, 2 moles of  $\text{NO}_2(\text{g})$  are provided for every mole of  $\text{N}_2\text{O}_5(\text{g})$  that reacts. So, per liter, we have:

$$\begin{aligned} \text{Molarity of } \text{NO}_2(\text{g}) \text{ produced} &= 0.8 \times 10^{-2} \text{ mol L}^{-1} \text{N}_2\text{O}_5 \left( \frac{2 \text{ mol L}^{-1} \text{NO}_2}{1 \text{ mol L}^{-1} \text{N}_2\text{O}_5} \right) \\ &= 1.6 \times 10^{-2} \text{ mol L}^{-1} \end{aligned}$$

Similarly, for  $\text{O}_2(\text{g})$  we have:

$$\begin{aligned} \text{Molarity of } \text{O}_2(\text{g}) \text{ produced} &= 0.8 \times 10^{-2} \text{ mol L}^{-1} \text{N}_2\text{O}_5 \left( \frac{\frac{1}{2} \text{ mol L}^{-1} \text{O}_2}{1 \text{ mol L}^{-1} \text{N}_2\text{O}_5} \right) \\ &= 0.4 \times 10^{-2} \text{ mol L}^{-1} \end{aligned}$$

Often, chemists want to know the rate of a reaction at a specific time  $t$  rather than the rate averaged over a time interval  $\Delta t$ . For example, what is the rate of formation of  $\text{NO}_2$  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 4.3

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,  $t = 2$  s.

Time (s)	0	1	2	3	4	5	6	7	8
[ICl] (mol L <sup>-1</sup> )	2.000	1.348	1.052	0.872	0.748	0.656	0.586	0.530	0.484
[H <sub>2</sub> ] (mol L <sup>-1</sup> )	1.000	0.674	0.526	0.436	0.374	0.328	0.293	0.265	0.242

**Solution:** First, plot H<sub>2</sub> concentration versus time for the reaction of 1.000 M H<sub>2</sub> 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.

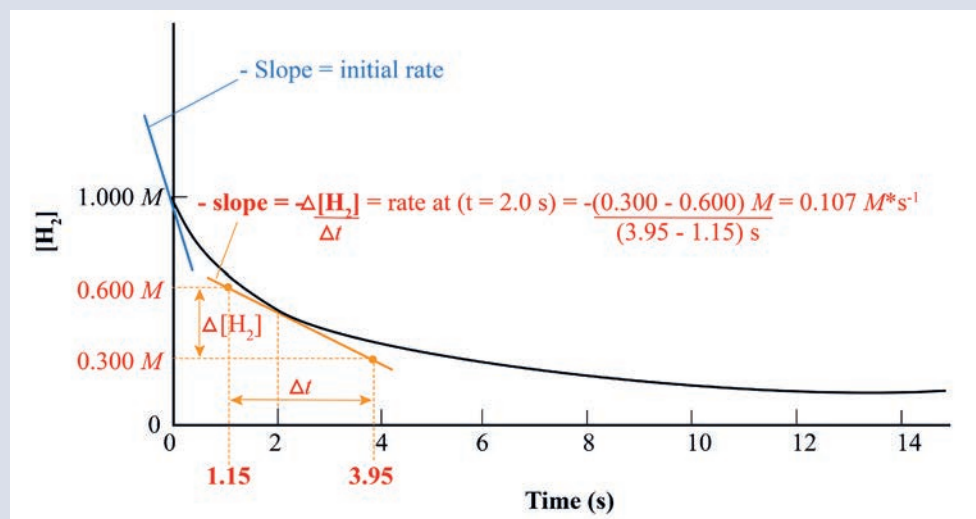


Figure 4.3: A plot of the hydrogen concentration versus time, using data of the above table

## Exercise 4.2

- Using the initial concentrations and the fact that  $[\text{O}_2] = 0.64 \times 10^{-2} \text{ mol. L}^{-1}$  at  $t = 600 \text{ s}$  in **Table 4.1**, calculate  $[\text{N}_2\text{O}_5]$  and  $[\text{NO}_2]$  at  $t = 600 \text{ s}$ .
- Consider the reaction:  

$$2\text{C}_2\text{H}_4(\text{g}) \rightarrow \text{C}_4\text{H}_8(\text{g})$$
 From the experimental data given in the table below, plot a graph for the consumption of ethylene,  $\text{C}_2\text{H}_4$ , versus time.
  - Calculate the rate of reaction between the time intervals 10 s to 30 s.
  - Calculate the rate of reaction at 45 s.

Time (s)	0	10	20	40	60	100
$[\text{C}_2\text{H}_4] (\text{mol L}^{-1})$	0.884	0.621	0.479	0.328	0.250	0.169

## Experiment 4.1

## Measuring the Rate Reaction

**Objective:** To measure the rate of reaction between marble chips ( $\text{CaCO}_3$ ) and dilute HCl acid.

**Apparatus:** Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

**Chemicals:** 2M dilute HCl acid, and marble chips/ $\text{CaCO}_3$ .

**Procedure:**

- Set up the apparatus as shown in **Figure 4.4**, but without the marble chips at first.
- Add 20 g of pure marble chips, in a clean 100 mL conical flask.
- Add 40 mL of 2M dilute HCl acid to the conical flask.
- Plug the cotton wool in position immediately.
- Read the mass of the flask and its contents and start the stopwatch.
- Record the mass at one minute intervals for 10 minutes.



Figure 4.4: The laboratory set up for the measurement of rate of reaction

#### Observations and analysis:

1. Use the following table to record your observations.

Time (min)	0	1	2	3	4	5	6	7	8	9	10
Mass (g)											
Decrease in mass (g)											

Plot a graph with time (minutes) on the horizontal axis and rate on the vertical axis. Draw a smooth curve through as many points as possible.

**Note** that in this experiment change in mass is proportional to change in concentration.

2. What happens to the mass during the reaction? Explain this with the help of a balanced equation.
3. What information can be obtained from the slope of this graph at any point?
4. Why is the graph
  - a. steep at the start of the reaction?
  - b. less steep in the middle of the reaction?
  - c. horizontal at the end of the reaction?

5. Calculate:
  - a. The average rate of the reaction.
  - b. The rate of reaction at 2 minutes.
6. Describe how the rate of reaction changes with time.
7. Can we measure the rate of this reaction by measuring the amount /volume of  $\text{CO}_2$  evolved?
8. Draw a graph of the expected result by plotting volume of  $\text{CO}_2$  evolved vs time.

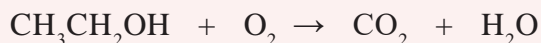
## Conditions needed for a chemical reaction



### Activity 4.2

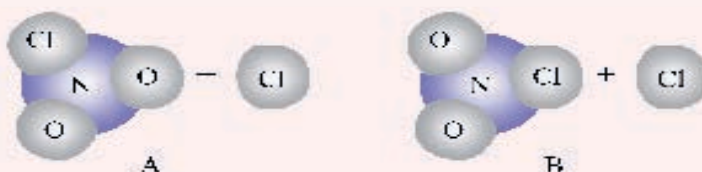
Form a group of three and discuss each of the following questions, then present your responses to the whole class.

1. Ethanol can easily burn in air due to the following reaction:



In actual practice, you are required to use a lighter (igniter) to start the reaction. Why?

2. Consider the following reaction  $\text{NO}_2\text{Cl} + \text{Cl} \rightarrow \text{NO}_2 + \text{Cl}$



Which of the above collisions might be successful to form the product?

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 4.5).

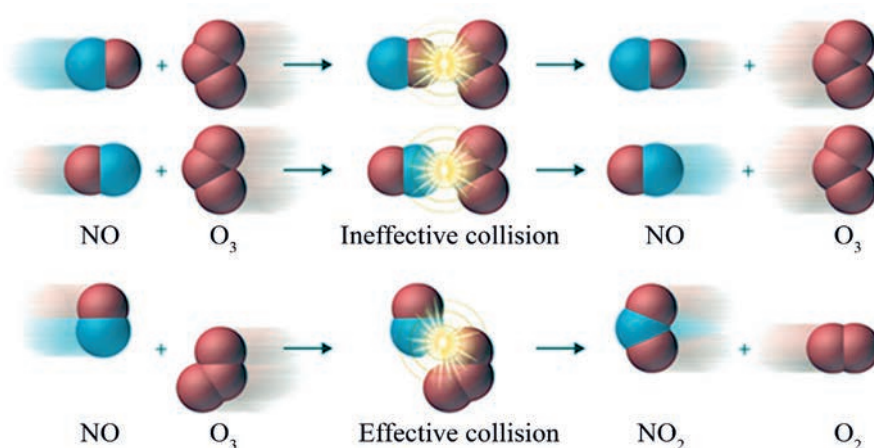


Figure 4.5: The effect of molecular orientation on the reaction of NO and O<sub>3</sub>





## 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,  $E_a$** .

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

*At the end of this section, you will be able to:*

-  list factors that affect the rate of a chemical reaction
-  describe the effects of changes in temperature, concentration or pressure and surface area on the rates of a chemical reaction
-  explain the effect of catalysts on the rates of chemical reaction
-  do an experiment on how the factors affect the rate of chemical reaction.



### Activity 4.3

Discuss each of the following questions in groups, and present your responses to the whole class.

1. How is the burning of charcoal affected by
  - a. increasing the amount of air used
  - b. adding more charcoal
2. How can you increase the rate of combustion of a given block of wood?
3. Why do sugar crystals dissolve more easily in hot water than in cold water?
4. Why does powdered sugar dissolved easily as compared to equivalent amounts of sugar crystals?

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



### Activity 4.4

Compare how fast the following substances burn and present your responses to the whole class.

- a. paper      b. wood charcoal      c. alcohol      d. copper wire

Consider **Experiment 4.2** to study the effect of the nature of reactants on rate of reaction.

## Experiment 4.2

### The Effect of Nature of Reactants on Rate of Reaction

**Objective:** To study the effect of the nature of reactant for the reaction of copper and magnesium metals with hydrochloric acid.

**Apparatus:** Balance, test tubes, test tube stand.

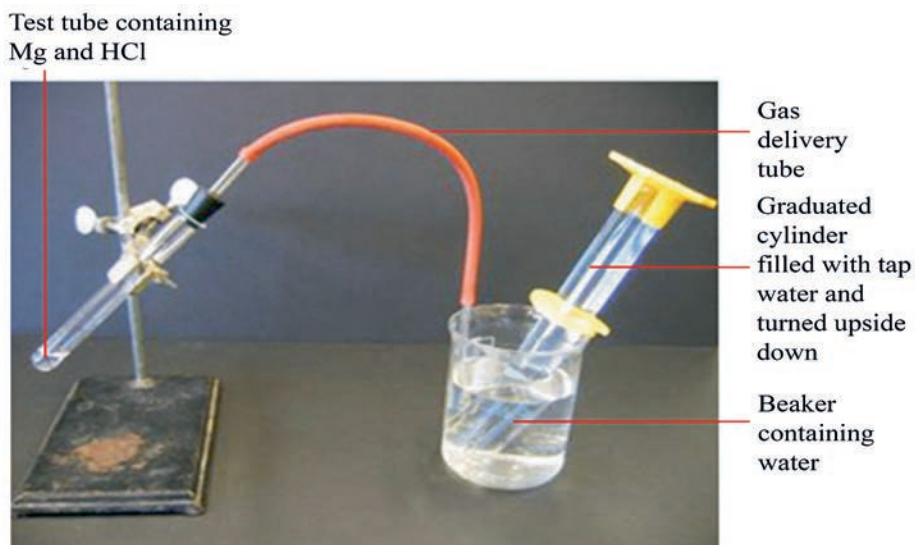
**Chemicals:** Copper (Cu), magnesium (Mg), 2M hydrochloric acid (HCl).

#### Procedure:

1. Measure equal masses of copper and magnesium metals using a balance.
2. Record the weighed mass of these metals and add each to separate test tubes.
3. Assemble the test tubes as shown in **Figure 4.6**.
4. Add equal volume of 5 mL of 1M HCl to both the test tubes.

**Wear your safety goggles and gloves.**

5. Observe relative rates of reaction in both test tubes and record your observations.



**Figure 4.6: The reaction of magnesium with HCl acid Observations and analysis**

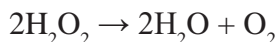
1. Which of these two metals, copper or magnesium, reacts faster? Why?

- Write the balanced chemical equation for the reaction of
  - copper with HCl acid
  - magnesium with HCl acid
- What do you learn from this experiment?
- Perform a similar activity using different metals such as aluminum, and zinc. In which case do you expect the reaction to be faster and why?

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.



Even similar reactions may have different rates under the same conditions. For example, if small pieces of the metal iron and sodium are left in air, the sodium reacts completely overnight, whereas the iron is barely affected. The active metals sodium and calcium both react with water to form hydrogen gas and the corresponding metal hydroxide. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

Can you write the balanced equation for the reaction of sodium and calcium with water?

## ii. Surface Area of Reactants



### Activity 4.5

Form a group of three or four and answer the following questions, then present your responses to the whole class.

- Why does a wood fire burn faster if the logs are chopped into smaller pieces?
- Which form of zinc metal is easier to dissolve in dilute HCl, large pieces of Zn or powdered Zn? Why? Consider the **Experiment 4.3** to study the effect of surface area on rate of reaction.

### Experiment 4.3

#### Effect of surface Area on Reaction Rate

**Objective:** To study the effect of surface area of reactants on the rate of reaction using cube chalk and powdered chalk with dilute hydrochloric acid.

**Apparatus:** Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

**Chemicals:** Cube chalk, powdered chalk and 2M dilute HCl solution

**Procedure:** Repeat **Experiment 4.1** but use 20 g of small cubical chalk and then powdered chalk in place of marble chips.

**Observations:** In which case is the gas produced faster?

#### Observations and analysis:

1. Compare the rate curve, average rate and reaction rate at 2 minutes with that of **Experiment 4.1**. Explain your observations.
2. Sketch a graph for the consumption of each size of chalk (cube chalk and powdered chalk) against time on the same graph sheet.
3. Write a conclusion to the experiment.

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:



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



#### Activity 4.6

Answer the following questions in groups and present your responses to the whole class.

1. Why does wood burn more rapidly in pure oxygen than in air?
2. Why does limestone ( $\text{CaCO}_3$ ) deteriorate more rapidly in highly polluted air than in less polluted air?

Consider **Experiment 4.4** to study the effect of concentration of acid on the rate of reaction between  $\text{CaCO}_3$  and hydrochloric acid.

#### Experiment 4.4

##### Effect of Concentration on Reaction Rate

**Objective:** To study the effect of concentrations of hydrochloric acid on rate of reaction with marble chips.

**Apparatus:** Direct reading balance, 100 mL conical flask, stopwatch, cotton wool

**Chemicals:** 1M HCl, 2M HCl dilute solutions and marble chips ( $\text{CaCO}_3$ ).

**Procedure:** Repeat **Experiment 4.1** but you have to use 1M dilute HCl acid in place of 2M dilute HCl acid.

##### Observations and analysis:

1. Compare the rate of reaction with that in **Experiment 4.1**. Which reaction is more vigorous? Explain.
2. Which of the two reactions will produce more carbon dioxide? Explain your answer.
3. What would happen to the rate curve and average rate if:
  - a. 1M HCl is replaced with 4M dilute HCl acid? Explain.
  - b. 1M HCl is replaced with 0.5M dilute HCl acid? Explain.
4. Sketch a graph for each of 0.5 M, 1M, 2M and 4M dilute HCl acid against time on the same graph sheet.

At a fixed temperature, the rate of a given reaction depends on the concentration of the reactants. Reaction rates often increase 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



#### Activity 4.7

Form a group and answer the following questions, then present your responses to the whole class.

1. Why do we keep foods in refrigerator rather than at room temperature?
2. Compare the oxidation of wood or coal at ordinary and high temperatures?

In **Experiment 4.5**, you will study the effect of temperature on the rate of reaction of  $\text{Na}_2\text{S}_2\text{O}_3$  with HCl.

#### Experiment 4.5

##### The Effect of Temperature on Reaction Rate

**Objective:** To study the effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid.

**Apparatus:** 100 mL beakers, test tubes, thermometers, white paper, pencil.

**Chemicals:** 0.5M HCl acid, 0.1M  $\text{Na}_2\text{S}_2\text{O}_3$  solution, pieces of ice.

##### Procedure:

1. Take 25 mL of 0.1M  $\text{Na}_2\text{S}_2\text{O}_3$  solution in a test tube and 25 mL of 0.5M HCl acid in another test tube.
2. Prepare three such sets and maintain them at different temperatures.  
Set (i) at 0 °C [by keeping them in an ice bath as shown in **Figure 4.7 (a)**].  
Set (ii) at room temperature.  
Set (iii) at 40 °C (by heating the two solutions in a water bath).

- Put a cross sign on a white cardboard and place a clean dry 100 mL beaker above it.
- Now, pour the contents of set (i) in the beaker and start a stopwatch immediately.
- Carefully stir the mixture with thermometer and record the time taken for the cross to disappear [Figure 4.7 (b)].
- Repeat steps 3, 4, and 5 with set 2 and set 3, respectively.
- Tabulate your results as temperature in  $^{\circ}\text{C}$  versus time in minutes.

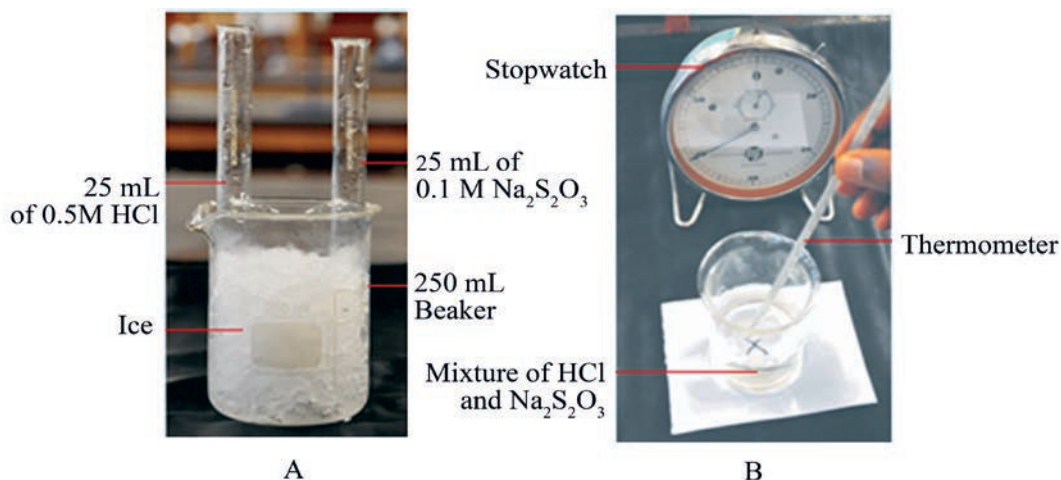


Figure 4.7: Laboratory set-up for the study of the effect of temperature on rate of reaction

#### Observations and analysis:

- What was the appearance of the mixture at the start of the reaction, and at the end of the reaction? Explain the changes using the equation for the reaction.
- Plot the graph of time (minutes) on the horizontal axis against rate on the vertical axis.
- Under which condition of temperature does the cross take:
  - the shortest time to disappear, and
  - the longest time to disappear.
- Draw a conclusion about the relationship between the average reaction rate and temperature.



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 raises, 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



#### Activity 4.8

Answer the following questions in groups and present your response to the whole class.

1. How do inhibitors extend the shelf-life of a package of food?
2. What catalyst do you know in your body and the surroundings?
3. Why is yeast added to the dough in the making of bread? What happens if you don't add yeast to the dough?

Now, you will perform **Experiment 4.6** to study the effect of a catalyst on the rate of decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2$

#### Experiment 4.6:

##### The Effect of a Catalyst on the Rate of Reaction

**Objective:** To investigate the effect of a catalyst on rate of decomposition of hydrogen peroxide.

**Apparatus:** Conical flask, gas syringe, delivery tube.

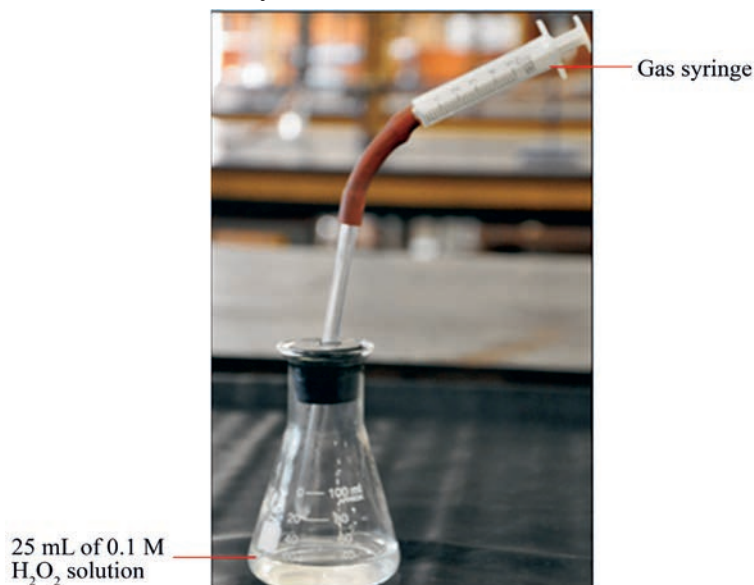
**Chemicals:** 0.5% by volume  $\text{H}_2\text{O}_2$  solution,  $\text{MnO}_2$ .

**Procedure:**

1. Set-up the apparatus as shown in **Figure 4.8**. Set the volume of the gas syringe at 0 mL. Add 25.0 mL of 0.1M  $\text{H}_2\text{O}_2$  solution, but without manganese (IV) oxide,  $\text{MnO}_2$ , and start stopwatch immediately.
2. Record the volume of gas collected in gas syringe at minute intervals until each reaction is almost complete.
3. Repeat steps 1 and 2 with 1 g of  $\text{MnO}_2$ .

**Observations and analysis:**

1. Identify the gas and write a balanced chemical equation for the reaction.
2. Under which condition does gas syringe contains more of the gas at any one time? Give an explanation for this observation.
3. Describe the appearance of  $\text{MnO}_2$  before and after the reaction.
4. Plot graphs of rate on the vertical axis and time (minutes) on the horizontal axis for two different sets of readings. Which set of reading were used? Why?
5. Write a conclusion about the reaction rate:
  - a. in the presence of a catalyst
  - b. in the absence of a catalyst



**Figure 4.8:** Investigation into the effect of manganese (IV) oxide on hydrogen peroxide

A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy,  $E_a$ . An 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.

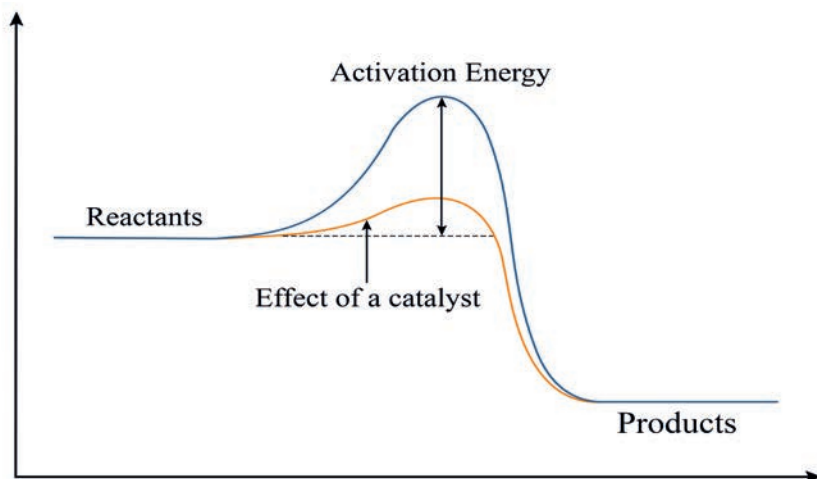


Figure 4.9: A catalyst provides an alternate pathway with a lower activation energy barrier for the reaction

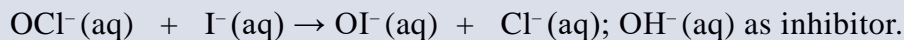
Chemical catalysts can be either positive or negative. Positive catalysts increase the rate of reaction by lowering the  $E_a$ .

### Example 4.4



Negative catalysts or inhibitors decrease the rate of reaction by increasing the value of  $E_a$ .

### Example 4.5



Example 4.4 represents heterogeneous catalysts as state of reactants and catalyst is different, while Example 4.5 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).

## CHECKLIST

### KEY TERMS

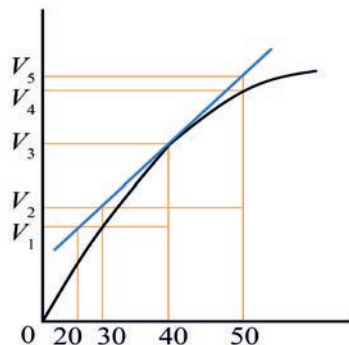
- Activation energy*
- Average rate*
- Catalyst*
- Chemical kinetics*
- Collision theory*
- Effective collision*
- Heterogeneous catalyst*

- Homogeneous catalyst*
- Initial rate*
- Instantaneous rate*
- Kinetics*
- Rate of reaction*
- Surface area*

**REVIEW EXERCISE****Part I: Choose the correct answer from the given alternatives**

- When the concentration of reactant molecules is increased, the rate of reaction increases. The best explanation is: As the reactant concentration increases,
  - the average kinetic energy of molecules increases.
  - the frequency of molecular collisions increases.
  - the rate constant increases.
  - the activation energy increases.
- A catalyst:
  - actually participates in the reaction.
  - changes the equilibrium concentration of the products.
  - does not affect a reaction energy path.
  - always increases the activation energy for a reaction.
- 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.
  - only I & II
  - only II
  - only II & III
  - only I & III
- The combustion of ethane ( $C_2H_6$ ) is represented by the equation:  
 $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$  In this reaction:
  - the rate of consumption of ethane is seven times faster than the rate of consumption of oxygen.
  - $CO_2$  is formed twice as fast as ethane is consumed.
  - water is formed at a rate equal to two-thirds the rate of formation of  $CO_2$ .
  - the rate of consumption of oxygen equals the rate of consumption of water.
- The speed of a chemical reaction
  - is constant no matter what the temperature is.
  - is independent of the amount of contact surface of a solid involved.
  - between ions in aqueous solution is extremely rapid because there are no bonds that need to be broken.
  - 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 4.10**. On the basis of this mark the correct option.



**Figure 4.10:** A reaction between zinc and dilute hydrochloric acid

- 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  $\frac{V_3 - V_1}{40 - 20}$
7. Consider the graph given in **Figure 4.10**. Which of the following options does not show instantaneous rate of reaction at 40<sup>th</sup> 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?
- The rate of a reaction decreases with passage of time as the concentration of reactants decreases.
  - The rate of a reaction is same at any time during the reaction.
  - The rate of a reaction is independent of temperature change.
  - 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?  $5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
- a.  $\frac{\Delta[\text{Br}^-]}{\Delta t} = 5 \frac{\Delta[\text{H}^+]}{\Delta t}$       b.  $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{6}{5} \frac{\Delta[\text{H}^+]}{\Delta t}$
- b.  $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$       d.  $\frac{\Delta[\text{Br}^-]}{\Delta t} = 6 \frac{\Delta[\text{H}^+]}{\Delta t}$
10. During the decomposition of  $\text{H}_2\text{O}_2$  to give dioxygen, 48 g  $\text{O}_2$  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.  $1.5 \text{ mol min}^{-1}$       c.  $2.25 \text{ mol min}^{-1}$       d.  $3.0 \text{ mol min}^{-1}$

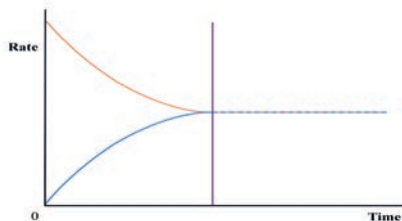
### Part II: Give short answers to each of the following questions

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  $A(g) \rightarrow B(g)$ , 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
 
$$2AX_2(g) \rightarrow 2AX(g) + X_2(g)$$
 In one experiment,  $[AX_2]$  was measured at various times and these data were obtained:

Time (s)	0	2	6	8	10	20
$[AX_2]$ (mol L <sup>-1</sup> )	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:  $A(g) + 2B(g) \rightarrow C(g)$  When  $[B]$  is decreasing at  $0.5 \text{ mol L}^{-1} \text{ s}^{-1}$ , how fast is  $[A]$  decreasing?
  21. Reaction rate is expressed in terms of changes in concentration of reactants and products. Write a balanced equation for
 
$$\text{Rate} = -\frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$
  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:  $3O_2(g) \rightarrow 2O_3(g)$ 
    - a. Express the reaction rate in terms of  $[O_2]$  and  $[O_3]$ .
    - b. 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  $[O_3]$ ?

# UNIT 5



## CHEMICAL EQUILIBRIUM

### Unit Outcomes

*At the end of this unit, you will be able to:*

- ☞ *discuss how equilibrium is established*
- ☞ *explain characteristics of dynamic equilibrium*
- ☞ *state the law of mass action and write an expression for equilibrium constants,  $K_c$  and  $K_p$  from a given chemical reaction*
- ☞ *apply the law of mass action to calculate  $K_c$ ,  $K_p$ , concentration and pressure of substances in equilibrium*
- ☞ *explain how the reaction quotient is used to indicate position of the equilibrium*
- ☞ *state Le-Chatlier's principle and use it to predict and explain the effects of changes in temperature, pressure, concentration and presence of a catalyst on a reaction*
- ☞ *perform an activity to demonstrate the effects of changes in concentration on the position of equilibrium and to determine  $K_c$  or  $K_p$  values*
- ☞ *explain how equilibrium principles may be applied to optimize the production of industrial chemicals (e.g., production of ammonia and sulphuric acid)*
- ☞ *describe scientific enquiry skills along this unit: observing, predicting, comparing and contrasting, communicating, asking questions and making generalizations.*





## Start-up Activity

Form a group and perform the following activity:

Mix 10 mL of 0.1 mol L<sup>-1</sup> HCl solution with 10 mL of 0.1 mol L<sup>-1</sup> NaOH solution. Now, discuss each of the following questions:

- What is the concentration of NaCl formed?
- How much HCl and NaOH remain unreacted?
- Is the reaction complete?

Share your ideas with the rest of the class.

## 5.1 Introduction

In Unit 4 you have learned about the rate of reaction. You have also studied the time taken for half of the reaction to be completed. However, some questions have not been answered yet. These questions include: 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

*At the end of this section, you will be able to:*

- ☞ explain reversible and irreversible reactions*
- ☞ define dynamic chemical equilibrium*
- ☞ state the necessary conditions for attainment of equilibrium*
- ☞ describe the microscopic event that occur when a chemical system is in equilibrium*
- ☞ explain the characteristics of chemical equilibrium*
- ☞ state the law of mass action*
- ☞ define equilibrium constant*
- ☞ write the equilibrium constant expression for chemical reactions that involve concentration*

- ☞ calculate values for equilibrium constant involving concentration
- ☞ state the relationship of  $K_{eq}$  to the relative amounts of products and reactants in a given reaction
- ☞ write the equilibrium constant expression for chemical reactions that involve partial pressure
- ☞ calculate values for equilibrium constant involving partial pressure
- ☞ show the relationship between  $K_C$  and  $K_p$
- ☞ distinguish between homogeneous and heterogeneous equilibrium reactions
- ☞ define reaction quotient
- ☞ use the equilibrium quotient to predict the direction of the reaction and the position of equilibrium
- ☞ calculate equilibrium concentrations given initial concentrations
- ☞ determine whether the reactants or products are favored in a chemical reaction given the equilibrium constant
- ☞ list factors that affect chemical equilibrium
- ☞ state Le-Chatliers principle
- ☞ use Le-Chatliers principle to explain the effect of changes in temperature, pressure, concentration and presence of catalyst on a reaction
- ☞ state the effect of changes in concentration, pressure/volume and temperature on  $K_{eq}$
- ☞ perform an activity to demonstrate the effect of changes in concentration on the position of equilibrium
- ☞ perform an activity to demonstrate the effect of changes in temperature on the position of equilibrium
- ☞ perform an activity to determine  $K_C$  for esterification of an organic acid;
- ☞ define optimum conditions
- ☞ explain how Le-Chatliers principle is applied in the Haber process (production of  $NH_3$ ) and in the Contact process (production of  $H_2SO_4$ ).

## 5.2.1 Reversible and Irreversible Reactions



## Activity 5.1

Perform the following activities in pairs and write a report of your findings.

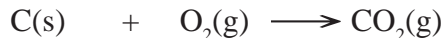
Consider the reactions that involve both gaseous reactants and products.

What will happen if the reaction takes place in:

- an open vessel (container)?
- a closed vessel?

Share your findings to the whole class.

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 ( $\longrightarrow$ ) is used to indicate that the reaction proceeds in only one direction. For instance, the reaction between carbon and oxygen is an irreversible reaction:

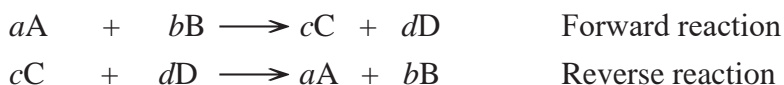


On the other hand, some reactions do not go to completion. Such reactions are called **reversible reactions** or **two-way reactions**. These reactions usually proceed both in the forward and reverse reactions. The reaction in which the original reactants form products is the **forward reaction** and 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.

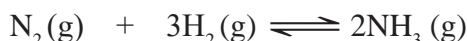
Reversible reactions have the following general form:



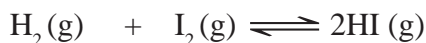
Where A and B are reactants, C and D are products and a, b, c, and d are balancing coefficients. In this reaction:



For example, the formation of ammonia is a reversible reaction:



Another example of a reversible reaction is the formation of hydrogen iodide from hydrogen gas and iodine vapours:



### Exercise 5.1

Answer the following questions:

1. How do you distinguish between reversible and irreversible reactions?
2. Give examples of reversible and irreversible reactions.

## 5.2.2 Attainment and Characteristics of Chemical Equilibria



### Activity 5.2

Discuss the following idea in pairs and present your findings to the whole class.

Why do chemical reactions reach an equilibrium state?

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 increases (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: Rate of forward reaction ( $r_f$ ) = Rate of reverse reaction ( $r_r$ )

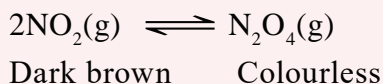
### 5.2.3 Conditions for Attainment of Chemical Equilibria



#### Activity 5.3

Sit in a group of three or four and discuss the following reactions. Share your findings with the whole class.

1. Dimerization of nitrogen dioxide is a reversible reaction:



When  $\text{NO}_2$  is placed in an evacuated, sealed glass vessel, the intensity of the initial dark brown color gradually decreases. However, after sometime the intensity of the brown color becomes constant.

- a. Why does the dark brown colour intensity decrease at the start?
- b. Why does the brown colour become constant, eventually?
- c. What will happen to the colour, if you check after a month?

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**.

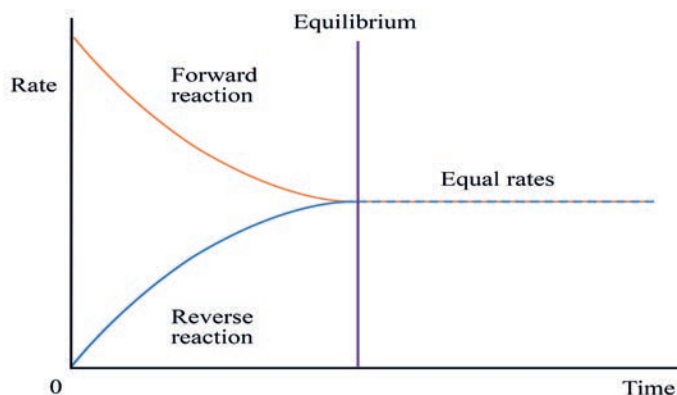
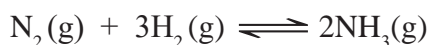


Figure 5.1: Change in the rate of reaction with time for forward and reverse reactions

For example, synthesis of ammonia from nitrogen and hydrogen is a reversible process.



At the beginning of the reaction, only nitrogen and hydrogen are present. They combine to form ammonia at a large rate. As the reaction progresses, the concentrations of nitrogen and hydrogen decrease so the rate of formation of ammonia decreases. As more and more ammonia molecules are formed, some of the molecules start decomposing to give back nitrogen and hydrogen molecules. As the reaction progresses, the number of ammonia molecules increases, the rate of decomposition of ammonia also increases. As the reaction proceeds, the rate of formation of ammonia decreases while the rate of decomposition ammonia increases. At a given point the two rates become equal, and equilibrium is reached.

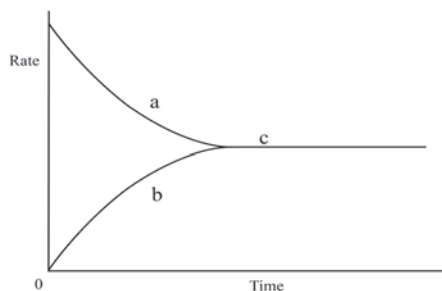
Note that the concentrations of products and reactants are not necessarily equal at equilibrium, only the rate of forward and reverse reactions are equal. Generally, a reaction at equilibrium has the following characteristics:

- 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.

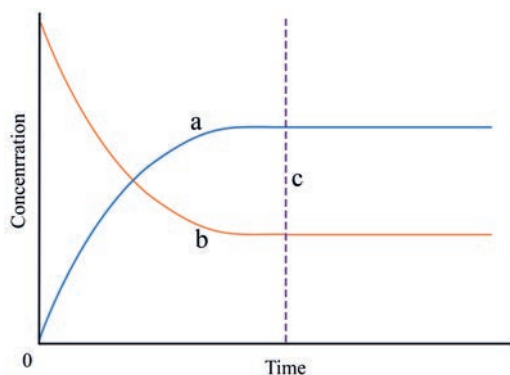
## Exercise 5.2

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?

### 5.2.4 Equilibrium Expression and Equilibrium Constant

#### A. Law of Mass Actions

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:



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:

$$\begin{aligned} r_f &\propto [A]^a[B]^b & \text{or} & & r_f &= k_f [A]^a[B]^b \\ r_r &\propto [C]^c[D]^d & \text{or} & & r_r &= k_r [C]^c[D]^d \end{aligned}$$

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:

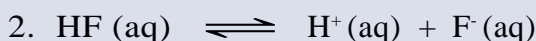
$$\begin{aligned} K_C &= \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{[\text{mol L}^{-1}]^c [\text{mol L}^{-1}]^d}{[\text{mol L}^{-1}]^a [\text{mol L}^{-1}]^b} \\ &= (\text{mol L}^{-1})^{(c+d)-(a+b)} \end{aligned}$$

### Example 5.1

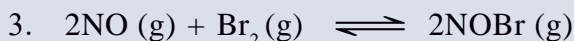
$K_C$  expressions and units as well as  $K_C$  value determinations:



$$K_C = \frac{[\text{NH}_4^+][\text{CH}_3\text{COO}^-]}{[\text{NH}_3][\text{CH}_3\text{COOH}]} = \frac{(\text{mol L}^{-1})(\text{mol L}^{-1})}{(\text{mol L}^{-1})(\text{mol L}^{-1})} = 1$$

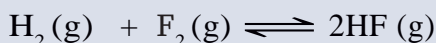


$$K_C = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(\text{mol L}^{-1})(\text{mol L}^{-1})}{(\text{mol L}^{-1})} = \text{mol L}^{-1}$$



$$K_C = \frac{[\text{NOBr}]^2}{[\text{NO}]^2 [\text{Br}_2]} = \frac{[\text{mol L}^{-1}]^2}{[\text{mol L}^{-1}]^2 (\text{mol L}^{-1})} = [\text{mol L}^{-1}]^{-2}$$

4. For the reaction



An equilibrium mixture at 425 °C contains  $4.79 \times 10^{-4}$  mol/L of  $\text{H}_2$ ,  $4.79 \times 10^{-4}$  mol/L of  $\text{F}_2$  and  $3.53 \times 10^{-3}$  mol/L of HF. Determine the equilibrium constant of the reaction.

**Solution:**

**Given:**  $[H_2] = [F_2] = 4.79 \times 10^{-4} \text{ mol/L}$

$[HF] = 3.53 \times 10^{-3} \text{ mol/L}$

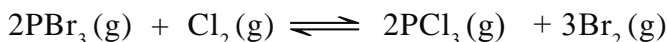
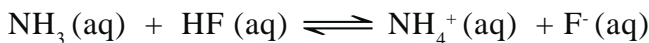
$K_C$  expression for the reaction is  $K_C = \frac{[HF]^2}{[H_2][F_2]}$

Substitution of the give values in the expression gives:

$$K_C = \frac{[3.53 \times 10^{-3} \text{ mol/L}]^2}{(4.79 \times 10^{-4} \text{ mol/L})(4.79 \times 10^{-4} \text{ mol/L})} = 5.43$$

**Exercise 5.3**

1. Write the equilibrium constant expressions ( $K_C$ ) for the following reactions:



2. For the reaction  $N_2(g) + 3Cl_2(g) \rightleftharpoons 2NCl_3(g)$  an analysis of an equilibrium mixture is performed at a certain temperature. It is found that  $[NCl_3] = 1.9 \times 10^{-1} \text{ M}$ ,  $[N_2] = 1.4 \times 10^{-3} \text{ M}$ , and  $[Cl_2] = 4.3 \times 10^{-4} \text{ M}$ . Calculate  $K_C$  for the reaction at this temperature

**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:

$$\frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} = K_p$$



The expression of equilibrium constant in terms of molarities is:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = K_C$$

The expression of  $K_p$  is:

$$\frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = K_p$$

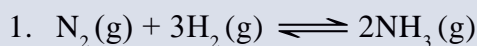
The unit of  $K_p$  is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of  $K_p$ , will be:

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} = \frac{[\text{atm}]^c [\text{atm}]^d}{[\text{atm}]^a [\text{atm}]^b} = (\text{atm})^{(m+n)-(a+b)}$$

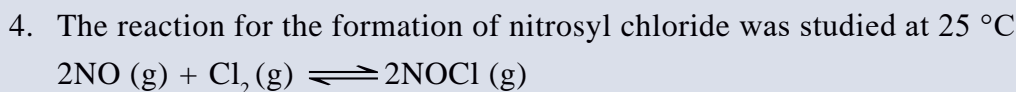
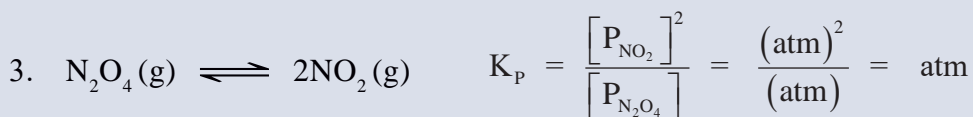
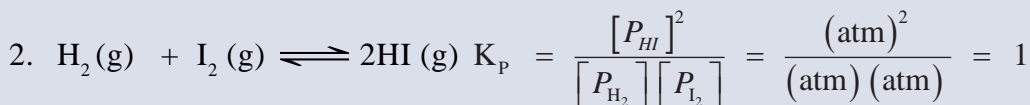
If the partial pressure is measured in kPa, then the unit of  $K_p$  will be  $(\text{kPa})^{(m+n)-(a+b)}$

### Example 5.2

$K_p$  expressions and units as well as  $K_p$  value determinations:



$$K_p = \frac{[P_{\text{NH}_3}]^2}{[P_{\text{N}_2}][P_{\text{H}_2}]^3} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})^3} = \frac{1}{\text{atm}^2} = \text{atm}^{-2}$$



At equilibrium, the partial pressures were found to be 1.2,  $5.0 \times 10^{-2}$  and  $3.0 \times 10^{-1}$  atm for NOCl, NO and  $\text{Cl}_2$ , respectively. Calculate the value of  $K_p$  for this reaction at 25 °C.

#### Solution:

**Given:**  $P_{\text{NOCl}} = 1.2$  atm,  $P_{\text{NO}} = 5.0 \times 10^{-2}$  atm and  $P_{\text{Cl}_2} = 3.0 \times 10^{-1}$  atm

$K_p$  expression for the reaction is

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{NO}})^2 P_{\text{Cl}_2}}$$

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

- Write the equilibrium constant expressions ( $K_p$ ) for the following reactions:
  - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
  - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{NOBr}(\text{g})$
- The following equilibrium pressures were observed at a certain temperature for the reaction  $2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ 

$$P_{\text{NO}_2} = 0.55 \text{ atm}$$

$$P_{\text{NO}} = 6.5 \times 10^{-5} \text{ atm,}$$

$$P_{\text{O}_2} = 4.5 \times 10^{-5} \text{ atm}$$
 Calculate the value for the equilibrium constant at this temperature

**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. See these examples:



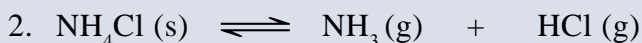
When we write the equilibrium constant expression for heterogeneous reactions, we do not include the concentration of pure solids or pure liquids in the expression. This is because, the position of equilibrium does not depend on the amounts of pure solids or pure liquids present. The molar concentrations of pure solids liquids are constant at a given temperature.

### Example 5.3

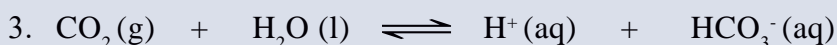
The equilibrium constant expressions for some heterogeneous reactions are shown below:



$$K_c = [\text{CO}_2] \quad \text{or} \quad K_p = P_{\text{CO}_2}$$



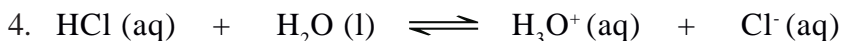
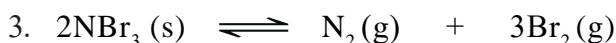
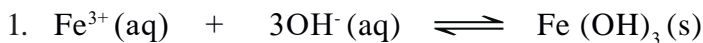
$$K_c = [\text{NH}_3][\text{HCl}] \quad \text{or} \quad K_p = P_{\text{NH}_3}P_{\text{HCl}}$$



$$K_c = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

### Exercise 5.5

Write the equilibrium constant expression for the following reactions:



### E. Relation between $K_c$ and $K_p$

For the general reaction



$K_c$  and  $K_p$  expressions are:

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = \frac{C_c^c C_D^d}{C_A^a C_B^b}$$

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

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:

$$P = nRT/V \quad \text{and} \quad n/V = C$$

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:

$$P_A = n_A RT/V = C_A RT$$

$$P_B = n_B RT/V = C_B RT$$

$$P_C = n_C RT/V = C_C RT$$

$$P_D = n_D RT/V = C_D RT$$

$$K_p = \frac{[n_C RT/V]^c [n_D RT/V]^d}{[n_A RT/V]^a [n_B RT/V]^b} = \frac{C_C^c C_D^d}{C_A^a C_B^b} (RT)^n$$

Where  $\Delta n = (c + d) - (a + b)$  for gaseous species

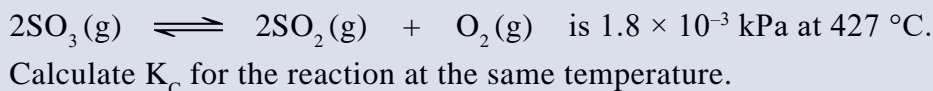
$$K_p = K_c (RT)^{\Delta n}$$

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

1. The equilibrium constant ( $K_p$ ) for the reaction:



#### Solution:

Given:  $K_p = 1.8 \times 10^{-3} \text{ kPa} = 1.8 \text{ Nm}^{-2}$ ,  $T = 427^\circ\text{C} = 700 \text{ K}$  and  $R = 8.314 \text{ N m K}^{-1} \text{ mol}^{-1}$

We know that  $K_p = K_c (RT)^{\Delta n}$

For the given reaction,  $\Delta n = (2 + 1) - 2 = 1$

Therefore,  $K_c = K_p / (RT)$

$$K_c = \frac{K_p}{RT} = K_c = \frac{1.8 \text{ Nm}^{-2}}{8.314 \text{ N m K}^{-1} \text{ mol}^{-1} \times 700 \text{ K}} = 3.1 \times 10^{-4} \text{ m}^{-3} \text{ mol}$$

2. What are the values of  $K_p$  and  $K_c$  at  $1000^\circ\text{C}$  for the reaction  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  if the pressure of  $\text{CO}_2$  in equilibrium with  $\text{CaCO}_3$  and  $\text{CaO}$  is  $3.87 \text{ atm}$ ?

**Solution:**

Enough information is given to find  $K_p$  first. Writing the  $K_p$  expression

for the reaction:  $K_p = P_{\text{CO}_2} = 3.87 \text{ atm}$ ,

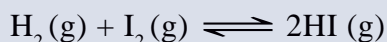
$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$  and

$T = 1273 \text{ K}$

Then to get  $K_c$ , rearrange the equation,  $K_p = K_c(RT)^{\Delta n}$  Where  $n$ , the change in the number of moles of gas in the reaction is  $+1$ .

$$K_c = \frac{3.87 \text{ atm}}{0.082 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \text{ mol}^{-1} \times 1273 \text{ K}} = 0.037 \frac{\text{mol}}{\text{L}} = 0.037 \text{ M}$$

3. At  $400^\circ\text{C}$ ,  $K_c = 64$  for the reaction



- What is the value of  $K_p$  for this reaction?
- If at equilibrium, the partial pressures of  $\text{H}_2$  and  $\text{I}_2$  in a container are  $0.20 \text{ atm}$  and  $0.50 \text{ atm}$ , respectively, what is the partial pressure of  $\text{HI}$  in the mixture?

**Solution:**

The equation relating  $K_p$  to  $K_c$  is:

$$K_p = K_c(RT)^{\Delta n}$$

The change in the number of moles of gas  $\Delta n$  is:

$$\Delta n = 2 \text{ mol HI} - 1 \text{ mol H}_2 - 1 \text{ mol I}_2 = 0$$

Since,  $\Delta n = 0$ ,  $K_p = K_c$

$$K_p = K_c(RT)^0 = K_c = 64$$

b. Write the equilibrium constant expression:

$$K_p = \frac{[\text{P}_{\text{HI}}]^2}{[\text{P}_{\text{H}_2}][\text{P}_{\text{I}_2}]}$$

by rearranging the above equation, we can find  $\text{P}_{\text{HI}}$

$$\text{P}_{\text{HI}} = \sqrt{K_p [\text{P}_{\text{H}_2}][\text{P}_{\text{I}_2}]} = \sqrt{64 \times 0.2 \text{ atm} \times 0.5 \text{ atm}} = 2.53 \text{ atm}$$

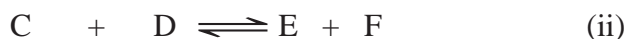
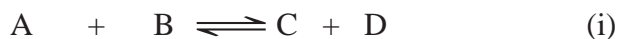
## Exercise 5.6

- 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:  

$$\text{CH}_3\text{OH}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 2\text{H}_2(\text{g})$$
 Calculate  $K_p$  at this temperature.
- At 1100 K,  $K_p = 0.25$  for the reaction:  

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$
 What is the value of  $K_c$  at this temperature?
- When 0.500 mol of  $\text{N}_2\text{O}_4$  is placed in a 4.00 L reaction vessel and heated at 400 K, 79.3% of the  $\text{N}_2\text{O}_4$  decomposes to  $\text{NO}_2$ . 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.

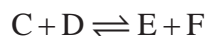
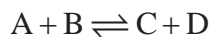
Consider the reactions in which the product species in one equilibrium system are involved in the second equilibrium process.



The equilibrium constant expressions for reaction (i) and (ii), respectively, are

$$K_1 = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \quad \text{and} \quad K_2 = \frac{[\text{E}][\text{F}]}{[\text{C}][\text{D}]}$$

The overall reaction is given by the sum of the two reactions:



The equilibrium constant expression for the overall reaction is:

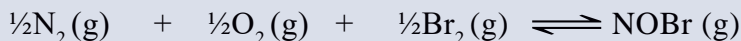
$$K_{\text{overall}} = \frac{[\text{E}][\text{F}]}{[\text{A}][\text{B}]} = K_1 \times K_2 = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \times \frac{[\text{E}][\text{F}]}{[\text{C}][\text{D}]}$$

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:  $K_{\text{overall}} = K_1 \times K_2 \times K_3 \dots$

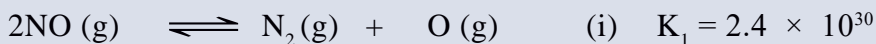


## Example: 5.5

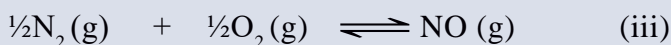
1. Determine  $K_c$  for this reaction:



from the following information at 298 K.

**Solution:**

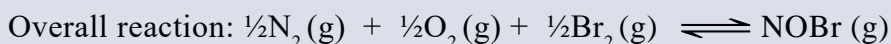
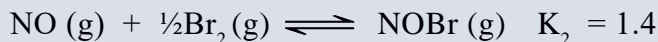
To calculate  $K_c$  of the overall reaction, reactions (i) and (ii) must add up to give the overall reaction. To do this, first reverse reaction (i) and multiply  $\frac{1}{2}$ , so that it will have the form:



Since the reaction equation is reversed and multiplied by  $\frac{1}{2}$ , the equilibrium constant for reaction (iii),  $K_1'$  is calculated as:

$$K_1' = \left(\frac{1}{K_1}\right)^{1/2} = \left(\frac{1}{2.4 \times 10^{30}}\right)^{1/2} = 6.5 \times 10^{-16}$$

Now, add reactions (ii) and (iii):



$$K_{\text{Overall}} = K_2 \times K_1'$$

Thus, the equilibrium constant for the overall reaction is:

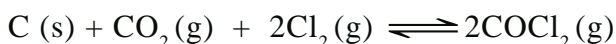
$$K_{\text{overall}} = K_2 \times K_1' = 1.4 \times 6.5 \times 10^{-16} = 9.1 \times 10^{-16}$$

## Exercise 5.7

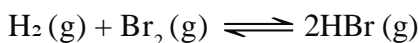
1. The following equilibrium constants were determined at 1123 K:



Write the equilibrium constant expression  $K_C$  and calculate the equilibrium constant at 1123 K for the following reaction.

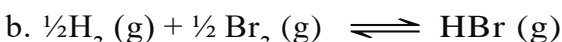
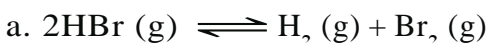


2. For the reaction:

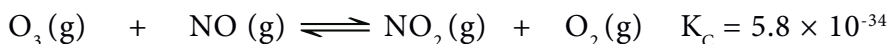
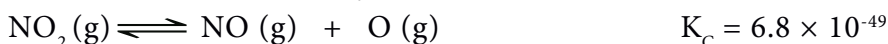
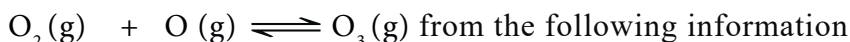


$$K_p = 7.1 \times 10^4 \text{ at } 700 \text{ K.}$$

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:



### 5.2.5 Applications 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

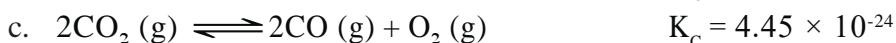
$K_C$  or  $K_p$  value is used predict the extent of the reactions at equilibrium. Very large values of  $K_C$  or  $K_p$  indicate that at equilibrium the reaction system consists of mainly products and the equilibrium lies to the right, i.e., the reaction goes near to completion. An equilibrium mixture 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.

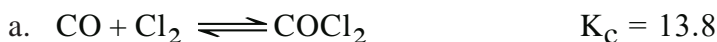
Note that a reaction goes essentially to completion if  $K_c$  or  $K_p > 10^{10}$  and not at all if  $K_c$  or  $K_p < 10^{-10}$ .

### Exercise 5.8

1. Predict whether the formation of product is favoured for the following reactions:



2. Arrange the following reactions in order of their increasing tendency to proceed towards completion (least extent to greatest extent):



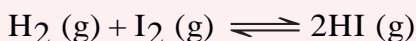
## B. Predict the direction of the reaction



### Activity 5.4

Form a group and discuss the following. Share your ideas with the rest of the class.

The equilibrium constant,  $K_c$  for the following reaction is 54.3 at 430 °C.



Suppose that in a certain experiment, 0.243, 0.146, and 1.98 moles of  $\text{H}_2$ ,  $\text{I}_2$  and HI, respectively, are placed in a 1.0 L container at 430 °C. Will there be a net reaction to form the  $\text{H}_2$ ,  $\text{O}_2$  or more HI?

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:



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

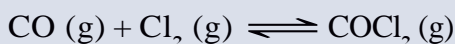
Where [A], [B], [C] and [D] are concentrations at any stage during the reaction. At the initial stages of the reaction, the amount of product formed is low, therefore, the value of  $Q$  is small. As the reaction progresses, the value of  $Q$  also increases due to the increase in concentration of the 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

1. At a certain temperature, the reaction:



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:**

$$\begin{aligned} \text{Given: } [\text{CO}]_0 &= 2.5 \text{ mol L}^{-1} & [\text{COCl}_2]_0 &= 5.0 \text{ mol L}^{-1} \\ [\text{Cl}_2]_0 &= 1.2 \text{ mol L}^{-1} & K_C &= 13.8 \end{aligned}$$

The expression for  $Q_C$  is:

$$Q_C = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{5.0 \text{ mol L}^{-1}}{2.5 \text{ mol L}^{-1} \times 1.2 \text{ mol L}^{-1}} = 1.67$$

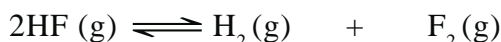
$Q_C < K_C$  thus the reaction mixture is not an equilibrium mixture. So, the reactants should combine to form more products to reach equilibrium, i.e., the reaction should proceed further to the right (the forward direction).

## Exercise 5.9

1. At a start of a reaction, there are 0.0218, 0.0145, and 0.0783 moles of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$ , respectively, in a 3.5 liter reaction vessel at  $430^\circ\text{C}$ . Decide whether or not the reaction is at equilibrium. If not, predict in which direction the reaction will proceed. The equilibrium reaction is:

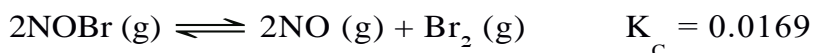


2. At a very high temperature, the following reaction has  $K_{\text{C}} = 1.0 \times 10^{-13}$



At a certain time, the concentrations of  $\text{HF}$ ,  $\text{F}_2$  and  $\text{H}_2$  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  $\text{NOBr}$  is represented by the equation:



At equilibrium the concentrations of  $\text{NO}$  and  $\text{Br}_2$  are  $1.05 \times 10^{-2}$  M and  $5.24 \times 10^{-3}$  M, respectively. What is the concentration of  $\text{NOBr}$ ?

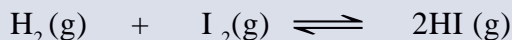
## C. Calculate the equilibrium concentrations

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:

1. Write the balanced equation for the reaction and then the  $K_{\text{C}}$  or  $K_{\text{p}}$  expressions.
2. List the initial concentrations.
3. Calculate  $Q_{\text{C}}$  or  $Q_{\text{p}}$  to determine the direction of the reaction, if initial concentrations of the reactants and products are given.
4. Define the change in concentration needed to reach equilibrium and find the equilibrium concentrations by using the change of the initial concentrations.
5. Substitute the equilibrium concentrations into the  $K_{\text{C}}$  or  $K_{\text{p}}$  expression, solve for the unknown.
6. Check whether the calculated equilibrium concentrations give the correct value of  $K_{\text{C}}$  or  $K_{\text{p}}$ .

### Example 5.7

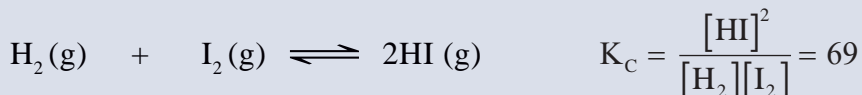
1. The equilibrium constant,  $K_C$  is 69 for the following reaction:



Given that 1 mole of  $\text{H}_2$  and 2 moles of  $\text{I}_2$  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:



$$[\text{HI}]_{\text{initial}} = [\text{HI}]_0 = 0$$

$$[\text{H}_2]_0 = \frac{1 \text{ mol}}{0.5 \text{ L}} = 2 \frac{\text{mol}}{\text{L}} = 2 \text{ M}$$

$$[\text{I}_2]_0 = \frac{2 \text{ mol}}{0.5 \text{ L}} = 4 \frac{\text{mol}}{\text{L}} = 4 \text{ M}$$

2. No need to calculate  $Q_C$  since  $[\text{HI}]_0 = 0$
3. Let the number of moles of  $\text{H}_2$  (or  $\text{I}_2$ ) consumed per liter to reach an equilibrium is  $x$ . Since the stoichiometric proportion of each reactant ( $\text{H}_2$  and  $\text{I}_2$ ) 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	$\text{H}_2$	+	$\text{I}_2$	$\rightleftharpoons$	$2\text{HI}$
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:

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$64 = \frac{(2x)^2}{(2.0 \text{ M} - x)(4.0 \text{ M} - x)} = \frac{(2x)^2}{x^2 - 6x + 8}$$

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:

$$\begin{aligned} x &= \frac{-(-384) \pm \sqrt{(-384)^2 - 4(60 \times 512)}}{2 \times 60} \\ &= \frac{384 \pm \sqrt{2.5 \times 10^4}}{120} = \frac{384 \pm 158}{120} \end{aligned}$$

$$x = 1.9 \text{ M or } 4.5 \text{ M}$$

But the change in concentration cannot be greater than the initial concentrations of the  $\text{H}_2$ , i.e., 2 M. Thus, only 1.9 is a reasonable value. Therefore, the equilibrium concentration of each species is:

$$[\text{H}_2] = 2.0 - x = 2.0 \text{ M} - 1.9 \text{ M} = 0.1 \text{ M}$$

$$[\text{I}_2] = 4.0 - x = 4.0 \text{ M} - 1.9 \text{ M} = 2.1 \text{ M}$$

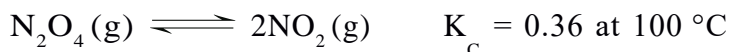
$$[\text{HI}] = 2x = 2(1.9 \text{ M}) = 3.8 \text{ M}.$$

$$\text{Check } K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(3.8 \text{ M})^2}{0.1 \text{ M} \times 2.1 \text{ M}} = 68.76 \approx 69$$

Therefore, the calculated equilibrium concentrations are correct.

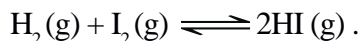
## Exercise 5.10

1. For the equilibrium:



A sample of 0.25 mol  $\text{N}_2\text{O}_4$  is allowed to dissociate and come to equilibrium in a 1.5 L flask at  $100^\circ\text{C}$ . What are the equilibrium concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ ?

2. At  $400^\circ\text{C}$ , the equilibrium constant for the reaction is 64:



A mixture of 0.250 mol  $\text{H}_2$  and 0.250 mol  $\text{I}_2$  was introduced into an empty 0.75 L reaction vessel at  $400^\circ\text{C}$ , find the equilibrium concentrations of all components.

### 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 is 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.

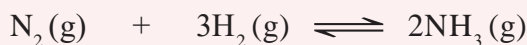
The factors whose change may affect a reaction equilibrium include **concentration of a reactant or product**, **reaction volume** or **applied pressure**, and **temperature**.

#### A. Effect of Change in The Concentration



#### Activity 5.5

Sit in pair and discuss the following idea. Share your discussion with the whole class. Consider the following equilibrium reaction:



Suppose at equilibrium position the concentrations of  $[\text{N}_2] = 0.399 \text{ M}$ ,  $[\text{H}_2] = 1.197 \text{ M}$ , and  $[\text{NH}_3] = 0.202 \text{ M}$ .

- a. What will happen if 1.000 M of  $\text{N}_2$  is suddenly injected into the system?

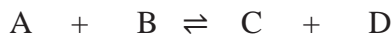


- b. What are the new concentrations of  $[\text{N}_2]$ ,  $[\text{H}_2]$  and  $[\text{NH}_3]$  after the system reaches the new equilibrium? (Hint: assume the  $K_c$  value at both equilibrium positions is equal.)

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:

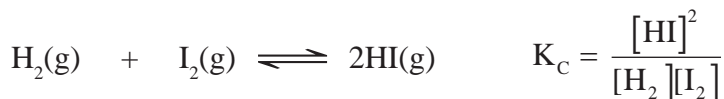
- If the concentration increases, the system reacts to reduce some of it.
- If the concentration decreases, the system reacts to produce some of it.

Consider the general reaction:



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.

Consider the following reversible reaction:



If you wish to convert as much  $\text{H}_2$  to  $\text{HI}$  as possible, you might increase the concentration of  $\text{I}_2$ . To understand the effect of this, first suppose that a mixture of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  is at equilibrium. If  $\text{I}_2$  is now added to this mixture, the equilibrium is disturbed. Thus, the reaction will now go in the direction that will use up some of the added  $\text{I}_2$ . Consequently, adding more  $\text{I}_2$  has the effect of converting a greater quantity of hydrogen to  $\text{HI}$ .

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?

## Experiment 5.1

### The Effect of Change in Concentration on Equilibrium Position

**Objective:** To study the effect of concentration on the position of equilibrium.

**Apparatus:** Test tubes, test tube stands, 100 mL beakers

**Chemicals:** 0.1M  $\text{HNO}_3$  solution, 0.05M  $\text{Fe}(\text{NO}_3)_3$  solution in 0.1M  $\text{HNO}_3$ , 0.01M  $\text{KSCN}$  solution in 0.1M  $\text{HNO}_3$ .

#### Procedure:

1. Take 5 test tubes and label them as 1, 2, 3, 4 and 5. Keep them in a test tube rack.
2. Take 50 mL of 0.05 M solution of  $\text{Fe}(\text{NO}_3)_3$  in a beaker.
3. In separate beakers take 10 mL of 0.01 M  $\text{KSCN}$  solution and 20 mL of 0.1 M  $\text{HNO}_3$  acid solution.
4. Mix the solutions as in the given table to prepare 5 different solutions

Volume in mL of:			
Test tube	0.05M $\text{Fe}(\text{NO}_3)_3$	0.1M $\text{HNO}_3$	0.01M $\text{KSCN}$
1	1.0	4.0	5.0
2	2.0	3.0	5.0
3	3.0	2.0	5.0
4	4.0	1.0	5.0
5	5.0	0.0	5.0

5. Note the color of the solution in each test tube.
6. Arrange the test tubes in increasing order of color intensity.

#### Observations and analysis:

1. Which direction is exothermic and which is endothermic? Explain your results.
2. Correlate the colour intensity with the concentration of  $\text{Fe}^{3+}$  in the test tube.  
Hint:  $\text{Fe}^{3+}$  forms deep red colour complex with  $\text{SCN}^-$  ions.  
$$\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{SCN})^{2+}(\text{aq}) \text{ deep red}$$
3. By taking different volumes of  $\text{Fe}(\text{NO}_3)_3$  in the test tubes the concentration of  $\text{Fe}^{3+}$  is varied in the solution. Calculate the concentration of  $\text{Fe}^{3+}$  ions in each test tube and correlate with the color intensity.

4. In the test tube take 1.0 mL of  $\text{Fe}(\text{NO}_3)_3$  solution and add 4.0 mL of  $\text{HNO}_3$  solution followed by 1.0 mL of  $\text{KSCN}$  solution. Mix well and note the color. Add 1.0 mL of  $\text{Fe}(\text{NO}_3)_3$  solution and again note the color of the solution.

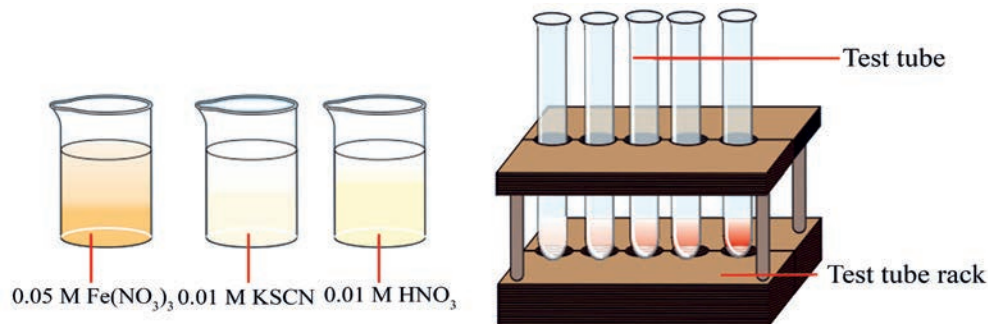


Figure 5.2: Laboratory set-up for the effect of changes in concentration on equilibrium of  $\text{Fe}^{3+}(\text{aq})$  and  $\text{SCN}^{-}(\text{aq})$

## B. Effect of Change in Pressure



### Activity 5.6

Explain why changes in pressure have little effect on the concentrations of solids or liquids. Hint: Refer to Unit 3 Physical States of Matter.

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 Chatelier'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:

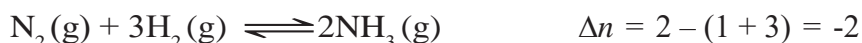


The effect of pressure is decided by:

$$\Delta n. \Delta n = (c + d) - (a + b)$$

- 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 dinitrogen 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.
  - a.  $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$
  - b.  $2\text{H}_2\text{S}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{S}_2(\text{g})$
  - c.  $\text{C}(\text{s}) + \text{S}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g})$

### C. Effect of Change in Temperature



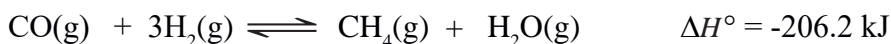
#### Activity 5.7

Sit in pair and discuss the similarities and differences between to the following two reactions. Share your discussion with the whole class.

- $$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \quad \Delta H^\circ_{\text{rxn}} = -9.4 \text{ kJ}$$
- $$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) \quad \Delta H^\circ_{\text{rxn}} = +182.6 \text{ kJ}$$

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  $K_c$  values of the methanation reaction at different temperatures:



<b><math>K_c</math> for methanation at different temperatures</b>	
298	$4.7 \times 10^{27}$
800	$1.38 \times 10^5$
1000	$2.54 \times 10^2$
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 favours the endothermic reaction. Whereas, a decrease in temperature favors the exothermic reaction.

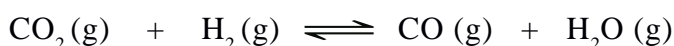
For example, formation of ammonia is an exothermic process:



From the equation we can see that 92 kJ of heat is released when  $\text{NH}_3$  is produced from  $\text{N}_2$  and  $\text{H}_2$ . Therefore, the forward reaction is exothermic, while the reverse reaction is endothermic. Thus, an increase in temperature favors the decomposition of ammonia to  $\text{N}_2$  and  $\text{H}_2$ , 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  $\text{CO}_2$  to  $\text{CO}$  by the endothermic reaction:



Is a high or a low temperature more favorable for the production of carbon monoxide? Explain.

## Experiment 5.2

### The Effect of Change in Temperature on the Equilibrium Position

**Objective:** Determination of the effect of changes in temperature on the position of equilibrium of iodine and starch.

**Apparatus:** Test tubes, water bath, stands, Bunsen burner, thermometer.

**Chemicals:** Iodine, starch.

#### Procedure:

1. Add a few drops of iodine to some starch solution in a test tube. Record your observations.
2. Heat the solution to about  $80^\circ\text{C}$  using a water bath. Record your observation. What do you conclude from this?
3. Cool the container by placing it in an ice box. Record your observation.

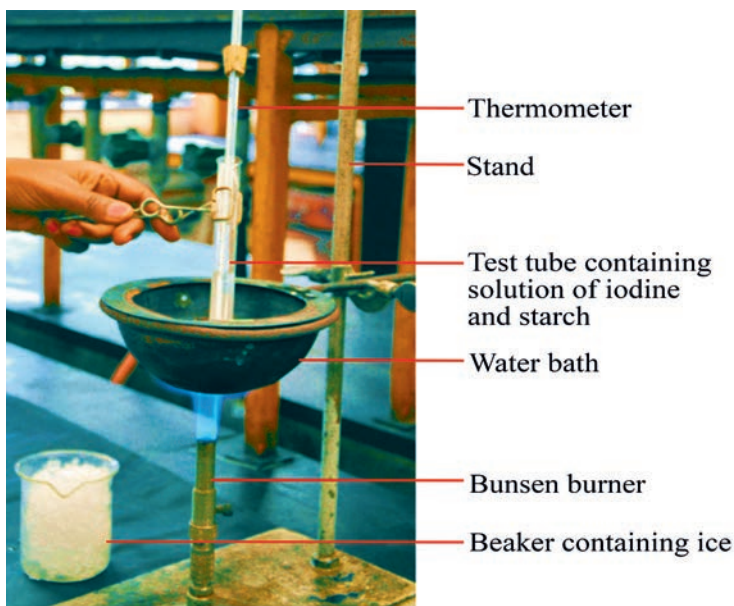


Figure 5.3: Laboratory set-up for the effect of changes in temperature on equilibrium of iodine and starch

**Observations and analysis:**

1. Is this reaction an example of an equilibrium reaction?
2. Which direction is exothermic and which is endothermic? Explain your results.
3. What can you conclude based on your observations?

#### D. Effect of Catalyst

As we learned in Unit 4, 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 an equilibrium constant or in the reaction quotients.

For instance,  $\text{SO}_3$  is formed by the reaction of  $\text{SO}_2$  with  $\text{O}_2$ :



The reaction is very exothermic, but very slow. It is catalyzed commercially in the Contact process by Pt,  $\text{SiO}_2$ , or  $\text{V}_2\text{O}_5$ , at high temperatures (400 to 700 °C).

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.

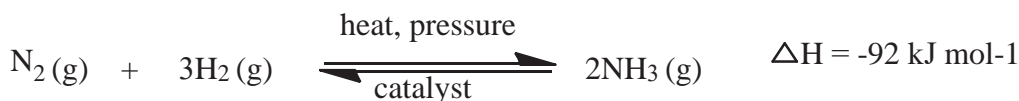
## 5.2.7 Equilibrium and Industry

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,  $\text{N}_2$ , would be converted to ammonia,  $\text{NH}_3$ , by reacting it with hydrogen,  $\text{H}_2$ . The Haber synthesis was developed into an industrial process by Carl Bosch.

The reaction between  $\text{N}_2$  and  $\text{H}_2$  to produce  $\text{NH}_3$  is an exothermic equilibrium reaction. It releases 92.4 kJ/mol of energy at 298 K.



According to **Le Chatelier's principle**, the production of ammonia is favoured 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:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$



As the temperature increases, the equilibrium constant decreases and the yield of ammonia decreases.

Temperature (°C)	$K_{eq}$
25	$6.4 \times 10^2$
200	$4.4 \times 10^{-1}$
300	$4.3 \times 10^{-3}$
400	$1.6 \times 10^{-4}$
500	$1.5 \times 10^{-5}$

In the industrial production of  $\text{NH}_3$  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  $\text{N}_2$  bonds and  $\text{H}_2$  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 5.4**.

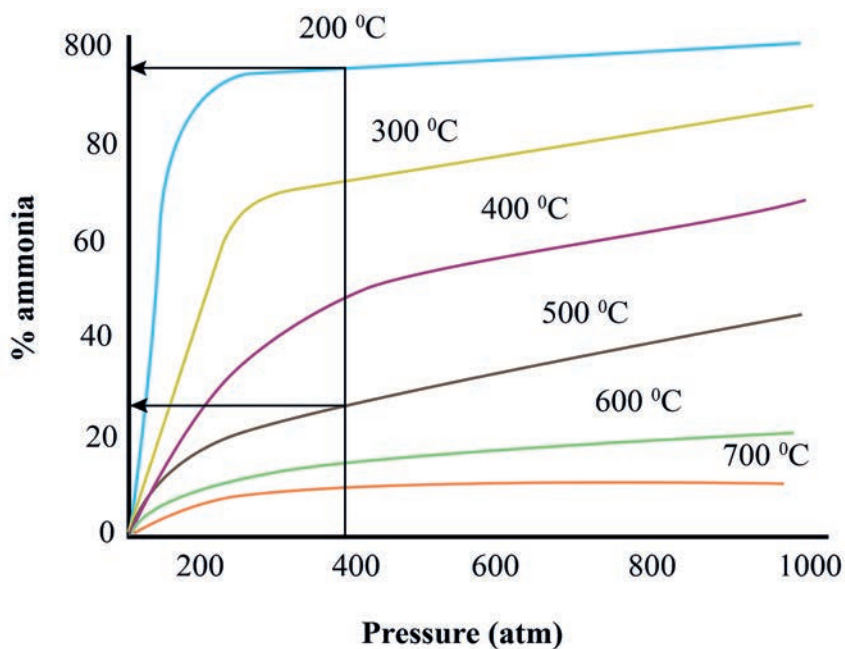


Figure 5.4: The effects of temperature and pressure on the percentage yields of ammonia for the Haber process

In the commercial production of ammonia,  $\text{NH}_3$  is continuously removed as it is produced. Removing the products causes more  $\text{N}_2$  and  $\text{H}_2$  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 5.5 shows a simplified flow diagram for the Haber process:

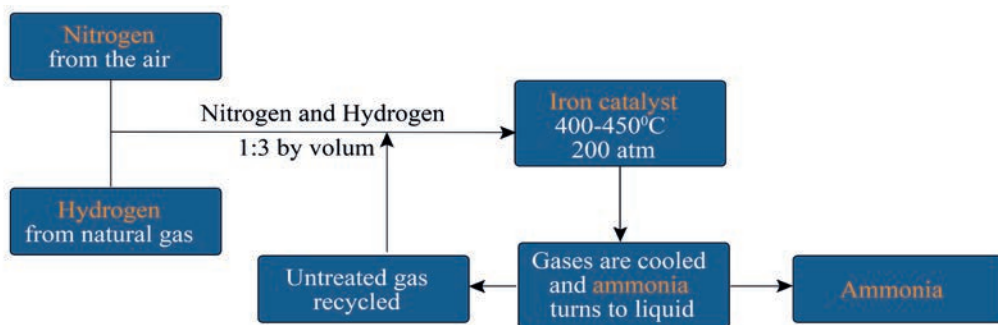


Figure 5.5: A flow diagram of the Haber process

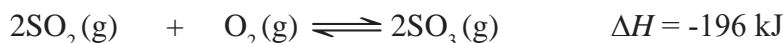
### Exercise 5.15

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?

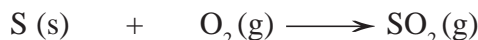
### B. Contact Process for the Manufacture of Sulphuric acid

The Contact process is the production of sulphuric acid,  $\text{H}_2\text{SO}_4$ , by the catalytic oxidation of sulphur dioxide,  $\text{SO}_2$ , to sulphur trioxide,  $\text{SO}_3$ . It is a reversible reaction:



The Contact process involves the following steps:

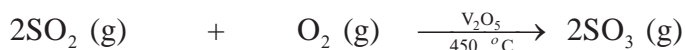
- i. Preparation of sulphur dioxide gas,  $\text{SO}_2$ , by burning pure sulphur in the presence of excess air:



To improve the efficiency of a catalyst (in the next step), various impurities present in the mixture of  $\text{SO}_2$  and air are first removed.

- ii. Conversion of  $\text{SO}_2$  to sulphur trioxide,  $\text{SO}_3$

Oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  takes place at  $450^\circ\text{C}$  in the presence of a catalyst, a vanadium (V) oxide ( $\text{V}_2\text{O}_5$ ):



- iii. Converting sulfur trioxide into sulfuric acid,  $\text{H}_2\text{SO}_4$

$\text{SO}_3(\text{g})$  is dissolved in concentrated  $\text{H}_2\text{SO}_4$  (98 %) to produce disulphuric acid or pyrosulphuric acid, also known as fuming sulphuric acid or oleum,  $\text{H}_2\text{S}_2\text{O}_7$ :



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  $\text{H}_2\text{S}_2\text{O}_7$  to obtain  $\text{H}_2\text{SO}_4$

A calculated amount of water is added to obtain sulphuric acid of desired strength:



The oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  (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  $\text{SO}_2$ , whereas lower temperatures would favor the production of  $\text{SO}_3$ . However, the rate of reaching equilibrium at the lower temperatures is extremely low. At higher temperature, equilibrium is reached rapidly but the yield of  $\text{SO}_3$  is lower. The temperature about  $450\text{ }^\circ\text{C}$  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.,  $\text{SO}_3$ . In the Contact process,  $\text{V}_2\text{O}_5$  is also used to speed up the rate of the reaction. Figure 5.6 shows the Contact process for the manufacture of  $\text{H}_2\text{SO}_4$ .

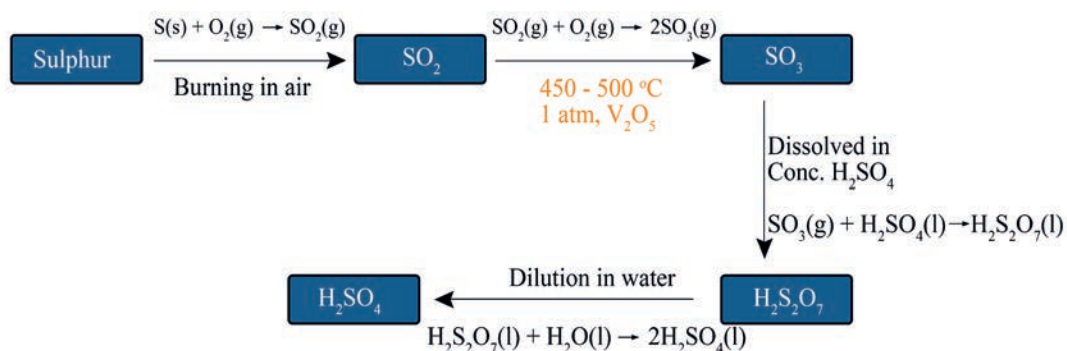


Figure 5.6: A flow diagram of the Contact process

### Exercise 5.16

Answer the following questions:

1. What is a mixture of  $\text{H}_2\text{SO}_4$  and free  $\text{SO}_3$ ?
2. What are the raw materials for making  $\text{SO}_2$  in the Contact process?
3. Why is  $\text{SO}_3$  not directly added to make  $\text{H}_2\text{SO}_4$ ?



## 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  $a A + bB \rightleftharpoons mM + nN$  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 products.
- Removing the products from the reaction vessel shifts the reaction in the forward direction.

## CHECKLIST

### KEY TERMS

- *Chemical equilibrium*
- *Components*
- *Equilibrium constant*
- *Law of mass action*

- *Le Chatelier's principle*
- *Reaction quotient*
- *Haber process*
- *Contact process*

## REVIEW EXERCISE

## Part I: Multiple Choice Type Questions

Choose the correct answer from the given alternatives

- Which of the following is correct about a reaction at equilibrium?
  - The concentrations of reactants and products are equal.
  - The system is static in nature.
  - The forward and backward rates are equal.
  - None.
- For a reaction to shift towards the product direction, which of the following conditions holds true?
  - $Q_c = K_c = 0$
  - $Q_c < K_c$
  - $Q_c > K_c$
  - $Q_c = K_c$
- Given the equation  $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ , the expression for  $K_c$  is:
  - $\frac{2[CO]}{2[C][O_2]}$
  - $\frac{[CO]^2}{[C]^2[O_2]}$
  - $\frac{[CO]^2}{[O_2]}$
  - $\frac{2[CO]}{[O_2]}$
- In which of the following cases does the reaction go fastest towards completion:
  - $K = 10^3$
  - $K = 10^{-2}$
  - $K = 10$
  - $K = 1$
- 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?
  - 0.5 atm
  - 4.0 atm
  - 8.0 atm
  - 32.0 atm
- 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:
  - 0.1
  - 10
  - 0.05
  - 20
- Which of the following is likely to happen when pressure is applied to the following system at equilibrium:  $H_2O(s) \rightleftharpoons H_2O(l)$ 
  - More water will be formed
  - More ice will be formed
  - Water will evaporate
  - No change occurs

8. The equilibrium constant for the reaction  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  is  $K_1$  and for the reaction  $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$  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?  
 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- a. No change occurs.  
b. Reaction shifts in the forward direction  
c. More CaCO<sub>3</sub> 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 questions**

11. For the reaction at equilibrium:  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$   
 $\Delta H = -196$  kJ/mol. Predict the direction of the change on:
- a. Removal of SO<sub>2</sub>  
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  $K_p$ .
- a.  $NH_3(g) + O_2(g) \rightleftharpoons N_2(g) + H_2O(g)$   
b.  $N_2(g) + H_2(g) \rightleftharpoons NH_3(g)$   
c.  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
13. For the reaction at 200 °C:  $2A(g) + B(g) \rightleftharpoons 3C(g)$  the equilibrium constant is 3.0. Given the following information,

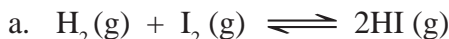
Species	Concentration
[A]	2.0 M
[B]	3.0 M
[C]	2.0 M

predict the direction in which the reaction should proceed to reach equilibrium.



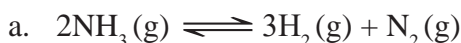
14. Given the reaction:  $2\text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$  what is the concentration of CO in equilibrium at 25 °C in a sample of gas originally containing 1.00 mol L<sup>-1</sup> of CO<sub>2</sub>? For the dissociation of CO<sub>2</sub> at 25 °C,  $K_c = 2.96 \times 10^{-92}$ .

15. Hydrogen and iodine react according to the equation:



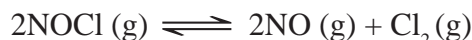
Suppose 1.00 mol H<sub>2</sub> and 2.00 mol I<sub>2</sub> are placed in a 1.00 L vessel. How many moles of substances are in the gaseous mixture when it comes to equilibrium at 458 C? The equilibrium constant  $K_c$  at this temperature is 49.7.

16. 5.0 moles of ammonia were introduced into a 5.0 L reaction chamber in which it partially decomposed at high temperatures;

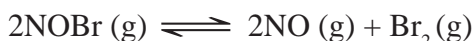


b. At equilibrium at a particular temperature, 80.0% of the ammonia had reacted. Calculate  $K_c$  for the reaction.

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.

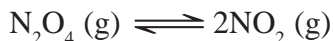


18. A sample of nitrosyl bromide was heated to 100°C in a 10.0 L container in order to partially decompose it.



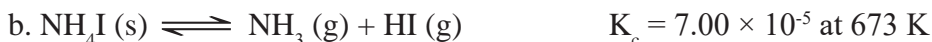
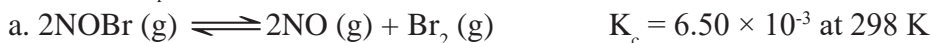
At equilibrium the container was found to contain 0.0585 mole of NOBr, 0.105 mole of NO, and 0.0524 mole of Br<sub>2</sub>. Calculate the value of  $K_c$ .

19. The brown gas NO<sub>2</sub> and the colorless gas N<sub>2</sub>O<sub>4</sub> exist in equilibrium.

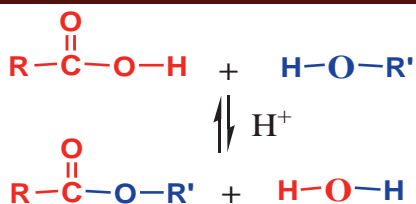


0.625 mole N<sub>2</sub>O<sub>4</sub> was introduced into a 5.00 L vessel and was allowed to decompose until it reached equilibrium with NO<sub>2</sub>. The concentration of N<sub>2</sub>O<sub>4</sub> at equilibrium was 0.0750 M. Calculate  $K_c$  for the reaction.

20. Calculate  $K_p$  for the following reactions at the indicated temperature.



# UNIT 6



## SOME IMPORTANT OXYGEN-CONTAINING ORGANIC COMPOUNDS

### Unit Outcomes

*At the end of this unit, you will be able to:*

- ☞ *classify organic compounds*
- ☞ *write the structural formula and IUPAC names of alcohols, ethers, aldehydes, ketones, carboxylic acids and esters*
- ☞ *give the general formulas of alcohols, ethers, aldehydes, ketones, carboxylic acids and esters*
- ☞ *describe some physical and chemical properties of alcohols, ethers, aldehydes, ketones, carboxylic acids and esters*
- ☞ *develop skills in naming and writing the molecular and structural formulas of alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, anhydrides, amides, and acid chlorides*
- ☞ *predict and correctly name the products of organic reactions, including substitution, addition, elimination, esterification, hydrolysis and oxidation reactions*
- ☞ *perform activities to prepare an alcohol (Katikalla), and a carboxylic acid*
- ☞ *test for the carboxylic acid and ester functional groups*
- ☞ *write the general formula of fats and oil and the structures for some common triglycerides*
- ☞ *give the structures, properties and uses of fats and oils, and demonstrate scientific enquiry skills, including: observing, classifying, comparing and contrasting, asking questions, drawing conclusions, applying concepts and problem solving.*



## Start-up Activity

Perform the following activity in groups and present your response to the rest of the class.

Take turns to name an item that contains organic molecules that we use in daily life, and identify what class of organic compound (s) it contains.

## 6.1 Introduction

*At the end of this section, you will be able to:*

☞ *classify organic compounds.*

### Classification of organic compounds

Why is classification of organic compounds needed? What is the basis of the classification?

In Grade 10, you have learned about some general organic reactions of hydrocarbons. In this unit, you will continue to learn about more functional groups: oxygen-containing functional groups. 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.

*Can you name the common functional groups and give an example for each functional group?*

Aldehydes and ketones contain a carbonyl group that consists of a carbon–oxygen double bond (C=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. In this unit, you will also learn about fats and oils which are esters.

## 6.2 Alcohols and Ethers

*At the end of this section, you will be able to:*

- ☞ define alcohols*
- ☞ tell the functional group of alcohols*
- ☞ classify alcohols based on the number of hydroxyl groups*
- ☞ write the general formulas of monohydric alcohols*
- ☞ write the molecular formulas and the names of the first six members of the monohydric alcohols*
- ☞ give the IUPAC names for the given alcohols*
- ☞ classify monohydric alcohols based on the number of alkyl groups attached to the carbon atom carrying the hydroxyl group*
- ☞ give some examples for primary, secondary and tertiary alcohols*
- ☞ describe the physical properties of alcohols*
- ☞ explain general methods of preparation of alcohols*
- ☞ explain the industrial preparation of ethanol*
- ☞ perform an experiment to prepare ethanol from sugar*
- ☞ explain the chemical reactions of alcohols such as oxidation, reaction with active metals, esterification and dehydration*
- ☞ carry out an activity to show chemical reactions of alcohols with active metals*
- ☞ write the molecular formulas and names of the first six members of ethers*
- ☞ give the IUPAC names for given ethers*
- ☞ describe the physical properties of ethers*
- ☞ explain the general methods of preparation of ethers*
- ☞ explain the use of ethers, such as solvent inorganic reactions.*



## Activity 6.1

Discuss the following questions in groups, and write a report. Present your report to the class.

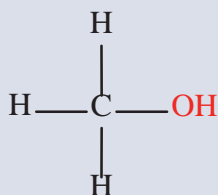
1. List some alcohols you know. Name the alcohol used in alcoholic beverages. What are the uses of alcohols in industry?
2. Ethiopia uses an alcohol blended with gasoline to drive cars. What is the name of the alcohol?
3. Hand sanitizers are used as an alternative to washing hands to kill most bacteria and viruses that spread colds and flu. Which alcohol (s) is present in hand sanitizers?
4. Explain the effects of using carbon-based fuels on the increase in carbon dioxide in the atmosphere and its consequences.

What do you think when you hear the word “alcohol”? Can you define alcohol?

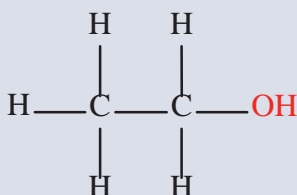
Give a few examples of the uses of alcohols. Most people think of two common alcohols: the substance that intoxicates people, and the one used in clinics and hospitals. However, there are many types of alcohol. The only alcohol present in all alcoholic beverages is called **ethanol**. Other alcohols are used for different purposes.

Alcohols are derivatives of hydrocarbons in which one or more of the hydrogen atoms in the hydrocarbon have been replaced by a hydroxyl group (–OH). The functional group in an alcohol is **an –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.

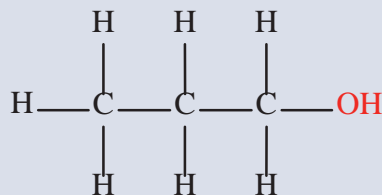
### Example 6.1



Methanol



Ethanol



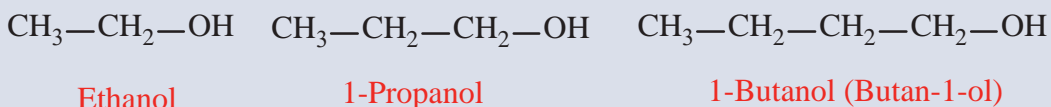
1-Propanol (Propan-1-ol)

### 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 ( $-\text{OH}$ ) groups respectively in their structures.

i. **Monohydric alcohols** are alcohols containing only one hydroxyl group.

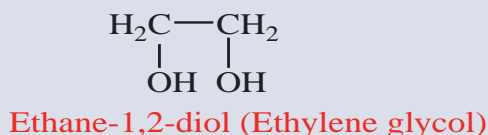
#### Example 6.2



Which one of the above monohydric alcohols is present in any drinking alcohol?

ii. **Dihydric alcohols** are those containing two hydroxyl groups per molecule. They are also named **glycols** or **diols**.

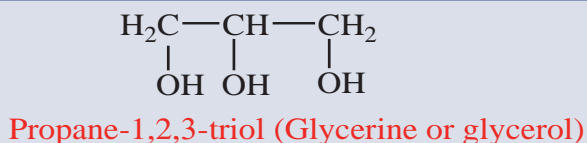
#### Example 6.3



Can you give more examples of dihydric alcohols?

iii. **Trihydric alcohols** are those containing three hydroxyl groups in their molecular structure.

#### Example 6.4



iv. **Polyhydric alcohols** are those alcohols containing three or more hydroxyl groups in their molecular structure.

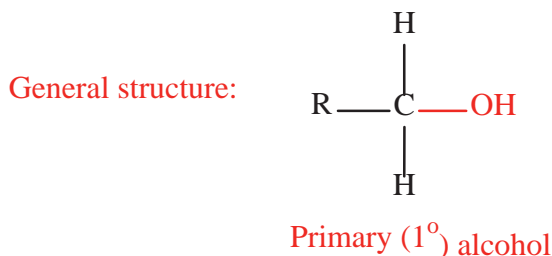
Can you give examples of polyhydric alcohols?

### Classification of Monohydric Alcohols

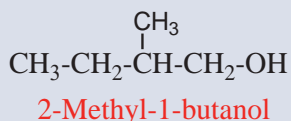
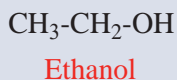
Monohydric alcohols may be further classified according to the carbon atom to which the hydroxyl group is attached.

#### Primary alcohols

In a primary alcohol, the carbon with the hydroxyl group is only attached to one alkyl group.

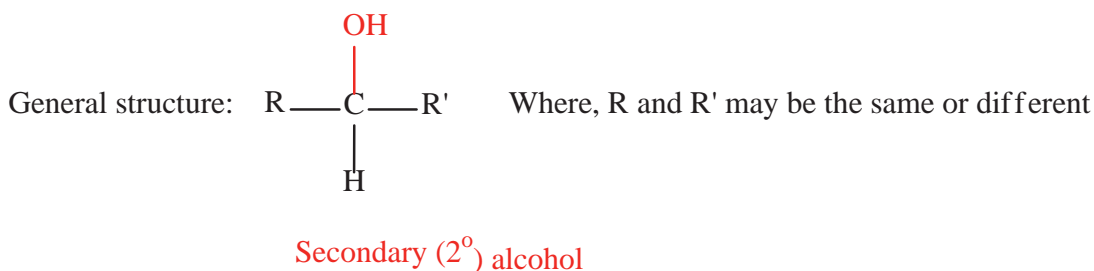


#### Example 6.5

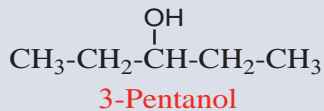
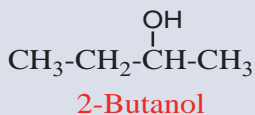
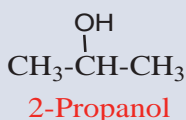


#### Secondary alcohols

In a secondary alcohol, the carbon with the hydroxyl group is attached to two alkyl groups.

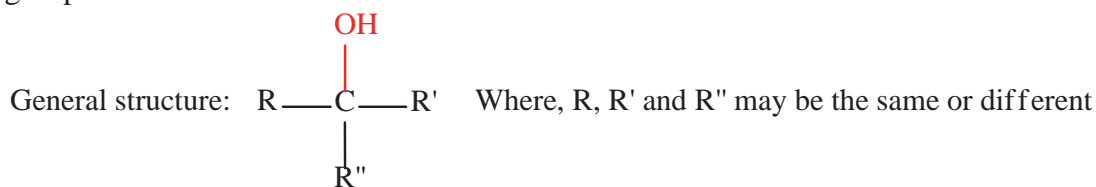


#### Example 6.6



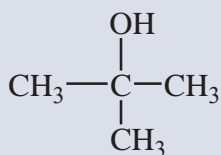
## Tertiary alcohols

In a tertiary alcohol, the carbon with the hydroxyl group is attached to three other alkyl groups.

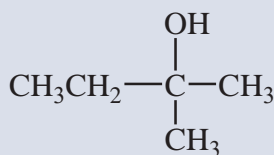


Tertiary ( $3^\circ$ ) alcohol

### Example 6.7



2-Methyl-2-propanol

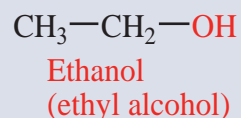
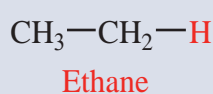
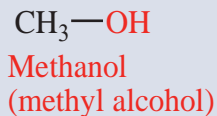
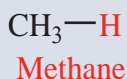


2-Methyl-2-butanol

## 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*.

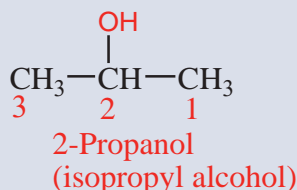
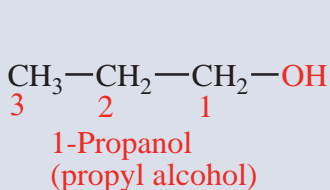
### Example 6.8



When an alcohol consists of a chain with three or more carbon atoms, the chain is numbered to give the position for the  $-\text{OH}$  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  $-\text{OH}$  group and other substituents are indicated by using the numbers of carbon atoms to which these are attached.



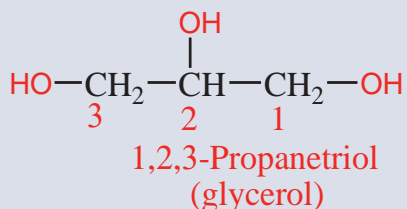
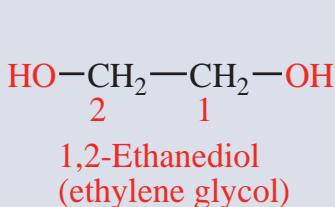
## Example 6.9



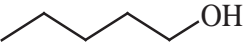

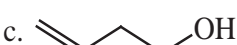
Is neopentyl alcohol a 1°, 2°, or 3° alcohol?

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'.

## Example 6.10



## Exercise 6.1

- Give the general formula for the homologous series of monohydric alcohols.
- Classify the following alcohols as monohydric, dihydric and trihydric alcohols.
  - 2-propanol
  - 1,3-propanediol
  - 1,2,3-butanetriol
- Classify the following monohydric alcohols as primary, secondary or tertiary alcohols.
  - 1-pentanol
  - 2-pentanol
  - 2-methyl-2-butanol
- Give the IUPAC name for the following alcohols:
  - 
  - 
  - 

## 6.2.3 Physical Properties of Alcohols



## Activity 6.2

Answer the following questions in groups, and share your answers with the whole class.

1. Is the bond in  $\text{-O-H}$  polar or non-polar? Why?
2. Compare the physical state of the first four members of monohydric alcohols and alkanes.
3. Lower alcohols, like methanol and ethanol, are miscible with water in all proportions, while lower hydrocarbons are not so. Explain.

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**).

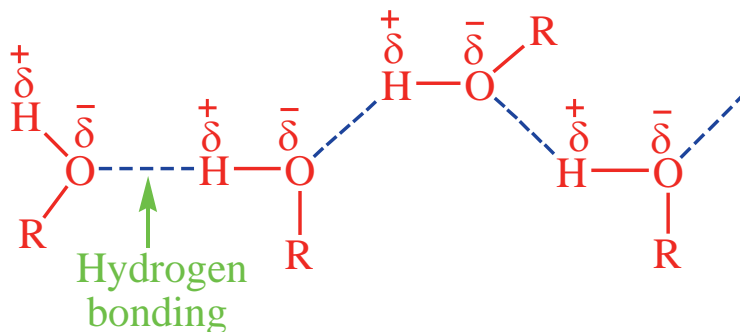


Figure 6.1: Hydrogen bonding between molecules of an alcohol

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.

## Group Assignment 6.1



Form a group of five and explain the following facts by searching information from the internet and any other sources. Submit your report in Word and PDF formats.

1. Dihydric and the trihydric alcohols have higher boiling points than monohydric alcohols of similar molecular size (mass).
2. The solubility of alcohols in water decreases with increasing carbon number.
3. The water solubilities of dihydric and trihydric alcohols are higher than those of monohydric alcohols of similar molecular mass.
4. The boiling point of a branched isomer is lower than that of its isomeric straight-chain alcohol.

**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 <sub>3</sub> OH	Methanol	-97	64.7	0.792
CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	-117	78.3	0.789
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1-Propanol	-126	97.2	0.804
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	1-Butanol	-90	117.7	0.810
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH	1-Pentanol	-78.5	138	0.817
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OH	1-Hexanol	-52	156.5	0.819

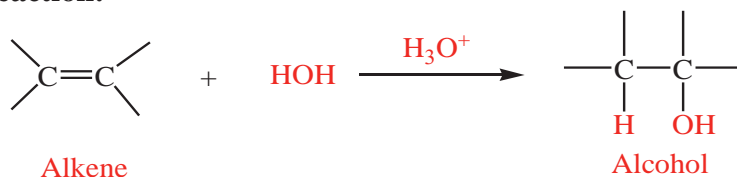
## 6.2.4 Preparation of Alcohols

The general laboratory methods of preparation of alcohols are:

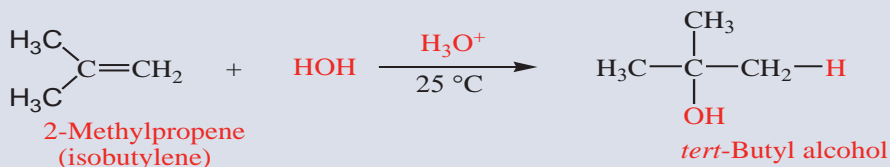
### A. Acid-catalyzed hydration of alkenes:

Water is added to the double bond of an alkene in the presence of dilute acid such as  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ .

#### General Reaction:



### Example 6.11



Note that hydrogen of the water goes to the carbon of the alkene that contains more hydrogens.

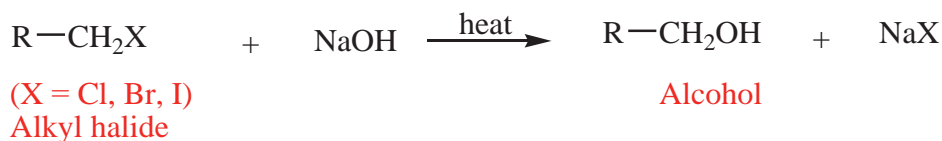
Does addition reaction change the hybridization of the carbon items initially held by the double bond? Explain.

### B. Hydrolysis of alkyl halides:

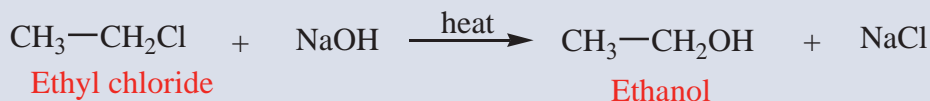
Warming alkyl halides with sodium hydroxide forms alcohols.

What does hydrolysis mean?

#### General Reaction:



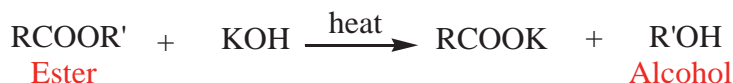
### Example 6.12



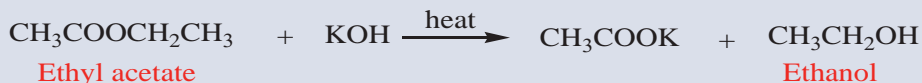
### C. Hydrolysis of Esters:

Heating esters with potassium hydroxide produces alcohols.

**General reaction:**



### Example 6.13



Methods **B** and **C** involve the replacement of other groups by the  $\text{—OH}$  group. Hence, they are examples of substitution reactions.

### Ethanol (Ethyl Alcohol), $\text{CH}_3\text{CH}_2\text{OH}$



### Activity 6.3

Answer the following questions individually and share your answers with others in the class.

1. Why is the shelf-life of some alcoholic beverages low, while for others it is high?
2. How can you improve the shelf-life of those alcoholic beverages with a low shelf-life?

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.

Can you categorize the alcoholic beverages as distilled and non-distilled?

## Industrial preparation of ethanol

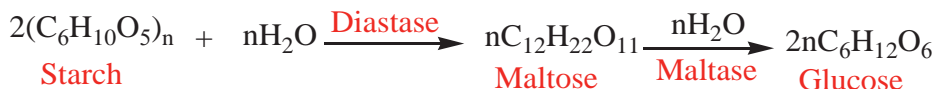
Ethanol is manufactured industrially by:

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:

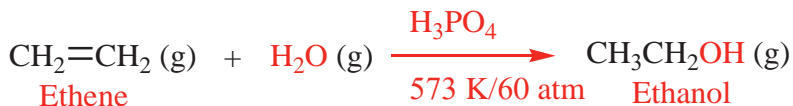


Fermentation can produce an alcoholic beverage whose ethanol content is 12–15% only. Why is it that difficult to produce a higher percentage of alcohols by fermentation? How can a higher ethanol-containing beverage be produced?

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,  $\text{H}_3\text{PO}_4$ , catalyst.



## Experiment 6.1

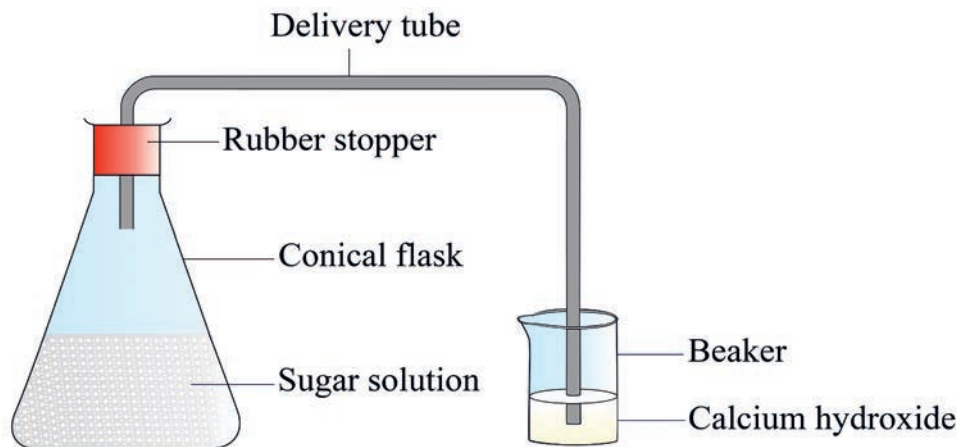
### Preparation of Ethanol by Fermentation

**Objective:** To prepare ethanol from sugar.

**Materials and chemicals:** Conical flask, glass rod, distillation flask, condenser, spatula, thermometer, watch glass, Bunsen burner, tripod, boiling chips, beaker, stopper and delivery tube. Sugar, ammonium phosphate or ammonium sulphate, yeast,  $\text{Ca}(\text{OH})_2$ .

### Procedure:

1. Take 50 mL of distilled water in a conical flask, add 15 g of sugar to it and stir. Add about 1 gram of yeast and a small amount of ammonium phosphate or ammonium sulphate to the solution. Arrange the setup, as shown in **Figure 6.2**, and let the flask stand for three days at a warm place.

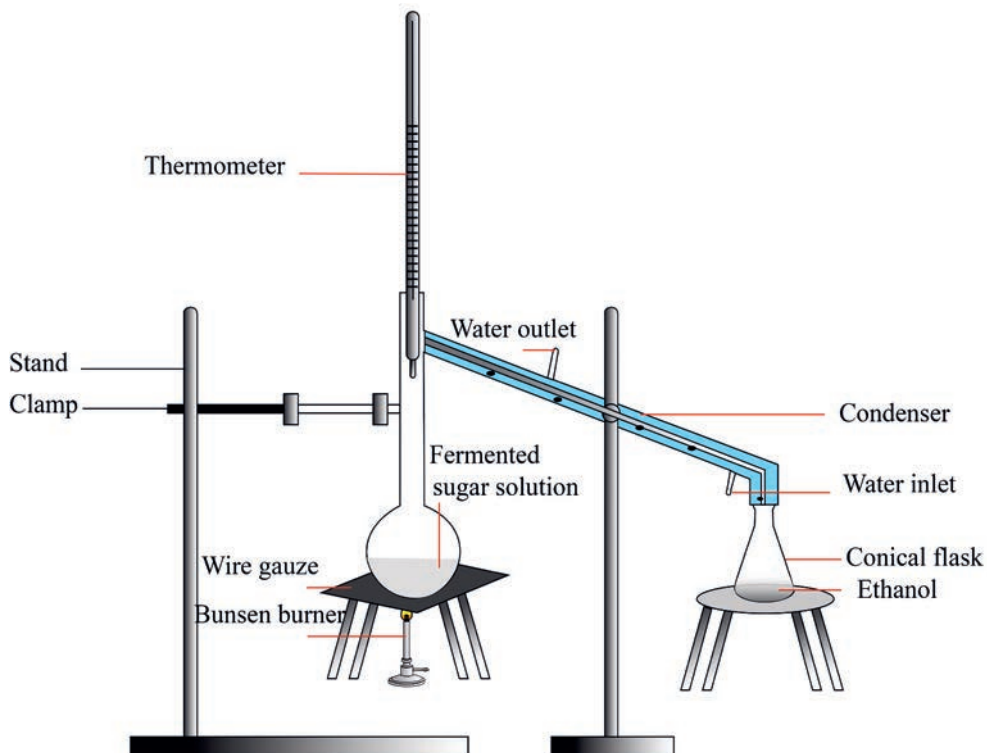


**Figure 6.2:** The fermentation of sugar

### Observations and analysis:

- A. What is the purpose of adding yeast to the solution?
- B. Why do we add ammonium phosphate or ammonium sulphate to the sugar solution?
- C. What happened to the calcium hydroxide solution at the end of the first or second day? Which gas is produced?
- D. What is the smell of the solution in the flask after three days?
- E. What has happened in the flask containing the sugar solution as it stood for three days?

- F. After three days, filter the solution, and arrange the set up as in **Figure 6.3**. Pour 20 mL of the filtrate in a distilling flask, with a few boiling chips, heat the solution, and collect the liquid in a receiver.



**Figure 6.3: Separation of ethanol by distillation**

**Points to observe:**

- Observe the colour and identify the smell of the distillate.
- Pour a small amount of the distillate on a watch glass, strike a match and bring the flame close to the distillate. Does it catch fire?
- Write a complete laboratory report on this experiment and submit it to your teacher.



## Project 6.1

Form a group of five and do the following activities. Submit Word and PDF documents to your teacher.

1. Search the preparation of “Katikalla”, “Tela”, “Tej”, and other locally prepared alcoholic beverages in your community by interviewing elders. Report your findings to the whole class.
2. Choose one locally prepared non-distilled alcoholic beverage in your community and illustrate its preparation.
3. Compare the traditional and industrial methods of preparing alcoholic beverages.
4. Search the internet or any other sources to summarize the properties and uses of ethanol.

### 6.2.5 Chemical Properties of Alcohols



#### Activity 6.4

Discuss the following questions in groups, and write a report. Present your report to the class.

1. Why do alcoholic beverages such as “Tela”, “Tej”, beer and wine turn sour if they are not properly stored? Which reaction of alcohols is responsible for this? Write a chemical equation to support your answer.
2. What types of reactions do alcohols undergo? Alcohols contain a hydrocarbon group and a functional group (–OH). Which part of alcohols is responsible for most of their chemical reactions?

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 6.14****Experiment 6.2****Reactions of Alcohols with Active Metals**

**Objective:** To observe the reaction of alcohols with sodium and magnesium.

**Materials required:** Ethanol, sodium and magnesium metal. Test tubes, test tube holder, test tube rack, measuring cylinder, Bunsen burner, scissors or knife.

**Procedure:**

Take two test tubes and add 2-5 mL of ethanol to each of the test tubes. Cut a very small piece of sodium with a knife and drop it into the first test tube. Take magnesium ribbon and drop it in the second test tube.

**Observations and analysis:**

- A. What do you observe
  - a. in the first test tube?
  - b. in the second test tube?
- B. Is there an evolution of gas? How do you check this gas is hydrogen?
- C. If no reaction occurs in any of the test tubes, heat the mixture gently using a Bunsen burner and write your observation.
- D. Which bond of the alcohol is broken in the reaction?
- E. Write a general reaction for such reactions.
- F. What type of metals reacts in this manner?

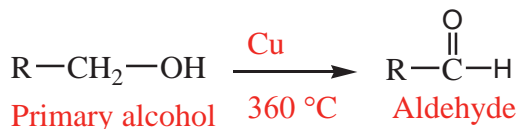
**b. Oxidation of alcohols**

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.

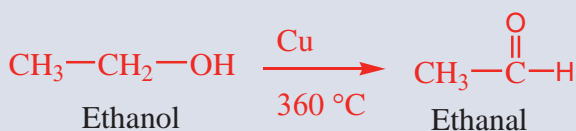
### i. Oxidation of primary alcohols

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:**

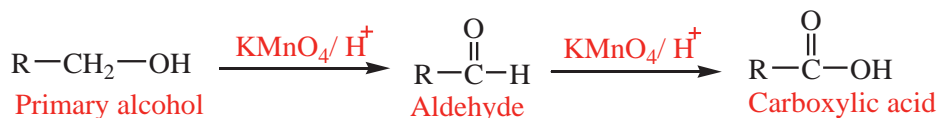


#### Example 6.15

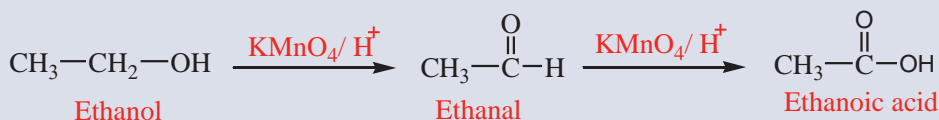


Strong oxidizing agents, such as acidified  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{CrO}_3$  in  $\text{H}_2\text{SO}_4$ , oxidize primary alcohol first to aldehydes and then to carboxylic acids. It is difficult to stop the reaction at the aldehyde stage.

**General reaction:**



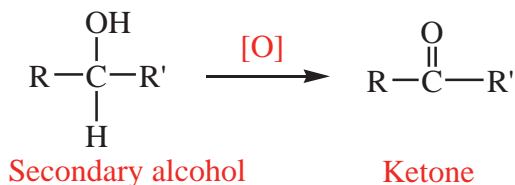
#### Example 6.16



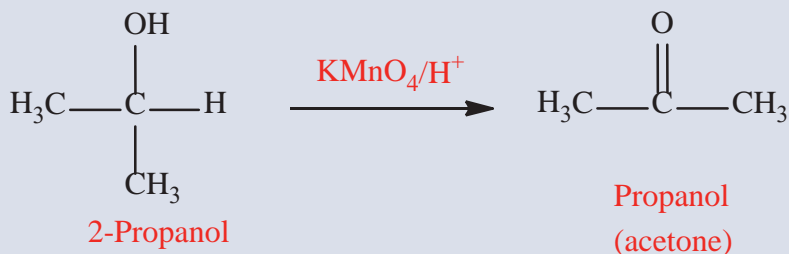
Is there any possibility to prepare aldehydes from primary alcohols?

### ii. Oxidation of secondary alcohols yields ketones

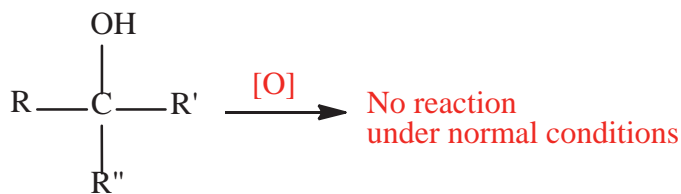
**General reaction:**



## Example 6.17



## iii. Tertiary alcohols and ketones are generally resistant to oxidation



Tertiary alcohol

What happens if 3° alcohols subject to oxidation under drastic conditions?

## Group Assignment 6.2

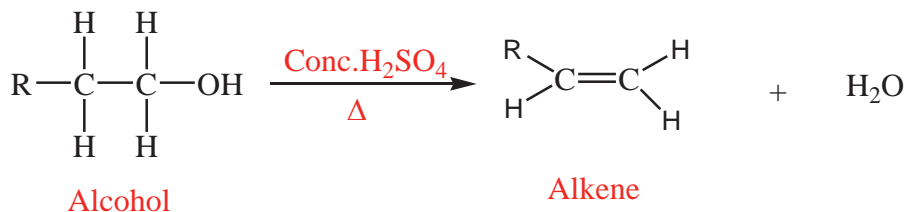


Do the following activity in a group of five and share your responses with the whole class.

Alcohols A, B, and C all have the composition  $\text{C}_4\text{H}_{10}\text{O}$ . Molecules of alcohol A contain a branched carbon chain and can be oxidized to an aldehyde; molecules of alcohol B contain a linear carbon chain and can be oxidized to a ketone; and molecules of alcohol C can be oxidized to neither an aldehyde nor a ketone. Predict the structural formulas of these molecules.

## 2. Reactions involving cleavage of carbon–oxygen (C – O) bond in alcohols

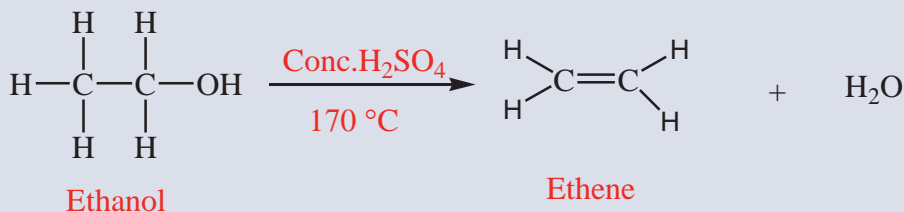
- a. **Dehydration of alcohols:** Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with an acid such as concentrated  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  and heating.

**General reaction:**

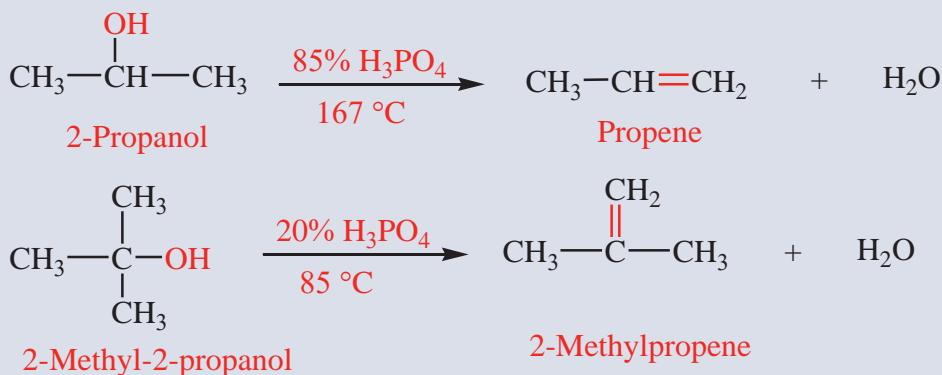
In general, dehydration of primary alcohols is difficult and requires concentrated acid and high temperature.

**Example 6.18**

Ethanol dehydrates in the presence of concentrated  $\text{H}_2\text{SO}_4$  and heating at  $170^\circ\text{C}$ .

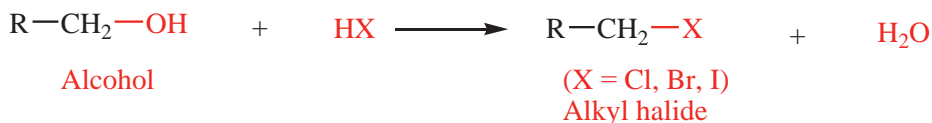
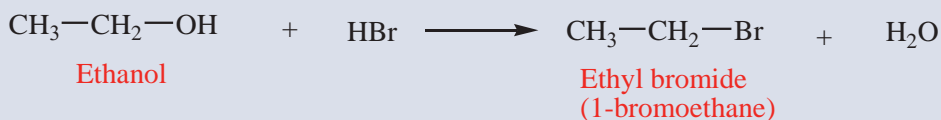


Secondary and tertiary alcohols dehydrate under milder conditions.

**Example 6.19**

Arrange primary, secondary, and tertiary alcohols in the degree of dehydration order.

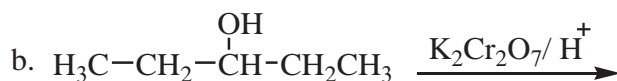
**b. Reactions of alcohols with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides.

**General reaction:****Example 6.20**

Is it possible to produce alcohols from alkyl halides?

**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:



## 6.2.6 Structure and Nomenclature of Ethers



## Activity 6.5

Try to answer the following questions in groups, and present your responses to the whole class.

1. Diethyl ether ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$ ) is prepared from ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{-OH}$ ). Based on these information and your prior knowledge of molecular structures, discuss these questions.
  - a. From  $\text{CH}_3\text{CH}_2\text{-OH}$  and  $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$ , which one do you expect to have higher boiling point?
  - b. Which one of these compounds is more soluble in water? Why?

**Ethers** are compounds in which an oxygen is bonded to two alkyl substituents ( $\text{R-O-R'}$ ), where R and R' may be the same or different. If the alkyl substituents are identical, the ether is a symmetrical ether. If the substituents are different, the ether is an unsymmetrical ether.

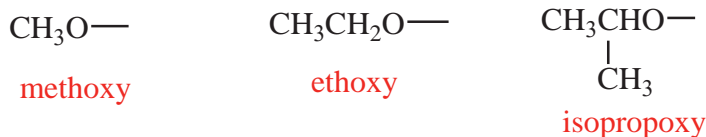


The common name of an ether consists of the names of the two alkyl substituents (in alphabetical order), followed by the word “ether”. The smallest ethers are almost always named by their common names.

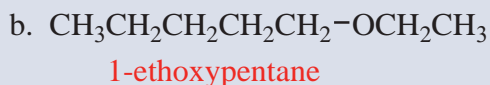
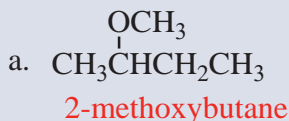
## Example: 6.21

- |  |   |  |
|--|---|--|
| a. $\text{CH}_3\text{-O-CH}_2\text{CH}_3$<br>ethylmethyl ether | b. $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$<br>diethyl ether | c. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH-O-CH}_2\text{CH}_3 \end{array}$<br>ethylisopropyl ether |
|--|---|--|

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 6.22



## Exercise 6.3

1. Give the systematic (IUPAC) name for each of the following ethers:



2. What are the common names of the compounds given in question 1?

## 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 (**Figure 6.4**).

How do ethers differ from alcohols?

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. How do you rate the boiling points of ethers and hydrocarbons of comparable molecular weight?

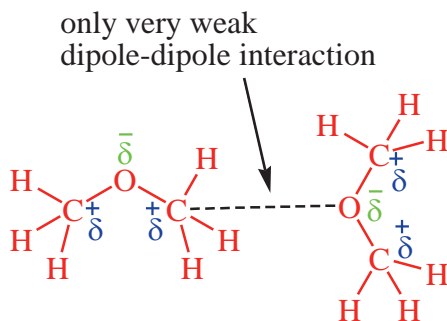


Figure 6.4: Weak attractive interactions exist between diethyl ether molecules in the pure liquid



Because the oxygen atom of ether carries a partial negative charge, ethers form hydrogen bonds with water (**Figure 6.5**) and are more soluble in water than are hydrocarbons of comparable molecular weight and shape.

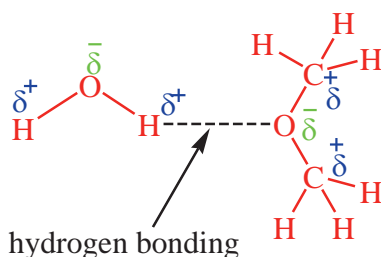


Figure 6.5: Hydrogen bonding between diethyl ether and water

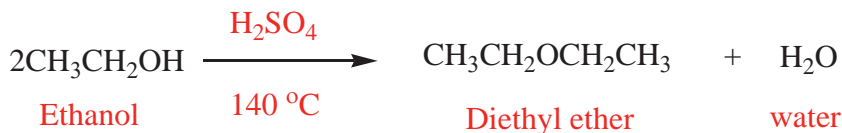
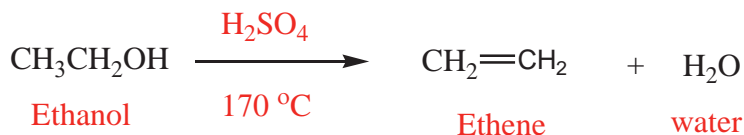
### Exercise 6.4

- Arrange these compounds in order of increasing solubility in water:
  - $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$
  - $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- Arrange these compounds in order of increasing boiling point:
  - $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$
  - $\text{HOCH}_2\text{CH}_2\text{OH}$
  - $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$
- 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.

### 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  $170^\circ\text{C}$  in the presence of sulphuric acid. On the other hand, ethanol yields ethoxyethane in the presence of sulphuric acid at  $140^\circ\text{C}$ . The method is limited to use with primary alcohols.



What is the problem if we use secondary and tertiary alcohols? Does this method work for the synthesis of both symmetrical and unsymmetrical ethers?

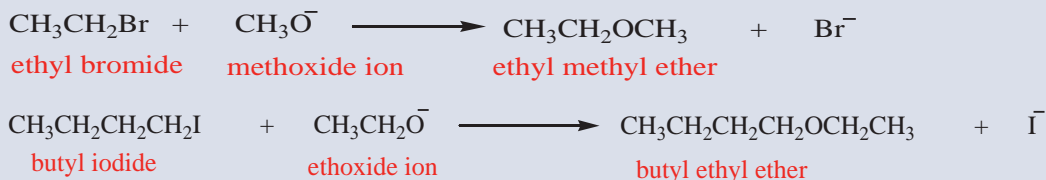
## 2. Williamson ether synthesis

In this method, an alkyl halide is made to react with an alkoxide which leads to the formation of ether.



Can this method be used for the preparation of both symmetrical and unsymmetrical ethers?

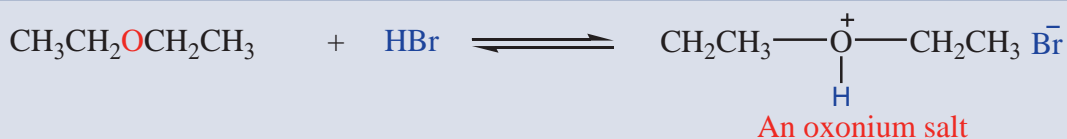
### Example 6.23



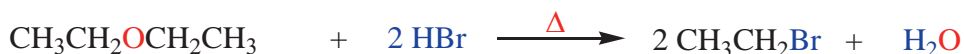
## 6.2.9 Reactions of Ethers

Ethers, R–O–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  $\text{KMnO}_4$ . Ethers are not affected by bases, however, they can react with proton donors to form oxonium salts.

### Example 6.24



Heating dialkyl ethers with very strong acids (HI, HBr, and  $\text{H}_2\text{SO}_4$ ) 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.

## 6.3 Aldehydes and Ketones

*At the end of this section, you will be able to:*

- ☞ write the general structural formulas of aldehydes and ketones
- ☞ give the structures and names of common members of each group
- ☞ describe the physical properties of aldehydes and ketones
- ☞ explain some methods of preparation of aldehydes and ketones
- ☞ explain the chemical reactions of aldehydes and ketones such as addition, oxidation and reduction
- ☞ give some chemical tests that differentiate aldehydes from ketones.

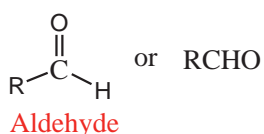


### Activity 6.6

Answer the following questions in groups then present your response to the whole class.

1. What functional group form if one of the carbon in the  $C=C$  is replaced by an oxygen atom?
2. What is the common type of reaction for alkenes?
3. Which type of reaction do you expect for 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.

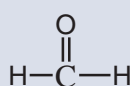


What are the simplest ketone and simplest aldehyde?

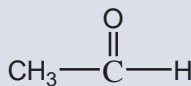
### 6.3.1 Nomenclature

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  $-\text{CHO}$ .

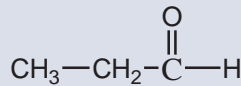
#### Example 6.25



Methanal



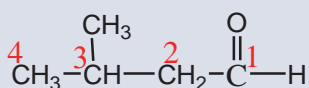
Ethanal



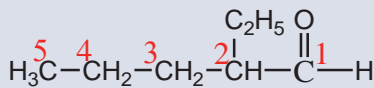
Propanal

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.

#### Example 6.26



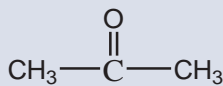
3-Methylbutanal



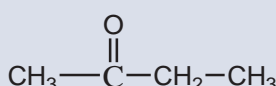
2-Ethylpentanal

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  $-\text{RCOR}'$ .

#### Example 6.27



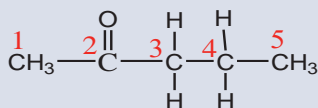
Propanone



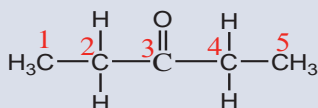
Butanone

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.

### Example 6.28



2-Pentanone or pentan-2-one

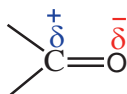


3-Pentanone or pentan-3-one

Give structures and name of ketones containing six (6) carbon atoms. Hint: consider isomeric forms including cyclic ones.

### 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 solubilities 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 <sub>3</sub> CHO	20	infinity
Propanal	Propionaldehyde	CH <sub>3</sub> CH <sub>2</sub> CHO	49	16
Butanal	Butyraldehyde	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	76	7
Hexanal	Caproaldehyde	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CHO	129	slight
Propanone	Acetone	CH <sub>3</sub> COCH <sub>3</sub>	56	infinity
2-Butanone	Methyl ethyl ketone	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	80	26
3-pentanone	Diethyl ketone	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>2</sub> CH <sub>3</sub>	101	5

## Project 6.2

Form a group of five and write on the following topics by searching information from the internet or any other sources. For each case, give the general reaction and specific examples.

i. Method of preparation of aldehydes and ketones. These may include:

**a. ozonolysis of alkenes**

**b. oxidation of alcohols:** oxidation of a primary alcohols using mild oxidizing agents  
oxidation of a secondary alcohol

ii. Reactions of aldehydes and ketones. Here focus on addition, oxidation, and reduction reactions.

a. Addition

- Addition of Grignard reagents to aldehydes and ketone
- Addition of alcohol: formation of hemiacetals and acetals

b. Oxidation

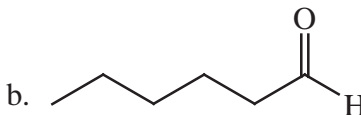
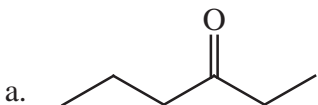
- Oxidation of aldehydes and ketones

c. Reduction

- Catalytic reduction of aldehydes and ketones
- Metal hydride reductions

## 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  $C_4H_8O$  and for the two aldehydes with molecular formula  $C_4H_8O$ .
- 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:



- Formalin helps in the preservation of biological specimens. What is the main constituent of formalin?

## 6.4 Carboxylic Acids

*At the end of this section, you will be able to:*

- ☞ *list common organic acids and name their sources*
- ☞ *write the general formula of saturated monocarboxylic acids*
- ☞ *write the molecular formulas and names of the first six members of the saturated monocarboxylic acids*
- ☞ *give the structural formula for the first four members of the saturated monocarboxylic acids*
- ☞ *give the examples of mono, di and tricarboxylic acids*
- ☞ *name some branched carboxylic acids]*
- ☞ *explain why “Tella” or “Tej” turns sour*
- ☞ *describe the physical and chemical properties of saturated monocarboxylic acids*
- ☞ *explain the general methods of preparation of saturated monocarboxylic acids*
- ☞ *explain the industrial and laboratory preparation of acetic acid*
- ☞ *conduct an experiment to prepare acetic acid in the laboratory*
- ☞ *name and write structural formulas of some fatty acids*
- ☞ *describe some uses of common carboxylic acids.*

### 6.4.1 Structure and Nomenclature of Carboxylic Acids



#### Activity 6.7

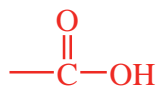
Discuss the following questions in groups, then present your response to the whole class.

1. What are acids?
2. Name some common house-hold carboxylic acids.



### 6.4.1.1 Structure of Carboxylic Acids

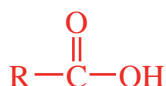
Carboxylic acid is one of the class of organic compounds containing the carbonyl functional group (C=O). A carboxyl group (COOH) is a functional group consisting of a carbonyl group (C=O) with a hydroxyl group (O–H) attached to the same carbon atom. It is usually written as —COOH or —CO<sub>2</sub>H.



Carboxyl group

#### A. Saturated monocarboxylic acids

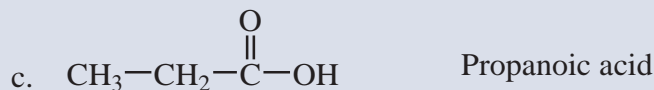
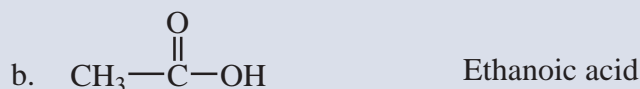
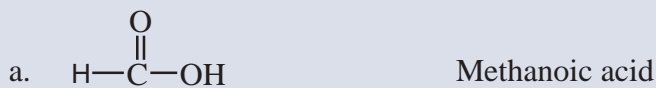
The general formula for saturated monocarboxylic acids can be written as:



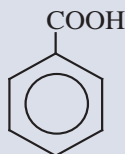
where R is either hydrogen or an alkyl group for aliphatic carboxylic acids. When R is phenyl (aryl) group, the structure represents aromatic carboxylic acids.

#### Example 6.29

1. The structure of the first three saturated monocarboxylic acids are written as follows:



2. The simplest aromatic acid is benzoic acid.



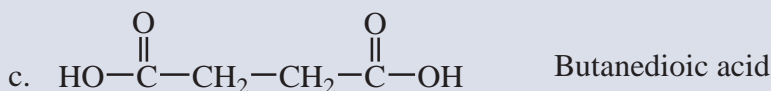
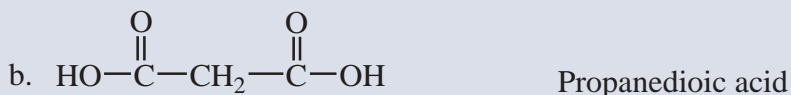
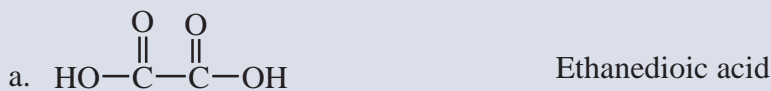
Benzene carboxylic acid (Benzoic acid)

**B. Di- and tricarboxylic acids**

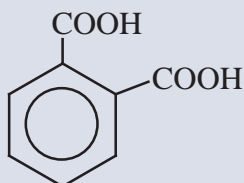
Carboxylic acids containing two carboxyl groups in their structure are called **dicarboxylic acids**.

**Example 6.30**

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- Benzenedicarboxylic acid (phthalic acid)

Give the structures, IUPAC and common names of the other two isomers.

Similarly, carboxylic acids that contain three carboxyl groups in their structure are called tricarboxylic acids. Example: citric acid is a typical tricarboxylic acid.

Can you give the structure of citric acid?

**Activity 6.8**

Form a group and make a list of some fruits containing carboxylic acid.

Which acid is commonly present in most fruits? Which carboxylic acid is present in wine fruits? Is this acid a monocarboxylic, a dicarboxylic or a tricarboxylic acid?

Present your responses to the whole class.

### Exercise 6.7

- Write the structure of the following monocarboxylic acids:
  - Butanoic acid
  - Pentanoic acid
- Write the structure of the following dicarboxylic acids:
  - Pentanedioic acid
  - Hexanedioic acid
  - 1,3-Benzenedicarboxylic acid
- A great many carboxylic acids are encountered in nature. List some of them and their respective sources.

#### 6.4.1.2 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.

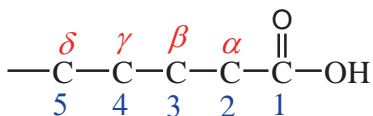
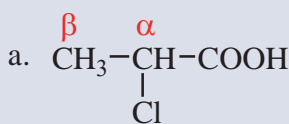
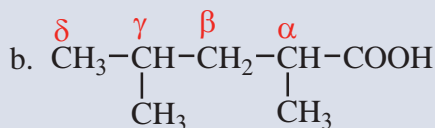
**Table 6.3: Common names of some monocarboxylic acids.**

Structure of Acid	Natural Source	Common Name
HCOOH	Ants (Formica)	Formic acid
CH <sub>3</sub> COOH	Vinegar (Acetum)	Acetic acid
CH <sub>3</sub> CH <sub>2</sub> COOH	Basic Fat (Propio)	Propionic acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Rancid butter (Butyrum)	Butyric acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Present in a Valerian herb	Valeric acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> 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,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ... for designating the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, ... position of carbon atoms as shown below:

**Example 6.31** $\alpha$ -chloropropionic acid $\alpha, \gamma$ -dimethylvaleric acid**C. Dicarboxylic acids**

Dicarboxylic acids also possess common names which are based on their sources.

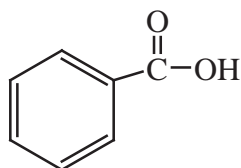
**Table 6.4** lists common and IUPAC names of some of the most important dicarboxylic acids.

**Table 6.4: Common and IUPAC names of some dicarboxylic acids.**

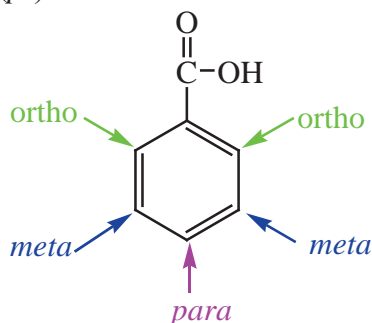
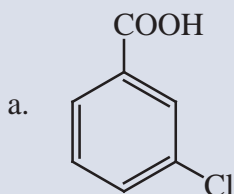
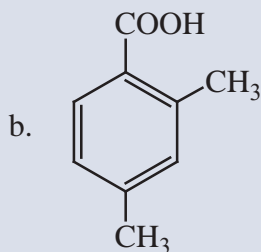
Structure	Common Name	IUPAC Name
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC-CH <sub>2</sub> -COOH	Malonic acid	Propanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>2</sub> -COOH	Succinic acid	Butanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>3</sub> -COOH	Glutaric acid	Pentanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>4</sub> -COOH	Adipic acid	Hexanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>5</sub> -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 6.32*****m*-chlorobenzoic acid*****o,p*-dimethylbenzoic acid.**

**Exercise 6.8**

- Write the common names for the following carboxylic acids:
  - $$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}-\text{COOH} \\ | \qquad \qquad | \\ \text{Br} \qquad \qquad \text{Cl} \end{array}$$
  - $\text{HOOC}-(\text{CH}_2)_2-\text{CH}_2-\text{COOH}$
- Write the structures of carboxylic acids for the given common names:
  - $\beta$ -Bromobutyric acid
  - p*-bromobenzoic acid
  - glutaric acid

**ii. IUPAC names of carboxylic acids**
**A. Straight chain monocarboxylic acid**

In IUPAC system, monocarboxylic acids are named by replacing the terminal “-e” of the corresponding alkane name with “-oic acid.” They are named as alkanonic acids.

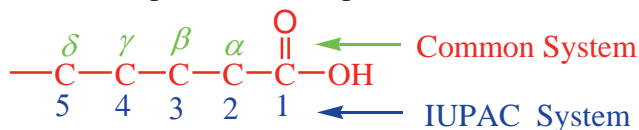
**Example 6.33**

- Write the IUPAC names for:
  - H-COOH
  - CH<sub>3</sub>-CH<sub>2</sub>-COOH
  - CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-COOH

methanoic acid                  propanoic acid                  pentanoic acid
- Write the structure of the following carboxylic acids:
  - Ethanoic acid
  - Butanoic acid
  - Hexanoic acid
  - $$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$$
  - $$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$$
  - $$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$$

**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 substituents 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  $\alpha$ -position in the common naming system.

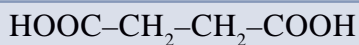

**Example 6.34**

- $\text{CH}_3-\text{CH}(\text{CH}_3)\text{CH}_2-\text{COOH}$   
 3-methylbutanoic acid
- $\text{CH}_3-\text{CH}_2\text{CH}(\text{Cl})-\text{CH}(\text{CH}_3)-\text{COOH}$   
 3-Chloro-2-methylpentanoic acid

### 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 6.35

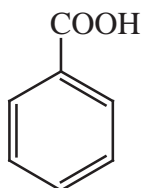


Butanedioic acid

Write the structure of hexanedioic acid.

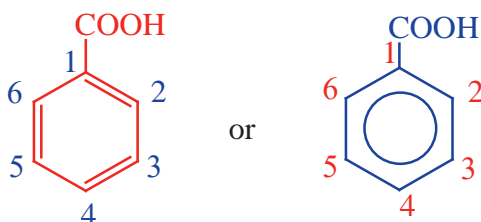
### D. Aromatic carboxylic acids

IUPAC name of the simplest aromatic carboxylic acid is benzenecarboxylic acids.

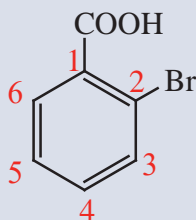


Benzenecarboxylic acid

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.



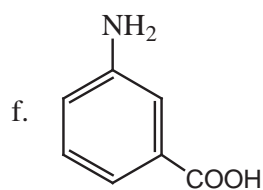
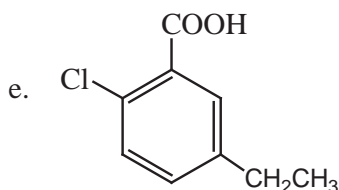
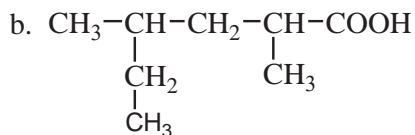
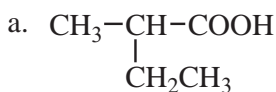
#### Example 6.36



2-bromobenzenecarboxylic acid

## Exercise 6.9

1. Write the IUPAC names for the following carboxylic acids:



2. Draw the structures of the following carboxylic acids:

- 3-chloro-2,3-dimethylpentanoic acid
- 4-bromo-2-hydroxybenzoic acid
- p*-Methylbenzoic acid
- 2-ethyl-3-methylpentanedioic acid

## 6.4.2 Physical Properties of Carboxylic Acids



## Activity 6.9

Discuss the following questions in groups, then present your ideas to the whole class.

- The solubility of monocarboxylic acids in water decreases with increase in molecular mass. Explain.
- Higher members of monocarboxylic acids are almost odourless. Why?
- Compare the boiling points of monocarboxylic acids with alcohols, aldehydes and ketones of similar molar masses?

## 1. State

The lower aliphatic acids containing up to 9 carbon atoms are liquids, whereas the higher members are colourless waxy solids. Benzoic acid and most of its derivatives are also colourless solids.



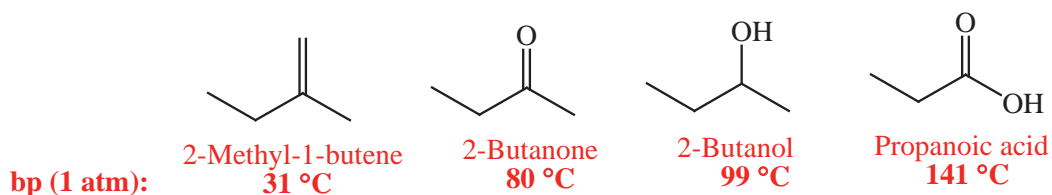
## 2. Odor

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

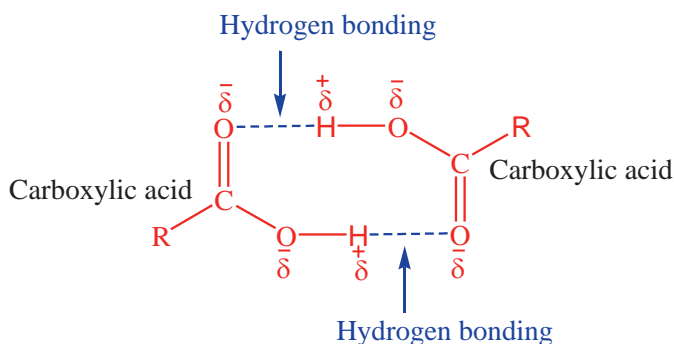
The melting points and boiling points of carboxylic acids are higher than those of hydrocarbons and oxygen-containing organic compounds of comparable size and shape and indicate strong intermolecular attractive forces. **Figure 6.6** gives boiling point comparison of carboxylic acid with alkene, ketone, and alcohol.

What is the molecular mass of each compound shown in **Figure 6.6**?



**Figure 6.6:** Boiling point comparison of carboxylic acid with alkene, ketone, and alcohol

A unique hydrogen-bonding arrangement, shown in **Figure 6.7**, contributes to these attractive forces. 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 shows hydrogen bonding between carboxylic acids and water molecules.

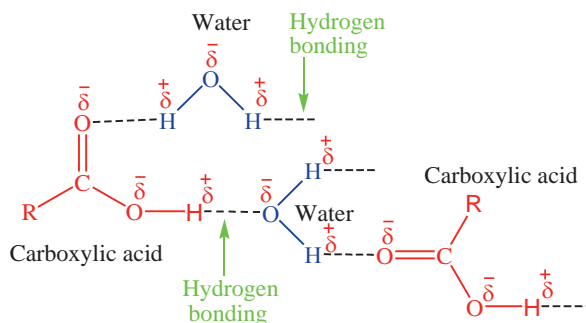


Figure 6.8: Formation of hydrogen bonding between carboxylic acids and water molecules

Does the solubility carboxylic acids in water decrease or increase with increasing molecular mass? Why? Do you predict that carboxylic acids will be soluble in organic solvents? Explain.

The boiling points, melting points and solubilities 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 <sub>2</sub> O at 25 °C
HCOOH	Methanoic acid	100.5	∞*
CH <sub>3</sub> COOH	Ethanoic acid	118	∞*
CH <sub>3</sub> CH <sub>2</sub> COOH	Propanoic acid	141	∞*
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	Butanoic acid	164	∞*
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	Pentanoic acid	187	4.97
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	Hexanoic acid	205	1.08

Structure	IUPAC Name	Boiling point (°C)	Solubility (g/100 mL) H <sub>2</sub> O at 25 °C
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COOH	Heptanoic acid	223	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH	Octanoic acid	239	0.07
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> COOH	Nonanoic acid	253	—
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOH	Decanoic acid	269	0.015

∞\* means miscible in all proportions.

### Exercise 6.10

- Arrange the following aliphatic carboxylic acids in the decreasing order of boiling point:
  - butanoic acid
  - decanoic acid
  - octanoic acid
  - propanoic acid
- Which of these aliphatic carboxylic acids has the lowest boiling point?
  - pentanoic acid
  - methanoic acid
  - hexanoic acid
  - propanoic acid
- Arrange the following compounds in increasing order of their boiling points:
  - C<sub>5</sub>H<sub>12</sub>
  - C<sub>2</sub>H<sub>5</sub>COOH
  - C<sub>4</sub>H<sub>11</sub>OH
  - CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>COOH

### 6.4.3 Chemical Properties of Carboxylic Acids



#### Activity 6.10

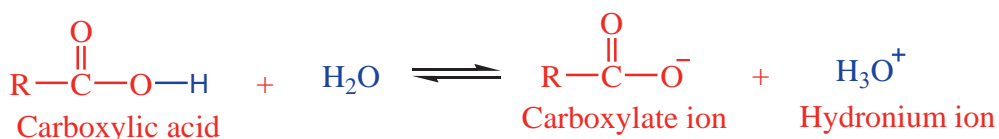
Form a group, discuss the following questions and present your responses to the whole class.

- Why does 'Tella' or 'Tej' turn sour when kept for a longer time but not Katikalla?
- Why does beer have a longer shelf life than 'Tella'?
- What is the practical use of metal salts of carboxylic acids in your daily life?

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:

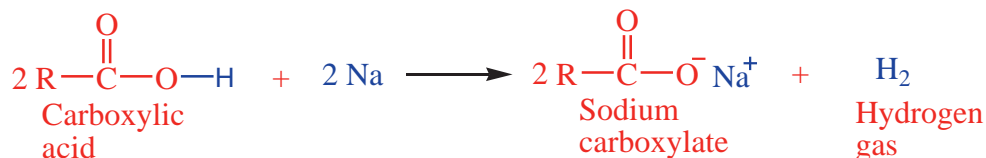
### i. Reaction as an acid

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.

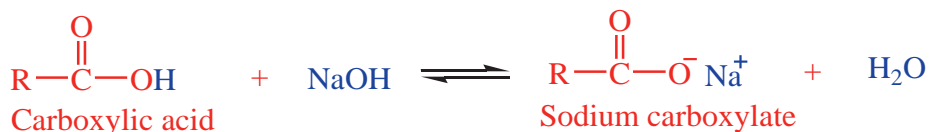


The salts of carboxylic acids are named by writing the name of the metal first, followed by the name of the acid replacing the ending *-ic acid* by *-ate*.

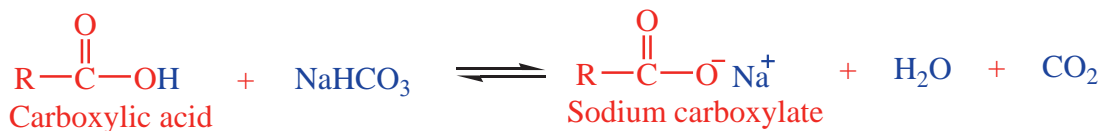
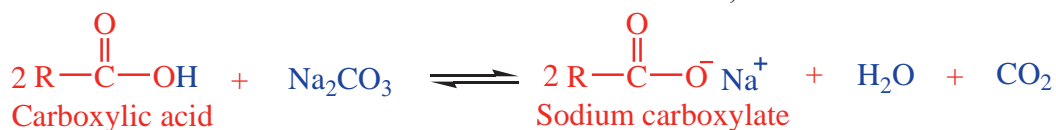
For example, sodium reacts with ethanoic acid to form sodium ethanoate and hydrogen.



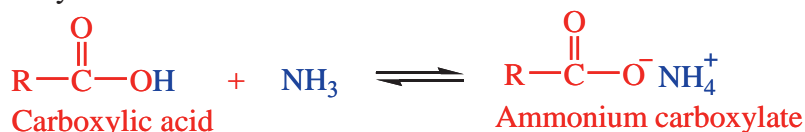
**b. Reaction with Bases:** Carboxylic acids react with strong bases like sodium hydroxide or potassium hydroxide to form the corresponding metal carboxylate salts and water.



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.

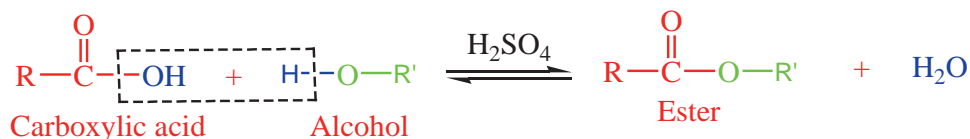


They also react with ammonia to form ammonium salts of carboxylic acids.



## ii. Formation of Esters

One of the important reactions of carboxylic acids involves the replacement of  $-\text{OH}$  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

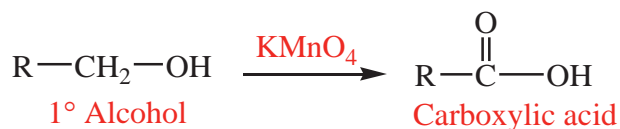
- Write the chemical equations for the reaction between ethanoic acid and each of the following reagents and write the names of the products formed:
  - KOH
  - $\text{Na}_2\text{CO}_3$
  - $\text{NH}_3$
- Write the chemical equations for the reaction between methanoic acid and ethanol and write the name of the product.

### 6.4.4 Preparation of Carboxylic Acids

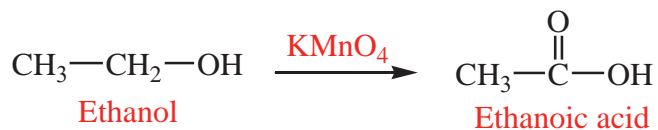
One of the important methods for preparation of carboxylic acids is **oxidation**. Many saturated monocarboxylic acids are obtained by the oxidation of the corresponding primary alcohols, whereas aromatic acids are obtained from the corresponding alkylbenzenes.

#### 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  $KMnO_4$ .



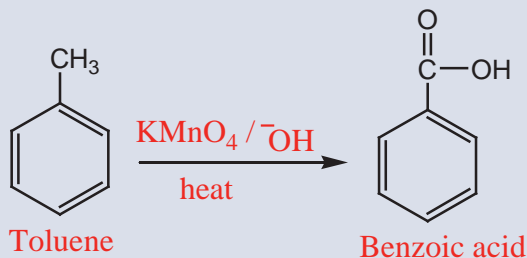
For example, oxidation of ethanol yields acetic acid (ethanoic acid).



#### ii. Oxidation of Alkylbenzenes

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 ethylbenzene, both give benzoic acid on refluxing with  $KMnO_4$  in alkaline medium.

## Example 6.37



Write the chemical equations for the oxidation of ethylbenzene with  $\text{KMnO}_4$  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. It can also be obtained by passing the vapours of ethanol through copper oxide as described in [Experiment 6.3](#).

## Experiment 6.3

## Laboratory Preparation of Acetic Acid

**Objective:** To prepare acetic acid in the laboratory by oxidation of ethanol.

**Apparatus:** Goggles, test tubes, test tube rack, quickfit distillation apparatus, 250 mL beaker, pipettes, Bunsen burner, stand, clamp, tripod, wire gauze, digital balance, blue litmus paper, boiling chips such as fine gravels, broken porcelain pieces, etc.

**Chemicals:** Ethanol, sodium dichromate, 1M sulphuric acid, 0.5M sodium carbonate solution.

**Procedure:****Oxidation of ethanol to ethanoic acid**

1. Set up the Quickfit distillation apparatus for refluxing as shown in [Figure 6.9a](#).
2. Place about 10 mL of 1M sulphuric acid into the 250 mL round-bottom flask.

3. Add 2-3 g of sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) and a few pieces of boiling chips. Swirl the contents of the flask until the solution is complete (warm if necessary).
4. Cool the mixture under a running tap since the process is exothermic.
5. Add 1 mL of ethanol dropwise into the flask.
6. Boil under reflux (Figure 6.9 a) for 20 minutes
7. Arrange the distillation set up as shown in (Figure 6.9 b) and distil up to 2-3 mL
8. Notice the smell of the product (distilled liquid) and compare it with that of ethanol.
9. Add a few drops of the distilled liquid to a small amount of solid sodium carbonate.
10. Add a drop of the distilled liquid to moistened blue litmus paper.

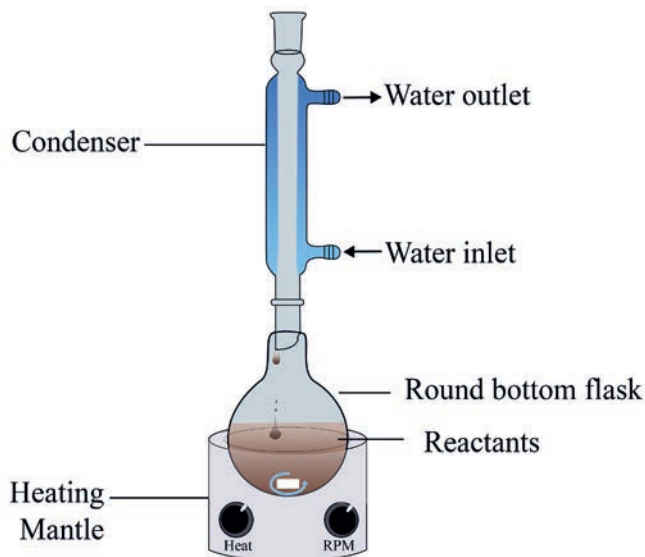


Figure 6.9a: Reflux set-up

### Observation and analysis

1. What happened to the colour of the solution in the flask?
2. What is the role of sodium dichromate in the above reaction? Is it oxidized or reduced?
3. Write the chemical equation for this reaction.
4. What do you conclude from this experiment?



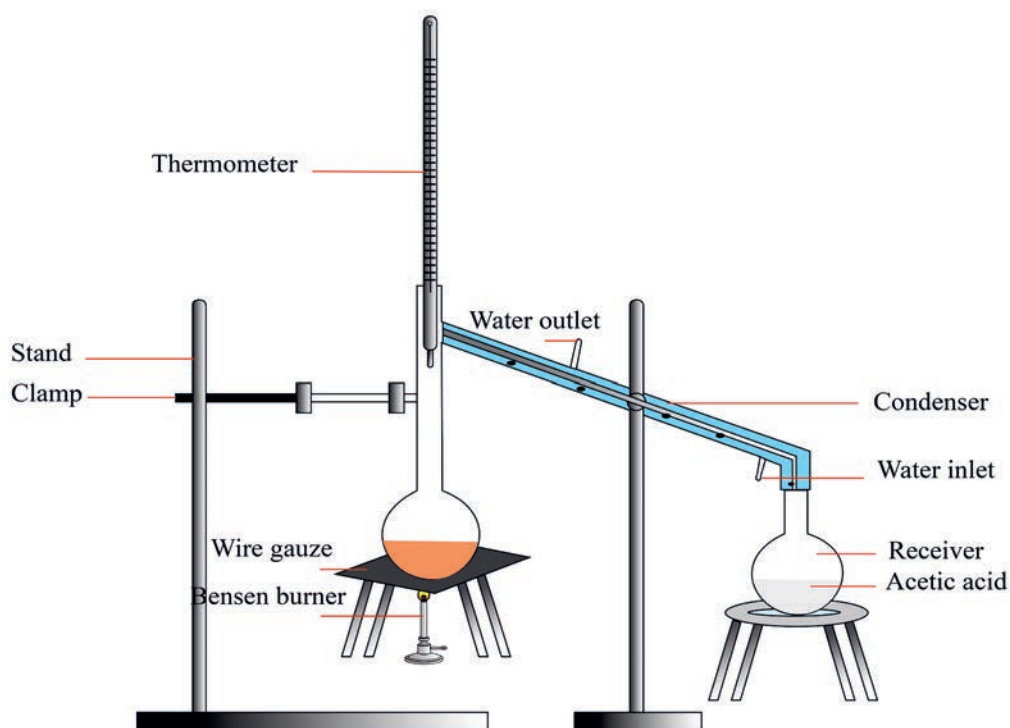


Figure 6.9b: Laboratory set-up for distillation of acetic acid

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 (Figure 6.10) 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).

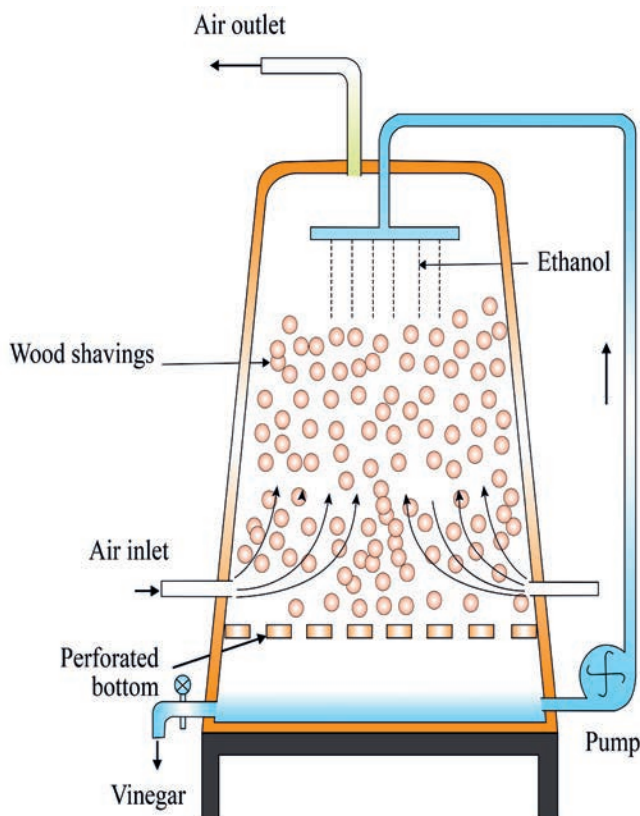


Figure 6.10: Industrial preparation of acetic acid

### 6.4.5 Fatty Acids



#### Activity 6.11

Discuss the following questions in groups and present your answer to the class. You have learned about the six foodstuffs in your lower grade biology lesson. Which one of these foodstuffs produces fatty acid during digestion? Why are they named 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 unbranched. Fatty acids can be classified as saturated or unsaturated.

*What is the main difference between saturated and unsaturated compounds?*

Double bonds in naturally occurring unsaturated fatty acids are never conjugated.

*How many methylene ( $-\text{CH}_2-$ ) group(s) usually separates the double bonds in unsaturated fatty acids?* (See Table 6.6).

**Table 6.6:** Some common naturally occurring fatty acids

Number of carbons	Common Name	Structure / Formula	Melting Point ( $^{\circ}\text{C}$ )
<b>Saturated</b>			
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
<b>Unsaturated</b>			
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.

Why do unsaturated fatty acids have lower melting points than saturated fatty acids with comparable molecular weights?

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.

Can you suggest some more examples of the use of carboxylic acids in daily life?

#### 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’?

### Project 6.3

Form a group of five and share information on some carboxylic derivatives (anhydrides, amides, and acid chloride), then submit a written word and PDF documents to your teacher. In your write-up, put the following key points into consideration:

- structures and naming (both IUPAC and common systems) of anhydrides, amides, and acid chloride
- physical properties of anhydrides, amides, and acid chloride
- common reactions and methods of preparations.

## 6.5 Esters

*By the end of this section, you will be able to:*

- ☞ list common sources of esters
- ☞ write the general structural formula of esters
- ☞ write the molecular formulas and names of some simple esters
- ☞ describe physical properties of esters
- ☞ explain the chemical properties of esters
- ☞ explain the general methods of preparation of esters
- ☞ describe some uses of common esters.

### 6.5.1 Sources of Esters

Why do some fruits and flowers give out a pleasant smell?

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

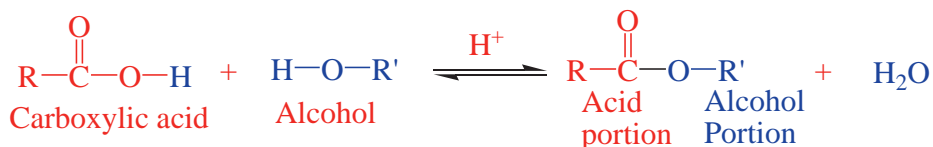
Esters are derivatives of carboxylic acids in which the hydroxyl group (-OH) of a carboxylic acid is replaced by an alkoxy group (-OR). Esters can be formed by the reaction between acids and alcohols or phenols. In such cases, the hydroxyl group is replaced by an alkoxy group.

Esters have the general formula  $\text{RCO}_2\text{R}'$  (or  $\text{RCOOR}'$ ), which can be represented by the general formula:

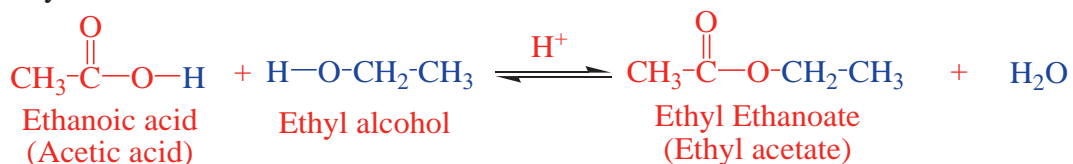


Where  $\text{R}$  = hydrogen, alkyl or an aryl group and  $\text{R}'$  = alkyl or an aryl group.

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

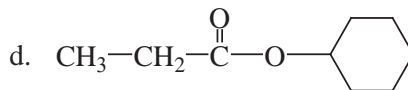
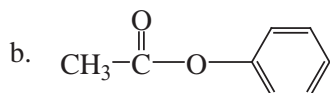
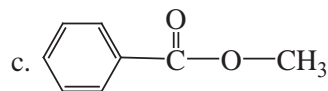
Molecular Formula	Structure/Formula	Common Name	IUPAC Name
C <sub>2</sub> O <sub>2</sub> H <sub>4</sub>	HCOOCH <sub>3</sub>	Methyl formate	Methyl methanoate
C <sub>3</sub> O <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> COOCH <sub>3</sub>	Methyl acetate	Methyl ethanoate
C <sub>3</sub> O <sub>2</sub> H <sub>6</sub>	HCOOCH <sub>2</sub> CH <sub>3</sub>	Ethyl formate	Ethyl methanoate
C <sub>4</sub> O <sub>2</sub> H <sub>8</sub>	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	Ethyl acetate	Ethyl ethanoate
C <sub>4</sub> O <sub>2</sub> H <sub>8</sub>	HCOOCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Propyl formate	Propyl methanoate
C <sub>5</sub> O <sub>2</sub> H <sub>10</sub>	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	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 methanoate 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

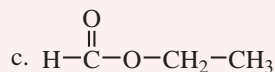
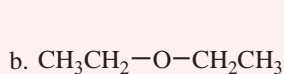
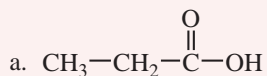
### 6.5.3 Physical Properties



#### Activity 6.12

Form a group and discuss the following questions. After the discussion, share your ideas with the rest of the class.

Which one of the following compounds do you expect to have the highest boiling point? Why?



#### 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 **Figure 6.11**, the solubility of esters in water decreases as their molecular mass increase. All esters are soluble in organic solvents.

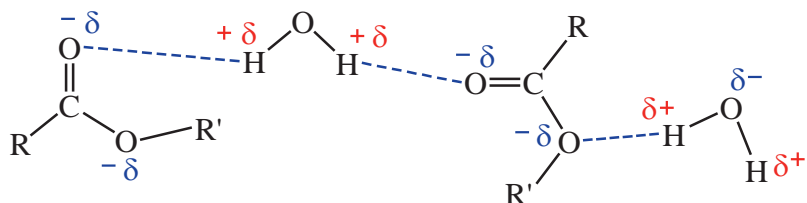


Figure 6.11: Hydrogen bonding between water and ester molecules

## 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



#### Activity 6.13

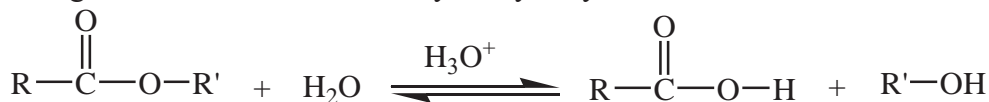
Form a group and discuss the following questions. After the discussion, share your ideas with the rest of the class.

1. What would happen when esters are treated with water?
2. Recall the reactants that form esters. What was the by-product of the reaction?

## i. Hydrolysis

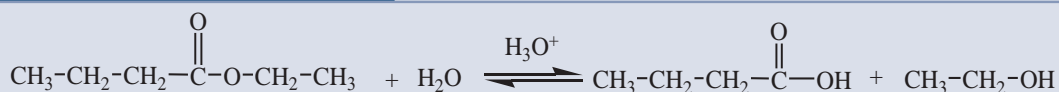
The most important reaction of carboxylic esters is their hydrolysis, which may be catalyzed by either mineral acids or bases. The reaction yields the corresponding carboxylic acid and alcohol of the ester.

The general reaction for acid-catalyzed hydrolysis of esters can be written as:



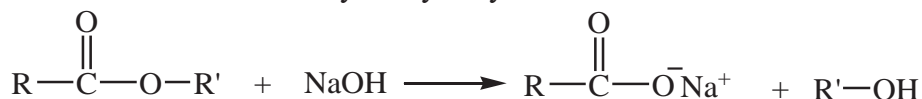


### Example 6.38



For synthetic purposes, base catalysis is often preferred because the reaction is not reversible. Base-catalyzed ester hydrolysis is called **saponification**.

The general reaction for base-catalyzed hydrolysis of esters can be written as:



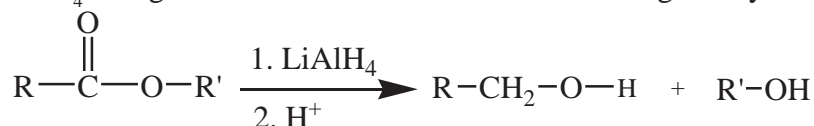
### Example 6.39



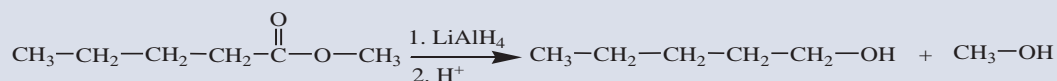
In biological systems, many ester hydrolysis reactions take place, for example, in the digestion of fats. These reactions occur under very mild conditions, and in the presence of certain biological catalysts known as **enzymes**.

#### ii. Reduction

Esters are reduced to primary alcohols by special reducing agents like lithium aluminum hydride,  $\text{LiAlH}_4$ . The general reaction for reduction of esters is given by:

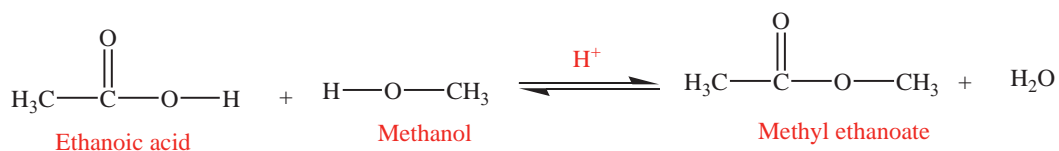


### Example 6.40



### 6.5.5 Preparation of Esters

Esters can be synthesized by heating a mixture of a carboxylic acid and an alcohol in the presence of an acid (usually  $\text{H}_2\text{SO}_4$ ) as catalyst. This reaction is called esterification and is a common method for the preparation of esters. In esterification, the  $-\text{OH}$  group from the carboxylic acid and the  $-\text{H}$  from the alcohol are removed and combine to form water molecule.



In this condensation reaction, the hydroxyl group ( $-\text{OH}$ ) from the acid and a hydrogen atom ( $-\text{H}$ ) 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

- Write the reactions for the preparation of each of the following esters using appropriate acids and alcohols:
  - ethylacetate
  - ethyl butanoate
  - methylbenzoate
  - phenylethanoate
- 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-propanol.

### 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	$C_4H_9COOC_5H_{11}$	Isoamyl isovalerate
Pineapple	$C_3H_7COOC_2H_5$	Ethyl butyrate
Banana	$CH_3COOC_5H_{11}$	Isopentyl acetate
Orange	$CH_3COOC_8H_{17}$	Octyl acetate
Grape	$C_6H_4(NH_2)(COOCH_3)$	Methyl anthranilate
Pear	$CH_3CO_2(CH_2)_2CH(CH_3)_2$	Isopentyl acetate

## 6.6 Fats and Oils

*By the end of this section, you will be able to:*

- ☞ *define fats and oils*
- ☞ *write the general structural formula for fats and oils*
- ☞ *write the structures of some common triglycerides*
- ☞ *describe physical properties of fats and oils*
- ☞ *explain hardening of oils (process of converting oils to hard fats)*
- ☞ *explain rancidity.*

### 6.6.1 Source of Fats and Oils



#### Activity 6.14

Perform the following activity in groups, then present your conclusion to the whole class.

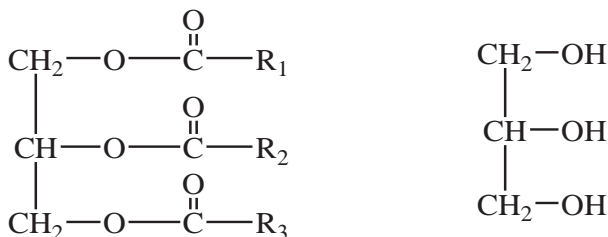
Collect samples of butter, lard, tallow, peanut oil, soybean oil and olive oil. Classify them to as vegetable or animal origin based on their physical state. Do you find any relation between the origin and the physical state?

Fats and oils are esters. They are triesters of glycerol which are collectively known as triglycerides or triacylglycerols. 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:



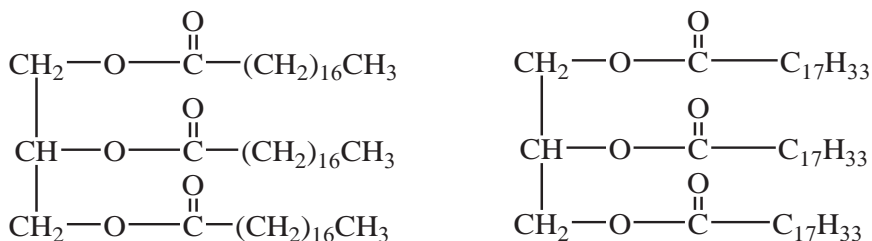
A triglyceride (triacylglycerol)

Glycerol

Where  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  may be the same or different hydrocarbon groups.

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:



Glyceryl tristearate (stearin) fat

Glyceryl trioleate (olein) oil

**Exercise 6.15**

- Write the structure of the following compounds
  - Glyceryl trimyristate
  - Glyceryl palmitooleostreatate
- 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.

**6.6.3 Physical Properties of Fats and Oils****Activity 6.15**

From a group and compare vegetable oils with mineral oils.

- Do they behave in a similar fashion? Explain.
- Present your responses to the whole class.

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, cottonseed 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



## Activity 6.16

Form a group and classify the following fatty acids as saturated or unsaturated fatty acids.

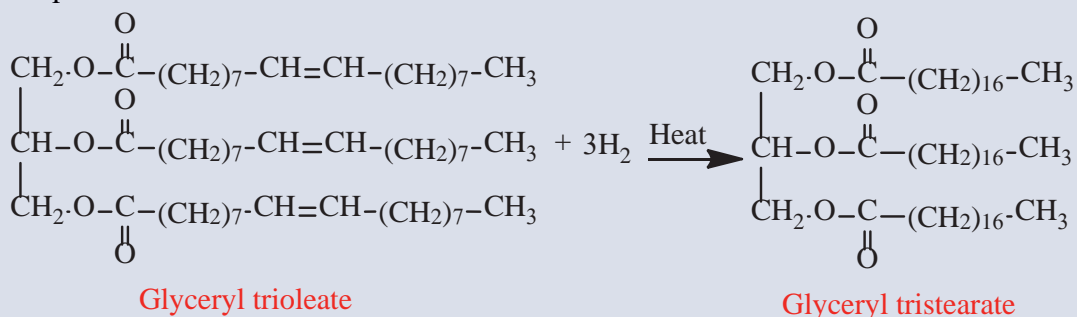
- Myristic acid      - Oleic acid                      -Linolic acid      - Lauric acid  
 -Palmitic acid      - Linolenic acid and      -Stearic acid.

Can you suggest a method of converting unsaturated fatty acids to saturated fatty acids? Present your findings to the whole class.

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.

## Example 6.41

A glyceryl tristearate (found in animal fat) can be prepared by hydrogenation of glyceryl trioleate (oil found in olive oil and whole oil) is shown in the equation below:



## Exercise 6.16

Write the equation for the hydrogenation of:

- Glyceryl trilinoleate, and
- Glyceryl tripalmitoleate

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 fat**, 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



#### Activity 6.17

Perform the following activity in groups, then present your findings to the whole class.

Obtain two packets of fried potato chips from the market. Open one packet and smell it. Now place half the contents in a close tight container and other half in an open container. Let the second packet be kept as such. After 15 days, smell the chips kept in the open container, closed container and sealed packet. Record your observations and find out what is the best method to keep such items.














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 ( $\text{-OH}$ ) group as their functional group and represented by the general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$ .
-  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  $\text{-OH}$  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  $\text{-COOH}$  functional group.
-  Because of the  $\text{-COOH}$  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.

## CHECKLIST

## KEY TERMS

➤ *Addition reaction*

➤ *Alcohol*

➤ *Aldehyde*

➤ *Carboxyl group*

➤ *Carboxylic acid*

➤ *Ester*

➤ *Esterification*

➤ *Ether*

➤ *Fat*

➤ *Fermentation*

➤ *Hardening of oils*

➤ *Hydrogenation*

➤ *Ketone*

➤ *Lipid*

➤ *Oil*

➤ *Ozonolysis*

➤ *Rancidity*

➤ *Substitution reaction*

➤ *Triglycerides*

## REVIEW EXERCISE

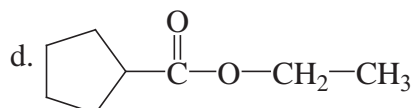
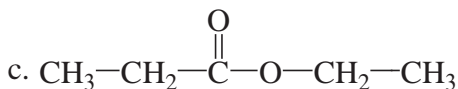
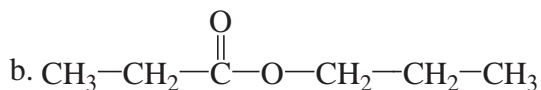
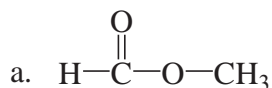
### Part I: Multiple choice Type Questions

- Which one is the least soluble in water?
  - methanol
  - butanal
  - hexane
  - hexanedioic acid
- Which of the following compounds is ether?
  - $\text{CH}_3\text{CH}_2\text{COOCH}_3$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
  - $\text{CH}_3\text{CH}_2\text{OCH}_3$
- The compounds  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{COOH}$  react in the presence of an acid catalyst to form:
  - a carboxylic acid
  - an aldehyde
  - a ketone
  - an ester
- Alcohols that yield ketones on oxidation are classified as:
  - primary alcohols
  - secondary alcohols
  - dihydric alcohols
  - trihydric alcohols
- What is the product of the reduction of 3-methyl-2-pentanone?
  - 3-methyl-2-pentanol
  - 2-methyl-3-pentanol
  - 3-methyl-2-pentanal
  - 3-methyl-2-pentene
- Acetic acid is manufactured by the fermentation of:
  - ethanol
  - methanol
  - ethanal
  - methanal
- Fats and oils are:
  - acids
  - alcohols
  - esters
  - hydrocarbons
- Which pair of compounds can react to form a hemiacetal?
  - $\text{CH}_3\text{CH}_2\text{CHO}$  and  $\text{CH}_3\text{CH}_2\text{OH}$
  - $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{CH}_2\text{CHO}$
  - $\text{CH}_3\text{CH}_2\text{CHO}$  and  $\text{CH}_3\text{COOH}$
  - $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{COOH}$

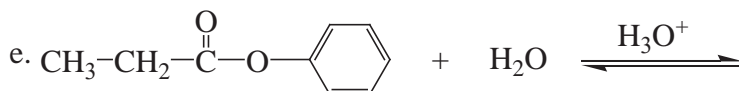
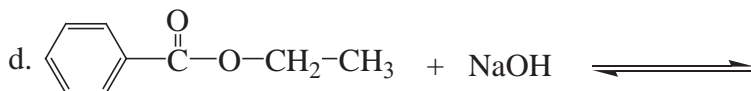
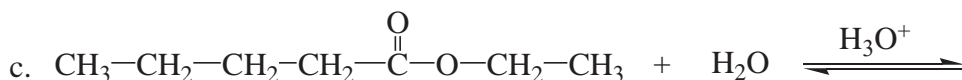
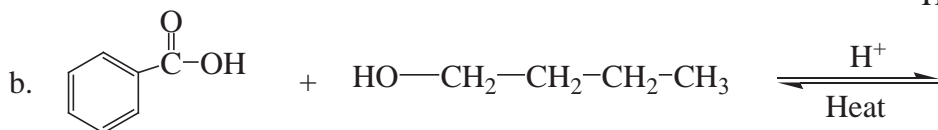
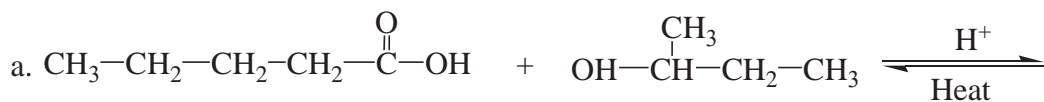
### Part II: Answer the following questions:

- Why is there a large difference in the boiling points of butanal and 1-butanol?
- Write a test to differentiate between 2-pentanone and pentanal.
- Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to an oxygen atom ( $-\text{O}-\text{H}$ )?
- Draw the structural formula for the ester formed when each of the following reacts with methyl alcohol:
  - Acetic acid
  - Benzoic acid
  - Formic acid
  - 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:



15. Identify each of the following as a saturated, monounsaturated, polyunsaturated:

