THE GOVERNMENT OF
THE REPUBLIC OF THE UNION OF MYANMAR

MINISTRY OF EDUCATION

TEXTBOOK

CHEMISTRY

GRADE 11

2022-2023

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PREFACE

Chemistry is central to understanding many fields including agriculture, geology, medicine, anatomy, applied health technology, biology, molecular biology, pharmacology, astronomy, dental science, veterinary science, and materials science. Even if students are not planning to work in any of these fields, chemistry is used by each of us every day in our struggle to cope with our technological world. Learning about the benefits and risks associated with our chemicals will help students to be informed citizens, able to make intelligent choices concerning the world around them.

Six fundamental higher order thinking skills have been identified in the Chemistry Syllabus. They are problem solving skills, inquiring skills, reasoning skills, communicating skills, conceptualizing skills, and creative and innovative skills. These skills, together with intertwining ways of learning chemistry, thinking and using chemical knowledge are considered important in chemistry education.

21st Century Skills

After learning this course, students will develop and practise higher order thinking skills: comprehension, analysis, synthesis and evaluation. They will be able to participate actively in all lessons through the **5 Cs** as important **21st century skills for learning**:

- ✓ **Collaboration** – In lessons students will be working in groups, to share ideas with their classmates and to find the solution together.
- ✓ **Communication** – Students will develop verbal and non-verbal communication skills in group works.
- ✓ **Critical thinking and problem solving** – Students will be given interesting problems to solve – finding and explaining solutions, looking for correcting errors.
- ✓ **Creativity and innovation** – Thinking 'outside the box' is an important 21st century skills. Students will be encouraged to explore new ideas and solve problems in new ways.
- ✓ **Citizenship** – Students will take part in the school community and develop fairness and conflict resolution skills.

Important Features of This Textbook

- ♦ The High School Chemistry Curriculum covers **six main themes**: Particulate Nature of Substances, Periodicity, Chemical Calculations, Chemistry of Reactions, The Environment, and Organic Chemistry.
- ♦ There are **eight chapters** comprised in this Textbook:
  - Chapter 1: The Behaviour of Gases
  - Chapter 2: Stoichiometry
  - Chapter 3: Oxidation and Reduction
  - Chapter 4: Electrolysis
  - Chapter 5: The Behaviour of Metals and Metallurgy
  - Chapter 6: Non-metals and Their Compounds: Nitrogen and Sulphur
  - Chapter 7: Atmospheric Chemistry
  - Chapter 8: Organic Chemistry: Hydrocarbons and Alcohols

- Each chapter starts with the ***introductory*** of the topic, containing an example of how the material is covered in the chapter, followed by the **Learning Outcomes** of the chapter.
- In each section of the chapter, the text and illustrations describe and explain all of the facts and concepts that students need to know. **Review Questions** after each section, give students a chance to check that they have understood the topic they have just read about. There is a summary of **Key Terms**, which are highlighted in the text, at the end of each section. All end-of-chapter **Exercises** are designed to ensure that students have grasped major concepts, in addition to testing their understanding of the materials covered in the chapter. At the end of each chapter, the **Chapter Review** (a concept link) points out the summary and highlights of the chapter.
- In addition, the **"Chemistry in Society"** highlighted in colour, introduces students to the important chemicals and substances that are the basis for the high standard of living and modern technology that they now enjoy as well as that chemistry is intimately involved in almost every aspect of our material world. It is suggested that teachers should not emphasise this section as exam-oriented teaching.
- The **Glossary** at the end of the Textbook is a listing of key terms mentioned in all chapters.

Goals of Grade 11 Chemistry

In this chemistry course, students will develop the basic knowledge and skills which will help to understand more about chemistry and to apply in their daily life. They will learn how to demonstrate an interest in the creativity and innovation found in chemistry. In some lessons, students will participate in group activities to develop skills in scientific methods of investigation based on the concepts, theory, terms, facts, laws and principles related to main themes, skills in solving problems demonstrating proper use of units, quantities and scientific notation. They will also recognise the high school chemistry courses as a foundation for vocational applications and further study in science and technology.

Additionally, studying chemistry teaches a student to solve problems and communicate with others in an organized and logical manner. By participating actively in all lessons, they will achieve soft skills/ employability skills, including **5Cs** which will be helpful in their further study and throughout their career. We hope that students will understand the benefits and hazards to the Material World through the knowledge they learned.

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COVER STORY

Thorough knowledge of the chemistry world – living or non-living, the student can appreciate the role of chemistry in society, and to a large extent of applying environmental protection to achieve sustainable development. Understanding green chemistry leads to a better future of life on the planet Earth.

The Periodic Table

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Group	I	II											III	IV	V	VI	VII	0
1	1 H Hydrogen 1																	2 He Helium 4
2	3 Li Lithium 7	4 Be Beryllium 9											5 B Boron 11	6 C Carbon 12	7 N Nitrogen 14	8 O Oxygen 16	9 F Fluorine 19	10 Ne Neon 20
3	11 Na Sodium 23	12 Mg Magnesium 24											13 Al Aluminium 27	14 Si Silicon 28	15 P Phosphorus 31	16 S Sulphur 32	17 Cl Chlorine 35.5	18 Ar Argon 40
4	19 K Potassium 39	20 Ca Calcium 40	21 Sc Scandium 45	22 Ti Titanium 48	23 V Vanadium 51	24 Cr Chromium 52	25 Mn Manganese 55	26 Fe Iron 56	27 Co Cobalt 59	28 Ni Nickel 59	29 Cu Copper 64	30 Zn Zinc 65	31 Ga Gallium 70	32 Ge Germanium 73	33 As Arsenic 75	34 Se Selenium 79	35 Br Bromine 80	36 Kr Krypton 84
5	37 Rb Rubidium 85	38 Sr Strontium 88	39 Y Yttrium 89	40 Zr Zirconium 91	41 Nb Niobium 93	42 Mo Molybdenum 96	43 Tc Technetium 99	44 Ru Ruthenium 101	45 Rh Rhodium 103	46 Pd Palladium 106	47 Ag Silver 108	48 Cd Cadmium 112	49 In Indium 115	50 Sn Tin 119	51 Sb Antimony 122	52 Te Tellurium 128	53 I Iodine 127	54 Xe Xenon 131
6	55 Cs Caesium 133	56 Ba Barium 137	57-71 Lanthanoids	72 Hf Hafnium 178	73 Ta Tantalum 181	74 W Tungsten 184	75 Re Rhenium 186	76 Os Osmium 190	77 Ir Iridium 192	78 Pt Platinum 195	79 Au Gold 197	80 Hg Mercury 201	81 Tl Thallium 204	82 Pb Lead 207	83 Bi Bismuth 209	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222
7	87 Fr Francium 223	88 Ra Radium 226	89-103 Actinoids	104 Rf Rutherfordium 267	105 Db Dubnium 268	106 Sg Seaborgium 269	107 Bh Bohrium 270	108 Hs Hassium 277	109 Mt Meitnerium 278	110 Ds Darmstadtium 281	111 Rg Roentgenium 281	112 Cn Copernicium 285	113 Nh Nihonium 286	114 Fl Flerovium 289	115 Mc Moscovium 289	116 Lv Livermorium 293	117 Ts Tennessine 294	118 Og Oganesson 294

Z
X
A

Z = atomic number

X = atomic symbol

A = atomic mass or mass number

Metals

■ alkali metals

■ alkaline-earth metals

■ transition metals

■ other metals

Non-metals

■ halogens

■ noble gases

■ other non-metals

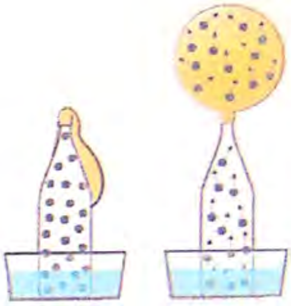
■ metalloids

Lanthanide series	57 La Lanthanum 139	58 Ce Cerium 140	59 Pr Praseodymium 141	60 Nd Neodymium 144	61 Pm Promethium 145	62 Sm Samarium 150	63 Eu Europium 152	64 Gd Gadolinium 157	65 Tb Terbium 159	66 Dy Dysprosium 162	67 Ho Holmium 165	68 Er Erbium 167	69 Tm Thulium 169	70 Yb Ytterbium 173	71 Lu Lutetium 175
Actinide series	89 Ac Actinium 227	90 Th Thorium 232	91 Pa Protactinium 231	92 U Uranium 238	93 Np Neptunium 237	94 Pu Plutonium 244	95 Am Americium 243	96 Cm Curium 247	97 Bk Berkelium 247	98 Cf Californium 251	99 Es Einsteinium 252	100 Fm Fermium 257	101 Md Mendelevium 258	102 No Nobelium 259	103 Lr Lawrencium 262

CHAPTER 1

THE BEHAVIOUR OF GASES

We recognise gases, liquids and solids quite easily because an important example of each is all around us: air, water and soil. The gaseous state is the simplest state of matter to understand. Gases are very important since the air around us making up the atmosphere is gas. Oxygen gas is required to keep our bodies alive. Carbon dioxide is a gas given off as waste by animals and used as a raw material by plants. Methane gas is used as fuel. Ammonia gas which is a combination of nitrogen and hydrogen gases is used to make fertiliser. Thus, it is important to study the behaviour of gases and their reactions.



The volume and shape of all gases can be assumed as those of their containers. The intermolecular forces of gases are much weaker than those of other physical states. Being the most compressible of the states of matter, they can be mixed evenly and completely when confined to the same container. Gases have much lower densities than liquids and solids. In this chapter we shall explore some of the characteristic properties of the gaseous state, and the laws that govern the behaviour of gases.

Learning Outcomes

After completing this chapter, students will be able to:

- explain the Kinetic Molecular Theory of gases;
- apply ways of identifying and collecting measurable quantities of some common gases;
- interpret the gas laws;
- solve problems involving gas laws and theories.

1.1 KINETIC MOLECULAR THEORY OF GASES

The **Kinetic Molecular Theory** is a model that is used to predict gas behaviour.

The principal assumptions for the kinetic molecular theory of gases are very simple.

(1) The volume of the particles themselves is negligible compared with the total volume of the gas. Most of the volume of the gas is empty space.

(2) Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic. In other words, energy can be transferred from one molecule to another as a result of a collision. Nevertheless, the total energy of all the molecules in a system remains the same.

Gas molecules moving in random directions

(3) Gas molecules exert neither attractive nor repulsive forces on one another.
(4) The average kinetic energy of molecules is the same for all gases at the same temperature, and its value is directly proportional to the Kelvin temperature.

REVIEW QUESTIONS

(1) Which of the following statements is suitable for gas, according to the kinetic molecular theory?
   (a) Gas molecules exert forces on each other.
   (b) The average kinetic energy is directly proportional to the Kelvin temperature.
   (c) There are small spaces separating the gas molecules.
   (d) Gas molecules move in a circular way.

(2) According to the kinetic molecular theory, what can we assume is a correct approximation of the volume of a gaseous molecule?
   (a) 1 L (b) essentially zero (c) 10 mL (d) 100 mL

(3) Which of the following collisions correctly characterises gas particles according to the kinetic molecular theory?
   (a) inelastic collisions (b) elastic collisions
   (c) linear collisions (d) circular and inelastic collisions

1.2 MEASURABLE QUANTITIES OF GASES

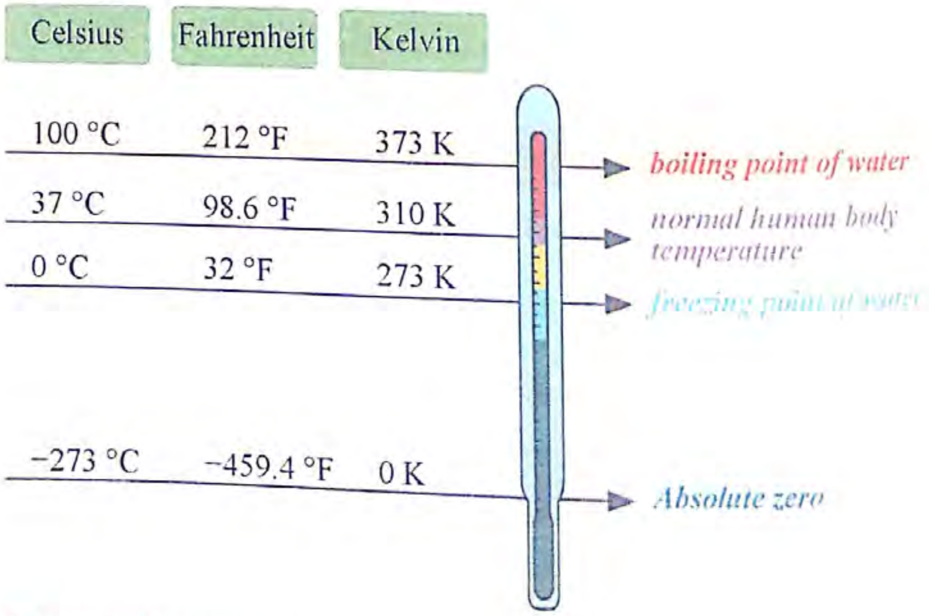
For any trapped sample of gas, we can measure its temperature (T), the volume (V) of the space it occupies, its pressure (P) against the confining wall and its mass (m).

Temperature (T)

The units of temperature are degree Celsius, degree Fahrenheit and Kelvin. Their relations are expressed as follows:

$$\mathbf{T\,^{\circ}C + 273 = T\,K}$$

$$\mathbf{\frac{9}{5}\,T\,^{\circ}C + 32 = T\,^{\circ}F}$$



Relationship among temperature scales

Volume (V)

The units of volume and their relations are as follows:

$1000\ \text{cm}^3 = 1000\ \text{mL} = 1\ \text{L} = 1\ \text{dm}^3 = 1 \times 10^{-3}\ \text{m}^3$

Pressure (P)

A gas exerts a force on the walls of any container; for example, the gas in an inflated balloon exerts pressure on the wall of the balloon. Pressure is in fact the force that acts on a given area.

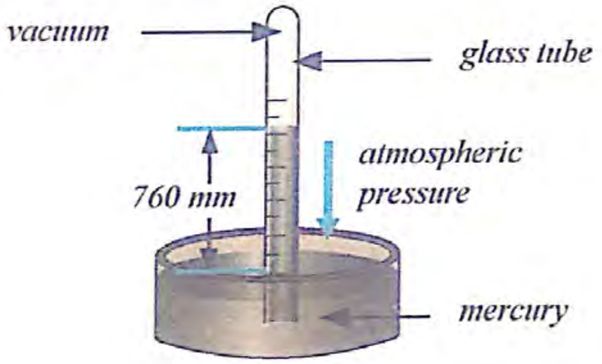
Force = mass × acceleration = kg m s^{-2} = N (newton)

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{N}}{\text{m}^2} \qquad [1\ \text{N m}^{-2} = 1\ \text{Pa (pascal is SI unit of pressure)}]$$

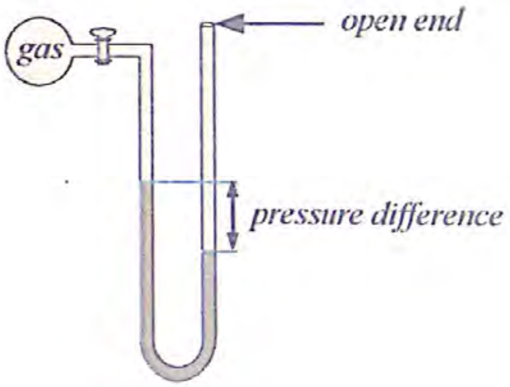
The effects of pressure are observed in the mixture of gases surrounding the Earth–our atmosphere, which is composed of nitrogen, oxygen, argon and other minor constituents. These gases in the atmosphere exert pressure. This pressure is known as **atmospheric pressure**. The actual value of atmospheric pressure depends on location, temperature and weather conditions.

Instruments used for measuring atmospheric pressure and gas pressure are barometer and manometer, respectively. **Standard atmospheric pressure** (1 atm) is equal to the pressure that supports a column of mercury exactly 760 mm (or) 76 cm high at 0 °C at sea level. Hence, the standard atmospheric pressure can also be expressed as 760 mmHg. The mmHg unit is also the same as the torr.

$1\ \text{atm} = 760\ \text{mmHg} = 760\ \text{torr} = 101{,}325\ \text{Pa} = 101{,}325\ \text{N m}^{-2} = 101.325\ \text{kPa}$



Barometer



Manometer

Mass (m)

The mass of a gas can be determined by weighing the gas in an enclosed container by gram(g)or kilogram (kg).

REVIEW QUESTIONS

(1) The normal boiling point of ethanol is 78 °C. Convert this to Kelvin temperature.

(2) What is the pressure in atm and Pa in a room if the barometer reading is 688 mmHg?

(3) The capacity of an inflated balloon is 100 cm^3. How many balloons can be filled with the gas from a 20 L helium gas tank?

Key Terms

- **Atmospheric pressure** is the force exerted on a surface by the air above it as gravity pulls it to the Earth.
- **Standard atmospheric pressure** is equivalent to the pressure exerted by a column of mercury 760 mm high at 0 °C at sea level.

1.3 RELATIONSHIP AMONG PRESSURE, VOLUME AND TEMPERATURE OF GASES

In spite of wide differences in chemical properties, all the gases more or less obey the gas laws. The gas laws deal with how gases behave with respect to pressure, volume, temperature and amount.

(a) Pressure -Volume Relationship: Boyle's Law

In the 17th century, Robert Boyle, an Irish scientist, studied the behaviour of gases systematically and quantitatively. **Boyle's law** can be stated as:

When the temperature of a given mass of gas is kept constant, the volume of the gas is inversely proportional to its pressure.

The volume and pressure relationship for a given mass of any gas may be mathematically expressed as:

$V \propto \frac{1}{P}$ (a given mass of gas, kept at a constant temperature)

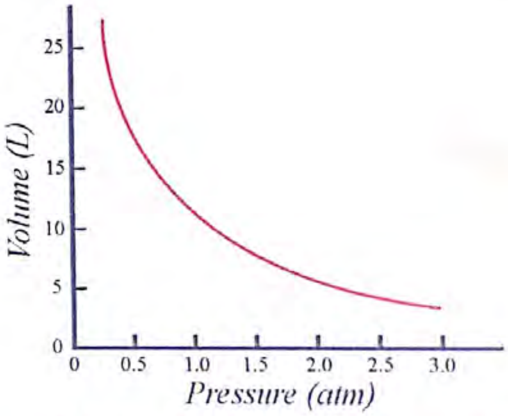
$V = \text{constant} \times \frac{1}{P}$

$PV = \text{constant}$

$P_1V_1 = P_2V_2$

where P_1 and V_1 are for the initial conditions;

P_2 and V_2 are for the final conditions.



Relationship between volume and pressure of the gas

Example 1: A volume of a certain mass of gas occupies 952 cm^3 at 561 mmHg. What is the volume under 760 mmHg at the same temperature?

Solution:

Initial state	Final state
$P_1 = 561$ mmHg	$P_2 = 760$ mmHg
$V_1 = 952\ cm^3$	$V_2 = ?$

Using Boyle's law, $P_1V_1 = P_2V_2$

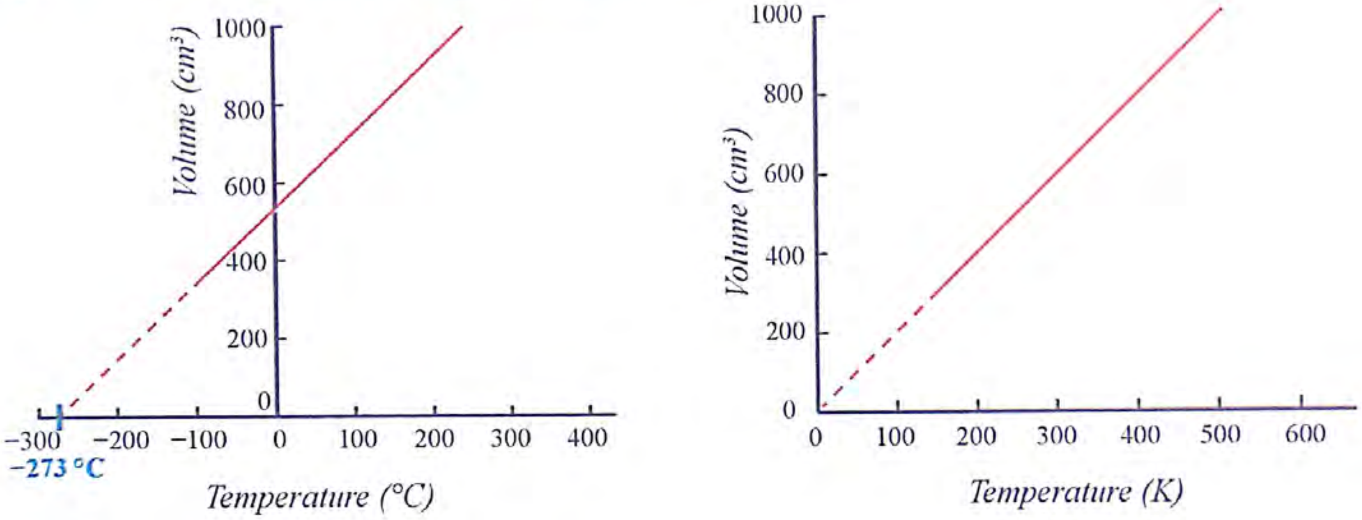
$$V_2 = \frac{P_1V_1}{P_2} = \frac{561\ \text{mmHg} \times 952\ \text{cm}^3}{760\ \text{mmHg}} = 702.7\ \text{cm}^3$$

Check: The increase in pressure decreases the volume. So, the answer is reasonable.

(b) Temperature - Volume Relationship: Charles' Law

In the 18th century, the French physicist Jacques Charles studied the effect of temperature on the volume of a gas at constant pressure. **Charles' law** can be stated as:

When the pressure of a given mass of gas is kept constant, the volume of the gas is directly proportional to its temperature on the Kelvin scale.



Relationship between volume and temperature of the gas

The volume and temperature relationship for a given mass of any gas may be mathematically expressed as:

$$V \propto T \text{ (a given mass of gas, kept at constant pressure)}$$

$$\therefore \; V = \text{constant} \times T$$

$$\therefore \; \frac{V}{T} = \text{constant}$$

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

where V_1 and T_1 are for the initial conditions; V_2 and T_2 are for the final conditions.

Example 2: A certain mass of gas occupies 617 cm^3 at 9 °C. What is the volume at 0 °C under the same pressure?

Solution:

Initial state	Final state
$V_1 = 617\ cm^3$	$V_2 = ?$
$T_1 = 9\ °C + 273 = 282\ K$	$T_2 = 0\ °C + 273 = 273\ K$

Using Charles' law, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{617\ \text{cm}^3 \times 273\ \text{K}}{282\ \text{K}} = 597.3\ \text{cm}^3$$

Check: The decrease in temperature decreases the volume. So, the answer is reasonable.

Absolute zero temperature: The volume of a given mass of gas decreases regularly with a regular decrease in temperature. If the constant contraction rate is continued, the volume of the gas will become zero at - 273 °C (more precisely - 273.15 °C). This temperature is taken as the zero point of a new scale of temperature (Kelvin temperature scale), and is also known as absolute zero temperature.

(c) Temperature – Pressure Relationship: Gay-Lussac's Law

Early in the 19th century, Joseph Louis Gay-Lussac, a French scientist, determined that the pressure of a gas sample increases when heated and decreases when cooled at constant volume. **Gay-Lussac's law** can be stated as;

When a volume of a given mass of gas is kept constant, the pressure of the gas is directly proportional to its temperature on the Kelvin scale.

The pressure and temperature relationship for a given mass of any gas may be mathematically expressed as:

$P \propto T$ (a given mass of gas, kept at constant volume)

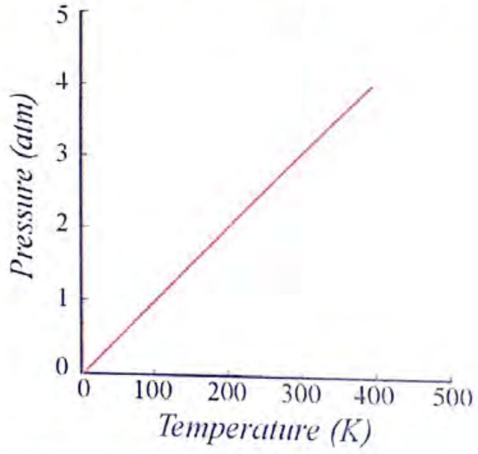
$\therefore\ P = \text{constant} \times T$

$\therefore\ \frac{P}{T} = \text{constant}$

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

where P_1 and T_1 are for the initial conditions;

P_2 and T_2 are for the final conditions.



Relationship between pressure and temperature of the gas

Example 3: The pressure of a gas at 27 °C is 760 mmHg. What is the pressure of the gas at 87 °C at constant volume?

Solution:

Initial state	Final state
$P_1 = 760$ mmHg	$P_2 = ?$
$T_1 = 27\ °\text{C} + 273 = 300$ K	$T_2 = 87\ °\text{C} + 273 = 360$ K

Using Gay-Lussac's law, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{760 \text{ mmHg} \times 360 \text{ K}}{300 \text{ K}} = \mathbf{912 \text{ mmHg}}$$

Check: The increase in temperature increases the pressure. So, the answer is reasonable.

Standard temperature and pressure, STP

STP in chemistry is the abbreviation for Standard Temperature and Pressure. It is commonly used when calculating gas density and volume of gas.

standard temperature = 0 °C (or) 273 K; standard pressure = 760 mmHg (or) 760 torr (or) 1 atm

Room temperature and pressure, r.t.p.

room temperature = 25 °C (or) 298 K; standard pressure = 760 mmHg (or) 760 torr (or) 1 atm

(d) Combined Gas Law

There is a single expression, called the **Combined Gas Law** that combines Boyle's Law, Charles' Law and Gay-Lussac's Law. When only the amount of gas is constant, the combined gas law describes the relationship among pressure (P), volume (V) and temperature (T).

The P, V and T relationship for a given mass of any gas may be mathematically expressed as:

$$V \propto \frac{T}{P} \text{ (a given mass of gas)}$$

$$\therefore V = \text{constant} \times \frac{T}{P}$$

$$\therefore \frac{PV}{T} = \text{constant}$$

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

where P_1, V_1 and T_1 are for the initial conditions and P_2, V_2 and T_2 are for the final conditions. This equation is known as the **combined gas law equation**.

Example 4: At 27 °C and 750 mmHg, a gas occupies 380 cm^3. What is the volume of this gas at STP?

Solution:

Initial state	Final state (STP)
P_1 = 750 mmHg	P_2 = 760 mmHg
T_1 = 27 °C + 273 = 300 K	T_2 = 273 K
V_1 = 380 cm^3	V_2 = ?

Using combined gas law, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{750 \text{ mmHg} \times 380 \text{ cm}^3 \times 273 \text{ K}}{300 \text{ K} \times 760 \text{ mmHg}} = \mathbf{341.3 \text{ cm}^3}$$

Check: The volume will decrease by decreasing temperature as well as by increasing pressure. So, the answer is reasonable.

(e) Volume-Amount Relationship:

(i) Gay- Lussac's Law

Early in the 19th century, Gay-Lussac studied the volume relationship of reacting gases, and summarised the results known as **Gay-Lussac's law of combining volumes of gases**. It can be stated as:

At the same temperature and pressure, the volumes of reacting gases and gaseous products are in simple ratios of small whole numbers.

For instance, H_2 and N_2 react to form NH_3.

hydrogen	+	nitrogen	⟶	ammonia
$3H_2(g)$	+	$N_2(g)$	⟶	$2NH_3(g)$
3 mol		1 mol		2 mol
3 volumes		1 volume		2 volumes

The volume ratios of $H_2 : N_2 : NH_3 = 3 : 1 : 2$ (simple ratios of small whole numbers)

Example 5: Calculate the volume of O_2 required for complete combustion of 16 L of butane (C_4H_{10}) at constant temperature and pressure.

Solution:

$2C_4H_{10}(g)$	+	$13O_2(g)$	⟶	$8CO_2(g)$	+	$10H_2O(l)$
2 mol		13 mol				
2 volumes		13 volumes				

$$\text{volume of } O_2 = 16 \text{ L of butane} \times \frac{13 \text{ volumes of oxygen}}{2 \text{ volumes of butane}} = \mathbf{104 \text{ L of oxygen}}$$

Check: Mole ratio of butane to oxygen is 2:13. Thus, the volume of oxygen required is also 6.5 times greater.

(ii) Avogadro's law

The Italian scientist Amedeo Avogadro expressed that the volume of any given gas must be proportional to the number of moles or molecules present. **Avogadro's law** can be stated as:

At constant temperature and pressure, the volume, V, occupied by a gas sample is directly proportional to the number of moles, n, of gas.

$$V \propto n \text{ (at constant temperature and pressure)}$$

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

Avogadro's law can also be stated as:

Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (or atoms if the gas is monoatomic).

The relationship may be mathematically expressed as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \text{ (at the same temperature and pressure)}$$

where V_1 and n_1 are for the initial conditions; V_2 and n_2 are for the final conditions.

(f) Ideal Gas Law

By summarising the gas laws,

Boyle's law: $V \propto \frac{1}{P}$ (a given mass of gas, kept at constant temperature)

Charles' law: $V \propto T$ (a given mass of gas, kept at constant pressure)

Avogadro's law: $V \propto n$ (temperature and pressure are kept constant)

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

$$V = R\frac{nT}{P}$$

$$\mathbf{PV = nRT}$$

This equation is known as the **ideal gas law equation**. The proportionality constant **(R)** is called the **gas constant**.

PV = nRT for 1 mol of gas at standard temperature and pressure,

$$R = \frac{PV}{nT} = \frac{(1\text{ atm})(22.4\text{ L})}{(1\text{ mol})(273\text{ K})} = \mathbf{0.0821\ L\ atm\ K^{-1}\ mol^{-1}}$$

The value of the gas constant 'R' depends on the units used for pressure, volume and temperature.

Ideal gas versus real gas

An ideal gas is a hypothetical gas. The molecules of an ideal gas do not attract or repel one another. Although the gas takes up the volume, the ideal gas molecules are approximated as point particles that have no volume in and of themselves. In other words, the volumes of ideal gas molecules are negligible. However, the particles in a real gas have volume, and there are attractions between the particles. Because of these attractions, a real gas can condense, or even solidify, when it is compressed or cooled.

Although real gases differ mostly from ideal gas behaviour at low temperatures and high pressures, the real gases behave mostly like an ideal gas at high temperatures and low pressures.

The ideal gas equation can be used to solve many gas problems as the ideal gas works rather well for most reasonable temperature and pressure ranges.

Example 6: Calculate the volume of a 0.4 mol of a gas in a container at 265 K and 0.9 atm. ($R = 0.0821$ L atm K^{-1} mol^{-1})

Solution:

$n = 0.4$ mol $T = 265$ K $P = 0.9$ atm $V = ?$

Using ideal gas law, $PV = nRT$;

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

$$V = \frac{0.4 \text{ mol} \times 0.0821 \text{ L atm K}^{-1}\text{ mol}^{-1} \times 265 \text{ K}}{0.9 \text{ atm}} = \mathbf{9.7\ L}$$

Check: The given conditions of temperature and pressure are close to STP. Thus 0.4 mol of gas may occupy approximately 10 L.

The molar mass of a gaseous substance

For known gaseous substances, the molar mass can be found easily. In practice, chemists often deal with the unknown gases. To determine the molar mass of an unknown gas, chemists need to determine the density of gas experimentally and use the rearranged ideal gas law.

Ideal gas law, $PV = nRT$ (where n = mole of gas $= \frac{\text{mass}}{\text{molar mass}}$)

$$P = \frac{\text{mass}}{\text{molar mass}} \times \frac{1}{V} \times RT$$

$$= \frac{1}{\text{molar mass}} \times \frac{\text{mass}}{\text{volume}} \times RT$$

$$= \frac{1}{M} \times d \times RT \quad (\text{since, density } (d) = \frac{\text{mass}}{\text{volume}})$$

$$M = \frac{dRT}{P}$$

where R = gas constant, T = Kelvin temperature, P = pressure, d = density, M = molar mass

Example 7: The density of a gaseous compound is 3.38 g L^{-1} at 40 °C and 1.97 atm. What is its molar mass? Based on molar mass, predict the name of gas which is either carbon monoxide or carbon dioxide. ($C = 12$, $O = 16$, $R = 0.0821$ L atm K^{-1} mol^{-1})

Solution:

$d = 3.38$ g L^{-1} $T = 40\ ^\circ C + 273 = 313$ K

$P = 1.97$ atm $R = 0.0821$ L atm K^{-1} mol^{-1} $M = ?$

$$M = \frac{dRT}{P} = \frac{3.38 \text{ g L}^{-1} \times 0.0821 \text{ L atm K}^{-1}\text{ mol}^{-1} \times 313 \text{ K}}{1.97 \text{ atm}} = \mathbf{44.09\ g\ mol^{-1}}$$

molar mass of CO $= 12 + 16 = 28$ g mol^{-1}; molar mass of $CO_2 = 12 + (2 \times 16) = 44$ g mol^{-1}

Thus, the name of gas is **carbon dioxide**.

REVIEW QUESTIONS

(1) A gas at 155 kPa and 25 °C has an initial volume of 1.00 L. The pressure of the gas increases to 605 kPa as the temperature is raised to 125 °C. What is the final volume?

(2) The volume of a gas-filled balloon is 30.0 L at 313 K and 153 kPa pressure. What would the volume be at standard temperature and pressure (STP)?

(3) How many moles are present in each of the volumes of the following gases at r.t.p.?

(a) 54.5 dm^3 of CH_4 (b) 250 cm^3 of CO_2 (c) 1.0 m^3 of O_2

Key Terms

- **Real gases** are gases whose molecules occupy spaces and have interactions; consequently, they only approach to the ideal gas law at high temperature and low pressure.
- **Ideal gases** are gases whose molecules occupy negligible space and have no interactions and which consequently obey the gas laws.

1.4 A GAS MIXTURE AND MOVEMENT OF GASES

(a) Dalton's Law of Partial Pressures

In the early 19th century, the English chemist, John Dalton formulated the law for the pressure of the mixture of non-reacting gases. Each gas in the mixture exerts a pressure that is independent of the other gases present. These pressures are called partial pressures. Dalton's law of partial pressures can be stated as:

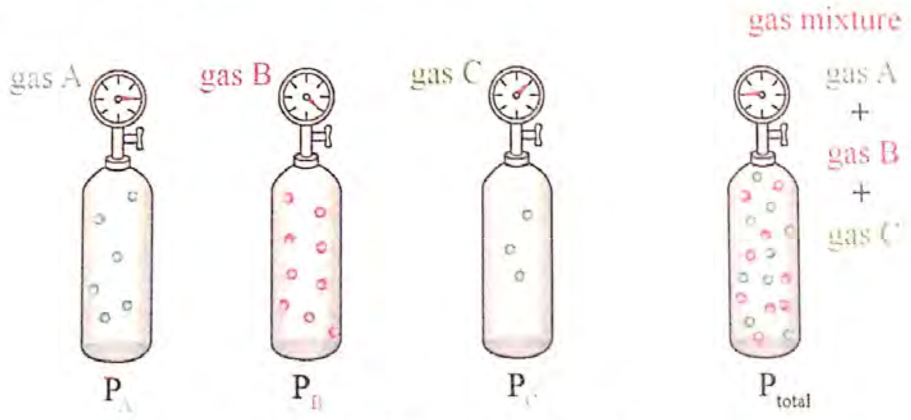
When the temperature is kept constant, the total pressure of a gas mixture is the sum of the partial pressures of different gases.

The phenomenon of gas pressure in a gas mixture can be summarised as follows:

$P_{total} = P_A + P_B + P_C + \ldots$ (at constant temperature)

P_{total} = total pressure of a gas mixture

$P_A, P_B, P_C \ldots$ = partial pressures of different gases



$$P_{total} = P_A + P_B + P_C$$

Relationship between total pressure and partial pressures of different gases in a gas mixture

Example 8: A gas occupies 500 cm^3 at 17 °C and 785 mmHg when it is collected over water. The vapour pressure of water at this temperature is 15 mmHg. What is the pressure of the dry gas at 17 °C?

Solution:

$P_{\text{water vapour}} = 15$ mmHg $\quad P_{\text{total}} = 785$ mmHg $\quad P_{\text{dry gas}} = ?$

Using Dalton's law of partial pressures, $P_{\text{total}} = P_{\text{dry gas}} + P_{\text{water vapour}}$

$$P_{\text{dry gas}} = P_{\text{total}} - P_{\text{water vapour}} = 785 \text{ mmHg} - 15 \text{ mmHg} = \mathbf{770 \text{ mmHg}}$$

Check: A gas collected over water contains water vapour. So, the pressure of dry gas which is lower than the pressure of the gas collected over water is reasonable.

(b) Diffusion and Effusion of Gas: Graham's Law

Due to their molecular motions, gases have the property of diffusion; the ability of two or more gases to mix spontaneously until they form a uniform mixture. For example, when perfume is sprayed in one corner of a room, we can smell it in another corner of the room. This is because the gas spreads as a result of diffusion. Thus, **diffusion** is the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties.

Effusion is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening. If we put a pinhole in a balloon, the gas inside will effuse or flow out of the balloon. This phenomenon is the effusion of the balloon gas into the atmosphere. Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same as the rate of diffusion from Graham's law.

Graham's law of gaseous diffusion can be stated as:

At the given temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density.

The relationship between the rate and the density of a gas can be mathematically expressed as:

$$r \propto \frac{1}{\sqrt{d}} \quad \text{(at the given temperature and pressure)}$$

$$r = \text{constant} \times \frac{1}{\sqrt{d}}$$

$$r\sqrt{d} = \text{constant}$$

where r = rate of diffusion of gas
d = density of gas

At the same temperature and pressure, the relationship between the rates of diffusion to mola masses of gaseous particles can be mathematically expressed as:

$$\mathbf{r_1\sqrt{d_1} = r_2\sqrt{d_2}} \quad \text{or} \quad r_1\sqrt{M_1} = r_2\sqrt{M_2} \quad \text{or} \quad \mathbf{\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}}$$

where r_1, d_1, M_1 are for gas 1; r_2, d_2, M_2 are for gas 2.
M = molar mass

Example 9: Helium gas diffuses 4 times as fast as an unknown gas. What is the relative molecular mass of the gas? (He = 4)

Solution:

$r_{He} = 4 \times r_{gas}$ $\qquad M_{He} = 4\ g\ mol^{-1}$

$\frac{r_{He}}{r_{gas}} = 4$ $\qquad M_{gas} = ?$

Using Graham's law of gaseous diffusion, $\frac{r_{He}}{r_{gas}} = \sqrt{\frac{M_{gas}}{M_{He}}}$

$$4 = \sqrt{\frac{M_{gas}}{4}}$$

$$16 = \frac{M_{gas}}{4}$$

$$M_{gas} = 64\ g\ mol^{-1}$$

molar mass of the gas = $64\ g\ mol^{-1}$

relative molecular mass = **64**

Check: The molar mass of gas is inversely proportional to its rate of diffusion. Therefore, the greater value of molar mass of unknown gas is as expected.

REVIEW QUESTIONS

(1) The gases chlorine, carbon dioxide, argon and nitrogen are mixed together in a container. Arrange the rate of diffusion of these gases in increasing order. (Cl = 35.5, C = 12, Ar = 40, N = 14, O = 16)

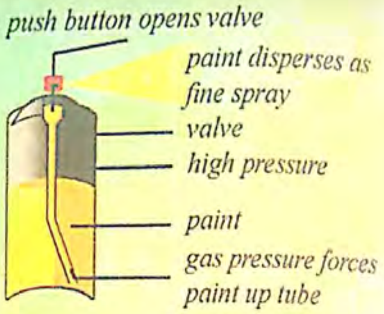
(2) At the same temperature and pressure, which molecule travels faster, CH_4 or C_2H_4? (H = 1, C = 12)

(3) The atmospheric pressure reading is 102 kPa. Pressure of oxygen is 20.9 kPa, pressure of carbon dioxide is 0.05 kPa and pressure of other minor gases is 1.55 kPa. What is the pressure of nitrogen gas?

Key Terms

- **Diffusion** is the process by which gas molecules spread together until they form a uniform mixture.
- **Effusion** is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening.

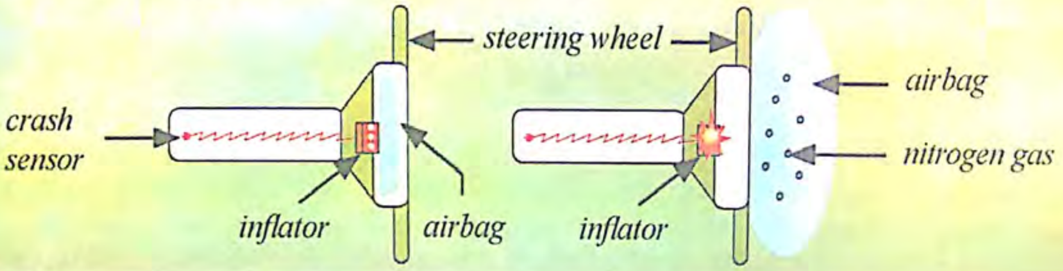
Chemistry in Society



- Gas pressure inside a new spray paint can is greater than the air pressure outside the can. As the can is used, the pressure inside the can decreases until there is not enough pressure inside the can to force the paint out. This same principle can be seen in fire extinguishers too.
- Airbags are designed to reduce injury when crashing. Its function is associated with seat belts. Seat belt makes you stay only on your seat and right position to be protected by airbag. Sodium azide (NaN_3) is used in some automobile airbags. By the collision, $NaN_3(s)$ decomposes as:

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$

The nitrogen gas produced quickly inflates the bag between the driver and dashboard.



EXERCISES

Q 1 to Q 4 (Understanding)

1. Diagrammatically illustrate the Boyle's law and Charles' law which show the relationship between volume, temperature and pressure for a given mass of gas.
2. Which of the following changes would increase the pressure of a gas in a closed container?
   I. Part of the gas is removed.
   II. The container size is decreased.
   III. Temperature is increased.
   (A) I and II only; (B) II and III only; (C) I and III only; (D) I, II, and III; (E) III only
3. How many litres of propane gas C_3H_8 will undergo complete combustion with 34 L of oxygen gas?

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

4. Determine the volume of hydrogen gas needed to react completely with 5.0 L of oxygen gas to form water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Q 5 to Q 11 (Analysing)

5. The pressure in an automobile tyre is 1.88 atm at 25 °C. What will be the pressure if the temperature increases to 37 °C?

6. Four identical containers under the same conditions are filled with nitrogen, oxygen, hydrogen and neon gases. Which container will have the highest mass? (N = 14, O = 16, H = 1, Ne = 20)
7. If the Kelvin temperature of an ideal gas is tripled and the volume is doubled, which of the following will be a new pressure?

   (a) $\frac{1}{6}$ of the original pressure (b) $\frac{2}{3}$ of the original pressure

   (c) $\frac{3}{2}$ of the original pressure (d) 5 times the original pressure
8. A gas evolved during the fermentation of glucose (wine making) has a volume of 0.78 L at 20 °C and 1 atm. What was the volume of this gas at the fermentation temperature of 36 °C and 1 atm pressure?
9. How many grams of carbon dioxide gas are in a 1 L balloon at STP? (C = 12, O = 16).
10. At 30 °C, a sample of nitrogen gas kept in a container of volume 3 L exerts a pressure of 4.5 atm. Calculate the number of moles of the nitrogen gas. ($R = 0.0821$ L atm K^{-1} mol^{-1})
11. Calculate the volume of N_2 generated at 80 °C and 823 mmHg by the decomposition of 60.0 g of NaN_3. (Na = 23, N = 14, $R = 0.0821$ L atm K^{-1} mol^{-1})

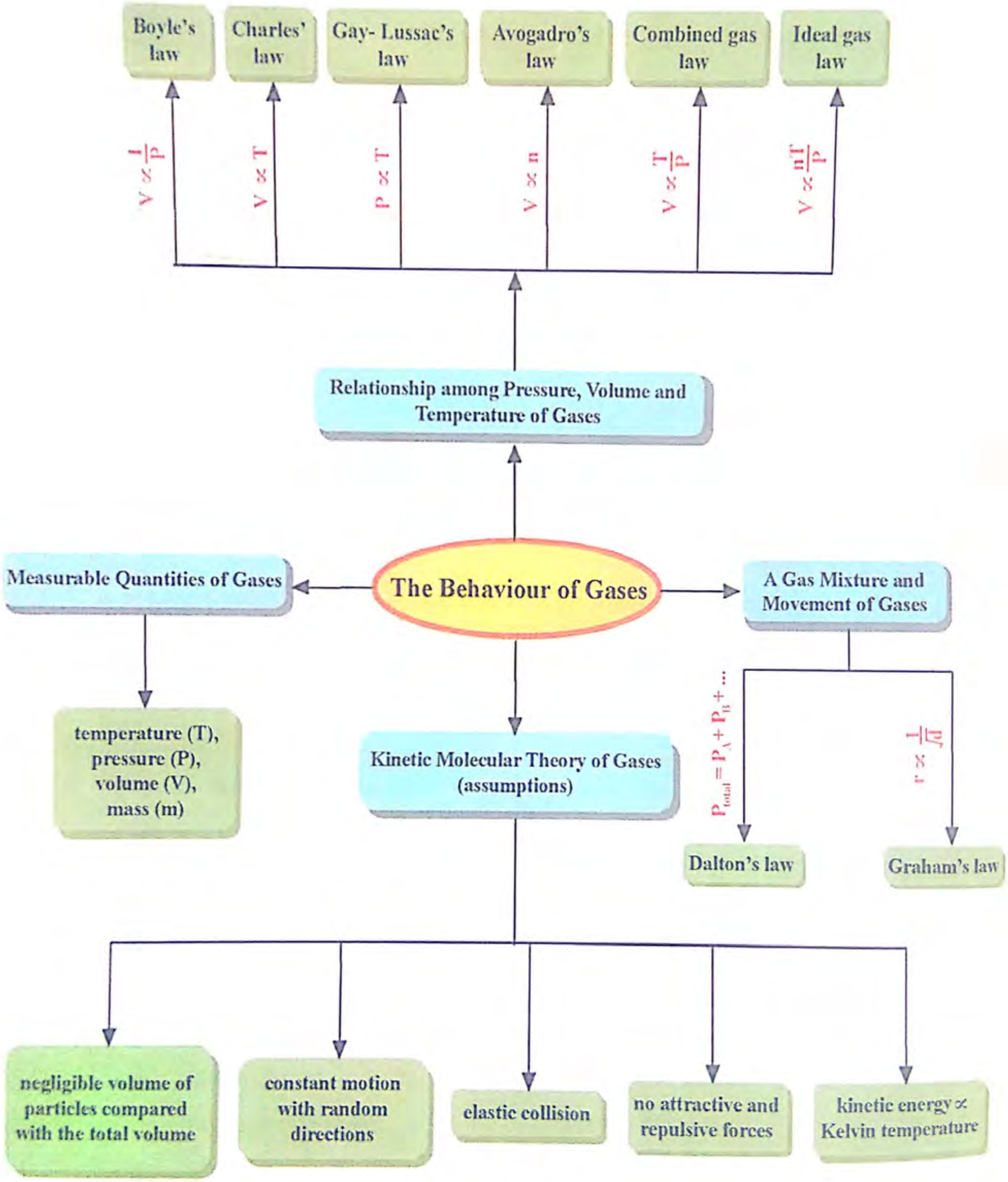
Q 12 and Q 13 (Problem solving)

12. A 0.21 g of gas occupies a volume of 186 cm^3 measured over water at 766 mmHg and 23 °C. Vapour pressure of water at 23 °C is 21.1 mmHg. What is the approximate molecular mass of the gas? ($R = 0.0821$ L atm K^{-1} mol^{-1})
13. A 10 g of limestone is treated with dilute hydrochloric acid. The liberated gas measured at 27 °C and 750 mmHg is 1.85 dm^3. Find the percentage purity of calcium carbonate.
    (C = 12, O = 16, Ca = 40, $R = 0.0821$ L atm K^{-1} mol^{-1})

Q 14 to Q 17 (Critical thinking)

14. At 46 °C, a sample of ammonia gas exerts a pressure of 5.0 atm. What is the pressure when the volume of the gas is reduced to one tenths (0.10) of the original value at the same temperature?
15. A rigid plastic container holds 1.0 L of methane gas at 660 torr pressure when the temperature is 22 °C. How much pressure will the gas exert if the temperature raised to 44 °C?
16. At 5 °C, a balloon containing 150 cm^3 of gas exerts a pressure of 1.3 atm. What will be the volume of gas in the balloon when the pressure doubles and the temperature decreases to 2 °C?
17. If it takes 1 minute for 50 cm^3 of oxygen to diffuse through a pinhole, how long will it take for the same volume of hydrogen to diffuse through the same hole? (H = 1, O = 16)

CHAPTER REVIEW
(Concept Map)

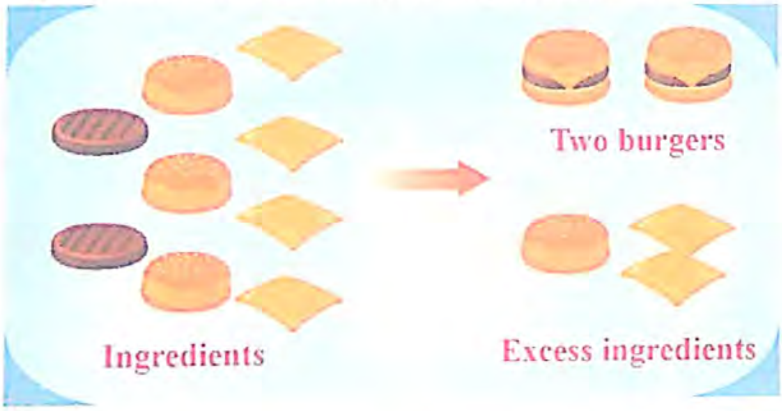


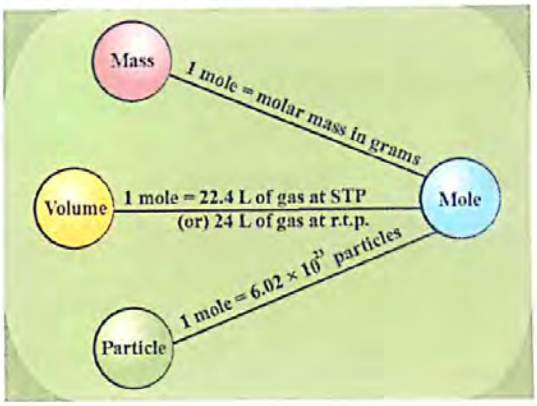
CHAPTER 2

STOICHIOMETRY

In the world today, we continually strive to express information in a concise, useful manner. Chemists use chemical equations to describe reactions observed in the laboratory or in nature. We often need to calculate the amount of substance that is either produced from or needed to react with, a given quantity of another substance. The study of the quantitative relationships implied by a chemical reaction is called stoichiometry. The word, stoichiometry derives from the Greek words: *stoicheion* (meaning 'element') and *metron* (meaning to 'measure'). Stoichiometry is based on the laws and principles of chemistry.

In this chapter, different types of quantitative measurements based on chemical reactions will be highlighted and the calculations for problems will be solved by using the unit factor method.





Learning Outcomes

After completing this chapter, students will be able to:

- determine the significant figures and round off numerical results;
- solve the problems related to the determination of mole and millimole of a substance;
- perform calculations involving chemical formulae and chemical equations;
- solve the problems related to calculations involving limited quantities;
- conduct volumetric analysis related to stoichiometry in solutions;
- demonstrate proper use of terms and units used in volumetric analysis;
- determine the concentrations of solutions in acid-base titrations.

2.1 MEASURABLE STANDARD VARIABLES

Chemistry is a quantitative science, which means that in many cases we measure a property of a substance and compare it with a standard having a known value of that property. We express the measurement as the product of a number and a unit. The unit indicates the standard against which the measured quantity is being compared, e.g., the length of a football field is 100 m, and it is 100 times longer than a standard of length which is called the metre (m).

The scientific system of measurement is called the International System of Units and is abbreviated as **SI** (Système Internationale). It is a modern version of the metric system. The basic quantities of SI units are shown in Table 2.1, and SI prefixes are described in Table 2.2.

Table 2.1 SI Basic Quantities

Physical quantity	Unit	Symbol
length	metre	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

Table 2.2 SI Prefixes

Factor	Prefix
10^{18}	exa (E)
10^{15}	peta (P)
10^{12}	tera (T)
10^{9}	giga (G)
10^{6}	mega (M)
10^{3}	kilo (k)
10^{2}	hecto (h)
10^{1}	deca (da)

Factor	Prefix
10^{-1}	deci (d)
10^{-2}	centi (c)
10^{-3}	milli (m)
10^{-6}	micro (μ)
10^{-9}	nano (n)
10^{-12}	pico (p)
10^{-15}	femto (f)
10^{-18}	atto (a)

(a) Significant Figures

The significant figures in a measurement consist of all the certain digits in that measurement plus one uncertain or estimated digit. Rules for significant figures and their respective examples are shown in Table 2.3.

According to the rules mentioned in Table 2.3, a measurement of 140 has two significant figures. The measurement 140 can also be written as 1.4×10^{2}, with two significant figures in the coefficient. A number with left end zeros, such as 0.000416, can be written as 4.16×10^{-4}, which has three significant figures. In some cases, scientific notation is the only way to indicate the correct number of significant figures. In order to report a value of 15000000 with four significant figures, it would need to be written as 1.500×10^{7}. The right end zeros after the 5 are significant. The original number of 15000000 only has two significant figures.

Table 2.3 Rules for Significant Figures

Rule	Example
1. All nonzero digits in a measurement are significant.	• 612 has three significant figures. • 1975 has four significant figures.
2. Zeros that appear between other nonzero digits are always significant.	• 20019 has five significant figures. • 309 has three significant figures.
3. Zeros that appear in front of all of the nonzero digits are called left end zeros. Left end zeros are never significant.	• 0.006 has one significant figure. • 0.000513 has three significant figures.
4. Zeros that appear after all nonzero digits are right end zeros. Right end zeros in a number that lacks a decimal point are not significant.	• 210 has two significant figures. • 3522000 has four significant figures.
5. Right end zeros in a number with a decimal point are significant.	• 820.0 has four significant figures.

Example 1: Find significant figures in each of the following measurements:
(a) 19.5 m (b) 0.0051 L (c) 204.80 g (d) 700 kg (e) 1.90×10^5 s (f) 700.0 kg

Solution: (a) **three** significant figures (b) **two** significant figures
(c) **five** significant figures (d) **one** significant figure
(e) **three** significant figures (f) **four** significant figures

(b) Rounding off Numerical Results

To get the specifics of the rules for determining the significant figures in a calculated result, it is needed to be able to round numbers correctly. If it is needed to drop just one digit to round off a number, the rule that must follow is to increase the final digit by one unit if the digit dropped is 5, 6, 7, 8 or 9 and to leave the final digit unchanged if the digit dropped is 0, 1, 2, 3 or 4.

For example, three significant figures for 3.567 = 3.57 (rounded up)
three significant figures for 4.623 = 4.62 (rounded drop)

Example 2: Consider the measurement of 207.518 m. Right now, the measurement contains six significant figures. How would you successively round it to fewer and fewer significant figures?

Solution: Significant figures and rounding off numerical results of 207.518 m are:

Number of significant figures	Rounded value	Reason
6	**207.518**	All digits are significant
5	**207.52**	8 rounds the 1 up to 2
4	**207.5**	2 is dropped
3	**208**	5 rounds the 7 up to 8
2	**210**	8 is replaced by a 0 and rounds the 0 up to 1
1	**200**	1 is replaced by a 0

REVIEW QUESTIONS

(1) How many significant figures are there in each of the following measurements?

(a) 0.00090 L (b) 255 g (c) 1435210 m (d) 40.1 kg (e) 9.0026×10^{-6} mm

(2) Round off the measured quantity of 31.0753 g according to each of the following significant figures:

(a) five (b) four (c) three (d) two (e) one

(3) Students A, B and C had done an experiment of weighing the salt and the resultant values were 8.3421 g, 8.3681 g and 8.4078 g, respectively. Round off the resultant values with three significant figures.

Key Term

- The **significant figures** of a number are digits that carry meaningful contribution to its measurement resolution.

2.2 COMPOSITION STOICHIOMETRY

Composition stoichiometry describes the quantitative relationships among elements in compounds. The calculation of molecular mass, relative molecular mass and relative formula mass, calculation of molecular formula and empirical formula, and calculation of percentage composition by mass of a particular element in a compound are included in composition stoichiometry.

In stoichiometric calculation, the SI unit for the amount of chemical substances is the **mole**, abbreviated as **mol**. **One mole of a substance is defined as the amount of substance that contains the same number of particles (atoms, molecules, or other particles) as there are atoms in exactly 12 g of pure carbon-12 atom.**

$$1 \text{ mole} = 6.02214179 \times 10^{23} \text{ particles}$$

This number is often rounded to 6.02×10^{23}, and it is called **Avogadro's number**. The mass of one mole of atoms of a pure element in grams is numerically equal to the atomic mass of that element in atomic mass units. On the other hand, the mass of one mole of molecules of a compound in grams is numerically equal to the molecular mass of that compound. This is called the **molar mass** of the element or compound; its units are **gram per mole (g mol^{-1})** or **milligram per millimole (mg mmol^{-1})**.

Hydrated salts are salts in which one or more water molecules are chemically combined. The number of water molecules in hydrated salt can also be determined by composition stoichiometry. The water found in crystals is called **water of crystallisation** and it is defined as water that occurs as a constituent of crystalline substances in a definite stoichiometric ratio. Some examples of hydrated salts are oxalic acid dihydrate, $(COOH)_2.2H_2O$ and copper(II) sulphate pentahydrate, $CuSO_4.5H_2O$.

Example 3: Calculate the mass of water that is contained in 5.24 g of $Zn(NO_3)_2.6H_2O$. (Zn = 65, N = 14, O = 16, H = 1)

Solution: molar mass of $Zn(NO_3)_2.6H_2O = 65 + (2 \times 14) + (6 \times 16) + 6[(2 \times 1) + 16] = 297 \text{ g mol}^{-1}$

mass of water in $Zn(NO_3)_2.6H_2O = 6[(2 \times 1) + 16] = 108 \text{ g}$

$$\text{g of } H_2O = 5.24 \text{ g of } Zn(NO_3)_2.6H_2O \times \frac{108 \text{ g of } H_2O}{297 \text{ g of } Zn(NO_3)_2.6H_2O} = \textbf{1.91 g of water}$$

Example 4: When 6.41 g of blue copper(II) sulphate crystals, $CuSO_4.nH_2O$, was heated until mass of white anhydrous copper(II) sulphate, $CuSO_4$, remained constant, 4.11 g of anhydrous salt was obtained. Calculate the number of moles of water (n) in the formula of $CuSO_4.\ nH_2O$.
(Cu = 63.5, S = 32, H = 1, O = 16)

Solution: mass of $CuSO_4.nH_2O$ = 6.41 g

mass of $CuSO_4$ = 4.11 g

mass of water = 6.41 g − 4.11 g = 2.3 g

molar mass of water = $(2 \times 1) + 16 = 18\ g\ mol^{-1}$

$$\text{mol of water} = 2.3\ g \times \frac{1\ \text{mol of}\ H_2O}{18\ g\ \text{of}\ H_2O} = 0.1278\ \text{mol}$$

molar mass of $CuSO_4$ = $63.5 + 32 + (4 \times 16) = 159.5\ g\ mol^{-1}$

$$\text{mol of}\ CuSO_4 = 4.11\ g \times \frac{1\ \text{mol of}\ CuSO_4}{159.5\ g\ \text{of}\ CuSO_4} = 0.0258\ \text{mol}$$

mole ratio of $CuSO_4$ to water in $CuSO_4.nH_2O$ = 0.0258 : 0.1278 = 1 : 4.95 = 1: 5

Thus the number of moles of water (n) in the hydrated crystal = 5

REVIEW QUESTIONS

(1) Calculate mass in kilograms of 5 moles of aluminium sulphate, $Al_2(SO_4)_3$. (Al = 27, S = 32, O =16)

(2) How many moles are there in 250 g of barium chloride? (Ba = 137, Cl = 35.5)

(3) Calculate the masses of magnesium, sulphur and water in 1 mole of Epsom salt, $MgSO_4.7H_2O$.
(Mg = 24, S = 32, O = 16, H = 1)

Key Terms

- **Stoichiometry** is a part of chemistry which deals with the quantities of substances taking part in a chemical reaction.
- **Water of crystallisation** is defined as water that occurs as a constituent of crystalline substances in a definite stoichiometric ratio.

2.3 REACTION STOICHIOMETRY

Reaction stoichiometry is the field of chemistry that is concerned with the relative quantities of reactants and products in chemical reactions.

(a) Chemical Equations in Stoichiometry

Balanced chemical equations are used to describe chemical reactions; the amount of reactants used up must be equal to the amount of products formed. There is no detectable change in the quantity of matter during an ordinary chemical reaction. There are three laws of matter concerning chemical reactions: the **Law of Conservation of Mass**, the **Law of Definite Proportions** and the **Law of Multiple Proportions**. The concepts of these laws provided the basis for balancing chemical equations and for performing calculations based on the chemical reactions. Some common types of chemical reactions are given below:

Combination reaction	$\text{phosphorus} + \text{chlorine} \longrightarrow \text{phosphorus(III) chloride}$ $P_4\,(s) + 6Cl_2\,(g) \longrightarrow 4PCl_3\,(l)$
Decomposition reaction	$\text{hydrogen peroxide} \longrightarrow \text{oxygen} + \text{water}$ $2H_2O_2\,(l) \longrightarrow O_2\,(g) + 2H_2O\,(l)$
Displacement reaction	$\text{chlorine} + \text{sodium bromide} \longrightarrow \text{sodium chloride} + \text{bromine}$ $Cl_2\,(g) + 2NaBr\,(aq) \longrightarrow 2NaCl\,(aq) + Br_2\,(g)$
Combustion reaction	$\text{carbon} + \text{oxygen (excess)} \xrightarrow{\Delta} \text{carbon dioxide}$ $C\,(s) + O_2\,(g) \xrightarrow{\Delta} CO_2\,(g)$

In all reactions, they follow the Law of Conservation of Mass. That is, the total number of atoms of each element in reactants and products must be equal. So, the chemical equation is also balanced.

(b) Limiting Reactants

The **limiting reactant** (limiting reagent) is a substance that stoichiometrically limits the amount of product(s) that can be formed in a reaction. The reaction will stop when all amount of the limiting reactant is used up.

Magnesium reacts with dilute sulphuric acid according to the following chemical equation:

$$\text{magnesium} + \text{sulphuric acid (dil.)} \longrightarrow \text{magnesium sulphate} + \text{hydrogen}$$

$$Mg\,(s) + H_2SO_4\,(aq) \longrightarrow MgSO_4\,(aq) + H_2\,(g)$$

This means 1 mole of Mg reacts with 1 mole of H_2SO_4. If 1 mole of Mg and 1 mole of H_2SO_4 are mixed together, both reactants will be completely used up by the time, the reaction stops.

However, if 1 mole of Mg is mixed with 2 moles of H_2SO_4 there is an insufficient amount of Mg to react with all of the sulphuric acid. There will be left 1 mole of sulphuric acid when 1 mole of Mg is used up and the reaction stops. In this case, magnesium is the limiting reactant, because it stops the reaction before all the H_2SO_4 has reacted.

Another example of the limiting reactant is burning a fuel such as natural gas; it is the oxygen in the air which is present in excess. The amount of carbon dioxide produced is limited by the amount of natural gas burnt, not by the amount of oxygen. So, the natural gas is the limiting reactant.

Example 5: When gaseous ammonia is passed over solid copper(II) oxide at high temperature, nitrogen gas, solid copper and water vapour are produced. Which is the limiting reactant when 18.5 g of NH_3 is reacted with 96.5 g of CuO? (Cu = 63.5, O = 16, N = 14, H = 1)

Solution:

$$2NH_3\,(g) + 3CuO\,(s) \longrightarrow N_2\,(g) + 3Cu\,(s) + 3H_2O\,(g)$$

2 mol 3 mol

$$\text{molar mass of CuO} = 63.5 + 16 = 79.5\ \text{g mol}^{-1}$$

$$\text{molar mass of } NH_3 = 14 + (3 \times 1) = 17\ \text{g mol}^{-1}$$

$$\text{mol of } NH_3 = 18.5\ \text{g of } NH_3 \times \frac{1\ \text{mol of } NH_3}{17\ \text{g of } NH_3} = 1.09\ \text{mol of } NH_3$$

$$\text{mol of CuO} = 96.5\ \text{g of CuO} \times \frac{1\ \text{mol of CuO}}{79.5\ \text{g of CuO}} = 1.21\ \text{mol of CuO}$$

According to the chemical equation, 2 mol of NH_3 reacts with 3 mol of CuO.

$$\text{mol of } NH_3 \text{ required} = 1.21 \text{ mol of CuO} \times \frac{2 \text{ mol of } NH_3}{3 \text{ mol of CuO}} = 0.81 \text{ mol of } NH_3$$

$$\text{mol of CuO required} = 1.09 \text{ mol of } NH_3 \times \frac{3 \text{ mol of CuO}}{2 \text{ mol of } NH_3} = 1.64 \text{ mol of CuO}$$

0.81 mol of NH_3 is required and we have 1.09 mol of NH_3. Therefore, NH_3 is an excess amount.
1.64 mol of CuO is required, but we have only 1.21 mol of CuO.

∴ **CuO is a limiting reactant.**

(c) Percentage Yields and Percentage Purity

In the laboratory, a little of the chemical is always lost by evaporating into the air or is remaining in the solution. Some of the reactants may not react and lose. Therefore, the amount of chemical produced is always less than the maximum amount that is expected. This is expressed by the percentage yield.

$$\textbf{The percentage yield} = \frac{\textbf{experimental or actual yield of product}}{\textbf{theoretical yield of product}} \times 100\ \%$$

In some cases, chemicals are not pure and it is needed to calculate the percentage purity of the substance.

$$\textbf{The percentage purity} = \frac{\textbf{mass of pure substance present}}{\textbf{mass of sample}} \times 100\ \%$$

Example 6: If 128 g of sulphur dioxide reacts with oxygen, 140 g of sulphur trioxide will be produced according to the chemical equation: $2SO_2 (g) + O_2 (g) \longrightarrow 2SO_3 (g)$. Calculate the percentage yield of the sulphur trioxide. (S = 32, O = 16)

Solution: $2SO_2 (g) + O_2 (g) \longrightarrow 2SO_3 (g)$

2 mol 1 mol 2 mol

molar mass of $SO_2 = 32 + (2 \times 16) = 64 \text{ g mol}^{-1}$

molar mass of $SO_3 = 32 + (3 \times 16) = 80 \text{ g mol}^{-1}$

$$\text{mol of } SO_2 = 128 \text{ g of } SO_2 \times \frac{1 \text{ mol of } SO_2}{64 \text{ g of } SO_2} = 2 \text{ mol of } SO_2$$

According to the chemical equation, 2 mol of SO_3 is produced by 2 mol of SO_2.
∴ mol of SO_3 = 2 mol

$$\text{mass of } SO_3 = 2 \text{ mol of } SO_3 \times \frac{80 \text{ g of } SO_3}{1 \text{ mol of } SO_3} = 160 \text{ g of } SO_3$$

$$\text{percentage yield} = \frac{\text{experimental mass of } SO_3}{\text{theoretical mass of of } SO_3} \times 100\ \% = \frac{140 \text{ g}}{160 \text{ g}} \times 100\ \% = 87.50\ \%$$

Example 7: When hydrochloric acid was added to 8 g of impure calcium carbonate, 1200 cm^3 of gas was produced. This experiment was done at r.t.p. Find the percentage purity of the calcium carbonate. (Ca = 40, C = 12, O = 16)

Solution:

$$\underset{1\text{ mol}}{CaCO_3\,(s)} + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + H_2O\,(l) + \underset{1\text{ mol}}{CO_2\,(g)}$$

molar mass of $CaCO_3 = 40 + 12 + (3 \times 16) = 100\ g\ mol^{-1}$

molar mass of $CO_2 = 12 + (2 \times 16) = 44\ g\ mol^{-1}$

molar volume of gases at r.t.p. = $24\ dm^3 = 24000\ cm^3$

$$\text{mol of } CO_2 = 1200\ cm^3 \times \frac{1\text{ mol of } CO_2}{24000\ cm^3 \text{ at r.t.p.}} = 0.05\text{ mol of } CO_2$$

According to the chemical equation, 1 mol of CO_2 is produced from 1 mol of $CaCO_3$.

$$\boxed{\text{mol of } CO_2} \longrightarrow \boxed{\text{mol of } CaCO_3} \longrightarrow \boxed{\text{g of } CaCO_3}$$

$$\text{g of } CaCO_3 = 0.05\text{ mol of } CO_2 \times \frac{1\text{ mol of } CaCO_3}{1\text{ mol of } CO_2} \times \frac{100\text{ g of } CaCO_3}{1\text{ mol of } CaCO_3} = \mathbf{5\ g\ of\ CaCO_3}$$

$$\text{percentage purity} = \frac{\text{mass of pure } CaCO_3}{\text{mass of sample}} \times 100\ \% = \frac{5\ g}{8\ g} \times 100\ \% = \mathbf{62.5\ \%}$$

(d) Sequential Reactions

Often more than one reaction is required to convert starting materials into the desired products. This is true for many reactions that are carried out in the laboratory and for many industrial processes. These are called **sequential reactions**. The desired product from each reaction is taken as the starting material for the next reaction. Some examples of sequential reactions are described below:

(1) carbon + steam ⟶ carbon monoxide + hydrogen

$$C\,(s) + H_2O\,(g) \longrightarrow CO\,(g) + H_2\,(g)$$

nickel + carbon monoxide ⟶ tetracarbonylnickel

$$Ni\,(s) + 4CO\,(g) \longrightarrow Ni(CO)_4\,(s)$$

(2) phosphorus + oxygen ⟶ phosphorus(V) oxide

$$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s)$$

phosphorus(V) oxide + water ⟶ phosphoric acid

$$P_4O_{10}\,(s) + 6H_2O\,(l) \longrightarrow 4H_3PO_4\,(aq)$$

Example 8: Phosphoric acid, H_3PO_4 can be prepared by two steps:

$P_4\ (s) + 5O_2\ (g) \longrightarrow P_4O_{10}\ (s)$ and $P_4O_{10}\ (s) + 6H_2O\ (l) \longrightarrow 4H_3PO_4\ (aq)$.

When 250 g of phosphorus reacts with excess oxygen, 80.2 % yield of P_4O_{10} is produced.
If 90.3 % yeild of H_3PO_4 is obtained in the second step reaction, what would be the mass of H_3PO_4?
(P = 31, O = 16, H = 1)

Solution:

$$\begin{array}{cccccc} P_4\ (s) & + & 5O_2\ (g) & \longrightarrow & P_4O_{10}\ (s) \\ 1\ \text{mol} & & 5\ \text{mol} & & 1\ \text{mol} \end{array}$$

molar mass of P_4 = 4×31 = $124\ g\ mol^{-1}$

molar mass of P_4O_{10} = $(4 \times 31) + (10 \times 16)$ = $284\ g\ mol^{-1}$

$$\boxed{\text{g of } P_4} \rightarrow \boxed{\text{mol of } P_4} \rightarrow \boxed{\text{mol of } P_4O_{10}} \rightarrow \boxed{\text{g of } P_4O_{10}}$$

$$\text{g of } P_4O_{10} = 250\ \text{g of } P_4 \times \frac{1\ \text{mol of } P_4}{124\ \text{g of } P_4} \times \frac{1\ \text{mol of } P_4O_{10}}{1\ \text{mol of } P_4} \times \frac{284\ \text{g of } P_4O_{10}}{1\ \text{mol of } P_4O_{10}} \times \frac{80.2\ \text{g of } P_4O_{10}}{100\ \text{g of } P_4O_{10}}$$

$$= \mathbf{459\ g\ of\ P_4O_{10}}$$

$$\begin{array}{cccccc} P_4O_{10}\ (s) & + & 6H_2O\ (l) & \longrightarrow & 4H_3PO_4\ (aq) \\ 1\ \text{mol} & & 6\ \text{mol} & & 4\ \text{mol} \end{array}$$

molar mass of H_3PO_4 = $(3 \times 1) + 31 + (4 \times 16)$ = $98\ g\ mol^{-1}$

$$\boxed{\text{g of } P_4O_{10}} \rightarrow \boxed{\text{mol of } P_4O_{10}} \rightarrow \boxed{\text{mol of } H_3PO_4} \rightarrow \boxed{\text{g of } H_3PO_4}$$

$$\text{g of } H_3PO_4 = 459\ \text{g of } P_4O_{10} \times \frac{1\ \text{mol of } P_4O_{10}}{284\ \text{g of } P_4O_{10}} \times \frac{4\ \text{mol of } H_3PO_4}{1\ \text{mol of } P_4O_{10}} \times \frac{98\ \text{g of } H_3PO_4}{1\ \text{mol of } H_3PO_4} \times \frac{90.3\ \text{g of } H_3PO_4}{100\ \text{g of } H_3PO_4}$$

$$= \mathbf{572\ g\ of\ H_3PO_4}$$

REVIEW QUESTIONS

(1) What will be the volume of ammonia gas when 100 cm^3 of nitrogen reacts with 150 cm^3 of hydrogen? Which is the limiting reactant? (All gases are measured at the same temperature and pressure.)

(2) In the combustion of propane, C_3H_8, 32 g of O_2 is needed to form 10 g of H_2O.
What are the theoretical yield and percentage yield of H_2O? (C = 12, O = 16, H = 1)

$C_3H_8\ (g) + 5O_2\ (g) \longrightarrow 3CO_2\ (g) + 4H_2O\ (l)$.

(3) Magnesium metal reacts with dilute hydrochloric acid to produce magnesium chloride and hydrogen. The chemical equation for the reaction is shown below.

$Mg\ (s) + 2HCl\ (aq) \longrightarrow MgCl_2\ (aq) + H_2\ (g)$

Starting with the known mass, 12.0 g of Mg, calculate the following:
(a) the mass of HCl reacted; (b) the mass of $MgCl_2$ produced. (Mg = 24, Cl = 35.5, H = 1)

Key Terms

- **Law of Conservation of Mass** states that the total mass of reactant(s) is equal to the total mass of the product(s).
- **Law of Definite Proportions** states that every chemical compound contains fixed and constant proportions (by mass) of its constituent elements.
- **Law of Multiple Proportions** states that when two elements combine with each other to form more than one compound, the different masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers.
- **Limiting reactant** is the reactant in a chemical reaction that limits the amount of product because the reaction stops when the limiting reactant is completely consumed.
- **Sequential reactions** consist of linked reactions in which the product of the first reaction becomes the reactant of the second reaction.

2.4 SOLUTION STOICHIOMETRY

Solution stoichiometry deals with the quantities in chemical reactions taking place in solutions such as to prepare solutions of desirable concentrations, to carry out chemical reactions using correct amount of solutions, and to predict the amount produced in solutions.

(a) Concentration of Solutions

In chemical reactions, it is required to know how much of the reactants are present in a solution and how to control the amount of reactants used to bring about a reaction in aqueous solution. On this context, the amount of substance (solute) present in aqueous solution is needed to know. In chemistry, the amount of solute can be measured by two ways: (a) mass in gram of solute and (b) number of moles of solute. To measure volume, chemists use cubic decimetre (dm^3) or litre (L) as the standard unit. In some cases, cubic centimetre (cm^3) or millilitre (mL) is also used.

$$\text{concentration} = \frac{\text{amount of solute (gram or mole or millimole)}}{\text{volume of solution (dm}^3\text{ or L or cm}^3\text{ or mL)}}$$

For example,

- a concentration of 10 g dm^{-3} means that there are 10 g of solute in 1 dm^3 of solution.
- a concentration of 2 mol dm^{-3} means that there are 2 moles of solute in 1 dm^3 of solution.

Molarity (M) of a solution is the quantity in moles of solute dissolved in one cubic decimetre (1 dm^3) of solution.

$$\text{molarity} = \frac{\text{mole of solute}}{\text{volume of solution (dm}^3\text{ or L)}}$$

$$\text{molarity} = \frac{\text{millimole of solute}}{\text{volume of solution (cm}^3\text{ or mL)}}$$

A **molar solution** of a compound is a solution which contains one mole of the compound in one cubic decimetre (1 dm^3) of the solution. (Note that it is one cubic decimetre of the solution, not solvent that is specified.)

Example 9: What is the molarity (M) of a solution that contains 7.3 g of HCl in 4.00 L of solution? (H = 1, Cl = 35.5)

Solution: molar mass of HCl = 1 + 35.5 = 36.5 g mol^{-1}

$$\boxed{\text{g of HCl}} \rightarrow \boxed{\text{mol of HCl}}$$

$$\text{mol of HCl} = 7.3\text{ g of HCl} \times \frac{1\text{ mol of HCl}}{36.5\text{ g of HCl}} = 0.2\text{ mol of HCl}$$

$$\text{molarity of HCl} = \frac{0.2\text{ mol of HCl}}{4.00\text{ L of solution}} = 0.05\text{ M}$$

Example 10: The concentration of NaCl in typical blood serum is about 0.14 M. What volume of blood contains 1.00 mg of NaCl? (Na = 23, Cl = 35.5)

Solution: molar mass of NaCl = 23 + 35.5 = 58.5 g mol^{-1}

$$\boxed{\text{mg of NaCl}} \rightarrow \boxed{\text{g of NaCl}} \rightarrow \boxed{\text{mol of NaCl}}$$

$$\text{mol of NaCl} = 1.00\text{ mg of NaCl} \times \frac{1\text{ g of NaCl}}{1000\text{ mg of NaCl}} \times \frac{1\text{ mol of NaCl}}{58.5\text{ g of NaCl}} = 1.71 \times 10^{-5}\text{ mol of NaCl}$$

$$\boxed{\text{mol of NaCl}} \rightarrow \boxed{\text{L of blood}}$$

$$\text{volume of blood serum} = 1.71 \times 10^{-5}\text{ mol of NaCl} \times \frac{1\text{ L of blood serum}}{0.14\text{ mol of NaCl}}$$

$$= \mathbf{1.22 \times 10^{-4}\ L\ of\ blood\ serum}$$

(b) Dilution of a Solution

Dilution is the procedure for preparing a less concentrated solution from a more concentrated one. The amount of solute does not change due to dilution; this is because only water (no solute) is added to accomplish the dilution. The volume of solution is changed.

$$\text{Since, molarity} = \frac{\text{mole of solute}}{\text{volume of solution (dm}^3\text{ or L)}}$$

number of mole of solute = molarity (M) × volume (V)

mole of solute before dilution = mole of solute after dilution

$$\mathbf{M_1 V_1 = M_2 V_2}$$

where M_1, V_1 = molarity and volume before dilution, respectively

M_2, V_2 = molarity and volume after dilution, respectively

Example 11: Calculate the volume in millilitres of 18.0 M HNO_3 that is required to prepare 1.00 L of a 0.900 M solution of HNO_3.

Solution:

Before dilution	After dilution
$M_1 = 18.0\ M$	$M_2 = 0.900\ M$
$V_1 = ?$	$V_2 = 1.00\ L$

$$M_1V_1 = M_2V_2$$

$$V_1 = \frac{M_2V_2}{M_1} = \frac{0.900\ M \times 1.00\ L}{18.0\ M} = 0.0500\ L = \mathbf{50.0\ mL}$$

(c) Titration

In volumetric analysis, the term **"titration"** is used for the procedure in which a solution of a standard reagent (reactant) is added to a specific volume of a solution of unknown molarity. The volume of the standard reagent solution which just reacts completely with the unknown solution is measured to get the exact titre. From this measurement, the amount in moles of standard reagent required for the reaction can be calculated. Knowing the chemical equation for the reaction, we can determine the amount in moles of the other reactants.

In a titration, a solution of accurately known concentration is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete.

Standard solution

The reagent of exactly known concentration that is used in a titration is called a **standard solution**. The concentration of a standard solution is established either directly or indirectly. In either method, a highly purified chemical compound called a primary standard is required as the reference material.

Primary standard

A primary standard is a highly pure and stable compound, used to establish the concentration of the standard solution. The accuracy of a volumetric analysis depends upon the primary standard.

The common types of titrations are:

(1) acid-base titration (neutralisation titration),
(2) precipitation titration,
(3) oxidation-reduction titration (redox titration) and
(4) complexometric titration.

The apparatus used for titration are burette, pipette, conical flask, beaker, funnel and stand. In general, a precisely known volume of the unknown solution (titrate), usually measured out by a pipette is placed in a conical flask. A solution of known concentration (titrant) is then added gradually from a burette for simple titration. This addition is continued until the exact mole ratio required by the balanced chemical equation is reached and this point is known as the **equivalence point**. The equivalence point of a chemical reaction is the point at which chemically equivalent quantities of reactants have been reacted.

In practice, the equivalence point cannot be seen and only the end point can be seen. **End point** is the point at which a titration is complete, usually marked by a change in colour of an indicator. Therefore, **titration error** occurs due to the difference between end point and equivalence point of the titration. To detect the end point of the titration, different indicators (organic dyes), such as methyl orange, phenolphthalein, etc., are used in acid-base titration. We will only focus acid-base titration in this section.

Example 12: A 2.792 g of sodium carbonate reacted with 0.324 M sulphuric acid solution. What volume in litre and in millilitre of sulphuric acid was required to complete this reaction?
(Na = 23, C = 12, O = 16, S = 32, H = 1)

Solution:

$$\underset{1\ \text{mol}}{H_2SO_4\,(aq)} + \underset{1\ \text{mol}}{Na_2CO_3\,(aq)} \longrightarrow Na_2SO_4\,(aq) + CO_2\,(g) + H_2O\,(l)$$

$$\text{molar mass of } Na_2CO_3 = (2 \times 23) + 12 + (3 \times 16) = 106\ \text{g mol}^{-1}$$

$$\boxed{\text{g of } Na_2CO_3} \rightarrow \boxed{\text{mol of } Na_2CO_3} \rightarrow \boxed{\text{mol of } H_2SO_4} \rightarrow \boxed{\text{L of } H_2SO_4}$$

$$\text{volume of } H_2SO_4 = 2.792\ \text{g of } Na_2CO_3 \times \frac{1\ \text{mol of } Na_2CO_3}{106\ \text{g of } Na_2CO_3} \times \frac{1\ \text{mol of } H_2SO_4}{1\text{mol of } Na_2CO_3} \times \frac{1\ \text{L of } H_2SO_4}{0.324\ \text{mol of } H_2SO_4}$$

$$= \mathbf{0.0813\ L\ of\ H_2SO_4\ solution} = \mathbf{81.30\ mL\ of\ H_2SO_4\ solution}$$

Example 13: A 3.0 g of a mixture of sodium carbonate and sodium chloride was made up to 250 mL of solution. A 25 mL of this solution required 21 mL of 0.1050 M hydrochloric acid for neutralisation. Calculate the percentage by mass of sodium chloride in the mixture. (C = 12, O = 16, Na = 23)

Solution:

$$\underset{1\ \text{mol}}{Na_2CO_3\,(aq)} + \underset{2\ \text{mol}}{2HCl\,(aq)} \longrightarrow 2NaCl\,(aq) + H_2O\,(l) + CO_2\,(g)$$

$$\boxed{\text{mL of HCl}} \longrightarrow \boxed{\text{L of HCl}} \longrightarrow \boxed{\text{mol of HCl}} \longrightarrow \boxed{\text{mol of } Na_2CO_3}$$

$$\text{mol of } Na_2CO_3 = 21\ \text{mL of HCl} \times \frac{1\ \text{L of HCl}}{1000\ \text{mL of HCl}} \times \frac{0.1050\ \text{mol of HCl}}{1\ \text{L of HCl}} \times \frac{1\ \text{mol of } Na_2CO_3}{2\ \text{mol of HCl}}$$

$$= 1.10 \times 10^{-3}\ \text{mol of } Na_2CO_3$$

25 mL of mixture contains 1.10×10^{-3} mol of Na_2CO_3

$$\text{250 mL of mixture contains} = \frac{1.10 \times 10^{-3} \times 250}{25} = 1.10 \times 10^{-2}\ \text{mol of } Na_2CO_3$$

$$\text{molar mass of } Na_2CO_3 = (2 \times 23) + 12 + (3 \times 16) = 106\ \text{g mol}^{-1}$$

$$\text{g of } Na_2CO_3 = 1.10 \times 10^{-2}\ \text{mol of } Na_2CO_3 \times \frac{106\ \text{g of } Na_2CO_3}{1\ \text{mol of } Na_2CO_3} = 1.17\ \text{g of } Na_2CO_3$$

$$\text{mass of NaCl} = 3.0\ \text{g} - 1.17\ \text{g} = 1.83\ \text{g of NaCl}$$

$$\text{percentage by mass of NaCl} = \frac{\text{mass of NaCl}}{\text{mass of mixture}} \times 100\ \% = \frac{1.83\ \text{g}}{3.0\ \text{g}} \times 100\ \% = \mathbf{61.00\ \%}$$

REVIEW QUESTIONS

(1) Calculate the molarity of an acid solution containing 9.8 g of sulphuric acid in 10 dm^3 of solution
(H = 1, O = 16, S = 32)

(2) What volume of water is needed to dilute a molar hydrochloric acid solution to make 2 dm^3 of 0.25
hydrochloric acid solution?

(3) A 10 cm^3 of sulphuric acid required 20 cm^3 of 0.2 M potassium hydroxide to neutralise it. Calcul
the molarity of sulphuric acid solution.

Key Terms

- The **molarity (M)** of a solution is the quantity in moles of the solute dissolved in one cu decimetre of the solution.
- A **molar solution** of a compound is a solution which contains one mole of the compound one cubic decimetre (1 dm^3) of the solution.
- **Titration** is the procedure in which a solution of a standard reagent (reactant) is added to a spec volume of a solution of unknown molarity.
- A **standard solution** is a solution of accurately known concentration that is used in titration.
- The **equivalence point** of a chemical reaction is the point at which chemically equival quantities of reactants have been mixed.
- **End point** is the point at which a titration is complete, usually marked by a change in colour an indicator.
- **Titration error** is the difference between end point and equivalence point of the titration.

Chemistry in Society

- Stoichiometry is essential for the production of many things we use in our daily life.
- Stoichiometry is needed to figure out exactly what quantities of reactants are required in order to yield the product in industry.
- Stoichiometry is used to get the certain taste of recipe for cooking.
- Productions of soaps, tyres, fertilisers, gasoline, deodourants, medicines and chocolates are the examples of the use of stoichiometry.

EXERCISES

Q 1 and Q 2 (Remembering and Understanding)

1. Write TRUE or FALSE for each of the following statements. If FALSE, correct it.
   (a) When a given aqueous solution is diluted with water, the quantity or mole of the solute changes
   (b) A molar solution of sodium carbonate contains 1 mole of pure Na_2CO_3 in 1 litre of solution.
   (c) The procedure in which a solution of a standard reagent is added to the specific volume of unknow molarity is called dilution.
   (d) An indicator indicates the equivalence point of the titration.

(e) The significant figures of a number are digits that carry meaningful contribution to its measurement

2. Choose the correct answer.

(a) Butane burns in oxygen according to the following chemical equation:

$$2C_4H_{10}\,(g) + 13O_2\,(g) \longrightarrow 8CO_2\,(g) + 10H_2O\,(l)$$

If 11.6 g of butane is burnt in 11.6 g of oxygen, which one is the limiting reagent?

(i) butane (ii) oxygen (iii) oxygen and butane (iv) neither

(b) Which is not a correct statement?

(i) One mole of methane contains four moles of hydrogen atoms.

(ii) One mole of ^{12}C has a mass of 12.00 g.

(iii) One mole of hydrogen gas contains 6.02×10^{23} atoms of hydrogen.

(iv) One mole of methane contains 75 % of carbon by mass.

(c) A 300 cm^3 of water is added to a solution of 200 cm^3 of 0.5 mol dm^{-3} sodium chloride. What is the concentration of the new solution?

(i) 0.05 mol dm^{-3} (ii) 0.2 mol dm^{-3} (iii) 0.1 mol dm^{-3} (iv) 0.3 mol dm^{-3}

(d) Glucose has a relative molecular mass of 180. How many grams of glucose are added to 50 cm^3 of water to make a solution of concentration 0.4 mol dm^{-3}?

(i) 3.6 g (ii) 9 g (iii) 36 g (iv) 72 g

(e) The three significant figures for the measurement 61.372 is:

(i) 61.3 (ii) 61.4 (iii) 6.137×10^2 (iv) 6.13×10^2

Q 3 to Q 11 (Analysing and Problem solving)

3. There are 0.5 mol of CH_4 gas and 1.0 mol of HCl gas. (C = 12, H = 1, Cl = 35.5)

(a) Which has more molecules?

(b) Which has the greater mass?

(c) Which has the greater volume at STP?

(d) Which has the greater percentage of hydrogen?

4. How many hydrogen atoms are present in 15 g of urea, $CO(NH_2)_2$, which is used as a fertiliser, in animal feed, and in the manufacture of polymers? (N = 14, H = 1, C = 12, O = 16)

5. Calculate the mass of water in each of the following compounds:

(a) 49.6 g of $Na_2S_2O_3.5H_2O$ (Na = 23, S = 32, O = 16, H = 1)

(b) 54.1 g of $FeCl_3.6H_2O$ (Fe = 56, Cl = 35.5, O = 16, H = 1)

6. Cyanogen gas, C_2N_2 can react with fluorine to form carbon tetrafluoride and nitrogen trifluoride.

$$C_2N_2\,(g) + 7F_2\,(g) \longrightarrow 2CF_4\,(g) + 2NF_3\,(g)$$

(a) How many moles of fluorine react with 1.37 mol of cyanogen?

(b) How many moles of carbon tetrafluoride are obtained from 13.75 mol of fluorine?

(c) How many moles of cyanogen are required to produce 0.8974 mol of nitrogen trifluoride?

(d) How many moles of fluorine will yield 4.981 mol of nitrogen trifluoride?

7. Sulphuric acid and sodium hydroxide react together according to the chemical equation:

$$H_2SO_4\,(aq) + 2NaOH\,(aq) \longrightarrow Na_2SO_4\,(aq) + 2H_2O\,(l)$$

What volume of 0.250 mol dm^{-3} NaOH is required to neutralise exactly 25.0 cm^3 of 0.125 mol dm H_2SO_4?

8. When 32 g of methane (CH_4) was burnt with 96 g of oxygen, what mass of carbon dioxide would formed? (C = 12, H = 1, O = 16)

9. An exactly 250 cm^3 of solution was prepared by dissolving a 2.5 g of mixture of anhydrous sodiu carbonate and sodium chloride. 25 cm^3 of this solution required 20 cm^3 of 0.1 M hydrochloric acid react completely. Calculate the percentage by mass of sodium chloride in the mixture. (Na = 23, C = 12, O = 16, Cl = 35.5)

10. To remove exhaled carbon dioxide from the living environment in space vehicles, solid lithiu hydroxide is used. Calculate the mass of gaseous carbon dioxide with four significant figures th can be observed by 1.00 kg of lithium hydroxide? (Li = 7, O = 16, H = 1, C = 12)

$$2LiOH\,(s) + CO_2\,(g) \longrightarrow Li_2CO_3\,(s) + H_2O\,(l)$$

11. Magnesium carbonate reacts with 500 cm^3 of 0.2 M nitric acid as follows:

$$MgCO_3\,(s) + 2HNO_3\,(aq) \longrightarrow Mg(NO_3)_2\,(aq) + H_2O\,(l) + CO_2\,(g)$$

(a) How many moles of magnesium carbonate will react with the nitric acid?
(b) How many grams of magnesium nitrate will be produced from the reaction?
(c) What volume in cm^3 of carbon dioxide gas will be produced from the reaction at STP?
(H = 1, C = 12, N = 14, O = 16, Mg = 24)

Q 12 and Q 13 (Critical thinking)

12. When 200 cm^3 of iron(III) chloride was boiled with excess ammonium hydroxide, the reddish-brow precipitate, $Fe(OH)_3$, was formed. After heating this precipitate, a 0.36 g of dried residue, Fe_2O_3, wa obtained. What is the concentration in mol dm^{-3} of iron(III) chloride solution? Give your answer wit three significant figures. (Fe = 56, O = 16, Cl = 35.5, H = 1)

13. Sulphur containing acid **J** has a relative molecular mass of 98. A 200 cm^3 of the aqueous sample contai 196 g of **J**.
(a) Calculate the concentration of **J** in g dm^{-3} and mol dm^{-3}.
(b) What is the formula of the acid **J**?
(c) When **J** is mixed with acidified aqueous barium nitrate, a white precipitate **K** forms. Write down the chemical equation for the reaction between acid **J** and barium nitrate. Name the precipitate K

CHAPTER 3

OXIDATION AND REDUCTION

Oxidation and reduction reactions are important because they are the principal sources of energy of chemistry and physico-biochemical entities, naturally or artificially. Thousands of different reactions in industries and homes undergo these reactions. The varieties of oxidation-reduction reactions that affect us every day are amazing. Rusting of iron is one familiar example of oxidation and reduction reactions. Painting iron railings and galvanising nails to combat corrosion, electroplating jewellery with very thin coatings of gold or silver, bleaching clothes and developing photographs in solutions using chemical reactions are indeed oxidation-reduction reactions. Photosynthesis in plants takes place through a series of chemical reactions involving oxidation-reduction processes. Some important concepts in oxidation and reduction reactions and their usefulness in our daily life and society are described in this chapter.


Rusting


Electroplating


Combustion


Rancidification


Changing colour

Learning Outcomes

After completing this chapter, students will be able to:

- explain how to assign the oxidation numbers;
- define oxidation and reduction reactions in terms of oxygen, hydrogen, electron transfer and changes in oxidation number;
- describe the concepts and process of oxidation and reduction;
- explain the oxidation and reduction (redox) reactions;
- identify and describe the properties and behaviours of oxidising and reducing agents;
- balance the redox equations.

3.1 OXIDATION NUMBERS

Oxidation numbers have a variety of uses in chemistry – from writing formulae to predicting properties of compounds and assisting in the balancing of oxidation-reduction reactions in which electrons are transferred.

The oxidation number (or oxidation state) of an atom can be zero, positive, or negative.

An oxidation number of zero means the atom has the same number of electrons assigned to it as there are in the free neutral atom. All elements in their free state (uncombined with other elements) have an oxidation number of zero (e.g., Na, Mg, H_2, O_2, Cl_2).

A **positive oxidation number** means the atom has fewer electrons assigned to it than in the neutral atom, and a **negative oxidation number** means the atom has more electrons assigned to it than in the neutral atom. The oxidation number of an atom that has lost or gained electrons to form an ion is the same as the positive or negative charge of the ion. For example, in NaCl, the oxidation numbers are +1 for the Na^+ ion and -1 for the Cl^- ion. The Na^+ ion has one less electron than the neutral Na atom, and the Cl^- ion has one more electron than the neutral Cl atom.

Rules for Assigning Oxidation Number

Assigning correct oxidation numbers to elements is essential for balancing the oxidation-reduction equation. Rules for assigning oxidation numbers are summarised as follows:

(1) All elements regardless of whether they are monoatomic, diatomic or triatomic have an oxidation number of zero (e.g., Cu, He, H_2, O_2, I_2, F_2, O_3).

(2) The algebraic sum of the oxidation numbers of the atoms in a neutral molecule is zero (e.g., $KMnO_4$, NaCl).

(3) The algebraic sum of the oxidation numbers of the atoms in a polyatomic ion is equal to the charge on the ion (e.g., MnO_4^-, NH_4^+).

(4) Oxidation number of H is +1, except in metal hydrides, where it is -1 (e.g., NaH, LiH, CaH_2).

(5) Oxidation number of O is −2, except in peroxides (e.g., H_2O_2, BaO_2, Na_2O_2), where it is −1, and in OF_2, where it is +2.

(6) The metallic element in an ionic compound has a positive oxidation number. **Alkali metals** in combined state have an oxidation number +1. **Alkaline earth metals** in combined state have an oxidation number +2.

(7) The oxidation number of halogen in compounds (e.g., $BaCl_2$, NaBr, KI) is -1. In interhalogen compounds (e.g., BrF_5, IF_7, ClF_3), and other compounds (e.g., $KClO_3$, NaOCl), the oxidation number of halogen is positive.

(8) In covalent compounds, the negative oxidation number is assigned to the more electronegative atom.

Use the following steps to find the oxidation number of an element within a compound or an ion.

Step (1) Write the oxidation number of each known atom below the correct position of atom in the formula.

Step (2) Multiply each oxidation number by the number of atoms of the element in the compound.

Step (3) Write an expression indicating the sum of all the oxidation numbers in the compound or ion. (The sum of the oxidation numbers in a compound must equal zero; the sum of the oxidation numbers in an ion must equal to the charge on that ion.)

Example 1: Determine the oxidation number of sulphur in sulphuric acid.

Solution: H_2SO_4

$2(H) + (S) + 4(O)$

Step 1 $(+1) \quad (S) \quad (-2)$

Step 2 $2(+1) \quad\quad 4(-2)$

Step 3 $+2 \quad + (S) \quad + (-8) = 0$

$S = +6$

$\therefore$ Oxidation number of sulphur = $+6$

Example 2: Determine the oxidation number of manganese in the permanganate ion MnO_4^-.

Solution: MnO_4^-

$(Mn) + 4(O)$

Step 1 $(Mn) \quad (-2)$

Step 2 $(Mn) \quad 4(-2)$

Step 3 $(Mn) + (-8) = -1$ (the charge on the ion)

$Mn = +7$

$\therefore$ Oxidation number of manganese = $+7$

REVIEW QUESTIONS

(1) Determine the oxidation number of a chlorine atom in each of the following:
(a) $KClO_4$ (b) $CaCl_2$ (c) ClF_3 (d) Cl_2

(2) Assign the oxidation number of a chromium atom in each of the following:
(a) CrO_3 (b) CrO_2 (c) Cr_2O_3 (d) $Cr_2O_7^{2-}$ (e) Cr

(3) Give the oxidation number of underlined element in each of the following:
(a) $\underline{S}O_4^{2-}$ (b) $\underline{Sn}$ (c) $H_2\underline{S}$ (d) $\underline{Fe}Cl_3$ (e) $\underline{N}O_3^-$ (f) $\underline{N}H_4^+$

Key Terms

- The **oxidation number** (or oxidation state) of an atom represents the number of electrons lost or gained by an atom. Oxidation number can be zero, positive, or negative.
- A **positive oxidation number** indicates the number of electrons removed from a neutral atom.
- A **negative oxidation number** indicates the number of electrons added to a neutral atom.

3.2 CONCEPTS OF OXIDATION AND REDUCTION

Oxidation and reduction reactions involve the transfer of oxygen atoms, or hydrogen atoms, or electrons, or change in oxidation numbers. Hence, oxidation and reduction reactions can be defined in various ways.

(a) Oxidation and Reduction in Terms of Oxygen

When a substance **gains oxygen** in a chemical reaction, it is **oxidised**. This reaction is called **oxidation**. For example, in a reaction that occurs when lightning, nitrogen has been oxidised to nitrogen oxide because it gains oxygen.

nitrogen + oxygen ⟶ nitrogen oxide

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

When a substance **loses oxygen** in a chemical reaction, it is **reduced**. The reaction is called **reduction**. For example, when copper(II) oxide reacts with coke at high temperature, copper(II) oxide has been reduced to copper because it loses oxygen.

$$\text{copper(II) oxide} + \text{carbon} \xrightarrow{\Delta} \text{copper} + \text{carbon dioxide}$$

$$2CuO\,(s) + C\,(s) \xrightarrow{\Delta} 2Cu\,(s) + CO_2\,(g)$$

(b) Oxidation and Reduction in Terms of Hydrogen

When a substance **loses hydrogen** in a chemical reaction, it is **oxidised**. The reaction is called **oxidation**. An example is the chemical reaction of chlorine and hydrogen sulphide.

$$\text{chlorine} + \text{hydrogen sulphide} \longrightarrow \text{sulphur} + \text{hydrogen chloride}$$

$$Cl_2\,(g) + H_2S\,(g) \longrightarrow S\,(s) + 2HCl\,(g)$$

In this reaction, hydrogen sulphide loses hydrogen and it is oxidised.

When a substance **gains hydrogen** in a chemical reaction, it is **reduced**. The reaction is called **reduction**. An example is the reaction of hydrogen and chlorine.

$$\text{hydrogen} + \text{chlorine} \longrightarrow \text{hydrogen chloride}$$

$$H_2\,(g) + Cl_2\,(g) \longrightarrow 2HCl\,(g)$$

In this reaction, chlorine gains hydrogen and it is reduced.

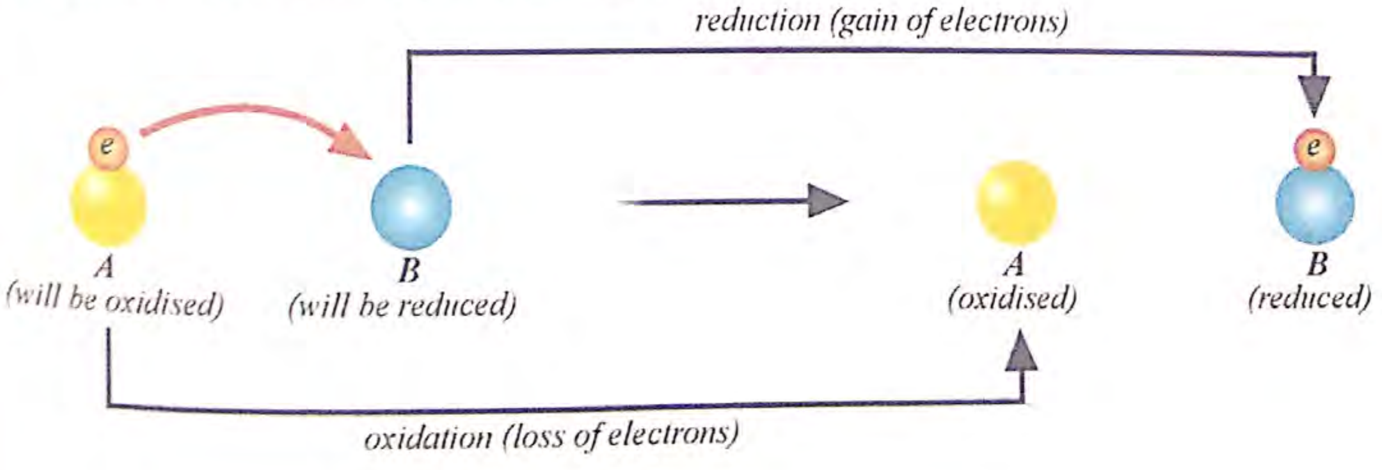
Oxygen belongs to a class of electronegative elements and hydrogen belongs to electropositive elements. Based on this classification, the concept of oxidation and reduction was extended to electronegative and electropositive elements. Thus, oxidation and reduction may now be defined as:

Oxidation is the **addition of oxygen** (or electronegative element) to a substance.
Reduction is the **removal of oxygen** (or electronegative element) from a substance.

Oxidation is the **removal of hydrogen** (or electropositive element) from a substance.
Reduction is the **addition of hydrogen** (or electropositive element) to a substance.

(c) Oxidation and Reduction in Terms of Electron Transfer

There are several oxidation-reduction reactions where no oxygen or hydrogen is involved. Hence, one of the most important ways to define oxidation-reduction is **electron transfer**, in which one substance gives up electrons and another substance takes electrons.



Example of this type of oxidation-reduction reaction is shown below.

$Zn\ (s) + Cu^{2+}\ (aq) \longrightarrow Zn^{2+}\ (aq) + Cu\ (s)$

The above equation can also be written as two ionic half-equations.

$Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e$ (loss of electrons) **(oxidation)**

$Cu^{2+}\ (aq) + 2e \longrightarrow Cu\ (s)$ (gain of electrons) **(reduction)**

It is obvious that zinc is oxidised. The formation of Zn^{2+} ion is due to the loss of two electrons each Zn atom. The copper(II) ion is reduced. The change from Cu^{2+} ion into copper metal is due to the ga of two electrons by each ion. Thus, oxidation and reduction can be defined as:

Oxidation is the **loss of electrons** by an element, compound or ion.

Reduction is the **gain of electrons** by an element, compound or ion.

(d) Oxidation and Reduction in Terms of Oxidation Number

Oxidation-reduction reactions are characterised by a change in **oxidation numbers (oxidatio states)** of some of the elements in the reactants. For example,

oxidised

$$\overset{0}{P_4} + 5O_2 + 6H_2O \longrightarrow 4H_3\overset{+5}{P}O_4$$

reduced

$$P_4 + 5\overset{0}{O_2} + 6H_2O \longrightarrow 4H_3P\overset{-2}{O_4}$$

In the above reaction, the oxidation number of **phosphorus** increases from '0' (in P_4) to +5 (in H_3PO and therefore P_4 has been oxidised to H_3PO_4. Similarly, the oxidation number of **oxygen** is decreased fro '0' (in O_2) to -2 (in H_3PO_4) and the oxygen has therefore been reduced. Thus, oxidation and reduction ma now be defined as:

Any element which **increases in oxidation number** is said to be **oxidised**.

Any element which **decreases in oxidation number** is said to be **reduced**.

REVIEW QUESTIONS

(1) Select the reaction which involves oxidation and reduction.

(i) $NH_3\ (g) + H_2O\ (l) \longrightarrow NH_4^+\ (aq) + OH^-\ (aq)$ (ii) $2H_2O_2\ (l) \longrightarrow 2H_2O\ (l) + O_2$ (g

(iii) $Ba^{2+}\ (aq) + SO_4^{2-}\ (aq) \longrightarrow BaSO_4(s)$

(2) By using oxidation numbers, determine which elements are oxidised, and which are reduced in th following reactions:

(a) $C\ (s) + 2H_2SO_4\ (l) \longrightarrow CO_2\ (g) + 2SO_2\ (g) + 2H_2O\ (l)$

(b) $2HNO_3\ (l) + 6HI\ (g) \longrightarrow 2NO\ (g) + 3I_2\ (s) + 4H_2O\ (l)$

(3) The compound $KBrO_3$ decomposes when heated. $2KBrO_3\ (s) \xrightarrow{\Delta} 2KBr\ (s) + 3O_2\ (g)$ Using oxidation numbers, explain why this reaction is oxidation-reduction reaction.

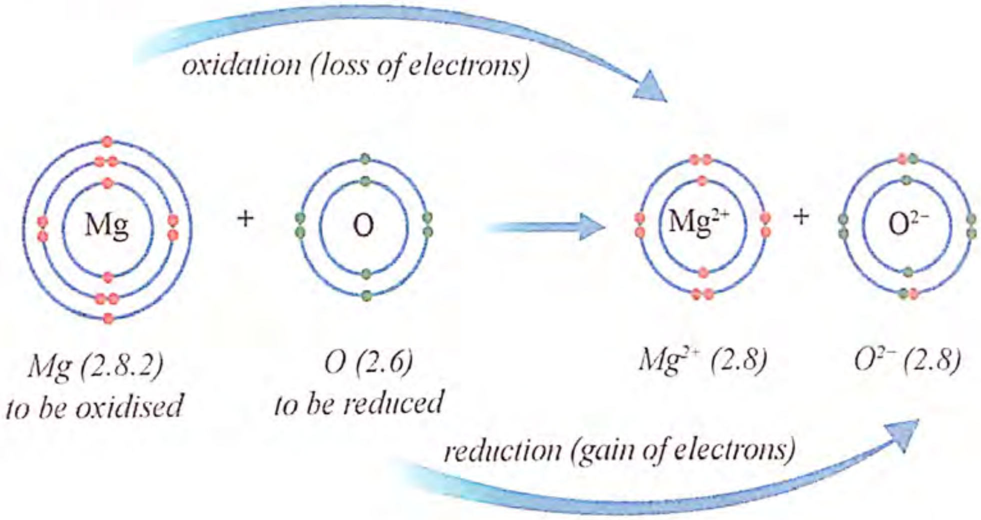
Key Terms

- **Oxidation** is the addition of oxygen (or electronegative element) to a substance or the removal of hydrogen (or electropositive element) from a substance. It is the loss of electrons by an element, compound or ion, or an increase in oxidation number.
- **Reduction** is the removal of oxygen (or electronegative element) from a substance or the addition of hydrogen (or electropositive element) to a substance. It is the gain of electrons by an element, compound or ion, or a decrease in oxidation number.

3.3 OXIDATION-REDUCTION REACTION (REDOX REACTION)

Chemical reactions which involve oxidation as well as reduction processes simultaneously, are known as **redox reactions.** Redox reactions are very important in living things. For example, one redox reaction, photosynthesis, provides food for the plant, and another one, respiration, keeps you alive. Even though the oxidation and reduction reactions take place simultaneously, chemists describe these reactions separately. The separate oxidation and reduction reactions are called **half-reactions**. Redox reactions require a track of each electron to each atom in chemical reactions. Redox reactions are also encountered in electrochemistry.

Consider the combustion of magnesium ribbon.



$$\mathrm{Mg} \longrightarrow \mathrm{Mg}^{2+} + 2e \text{ (oxidation, loss of electrons)}$$

$$\frac{1}{2}\mathrm{O}_2 + 2e \longrightarrow \mathrm{O}^{2-} \text{ (reduction, gain of electrons)}$$

In the above chemical reaction, magnesium loses electrons and so it is oxidised. At the same time, oxygen gains electrons and so it is reduced. Thus, the reaction between magnesium and oxygen is a redox reaction.

REVIEW QUESTIONS

(1) Which of the following chemical equations represents a redox reaction? For this redox reaction, determine which reactant is oxidised and which reactant is reduced.

(i) $MgO\ (s) + H_2CO_3\ (aq) \longrightarrow MgCO_3\ (s) + H_2O\ (l)$

(ii) $2Na\ (s) + 2H_2O\ (l) \longrightarrow 2NaOH\ (aq) + H_2\ (g)$

(2) Determine which elements are oxidised and which are reduced in the following reactions by using oxidation numbers

(a) $2KMnO_4\ (s) + 16HCl\ (l) \longrightarrow 2MnCl_2\ (aq) + 5Cl_2\ (g) + 8H_2O\ (l) + 2KCl\ (aq)$

(b) $2KNO_3\ (s) \longrightarrow 2KNO_2\ (s) + O_2\ (g)$

(3) Which of the following chemical reactions is not a redox reaction?

(i) $CuO\ (s) + H_2\ (g) \longrightarrow Cu\ (s) + H_2O\ (l)$

(ii) $Fe_2O_3\ (s) + 3CO\ (g) \longrightarrow 2Fe\ (s) + 3CO_2\ (g)$

(iii) $BaCl_2\ (aq) + H_2SO_4\ (aq) \longrightarrow BaSO_4\ (s) + 2HCl\ (aq)$

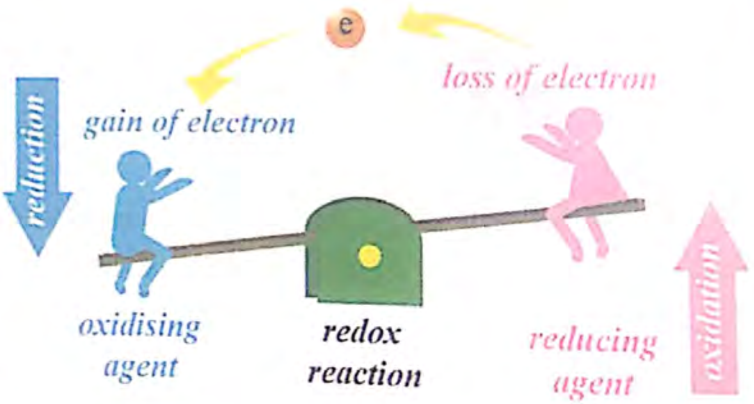
Key Term

- **Redox reactions** are the chemical reactions which involve oxidation as well as reduction processes simultaneously.

3.4 OXIDISING AGENT AND REDUCING AGENT

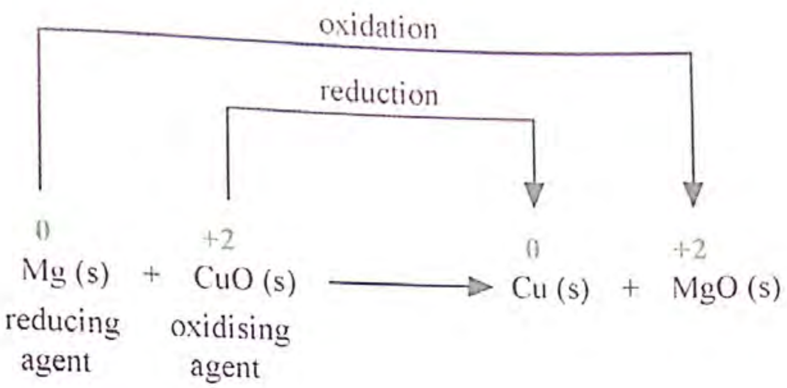
This section describes how to define an oxidising or reducing agent and how to determine an oxidising or reducing agent in a chemical reaction.

An oxidising agent or **oxidant** is an acceptor of electrons and is reduced itself in a chemical reaction. The oxidising agent is normally in one of its higher possible oxidation states because it will gain electrons and be reduced. The oxidising agent helps the other substance to get oxidised, and it gets reduced. **Examples of oxidising agents** include oxygen, halogens, concentrated sulphuric acid, nitric acid, hydrogen peroxide, potassium permanganate, potassium dichromate, metallic oxides, etc.



A **reducing agent** or **reductant** is a donor of electrons and is oxidised itself in a chemical reaction. The reducing agent is typically in one of its lower possible oxidation states because it will lose electrons and be oxidised in the redox reaction. The reducing agent helps the other substance to get reduced, and it gets oxidised. **Examples of reducing agents** include carbon, carbon monoxide, sulphur dioxide, hydrogen, hydrogen sulphide, metal, etc.

In the reaction between magnesium and copper(II) oxide, copper(II) oxide is reduced by gaining electrons from magnesium. So, copper(II) oxide is an oxidising agent. In a similar way, magnesium causes the reduction of copper(II) oxide by losing electrons from it. Therefore, magnesium is a reducing agent.



REVIEW QUESTIONS

(1) In each of the following redox reactions, which reactant is oxidised and which one is reduced? Identify the oxidising agent and reducing agent.

(a) $Mg (s) + H_2O (g) \longrightarrow MgO (s) + H_2 (g)$ (b) $CuO (s) + H_2 (g) \longrightarrow Cu (s) + H_2O (l)$

(c) $Cu^{2+} (aq) + Zn (s) \longrightarrow Zn^{2+} (aq) + Cu (s)$ (d) $Mg (s) + 2H^{+} (aq) \longrightarrow Mg^{2+} (aq) + H_2 (g)$

(2) Identify the oxidising agent and the reducing agent in each of the following reactions. Give reasons for your answer.

(a) $2Sr (s) + O_2 (g) \longrightarrow 2SrO (s)$

(b) $3Mg (s) + N_2 (g) \longrightarrow Mg_3N_2 (s)$

(c) $Cl_2 (g) + 2NaBr (aq) \longrightarrow 2NaCl (aq) + Br_2 (aq)$

(d) $2Na (s) + 2H_2O (l) \longrightarrow 2NaOH (aq) + H_2 (g)$

(3) Select the oxidising and reducing agents from the following list:

carbon, potassium dichromate, sulphur, carbon monoxide, nitric acid, aluminium, oxygen

Key Terms

- An **oxidising agent** or **oxidant** is an acceptor of electrons and is reduced itself in a chemical reaction. An oxidising agent helps the other substance to get oxidised, and it gets reduced.
- A **reducing agent** or **reductant** is a donor of electrons and is oxidised in a chemical reaction. A reducing agent helps the other substance to get reduced, and it gets oxidised.

3.5 BALANCING OXIDATION-REDUCTION EQUATIONS

Most redox reactions are relatively simple, and balancing them is straightforward. When redox reactions occur in an aqueous solution, however, the equations are more complex and more difficult to balance by inspection. The balanced chemical equation is the most important criterion for solving any stoichiometry problem.

(a) Balancing the Redox Equation Using Oxidation Number

One way to balance oxidation-reduction equations is by keeping track of the electron transfer using the oxidation numbers of each of the atoms. Procedures for balancing oxidation-reduction equations are as follows: (In the given example we shall use "ox. no." as an abbreviation for oxidation number.)

Step (1) Write the unbalanced chemical equation for the reaction.

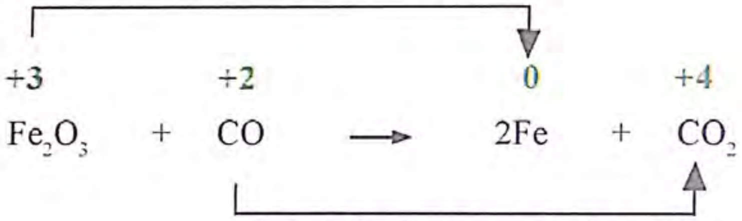
$$Fe_2O_3\,(s) + CO\,(g) \longrightarrow Fe\,(s) + CO_2\,(g)$$

Step (2) Assign oxidation numbers to all atoms or elements in the reactants and the products, and determine which atoms change oxidation state.

$$\overset{+3\ -2}{Fe_2O_3} + \overset{+2\ -2}{CO} \longrightarrow \overset{0}{Fe} + \overset{+4\ -2}{CO_2}$$

Step (3) Deduce the oxidation number changes by using the line to connect the atoms that are undergoing a change in oxidation number (ox. no. of product − ox. no. of reactant). Balance the connected atoms. On the line, write the oxidation number change.

change in ox. no. −3 × 2 = −6 (reduced)

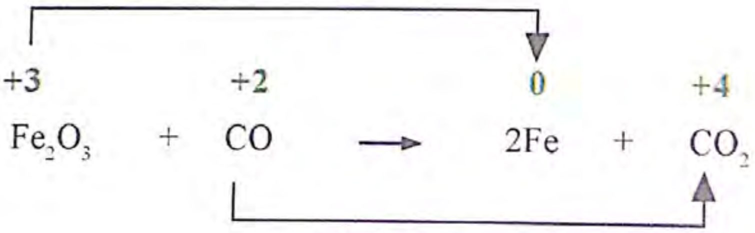


$$\overset{+3}{Fe_2O_3} + \overset{+2}{CO} \longrightarrow \overset{0}{2Fe} + \overset{+4}{CO_2}$$

change in ox. no. +2 (oxidised)

Step (4) Balance the oxidation number changes by multiplying appropriate coefficients to make the total increase in oxidation number equal to the total decrease in oxidation number.

reduced −6



$$\overset{+3}{Fe_2O_3} + \overset{+2}{CO} \longrightarrow \overset{0}{2Fe} + \overset{+4}{CO_2}$$

oxidised (+2 × 3) = +6

Step (5) Balance the atoms and total charges by showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in Step (4).

$$Fe_2O_3\,(s) + 3CO\,(g) \longrightarrow 2Fe\,(s) + 3CO_2\,(g)$$

Note : Remember that a change in oxidation number represents the number of electrons transferred. Instead of using a change in oxidation number, the number of electrons transferred may also be used for balancing redox equations.

(b) Balancing the Ionic Redox Equation Using Half-equations

Two ionic half-reactions form a total net equation. Examples of acidic and alkaline conditions can be demonstrated by half-reactions. Besides the general rules for neutral conditions, additional rules must be applied for aqueous reactions in acidic or alkaline conditions. In this method, the equation is separated into two half-equations; one for oxidation and one for reduction. Each equation is balanced by adjusting the coefficients of elements and adding H_2O, H^+ or OH^- and electron(s) in the following order:

(1) Write the unbalanced chemical equation in ionic form (if necessary).

(2) Write separate half-reactions for the oxidation and reduction processes.

(3) Balance the number of atoms of the elements in the chemical equation other than O and H.

(4) Balance the oxygen atoms by adding water molecules.

(5) Balance the hydrogen atoms by adding H^+ ions.

(6) Balance the charge of each chemical equation with electrons.

(7) The electron(s) on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers.

(8) The half-equations are added together, cancelling out the electrons to form one balanced chemical equation. Common terms should also be cancelled out. (If the equation is being balanced in a basic solution, through the addition of one more step, the appropriate number of OH^- must be added to balance the remaining H^+.)

(i) ***Acidic condition***

Acidic condition usually implies a solution with an excess of H^+ concentration, hence making the solution acidic. Let balance the given redox reaction in acidic condition as follows:

Step (1) Write the given unbalanced chemical equation.

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \longrightarrow Cr^{3+}(aq) + NO_3^-(aq)$$

Step (2) Separate it into two half-reactions.

$$Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$$

$$HNO_2(aq) \longrightarrow NO_3^-(aq)$$

Step (3) Balance the elements other than O and H. In this example, only chromium needs to be balanced.

$$Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq)$$

$$HNO_2(aq) \longrightarrow NO_3^-(aq)$$

Step (4) Add H_2O to balance oxygen. The chromium reaction needs to be balanced by adding $7H_2O$ molecules. The other reaction also needs to be balanced by adding one water molecule.

$$Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$HNO_2(aq) + H_2O(l) \longrightarrow NO_3^-(aq)$$

Step (5) Balance hydrogen by adding H^+ ions.

$$14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$HNO_2(aq) + H_2O(l) \longrightarrow 3H^+(aq) + NO_3^-(aq)$$

Step (6) Balance the charge of each equation with electrons. The first reaction in Step (5) ha +12, i.e., $(+14) + (-2) = +12$ on the left side and +6, i.e., $2 \times (+3) = +6$ on the rig side. To balance, add 6 electrons to the left side.

$$6e + 14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

For the second reaction in Step (5), there is no charge on the left and +2, i.e. $(+3) + (-1) = +2$ charge on the right. So, add 2 electrons to the right side.

$$HNO_2(aq) + H_2O(l) \longrightarrow 3H^+(aq) + NO_3^-(aq) + 2e$$

Step (7) Check and balance the reactions so that the electrons are equal. The first reaction i Step (5) has 6e and the second reaction has 2e, so the second one is multiplied by 3.

$$6e + 14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$3HNO_2(aq) + 3H_2O(l) \longrightarrow 9H^+(aq) + 3NO_3^-(aq) + 6e$$

Step (8) Add the half-reactions and cancel out common terms.

$$\cancel{6e} + 14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$3HNO_2(aq) + 3H_2O(l) \longrightarrow 9H^+(aq) + 3NO_3^-(aq) + \cancel{6e}$$

$$3HNO_2(aq) + 5H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 3NO_3^-(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$$

Check: The total charges of reactants must be equal to total charges of products. Here, +3 = +3

(ii) ***Alkaline condition***

Bases produce OH^- ions in solution; hence, balancing a redox reaction in basi condition requires OH^-. It follows the same steps as for acidic condition. The only differenc is adding hydroxide ions (OH^-) to each side of the net reaction to balance any H^+, and OH^- an H^+ ions on the same side of a reaction should be added together to form water. Again, an common terms can be cancelled out. Let balance the given redox reaction in alkaline conditio as follows:

Step (1) Write the given unbalanced chemical equation in ionic form.

$$Ag(s) + Zn^{2+}(aq) \longrightarrow Ag_2O(aq) + Zn(s)$$

Step (2) Separate it into two half-reactions.

$$Ag(s) \longrightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \longrightarrow Zn(s)$$

Step (3) Balance the elements other than oxygen and hydrogen.

$$2Ag(s) \longrightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \longrightarrow Zn(s)$$

Step (4) Add H_2O to balance oxygen.

$$H_2O\,(l) + 2Ag\,(s) \longrightarrow Ag_2O\,(aq)$$
$$Zn^{2+}\,(aq) \longrightarrow Zn\,(s)$$

Step (5) Balance the hydrogen with H^+ ions.

$$H_2O\,(l) + 2Ag\,(s) \longrightarrow Ag_2O\,(aq) + 2H^+\,(aq)$$
$$Zn^{2+}\,(aq) \longrightarrow Zn(s)$$

Step (6) Balance the charge with electrons.

$$H_2O\,(l) + 2Ag\,(s) \longrightarrow Ag_2O\,(aq) + 2H^+(aq) + 2e$$
$$Zn^{2+}(aq) + 2e \longrightarrow Zn(s)$$

Step (7) Check and balance the reactions so that they have an equal number of electrons. In this case, the electrons are balanced.

Step (8) Add the half-reactions and cancel the electrons.

$$H_2O\,(l) + 2Ag\,(s) \longrightarrow Ag_2O\,(aq) + 2H^+(aq) + \cancel{2}e$$
$$Zn^{2+}\,(aq) + \cancel{2}e \longrightarrow Zn\,(s)$$

$$H_2O\,(l) + 2Ag\,(s) + Zn^{2+}\,(aq) \longrightarrow Zn(s) + Ag_2O\,(aq) + 2H^+\,(aq)$$

Add OH^- to balance H^+. There are two net H^+ ions, so two OH^- ions are added on both sides.

$$H_2O\,(l) + 2Ag\,(s) + Zn^{2+}\,(aq) + 2OH^-\,(aq) \longrightarrow Zn(s) + Ag_2O\,(aq) + 2H^+\,(aq) + 2OH^-\,(aq)$$

Combine OH^- ions and H^+ ions that are present on the same side to form water.

$$H_2O\,(l) + 2Ag\,(s) + Zn^{2+}\,(aq) + 2OH^-\,(aq) \longrightarrow Zn(s) + Ag_2O\,(aq) + 2H_2O\,(l)$$

Cancel common terms

$$2Ag\,(s) + Zn^{2+}\,(aq) + 2OH^-\,(aq) \longrightarrow Zn\,(s) + Ag_2O\,(aq) + H_2O\,(l)$$

Check: The total charges of reactants must be equal to total charges of products. Here, 0 = 0

REVIEW QUESTIONS

(1) Balance each of the following redox reactions assuming it occurs in an acidic condition.

(a) $Zn\,(s) + NO_3^-\,(aq) \longrightarrow Zn^{2+}\,(aq) + NH_4^+\,(aq) + H_2O\,(l)$

(b) $HNO_3\,(aq) + Cu\,(s) \longrightarrow Cu(NO_3)_2\,(aq) + NO\,(g) + H_2O\,(l)$

(c) $Al\,(s) + SO_4^{2-}\,(aq) \longrightarrow Al^{3+}\,(aq) + SO_2\,(g)$

(2) Balance each of the following reactions assuming it occurs in an alkaline medium.

(a) $S\,(s) + NaIO_3\,(aq) + NaOH\,(aq) \longrightarrow Na_2SO_4\,(aq) + NaI\,(aq) + H_2O\,(l)$

(b) $Cl_2\,(g) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + NaClO_3\,(aq) + H_2O\,(l)$

(c) $Cr_2(SO_4)_3$ (aq) + NaOH (aq) + H_2O_2 (l) ⟶ Na_2CrO_4 (aq) + Na_2SO_4 (aq) + H_2O (l)

(d) MnO_4 (aq) + $C_2O_4^{2-}$ (aq) ⟶ MnO_2 (s) + CO_2 (g)

Chemistry in Society

- The oxidation of fuels such as petrol, gas, wood, etc. produces a large amount of energy which we need for various purposes in daily life.
- Oxidation of food in the digestive system causes the changes in proteins and nutrients required for biochemical reactions.

- Oxidation of fats and oils lead to rancidity, and in fruits such as apples, it can result in the formation of compounds which change the colour of fruit.
- Margarine and other butter substitutes are produced by using reduction of oils from corn, peanuts and soybeans.

- The breathalysers, to estimate the content of alcohol in drivers' breathes employ the chemical principle of redox reaction.
- Oxidising and reducing agents are important in industrial application. They are used in processes such as purifying water, bleaching fabrics, and storing energy (batteries, fuel cells, etc.).

EXERCISES

Q 1 to Q 8 (Understanding)

1. Write TRUE or FALSE for each of the following statements. If FALSE, correct it.
   - (a) Oxidation is the addition of oxygen to a substance.
   - (b) Reduction is the addition of hydrogen to a substance.
   - (c) Oxidation number of hydrogen in hydrogen peroxide is one.
   - (d) Reduction is the loss of electrons by a molecule, atom and ion.
   - (e) Oxidising agent is an electron donor.
2. Fill in the blanks with a suitable word or phrase or numerical value with units as necessary.
   - (a) The reaction in which oxidation and reduction are occurring simultaneously, is known as _____ reaction.
   - (b) An oxidising agent is a (an) _____ of electrons.
   - (c) Oxidation number of Cr in $Cr_2O_7^{2-}$ is _____.
   - (d) When the oxidation number of elements is decreased, it is said to be _____.
   - (e) Oxidation number of elements in pure form is _____.
3. Calculate the oxidation number of underlined elements in each of the following:

   (a) $Pb\underline{S}O_4$ (b) $Na\underline{I}O_3$ (c) $Na\underline{B}H_4$ (d) $Ca\underline{H}_2$ (e) $\underline{Al}H_3$

4. Hydrogen peroxide, H_2O_2, reacts with silver oxide:

$$Ag_2O\ (aq) + H_2O_2\ (l) \longrightarrow 2Ag\ (s) + H_2O\ (l) + O_2\ (g)$$

(a) What is the oxidation state of silver in Ag_2O?
(b) Which substance is reduced in the reaction?
(c) What property of hydrogen peroxide is shown in this reaction?

5. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) reducing agent	(i) −1
(b) reduction	(ii) CO
(c) oxidising agent	(iii) +3
(d) sum of the oxidation number in MnO_4^-	(iv) electron acceptor
(e) oxidation number of Al^{3+}	(v) addition of hydrogen

6. Identify the oxidising agent and the reducing agent for each of the following:

(a) $PbS\ (s) + 4H_2O_2\ (l) \longrightarrow PbSO_4\ (aq) + 4H_2O\ (l)$
(b) $3Mg\ (s) + N_2\ (g) \longrightarrow Mg_3N_2\ (s)$
(c) $4Fe\ (s) + 3O_2\ (g) \longrightarrow 2Fe_2O_3\ (s)$
(d) $3HCl\ (aq) + HNO_3\ (aq) \longrightarrow Cl_2\ (g) + NOCl\ (g) + 2H_2O\ (l)$

7. Explain why this reaction is a redox reaction.

$$2Mg\ (s) + O_2\ (g) \longrightarrow 2MgO\ (s)$$

8. By using oxidation numbers, identify which elements are oxidised and which are reduced in these reactions.

(a) $C_2H_6\ (g) + \frac{7}{2}O_2\ (g) \longrightarrow 2CO_2\ (g) + 3H_2O\ (g)$

(b) $2Sb\ (s) + 2HNO_3\ (aq) \longrightarrow Sb_2O_3\ (s) + 2NO\ (g) + H_2O\ (l)$

9. In the chemical equation: $2Br^-\ (aq) + Cl_2\ (g) \longrightarrow 2Cl^-\ (aq) + Br_2\ (l)$

(i) What is being oxidised? (ii) What is being reduced?
(iii) Which is the oxidising agent? (iv) Which is the reducing agent? **(Remembering)**

Q 10 and Q 11 (Applying and Analysing)

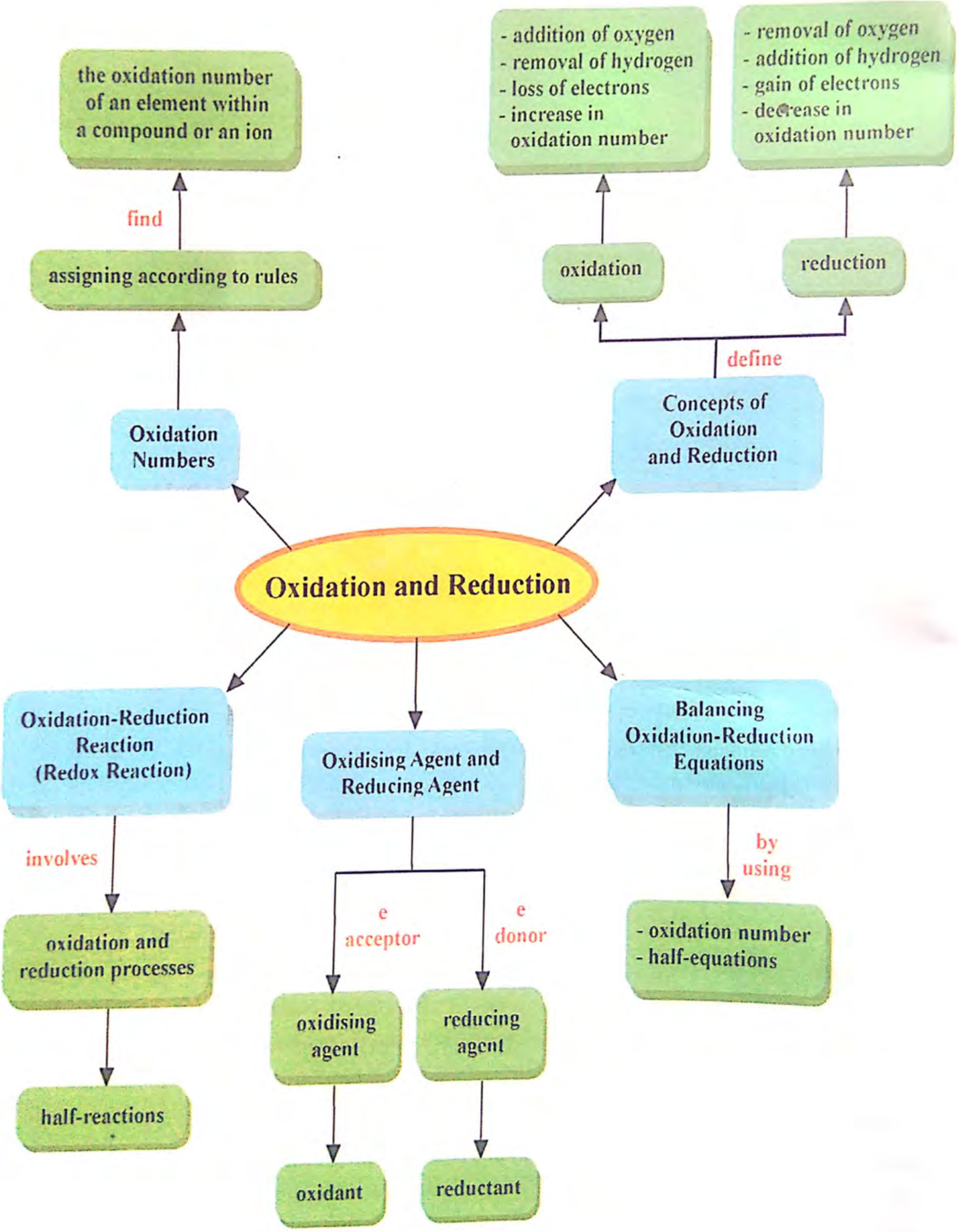
10. Complete and balance each reaction by using half-equations.

(a) $MnO_4^-\ (aq) + NO_2^-\ (aq) \longrightarrow MnO_2\ (s) + NO_3^-\ (aq)$ (in alkaline medium)
(b) $Sn^{2+}\ (aq) + IO_3^-\ (aq) \longrightarrow Sn^{4+}\ (aq) + I^-\ (aq)$ (in acidic medium)
(c) $Bi\ (s) + NO_3^-\ (aq) \longrightarrow Bi^{3+}\ (aq) + NO_2\ (g)$ (in acidic medium)
(d) $Cr_2O_7^{2-}\ (aq) + I^-\ (aq) \longrightarrow Cr^{3+}\ (aq) + I_2\ (aq)$ (in acidic medium)

11. Complete and balance each reaction by using oxidation numbers.

(a) $Ba\ (s) + AlF_3\ (s) \longrightarrow BaF_2\ (s) + Al\ (s)$
(b) $H_2SO_4\ (aq) + HBr\ (aq) \longrightarrow SO_2\ (g) + Br_2\ (aq) + H_2O\ (l)$
(c) $H_2O\ (l) + Cl_2\ (g) \longrightarrow HCl\ (g) + O_2\ (g)$
(d) $P_4\ (s) + HNO_3\ (aq) \longrightarrow H_3PO_4\ (aq) + NO_2\ (g) + H_2O\ (l)$

CHAPTER REVIEW
(Concept Map)



CHAPTER 4

ELECTROLYSIS

Many important chemical processes utilise electricity, whereas others can be used to produce it. In other words, chemical reactions can be used to produce electricity and vice versa. The conversion and storage of electrochemical energy are used in batteries like in smartphones and notebooks, car batteries and in fuel cells. In daily life, materials such as screws, nuts, electrical connectors have been surface finished by electroplating processes to protect from corrosion. Protective and decorative electroplating is also used in various industries and development of the electric automobiles and parts including other decorative items.The extraction of reactive metals such as sodium, magnesium, aluminium, and the refining of some metals, such as copper, are based on electrochemical methods.

Copper plated kettle

Gold plated coins

Silver and gold plated rings

Learning Outcomes

After completing this chapter, students will be able to:

- classify the conductors, non-conductors or insulators, electrolytes and non-electrolytes;
- describe the electrical conductivities of metals and electrolytes;
- explain the ionic theory;
- correlate the selective discharge of ions and electrolysis;
- differentiate between electrolytic cell and chemical cell;
- apply the Faraday's laws in electrolysis;
- describe the process of electroplating.

4.1 INTRODUCING ELECTROLYSIS

Electrolysis is the process whereby electrical energy is used to bring about a chemical change. In this section, some important terms used in electrolysis will be introduced.

(a) Conductors and Insulators

In a **conductor**, electric current can flow freely, but in **a non-conductor (an insulator)** it cannot. All metals either in the solid state or liquid state are conductors. For example, solid copper and liquid mercury conduct electricity. The non-metallic solid, graphite is a conductor. Solid substances such as wood, plastic and rubber do not conduct electricity and they are non-conductors or insulators. Semiconductors are substances which have an ability to conduct between conductors and non-conductors. Examples are elemental silicon, germanium, tin, selenium and gallium arsenide.

(b) Electrolytes and Non-electrolytes

Electrolytes are substances that ionise in solution or in a molten state and can conduct electricity. Most electrolytes are ionic compounds such as salt solutions. Acid and base solutions are also electrolytes: strong acid and strong base solutions are strong electrolytes, weak acid and weak base solutions are weak electrolytes.

Non-electrolytes do not dissociate into ions in solution and cannot conduct electricity. They are covalent compounds such as sugar solution.

(c) Electrodes

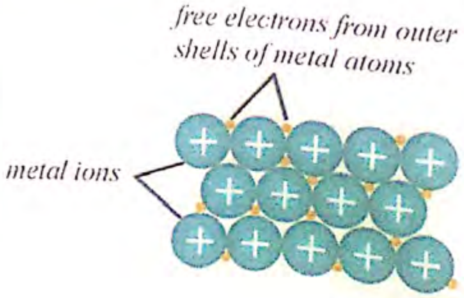
Electrodes are usually made of unreactive metals such as platinum or non-metal carbon (graphite) through which the electric current enters and leaves the electrolyte. Reduction and oxidation reactions take place at the electrodes. There are two types of electrodes: cathode and anode. **Cathode** attracts the positively charged ions (cations). **Anode** attracts negatively charged ions (anions). Thus, the reduction reaction takes place at the cathode and the oxidation reaction takes place at the anode.

(d) Electrical Conductivity

Electrical conductivity is a fundamental property of a material that quantifies how strongly it conducts electric current. If a substance has free electrons or mobile ions, it conducts electricity. Ionic substances do not conduct electricity when they are in solid state because the movement of ions is restricted. They can only conduct electricity in molten state or in aqueous solutions which contain positive ions (cations) and negative ions (anions). This is due to the ease of movement of ions in these states. The electrical conductance of a metal is much greater than that of a solution of an electrolyte.

(i) Electrical conductivity of metals

Metals contain free valence electrons. These valence electrons move freely through the entire **metallic lattice** (metallic framework). So metals can conduct electricity. For example, silver, copper, gold and aluminium have high electrical conductivity.



(ii) Electrical conductivity of electrolytes

The electrical conductivity of electrolytes is due to the presence of mobile ions. It can be explained by the following Arrhenius' Ionic Theory:

- Electrolytes contain electrically charged particles called ions.
- Electrolytes can conduct electricity due to the movement of these ions.
- Non-electrolytes do not contain ions and so they cannot conduct electricity.

(e) Electrochemical Cells

An electrochemical cell is a device that converts chemical energy into electrical energy or vice versa when a chemical reaction occurs by electrical energy. There are two fundamental types of electrochemical cells: electrolytic cell and chemical cell.

REVIEW QUESTIONS

(1) Why are the electrical wires coated with plastic or rubber?

(2) (a) Which metal is the most commonly used as conductor in electrical wiring and electrical circuits?
(b) Why is this metal used?

(3) Classify the given substances into conductors, non-conductors, electrolytes or non-electrolytes. Give reasons.
table salt solution, plastic, molten magnesium chloride, mercury, iron, sugar solution

Key Terms

- A **conductor** is a substance which conducts or allows the passage of electricity.
- A **non-conductor** or an **insulator** is a solid substance which does not conduct electricity.
- An **electrolyte** is a substance in the molten state or as a solution in water, which allows the passage of electricity.
- A **non-electrolyte** is a substance in a solution that does not conduct electric current.
- **Electrode** is an electrical conductor that emits or collects electrons in an electrolytic cell.
- **Cathode** is a negative electrode and donates electrons.
  Cation (positive ion) moves to the cathode and causes reduction during electrolysis.
- **Anode** is a positive electrode and accepts electrons.
  Anion (negative ion) moves to the anode and causes oxidation during electrolysis.
- **Metallic lattice** is a structure that consists of positively charged metal ions bound together by their inner electrons; however, their outer shell electrons are free to move around.
- **Electrolysis** is the decomposition of a compound, in solution or in the molten state, brought about by the passage of an electric current through it.

4.2 ELECTROLYTIC PROCESS

Electrolytic process is the use of electrolysis by which ionic substances are decomposed when an electric current is passed through them. It is commercially important as a stage in the separation of elements from minerals and ores using an electrolytic cell.

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table salt solution, plastic, molten magnesium chloride, mercury, iron, sugar solution

Key Terms

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4.2 ELECTROLYTIC PROCESS

Electrolytic process is the use of electrolysis by which ionic substances are decomposed when an electric current is passed through them. It is commercially important as a stage in the separation of elements from minerals and ores using an electrolytic cell.

(a) Electrolytic Cells

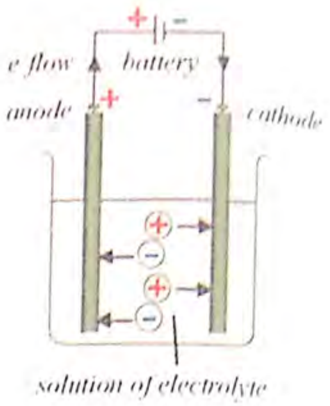


Figure 4.1 Electrolytic Cell

An **electrolytic cell** is the cell in which electrical energy is transformed into chemical energy. An electrolytic cell consists of a container with electrodes immersed in the reaction material (electrolyte) and connected to a source of direct current. Figure 4.1 represents an electrolytic cell. Electrolytes conduct electricity due to dissociation and discharge of ions at the respective electrodes. Electron transfer occurs between electrodes and electrolytes. During electrolysis, oxidation occurs at the positive electrode (anode) and reduction at the negative electrode (cathode). In the electrolytic cell, the cathode is connected to the negative terminal of battery and the anode is connected to the positive terminal.

(b) Electrolysis of Molten Salts

When an electric current is passed through the molten salt, the chemical reactions take place at the electrodes.

Electrolysis of molten sodium chloride using platinum electrodes

At sufficiently high temperature, sodium chloride is melted. This molten or fused sodium chloride contains Na and Cl ions. On electrolysis, Na ions accept electrons and discharge at the cathode and Cl ions give up electrons and discharge at the anode.

reaction at the cathode: $Na\ (l) + e \longrightarrow Na\ (l)$

reaction at the anode: $2Cl\ (l) \longrightarrow Cl_2\ (g) + 2e$

Net result: Liquid sodium floats to the top of the melt above the cathode and is drained off into a storage tank. Chlorine gas bubbles out of the melt above the anode.

(c) Electrolysis of Aqueous Solutions

Aqueous salt solutions contain cations and anions from the complete dissociation of salt and some H and OH ions from slight dissociation of water. Similarly, alkaline and aqueous acid solutions contain OH ions, H ions, acid radicals and basic radicals.

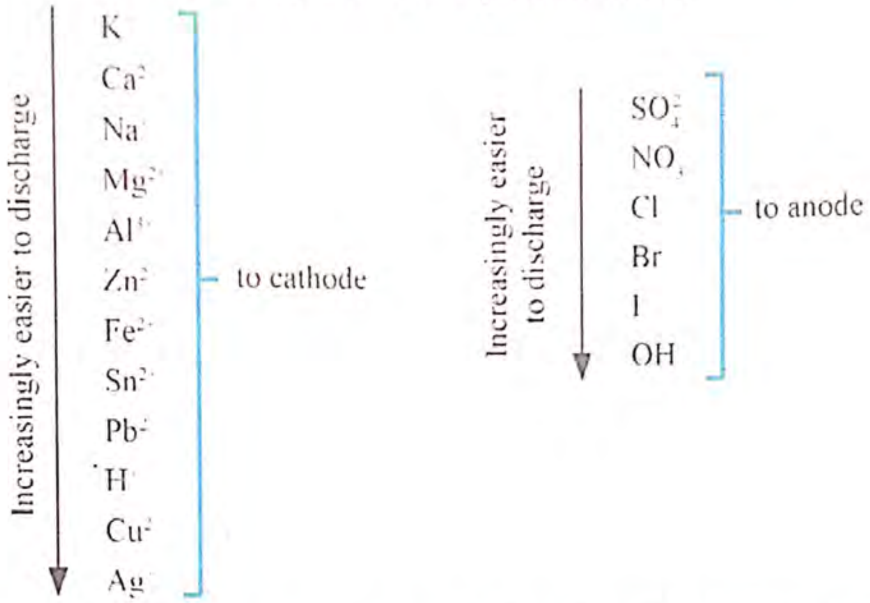
(i) Selective discharge of ions

In an aqueous solution of electrolyte, there are usually more than one species of cation (positive ion) or anion (negative ion). When electricity is passed through such a solution, the cations move towards the cathode and the anions move towards the anode. The preferential discharge of these ions depends on the following three factors: position of metal ions or groups in the electrochemical series, the concentration of electrolyte and the nature of the electrode used.

Position of the ions in the electrochemical series

Cations and anions are arranged in the order of increasing readiness with which they are discharged from solution on passage of electricity. This arrangement is known as the **electrochemical series**. It is built up by arranging in order of electrode potential values.

Arrangement of ions in the order of increasing readiness of discharge at electrodes (for aqueous solution)



If all other factors are equal, any ion lower in the series will be discharged from the solution in preference to those above it, positive ions at the cathode and negative ions at the anode. For example, on electrolysis of an aqueous sodium chloride solution which contains Na^+, H^+, Cl^- and OH^- ions, H^+ is discharged in preference to Na^+. Similarly, OH^- is discharged in preference to Cl^-.

Concentration of electrolyte

The concentration of electrolyte also means the concentration of ions in the electrolyte. As the concentration of an ion increases, the tendency of the ion to discharge from the solution also increases. The order of discharge stated by the electrochemical series may be reversed by the concentration effect.

The concentration effect can be seen when saturated sodium chloride solution (brine) and aqueous sodium chloride solution are electrolysed. In saturated sodium chloride (brine) solution, the concentration of Cl^- is much greater than that of OH^- ions. In these circumstances, Cl^- is discharged first. (Remember that in the electrolysis of aqueous sodium chloride solution, OH^- is discharged first.)

Nature of the electrode

The discharge of ions during electrolysis can be influenced by the types of electrodes used. Some electrodes are chemically inert (do not take part in the electrolytic reaction, e.g., graphite, platinum) while other electrodes are reactive (which may influence the ionic discharge, e.g., copper, mercury and silver).

For example, the products of the electrolysis of sodium chloride solution using platinum cathode and mercury cathode are quite different. With platinum cathode, H^+ ion which is lower in the electrochemical series than Na^+ ion, is discharged. If mercury is used as a cathode, Na^+ ion is discharged and sodium amalgam is produced.

(ii) Electrolysis of aqueous sodium chloride solution using graphite electrodes

The aqueous sodium chloride solution contains Na^+ and Cl^- ions from the salt, and H^+ an OH^- ions from water. On electrolysis, Na^+ and H^+ ions move to the cathode. H^+ ion is below the Na^+ ion i the electrochemical series. Therefore, H^+ ions accept electrons and are discharged. Cl^- ions and OH^- ion move to the anode. OH^- ion is below the Cl^- ion in the electrochemical series. Therefore, OH^- ions giv up electrons and are discharged.

reaction at the cathode: $2H^+ (aq) + 2e \longrightarrow H_2 (g)$

reaction at the anode: $4OH^- (aq) \longrightarrow 2H_2O (l) + O_2 (g) + 4e$

Net result : Hydrogen gas is evolved at the cathode and oxygen gas is evolved at the anode.

(iii) Electrolysis of saturated aqueous sodium chloride solution (brine) using platinum electrodes

Saturated sodium chloride solution contains Na^+ and Cl^- ions from the complete dissociation of sodium chloride, and some H^+ and OH^- ions from slight dissociation of water. On electrolysis, hydrogen gas is liberated at the cathode as described in the previous case. In brine, Cl^- and OH^- ions move to the anode. The concentration of Cl^- ions is very high compared to that of OH^- ions. Therefore, the Cl^- ions lose electrons and chlorine gas is evolved at the anode.

reaction at the cathode : $2H^+ (aq) + 2e \longrightarrow H_2 (g)$

reaction at the anode : $2Cl^- (aq) \longrightarrow Cl_2 (g) + 2e$

Net result: Hydrogen gas is evolved at the cathode and chlorine gas is evolved at the anode.

(iv) Electrolysis of aqueous copper(II) sulphate solution using platinum electrodes

Aqueous copper(II) sulphate solution contains Cu^{2+} and SO_4^{2-} ions from the dissociation of copper(II) sulphate, and H^+ and OH^- ions from slight dissociation of water. On electrolysis, Cu^{2+} and H^+ ions move to the cathode. Since Cu^{2+} ion is below H^+ ion in the electrochemical series, Cu^{2+} ions accept electrons more readily than H^+ ions and copper is deposited on the cathode. SO_4^{2-} ions and OH^- ions move to the anode. OH^- ion is below the SO_4^{2-} ion in the electrochemical series. Therefore, OH^- ions give up electrons and are discharged.

reaction at the cathode: $Cu^{2+} (aq) + 2e \longrightarrow Cu (s)$

reaction at the anode: $4OH^- (aq) \longrightarrow 2H_2O (l) + O_2 (g) + 4e$

Net result: Copper is deposited on the cathode and oxygen gas is liberated at the anode. The colour of solution becomes pale and more acidic due to the H^+ ions left in the solution.

(v) Electrolysis of aqueous copper(II) sulphate solution using copper electrodes

Aqueous copper(II) sulphate solution contains Cu^{2+}, SO_4^{2-}, H^+ and OH^- ions. As explained above, Cu^{2+} ions are discharged at the cathode where metallic copper is deposited. The SO_4^{2-} and OH^- ions move to the anode. However, both of these ions are not discharged at the anode. Instead of these ions, copper anode is dissolved into the solution. This is because copper electrodes are reactive and can dissolve in the solution forming Cu^{2+} ions. The effect of the nature of the electrode is more prominent than the other two factors when reactive electrodes are used in the electrolysis process.

reaction at the cathode:

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \text{ (copper deposits)}$$

reaction at the anode:

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e \text{ (copper dissolves)}$$

Net result: Copper deposits on the cathode and the mass of cathode increases. Copper anode dissolves and the mass of anode decreases. The colour of solution does not change (Figure 4.2).

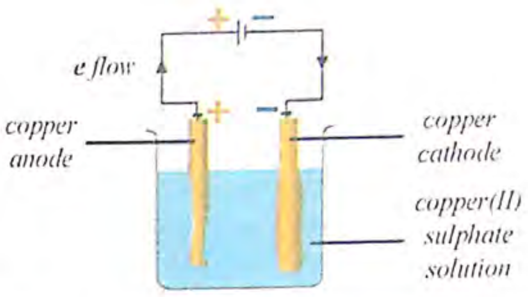


Figure 4.2 Electrolysis of Aqueous Copper(II) Sulphate Solution Using Copper Electrodes

(vi) Electrolysis of dilute acids and alkalis using platinum electrodes

Electrolysis of dilute sulphuric acid using platinum electrodes

Sulphuric acid solution contains H^+, SO_4^{2-} and OH^- ions. On electrolysis of dilute sulphuric acid as shown in Figure 4.3, H^+ ions go to the cathode and accept electrons, and H_2 gas is evolved.

SO_4^{2-} and OH^- ions both travel to the anode. OH^- ions lose electrons more easily and are discharged at the anode. Therefore, oxygen gas is liberated.

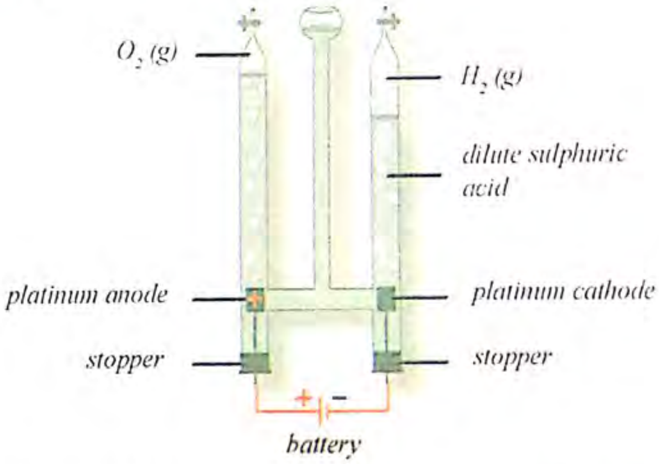


Figure 4.3 Electrolysis of Dilute Sulphuric Acid Using Platinum Electrodes

reaction at the cathode: $2H^+(aq) + 2e \longrightarrow H_2(g)$

reaction at the anode: $4OH^-(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e$

Net result: Two volumes of hydrogen gas and one volume of oxygen gas are evolved. The solution becomes more concentrated.

Note: The same result would be obtained from the electrolysis of alkali solution. The volume of gases evolved in the electrolysis can be measured by this type of apparatus known as the Hofmann's Voltameter.

REVIEW QUESTIONS

(1) A blue solution of copper(II) sulphate was divided into two portions. One portion was electrolysed using platinum electrodes. The other portion was electrolysed using copper electrodes. What changes in colour of the solution do you expect in each case?

(2) When brine solution was electrolysed using platinum electrodes, gas A and gas B were produced at cathode and anode, respectively.
   (a) Write down the electrode reactions and name the gases evolved.
   (b) Name the apparatus to measure the volume of these gases.

(3) In the electrolysis of water acidified with dilute sulphuric acid, predict the relative proportion of the gases evolved.

Key Terms

- An **electrochemical series** is an arrangement of cations and anions in the order of increasing readiness of discharge from solution on the passage of electricity.
- **Electrolytic cell** is the cell in which electrical energy is transformed into chemical energy.

4.3 CHEMICAL CELL

A chemical cell or **galvanic cell** as shown in Figure 4.4 is a type of cell in which an electric current can be produced from a chemical reaction. A car battery is one kind of galvanic cell, a device that can change chemical energy to electrical energy. There are many kinds of galvanic cells. These include dry cells, lead-acid batteries and fuel cells.

When the switch is pressed down to complete the circuit, the reaction will take place quite rapidly and the bulb will light up, indicating the flow of electric current in the circuit.

Zinc, the more electropositive of the two metals, ionises by loss of electrons and these electrons pass from zinc to copper through the wire. This is equivalent to the flow of current in the opposite direction.

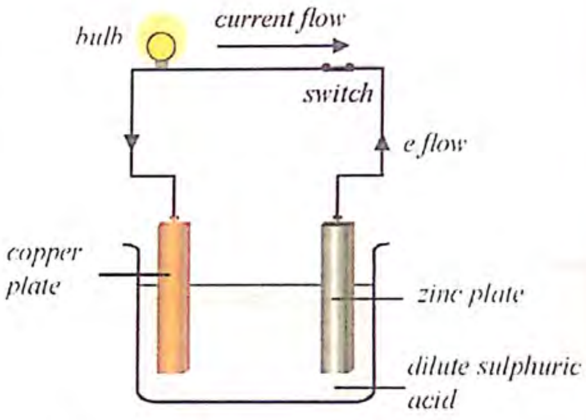


Figure 4.4 A Chemical Cell

reaction at zinc electrode: $Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2e$

At the copper surface, hydrogen ions from the dilute sulphuric acid (electrolyte) are reduced and hydrogen gas is liberated.

reaction at copper electrode: $2H^{+}\,(aq) + 2e \longrightarrow H_2\,(g)$

Net reaction : $Zn\,(s) + 2H^{+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)$

Current should continue to flow as long as materials last, but the bubbles of hydrogen adhere to the surface of the copper electrode, cutting off these surface areas of the electrode from contact with the electrolyte. This phenomenon, **polarisation**, slows down the reaction at the electrode and the cell is said to be polarised.

The two metals, that are used to convert chemical energy into electrical energy, must be widely separated in the electrochemical series, e.g., copper and magnesium, copper and zinc, etc. The greater the difference in reactivity between the two metals, the greater the voltage or **electromotive force (emf)** of the cell is observed.

REVIEW QUESTIONS

(1) What are the differences between electrolytic cell and chemical cell?

(2) Two plates, zinc and copper, held apart and connected to a small light bulb, are dipped into dilute sulphuric acid. The bulb lights up but the light soon becomes dim.
   (a) Name the type of cell.
   (b) What would be observed at the copper plate? Write a chemical equation for this reaction.
   (c) What would happen at the zinc plate? Write a chemical equation for this reaction.
   (d) Indicate the electron flow and current flow in chemical cell using zinc plate and copper plate.

(3) In a chemical cell, zinc plate and copper plate are used as electrodes and are dipped into dilute sulphuric acid. The bulb lights up.
   (a) If the zinc plate was replaced by an iron plate, would the lamp glow more or less brightly?
   (b) If the zinc plate was retained but the copper plate was replaced by a silver plate, would the lamp glow more or less brightly?

Key Terms

- **Chemical cell** is a cell in which chemical energy is transformed into electrical energy by forcing the electrons to travel through a wire.
- **Polarisation of the cell** is the chemical reaction that occurs when a current is flowing causes hydrogen bubbles to form on the surface of the electrode preventing further reaction.
- **Electromotive force (emf)** is the maximum potential difference between two electrodes of a galvanic or voltaic cell and it is measured in volt (V).

4.4 FARADAY'S LAWS OF ELECTROLYSIS

Faraday's laws of electrolysis are important to consider the quantitative relationship between the chemical change and the quantity of electricity involved.

(a) Faraday's First Law of Electrolysis

The statement of Faraday's first law of electrolysis is:

The amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the magnitude of the steady current (I) used, and the time (t) for which the current passes. That is, the amount of substance deposited or liberated is directly proportional to the quantity of electricity (Q) passed through the solution during electrolysis.

The quantity of electricity (Q) can be calculated from the steady current (I) used at time (t).

$Q = It$ unit of Q = coulomb (C);
unit of I = ampere (A); unit of t = second (s)

The faraday as a unit quantity of electricity

The quantity of electricity required to liberate one mole of a univalent element is 96500 coulombs. This quantity of electricity is given a special name which is **the faraday (F)**, in honour of the man who carried out a lot of work in the study of electrolysis.

For example, $M^{+}(aq) + e \longrightarrow M(s)$

1 mol   1 mol

Therefore, to liberate one mole of univalent element (M), one mole of electrons (e) is required. This one mole of electrons is equivalent to **one faraday** or 96500 C.

Example 1: Calculate the mass of copper in grams deposited by passing a steady current of 0.45 A for 25 minutes through an excess of copper(II) sulphate solution. (Cu = 63.5, 1F = 96500 C)

Solution: $I = 0.45\ A$, $t = 25\ min \times 60\ s = 1500\ s$

$Q = It = 0.45A \times 1500s = 675\ C$

reaction at the cathode: $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

2 mol   1 mol

2 F   63.5 g

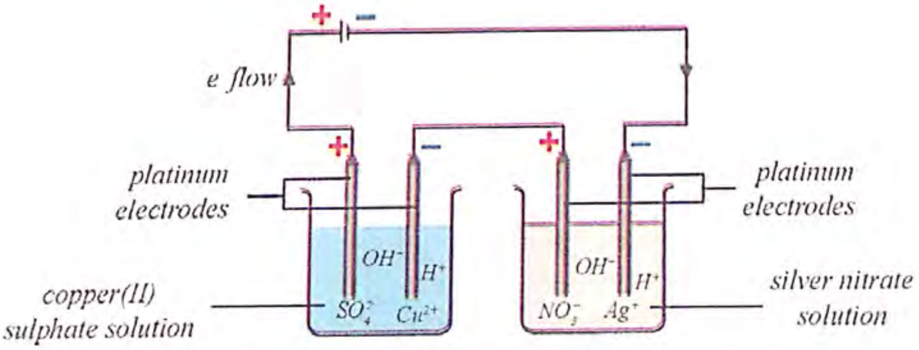
$2 \times 96500\ C$ of electricity was required to deposit 63.5 g of copper.

$$675\ C \text{ of electricity} = 63.5\ g \times \frac{675\ C}{2 \times 96500\ C} = 0.222\ g \text{ of copper}$$

(b) Faraday's Second Law of Electrolysis

The Faraday's second law of electrolysis can be stated as follows:

When the same quantity of electricity is passed through solutions of different electrolytes, the amounts of substances deposited or liberated are directly proportional to their chemical equivalent; in other words, the moles of substances deposited or liberated are inversely proportional to the valency of the elements, respectively.



A series of electrolytic cells with two different electrolytes

When a steady current is passed through a series of electrolytic cells with two different electrolytes, it is observed that:

In the first cell ($CuSO_4$ solution)	**In the second cell ($AgNO_3$ solution)**
$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$	$Ag^{+}(aq) + e \longrightarrow Ag(s)$
2 mol 1 mol	1 mol 1 mol
2 F 1 mol	1 F 1 mol

In order to produce 1 mol of copper, 2 F of electricity must be consumed.

In order to produce 1 mol of silver, 1 F of electricity must be consumed.

$$\therefore \text{ mole of element deposited} \propto \frac{1}{\text{charge on the ion}}$$

Example 2: A steady electric current is passed in turn through a series of two cells containing solutions of copper(II) sulphate and silver nitrate, respectively. If 0.146 g of copper were deposited at the cathode of the first cell, calculate the mass of silver deposited on the cathode of the second cell.
(Cu = 63.5, Ag = 108)

Solution: In $CuSO_4$ solution (first cell),

$$\begin{array}{lcl} Cu^{2+}(aq) + 2e & \longrightarrow & Cu(s) \\ \quad\quad 2\text{ mol} & & 1\text{ mol} \\ \quad\quad 2\text{ F} & & 63.5\text{ g} \end{array}$$

63.5 g of Cu was deposited by 2 F of electricity.

$$\therefore 0.146 \text{ g of Cu} = \frac{0.146\text{ g}}{63.5\text{ g}} \times 2\text{ F} = 0.0046\text{ F}$$

Since they were connected in series, the same quantity of electricity was passed through in $AgNO_3$ solution (second cell).

$$\begin{array}{lcl} \text{In } AgNO_3 \text{ solution (second cell), } Ag^{+}(aq) + e & \longrightarrow & Ag(s) \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 1\text{ mol} & & 1\text{ mol} \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 1\text{ F} & & 108\text{ g} \end{array}$$

1 F of electricity was required to deposit 108 g of Ag.

$$\therefore 0.0046\text{ F of electricity} = \frac{0.0046\text{ F}}{1\text{ F}} \times 108\text{ g} = 0.497\text{ g of silver}$$

Example 3: An electric current is passed through the solutions of silver nitrate and dilute sulphuric acid in series. If 5.4 g of silver were deposited in the first cell, what volume of hydrogen gas at STP was liberated at the cathode of the second cell? (Ag = 108)

Solution: In $AgNO_3$ solution (first cell),

$$\begin{array}{lcl} Ag^{+}(aq) + e & \longrightarrow & Ag(s) \\ \quad 1\text{ mol} & & 1\text{ mol} \\ \quad 1\text{ F} & & 108\text{ g} \end{array}$$

108 g of Ag was deposited by 1 F of electricity.

$$\therefore 5.4 \text{ g of Ag} = \frac{5.4\text{ g}}{108\text{ g}} \times 1\text{ F} = 0.05\text{ F}$$

Since they were connected in series, the same quantity of electricity was passed through in dilute sulphuric acid solution (second cell).

$$2H^{+}(aq) + 2e \longrightarrow H_2(g)$$

$$\begin{array}{ccc} & 2\text{ mol} & 1\text{ mol} \\ & 2\text{ F} & 22.4\text{ dm}^3\text{ at STP} \end{array}$$

2 F of electricity was required to liberate 22.4 dm^3 of H_2 gas at STP.

$$\therefore 0.05\text{ F of electricity} = \frac{0.05\text{ F}}{2\text{ F}} \times 22.4\text{ dm}^3\text{ at STP} = 0.56\text{ dm}^3\text{ of H}_2\text{ gas at STP}$$

Application of Faraday's laws of electrolysis

- The amount of substance produced in electrolysis by different quantities of electricity can be determined.
- The amounts of different substances produced from different electrolytes in a series of cells by the same quantity of electricity can be determined.
- The relative atomic masses of metals can also be determined.

REVIEW QUESTIONS

(1) The mass of silver deposited on a spoon during electrolysis was 0.976 g. Calculate the amount of electricity passed through the cell. (Ag = 108, 1 F = 96500 C)

(2) Silver nitrate, copper(II) sulphate and chromium(III) nitrate salt solutions are used in a series of electrolytic cells. When the same quantity of electricity (96500 C) is passed into these cells, how many moles of silver, copper and chromium will be deposited?

(3) Electric current was passed through the solutions of copper(II) sulphate and aqueous sodium hydroxide which were connected in series. If 6.35 g of copper were deposited in the first cell, calculate the volume of oxygen gas at STP liberated at the anode of second cell. (Cu = 63.5)

Key Term

- **One faraday** is the quantity of electricity (96500 coulombs) required to produce one mole of a univalent element.

4.5 ELECTROPLATING

Electroplating is a process where a coating of metal is added to a conductor using electricity via a reduction reaction. It is also known as electrodeposition. It is used to improve the appearance of the metal and to prevent the corrosion of metal. The cathode is the object to be plated. The electrolytic solution must contain ions of the same metal for plating. The ions will migrate to the cathode where they are discharged and deposited as a layer on the cathode. It is important to ensure that the cathode is electrically conductive.

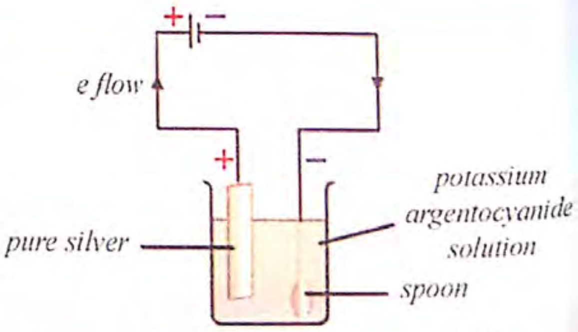


Figure 4.5(a) Electroplating of Silver

Figure 4.5(a) shows electroplating of silver. In silver plating, articles such as spoons or ornaments made of base alloys, (e.g., cupronickel) are used as cathode. Potassium argentocyanide, $K[Ag(CN)_2]$ solution in plating bath ionises as follows:

$$K[Ag(CN)_2]\,(aq) \rightleftharpoons K^+\,(aq) + Ag^+\,(aq) + 2CN^-\,(aq)$$

The anode is pure silver. When a direct current passes through this solution, the following reactions take place:

reaction at the cathode: $Ag^+\,(aq) + e \longrightarrow Ag\,(s)$ (silver deposits)

reaction at the anode: $Ag\,(s) \longrightarrow Ag^+\,(aq) + e$ (silver dissolves)

Figure 4.5(b) shows electroplating of chromium. In chromium plating, a steel object is plated first with nickel or copper, because chromium does not stick well onto a steel surface. The object is used as cathode in a plating bath containing acidified chromium(III) sulphate solution. The anode is made of lead. When a direct current passes through this solution, chromium deposits at the cathode as a bright coherent layer. This chromium layer resists rusting and gives a bright "silvery" surface.

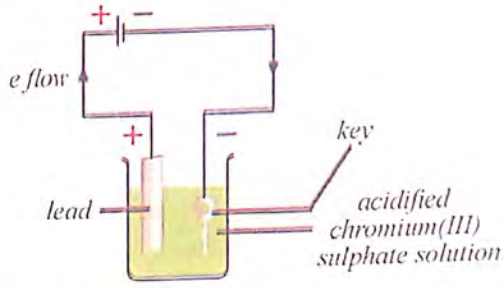


Figure 4.5(b) Electroplating of Chromium

reaction at the cathode: $Cr^{3+}\,(aq) + 3e \longrightarrow Cr\,(s)$

reaction at the anode: $4OH^-\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g) + 4e$

REVIEW QUESTIONS

(1) Name the electrolyte that is used in silver plating. Write down the electrode reactions.

(2) In chromium plating, steel parts are first plated with copper or nickel. Why?

(3) (a) In the electroplating of a spoon with silver using aqueous silver nitrate, is the spoon used as cathode or anode?

(b) In electrolytic refining, is the crude metal used as cathode or anode?

Key Term

- **Electroplating** is a process to coat one metal with a thin layer of another metal by electrolysis.

Chemistry in Society

- Copper wire is used in power distribution, telecommunications, electronic circuits and electrical equipment.
- Electrical insulators such as plastic and rubber are used to protect from the dangerous effects of electricity flowing through conductors.
- Body fluid contains electrolytes that are necessary for the body function. The important electrolytes in human bodies include chlorides of sodium, potassium and calcium.

- A battery consists of a galvanic cell or chemical cell connected in series that serves as a source of direct current. Lead storage battery, dry cell battery and alkaline battery are commonly used in daily life.

- Metal objects such as trophies become a better appearance and attraction after being plated.

EXERCISES

1. Arrange the following ions in order of decreasing readiness of discharge from solution during electrolysis if other factors are the same:

   (a) Al^{3+}, Na^{+}, Zn^{2+}, Ag^{+}, Fe^{2+} (b) NO_3^-, OH^-, SO_4^{2-}, Br^- **(Understanding)**

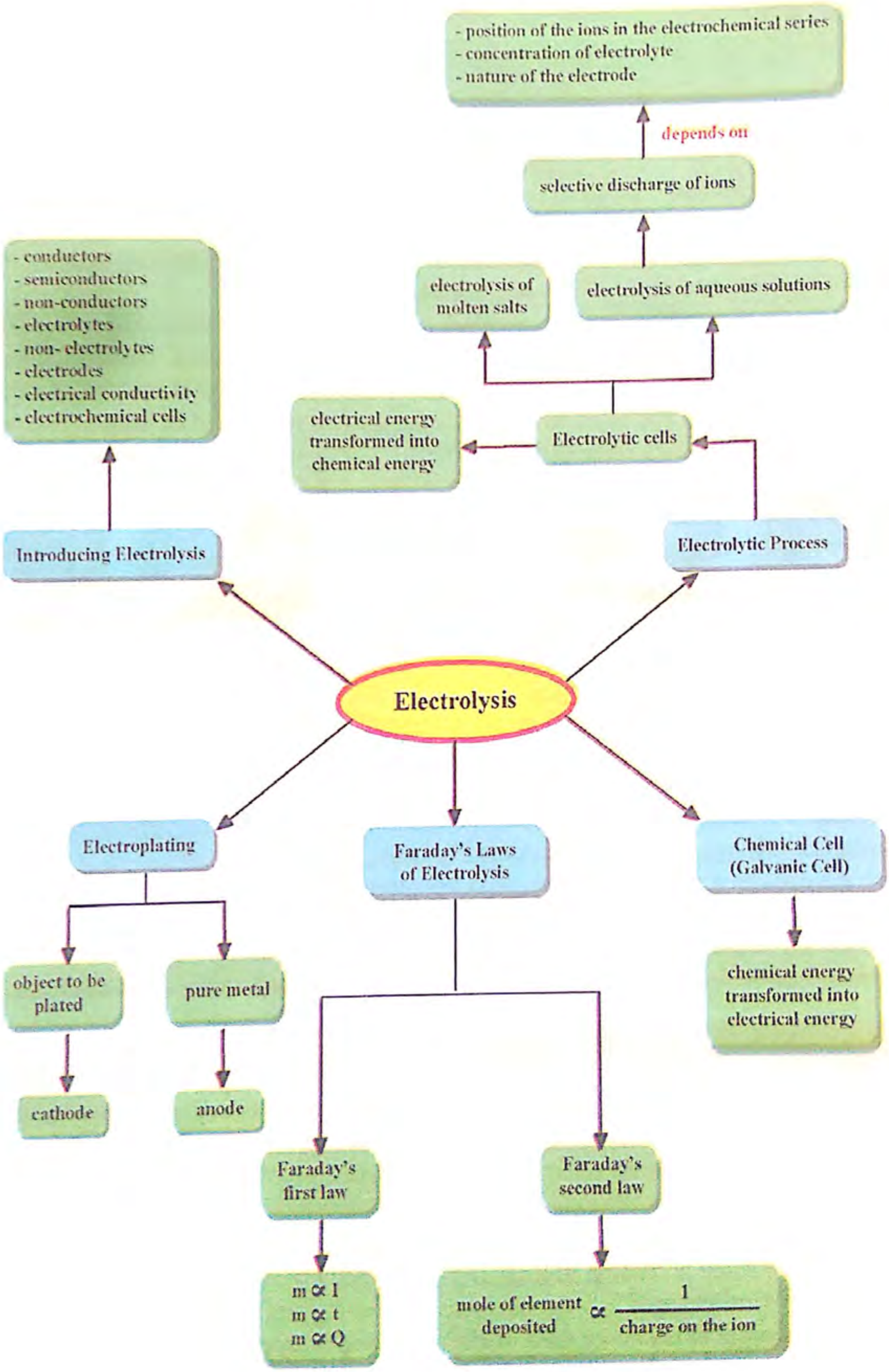
Q 2 to Q 4 (Critical thinking)

2. In the electrolysis of molten potassium bromide, the brown gas is produced at one of the electrodes. Name that electrode.
3. The following aqueous solutions are electrolysed using graphite electrodes: sodium sulphate, magnesium chloride and copper(II) chloride. Answer the following questions for each solution:
   (a) Name the ions present in the solution.
   (b) Predict the products at the anode and cathode.
   (c) Write the reactions at the anode and cathode.
4. Silver nitrate solution is electrolysed using silver electrodes. What products will be observed at the electrodes?

Q 5 to Q 11 (Problem solving)

5. In the electrolysis of aqueous copper(II) sulphate using inert electrodes, the negative electrode was found to increase in mass by 12 g. What volume of gas measured at r.t.p., would expect to be evolved at the positive electrode? (Cu = 63.5)
6. Brine is electrolysed using graphite electrodes and the volumes of the gases produced at the electrodes are measured.
   (a) Give the names of the gases evolved, and the volume ratio of these gases.
   (b) What will be the product of the reaction of these two gases?
   (c) What will be the actual volume at STP of this product, if 96500 C were used in the electrolysis, assuming that complete combination of the reacting gases occurred?
7. On passing a steady current of 0.75 A for 25 minutes through metal(II) sulphate solution, 0.365 g of metal is deposited. Calculate the relative atomic mass of metal. (1 F = 96500 C)
8. In the electrolysis of aqueous silver nitrate solution using inert electrodes, the negative electrode was found to increase in mass by 5.4 g. What volume of gas measured at STP, would expect to be evolved at the positive electrode? (Ag = 108)
9. Calculate the mass of aluminium deposited by the electrolysis of molten aluminium oxide using 193000 C of electricity. (Al = 27)
10. When the same quantity of electricity was passed through the solutions containing Zn^{2+} ions and unknown charge of gold ions, 13.0 g of zinc and 78.8 g of gold were deposited. What was the charge on the gold ion? (Zn = 65, Au = 197)
11. An electric current is passed in turn through the solutions of copper(II) sulphate, aluminium sulphate and dilute sulphuric acid in series. If 12.6 g of copper were deposited at the cathode of the first cell, calculate the mass of aluminium deposited in the second cell and the volume of hydrogen at STP in the third cell. (Cu = 63.5, Al = 27, H = 1)

CHAPTER REVIEW
(Concept Map)



CHAPTER 5

THE BEHAVIOUR OF METALS AND METALLURGY

Metals are a very important group of elements due to their properties and numerous applications. The main value results from their natural properties of rigidity, ductility, conductivity, tensile strength and lustre. Metals are used in construction, electronics, medicines, machinery, industries, agriculture, transportation and so on. Many things in our daily lives are made of metals. Popular examples are car, train, ship, TV, computer, mobile phone, refrigerator, electric stove, pot, jewellery, etc. Around 95 of 118 elements in the Periodic Table are classified as metals. Examples of metals are sodium, aluminium, potassium, copper, iron, zinc, lead, silver, gold, platinum, etc.

Therefore, in chemistry, it is very important to study the characteristics of metals, extraction of metals and reactions of their compounds. Moreover, Myanmar is rich in mineral resources, such as copper, gold, nickel, lead, zinc, silver, tin, tungsten and gemstones. Knowledge of chemistry principles on metals and their reactivity will help you to understand well the use and refinement of metals from our mineral resources.

Learning Outcomes

After completing this chapter, students will be able to:

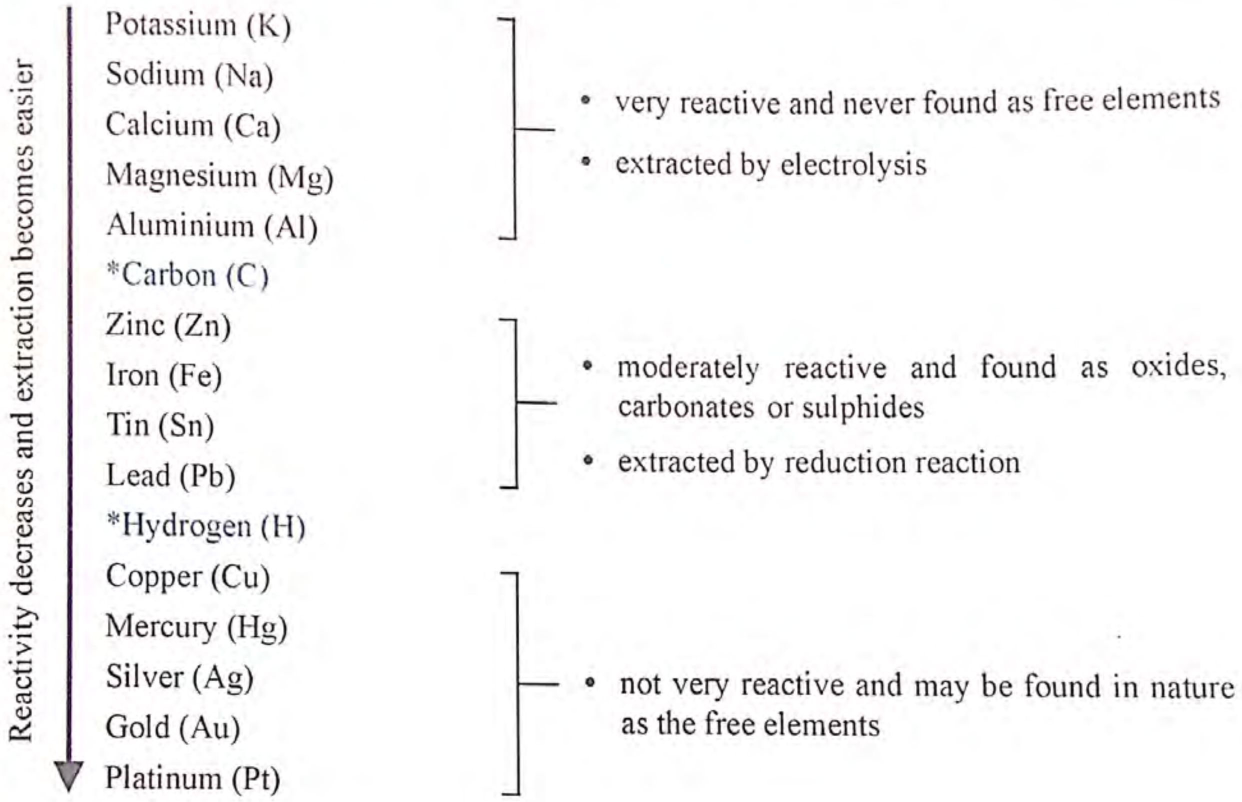
- describe the importance of metals in daily life;
- use the reactivity series of metals to determine whether a single displacement reaction will occur;
- recognise the characteristics and behaviours of metals;
- explain the extraction process of metals and their properties;
- describe how to improve the properties of some metals;
- apply the ways of protection of metal corrosion and metal recycling process.

5.1 METALS AND REACTIVITY SERIES

All metals have a tendency to lose electrons and form metal ions. In other words, all metals are good reducing agents and easily oxidised by themselves. Metals react differently with different substances. The more reactive a metal, the more vigorous its reactions are.

(a) The Reactivity Series

Metals can be listed according to their chemical reactivity. The **reactivity series** of metals is a series in which metals are arranged in order of reactivity from highest to lowest. Figure 5.1 displays some metals in decreasing order of reactivity, ease of extraction and the methods used to extract them. Carbon and hydrogen are included for comparison. Metals above carbon can only be extracted from their ores by electrolysis. Metals below carbon can be extracted from their ores by reduction with carbon (coke or charcoal). Generally, the metals placed above hydrogen in the series can displace it from acids. Metals below hydrogen can neither be reacted with water nor acid, and cannot easily be tarnished or corroded.



* Carbon and hydrogen are reference elements.

Figure 5.1 The Reactivity Series of Metals

(b) Reactions of Metals with Oxygen, Water and Dilute Acids

Metals react to different extents with oxygen, water and acids. Some metals react vigorously and fast, others slowly and some not at all.

(i) Reaction with oxygen

Metals can usually react with oxygen in the air to form oxides over various timescales; iron rusts over a long period, while potassium and sodium burn very quickly. Therefore, potassium and sodium must be stored in kerosene to avoid exposing it to moisture and oxygen in the air.

Some metals (such as iron, copper, zinc, and nickel) are slower to oxidise because they form a passive layer of oxide that protects the interior. Others, like platinum and gold do not react with the oxygen in the air at all. The reactivity of metals with oxygen and their respective flame colour are shown in Table 5.1.

Table 5.1 Reactivity of Metals with Oxygen

Metal	Reactivity	Chemical equation (in symbols)
potassium	- burns vigorously with a bright lilac flame	$4K(s) + O_2(g) \longrightarrow 2K_2O(s)$
sodium	- burns vigorously with a bright yellow flame	$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$
calcium	- burns quickly with a bright orange red flame	$2Ca(s) + O_2(g) \xrightarrow{\Delta} 2CaO(s)$
magnesium	- burns quickly with bright white flame	$2Mg(s) + O_2(g) \xrightarrow{\Delta} 2MgO(s)$
aluminium	- burns quickly with a bright yellow flame	$4Al(s) + 3O_2(g) \xrightarrow{\Delta} 2Al_2O_3(s)$
zinc	- burns quickly with a light blue flame	$2Zn(s) + O_2(g) \xrightarrow{\Delta} 2ZnO(s)$
iron	- burns quickly with yellow sparks	$3Fe(s) + 2O_2(g) \xrightarrow{\Delta} Fe_3O_4(s)$
tin lead copper mercury	- react slowly even at high temperature	$Sn(s) + O_2(g) \xrightarrow{\Delta} SnO_2(s)$
silver gold platinum	- no reaction	

(ii) Reaction with water

The reaction of metals with the water is shown in Table 5.2. Reactive metals such as potassium, sodium and calcium react with cold water to produce the metal hydroxide and hydrogen gas. The moderately reactive metals such as magnesium, zinc and iron react slowly with water. They will, however, react more rapidly with steam to form metal oxide and hydrogen.

Table 5.2 Reactivity of Metals with Water

Metal	Reactivity	Chemical equation (in symbols)
potassium sodium	- react violently with cold water, float, and catch fire	$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$
calcium	- reacts less vigorously with cold water	$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$
magnesium	- reacts very slowly with cold water, but vigorously with steam	$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$
aluminium	- apparently does not react with steam	

Continued from **Table 5.2** Reactivity of Metals with Water

Metal	Reactivity	Chemical equation (in symbols)
zinc iron	- do not react with cold water, react quite slowly with steam	$Zn\ (s) + H_2O\ (g) \longrightarrow ZnO\ (s) + H_2\ (g)$
tin	- does not react with cold water, reacts with steam while heating	$Sn\ (s) + 2H_2O\ (g) \xrightarrow{\Delta} SnO_2\ (s) + 2H_2\ (g)$
lead copper mercury silver gold platinum	- do not react with both water and steam	

(iii) Reaction with acids

The reactions of metals with dilute acids (HCl and H_2SO_4) produce the corresponding metallic salts and hydrogen gas. The reaction of metals with dilute hydrochloric acid is summarised as shown in Table 5.3.

Table 5.3 Reactivity of Metals with Dilute Hydrochloric Acid

Metal	Reactivity	Chemical equation (in symbols)
potassium sodium	- explode	$2K\ (s) + 2HCl\ (aq) \longrightarrow 2KCl\ (aq) + H_2\ (g)$
calcium	- reacts very fast	$Ca\ (s) + 2HCl\ (aq) \longrightarrow CaCl_2\ (aq) + H_2\ (g)$
magnesium	- reacts fast	$Mg\ (s) + 2HCl\ (aq) \longrightarrow MgCl_2\ (aq) + H_2\ (g)$
aluminium	- reacts moderately	$2Al\ (s) + 6\ HCl\ (aq) \longrightarrow 2AlCl_3\ (aq) + 3H_2\ (g)$
zinc iron tin	- react slowly	$Zn\ (s) + 2HCl\ (aq) \longrightarrow ZnCl_2\ (aq) + H_2\ (g)$
lead	- reacts very slowly	$Pb\ (s) + 2HCl\ (aq) \longrightarrow PbCl_2\ (s) + H_2\ (g)$
copper mercury silver gold platinum	- no reaction	

(c) Displacement of Metals

Displacement reaction is a chemical reaction in which a more reactive metal displaces a less reactive metal from its compound. The reactivity series is useful in predicting how metals react.

(i) Displacement of metals from solutions

When a piece of magnesium is placed in a copper(II) sulphate solution and the mixture is stirred, a brown solid forms on the surface of magnesium and the blue solution becomes colourless (Figure 5.2). The brown solid is copper metal. The solution turns colourless because the copper has been removed from the solution. The more reactive magnesium has displaced the less reactive copper from the copper(II) sulphate solution.

Figure 5.2 Reaction of Magnesium with Copper(II) Sulphate Solution

$$\text{magnesium} + \text{copper(II) sulphate} \longrightarrow \text{copper} + \text{magnesium sulphate}$$

$$Mg\ (s) + CuSO_4\ (aq) \longrightarrow Cu\ (s) + MgSO_4\ (aq)$$

(ii) Displacement of metals from metal oxides

In the displacement reaction between a metal and metal oxide, the more reactive metal will take the oxygen atom from the less reactive metal oxide. For example, when a mixture of magnesium powder and copper(II) oxide powder is heated, there is a very vigorous reaction with a lot of heat and light given out. The copper from copper(II) oxide is displaced by magnesium giving magnesium oxide.

$$\text{magnesium} + \text{copper(II) oxide} \xrightarrow{\Delta} \text{magnesium oxide} + \text{copper} + \text{heat}$$

$$Mg\ (s) + CuO\ (s) \xrightarrow{\Delta} MgO\ (s) + Cu\ (s) + \text{heat}$$

REVIEW QUESTIONS

(1) Use the reactivity series to predict which reactions will occur and which will not. If a reaction takes place, write a balanced chemical equation for the reaction.
(i) Zinc is heated with steam. (ii) Gold is heated with steam.
(iii) Silver is added to dilute hydrochloric acid.

(2) The metals: Ag, Na, Ca, Cu, Mg, Pb, Fe, Zn and Al are given. Answer the following questions based on the reactivity series.
Which metal(s) react(s) with (a) oxygen violently (b) cold water and (c) steam? Write down the chemical equation for each of the reactions.

(3) Give an example of a metal that can displace copper from copper(II) oxide. Explain why this reaction is possible. Write down the chemical equation for this reaction.

Key Term

- The **Reactivity Series** of metals is the arrangement of metals in the decreasing order of reactivity; the more reactive metals are easy to lose electrons and form positive ions.

5.2 PROCESSES OF THE EXTRACTION OF METALS

Metals occur in either a free state or chemically combined with other elements to form compounds. Gold, silver and platinum are examples of metals that occur in the free state. The oxide of iron, the sulphide of lead, and the phosphate of calcium are examples of compounds of metals that are found in the combined state. All these metals and compounds are minerals, inorganic substances found in the Earth's crust. **Ores** are those minerals from which metals are extracted economically. They consist of the desired metal compound and the impurities, and earthly substances called **gangue**. These ores contain a good percentage of metal.

The process of extracting a metal from its ore is called **metallurgy**. The three major steps of extracting metal from its ore are (a) concentration of the ore to remove impurities (b) isolation of the metal from its concentrated ore (reduction of the ore to get the metal) and (c) purification of the metal.

(a) Concentration of Ores

Removal of unwanted materials (e.g., clay, sand, stone, limestone, etc.) from the ore is known as concentration or dressing. Some processes of removal of mineral impurities from ore are described below.

(i) Gravity separation: The specific gravity of metal ores and that of clay, sand, stone, limestone and some other non-metals are different. The crushed ores are stirred with adding water or washed with blowing water. Thus, the lighter mineral impurities are washed away and the heavier ores are left behind.

(ii) Froth flotation process: This process as shown in Figure 5.3 is generally used to concentrate the sulphide ores. Sulphide ores get wet easily with oil. In this process, a suspension of the powdered ore is mixed with water and a small amount of appropriate oil (pine oil) in a big bowl. The mineral particles become wet by oils while the gangue particles by water. Thus, sulphide ore upon wetted with oil floats on water as foam. A rotating paddle agitates the mixture and draws air in it. As a result, froth bubbles which carry the mineral particles are formed. The froth is light and is skimmed off. It is then dried for recovery of the ore particles. The mineral impurities (gangue) settle at the bottom of the bowl as residues.

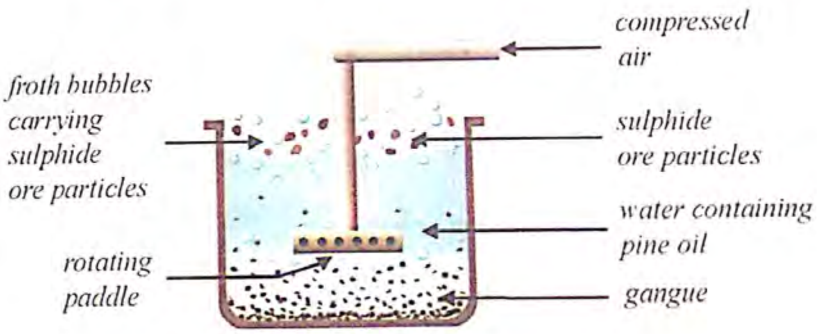


Figure 5.3 Froth Flotation Process

(iii) Magnetic separation: This is based on differences in the magnetic properties of the ore components. This process is used, if either of the ores or the gangue has the magnetic property. Crushed ores are passed through a plastic conveyor belt. The outer wheel of the conveyor belt has a magnetic property.

(iv) Chemical process: In this process the desired minerals of the ores are dissolved in a particular solution. The mineral impurities are separated by filtration. Then the concentrated ores are collected from the solution with the appropriate process. The mineral impurities are removed by filtration.

(b) Isolation of Metals from Concentrated Ores

The concentrated ore must be converted into a form which is suitable for reduction. Usually, the ore is converted to oxide before reduction. Oxides are easier to reduce. Thus, isolation of metals from concentrated ore involves two major steps: (i) conversion of ore to oxide, and (ii) reduction of the oxide to metal.

(i) Conversion of ore to oxide

Calcination: Calcination involves heating when the volatile matter escapes leaving behind the metal oxide. When the concentrated ores are heated at a temperature below the melting point in the absence of air, organic substances and moisture will be removed from the ore. In this process, hydrated metal oxides and metal carbonates are converted to metal oxides.

Roasting: In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. Generally roasting is applied for sulphide ores. If sulphide ores are heated at a temperature below the melting point in the presence of air, organic substances and moisture will be removed from the ore. Some mineral impurities, such as sulphur, arsenic, phosphorus, etc., are removed as volatile oxides during this process.

(ii) Reduction of oxide to metal

There are three main reduction methods of metal oxide. They are reduction of the ore with carbon, reduction of the molten ore by electrolysis, and reduction of the ore with a more reactive metal. Reduction of the metal oxide usually involves heating it with a reducing agent (C or CO or even another metal). For example, carbon combines with the oxygen of the metal oxide to produce metal and carbon dioxide. In this process, the metal ion is reduced. So, metal extraction is a reduction process.

(c) Purification of Metals

Some mineral impurities remain with metal up to the last stage. **Flux** is added to the ores to remove mineral impurities. At high temperature, metallic oxides of ores are reduced to free metals. Flux joins with impurities and forms metal slag. Metal **slag** does not dissolve in molten metal. It can easily be removed from the molten metal because of its relatively light mass. This process is called smelting.

Purification by electrolysis is done to make the metal becomes more pure than that obtained in the smelting process. In electrolysis, a chemical reaction occurs by using electrical energy.

REVIEW QUESTIONS

(1) What process would you use for the removal of impurities which have magnetic property?

(2) Which chemical form is suitable for the conversion of concentrated ore in the reduction process? Give a reason for your answer.

(3) Why is roasting a major source of air pollution and acid rain?

Key Terms

- **Ores** are the minerals from which the metals can be extracted conveniently and economically.
- **Gangue** is the earthy impurities (sand, silt, gravel, etc.) associated with the ore.
- **Metallurgy** is the process used for the extraction of pure metals from their ores.

- **Froth flotation** is a process that selectively separates materials based upon whether they are water repelling (hydrophobic) or have an affinity for water (hydrophilic).
- **Flux** is a substance added to the ores to promote fluidity and to remove mineral impurities.
- **Slag** is a fusible product formed when flux combined with gangue during the extraction of metals.

5.3 SOME IMPORTANT METALS

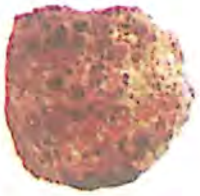
In Myanmar, copper and lead are rich mineral resources, and iron is a fairly rich resource. Iron ore can be found in more than 300 sites in Myanmar. Iron ore deposits are commonly found in Northern Shan State and in Kachin State. The locations of Pb–Zn–Ag deposits in Myanmar are mostly found in Shan State. There are other deposits found in Mandalay Region and Kayin State. Copper deposits start from the lower Chindwin area through Sabe Taung, Kyesin Taung and Letpadaung Taung, Monywa and continued to the Kawlin area of the Northern part of Myanmar. Copper is also found in Mandalay Region and Shan State.

The reactivity of a metal determines how it is extracted. If a metal (iron or lead) is less reactive than carbon, it can be extracted from its oxide by heating with carbon as a reducing agent. Otherwise, carbon cannot reduce the oxide of the elements above it in the reactivity series.

In this section, the extraction of aluminium (very reactive metal), extraction of iron and lead (moderately reactive metals) and extraction of copper (not very reactive metal) as well as the properties and uses of these metals and their compounds will be studied.

(a) Aluminium $^{27}_{13}\mathrm{Al}$

(i) Extraction of Aluminium



Aluminium ore

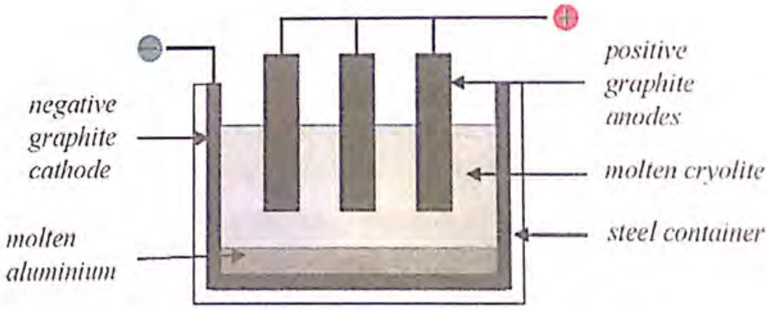


Figure 5.4 Electrolysis Tank for Extraction of Aluminium

Aluminium ore, bauxite ($Al_2O_3.H_2O$), is treated with sodium hydroxide to obtain pure alumina (Al_2O_3). Molten cryolite (Na_3AlF_6) is added into the container to dissolve the alumina because cryolite has a lower melting point than alumina and it can reduce the temperature of fusion. The mixture is electrolysed by using graphite electrodes as shown in Figure 5.4. Aluminium is produced at the cathode and oxygen is liberated at the anode.

reaction at the cathode: $2Al^{3+}\,(l) + 6e \longrightarrow 2Al\,(s)$

reaction at the anode: $3O^{2-}\,(l) \longrightarrow \frac{3}{2}O_2\,(g) + 6e$

(ii) Properties of Aluminium

Physical properties

Aluminium is a silvery-white metal. It is very **ductile** and **malleable.** It is a good conductor of heat and electricity. In moist air, a film of oxide is formed on the metal surface which prevents any further attack on the underlying metal. The melting point of aluminium is 660 °C.

Aluminium foil and a cup

Chemical properties

Direct combination reaction

Aluminium, on heating, combines directly with the halogens, sulphur, nitrogen and carbon to form halides, sulphide, nitride and carbide, respectively.

$$\text{aluminium} + \text{chlorine} \xrightarrow{\Delta} \text{aluminium chloride}$$
$$2Al\,(s) + 3Cl_2\,(g) \xrightarrow{\Delta} 2AlCl_3\,(s)$$

$$\text{aluminium} + \text{sulphur} \xrightarrow{\Delta} \text{aluminium sulphide}$$
$$2\,Al\,(s) + 3S\,(s) \xrightarrow{\Delta} Al_2S_3\,(s)$$

$$\text{aluminium} + \text{nitrogen} \xrightarrow{\Delta} \text{aluminium nitride}$$
$$2Al\,(s) + N_2\,(g) \xrightarrow{\Delta} 2AlN\,(s)$$

$$\text{aluminium} + \text{carbon} \xrightarrow{\Delta} \text{aluminium carbide}$$
$$4Al\,(s) + 3C\,(s) \xrightarrow{\Delta} Al_4C_3\,(s)$$

Reaction with acids

Aluminium reacts slowly with dilute sulphuric acid to give aluminium sulphate and hydrogen.

$$\text{aluminium} + \text{sulphuric acid (dil.)} \longrightarrow \text{aluminium sulphate} + \text{hydrogen}$$
$$2Al\,(s) + 3H_2SO_4\,(aq) \longrightarrow Al_2(SO_4)_3\,(aq) + 3H_2\,(g)$$

When aluminium is exposed to hot concentrated sulphuric acid, the result is aluminium sulphate, water and sulphur dioxide.

$$\text{aluminium} + \text{sulphuric acid (conc.)} \xrightarrow{\Delta} \text{aluminium sulphate} + \text{water} + \text{sulphur dioxide}$$
$$2Al\,(s) + 6H_2SO_4\,(l) \xrightarrow{\Delta} Al_2(SO_4)_3\,(s) + 6H_2O\,(l) + 3SO_2\,(g)$$

Both dilute and concentrated nitric acids react very slowly with aluminium.

Reaction with alkali

Aluminium reacts with alkalis.

aluminium + sodium hydroxide + water ⟶ sodium aluminate + hydrogen

$$2Al\,(s) + 2NaOH\,(aq) + 6H_2O\,(l) \longrightarrow 2NaAl(OH)_4\,(aq) + 3H_2\,(g)$$

Since aluminium can react with alkalis as well as with acids, it is an amphoteric metal.

Reducing property

The reduction of the metallic oxide with aluminium is known as the **Thermite reaction**. The reaction is initiated by the heat from burning magnesium ribbon used as a fuse which is placed in the mixture of iron(III) oxide and aluminium powder. The heat generated is sufficient to melt the iron and the aluminum oxide.

$$\text{aluminium} + \text{iron(III) oxide} \xrightarrow{\Delta} \text{aluminium oxide} + \text{iron} + \text{heat}$$

$$2Al\,(s) + Fe_2O_3\,(s) \xrightarrow{\Delta} Al_2O_3\,(s) + 2Fe\,(l) + \text{heat}$$

(iii) Uses of Aluminium

Long lasting uptakes of significant concentrations of aluminium can lead to serious health effect. However, metallic aluminium is very reactive with atmospheric oxygen forming a thin protective layer of aluminium oxide which is fairly chemically inert. Hence, aluminium is used in a huge variety of products including cans, foils, kitchen utensils and window frames. Aluminium-based light alloys are important in all branches of engineering construction and aeroplane parts.

(b) Iron $^{56}_{26}Fe$

(i) Extraction of Iron

Haematite (Fe_2O_3) and magnetite (Fe_3O_4) ores are suitable for the extraction of iron. The reaction s carried out in the blast furnace because a lot of heat is required.

Iron ore

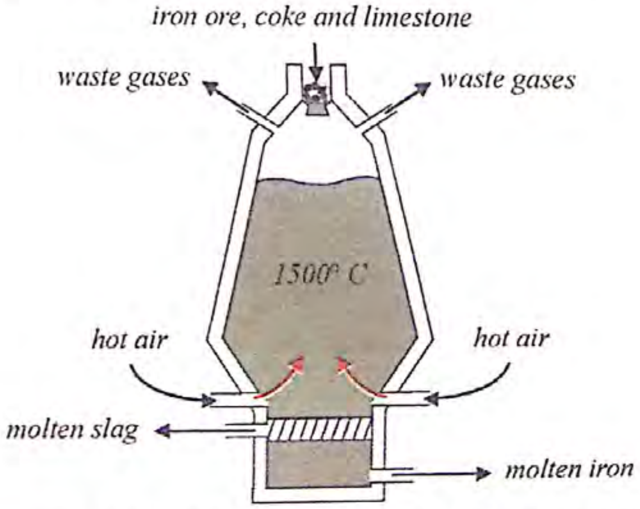


Figure 5.5 The Extraction of Iron in Blast Furnace

As shown in Figure 5.5, iron ore, limestone ($CaCO_3$) and coke (carbon) are introduced into th furnace from the top. A blast of hot air is forced up the furnace from the bottom. The coke burns to produ carbon dioxide.

coke + oxygen $\xrightarrow{\Delta}$ carbon dioxide

$$C\ (s) + O_2\ (g) \xrightarrow{\Delta} CO_2\ (g)$$

The CO_2 produced reacts with more carbon to form carbon monoxide.

carbon dioxide + carbon $\xrightarrow{\Delta}$ carbon monoxide

$$CO_2\ (g) + C\ (s) \xrightarrow{\Delta} 2CO\ (g)$$

The CO formed reduces the oxides of iron (Fe_2O_3 or Fe_3O_4) to iron.

iron(III) oxide + carbon monoxide $\xrightarrow{\Delta}$ iron + carbon dioxide

$$Fe_2O_3\ (s) + 3CO\ (g) \xrightarrow{\Delta} 2Fe\ (l) + 3CO_2\ (g)$$

iron(II,III) oxide + carbon monoxide $\xrightarrow{\Delta}$ iron + carbon dioxide

$$Fe_3O_4\ (s) + 4CO\ (g) \xrightarrow{\Delta} 3Fe\ (l) + 4CO_2\ (g)$$

Molten iron flows to the bottom of the furnace at 1500 ~ 1800 °C. The limestone ($CaCO_3$) brea down due to the heat of the furnace.

calcium carbonate $\xrightarrow{\Delta}$ calcium oxide + carbon dioxide

$$CaCO_3\ (s) \xrightarrow{\Delta} CaO\ (s) + CO_2\ (g)$$

Calcium oxide reacts with the sand (silicon dioxide or silica) to form calcium silicate (slag) whi floats on the molten iron.

calcium oxide + silicon dioxide $\longrightarrow$ calcium silicate

$$CaO\ (s) + SiO_2\ (s) \longrightarrow CaSiO_3\ (s)$$

The iron obtained by this process is known as pig or cast iron and contains about 4 % carbon well as some other impurities such as small amounts of manganese, phosphorus, silicon and sulphur. T removal of impurities from pig iron gives wrought iron, the purest form of industrial iron.

(ii) Properties of Iron

Physical properties

Iron is a silvery-grey in colour. Pure iron is soft and malleable. It rusts easily in the damp air. Unli most other metals, it is magnetic. It is a good conductor of heat and electricity. The melting point of pu iron is 1538 °C.

Chemical properties

Direct combination reaction

Reaction with oxygen

Iron oxides are products of a reaction between iron and oxygen. The best-known of them are iron(II) oxide (ferrous oxide, FeO), iron(III) oxide (ferric oxide, Fe_2O_3) and iron(II, III) oxide (ferrosoferric oxide, Fe_3O_4). Upon reacting with oxygen, iron will be oxidised to either the +3 oxidation state in Fe_2O_3, or to a combination of the +2 and +3 oxidation states in Fe_3O_4 (also known as magnetic iron oxide).

Reaction with halogen

When chlorine passes over heated iron, iron is oxidised to iron(III) chloride.

$$\text{iron} + \text{chlorine} \xrightarrow{\Delta} \text{iron(III) chloride}$$

$$2Fe\,(s) + 3Cl_2\,(g) \xrightarrow{\Delta} 2FeCl_3\,(s)$$

Reaction with sulphur

When a mixture of iron filings and sulphur powder is heated, black iron(II) sulphide is formed.

$$\text{iron} + \text{sulphur} \xrightarrow{\Delta} \text{iron(II) sulphide}$$

$$Fe\,(s) + S\,(s) \xrightarrow{\Delta} FeS\,(s)$$

Reaction with acids

Iron reacts with dilute sulphuric acid to form iron(II) sulphate and hydrogen.

$$\text{iron} + \text{sulphuric acid (dil.)} \longrightarrow \text{iron(II) sulphate} + \text{hydrogen}$$

$$Fe\,(s) + H_2SO_4\,(aq) \longrightarrow FeSO_4\,(aq) + H_2\,(g)$$

With hot concentrated sulphuric acid, iron gives iron(III) sulphate, water and sulphur dioxide.

$$\text{iron} + \text{sulphuric acid (conc.)} \xrightarrow{\Delta} \text{iron(III) sulphate} + \text{water} + \text{sulphur dioxide}$$

$$2Fe\,(s) + 6H_2SO_4\,(l) \xrightarrow{\Delta} Fe_2(SO_4)_3\,(s) + 6H_2O\,(l) + 3SO_2\,(g)$$

However, iron reacts with either dilute or concentrated hydrochloric acid to form iron(II) chloride and hydrogen gas. This reaction cannot produce iron(III) chloride due to the production of hydrogen gas which prevents the further oxidation of Fe^{2+} to Fe^{3+}.

$$\text{iron} + \text{hydrochloric acid (dil.)} \longrightarrow \text{iron(II) chloride} + \text{hydrogen}$$

$$Fe\,(s) + 2HCl\,(aq) \longrightarrow FeCl_2\,(aq) + H_2\,(g)$$

(iii) Uses of Iron

Iron is used in civil engineering like reinforced concrete, girders, etc. It is used to make magnets and alloys. It is used as a catalyst in the Haber process for manufacturing ammonia.

(c) Lead $^{207}_{82}\mathrm{Pb}$

(i) Extraction of Lead

Galena ore

Only about half of the lead materials used today is produced from mining, the rest is obtained from recycling, mostly from car batteries.

The lead ore, galena (PbS), is ground into small particles that are less than 0.1 mm in diameter. The lead powder is put through a flotation process: mixing the lead ore with water, the addition of oil, the introduction of air bubbles and agitation which forms the oil froth containing lead ore, on the surface. The froth is skimmed off and then filtered to remove the water. The powder is then heated to more than 1370 °C producing lead(II) oxide and volatile sulphur dioxide.

$$\text{lead(II) sulphide} + \text{oxygen} \xrightarrow{\Delta} \text{lead(II) oxide} + \text{sulphur dioxide}$$
$$2PbS\,(s) + 3O_2\,(g) \xrightarrow{\Delta} 2PbO\,(s) + 2SO_2\,(g)$$

The resulting powder is further heated in a blast furnace, with carbon producing molten lead which is drawn off into lead moulds.

$$\text{lead(II) oxide} + \text{carbon} \xrightarrow{\Delta} \text{lead} + \text{carbon monoxide}$$
$$PbO\,(s) + C\,(s) \xrightarrow{\Delta} Pb\,(s) + CO\,(g)$$

At this stage, the lead is about 95 % pure and is further refined to get greater than 99 % purity by melting and skimming impurities.

(ii) Properties of Lead

Physical properties

Pure lead

Lead is a bluish-grey metal. It is the softest of the metals in common use, and can be pressed into any form. It is a poor conductor of electricity and heat. On exposure to air, lead is tarnished owing to the formation of a layer of hydroxide and carbonate which prevents the further attack. It has a low melting point (328 °C).

Chemical properties

Lead does not react with water or steam. It reacts slowly with hydrochloric acid, either dilute or concentrated.

$$\text{lead} + \text{hydrochloric acid (dil.)} \longrightarrow \text{lead(II) chloride} + \text{hydrogen}$$
$$Pb\,(s) + 2HCl\,(aq) \longrightarrow PbCl_2\,(s) + H_2\,(g)$$

Dilute sulphuric acid has no appreciable action upon the lead, but hot concentrated sulphuric acid reacts with lead to form lead(II) sulphate and liberate sulphur dioxide.

$$\text{lead} + \text{sulphuric acid (conc.)} \xrightarrow{\Delta} \text{lead(II) sulphate} + \text{water} + \text{sulphur dioxide}$$
$$Pb\,(s) + 2H_2SO_4\,(l) \xrightarrow{\Delta} PbSO_4\,(s) + 2H_2O\,(l) + SO_2\,(g)$$

The metal also reacts with dilute nitric acid and with hot concentrated nitric acid.

$$\text{lead} + \text{nitric acid (dil.)} \longrightarrow \text{lead(II) nitrate} + \text{water} + \text{nitrogen oxide}$$

$$3Pb\,(s) + 8HNO_3\,(aq) \longrightarrow 3Pb(NO_3)_2\,(aq) + 4H_2O\,(l) + 2NO\,(g)$$

$$\text{lead} + \text{nitric acid (conc.)} \xrightarrow{\Delta} \text{lead(II) nitrate} + \text{water} + \text{nitrogen dioxide}$$

$$Pb\,(s) + 4HNO_3\,(l) \xrightarrow{\Delta} Pb(NO_3)_2\,(aq) + 2H_2O\,(l) + 2NO_2\,(g)$$

(iii) Uses of Lead

Lead is used as a shield against radioactive materials and X-rays. It is also used in car batteries and accumulators. Lead is also an important constituent in many important alloys, for example, soft solders (lead and tin) in connecting electronic circuits, and type metal (lead, antimony and tin) in printing.

(d) Copper $^{64}_{29}Cu$

(i) Extraction of Copper

The main source of copper ore is copper pyrites (also known as chalcopyrite), $CuFeS_2$. The ore typically contains a low percentage of copper and has to be concentrated by using a suitable method, such as froth flotation, before refining.


Copper pyrites ore

The concentrated ore is heated strongly with silicon dioxide (silica) and air or oxygen in a furnace. The copper in the copper pyrites is reduced to copper(I) sulphide. The iron in the copper pyrites is converted into an iron(II) silicate slag which is removed. Most of the sulphur in the copper pyrites turns into sulphur dioxide gas.

$$\text{copper pyrites} + \text{silicon dioxide} + \text{oxygen} \xrightarrow{\Delta} \text{copper(I) sulphide} + \text{iron(II) silicate} + \text{sulphur dioxide}$$

$$2CuFeS_2\,(s) + 2SiO_2\,(s) + 4O_2\,(g) \xrightarrow{\Delta} Cu_2S\,(s) + 2FeSiO_3\,(s) + 3SO_2\,(g)$$

The copper(I) sulphide produced is converted to copper with a final blast of air.

$$\text{copper(I) sulphide} + \text{oxygen} \xrightarrow{\Delta} \text{copper} + \text{sulphur dioxide}$$

$$Cu_2S\,(s) + O_2\,(g) \xrightarrow{\Delta} 2Cu\,(s) + SO_2\,(g)$$

The end product, **blister copper**, is a porous brittle form of copper which is about 98 ~ 99.5 % pure. Copper is then refined by electrolysis to get at least 99.92 % purity.

(ii) Properties of Copper

Physical properties

Copper is reddish coloured metal. A freshly exposed surface of pure copper has a pinkish-orange colour. It is malleable and ductile. It is a good conductor of electricity and heat. Its melting point is 1084 °C.


A piece of copper metal

Chemical properties

Reaction with acids

Copper can react with oxidising acids such as concentrated sulphuric acid and both dilute and concentrated nitric acids.

$$\text{copper} + \text{sulphuric acid (conc.)} \xrightarrow{\Delta} \text{copper(II) sulphate} + \text{water} + \text{sulphur dioxide}$$

$$Cu\,(s) + 2H_2SO_4\,(l) \xrightarrow{\Delta} CuSO_4\,(aq) + 2H_2O\,(l) + SO_2\,(g)$$

$$\text{copper} + \text{nitric acid (dil.)} \longrightarrow \text{copper(II) nitrate} + \text{water} + \text{nitrogen oxide}$$

$$3Cu\,(s) + 8HNO_3\,(aq) \longrightarrow 3Cu(NO_3)_2\,(aq) + 4H_2O\,(l) + 2NO\,(g)$$

$$\text{copper} + \text{nitric acid (conc.)} \xrightarrow{\Delta} \text{copper(II) nitrate} + \text{water} + \text{nitrogen dioxide}$$

$$Cu\,(s) + 4HNO_3\,(l) \xrightarrow{\Delta} Cu(NO_3)_2\,(aq) + 2H_2O\,(l) + 2NO_2\,(g)$$

Reaction with oxygen

The most common reaction product of heated copper and oxygen is copper(II) oxide.

$$\text{copper} + \text{oxygen} \xrightarrow{\Delta} \text{copper(II) oxide}$$

$$2Cu\,(s) + O_2\,(g) \xrightarrow{\Delta} 2CuO\,(s)$$

(iii) Uses of Copper

Copper is used in electrical equipment. It is used in roofing and guttering, and as rainspouts on a building. It is also used in plumbing and cooking utensils.

Copper plumbing and wire

REVIEW QUESTIONS

(1) Explain why aluminium is not extracted from its oxide by carbon reduction in a blast furnace.

(2) (a) Why can carbon be used for the extraction of lead? Write down the chemical equation for this reaction.
(b) What happens when lead is exposed to air?

(3) (a) Which reducing agent is used to extract iron from its ore?
(b) Why is limestone used for extracting iron?

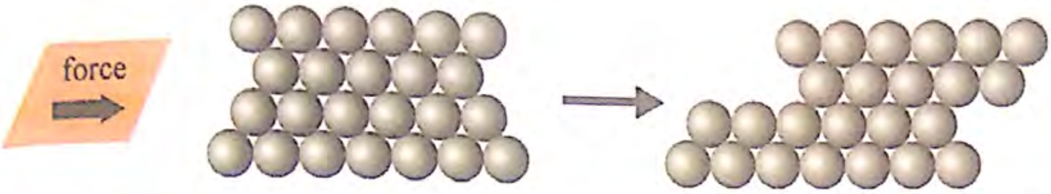
(4) (a) How is copper ore prepared for the extraction of copper?
(b) Write a chemical equation for the formation of slag in the extraction of copper.

Key Terms

- **Ductility** of a material is the ability to stretch under tensile stress.
- **Malleability** is the ability of a material to be shaped under force or pressure is exerted on it.
- **Thermite reaction** is a chemical reaction in which a lot of heat is released as a metal oxide is displaced by another metal which is more reactive than the metal in the metal oxide.

5.4 IMPROVING PROPERTIES OF METALS

In a pure metal, atoms are packed regularly in layers. These layers of atoms can slide over one another when force is applied.



It is easy to slide over one another

Pure metals have many useful properties but they are not widely used. This is because many pure metals are soft and may react with air and water resulting in corrosion. When a pure metal is alloyed, atoms of the added element have different sizes from those of the pure metal. The atoms of different sizes cannot slide over each other easily and this makes the alloy harder than the pure metals.

It is difficult to slide over one another

Alloying can also be used to improve the appearance and properties of the metal. Molten metals are mixed with other elements: metals or non-metals. This mixture is called an **alloy**. For example, mixing molten tin and copper gives a gold-coloured alloy called bronze. Although both metals are very soft and ductile, the resulting bronze will have much greater strength, hardness and corrosion resistance. It is used for door and window frames, locks, furniture hardware and musical instruments.

Steel is an alloy of iron containing carbon and other metals (see Table 5.4). Traces of sulphur, phosphorus and silicon are added as modifiers of alloys. There are many varieties of steel depending on their compositions. Some of the alloys along with their compositions, properties and uses are listed in Table 5.4. The percentage of metals to make alloy has been varied for particular applications.

Table 5.4 Alloys with Their Properties and Uses

Type of alloy	Parent metal (%)	Other metals (%)	Special properties	Uses
cupronickel	Cu (75)	Ni (25)	hard, shining and lasting	coins
brass	Cu (70)	Zn (30)	does not corrode easily	ship boiler
bronze	Cu (90)	Sn (10)	very hard and strong	ship propellers
solder	Pb (70)	Sn (30)	low melting point	soldering wires

Continued from **Table 5.4** Alloys with Their Properties and Uses

Type of alloy	Parent metal (%)	Other metals (%)	Special properties	Uses
duralumin	Al (93)	Cu (3) Mg (3) Mn (1)	light and strong	body of aeroplane and bullet train
magnalium	Al (70)	Mg (30)	hard but light	aircraft structure
pink gold	Au (75)	Cu (20) Ag (5)	soft, malleable, ductile	gold jewellery
rose gold	Au (75)	Cu (22.25) Ag (2.75)	soft, malleable, ductile	gold jewellery
mild steel	Fe (99.7)	C (0.3)	hard and strong	car bodies, building, ship and machinery
hard steel	Fe (99)	C (1)	hard and brittle	cutting tools, razor blades, chisels
soft steel	Fe (99.8)	C (0.2)	malleable and ductile	cable, nail, chain
stainless steel	Fe (73)	Cr (18) Ni (8) C (1)	hard and rustproof	cutlery, surgical instrument
nickel steel	Fe (98~96)	Ni (2~4) C (trace)	hard, elastic and rustproof	cable, automobile and aeroplane parts
tungsten steel	Fe (83~72)	W (14~20) Cr (3~8) C (trace)	hard, resistance to corrosion	high speed cutting tools, springs
manganese steel	Fe (89~88)	Mn (11~12) C (trace)	extremely hard, high melting point	rail tracks, rock crushers

REVIEW QUESTIONS

(1) What would be the result of alloying aluminium and magnesium?
(2) Why would it be advantageous to alloy iron and nickel?
(3) What would be the advantage in alloying tungsten and carbon?

Key Terms

- An **alloy** is a mixture of metals with other elements (usually metals but sometimes carbon), especially to give greater strength or resistance to corrosion.
- **Steel** is a mixture of the metal iron and the non-metal carbon.

5.5 METAL CORROSION, PROTECTION AND RECYCLING

(a) Corrosion

Corrosion is the deterioration of metals as a result of chemical reaction depending on the type of metal and the environmental conditions. When metal is corroded, it loses structural integrity and attractiveness. Corrosion of iron is called rusting. Most metals, except gold, can be corroded because they oxidise.

Some metals are attacked by substances in their surroundings. For example, silver reacts with sulphur in the air to form silver sulphide (Ag_2S), and turns black. Copper reacts with moist carbon dioxide in the air and gets a green coat called verdigris ($CuCO_3.Cu(OH)_2$). Iron acquires a coating of a brown flaky substance called rust ($Fe_2O_3.xH_2O$). Both air and moisture are necessary for rusting of iron.

Corrosion of silver

Corrosion of copper

Rusting of iron

(b) Corrosion Protection

There are many ways to protect metals from corrosion. Plating, painting, oiling or greasing and making alloy are commonly used to protect the exposure to oxygen and moisture.

Plating is a surface coating in which a metal is deposited on a conductive surface. The chrome plating (chromium plating) process is a method of applying a thin layer of chromium onto a metal object. The chromed layer is decorative, and provides corrosion resistance. Tin plating is commonly used in making food cans.

Galvanising is the process of immersing iron or steel in molten zinc. It produces a corrosion resistant layer on iron or steel. Galvanising is used to protect iron exposed to non-corrosive medium (air).

Sacrificial protection is used to protect iron exposed to corrosive medium. In this process, a zinc bar is attached to iron or steel.

Making alloys can improve the properties of metals in terms of strength, durability, conductivity and corrosion resistance.

(c) Metal Recycling

Recycling metals is an important way to make metals last longer. Metals can be recycled repeatedly without altering their properties. The highly recycled metals are steel, aluminium, copper, silver, gold and so on. Recycling can be beneficial to the environment by reducing mining operations, reducing air and water pollution, and conserving limited fossil fuel reserves.

The main stages of metal recycling process are:
(1) collection: Scrap metals are collected from a dust bin.

(2) sorting: Scrap metals are separated according to their types.
(3) processing: A series of mechanical and chemical operations is performed.
For example, shredding of aluminium to small sheet consists of the following operations:
- melting (mechanical operation),
- purification (chemical operation) (to be free from contaminant: mostly electrolysis),
- solidifying (mechanical operation) (to specific shape).

(4) distribution: Recycled metals are carried over to the consumers.

REVIEW QUESTIONS

(1) Choose the most and least corrosive metals among the following:
aluminium, silver, copper, iron, gold
(2) How would you protect iron from the corrosion?
(3) Why is a series of mechanical and chemical operations performed in the metal recycling process?

Key Term

- **Corrosion** is the deterioration of metals as a result of chemical reaction depending on the type of metal and the environmental conditions.

Chemistry in Society

- Potash alum ($K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$) can be used in water purification, leather tanning and dyeing.
- Lead(II,IV) oxide (Red lead, Pb_3O_4) can be used for surface coating.
- Brass finds uses in jewellery, machine bearings, electrical connections, door and furniture.
- Bronze is widely used in castings and machine parts.
- Stainless steel is hard and rustproof. This is used for cutlery and equipment in chemical factories.
- Bordeaux mixture, a suspension of copper(II) sulphate ($CuSO_4$) and calcium hydroxide ($Ca(OH)_2$) is used to control fungus on grapes, melons and other berries.

EXERCISES

Q 1 to Q 3 (Understanding)

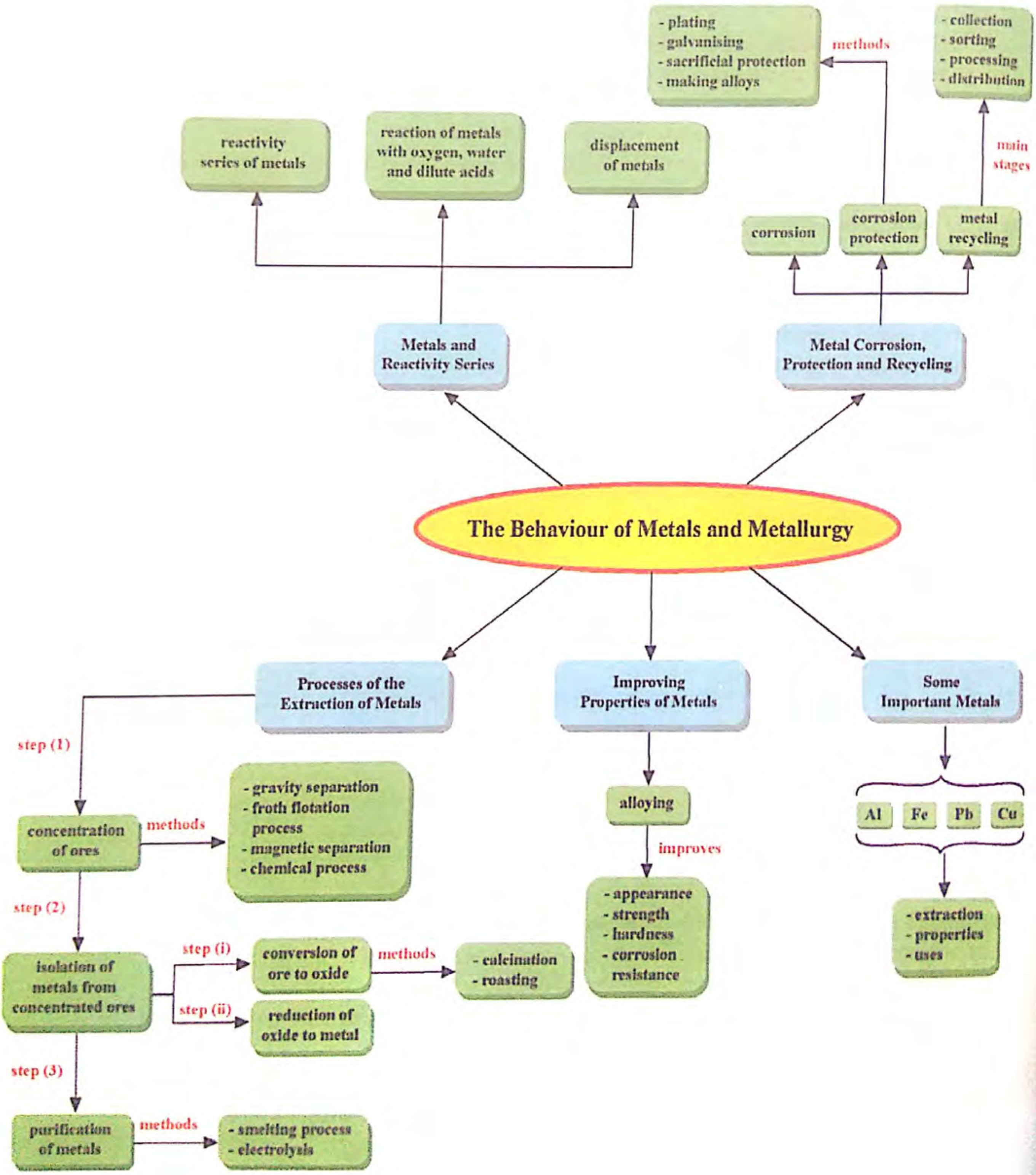
1. Fill in the blanks with a suitable word or phrase.
(a) Rusting is the common term for corrosion of _____.
(b) The elements between _____ and hydrogen in the reactivity series can be extracted by reduction reaction.
(c) In the extraction of copper, most of the sulphur in chalcopyrite is converted to _____ gas.
(d) Metals can be recycled repeatedly without altering their _____.
(e) Among the metals, _____ cannot be corroded even after thousands of years.

2. Use the following list of metals to answer the questions (a) to (h):
   iron, calcium, potassium, gold, aluminium, magnesium, sodium, zinc, platinum
   (a) Which metals can be extracted from the ores: (i) haematite and (ii) bauxite?
   (b) Which metal carbonate found in nature is called limestone (marble)?
   (c) Which of the metals will not react with oxygen to form oxides?
   (d) Which of the metals will react violently with cold water?
   (e) Choose one of the metals in your answer of (d) and write a balanced chemical equation for the reaction which takes place.
   (f) Which of the metals has a protective coating on its surface?
   (g) Which of the metals reacts very slowly with cold water but extremely vigorously with steam?
   (h) Which of the metals is used to galvanise iron?
3. What is the difference between galvanising and sacrificial protection?

Q 4 to Q 14 (Critical thinking)

4. If the reactions take place in the following statements, write the relevant chemical equations.
   (a) Iron is added to dilute hydrochloric acid.
   (b) Iron is added to potassium chloride solution.
   (c) Magnesium is heated with copper(II) oxide.
   (d) Lead is heated with calcium oxide.
5. Differentiate between roasting and calcination.
6. (a) In the extraction of aluminium, state the significant role of bauxite, cryolite and graphite.
   (b) Explain why it is necessary to renew the anode from time to time.
7. The reaction of metal **X** with iron(III) oxide is highly exothermic. The metal **X** is obtained from its oxide by electrolytic reduction. The oxide of metal **X** is an amphoteric oxide. Identify the metal **X** and write its reaction with iron(III) oxide. Give the evidence to show that the oxide of metal **X** is an amphoteric oxide.
8. Name two ores of iron. What are three raw materials used in the extraction of iron? Write chemical equations that occur in the blast furnace. What are the main constituents of steel?
9. Iron(III) oxide reacts with carbon monoxide in the extraction of iron. State which substance is oxidised and which substance is reduced.
10. Iron can react with sulphuric acid, but two different products can be obtained depending upon the acid strength. Explain this statement with appropriate chemical equations.
11. The extraction of copper from its ore involves the following steps. Write the relevant chemical equations for each step.
    (a) heating the concentrated ore with silica and oxygen in the furnace
    (b) roasting of copper(I) sulphide
    (c) cathode reaction in electrolytic refining of copper
12. You are given moderately reactive metal (Pb) and very reactive metal (Al). Compare the uses and extraction methods of these metals based on their reactivity.
13. Give reasons for the following questions/statements.
    (a) Why do silver and copper lose their brightness when they are exposed to air?
    (b) Tarnished copper vessels are cleaned with tamarind sherbet.
    (c) Aluminium is more reactive than iron, but there is less corrosion of aluminium as compared to iron when they are exposed to air.
14. Why is recycling of metals important for our society?

CHAPTER REVIEW
(Concept Map)



CHAPTER 6

NON-METALS AND THEIR COMPOUNDS: NITROGEN AND SULPHUR

Non-metals are the chemical elements that mostly lack the characteristics of metals. Physically, they tend to have relatively low melting points, boiling points, densities and electrical conductivities. So, they are good insulators of heat and electricity. Chemically, they tend to have relatively high ionisation energy, electron affinity and electronegativity. They gain or lose electrons when they react with other elements and chemical compounds. Non-metals are located on the right side of the Periodic Table. They usually have 4, 5, 6 or 7 electrons in their outermost shells. Among non-metals, 6 non-metals are solids (e.g., carbon, sulphur and phosphorus), and 11 non-metals are gases (e.g., hydrogen, nitrogen, oxygen and chlorine). Only one non-metal, bromine, is a liquid.

Non-metals are very useful in our daily life. Oxygen gas is absolutely essential to human life. Hydrogen gas is used in the hydrogenation of vegetable oils. Carbon is used for making electrodes in electrolytic cells. Nitrogen is important to the chemical industry and it is used in the manufacture of fertilisers. Sulphur is valued for its medical properties and as an important ingredient in many chemical solutions. Chlorine is a powerful disinfectant. It is used to purify water for drinking and in swimming pools. This chapter focuses on non-metallic elements, specifically nitrogen and sulphur, their properties, uses, and their important compounds.


Matches


Foods


Car tyres


Coffee beans

Sulphur ointment


Paint

Learning Outcomes

After completing this chapter, students will be able to:

- describe the preparation of nitrogen from the air;
- outline the preparations, properties and uses of oxides of nitrogen;
- recognise the conditions for the manufactures of ammonia and nitric acid;
- compare the properties and uses of ammonia and nitric acid;
- describe the extraction, properties and behaviours of sulphur and its compounds;
- explain the manufacture, properties and uses of sulphuric acid.

6.1 NITROGEN AND ITS BEHAVIOURS

Nitrogen is the non-metallic element with the symbol N and atomic number 7 having 7 protons, 7 neutrons and 7 electrons. Figure 6.1 shows the electronic structure of nitrogen atom.

A nitrogen molecule has two nitrogen atoms joined together by three covalent bonds. Nitrogen is a colourless gas, without any smell and is very unreactive. It has a very low boiling point of −196 °C.

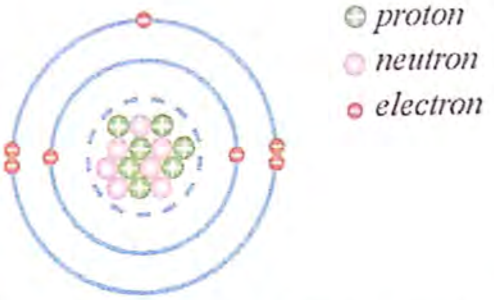


Figure 6.1 The Electronic Structure of Nitrogen Atom, $^{14}_{7}N$

(a) Occurrence of Nitrogen

The Earth's atmosphere is made up of 78 percentage of nitrogen,with the rest being oxygen, carbo dioxide and other trace elements. Even though there is so much nitrogen in the air, there is very little i the Earth's crust. It can be found in some fairly rare minerals such as Chile saltpetre ($NaNO_3$). Nitroge can also be found in all living organisms on the Earth including plants and animals. Industrially, elementa nitrogen can be manufactured by fractional distillation of liquid air from which carbon dioxide and wate have been removed.

(b) Preparation of Nitrogen from the Air

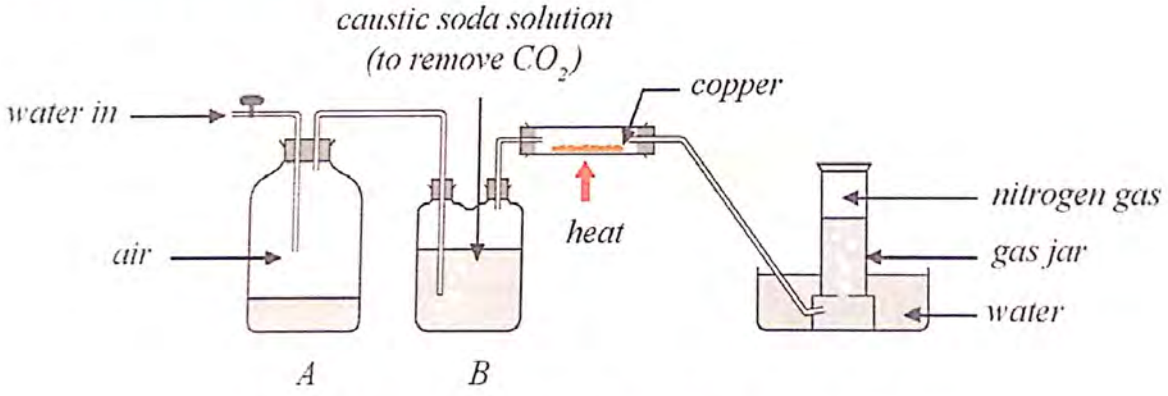


Figure 6.2 Preparation of Nitrogen Gas from the Air

The apparatus is set up as shown in Figure 6.2. Water is allowed to flow into bottle **A** at a slo rate. Air from this bottle is displaced and made to pass through another bottle **B** containing caustic sod solution to remove carbon dioxide. The carbon dioxide free air is then passed over heated copper whic absorbs oxygen to form copper(II) oxide. The nitrogen, which was freed from oxygen, comes out of th combustion tube. Since the nitrogen is only slightly soluble in water, it is collected by the downwar displacement of water. If the nitrogen is required dry, it may be passed through a U-tube containing glas beads wetted with concentrated sulphuric acid.

$$\text{copper} + \text{air} \longrightarrow \text{copper(II) oxide} + \text{nitrogen}$$
$$2Cu\,(s) + (N_2 + O_2)\,(g) \longrightarrow 2CuO\,(s) + N_2\,(g)$$

$$\text{sodium hydroxide} + \text{carbon dioxide} \longrightarrow \text{sodium carbonate} + \text{water}$$
$$2NaOH\,(aq) + CO_2\,(g) \longrightarrow Na_2CO_3\,(aq) + H_2O\,(l)$$

(c) Uses of Nitrogen

Nitrogen is also an important substance in the chemical industry, since it is used to make everything from nylon to various dyes and even explosives. Liquid nitrogen is used as a coolant. The main use of nitrogen is in the manufacture of ammonia gas, from which nitrogenous fertilisers, nitric acid and urea are mainly prepared. Some important **nitrogen fertilisers** are ammonium nitrate, NH_4NO_3, ammonium sulphate, $(NH_4)_2SO_4$ and urea, $CO(NH_2)_2$.

(d) Oxidation Numbers of Nitrogen

Nitrogen forms a large number of compounds with hydrogen and oxygen. Since nitrogen has 5 electrons in its outermost shell, the oxidation numbers of nitrogen vary from -3 to +5. Oxidation numbers of nitrogen in its compounds are shown in Table 6.1.

Table 6.1 Oxidation Numbers of Nitrogen in Its Compounds

Compound	Formula	Oxidation number
ammonia	NH_3	−3
hydrazine	N_2H_4	−2
hydroxylamine	NH_2OH	−1
nitrogen	N_2	0
dinitrogen oxide	N_2O	+1
nitrogen oxide	NO	+2
nitrous acid	HNO_2	+3
nitrogen dioxide	NO_2	+4
nitric acid	HNO_3	+5

REVIEW QUESTIONS

(1) Why does nitrogen show various oxidation numbers?
(2) Mention some important nitrogen fertilisers.
(3) Determine the oxidation number of nitrogen in $NaNO_3$, NCl_3 and N_2O_5.

Key Term

- **Nitrogen fertilisers** are compounds that contain or produce nitrate or ammonium ions in the soil.

6.2 COMPOUNDS OF NITROGEN

(a) Oxides of Nitrogen

Some common oxides of nitrogen are dinitrogen oxide, nitrogen oxide and nitrogen dioxide. Laboratory preparations and physical properties of these oxides are shown in Table 6.2.

Table 6.2 Laboratory Preparations and Physical Properties of Three Common Oxides of Nitrogen

Oxide of nitrogen	**Laboratory preparation**	**Method of collection**	**Physical properties**	
			Colour and odour	**Solubility**
dinitrogen oxide	ammonium sulphate + potassium nitrate $\xrightarrow{\Delta}$ ammonium nitrate + potassium sulphate $(NH_4)_2SO_4\ (aq) + 2KNO_3\ (aq) \xrightarrow{\Delta} 2NH_4NO_3\ (aq) + K_2SO_4\ (aq)$ ammonium nitrate → dinitrogen oxide + water $NH_4NO_3\ (aq) \longrightarrow N_2O\ (g) + 2H_2O\ (l)$	downward displacement of hot water	colourless gas, sweetish odour gas	soluble in cold water, insoluble in hot water
nitrogen oxide	copper + nitric acid (dil.) → copper(II) nitrate + nitrogen oxide + water $3Cu\ (s) + 8HNO_3\ (aq) \longrightarrow 3Cu(NO_3)_2\ (aq) + 2NO\ (g) + 4H_2O\ (l)$	downward displacement of cold water	colourless gas, odourless gas	insoluble in water
nitrogen dioxide	copper + nitric acid (conc.) $\xrightarrow{\Delta}$ copper(II) nitrate + nitrogen dioxide + water $Cu\ (s) + 4HNO_3\ (l) \xrightarrow{\Delta} Cu(NO_3)_2\ (aq) + 2NO_2\ (g) + 2H_2O\ (l)$	upward displacement of air	reddish brown gas, pungent and irritating smell	soluble in water

(i) Some chemical properties of oxides of nitrogen

Decomposition

Dinitrogen oxide is readily decomposed above 600 °C.

$$\text{dinitrogen oxide} \xrightarrow{> 600\ ^\circ C} \text{nitrogen} + \text{oxygen}$$

$$2N_2O\ (g) \xrightarrow{> 600\ ^\circ C} 2N_2\ (g) + O_2\ (g)$$

Thermal dissociation

At −10 °C, nitrogen dioxide exists as a solid, colourless dimer molecule, dinitrogen tetroxide, N_2O_4. It dissociates on heating to form the brown monomer NO_2 molecules. At about 150 °C, NO_2 begins to dissociate into the colourless nitrogen oxide and oxygen.

$$\text{dinitrogen tetroxide} \overset{\Delta}{\rightleftharpoons} \text{nitrogen dioxide} \overset{\Delta}{\rightleftharpoons} \text{nitrogen oxide} + \text{oxygen}$$

$$N_2O_4\ (s) \overset{\Delta}{\rightleftharpoons} 2NO_2\ (g) \overset{\Delta}{\rightleftharpoons} 2NO\ (g) + O_2\ (g)$$

Combustion

Dinitrogen oxide supports combustion as actively as oxygen and it produces nitrogen when heated.

carbon + dinitrogen oxide $\xrightarrow{\Delta}$ carbon dioxide + nitrogen
$C (s) + 2N_2O (g) \xrightarrow{\Delta} CO_2 (g) + 2N_2 (g)$
sodium + dinitrogen oxide $\xrightarrow{\Delta}$ sodium oxide + nitrogen
$2Na (s) + N_2O (g) \xrightarrow{\Delta} Na_2O (s) + N_2 (g)$

Formation of brown nitroso complex

A cold acidified solution of iron(II) sulphate is poured into a gas jar of nitrogen oxide to give rown nitroso iron(II) sulphate solution.

iron(II) sulphate + nitrogen oxide → nitroso iron(II) sulphate
$FeSO_4 (aq) + NO (g) \rightarrow FeSO_4.NO (aq)$ (brown)

Combination with chlorine

Nitrogen oxide combines directly with chlorine in the presence of charcoal to form yellow nitrosyl hloride gas. It is a strong oxidising agent.

nitrogen oxide + chlorine → nitrosyl chloride
$2NO (g) + Cl_2 (g) \rightarrow 2NOCl (g)$ (yellow)

Dissolution

Nitrogen dioxide, an acidic oxide, dissolves in water to form a mixture of nitric acid and nitrous cid.

nitrogen dioxide + water → nitric acid + nitrous acid
$2NO_2 (g) + H_2O (l) \rightarrow HNO_3 (aq) + HNO_2 (aq)$

Reaction with aqueous alkali

When nitrogen dioxide reacts with aqueous alkalis, the corresponding nitrates and nitrites are ormed.

sodium hydroxide + nitrogen dioxide → sodium nitrate + sodium nitrite + water
$2NaOH (aq) + 2NO_2 (g) \rightarrow NaNO_3 (aq) + NaNO_2 (aq) + H_2O (l)$

(ii) Some uses of oxides of nitrogen

Dinitrogen oxide gas (**laughing gas**) is used as anaesthetic for minor surgical operations. Since it poses a hazard it must be used with caution. Most oxides of nitrogen are used as oxidising agents in the production of rocket fuel and explosives.

(b) Hydride of Nitrogen: Ammonia

Hydride of nitrogen is the binary compound formed by the combination of hydrogen and nitrogen. The most thermally stable hydride of nitrogen is ammonia.

(i) The manufacture of ammonia: The Haber Process

Ammonia is manufactured on a large scale by the Haber process (Figure 6.3) which was invented in 1908 by Fritz Haber. In the Haber process, nitrogen and hydrogen gases are mixed together in the ratio of 1:3 by volume. The nitrogen is obtained from the air while hydrogen is derived mainly from natural gas. The mixture is passed over an iron catalyst at a high pressure of about 200 atm and a moderately high temperature of 450 °C.

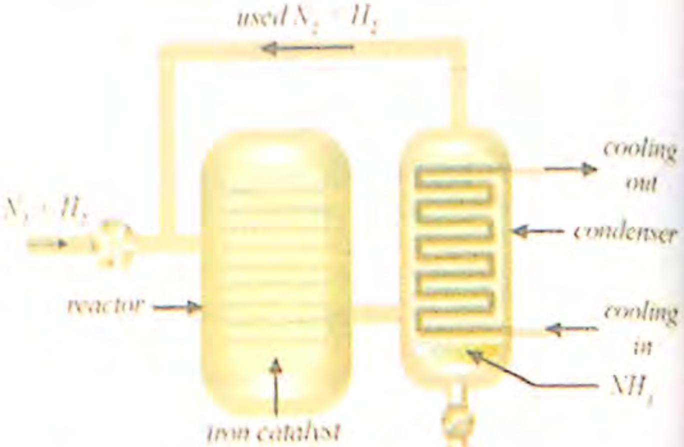


Figure 6.3 Manufacture of Ammonia Gas by Haber Process

$$\text{nitrogen} + \text{hydrogen} \rightleftharpoons \text{ammonia}$$

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

Ammonia is cooled to a low temperature, so it condenses to a liquid and is collected. The unreacted nitrogen and hydrogen are passed over the catalyst again. Recirculation is repeated as necessary.

(ii) Laboratory preparation of ammonia gas

An excess of the slaked lime, $Ca(OH)_2$ and ammonium chloride are mixed. The mixture is ground by using a mortar and pestle, and placed in a round-bottomed flask. The apparatus is set up as shown in Figure 6.4. When this mixture is heated, ammonia gas is evolved. It is dried by passage through a lime tower which contains the drying agent, quicklime, CaO.

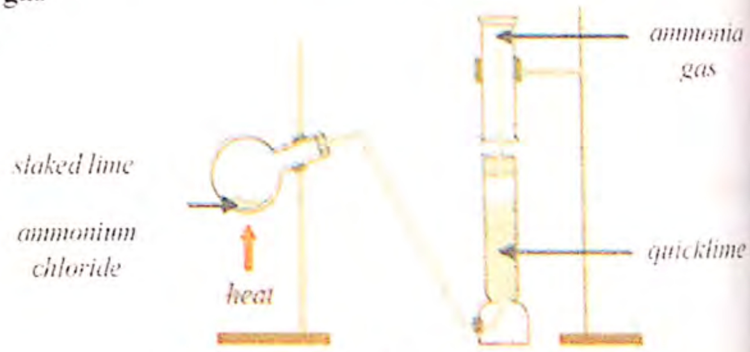


Figure 6.4 Laboratory Preparation of Ammonia Gas

$$\text{calcium hydroxide} + \text{ammonium chloride} \xrightarrow{\Delta} \text{calcium chloride} + \text{water} + \text{ammonia}$$

$$Ca(OH)_2\,(s) + 2NH_4Cl\,(s) \xrightarrow{\Delta} CaCl_2\,(aq) + 2H_2O\,(l) + 2NH_3\,(g)$$

Since ammonia is lighter than air and very soluble in water, it is collected by the downward displacement of air. The gas jar is known to be filled with ammonia if a moist red litmus paper placed at the mouth of the gas jar turns blue.

Note: Ammonia gas should not be dried by usual drying agents such as anhydrous calcium chloride, concentrated sulphuric acid and phosphorus(V) oxide. These compounds react with ammonia.

(iii) Physical properties of ammonia gas

Ammonia is a colourless gas with a characteristic pungent smell. It is less dense than air and very soluble in water producing a weak alkali. Liquid ammonia boils at 33.3 °C, and freezes at 77.7 °C to white crystals.

Solubility of ammonia gas

Ammonia is extremely soluble in water. This solubility level is often demonstrated in the laboratory by the "Fountain experiment". The round-bottomed flask is filled with dry ammonia gas and the apparatus is arranged as shown in Figure 6.5.

A few drops of water are allowed to pass through the inlet (dropper) attached to the round-bottomed flask. Ammonia dissolves into the water and the pressure in the flask drops. As a result, more water is forced into the flask creating a fountain effect.

The alkaline nature of ammonia can be shown in this experiment by adding a red litmus solution to the water in the trough. When ammonia in the flask dissolves in the litmus solution, it turns blue.

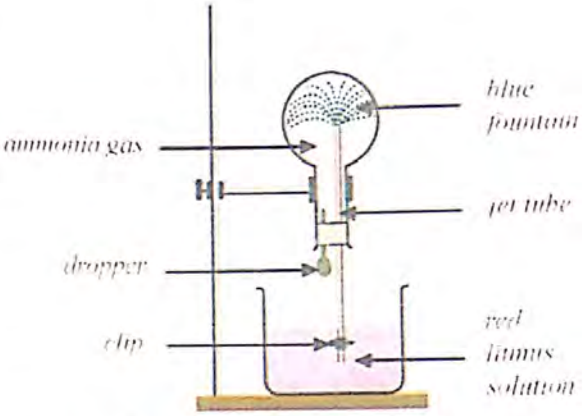


Figure 6.5 Fountain Experiment of Ammonia Gas

(iv) Chemical properties of ammonia gas

Reaction with acid

Dense white fumes are observed when ammonia gas reacts with hydrogen chloride gas to form solid ammonium chloride.

ammonia + hydrogen chloride ⟶ ammonium chloride

$$NH_3\,(g) + HCl\,(g) \longrightarrow NH_4Cl\,(s)$$

Reduction with copper(II) oxide

When ammonia is passed over heated copper(II) oxide, it reduces the copper(II) oxide to copper.

$$\text{copper(II) oxide} + \text{ammonia} \xrightarrow{\Delta} \text{copper} + \text{water} + \text{nitrogen}$$

$$3CuO\,(s) + 2NH_3\,(g) \xrightarrow{\Delta} 3Cu\,(s) + 3H_2O\,(l) + N_2\,(g)$$

Reaction with chlorine

When excess ammonia reacts with chlorine, nitrogen is obtained. If the chlorine is in excess, the explosive oily liquid substance, nitrogen trichloride is formed.

ammonia (excess) + chlorine ⟶ nitrogen + ammonium chloride

$$8NH_3\,(g) + 3Cl_2\,(g) \longrightarrow N_2\,(g) + 6NH_4Cl\,(s)$$

$$\text{ammonia} + \text{chlorine (excess)} \longrightarrow \text{nitrogen trichloride} + \text{hydrogen chloride}$$
$$NH_3\,(g) + 3Cl_2\,(g) \longrightarrow NCl_3\,(l) + 3HCl\,(g)$$

Reaction with metals

Ammonia combines directly with some metals on heating. Thus, dry ammonia passed over sodium metal heated to red heat forms sodium amide (sodamide). However, magnesium forms the nitride.

$$\text{ammonia} + \text{sodium} \xrightarrow{\Delta} \text{sodium amide} + \text{hydrogen}$$
$$2NH_3\,(g) + 2Na\,(s) \xrightarrow{\Delta} 2NaNH_2\,(s) + H_2\,(g)$$
$$\text{ammonia} + \text{magnesium} \xrightarrow{\Delta} \text{magnesium nitride} + \text{hydrogen}$$
$$2NH_3\,(g) + 3Mg\,(s) \xrightarrow{\Delta} Mg_3N_2\,(s) + 3H_2\,(g)$$

Both sodium amide and magnesium nitride are hydrolysed by water to regenerate ammonia.

$$\text{sodium amide} + \text{water} \longrightarrow \text{sodium hydroxide} + \text{ammonia}$$
$$NaNH_2\,(s) + H_2O\,(l) \longrightarrow NaOH\,(aq) + NH_3\,(g)$$
$$\text{magnesium nitride} + \text{water} \longrightarrow \text{magnesium hydroxide} + \text{ammonia}$$
$$Mg_3N_2\,(s) + 6H_2O\,(l) \longrightarrow 3Mg(OH)_2\,(s) + 2NH_3\,(g)$$

(v) Uses of ammonia

Ammonia is used in the manufacture of fertilisers, plastics, explosives, textiles, pesticides, dyes and other chemicals. It was used as a refrigerant gas in the past. Nowadays, more safer and more efficient refrigerants such as HFCs (hydrofluorocarbons), HCFCs (hydrochlorofluorocarbons) have been used.

(c) Oxoacid of Nitrogen: Nitric Acid

Nitric acid and nitrous acid are oxoacids of nitrogen. Among them, nitric acid (HNO_3), known as aqua fortis (Latin for "strong water"), is a more common and highly corrosive mineral acid. The pure compound is colourless.

(i) Manufacture of nitric acid

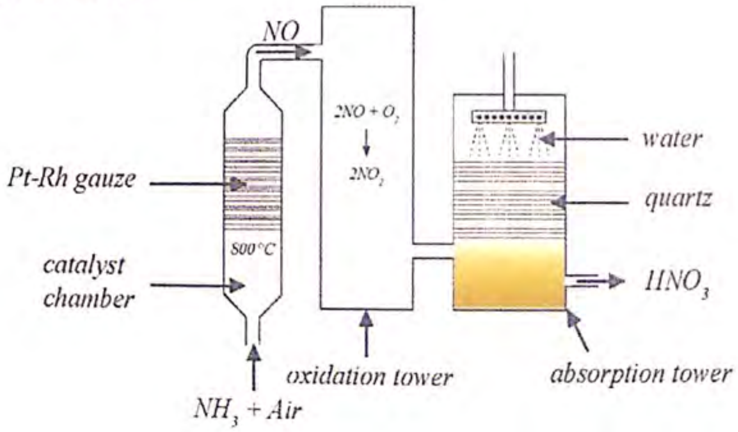


Figure 6.6 Ammonia Oxidation Process in Manufacture of Nitric Acid

Nitric acid is manufactured by the **Ammonia Oxidation Process** (Figure 6.6).

The oxidation of ammonia is carried out by passing ammonia gas and excess air through a multi-layered very fine gauze consisting of platinum (90 %) and rhodium (10 %) catalyst. The reaction is initiated by heating the catalyst to red heat, 800 °C. Once the reaction is started, the heat generated maintains the reaction temperature.

$$\text{ammonia} + \text{oxygen} \xrightarrow{\text{Pt-Rh, red heat}} \text{nitrogen oxide} + \text{water}$$
$$4NH_3\,(g) + 5O_2\,(g) \longrightarrow 4NO\,(g) + 6H_2O\,(g)$$

The nitrogen oxide so formed is rapidly cooled and made to combine with oxygen from excess of air to form nitrogen dioxide, a reddish-brown gas.

$$\text{nitrogen oxide} + \text{oxygen} \longrightarrow \text{nitrogen dioxide}$$
$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

The nitrogen dioxide in the presence of more air is then absorbed in water to yield nitric acid.

$$\text{nitrogen dioxide} + \text{oxygen} + \text{water} \longrightarrow \text{nitric acid}$$
$$4NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 4HNO_3\,(l)$$

Note: If nitric acid is subject to heat or light, decomposition occurs. For this reason, it should be stored in brown glass bottles.

(ii) Physical properties

Nitric acid is a colourless, fuming liquid.

(iii) Chemical properties

Acidic property

Dilute nitric acid neutralises bases, forming nitrates.

$$\text{potassium hydroxide} + \text{nitric acid (dil.)} \longrightarrow \text{potassium nitrate} + \text{water}$$
$$KOH\,(aq) + HNO_3\,(aq) \longrightarrow KNO_3\,(aq) + H_2O\,(l)$$

Oxidising property

Nitric acid oxidises metals to give metal nitrates.

$$\text{copper} + \text{nitric acid (conc.)} \xrightarrow{\Delta} \text{copper(II) nitrate} + \text{water} + \text{nitrogen dioxide}$$
$$Cu\,(s) + 4HNO_3\,(l) \xrightarrow{\Delta} Cu(NO_3)_2\,(aq) + 2H_2O\,(l) + 2NO_2\,(g)$$

Other metals react similarly to give oxides of nitrogen. The nature of the gaseous product depends on the metal, the concentration of the acid and the temperature employed.

With the reactive metal such as, magnesium and dilute nitric acid, hydrogen gas is liberated.

$$\text{magnesium} + \text{nitric acid (dil.)} \longrightarrow \text{magnesium nitrate} + \text{hydrogen}$$
$$Mg\,(s) + 2HNO_3\,(aq) \longrightarrow Mg(NO_3)_2\,(aq) + H_2\,(g)$$

With a less reactive metal such as zinc or aluminium and hot dilute nitric acid, ammonium nitrate is produced.

$$\text{zinc} + \text{nitric acid (dil.)} \xrightarrow{\Delta} \text{zinc nitrate} + \text{ammonium nitrate} + \text{water}$$
$$4Zn\,(s) + 10HNO_3\,(aq) \xrightarrow{\Delta} 4Zn(NO_3)_2\,(aq) + NH_4NO_3\,(aq) + 3H_2O\,(l)$$

Nitric acid can also oxidise certain non-metallic elements and certain compounds.

$$\text{carbon} + \text{nitric acid (conc.)} \xrightarrow{\Delta} \text{nitrogen dioxide} + \text{carbon dioxide} + \text{water}$$
$$C\,(s) + 4HNO_3\,(l) \xrightarrow{\Delta} 4NO_2\,(g) + CO_2\,(g) + 2H_2O\,(l)$$

$$\text{phosphorus} + \text{nitric acid (conc.)} \xrightarrow{\Delta} \text{phosphoric acid} + \text{nitrogen dioxide} + \text{water}$$
$$P_4\,(s) + 20HNO_3\,(l) \xrightarrow{\Delta} 4H_3PO_4\,(l) + 20NO_2\,(g) + 4H_2O\,(l)$$

$$\text{hydrogen iodide} + \text{nitric acid (dil.)} \xrightarrow{\Delta} \text{iodine} + \text{nitrogen oxide} + \text{water}$$
$$6HI\,(aq) + 2HNO_3\,(aq) \xrightarrow{\Delta} 3I_2\,(s) + 2NO\,(g) + 4H_2O\,(l)$$

Aqua regia as an oxidising agent

The ability of aqua regia (3 volumes concentrated HCl and 1 volume concentrated HNO_3) to dissolve the noble metal gold, is due to the oxidation of the hydrochloric acid by the nitric acid to liberate chlorine which converts the gold into gold(III) chloride. The latter dissolves in excess of hydrochloric acid to form the soluble chloroauric acid, $HAuCl_4$.

$$\text{hydrochloric acid (conc.)} + \text{nitric acid (conc.)} \longrightarrow \text{chlorine} + \text{nitrosyl chloride} + \text{water}$$
$$3HCl\,(l) + HNO_3\,(l) \longrightarrow Cl_2\,(g) + NOCl\,(g) + 2H_2O\,(l)$$

$$\text{gold} + \text{chlorine} \longrightarrow \text{gold(III) chloride}$$
$$2Au\,(s) + 3Cl_2\,(g) \longrightarrow 2AuCl_3\,(s)$$

$$\text{gold(III) chloride} + \text{hydrochloric acid} \longrightarrow \text{chloroauric acid}$$
$$AuCl_3\,(s) + HCl\,(aq) \longrightarrow HAuCl_4\,(aq)$$

(iv) Uses of nitric acid

Nitric acid is used in the manufacture of explosives and dyes, the production of ammonium nitrat fertiliser, and the preparation of aqua regia.

REVIEW QUESTIONS

(1) Among three oxides of nitrogen, which oxide is collected by the downward displacement of h water? Give reason for your answer.

(2) The following questions relate to the gases: nitrogen, nitrogen oxide, dinitrogen oxide, and nitroge dioxide.
  (i) Which gas(es) is(are) neutral oxide(s)?
  (ii) Which gas would be used to reduce pain for a person having a tooth extracted?

(iii) Which gas forms nitroso iron(II) sulphate?

(iv) Which gas can be manufactured from liquid air by fractional distillation?

(3) What happens when ammonia gas reacts with hydrogen chloride gas?

Key Terms

- **Laughing gas** is a chemical compound with the formula N_2O, which is used as an anaesthetic.
- **Haber process** is an industrial process of directly synthesising ammonia from hydrogen and nitrogen.
- **Aqua regia** is a mixture of concentrated hydrochloric acid and nitric acid in a volume ratio of 3:1.

6.3 SULPHUR AND ITS ALLOTROPES

Sulphur is the non-metallic solid element with the symbol S and atomic number 16 having 16 protons, 16 neutrons and 16 electrons. Figure 6.7 shows the electronic structure of sulphur atom which has 6 electrons in its outermost shell.

(a) Sulphur

Sulphur is a common element in the Earth's crust. It is a yellow, strong smelling solid element. Nowadays most sulphur is obtained from the sulphur compounds found in petroleum and natural gas. About 3 % of sulphur we use comes from the underground sulphur bed. It is also widely found in nature as iron pyrites (iron sulphide), galena (lead(II) sulphide), gypsum (calcium sulphate), epsom salts (magnesium sulphate) and many other minerals. Sulphur occurs as elemental sulphur, hydrogen sulphide gas and organosulphur compounds.

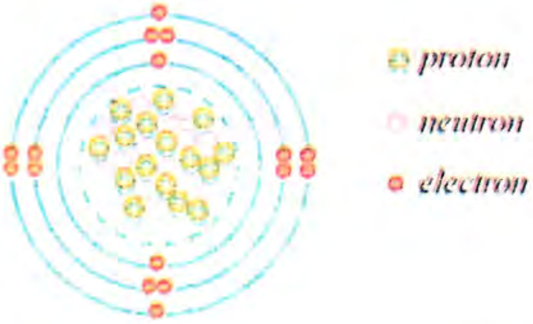
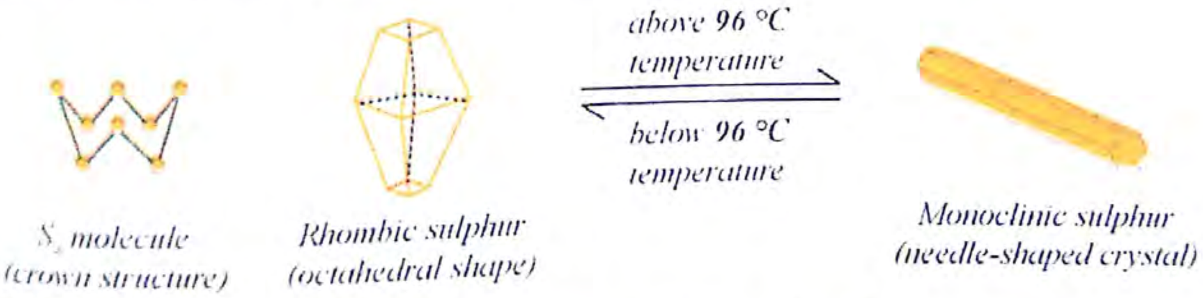


Figure 6.7 The Electronic Structure of Sulphur Atom, $^{32}_{16}S$

(i) Allotropes of sulphur

The structural unit in the solid state of sulphur is the S_8 ring structure. Sulphur can exist in different allotropic forms like carbon and oxygen. There are three allotropes of sulphur. Two of which are crystalline forms: rhombic sulphur and monoclinic sulphur and the other, non-crystalline form: plastic sulphur. Allotropic forms of sulphur and their transformations are illustrated in Figure 6.8.



S_8 molecule (crown structure)

Rhombic sulphur (octahedral shape)

Monoclinic sulphur (needle-shaped crystal)

Figure 6.8 Allotropic Forms of Sulphur and Their Transformations

Rhombic sulphur

When a solution of sulphur in carbon disulphide is allowed to evaporate slowly at room temperature, the octahedral crystals of rhombic sulphur are deposited from the solution.

Monoclinic sulphur

Molten sulphur is poured into a wet filter paper in a funnel. When the sulphur has nearly set to solidify, the filter paper is carefully unfolded. Long, dark yellow, needle-like crystals of monoclinic sulphur will be seen.

Monoclinic (or prismatic) sulphur slowly changes into the rhombic form at temperatures below 96 °C (369 K) which is the transition temperature.

Plastic sulphur

When any form of sulphur is heated almost to its boiling point and then poured into cold water, plastic sulphur is formed. Plastic sulphur is a soft, sticky, rubber-like substance with a transparent, brown colour. In the plastic sulphur, the S_8 ring molecules are ruptured and the sulphur atoms join together to form long chains with a zig-zag arrangement.

(ii) Extraction of sulphur

Different processes are used in mining sulphur according to the nature of the deposits. Sulphur is found in shallow or deep deposits below the Earth's surface. Sulphur, which is deposited at about 700 ft (~213 m) below the Earth's surface, is mined or extracted by the **Frasch Process**. The description for extracting sulphur by this process may be summarised as follows: three concentric pipes as shown in Figure 6.9 are driven down to the deposit of sulphur. Superheated steam at about 160 °C is forced down under pressure through the outermost pipe. When superheated steam reaches the deposit, it melts the sulphur, forming a pool of molten sulphur.

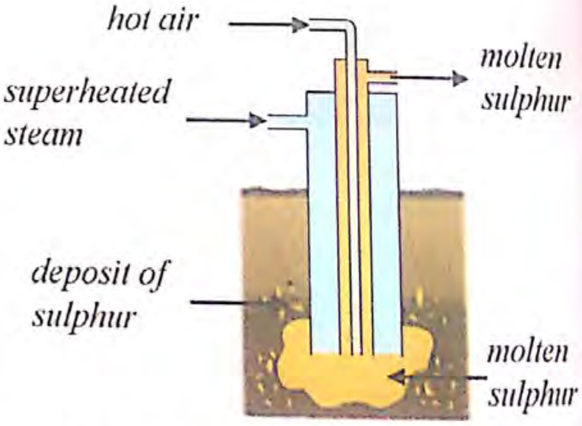


Figure 6.9 Extraction of Sulphur by the Frasch Process

Hot air under high pressure is forced down through the innermost pipe. The pressure of hot air forces up the molten sulphur through the central pipe, between the inner and outer pipes. The molten sulphur is collected in wooden containers and allowed to solidify. Sulphur obtained by this process is 99.5 % pure.

(b) Oxidation Numbers of Sulphur

Sulphur forms a large number of compounds with hydrogen and oxygen. Since sulphur has 6 electrons in the outermost shell, the oxidation numbers of sulphur vary from -2 to +6. Oxidation numbers of sulphur in its compounds are shown in Table 6.3.

Table 6.3 Oxidation Numbers of Sulphur in Its Compounds

Compound/Element	Formula	Oxidation number
hydrogen sulphide	H_2S	-2
sulphur	S	0
disulphur dichloride	S_2Cl_2	+1
sulphur dichloride	SCl_2	+2
sulphur dioxide	SO_2	+ 4
sulphur trioxide	SO_3	+6

REVIEW QUESTIONS

(1) Describe the different allotropic forms of sulphur.

(2) (a) Which crystalline form of sulphur exists at 90 °C? What is its shape?
(b) What is the structural difference between S_8 molecule and plastic sulphur?

(3) Determine the oxidation number of sulphur in H_2SO_3, Na_2S and $NaHSO_4$.

Key Terms

- **Rhombic sulphur** is an octahedral-shaped crystalline allotropic form of sulphur. It is the most stable form of sulphur.
- **Monoclinic sulphur** is a needle-shaped crystalline allotrope of sulphur and is obtained by heating rhombic sulphur to 96 °C (369 K).
- The **Frasch Process** is an industrial method to extract sulphur from underground elemental deposits.

6.4 COMPOUNDS OF SULPHUR

(a) Oxides of Sulphur

Sulphur has two important oxides: sulphur dioxide, SO_2 and sulphur trioxide, SO_3. In this section, laboratory preparation of sulphur dioxide and some of its physical properties (Table 6.4) have been discussed.

Table 6.4 Laboratory Preparation and Physical Properties of Sulphur Dioxide

Oxide of sulphur	Laboratory preparation	Method of collection	Physical properties	
			Colour and odour	Solubility
sulphur dioxide	sodium sulphite + sulphuric acid (dil.) $\xrightarrow{\Delta}$ sodium sulphate + water + sulphur dioxide $Na_2SO_3\ (s) + H_2SO_4\ (aq) \xrightarrow{\Delta} Na_2SO_4\ (aq) + H_2O\ (l) + SO_2\ (g)$	upward displacement of air	colourless gas with pungent odour	very soluble in water
	copper + sulphuric acid (conc.) $\xrightarrow{\Delta}$ copper(II) sulphate + water + sulphur dioxide $Cu\ (s) + 2H_2SO_4\ (l) \xrightarrow{\Delta} CuSO_4\ (aq) + 2H_2O\ (l) + SO_2\ (g)$			

(i) Chemical properties of sulphur dioxide

Addition reaction

Sulphur dioxide does not react with oxygen under ordinary conditions. However, it combines with oxygen in the presence of catalyst such as platinum or vanadium(V) oxide at the appropriate temperature.

$$\text{sulphur dioxide} + \text{oxygen} \xrightarrow{Pt/V_2O_5,\ 450\text{-}500\ ^\circ C} \text{sulphur trioxide}$$

$$2SO_2\ (g) + O_2\ (g) \xrightarrow{Pt/V_2O_5,\ 450\text{-}500\ ^\circ C} 2SO_3\ (g)$$

Sulphur dioxide directly combines with chlorine in the presence of sunlight to form sulphuryl chloride.

$$\text{sulphur dioxide} + \text{chlorine} \xrightarrow{\text{sunlight}} \text{sulphuryl chloride}$$

$$SO_2\ (g) + Cl_2\ (g) \xrightarrow{\text{sunlight}} SO_2Cl_2\ (l)$$

Acidic property

Sulphur dioxide reacts with basic oxide to form sulphite.

$$\text{sulphur dioxide} + \text{potassium oxide} \longrightarrow \text{potassium sulphite}$$

$$SO_2\ (g) + K_2O\ (s) \longrightarrow K_2SO_3\ (s)$$

Reducing property

Sulphur dioxide reduces halogens to hydrogen halides.

sulphur dioxide + water + bromine → sulphuric acid + hydrobromic acid

$$SO_2(g) + 2H_2O(l) + Br_2(aq) \rightarrow H_2SO_4(aq) + 2HBr(aq)$$

(yellowish-brown) (colourless)

Sulphur dioxide can also reduce violet coloured acidified potassium permanganate solution to a colourless solution

sulphur dioxide + water + potassium permanganate → potassium sulphate + manganese(II) sulphate + sulphuric acid

$$5SO_2(g) + 2H_2O(l) + 2KMnO_4(aq) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 2H_2SO_4(aq)$$

(violet) (colourless)

Sulphur dioxide can also reduce orange coloured acidified potassium dichromate solution to a green solution.

sulphur dioxide + sulphuric acid + potassium dichromate → potassium sulphate + chromium(III) sulphate + water

$$3SO_2(g) + H_2SO_4(aq) + K_2Cr_2O_7(aq) \rightarrow K_2SO_4(aq) + Cr_2(SO_4)_3(aq) + H_2O(l)$$

(orange) (green)

Sulphur dioxide bleaches colouring matter by reduction. Sulphur dioxide gas does not contain hydrogen atoms, and the gas alone cannot reduce other substances. But when water is present in the reaction, SO_2 reacts with water molecule to produce nascent hydrogen as shown in the chemical equation below

sulphur dioxide + water → sulphuric acid + nascent hydrogen

$$SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2[H]$$

nascent hydrogen + colouring substance → decolourised substance

[H] + dye → (dye-H)

The bleaching action of sulphur dioxide is due to the reducing property of nascent hydrogen, which may add hydrogen to the molecules of colouring substance, or remove oxygen from the molecules of the colouring substance. In this way, sulphur dioxide decolourises the colouring substances such as wet flowers, wet litmus papers, etc.

Oxidising property

Sulphur dioxide can oxidise magnesium and carbon monoxide.

sulphur dioxide + magnesium → magnesium oxide + sulphur

$$SO_2(g) + 2Mg(s) \rightarrow 2MgO(s) + S(s)$$

sulphur dioxide + carbon monoxide → carbon dioxide + sulphur

$$SO_2(g) + 2CO(g) \rightarrow 2CO_2(g) + S(s)$$

(ii) Uses of sulphur dioxide

Sulphur dioxide is used in the food industries, as a food preservative. It acts as a bleaching agent. It is a primary source material for manufacturing sulphuric acid which is a necessary chemical in many industries.

(b) Hydride of Sulphur: Hydrogen Sulphide

Hydrides of sulphur are important in the origin of life models and two of amino acids. Laboratory preparation of hydrogen sulphide, H_2S, and some properties are described in this section.

(i) Laboratory preparation of hydrogen sulphide gas

In the laboratory, hydrogen sulphide gas is prepared by the action of non-oxidising acids (dilute sulphuric acid and dilute hydrochloric acid) on metal sulphides.

A few pieces of iron(II) sulphide are put into a flat-bottomed flask. The apparatus is set up as shown in Figure 6.10. Dilute sulphuric acid is poured into the flask through a thistle funnel. Effervescence takes place and hydrogen sulphide gas is evolved. The gas evolved is soluble in water and heavier than air, so it is collected by the upward displacement of air. When a piece of paper soaked with lead(II) nitrate is placed near the mouth of the gas jar, the paper turns black if the gas jar is full with hydrogen sulphide.

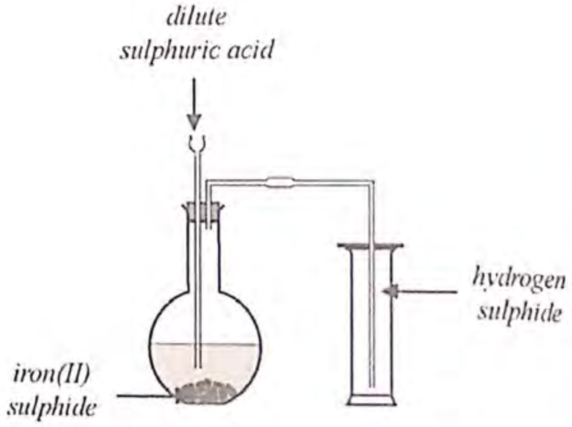


Figure 6.10 Laboratory Preparation of Hydrogen Sulphide Gas

$$\text{iron(II) sulphide} + \text{sulphuric acid (dil.)} \longrightarrow \text{iron(II) sulphate} + \text{hydrogen sulphide}$$

$$FeS\,(s) + H_2SO_4\,(aq) \longrightarrow FeSO_4\,(aq) + H_2S\,(g)$$

(ii) Physical properties of hydrogen sulphide

Hydrogen sulphide is a colourless gas with rotten egg smell. It is slightly acidic (turns blue litmus pink) and very poisonous.

(iii) Chemical properties of hydrogen sulphide

Reaction with oxygen under different conditions

In a limited supply of oxygen, hydrogen sulphide burns to produce water and sulphur.

$$\text{hydrogen sulphide} + \text{oxygen} \xrightarrow{\Delta} \text{water} + \text{sulphur}$$

$$2H_2S\,(g) + O_2\,(g) \xrightarrow{\Delta} 2H_2O\,(l) + 2S\,(s)$$

In an excess of oxygen, hydrogen sulphide burns to produce water and sulphur dioxide.

$$\text{hydrogen sulphide} + \text{oxygen (excess)} \xrightarrow{\Delta} \text{water} + \text{sulphur dioxide}$$

$$2H_2S\,(g) + 3O_2\,(g) \xrightarrow{\Delta} 2H_2O\,(l) + 2SO_2\,(g)$$

Reaction with metals

Hydrogen sulphide reacts with all metals in the reactivity series except gold and platinum. When the metal is heated in a stream of hydrogen sulphide, the following reaction occurs:

$$\text{zinc} + \text{hydrogen sulphide} \xrightarrow{\Delta} \text{zinc sulphide} + \text{hydrogen}$$

$$Zn\,(s) + H_2S\,(g) \xrightarrow{\Delta} ZnS\,(s) + H_2\,(g)$$

Reducing property

Hydrogen sulphide reduces halogens.

$$\text{hydrogen sulphide} + \text{chlorine} \longrightarrow \text{hydrogen chloride} + \text{sulphur}$$

$$H_2S\,(g) + Cl_2\,(g) \longrightarrow 2HCl\,(g) + S\,(s)$$

Hydrogen sulphide reduces acidified potassium permanganate solution (violet colour) to a colourless solution.

$$\text{hydrogen sulphide} + \text{potassium permanganate} + \text{sulphuric acid} \longrightarrow \text{manganese(II) sulphate} + \text{potassium sulphate} + \text{water} + \text{sulphur}$$

$$5H_2S\,(g) + \underset{\text{(violet)}}{2KMnO_4\,(aq)} + 3H_2SO_4\,(aq) \longrightarrow \underset{\text{(colourless)}}{2MnSO_4\,(aq)} + K_2SO_4\,(aq) + 8H_2O\,(l) + 5S\,(s)$$

Hydrogen sulphide reduces acidified potassium dichromate solution (orange colour) to a green solution.

$$\text{hydrogen sulphide} + \text{potassium dichromate} + \text{sulphuric acid} \longrightarrow \text{chromium(III) sulphate} + \text{potassium sulphate} + \text{water} + \text{sulphur}$$

$$3H_2S\,(g) + \underset{\text{(orange)}}{K_2Cr_2O_7\,(aq)} + 4H_2SO_4\,(aq) \longrightarrow \underset{\text{(green)}}{Cr_2(SO_4)_3\,(aq)} + K_2SO_4\,(aq) + 7H_2O\,(l) + 3S\,(s)$$

(c) Oxoacid of Sulphur: Sulphuric Acid

Oxoacids of sulphur are chemical compounds that contain sulphur, oxygen and hydrogen. The best known and most important industrially use of sulphur oxoacid is sulphuric acid. In this section, the manufacture of sulphuric acid and its properties have been discussed.

(i) Manufacture of sulphuric acid (The Contact Process)

Sulphuric acid is manufactured by the Contact Process as shown in Figure 6.11. In this process, sulphur or iron pyrites is burnt in excess air to produce sulphur dioxide.

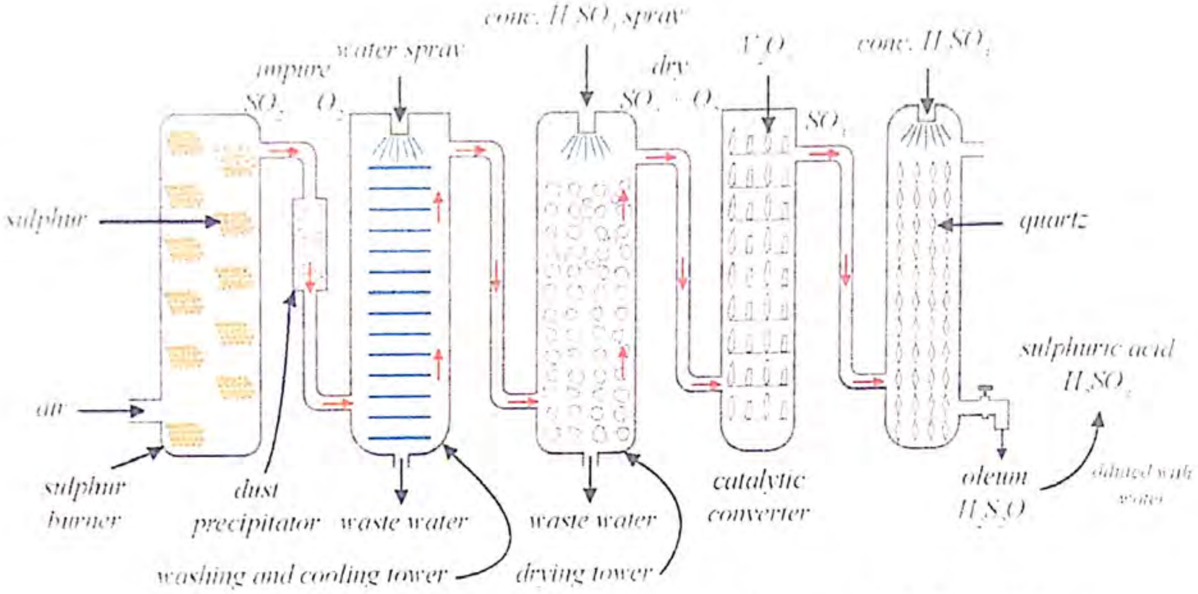


Figure 6.11 The Contact Process in the Manufacture of Sulphuric Acid

sulphur + oxygen ⟶ sulphur dioxide

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

iron pyrites + oxygen ⟶ iron(III) oxide + sulphur dioxide

$$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

The gas mixture, SO_2 and excess air, contains impurities (especially arsenious oxide). It is passed into a wash tower to remove impurities which might poison the catalyst.

The mixture of sulphur dioxide and excess air is passed into the drying tower and dried by spraying with concentrated sulphuric acid.

The dried sulphur dioxide and excess air are passed over platinum or vanadium(V) oxide catalyst at 450-500 °C to produce sulphur trioxide.

$$\text{sulphur dioxide} + \text{oxygen} \xrightarrow{Pt/V_2O_5,\ 450\text{-}500\ °C} \text{sulphur trioxide}$$

$$2SO_2(g) + O_2(g) \xrightarrow{Pt/V_2O_5,\ 450\text{-}500\ °C} 2SO_3(g)$$

Sulphur trioxide is easily dissolved in the concentrated sulphuric acid to form a product called oleum, $H_2S_2O_7$. The oleum is then diluted with water to produce the acid of any desired concentration.

sulphur trioxide + sulphuric acid (conc.) ⟶ oleum

$$SO_3(g) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l)$$

oleum + water ⟶ sulphuric acid

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$$

(ii) Physical properties of sulphuric acid

Sulphuric acid is a colourless, oily and heavy liquid. Its density is 1.84 g mL^{-1}. It boils at about 338 °C.

(iii) Chemical properties of sulphuric acid

Reaction with some metals

Dilute sulphuric acid reacts with iron and the metals above iron in the reactivity series producing sulphates and hydrogen.

iron + sulphuric acid (dil.) $\longrightarrow$ iron(II) sulphate + hydrogen

$Fe\,(s) + H_2SO_4\,(aq) \longrightarrow FeSO_4\,(aq) + H_2\,(g)$

Similar reactions occur with zinc and magnesium.

Dehydrating property

Concentrated sulphuric acid is a very powerful dehydrating agent. It can absorb not only free water, such as moisture, but also the combined water or the elements of water in some compounds.

Blue copper(II) sulphate becomes white when it is mixed with concentrated sulphuric acid.

copper(II) sulphate pentahydrate $\xrightarrow{\text{conc. } H_2SO_4}$ copper(II) sulphate + water

$\underset{\text{(blue)}}{CuSO_4.5H_2O\,(s)} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(white)}}{CuSO_4\,(s)} + 5H_2O\,(l)$

Methanoic acid (formic acid) reacts with concentrated sulphuric acid, decomposing into carbon monoxide and water.

methanoic acid $\xrightarrow{\text{conc. } H_2SO_4}$ carbon monoxide + water

$HCOOH\,(l) \xrightarrow{\text{conc. } H_2SO_4} CO\,(g) + H_2O\,(l)$

Sugar, starch and other carbohydrates are dehydrated by concentrated sulphuric acid. Carbon is formed as the final product. Hence, when concentrated sulphuric acid is added to these compounds, they turn black.

sugar $\xrightarrow{\text{conc. } H_2SO_4}$ carbon + water

$C_{12}H_{22}O_{11}\,(s) \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(black)}}{12C\,(s)} + 11H_2O\,(l)$

Oxidising property

Hot concentrated sulphuric acid oxidises metals and non-metals. Copper reacts with concentrated sulphuric acid to produce sulphur dioxide gas.

copper + sulphuric acid (conc.) $\xrightarrow{\Delta}$ copper(II) sulphate + water + sulphur dioxide

$Cu\,(s) + 2H_2SO_4\,(l) \xrightarrow{\Delta} CuSO_4\,(aq) + 2H_2O\,(l) + SO_2\,(g)$

Carbon is oxidised to carbon dioxide when it reacts with hot concentrated sulphuric acid.

carbon + sulphuric acid (conc.) $\xrightarrow{\Delta}$ sulphur dioxide + carbon dioxide + water

$$C\,(s) + 2H_2SO_4\,(l) \xrightarrow{\Delta} 2SO_2\,(g) + CO_2\,(g) + 2H_2O\,(l)$$

(iv) Uses of sulphuric acid

The major use of sulphuric acid is in the production of fertilisers, e.g., superphosphate, $Ca(H_2PO_4)_2.2CaSO_4$ and ammonium sulphate, $(NH_4)_2SO_4$. It is widely used in the manufacture of chemicals, e.g., hydrochloric acid, nitric acid, sulphate salts, synthetic detergents, dyes and pigments, explosives and drugs. Dilute sulphuric acid is used in lead-storage batteries. Sulphuric acid is used for the production of toilet bowl cleaners and drain cleaners.

REVIEW QUESTIONS

(1) Give the balanced chemical equation (with symbol only) for the laboratory preparation of hydrogen sulphide gas and mention some of its physical properties.
(2) In the Contact Process, why is the mixture of sulphur dioxide and excess air sprayed with concentrated sulphuric acid?
(3) Describe the relevant chemical equation for dehydrating property of concentrated sulphuric acid.

Key Term

- An **oxoacid** is an acid that contains hydrogen, oxygen and at least one other element.

Chemistry in Society

- Nitrogen is a refrigerant gas for freezing food. It is also used in food packaging to keep food fresh, for example, in crisp packets. Aircrafts and car tyres are filled with nitrogen because of its inert property.
- Ammonia is found in many household and industrial cleaning solutions.
- Nitric acid has been used as an oxidiser in liquid fuel rockets. Now, it is replaced by N_2O_4.
- Mineral sulphur is widely used in vulcanisation, a chemical process for converting natural rubber into more durable materials by heating them with sulphur.
- Sulphuric acid is one of the most important industrial chemicals. It is used in petroleum refining to wash impurities out of gasoline and other refinery products. Sulphuric acid is used in processing metals, e.g., in pickling (cleaning) iron and steel before plating them with tin or zinc.

EXERCISES

Q 1 to Q 7 (Understanding)

1. Write TRUE or FALSE for each of the following statements. If FALSE, correct it.
   (a) Nitrogen is present to the extent of about 21 percentage by volume of the air.
   (b) Nitrogen gas is relatively active and supports combustion.
   (c) Ammonia gas is collected by the upward displacement of air.
   (d) Sulphur is a yellow, strong, smelling solid element.
   (e) Hydrogen sulphide turns blue litmus slightly red.

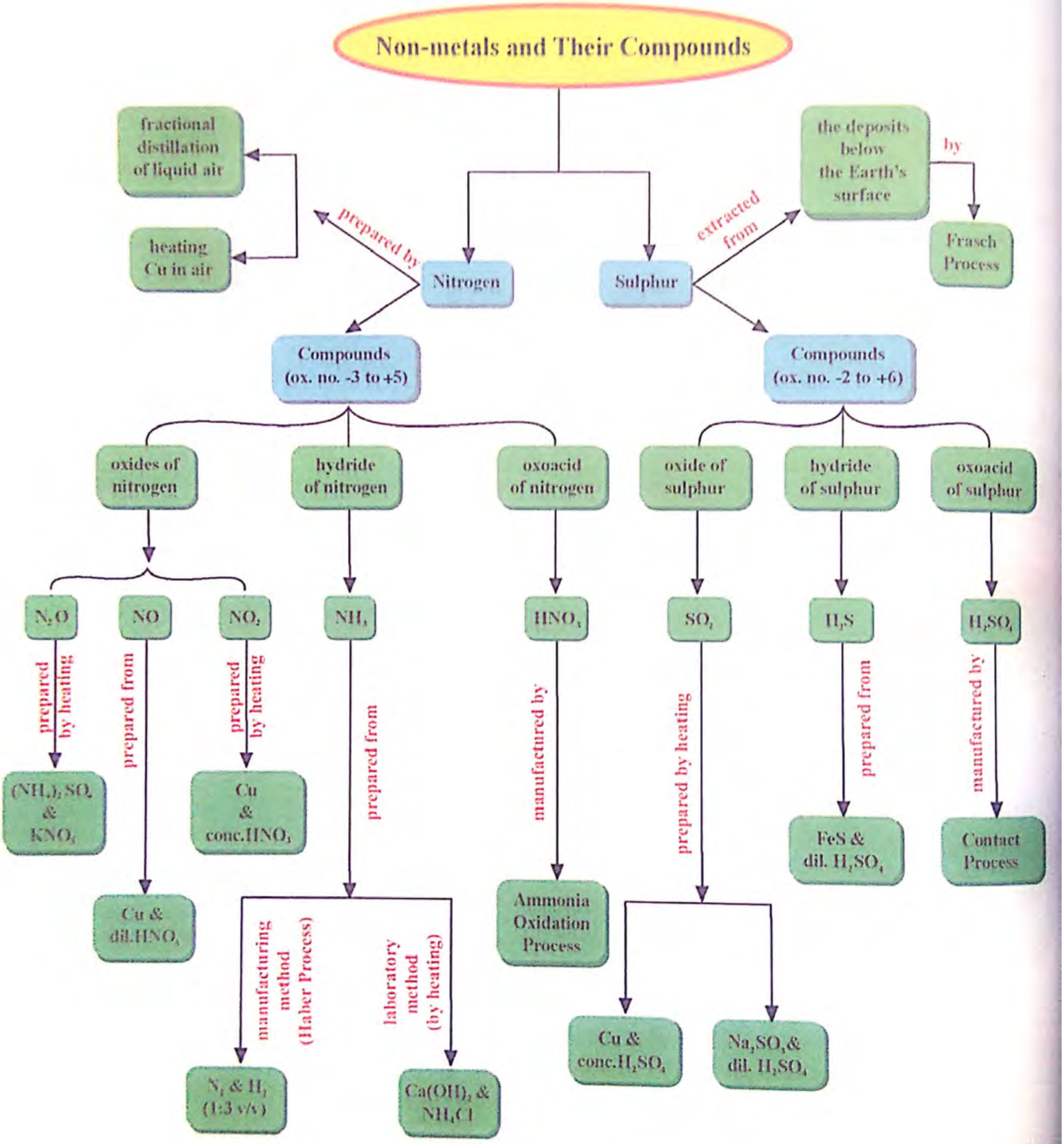
2. Fill in the blanks with suitable words or units or phrases.
   (a) Ammonia gas has a characteristic _____ smell.
   (b) The colour of nitroso iron(II) sulphate is_____.
   (c) Two crystalline forms of sulphur are _____ sulphur and _____ sulphur.
   (d) Sulphur dioxide decolourises colouring matter by _____.
   (e) Vanadium(V) oxide is used as a catalyst in the manufacture of _____.
3. Select the correct word or words given in the brackets.
   (a) Ammonia gas is prepared in the laboratory by heating ammonium chloride with (sodium oxide, calcium hydroxide, calcium oxide).
   (b) Nitrogen gas is manufactured in the industry by (destructive, fractional, vacuum) distillation of liquid air.
   (c) Dry ammonia gas passes over heated sodium to form (sodium oxide, sodium amide, sodium nitride).
   (d) Hydrogen sulphide (oxidises, reduces, displaces) halogens.
   (e) Sulphuric acid can be manufactured by the (Frasch, Haber, Contact) Process.
4. Briefly describe the preparation of each crystalline allotropic forms of solid sulphur.
5. Why is superheated steam forced down under pressure at 160 °C through the outermost pipe in the Frasch process?
6. What happens when sodium amide reacts with water? Give your answer with a relevant chemical equation.
7. Write balanced chemical equations for the following reactions:
   (a) oxidation of ammonia to nitrogen oxide
   (b) preparation of nitric acid from nitrogen oxide

Q 8 to Q 11 (Critical thinking)

8. In the laboratory, a steady stream of ammonia can be prepared by the reaction between ammonium sulphate and an alkali.
   (a) Name the alkali you would use. State whether it is necessary to heat the mixture or not.
   (b) Write the chemical equation (in words and symbols) for the preparation of ammonia gas.
   (c) If concentrated sulphuric acid is used as a drying agent, what would be produced (chemical formula)?
   (d) State how you would collect a sample of dry ammonia gas.
9. In a laboratory, solid substance **X** is obtained by heating of iron filings and sulphur. Gas **Y** is liberated when **X** reacts with dilute sulphuric acid and collected by the upward displacement of air.
   (a) Name solid substance **X** and write chemical equation in symbol only for the formation of solid substance **X**. What is gas **Y**? Give complete chemical equation for the preparation of gas **Y**.
   (b) Why is gas **Y** collected by the upward displacement of air?
10. When gas **Z** is mixed with hydrogen chloride gas, a dense white fume is observed. What is gas **Z**? Write complete chemical equation (in words and symbols) for this reaction.
11. You are provided with concentrated nitric acid, copper and water. Describe the chemical reactions you would use to prepare nitrogen oxide and nitrogen dioxide. How would you distinguish between these two gases?

CHAPTER REVIEW

(Concept Map)

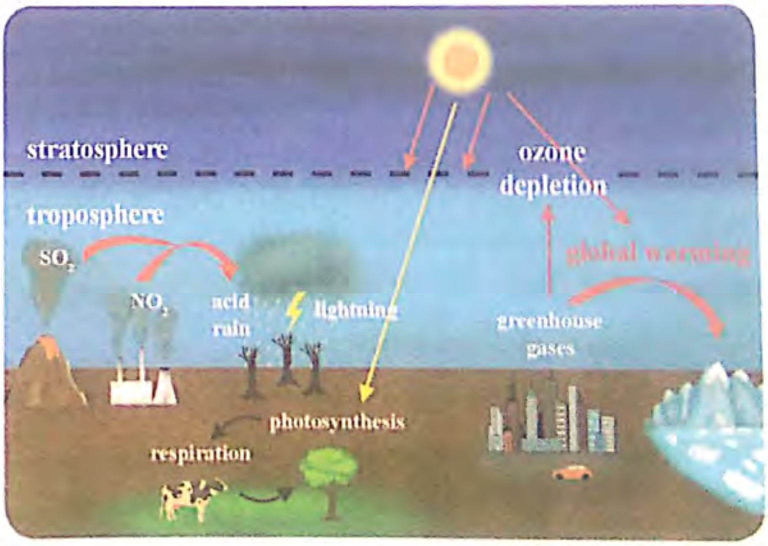


CHAPTER 7

ATMOSPHERIC CHEMISTRY

If we are passengers on a spaceship, we will see that the Earth lives under a thin blanket of air called the atmosphere. The **atmosphere** surrounds the Earth with a layer of gases, commonly known as air, and is retained by the Earth's gravity. Without food, we could live for about a month. Without water, we could live a few days. But, without air, we would die within minutes. We may run short of food, and we may run short of clean, fresh water, but we will not likely run out of air. What we may do is foul (pollute) the air so that we become sick from it and some of us may die prematurely. Nowadays, air pollution problems such as acid rain, ozone depletion, photochemical smog, greenhouse gases and global warming become a critical concern and these problems must be reduced by scientific strategies based on the concepts of atmospheric chemistry. Atmospheric chemistry studies the chemical composition of the natural atmosphere, including, the way gases, liquids and solids in the atmosphere interact with each other, with the Earth's surface and the associated biota, and how human activities may be changing the chemical and physical characteristics of the atmosphere.

This chapter presents the composition of the atmosphere, together with a brief background on some key chemical processes and substances (pollutants) involved in air pollution. In addition, it will look at the impact of these air pollutants, and the prospects for controlling them.



Learning Outcomes

After completing this chapter, students will be able to:

- analyse the composition and structure of the atmosphere;
- explain various types of air pollution and outline the pollutants and their sources;
- summarise the harmful effects of air pollution;
- describe ways of reducing air pollution.

7.1 THE EARTH'S ATMOSPHERE

The Earth is unique among the planets of the solar system, having an atmosphere that is chemically active and rich in oxygen. An abundance of oxygen makes our atmosphere almost unique in the known universe. Nearly all other environments of the universe are dominated by hydrogen or carbon dioxide. Mars, for example, has a much thinner atmosphere that is about 90 percent carbon dioxide. Jupiter has no solid surface; it is made up of 90 percent hydrogen, 9 percent helium and 1 percent other substances.

(a) Composition of Gases in Clean Air

The Earth's atmosphere is a mixture of several gases. It contains elements and compounds that are needed for all living things. As it is a mixture, its composition varies from time to time and from place to place. Table 7.1 shows the composition (percent by volume) of a typical sample of clean air. Out of several minor constituents, the most important is carbon dioxide. The composition of carbon dioxide in the atmosphere is believed to have being increased from 0.03 % in 1900 to its present value of about 0.04 %. It most likely will continue to rise as we burn more and more fossil fuels (coal, oil and gas).

Table 7.1 Composition of Gases in Clean Air

Gas	Composition (% by volume)
nitrogen	~ 78
oxygen	~ 21
carbon dioxide	~ 0.03
water vapour	0 ~ 4
noble gases: - argon - other	 ~ 0.9 ~ 0.002

Although the Earth's atmosphere is fairly simple in composition, its chemistry is very complex and not fully understood. The chemical processes that take place in our atmosphere are induced by solar radiation, but they are connected to natural events and human activities on the Earth's surface. The atmosphere protects life on the Earth by creating pressure allowing for liquid water to exist on the Earth's surface, absorbing ultraviolet solar radiation, warming the surface through heat retention, and reducing the temperature extremes between day and night.

(b) Layers of Atmosphere

The atmosphere is divided into four principal layers: troposphere, stratosphere, mesosphere and thermosphere. The characteristics of the atmosphere greatly depend on altitude (height), time (season), location (latitude) and even solar activity.

(i) Troposphere

Figure 7.1 shows that the troposphere is the lowest layer of the atmosphere and contains about three-fourths of the gases of the atmosphere. The layer nearest the Earth, the troposphere, harbours nearly all living things and almost all human activities. It is hotter near the Earth's surface because heat from the Earth warms this layer. In this layer, pressure and temperature decrease rapidly with height. Warm air rises to the top of the troposphere and cold air sinks. The rising and sinking of air in the troposphere mean that the weather of the Earth takes place in the troposphere.

At the top of the troposphere, there is a thin layer called the **tropopause**. The tropopause is a barrier that keeps air moving from the troposphere to the stratosphere. Sometimes breaks are found in the tropopause, and air from the troposphere and stratosphere can mix.

(ii) Stratosphere

The stratosphere, the second principal layer of the Earth's atmosphere, is above the tropopause. This layer is where we find the **ozone layer** that shields living creatures from life-destroying **ultraviolet radiation**. The maximum concentrations of ozone are found at about 25 km above the Earth's surface or near the middle of the stratosphere. It is a layer of ozone which absorbs most of the ultraviolet radiation from sunlight, resulting in the stratosphere being warmer. Many jet aircraft fly in the stratosphere.

The thin layer above the stratosphere is **stratopause**, which is the boundary between the stratosphere and the mesosphere.

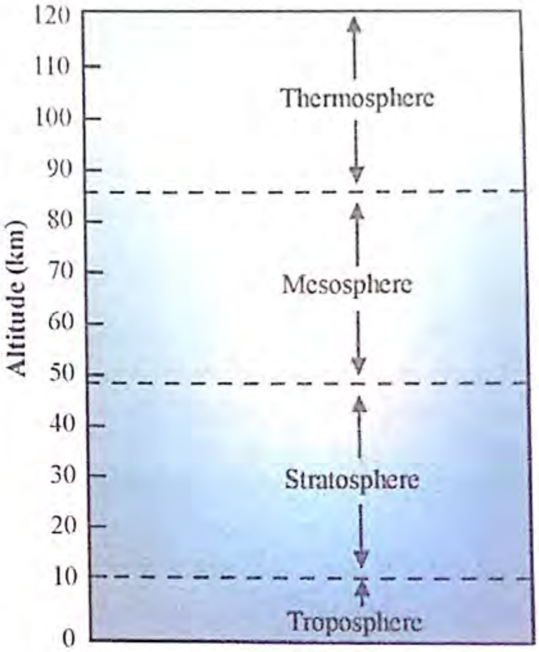


Figure 7.1 Major Layers of the Atmosphere

(iii) Mesosphere

The mesosphere is the third layer in the atmosphere. The air is extremely thin in this layer. Over 99 % of mass of the atmosphere lies below the mesosphere. The temperature decreases in the mesosphere with altitude because of the decrease in density of the air. The proportion of nitrogen to oxygen in this layer is about the same as in the troposphere.

The thin layer above the mesosphere is **mesopause**, which is the boundary between the mesosphere and thermosphere. Astronauts are the only people who travel through the mesopause.

(iv) Thermosphere

The thermosphere is the fourth layer in the atmosphere. The thermosphere is warmed by the absorption of solar X-rays by the nitrogen and oxygen molecules in this layer. The temperature of this layer increases with altitude. The space shuttles orbit the Earth in this layer.

(c) Importance of Nitrogen and Oxygen in the Atmosphere

(i) The nitrogen cycle

Although nitrogen makes up 78 % of the atmosphere, the inert molecular nitrogen (N_2) cannot be used directly by plants or animals. The nitrogen has to be fixed (i.e., combined) with other elements. Figure 7.2 shows the major processes involved in the cycle of nitrogen in nature. Certain types of bacteria convert atmospheric nitrogen to nitrogenous compounds, such as nitrates, ammonia and other compounds suitable for assimilation by algae and plants. Other bacteria convert the nitrogen in compounds back to N_2.

Another important mechanism for producing nitrates from nitrogen gas is lightning. Lightning also serves to fix nitrogen by causing it to combine with oxygen. Nitrogen oxide (NO) and nitrogen dioxide (NO_2) are formed. The chain reactions are:

$$\text{nitrogen} + \text{oxygen} \xrightarrow{\text{lightning}} \text{nitrogen oxide}$$

$$N_2(g) + O_2(g) \xrightarrow{\text{lightning}} 2NO(g)$$

nitrogen oxide + oxygen → nitrogen dioxide

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

Nitrogen dioxide reacts with water to form nitric acid (HNO_3).

nitrogen dioxide + oxygen + water → nitric acid

$$4NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 4HNO_3\,(aq)$$

The nitric acid falls in rainwater, adding to the supply of available nitrates in the oceans and the soil. Nitric acid is converted to nitrate salts in the soil. These nutrients are taken up by plants, which in turn are ingested by animals. Animals use the nutrients from plants to make proteins and other essential biomolecules by assimilation. **Denitrification** reverses **nitrogen fixation** to complete the cycle. For example, certain bacteria decompose animal wastes as well as dead plants and animals to produce free molecular nitrogen from nitrates.

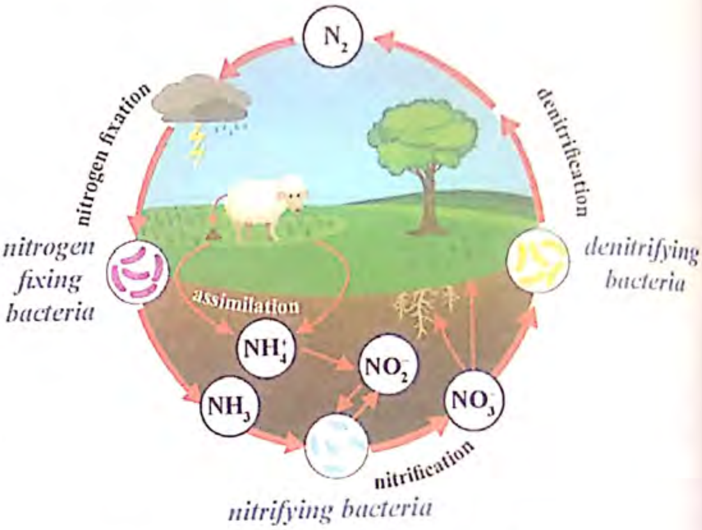


Figure 7.2 The Nitrogen Cycle

(ii) The oxygen cycle

Oxygen (O_2) makes up about 21 % of the atmosphere. Oxygen is used by both plants and animals in the metabolism of foods. It is also used in the decay and the combustion of plant and animal materials. However, the oxygen supply is constantly being replenished by green plants, including one-celled organisms, called phytoplankton, which live in the sea. A simplified oxygen cycle is illustrated in Figure 7.3.

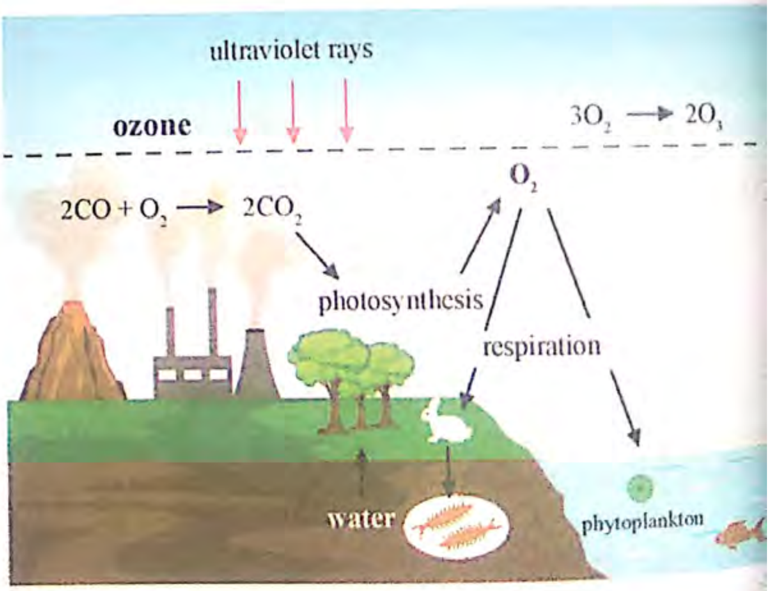


Figure 7.3 The Oxygen Cycle

In the stratosphere, some oxygen is formed by the action of ultraviolet radiation on moisture. Perhaps, some oxygen is converted to ozone (O_3), which in turn absorbs short-wavelength ultraviolet radiation.

oxygen $\xrightarrow{UV}$ ozone

$$3O_2\,(g) \xrightarrow{UV} 2O_3\,(g)$$

REVIEW QUESTIONS

(1) Why does the composition of carbon dioxide increase gradually in air?
(2) Why does the weather take place in the troposphere?
(3) Give the chemical equations by which lightning fixes nitrogen.
(4) How is the oxygen in the atmosphere used and how is it refilled back to the atmosphere?

Key Terms

- **Atmosphere** is the area of air and gas enveloping a celestial body in space, like stars and planets.
- **Troposphere** is the lowermost layer of the atmosphere.
- **Tropopause** is the interface between the troposphere and the stratosphere.
- **Stratosphere** is the second layer of the atmosphere, where temperature increases with altitude due to the presence of ozone.
- **Stratopause** is the thin transitional layer of the atmosphere between the stratosphere and the mesosphere.
- The **ozone layer** is a layer in the stratosphere where ozone gas is more highly concentrated and absorbs the UV radiation from sunlight.
- **Ultraviolet radiation** is a high energy radiation that comes from the Sun; there are three types of UV radiation: UVA, UVB and UVC. UVC has the shortest wavelength, and therefore it is the most dangerous.
- **Mesosphere** is the layer of the atmosphere between the stratosphere and the thermosphere; its temperature decreases with altitude.
- **Mesopause** is the thin transitional layer in the atmosphere, the boundary between the mesosphere and the thermosphere.
- **Thermosphere** is the fourth layer of the atmosphere where gases are extremely thinly distributed.
- **Denitrification** is the process which is the opposite of nitrogen fixation. In this process, some of the nitrates in soil convert to nitrogen gas by denitrifying bacteria.
- **Nitrogen fixation** is the conversion of molecular nitrogen into nitrogen compounds by combining with other elements.

7.2 AIR POLLUTION AND POLLUTANTS

Even before there were human beings, there were cases of natural air pollution. Volcanoes erupted, spewing ash and poisonous gases into the atmosphere. They still do so. In addition to natural activities, air pollution becomes worse as a result of human activities.

(a) Sources of Air Pollution

Air pollution occurs when various gases, finely divided solids, or finely dispersed liquid **aerosols** are released into the atmosphere at rates that exceed the natural capacity of the environment to deal with them. The chemical substances and particles causing air pollution are called **air pollutants**.

There are four main types of air pollution sources. They are *mobile sources* (cars, buses, planes, trucks and trains); *stationary sources* (power plants, oil refineries, industrial facilities and factories); *area sources* (agricultural areas, cities, and wood burning fireplaces); and *natural sources* (wind-blown dust, wildfires and volcanoes) (Figure 7.4).

The air pollutants from these sources can be categorised as:

(1) gaseous air pollutants: oxides of sulphur, nitrogen and carbon, hydrogen sulphide, ozone, volatile organic compounds, radon, etc., and

(2) particulate pollutants: smoke, dust, mist, fumes, smog (fuel smog and photochemical smog), etc.

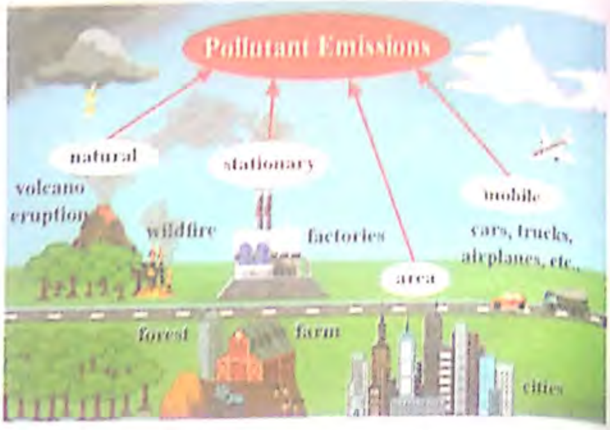


Figure 7.4 Releasing of Air Pollutants into the Atmosphere from Various Sources

(b) Gaseous Air Pollutants

(i) Oxides of sulphur: Oxides of sulphur are produced when sulphur containing fossil fuel is burnt. For example, when sulphur in coal burns, a choking, acid gas sulphur dioxide (SO_2) is formed.

$$\text{sulphur} + \text{oxygen} \longrightarrow \text{sulphur dioxide}$$
$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

Some of the sulphur dioxide reacts further with oxygen in the air to form sulphur trioxide (SO_3) which then reacts with water to form sulphuric acid (H_2SO_4).

$$\text{sulphur dioxide} + \text{oxygen} \longrightarrow \text{sulphur trioxide}$$
$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

$$\text{sulphur trioxide} + \text{water} \longrightarrow \text{sulphuric acid}$$
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Sulphur dioxide is poisonous to both animals and plants. High concentration of SO_2 leads to stiffness of flower buds which eventually fall off from plants. These oxides of sulphur and sulphuric acid are readily absorbed in the respiratory system. It makes life worse for the people who suffer from asthma, bronchitis and other lung diseases.

(ii) Oxides of nitrogen: Nitrogen and oxygen molecules are the main constituents of the air. These gases do not react with each other at normal temperature. When lightning strikes, they combine to form oxides of nitrogen at high altitudes. Then NO_2 is oxidised to nitrate ion, NO_3 which is washed into the soil, where it serves as a fertiliser. (Refer to Section 7.1 c-i.)

Power plants that burn fossil fuels are another major source of oxides of nitrogen. When fossil fuel is burnt at high temperatures, nitrogen and oxygen molecules combine to yield significant quantities of dinitrogen oxide (N_2O), nitrogen oxide (NO) and nitrogen dioxide (NO_2) as shown below:

$$\text{nitrogen} + \text{oxygen} \xrightarrow{\text{high temp.}} \text{dinitrogen oxide}$$
$$2N_2(g) + O_2(g) \xrightarrow{\text{high temp.}} 2N_2O(g)$$

$$\text{nitrogen} + \text{oxygen} \xrightarrow{\text{high temp.}} \text{nitrogen oxide}$$
$$N_2(g) + O_2(g) \xrightarrow{\text{high temp.}} 2NO(g)$$

Nitrogen oxide reacts instantly with oxygen to give NO_2. Rate of production of NO_2 becomes faster when nitrogen oxide reacts with ozone in the stratosphere.

$$\text{nitrogen oxide} + \text{oxygen} \longrightarrow \text{nitrogen dioxide}$$
$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

$$\text{nitrogen oxide} + \text{ozone} \longrightarrow \text{nitrogen dioxide} + \text{oxygen}$$
$$NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)$$

Automobile exhausts contain oxides of nitrogen, besides carbon dioxide, carbon monoxide and unburnt hydrocarbons. High concentration of nitrogen oxide leads to oxygen deprivation. Nitrogen dioxide is an irritant to the eyes and the respiratory system. Higher concentrations of NO_2 damage the leaves of plants and retard the rate of photosynthesis. The gases also contribute to the fading and decolourisation of fabrics. By forming nitric acid, they contribute to the acidity of rainwater.

(iii) Oxides of carbon: Carbon forms two important gases with oxygen: CO and CO_2. Carbon monoxide is produced as a result of the incomplete combustion of carbon. Carbon monoxide (CO) is mainly released into the air by automobile exhaust. Other sources involve incomplete combustion of coal, firewood, petrol, etc.

$$\text{carbon} + \text{oxygen} \xrightarrow{\Delta} \text{carbon monoxide (incomplete combustion)}$$
$$2C\,(s) + O_2\,(g) \xrightarrow{\Delta} 2CO\,(g)$$

Carbon monoxide is a highly poisonous gas to living beings because of its ability to block the delivery of oxygen to the organs and tissues resulting in headache, weak eyesight, nervousness, cardiovascular disorder and even death. In pregnant women who have the habit of smoking, the increased CO level in blood may induce premature birth, spontaneous abortions and deformed babies.

Carbon dioxide is released into the atmosphere by respiration, complete combustion of fuels such as coal, firewood, etc., burning of fossil fuels, and by decomposition of limestone during the manufacture of cement. It is also emitted during volcanic eruptions and deforestation.

$$\text{carbon} + \text{oxygen} \xrightarrow{\Delta} \text{carbon dioxide (complete combustion)}$$
$$C\,(s) + O_2\,(g) \xrightarrow{\Delta} CO_2\,(g)$$

Carbon dioxide (CO_2) emissions impact human health by displacing oxygen in the atmosphere. Breathing becomes more difficult as carbon dioxide levels rise. In closed areas, high levels of carbon dioxide can lead to health complaints such as headaches.

(iv) Hydrogen sulphide: It is estimated that volcanoes are the source of about two-thirds of the sulphur in the air. At high temperatures, the hydrogen sulphide (H_2S) gas given off by a volcanic eruption is oxidised by air.

$$\text{hydrogen sulphide} + \text{oxygen} \longrightarrow \text{sulphur dioxide} + \text{water}$$
$$2H_2S\,(g) + 3O_2\,(g) \longrightarrow 2SO_2\,(g) + 2H_2O\,(g)$$

Some of the SO_2 is reduced as more H_2S from volcanic eruptions forms more sulphur and water.

$$\text{hydrogen sulphide} + \text{sulphur dioxide} \longrightarrow \text{sulphur} + \text{water}$$

$$2H_2S\,(g) + SO_2\,(g) \longrightarrow 3S\,(s) + 2H_2O\,(g)$$

The rest of the SO_2 is released into the atmosphere, where it reacts with oxygen and water to form acid rain.

$$\text{sulphur dioxide} + \text{oxygen} + \text{water} \longrightarrow \text{sulphuric acid}$$

$$2SO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 2H_2SO_4\,(aq)$$

Hydrogen sulphide is responsible for many incidents of occupational toxic exposure. The clinical effects of H_2S depend on its concentration and the duration of exposure. H_2S has been referred to as the "knock down gas" because inhalation of high concentrations can cause immediate loss of consciousness and death.

(v) Ozone: Ground-level or "bad" ozone is not emitted directly into the air, but is created by chemical reactions between oxides of nitrogen (NO_x) and **volatile organic compounds (VOCs)** in the presence of sunlight. Emissions from industrial facilities and electric utilities, motor vehicle exhausts, gasoline vapours and chemical solvents are some of the major sources of NO_x and VOCs. Nitrogen dioxide molecules break apart with sunlight forming nitrogen oxide and atomic oxygen. Atomic oxygen is very reactive and combines with the O_2 in the air to produce ozone.

$$\text{nitrogen dioxide} \xrightarrow{\text{sunlight}} \text{nitrogen oxide} + \text{atomic oxygen}$$

$$NO_2\,(g) \xrightarrow{\text{sunlight}} NO\,(g) + O\,(g)$$

$$\text{atomic oxygen} + \text{oxygen} \longrightarrow \text{ozone}$$

$$O\,(g) + O_2\,(g) \longrightarrow O_3\,(g)$$

Ozone pollution is a concern during the summer months because strong sunlight and hot weather result in harmful ozone concentrations in the air we breathe. Breathing ozone can trigger a variety of health problems including chest pain, coughing and throat irritation. It can worsen bronchitis, emphysema and asthma. It can reduce lung function and inflame the linings of the lungs. Repeated exposure may permanently scar lung tissue.

(vi) Methane gas: It is a powerful greenhouse gas emitted by human activities such as leakage from the natural gas systems and the raising livestock, as well as by natural sources such as wetlands. It has a direct influence on climate, but also a number of indirect effects on human health, crop yields and the quality and productivity of vegetation. Its role is an important precursor to the formation of tropospheric ozone. Though methane (CH_4) is emitted into the atmosphere in smaller quantities than CO_2, it is more effective at trapping infrared radiation. As a result, methane emissions currently contribute to more than one-third of today's anthropogenic warming.

(vii) Volatile organic compounds (VOCs): They are organic chemicals that are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals such as benzene, chloroform, methanol, carbon tetrachloride, formaldehyde, etc. The sources of VOCs are household products including paints, wood preservatives, aerosol sprays, cleansers, disinfectants, moth repellents and air fresheners, automobile fuels, and pesticides. VOCs are also emitted from other products including building materials and furnishings, and office equipment such as copiers, printers, correction fluids, glues, adhesives and permanent markers. High concentrations of VOCs can cause deadly adverse effects on living organisms.

(viii)Radon gas: It is a naturally occurring radioactive gas that can cause lung cancer. Radon (Rn) gas is inert, colourless and odourless. Radon is naturally in the atmosphere in trace amounts. Radon gas seeps into homes from the soil, brick, concrete and stone. Radon flows easily through the porous soil and fissures in the rock. The level and effects of radon accumulation are very high in unventilated buildings. When it reaches the ground surface, the gas is dispersed and diluted to very low concentrations in the outdoor environment.

(c) Particulate Pollutants

Particulate matter (PM) is a term that describes extremely small solid particles and liquid droplets suspended in the air. Particle pollution mainly comes from motor vehicles, wood burning and industries. During forest fires or dust storms, particle pollution can reach extremely high concentrations. Particulate matter can be made up of a variety of components including nitrates, sulphates, organic chemicals, metals, soil or dust particles, allergens, smoke, mists, fumes and smog.

Smoke particulates consist of solid or mixture of solid and liquid particles formed during combustion of organic matter, e.g., cigarette smoke, smoke from burning of fossil fuels, garbage and dry leaves, oil smoke, etc.

Dust is composed of fine solid particles (over 1 μm in diameter), produced during crushing, grinding and attribution of solid materials, e.g., sand from sand blasting, sawdust from wood works, pulverised coal, cement and fly ash from factories, dust storms, etc.

Mists are produced by particles of spray liquids and by condensation of vapours in air, e.g., sulphuric acid mist, and herbicides and insecticides mists, etc.

Fumes are generally obtained by the condensation of vapours during sublimation, distillation, boiling and several other chemical reactions.

Smog is the term derived from the words *smoke* and *fog*. Two distinct types of smog can be recognised: fuel smog and photochemical smog. The fuel smog (sulphurous smog) usually accompanies cold damp air. It is caused by the combustion of sulphur-bearing fossil fuels, particularly coal. The combustion of coal produces ash, soot, CO_2, CO, high concentrations of oxides of sulphur such as SO_2 and SO_3. Usually, fuel smog is characterised by high levels of particulate matter, solid and liquid particles of greater than molecular size.

Figure 7.5 Air Pollution by Photochemical Smog around Hledan Centre, Yangon

The **photochemical smog** usually occurs during dry, sunny weather. It results from the action of sunlight on unsaturated hydrocarbons and oxides of nitrogen (NO_x) produced by automobiles and factories. When fossil fuels such as petrol, diesel, etc. are burnt, a variety of pollutants are emitted into the Earth's troposphere. Two of the major pollutants are hydrocarbons (unburnt fuels) and oxides of nitrogen (NO_x). Figure 7.5 illustrates the air pollution by photochemical smog around Hledan Centre, Kamayut Township where usually has heavy traffic.

The size of particles affects their potential to cause health problems.

Figure 7.6 Size of Particulate Matter Compared with Human Hair and Fine Beach Sand

PM_{10} (particles with a diameter of 10 μm or less): these particles (dust, pollen, mold, etc.) are small enough to pass through the throat and nose and enter the lungs.

$PM_{2.5}$ (particles with a diameter of 2.5 μm or less): these particles (combustion particles, organic compounds, etc.) are so small that they can get deep into the lungs and into the bloodstream. Note that PM_{10} includes $PM_{2.5}$ (Figure 7.6).

REVIEW QUESTIONS

(1) Where can the accumulation of radon be found in our environment? What are the impacts of radon?

(2) What is photochemical smog? Describe the factors that favour the formation of photochemical smog.

(3) What are the main types of air pollution sources? Categorise the sources of air pollution for each of the following: oil refineries, agricultural areas, volcanoes, buses.

Key Terms

- **Air pollution** can be defined as the presence of toxic chemicals, particulates, or biological materials in the air, at levels that cause discomfort, disease, or death to humans, damage other living organisms, or damage the natural environment.
- **Air pollutants** are any substances in the air that can, in high enough concentration, have adverse effects on humans and the environment.
- **Aerosols** are the suspension of fine solid or liquid particles in gas (e.g. smoke, fog).
- **Volatile Organic Compounds (VOCs)** are organic chemicals that are emitted as gases from certain solids or liquids.
- **Particulate matter (PM)** is a mixture of tiny pieces of solid particles and liquid droplets in the air, and can consist of hundreds of different chemicals, including carbon, sulphur, nitrogen and metal compounds.
- **Photochemical smog** is the haze in the atmosphere accompanied by high levels of ozone and oxides of nitrogen, caused by the action of sunlight on pollutants.
- **PM_{10}** refers to the particles with a diameter of 10 μm, and they are also called the fine particles.
- **$PM_{2.5}$** refers to the atmospheric particulate matter that has a diameter of less than 2.5 μm, which is about 3 % of the diameter of human hair.

7.3 CONSEQUENCES OF AIR POLLUTION

Air pollution threatens the health of humans and other living beings on our planet. It causes acid rain and depletion of the ozone layer contributing to global warming.

(a) Acid Rain

Rainwater normally has a pH of 5.6 due to the presence of H^+ ions formed by the reaction of rainwater with carbon dioxide present in the atmosphere producing carbonic acid (H_2CO_3).

water + carbon dioxide ⟶ carbonic acid ; carbonic acid ⟶ hydrogen ion + hydrogen carbonate ion

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)\ ;\ H_2CO_3\,(aq) \longrightarrow H^+\,(aq) + HCO_3^-\,(aq)$$

When the pH of the rainwater drops below 5.6, it is called **acid rain**. Acid rain usually has a pH between 4.2 and 4.4.

Industrial plumes contain sulphur dioxide and oxides of nitrogen. These gases convert to acids such as sulphuric acid and nitric acid. Nitric acid causes acid deposition that can damage trees and marine ecosystems due to a decrease in the pH of soil and water (Figure 7.7).

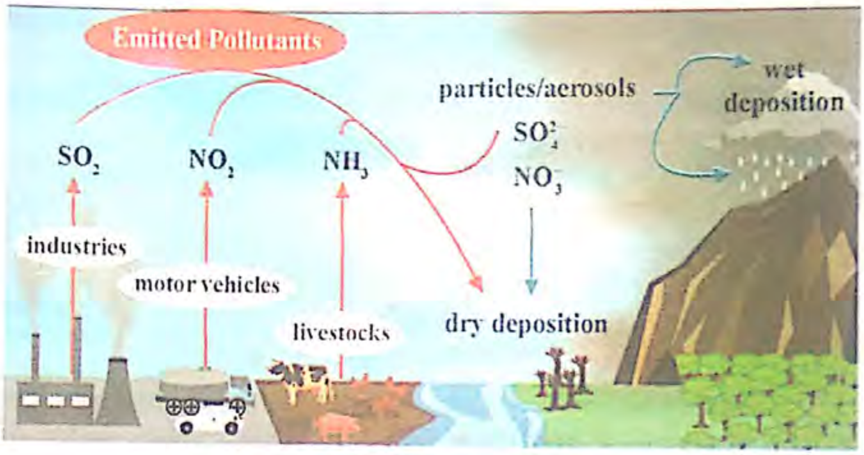


Figure 7.7 Deposition of Acids on the Earth's Surface

sulphur dioxide + oxygen + water ⟶ sulphuric acid

$$2SO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 2H_2SO_4\,(aq)$$

nitrogen dioxide + oxygen + water ⟶ nitric acid

$$4NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 4HNO_3\,(aq)$$

These acids may cause dry or wet deposition on both land and water. The deposition of acids can lamage the natural surface water system as well as the grasslands, forests and other vegetation.

b) Ozone Depletion

The depletion of the protective ozone layer could occur due to the presence of oxides of nitrogen ı the stratosphere. This ozone reacts rapidly with the NO to regenerate NO_2. NO_2 is a brown gas and at ufficiently high levels can contribute to haze.

nitrogen oxide + ozone ⟶ nitrogen dioxide + oxygen

$$NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)$$

The main reason for ozone layer depletion is the release of **chlorofluorocarbons (CFCs)**, also nown as freons. These compounds are non-reactive, non-flammable, non-toxic organic molecules and are ierefore used in refrigerators, air conditioners, in the production of plastic foam and by the electronic industry for cleaning computer parts. Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and eventually reach the stratosphere. In the stratosphere, they are broken down by powerful UV radiation, releasing chlorine free radicals.

dichlorodifluoromethane $\xrightarrow{UV}$ chlorine radical + chlorodifluoromethyl radical

$$CF_2Cl_2\,(g) \xrightarrow{UV} Cl^{\bullet}\,(g) + {}^{\bullet}CF_2Cl\,(g)$$

The chlorine radical ($Cl^{\bullet}$) then reacts with stratospheric ozone to form chlorine monoxide radicals ($ClO^{\bullet}$) and molecular oxygen.

chlorine radical + ozone $\longrightarrow$ chlorine monoxide radical + oxygen

$$Cl^{\bullet}\,(g) + O_3\,(g) \longrightarrow ClO^{\bullet}\,(g) + O_2\,(g)$$

Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

chlorine monoxide radical + atomic oxygen $\longrightarrow$ chlorine radical + oxygen

$$ClO^{\bullet}\,(g) + O\,(g) \longrightarrow Cl^{\bullet}\,(g) + O_2\,(g)$$

The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously releasing chlorine radicals into the stratosphere and damaging the ozone layer.

(c) Climate Change

Carbon dioxide is one of the most common greenhouse gases. These gases trap heat in the atmosphere and contribute to climate change. Other greenhouse gases include methane and chlorofluorocarbons (CFCs). Another pollutant associated with climate change is sulphur dioxide, a component of smog. But these gases also reflect light when released in the atmosphere. This keeps sunlight out and creates a cooling effect. Airborne particles, depending on their chemical makeup, can also have a direct effect on climate change. They can change or deplete nutrients in soil and waterways, harm forests and crops, and damage cultural icons such as monuments and statues.

(d) Harmful Effect of Pollutants on Natural Matter Cycles

The most common types of matter cycling between living and non-living things are the elements nitrogen and carbon. Tiny atoms of nitrogen and carbon are able to move around the planet through cycles. When people cut down forests, make more factories, and drive more cars that burn fossil fuels, the way that carbon and nitrogen move around the Earth changes. These changes form more greenhouse gases in the atmosphere; this causes climate change and various environmental problems.

(i) Harmful effect on the nitrogen cycle

The nitrogen cycle is discussed in Section 7.1 (c-i). Environmental problems can be caused in several ways when the nitrogen cycle has interfered. During fuel combustion, various compounds, including oxides of nitrogen, are released. Dinitrogen oxide (N_2O) is a greenhouse gas, which increases the Earth's temperature when it is present in the atmosphere too extensively. It can also react with ozone in the atmosphere, so that the ozone layer is broken down. When ozone depletion occurs, humans and animals can experience serious sunburns and skin cancer. Substantial intervention in the nitrogen cycle has resulted from humans by fixing nitrogen industrially in the manufacture of nitrogen-based fertiliser. Intensive fertilisation of agricultural soils can increase the rates at which nitrogen in the form of ammonia is volatilised and lost to the air. It can also speed the microbial breakdown of ammonium and nitrates in the soil, enhancing the release of oxides of nitrogen. Atmospheric nitrogen deposition has caused nitrogen enrichment and **eutrophication** of lakes.

(ii) Harmful effect on the carbon cycle

Figure 7.8 shows the carbon cycle in our global ecosystem. The transfer of carbon dioxide to and from the atmosphere is an essential part of the carbon cycle. Carbon dioxide is produced when any form of carbon or a carbon-containing compound is burnt in an excess of oxygen. Many carbonates give off CO_2 when heated, and all carbonates give off CO_2 when treated with acid.

$$\text{calcium carbonate} \xrightarrow{\Delta} \text{calcium oxide} + \text{carbon dioxide}$$

$$CaCO_3\,(s) \xrightarrow{\Delta} CaO\,(s) + CO_2\,(g)$$

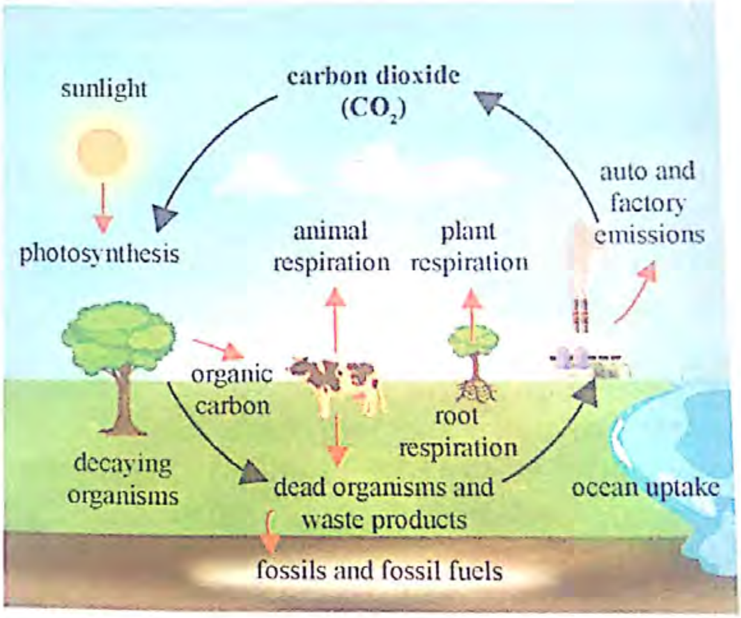


Figure 7.8 The Carbon Cycle

$$\text{calcium carbonate} + \text{hydrochloric acid} \longrightarrow \text{calcium chloride} + \text{water} + \text{carbon dioxide}$$

$$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)$$

Carbon dioxide is also a by-product of the fermentation of sugar (glucose).

$$\text{glucose} \xrightarrow{\text{yeast}} \text{ethanol} + \text{carbon dioxide}$$

$$C_6H_{12}O_6\,(aq) \xrightarrow{\text{yeast}} 2C_2H_5OH\,(aq) + 2CO_2\,(g)$$

Carbohydrates and other complex carbon-containing molecules are consumed by animals, which respire and release CO_2 as an end product of metabolism.

$$\text{glucose} + \text{oxygen} \longrightarrow \text{carbon dioxide} + \text{water}$$

$$C_6H_{12}O_6\,(aq) + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6H_2O\,(l)$$

Another major source of CO_2 is volcanic activity. Carbon dioxide is removed from the atmosphere by photosynthetic plants and certain microorganisms.

$$\text{carbon dioxide} + \text{water} \longrightarrow \text{glucose} + \text{oxygen}$$

$$6CO_2\,(g) + 6H_2O\,(l) \longrightarrow C_6H_{12}O_6\,(aq) + 6O_2\,(g)$$

When plants and animals die, the carbon in their tissues is oxidised to CO_2 and returns to the atmosphere. In addition, there is a dynamic equilibrium between atmospheric CO_2 and carbonates in the oceans and lakes.

Humans cause environmental problems by interfering with the carbon cycle in several ways. Depletion of plants and trees by deforestation can reduce the absorption of carbon dioxide. Humans cause the release of great amounts of carbon dioxide to the atmosphere through industrial processes, such as coal and oil combustion. As a result of these effects, the carbon dioxide levels in the atmosphere have increased greatly over recent years. Too much carbon dioxide in the atmosphere can cause the Earth to warm up. This will gradually cause all kinds of negative effects, for example, melting of ice from the Arctic and Antarctic causing floods on other continents, loss of animal habitats and changes in the types of natural vegetation.

REVIEW QUESTIONS

(1) How do you decide whether the acid rain occurs or not? Explain the formation of acid rain with the appropriate chemical equations.

(2) Explain the formation of haze. Describe how haze can impact a city and its inhabitants.

(3) How do humans cause environmental problems by influencing the carbon cycle?

Key Terms

- **Acid rain** is a term referring to the deposition of a mixture from wet (rain, snow, sleet, fog, cloud water and dew) and dry (acidifying particles and gases) acidic components.
- **Ozone depletion** is the gradual thinning of the Earth's ozone layer in the stratosphere caused by the release of chemical compounds containing gaseous chlorine or bromine from industry and other human activities.
- **Chlorofluorocarbons (CFCs)** are compounds of carbon, hydrogen, chlorine, and fluorine, typically gases used in refrigerants and aerosol propellants. They are harmful to the ozone layer in stratosphere owing to the release of chlorine atoms on exposure to ultraviolet radiation.
- **Eutrophication** is excessive richness of nutrients in a lake or other body of water, frequently due to run-off from the land. which causes a dense growth of plant life.

7.4 REDUCING AIR POLLUTION

Since air pollution is mainly caused by the combustion of fossil fuels, the controlled consumption of these fuels can reduce air pollution. There are ways to prevent, control and eventually reduce air pollution.

(1) The most basic solution for air pollution is to move away from fossil fuels, replacing them with alternative energies like solar, water and wind.

(2) By adopting responsible habits (i.e., turn off unnecessary lights and use natural light, unplug unused electronic devices) and use more efficient power saving devices.

(3) Shifting to electric vehicles and promoting shared mobility (i.e., carpooling and public transports) could reduce air pollution.

(4) The air pollution can be reduced by applying **green building technology** from planning to design, construction, operation, maintenance, renovation and demolition.

In addition, monitoring air quality has become very important to pollution detection. It can help to control air pollution and eventually improve air quality.

How air quality is measured

Air quality is measured by devices using laser-based technologies, flame ionisation, etc. These devices are located close to the traffic and close to industrial zones. In Myanmar, Yangon City Development Committee (YCDC) measures air quality in 74 places in Yangon in cooperation with the Ministry of Natural Resources and Environmental Conservation. Figure 7.9 illustrates the apparatus used in the measuring air quality at Kamayut Township, Yangon.

All the collected data are compiled into a value scale, called the **Air Quality Index (AQI)**.

An AQI is defined as an overall scheme that transforms weighted values of individual air pollution related parameters (PM_{10}, $PM_{2.5}$, NO_2, SO_2, CO, O_3, NH_3 and Pb) into a single number or set of numbers.

The purpose of AQI is to help people understand what local air quality means to their health. To make it easier to understand, the AQI is divided into six categories described in Table 7.2.

Figure 7.9 A Photo of the Measuring Air Quality at Kamayut Township, Yangon

Table 7.2 Air Quality Index Colour Code Chart

Air Quality Index levels of health concern	Numerical value	Meaning
good	0 to 50	Air quality is considered satisfactory, and air pollution poses little or no risk.
moderate	51 to 100	Air quality is acceptable; however, for some pollutants there may be a moderate health concern for a very small number of people who are unusually sensitive to air pollution.
unhealthy for sensitive groups	101 to 150	Members of sensitive groups may experience health effects. The general public is not likely to be affected.
unhealthy	151 to 200	Everyone may begin to experience health effects; members of sensitive groups may experience more serious health effects.
very unhealthy	201 to 300	Warnings are given for emergency conditions of health. The entire population is more likely to be affected.
hazardous	301 to 500	Health alert: everyone may experience more serious health effects.

REVIEW QUESTIONS

(1) How can we reduce air pollution?
(2) Why do you think it is important that air pollution be reduced?
(3) Which parameters should be measured for the determination of the air quality index?
(4) What is an air quality index and what are the benefits of AQI?

Key Terms

- **Green building technology** is the implementation of design in structures or buildings that are environmentally accountable and resource-efficient throughout the building's life cycle.
- **AQI** is an index for reporting the daily air quality index. It is an overall scheme that transforms weighted values of individual air pollution related parameters into a set of numbers.

Chemistry in Society

- Smoking tobacco through the use of cigarettes and cigars also releases toxic pollutants into the air.
- The garbage released out of houses gets dumped as landfills which generate methane, a highly inflammable gas. Methane can cause explosive compounds on reacting with the air.
- The plastic we use in our daily life, from bottles to bags, also releases greenhouse gases contributing to climate change.

EXERCISES

Q 1 to Q 6 (Understanding)

1. We generally divide the atmosphere into four regions. What are those four regions? Which characteristics define the specification of atmospheric layers? Where is ozone located?
2. Explain the processes that have a warming effect on the stratosphere.
3. What emissions from human activities lead to ozone depletion? What are the reactions involved for ozone layer depletion in the stratosphere?
4. Briefly outline the main processes of the nitrogen and carbon cycles.
5. (a) What is smog? Briefly describe the formation of photochemical smog.
   (b) Why is smog considered to be an environmental problem?
6. Identify and describe three detrimental effects of acid rain.

Q 7 to Q 10 (Critical thinking)

7. NO and NO_2 are both nitrogen compounds.
   (a) Explain how each of these compounds is formed.
   (b) What effect does each of these compounds have in the environment?

8. You are provided two statements (X) and (Y).

No.	Statement (X)	Statement (Y)
(a)	The pH of normal rainwater is 5.6	Carbon dioxide present in the atmosphere dissolves in rainwater and forms carbonic acid.
(b)	Photochemical smog is oxidising in nature.	Photochemical smog contains NO_2 and O_3, that are formed due to the sequential reactions.
(c)	Carbon dioxide is one of the greenhouse gases.	Respiratory functions of animals and plants produce a large amount of carbon dioxide.
(d)	Ozone is destroyed by solar radiation in upper stratosphere.	Thinning of the ozone layer allows excessive ultraviolet radiation to reach the surface of the Earth.
(e)	Greenhouse gases are observed in houses used to grow plants and these are made of green glass.	Greenhouse name has been given because glass houses are made of green glasses.

Choose the correct option out of the choices given below.

(i) Both (X) and (Y) are true and (Y) is the reason of (X).
(ii) Both (X) and (Y) are true but (Y) is not the reason of (X).
(iii) (X) is not correct but (Y) is correct.
(iv) Both (X) and (Y) are not correct.

9. Carbon dioxide is the most important minor constituent in the atmosphere. What would happen:
(a) if the amount of carbon dioxide in the atmosphere becomes very high?
(b) if the amount of carbon dioxide in the atmosphere becomes very low?

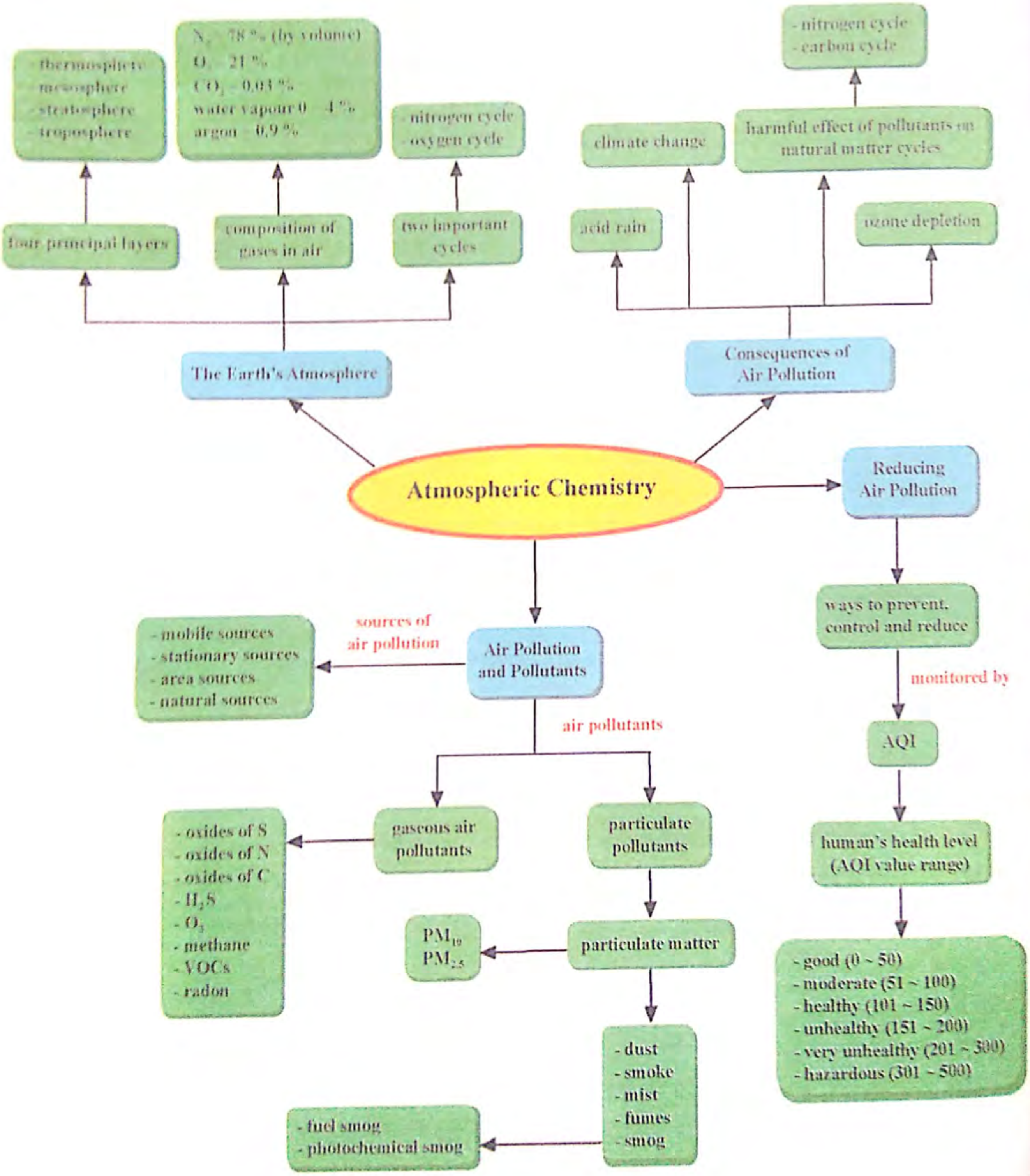
10. Sulphur dioxide, oxides of nitrogen and particulate matters are all atmospheric pollutants. Describe the causes and effects of these pollutants.

11. What are some of the human activities which release greenhouse gases? Give your suggestions on how you would reduce global warming. **(Analytical thinking)**

12. Explain briefly on the Real-Time AQI Map of Yangon showing 192 on 9th February, 2020. What should you do if AQI value is greater than 200? **(Problem solving)**

CHAPTER REVIEW

(Concept Map)



CHAPTER
8

ORGANIC CHEMISTRY: HYDROCARBONS AND ALCOHOLS

The existence and behaviour of carbon compounds are two of the most intriguing aspects of modern-day chemistry. Unlike compounds formed from other elements, carbon compounds are far more numerous and varied. In the living world, carbon combines with hydrogen, oxygen, nitrogen and sulphur to form millions of compounds. Compounds containing carbon and hydrogen as well as their derivatives are also known as organic compounds.

Organic compounds make up the cells and other structures of organisms and carry out life processes. They are also the basic components of many of the cycles that support and drive life on the Earth. For example, the carbon cycle includes the exchange of carbon between plants and animals in photosynthesis and cellular respiration. Organic compounds combine with metals that are important industrially. Hence, one should study organic chemistry which deals with organic compounds. The petroleum industry and the myriad of polymer products we find indispensable are among the many industries that depend on organic chemistry. Cold remedies, cleaning products, convenience foods, and countless drugs, both legal and illegal, have all come about from our understanding of organic chemistry.

In this chapter, you will have an opportunity to learn something about the system used to identify organic compounds by introducing the most common classes or "families" of organic compounds. These compounds are grouped according to their structural features, and the naming system. Moreover, you will also learn the chemical behaviour of the simplest organic compounds, the hydrocarbons and alcohols.


Sucrose


Starch


Cosmetic


Medicine


Wax


Glycerin


Methylated spirit


Hand sanitiser


Polyethylene

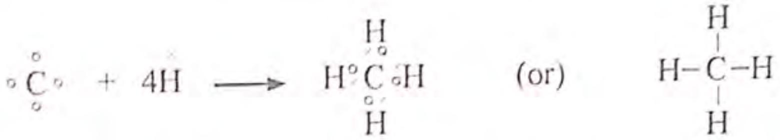
Learning Outcomes

After completing this chapter, students will be able to:

- outline the functional groups and families of organic compounds;
- identify the saturated and unsaturated hydrocarbons;
- describe the preparations and properties of hydrocarbons and their structural isomers;
- apply the preparation methods and properties of alcohols.

8.1 FAMILIES OF ORGANIC COMPOUNDS

There are at least ten million different organic compounds currently on the planet and every one of them is unique in its chemical structure and specific properties. The carbon atom is central to all organic compounds. Organic compounds contain carbon and hydrogen in which there is at least one C-C or C-H bond and sometimes a few other elements such as oxygen, nitrogen, sulphur, phosphorus and the halogens. The bonding between carbon and hydrogen in the simplest organic compound, methane, may be given as an example.



$$\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot + 4H \longrightarrow H{:}\overset{H}{\underset{H}{\overset{..}{\underset{..}{C}}}}{:}H \quad \text{(or)} \quad H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$$

The bonding patterns of carbon with its valence of four form single, double and triple bonds. Carbon forms a large number of compounds with hydrogen which are collectively called **hydrocarbons**. Hydrocarbons are compounds in which carbon and hydrogen atoms bonded to each other by covalent bonds. These molecules are further classified as saturated or unsaturated. The hydrocarbon compounds that contain only single bonds are called **saturated hydrocarbons**, and are classified as ***alkanes***. Those that contain double or triple bonds are called **unsaturated hydrocarbons** which include ***alkenes***, ***alkynes*** and ***aromatic compounds***.

(a) Formulae of Organic Compounds

The **general formula** is used to represent the families of organic compounds. The **molecular formula** of an organic compound is the actual number of atoms of each element present in a molecule. A **full structural formula** (graphic formula or displayed formula) shows every bond and atom in what order atoms are attached, but does not portray accurately the three-dimensional geometry of the molecule. A **condensed structural formula** is a more compact way of drawing the structural formula of a molecule.

(b) Functional Groups

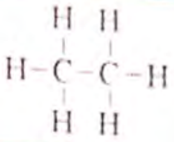
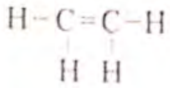
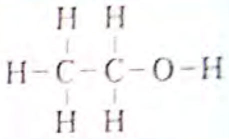
Organic compounds are classified according to the different types of **functional groups**. An alkane is a compound that lacks functional groups. The functional group in an alkene is a carbon-carbon double bond. The functional group in an alkyne is a carbon-carbon triple bond. Organic compounds typically contain other elements in addition to carbon and hydrogen. A functional group is an atom or a group of atoms that determine the chemical properties of a compound. An **alcohol** is an organic compound with a hydroxyl (OH) functional group attached to a carbon atom. Alcohols can often be represented by the general formula ROH, where R is an alkyl group.

(c) Homologous Series

A **homologous series** is a group of organic compounds, usually listed in order of increasing size, that have the same functional group and similar structure (and hence also similar chemical properties) and whose structures differ only by the number of CH_2 units in the main carbon chain.

In a homologous series, all the compounds fit the same general formula. As the chain gets longer, the compounds show a gradual change in properties. Different formulae, functional groups and homologous series for organic compounds are shown in Table 8.1.

Table 8.1 Different Formulae, Functional Groups and Homologous Series for Organic Compounds

Compound	Ethane	Ethene	Ethyne	Ethanol
general formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}	$C_nH_{2n+1}OH$ (or) $C_nH_{2n+2}O$
molecular formula	C_2H_6	C_2H_4	C_2H_2	C_2H_6O
full structural formula	 $\begin{array}{c}\quad H \quad H \\ \quad \vert \quad\; \vert \\ H-C-C-H \\ \quad \vert \quad\; \vert \\ \quad H \quad H\end{array}$	 $\begin{array}{c}H-C=C-H \\ \quad \vert \quad\; \vert \\ \quad H \quad H\end{array}$	$H-C\equiv C-H$	 $\begin{array}{c}\quad H \quad H \\ \quad \vert \quad\; \vert \\ H-C-C-O-H \\ \quad \vert \quad\; \vert \\ \quad H \quad H\end{array}$
condensed structural formula	CH_3CH_3	$CH_2=CH_2$	$CH\equiv CH$	CH_3CH_2-OH
functional group	-	$C=C$	$C\equiv C$	OH
homologous series	CH_4 C_2H_6 C_3H_8 etc.	C_2H_4 C_3H_6 C_4H_8 etc.	C_2H_2 C_3H_4 C_4H_6 etc.	CH_3OH C_2H_5OH C_3H_7OH etc.

REVIEW QUESTIONS

(1) What is the difference between two consecutive members in a homologous series in terms of:
(a) molecular mass (b) the number of atoms of each element?

(2) Ethanol is an organic compound.
(a) How many carbon atoms does it contain? (b) Which family does it belong to?
(c) Why does it belong to this family? (d) Draw a full structural formula of it.

(3) An alkane has five carbon atoms. Give its molecular formula.

Key Terms

- **Hydrocarbons** are the compounds that contain only carbon and hydrogen.
- **Saturated hydrocarbons** are hydrocarbons that contain only single bonds between carbon atoms.
- **Unsaturated hydrocarbons** are hydrocarbons that contain double or triple covalent bonds between adjacent carbon atoms.
- **Alkanes** are hydrocarbons that contain only single bonds.
- **Alkenes** are unsaturated hydrocarbons that contain a carbon-carbon double bond.
- **Alkynes** are unsaturated hydrocarbons that contain a carbon-carbon triple bond.
- A **general formula** is a type of empirical formula that represents the composition of any members of an entire class of compounds.
- The **molecular formula** is a chemical formula that gives the actual number of atoms of each element in each molecule of a substance.
- The **full structural formula** is a formula which shows every bond between every atom in the molecule.
- A **condensed structural formula** is a formula which omits bonds where they can be assumed, and groups atoms together.

- **A functional group** is a group of atoms that represents a potential reaction site in an organic compound.
- **Alcohol** is a hydrocarbon derivative in which a hydrogen atom attached to a carbon atom has been replaced by an OH group.
- **Homologous series** is a series of compounds in which each member differs from the next by a specific number and kind of atoms.

8.2 THE ALKANES

The alkanes are the simplest family of organic compounds and are referred to as the "saturated hydrocarbons".

Alkanes contain only carbon and hydrogen atoms. Every carbon in an alkane has a tetrahedral environment and is bonded to four other atoms, each of which is either carbon or hydrogen and is bonded by means of a single bond.

Alkanes form a homologous series, with the general formula C_nH_{2n+2}, where n is a number equal to or greater than 1. The representative alkane given here is ethane, C_2H_6. The ball-and-stick model shown is the more accurate three-dimensional model of ethane compared with its structural formula.

(a) Nomenclature of Alkanes

The root name for an organic compound indicates the number of carbon atoms in the longest continuous chain of carbon atoms as shown in Table 8.2.

Table 8.2 Root Names of Alkanes in the IUPAC (International Union of Pure and Applied Chemistry) Nomenclature System

Number of carbon atoms	Root name	Name of alkane	Molecular formula
1	meth-	methane	CH_4
2	eth-	ethane	C_2H_6
3	prop-	propane	C_3H_8
4	but-	butane	C_4H_{10}
5	pent-	pentane	C_5H_{12}
6	hex-	hexane	C_6H_{14}
7	hept-	heptane	C_7H_{16}
8	oct-	octane	C_8H_{18}
9	non-	nonane	C_9H_{20}
10	dec-	decane	$C_{10}H_{22}$

Alkyl groups

The alkyl groups (also known as alkyl radicals) are derived from the corresponding alkanes by the removal of a hydrogen (H) atom and are called alkyl radicals or groups. Alkyl groups are represented generally as R-, where R is C_nH_{2n+1}.

Alkane (R-H)	Name
CH_4	methane
CH_3-CH_3	ethane
$CH_3-CH_2-CH_3$	propane

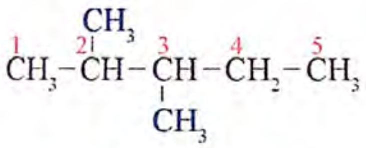
Alkyl group (R-)	Name
CH_3-	methyl
CH_3-CH_2	ethyl
$CH_3-CH_2-CH_2$	*n*-propyl
$H_3C-CH(CH_3)-$	*iso*-propyl

The naming system currently in use is the IUPAC system.

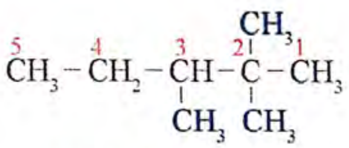
The IUPAC (International Union of Pure and Applied Chemistry) System or Geneva System:
In order to name the alkanes, a simple list of rule is as follows:

(1) Identify and name the longest carbon chain.
(2) Number the C atoms in this longest chain beginning at the end nearest the first branching.
(3) Assign the name and position number to each substituent. Arrange the substituents in alphabetical order.
(4) Use the appropriate prefix to group like substituents: di, tri, tetra, penta, and so on. Do not consider these prefixes when alphabetising attached groups.
(5) Write the name as a single word. Use hyphens to separate numbers and letters. Use comma to separate numbers. Do not leave any spaces.

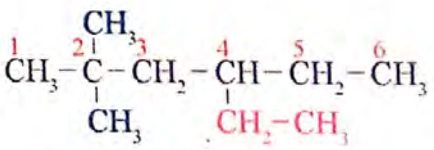
Some examples are:


$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H(CH_3)-\overset{4}{C}H_2-\overset{5}{C}H_3$

2,3-dimethylpentane


$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H(CH_3)-\overset{2}{C}(CH_3)_2-\overset{1}{C}H_3$

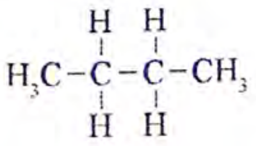
2,2,3-trimethylpentane


$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}H_2-\overset{4}{C}H(CH_2-CH_3)-\overset{5}{C}H_2-\overset{6}{C}H_3$

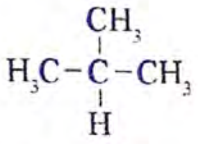
4-ethyl-2,2-dimethylhexane

(b) Isomers of Alkanes

Two or more compounds with the same molecular formula but different arrangements of atoms and have different properties from each other are called **isomers**. Several different types of isomerism are possible for organic compounds. *Straight chain* and *branched-chain* isomers are examples of **structural isomers** that differ in the order in which the atoms are bonded together. All of the alkanes containing four or more carbon atoms show structural isomerism. For example, there are two isomers of butane, C_4H_{10}. They can either arrange in a straight chain of four carbon atoms (*n*-butane) or they can form a chain of three carbon atoms with one side chain (*iso*-butane). So, the two compounds, *n*-butane and *iso*-butane are structural isomers of C_4H_{10}.


$H_3C-CH_2-CH_2-CH_3$

n-butane
(straight chain)

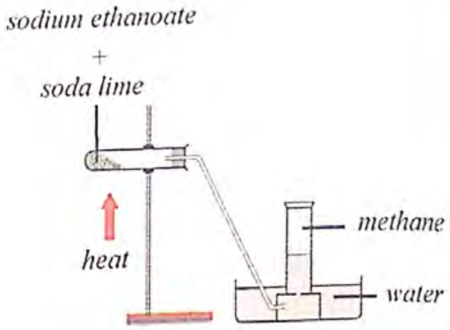

$H_3C-CH(CH_3)-CH_3$

iso-butane (2-methylpropane)
(branched-chain)

(c) Methods of Preparation of Alkanes

In the laboratory, alkanes are prepared by heating the sodium salt of a carboxylic acid with soda lime. Soda lime is a mixture of calcium oxide (lime) and sodium hydroxide.

$$\underset{\text{sodium ethanoate}}{CH_3COONa\ (s)} + NaOH\ (s) \xrightarrow[\Delta]{CaO} \underset{\text{methane}}{CH_4\ (g)} + Na_2CO_3\ (s)$$



Preparation of methane

The reaction is generally applicable for the preparation of other alkanes.

$$\underset{\text{sodium alkanoate}}{R\text{-}COONa} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{alkane}}{R\text{-}H} + Na_2CO_3$$

(or)

$$(C_nH_{2n+1})COONa + NaOH \xrightarrow[\Delta]{CaO} C_nH_{2n+2} + Na_2CO_3$$

Other methods of preparation of alkanes

Among the many other reactions which may be used for the preparation of alkanes, only two methods will be mentioned.

(i) Reduction of alkyl halides

The reduction of alkyl halides with molecular hydrogen takes place in the presence of catalyst like platinum, Pt or palladium, Pd.

$$\underset{\text{ethyl iodide}}{CH_3CH_2I\ (g)} + H_2\ (g) \xrightarrow{Pd} \underset{\text{ethane}}{CH_3CH_3\ (g)} + HI\ (g)$$

(ii) Reduction of alkenes (Hydrogenation)

Although platinum and palladium metals in finely divided form catalyse the addition of hydrogen to alkenes at room temperature, higher temperatures are required when nickel is used as the hydrogenating catalyst.

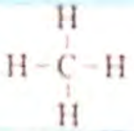
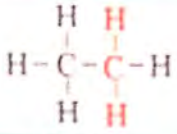
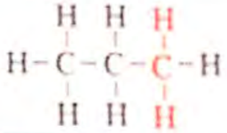
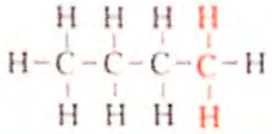
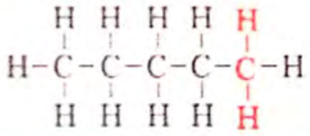
$$\underset{\text{propene}}{CH_3CH{=}CH_2\ (g)} + H_2\ (g) \xrightarrow[300\ ^\circ C]{Ni} \underset{\text{propane}}{CH_3CH_2CH_3\ (g)}$$

(d) Properties of Alkanes

(i) Physical properties

The normal alkanes from C_1 to C_4 (i.e., from methane to butane) are colourless gases, C_5 to C_{17} are colourless liquids and from C_{18} onwards are solids. The boiling points rise fairly regularly with an increasing number of carbon atoms (Table 8.3). As the chain gets longer: melting and boiling points rise, viscosity increases (the compounds flow less easily) and flammability decreases (the compounds burn less easily).

Table 8.3 Some Physical Properties of Alkanes

Alkane			Boiling point (°C)		
methane	CH_4	 $H-\overset{H}{\underset{H}{C}}-H$	− 162	boiling point and viscosity increase	flammability decreases
ethane	C_2H_6	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	− 89		
propane	C_3H_8	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	− 42		
butane	C_4H_{10}	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	− 1		
pentane	C_5H_{12}	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	36		

(ii) Chemical properties

The most important chemical reactions of these saturated hydrocarbons are the substitution and combustion reactions.

Substitution reaction

When methane is mixed with chlorine in diffused sunlight, the following stepwise reactions occur; where one chlorine atom replaces one hydrogen atom in each step.

$$\underset{\text{methane}}{CH_4\,(g)} + Cl_2\,(g) \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{methyl chloride}}{CH_3Cl\,(g)} + HCl\,(g)$$

$$CH_3Cl\,(g) + Cl_2\,(g) \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{methylene chloride}}{CH_2Cl_2\,(l)} + HCl\,(g)$$

$$CH_2Cl_2\,(l) + Cl_2\,(g) \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{chloroform}}{CHCl_3\,(l)} + HCl\,(g)$$

$$CHCl_3\,(l) + Cl_2\,(g) \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{carbon tetrachloride}}{CCl_4\,(l)} + HCl\,(g)$$

These reactions are known as **chlorination reactions** in alkane. Haloalkanes such as CH_2Cl_2, $CHCl_3$ and CCl_4 are important solvents.

Combustion reaction

The alkanes are unreactive toward acids, bases, metals and many other chemicals. Alkanes burn well in a good supply of oxygen, forming carbon dioxide and water vapour, and giving out plenty of heat. So, they are used as fuels. Methane burns most easily.

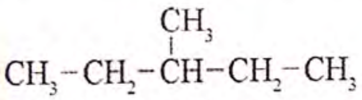
$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g) + \text{heat energy}$$

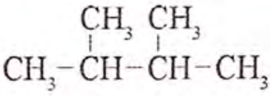
If there is not enough oxygen, the alkanes undergo incomplete combustion, giving off poisonous carbon monoxide and less heat energy.

$$2CH_4\,(g) + 3O_2\,(g) \longrightarrow 2CO\,(g) + 4H_2O\,(g) + \text{heat energy}$$

REVIEW QUESTIONS

(1) Give the IUPAC name for each of the following alkanes:

(a) 
$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$

(b) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(c) CH_3-CH_3

(2) Give the structural formula for each of the following compounds:
(a) octane (b) 3-methylhexane (c) 2,2,4-trimethylpentane

(3) Methane reacts with chlorine in a substitution reaction. Draw the full structural formula for each compound that can form as the reaction proceeds.

Key Terms

- **Isomers** are two or more compounds with the same molecular formula but different arrangements of atoms and have different properties.
- A **structural isomer** is a type of isomer in which molecules have the same molecular formula but different arrangements of atoms within the molecule.
- **Hydrogenation** is the reaction in which adding pairs of hydrogen atoms to a double or triple bond.
- **Substitution reaction** is a reaction in which an atom or a group of atoms attached to a carbon atom is replaced by another atom or group of atoms.
- **Chlorination reaction** is a chemical reaction in which a chlorine atom is introduced into a compound by substitution or by addition.

8.3 THE ALKENES

Alkene molecules which are unsaturated hydrocarbons contain at least one carbon-carbon double bond (C=C) (ethylenic bond). This ethylenic bond is the functional group of alkene, and largely dictates their reactions.

They form a homologous series, with the general formula C_nH_{2n}, where n is a number equal to or greater than 2. The representative alkene given here is ethene, C_2H_4. The picture shown is the ball-and-stick model of ethene, $CH_2=CH_2$.

(a) Nomenclature of Alkenes

The first member of the series is known as ethene. The common name of ethene is ethylene.

The IUPAC system: In order to name alkenes, a simple list of rule is as follows:

(1) Identify and name the longest carbon chain containing the double bond. Use the root name prefix with the ending *-ene*.
(2) Number the chain, starting at the end nearest to the double bond.
(3) Number the first carbon of the double bond directly in front of the root name.
(4) Identify and name the groups attached to this chain. Designate the location of each substituent group by an appropriate number and name.

$\overset{3}{C}H_3-\overset{2}{C}H=\overset{1}{C}H_2$

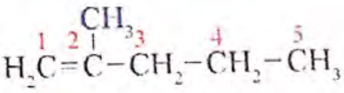
propene

$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$

1-butene

$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$

2-butene



$H_2\overset{1}{C}=\overset{2}{\underset{}{C}}(\overset{3}{C}H_3)-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3$

2-methyl-1-pentene

(b) Isomers of Alkenes

The first two members of the alkene family, ethene and propene, have only one structure but the higher members have more than one structure.

In alkenes, the chains can be in different ways, and the double bonds can be in different positions. For example, the following compounds have the same formula of C_4H_8 but they have different structures. So, they are isomers.

$CH_3-CH_2-CH=CH_2$

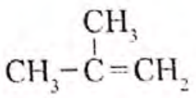
1-butene

I

$CH_3-CH=CH-CH_3$

2-butene

II



$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$

2-methylpropene (or) *iso*-butene

III

I and III or II and III are **chain isomers** due to the different structures of C-skeleton in the longer chain.

The basic carbon skeleton remains unchanged in the isomers I and II, but the double bonds are located in different positions. So, I and II are **positional isomers**.

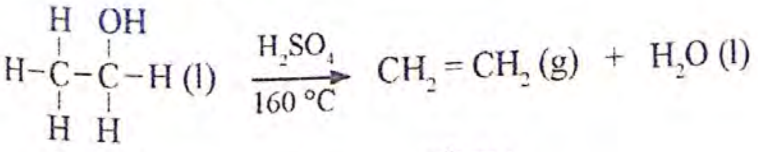
) Methods of Preparation of Alkenes

(i) Dehydration of alcohols

Two methods may be used for this dehydration.

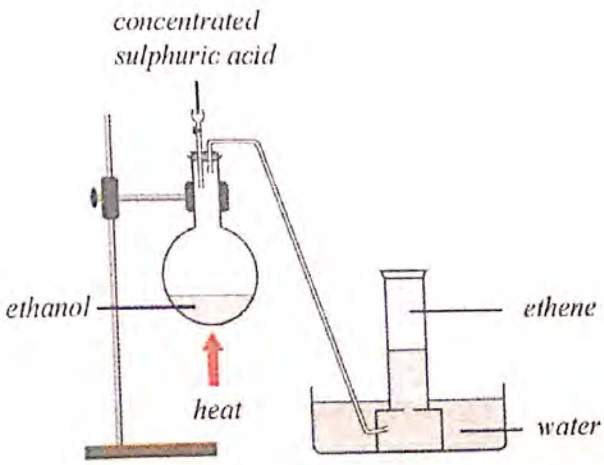
Heating with concentrated sulphuric acid at 160 °C

When ethanol is heated with concentrated sulphuric acid at 160 °C, ethene is formed. The reaction occurs, resulting in the loss of water.



$$H-\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-H\ (l)\ \xrightarrow[160\ °C]{H_2SO_4}\ CH_2=CH_2\ (g)\ +\ H_2O\ (l)$$

ethanol ethene



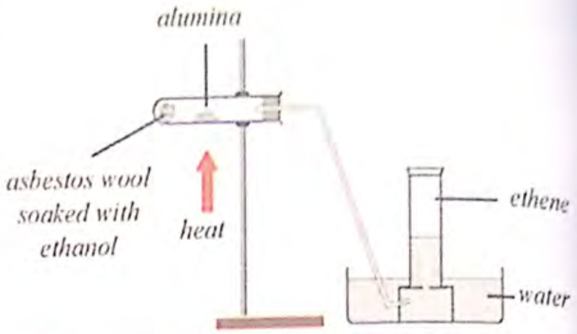
Preparation of ethene using conc. H_2SO_4

Passing the vapours of the alcohol over alumina, Al_2O_3, heated at 350 °C

Ethene can be prepared from ethanol as a result of being passed over the heated alumina.

$$CH_3CH_2OH\,(g) \xrightarrow[350\ ^\circ C]{Al_2O_3} CH_2{=}CH_2\,(g) + H_2O\,(l)$$

ethanol ethene

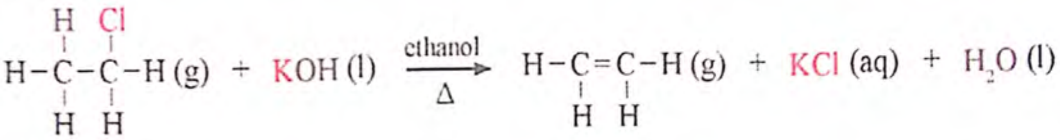


Preparation of ethene using alumina

(ii) Dehydrohalogenation of alkyl halides

The term dehydrohalogenation is used when a halogen atom and a hydrogen atom on an adjacent carbon of the same molecule are simultaneously removed as hydrogen halide.

When ethyl chloride is heated with an alcoholic solution of potassium hydroxide on a water bath, ethene is formed.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-H\,(g) + KOH\,(l) \xrightarrow[\Delta]{\text{ethanol}} H-\underset{H}{C}{=}\underset{H}{C}-H\,(g) + KCl\,(aq) + H_2O\,(l)$$

ethyl chloride ethene

(d) Properties of Alkenes

(i) Physical properties

At room temperature, alkenes containing two to four carbon atoms are gases; those containing five to fifteen carbon atoms are liquids; those containing more than sixteen carbon atoms are solids. They are all lighter than water in which they are insoluble. They burn in the air with a luminous, smoky flame.

(ii) Chemical properties

The unsaturated nature of alkenes (chemically reactive) is shown in the addition reactions of alkenes.

Addition of hydrogen (Hydrogenation)

When hydrogen is added to ethene using suitable catalyst, ethane is the product.

$$CH_2{=}CH_2\,(g) + H_2\,(g) \xrightarrow[300\ ^\circ C]{Ni} CH_3CH_3\,(g)$$

ethene or ethylene ethane

Addition of halogens (Halogenation)

Halogens react with alkenes to produce dihalogeno compounds. These reactions happen quickly at room temperature.

$$\underset{\text{ethene}}{CH_2=CH_2\,(g)} + Cl_2\,(g) \longrightarrow \underset{\text{ethene dichloride}}{CH_2Cl-CH_2Cl\,(l)}$$

$$\underset{\text{ethene}}{CH_2=CH_2\,(g)} + \underset{\text{(reddish-brown)}}{Br_2\,(aq)} \longrightarrow \underset{\text{ethene dibromide (colourless)}}{CH_2Br-CH_2Br\,(aq)}$$

The addition of Br_2 to alkenes is used as a simple qualitative test for unsaturation. When an alkene is added, the reddish-brown solution becomes colourless as the Br_2 reacts with the alkene to form a colourless compound. This reaction may be used to distinguish between alkanes and alkenes.

Addition of hydrogen halides or halogen acids (Hydrohalogenation)

$$\underset{\substack{\text{ethene}\\\text{(symmetrical)}}}{CH_2=CH_2} + \underset{\text{(unsymmetrical)}}{HX} \longrightarrow \underset{\text{ethyl halide (only one product)}}{CH_3CH_2X}$$

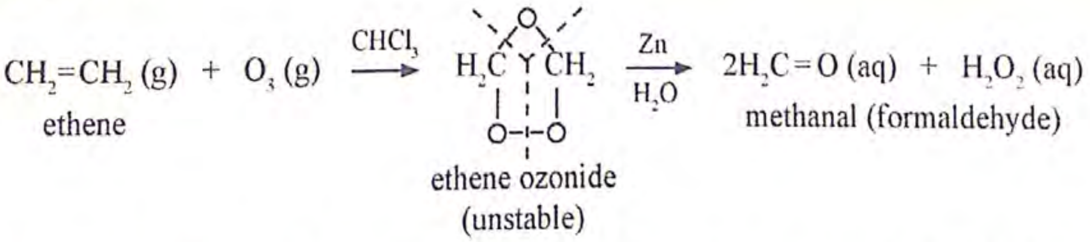
$$\underset{\substack{\text{propene}\\\text{(unsymmetrical)}}}{CH_3CH=CH_2} + \underset{\substack{(X = Cl, Br, I)\\\text{(unsymmetrical)}}}{HX} \longrightarrow \underset{\substack{\textit{iso}\text{-propyl halide}\\\text{I}\\\text{(major product)}}}{CH_3CHXCH_3} + \underset{\substack{\textit{n}\text{-propyl halide}\\\text{II}}}{CH_3CH_2CH_2X}$$

The halogen atom X is more electronegative than H. Although both products I and II are formed, I is usually produced in a larger proportion than II. This reaction provides the basis for **Markownikoff's rule** which may be stated as:

When an unsymmetrical addendum (HX) adds on to an unsymmetrical alkene, two products are formed; but that product where the negative part of the addendum adds on to the carbon with the least number of hydrogen atoms is the major product.

Ozonolysis

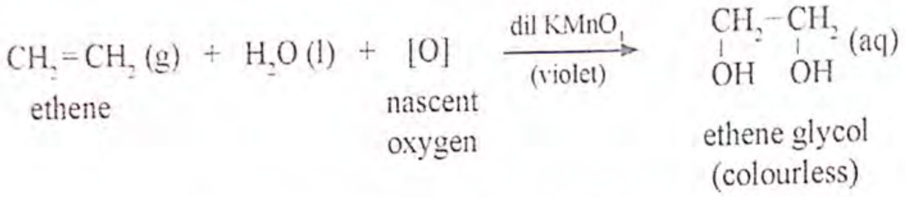
When a stream of ozonised oxygen is passed into a solution of alkene in glacial ethanoic acid (acetic acid) or chloroform, addition of ozone to alkene takes place with formation of alkene ozonide. This ozonide is unstable and reduced with zinc dust and water to give aldehydes or ketones depending upon the structure of alkene.



The complete process of preparing the ozonide followed by decomposing it, is called **ozonolysis**.

Hydroxylation of alkenes

When ethene is passed into cold dilute potassium permanganate solution, ethene glycol is formed.



$$\underset{\text{ethene}}{CH_2=CH_2\,(g)} + H_2O\,(l) + \underset{\text{nascent oxygen}}{[O]} \xrightarrow[\text{(violet)}]{\text{dil } KMnO_4} \underset{\text{ethene glycol (colourless)}}{\underset{OH\quad\ OH}{CH_2-CH_2}\,(aq)}$$

In this process, the colour of 1 % dilute $KMnO_4$ solution is discharged.

REVIEW QUESTIONS

(1) What makes alkenes react so differently from alkanes?

(2) Propene is an unsaturated hydrocarbon. (a) What does that mean? (b) Write a chemical equation for its reaction with cold dilute potassium permanganate solution.

(3) Give the structural isomers and the IUPAC names of the alkene, C_5H_{10}.

Key Terms

- **Chain isomers** are the isomers which are made up of two or more carbon or other compounds with the same molecular formula but different atomic arrangements, or branches.
- **Positional isomers** are the isomers which have the same carbon skeleton and the same functional groups but differ from each other in the location of the functional groups on or in the carbon chain.
- **Dehydration** reaction is the reaction in which H and OH are eliminated from adjacent carbon atoms to form water and a more unsaturated bond.
- **Dehydrohalogenation** is a type of chemical reaction in which a hydrogen halide is removed from an alkyl halide with formation of a double bond.
- **Addition reaction** is the reaction in which two atoms or groups of atoms are added to a molecule, one on each side of a double or triple bond.
- **Hydrohalogenation** is the addition of hydrogen halides, such as HCl and HBr, to alkenes to yield corresponding haloalkanes.
- **Halogenation** is a chemical reaction in which a halogen atom is introduced into a compound.
- **Ozonolysis** is the cleavage of an alkene or alkyne with ozone to form organic compounds, aldehydes or ketones.
- **Hydroxylation** is the reaction in which a hydroxyl group is introduced into an organic compound.

8.4 THE ALKYNES

Alkyne molecules which are unsaturated hydrocarbons contain at least one carbon-carbon triple bond ($C\equiv C$) (acetylenic bond). This acetylenic bond is the functional group of alkyne, and largely dictates the alkyne reactions.

They form a homologous series, with the general formula C_nH_{2n-2}, where n is a number equal to or greater than 2. The representative alkyne given here is ethyne, C_2H_2. The illustration given here is the ball-and-stick model of ethyne, $CH\equiv CH$.

(a) Nomenclature of Alkynes

The first member of the series is known as ethyne. It is commonly called acetylene.

The IUPAC system: The alkynes are named after the alkane having the same number of carbon atoms. The suffix -ane of the alkane is replaced by *-yne*. The rules for numbering are the same as for the alkenes.

$CH\equiv CH$

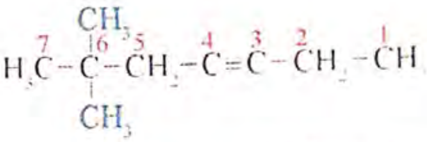
ethyne

$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$

1- butyne

$\overset{1}{C}H_3-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_3$

2- butyne



$H_3\overset{7}{C}-\overset{6}{C}(CH_3)_2-\overset{5}{C}H_2-\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{C}H_2-\overset{1}{C}H$

6,6- dimethyl-3-heptyne

(b) Isomers of Alkynes

The chains with four or more carbon atoms lead to the formation of structural isomers.

In alkynes, the chains can be in different ways, and the triple bonds can be in different positions. For example, the following compounds have the same formula of C_5H_8 but they have different structures. So, they are isomers.

$CH\equiv C-CH_2-CH_2-CH_3$

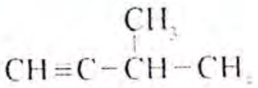
1- pentyne

I

$CH_3-C\equiv C-CH_2-CH_3$

2- pentyne

II



$CH\equiv C-CH(CH_3)-CH_3$

3- methyl-1-butyne

III

I and III or II and III are chain isomers due to the different structures of C-skeleton in the longer chain, whereas I and II are positional isomers due to the location of triple bonds in different positions.

(c) Methods of Preparation of Alkynes

Treatment of calcium carbide with water

Calcium carbide (CaC_2) reacts with water to produce acetylene.

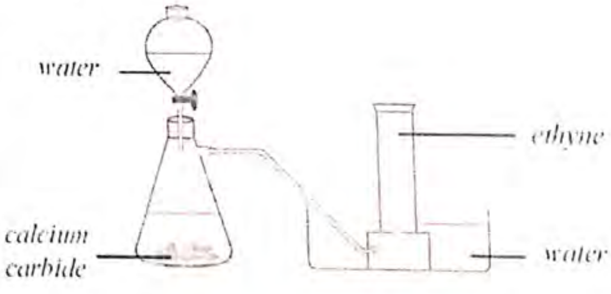
$$CaC_2\,(s) + 2H_2O\,(l) \longrightarrow CH\equiv CH\,(g) + Ca(OH)_2\,(aq)$$

calcium carbide ethyne or acetylene

The calcium carbide required for this reaction is industrially prepared by heating calcium oxide with coke in an electric furnace.

$$CaO\,(s) + 3C\,(s) \xrightarrow[\text{furnace}]{\text{electric}} CaC_2\,(s) + CO\,(g)$$

coke calcium carbide



Preparation of ethyne

(d) Properties of Alkynes

(i) Physical properties

At room temperature, alkynes containing two to four carbon atoms are gases; those containing five to twelve are liquids; containing more than thirteen carbon atoms are solids. They are all odourless and colourless except ethyne which has a slightly distinctive odour.

(ii) Chemical properties

Owing to the presence of the triple bond, the alkynes are also unsaturated. Reactions can be made to add to carbon-carbon triple bond (addition reaction) or to substitute acetylenic hydrogens (substitution reaction).

Addition of hydrogen (Hydrogenation)

The reaction proceeds in two distinct stages. It is possible to control the reaction and stop it after the first stage of 'hydrogenation'. Generally, it can be shown as follows:

$$\underset{\text{alkyne}}{R-C\equiv CH} + H_2 \xrightarrow{\text{Pd or Pt}} \underset{\text{alkene}}{R-CH=CH_2} \xrightarrow[\text{Pd or Pt}]{+H_2} \underset{\text{alkane}}{R-CH_2-CH_3}$$

Addition of halogens (Halogenation)

Chlorine or bromine can be added to ethyne in the dark to form ethyne di- and tetra-halides. Iodine can be added but only with difficulty.

$$\underset{\text{ethyne}}{CH\equiv CH\,(g)} + Cl_2\,(g) \longrightarrow \underset{\text{ethyne dichloride}}{CHCl=CHCl\,(l)} \xrightarrow{Cl_2} \underset{\text{ethyne tetrachloride}}{CHCl_2-CHCl_2\,(l)}$$

$$\underset{\text{ethyne}}{CH\equiv CH\,(g)} + \underset{\text{(reddish-brown)}}{Br_2\,(aq)} \longrightarrow \underset{\text{ethyne dibromide (colourless)}}{CHBr=CHBr\,(aq)}$$

$$\underset{\text{ethyne}}{CH\equiv CH\,(g)} + Br_2\,(l) \longrightarrow \underset{\text{ethyne dibromide}}{CHBr=CHBr\,(l)} \xrightarrow{Br_2} \underset{\text{ethyne tetrabromide}}{CHBr_2-CHBr_2\,(l)}$$

$$\underset{\text{ethyne}}{CH\equiv CH\,(g)} + \underset{\text{(violet)}}{I_2\,(g)} \xrightarrow{\text{ethanol}} \underset{\text{ethyne diiodide (colourless)}}{CHI=CHI\,(l)}$$

Addition of water (Hydration)

$$\underset{\text{ethyne}}{CH\equiv CH\,(g)} + H_2O\,(l) \xrightarrow[Hg^{2+}]{\text{dil } H_2SO_4,\ 60\ ^\circ C} \underset{\substack{\text{vinyl alcohol}\\ \text{(unstable)}}}{[CH_2=CHOH]} \longrightarrow \underset{\text{ethanal (acetaldehyde)}}{CH_3CH=O\,(aq)}$$

Addition of the hydrogen halides or halogen acids, HX (Hydrohalogenation)

The order of the readiness with which the hydrogen halides add to ethyne is HI > HBr > HCl > HF.

$$\underset{\text{ethyne}}{CH\equiv CH\,(g)} + HBr\,(g) \longrightarrow \underset{\text{vinyl bromide}}{CH_2=CHBr\,(l)} \xrightarrow{HBr} \underset{\text{ethylidene bromide}}{CH_3-CHBr_2\,(l)}$$

The addition reaction of vinyl bromide is in accordance with Markownikoff's rule.

Substitution reactions (Formation of metallic acetylides)

When acetylene is passed over heated sodium, one or both hydrogen atoms may be replaced or substituted by sodium to form mono- and di- sodium acetylides.

$$\underset{\text{ethyne (acetylene)}}{CH{\equiv}CH\,(g)} + Na\,(s) \xrightarrow{\Delta} \underset{\text{monosodium acetylide}}{CH{\equiv}CNa\,(s)} + \frac{1}{2}H_2\,(g)$$

$$\underset{\text{monosodium acetylide}}{CH{\equiv}CNa\,(s)} + Na\,(s) \xrightarrow{\Delta} \underset{\text{disodium acetylide}}{NaC{\equiv}CNa\,(s)} + \frac{1}{2}H_2\,(g)$$

The hydrogen atom on the triple bonded carbon is acidic and can be replaced by metals such as Na, Cu or Ag. When ethyne is added to an ammoniacal solution of copper(I) chloride or silver oxide, the corresponding metallic acetylides are precipitated.

$$\underset{\text{ethyne (acetylene)}}{HC{\equiv}CH\,(g)} + Cu_2Cl_2\,(aq) + 2NH_3\,(g) \longrightarrow \underset{\text{dicopper acetylide (red)}}{CuC{\equiv}CCu\,(s)} + 2NH_4Cl\,(aq)$$

Similarly,

$$\underset{\text{ethyne (acetylene)}}{HC{\equiv}CH\,(g)} + Ag_2O\,(aq) + NH_3\,(g) \longrightarrow \underset{\text{disilver acetylide (white)}}{AgC{\equiv}CAg\,(s)} + NH_4OH\,(aq)$$

$CH_3C{\equiv}CH$ contains a hydrogen atom on the triple bonded carbon and will form metallic acetylides. $CH_3C{\equiv}CCH_3$ contains no hydrogen on the triple bonded carbon and will not form metallic acetylides.

REVIEW QUESTIONS

(1) Draw the full structural formulae of the following compounds:
 (a) 4,4-dimethyl-2-pentyne (b) 3-octyne (c) 3-methyl-1-hexyne

(2) Compound X is an unsaturated hydrocarbon. Its general formula is C_nH_{2n-2}. Its relative molecular mass is 40.
 (a) (i) Which family does X belong to? (ii) What is its molecular formula?
 (b) (i) X reacts with bromine water. Write a chemical equation to show this reaction.
 (ii) Mention the type of reaction.

(3) Select the hydrocarbon(s) which has (have) the acidic character from the following:
 (a) C_2H_6, C_2H_4, C_2H_2 (b) $CH_3{-}C{\equiv}CH$, $CH{\equiv}CH$, $CH_3{-}C{\equiv}C{-}CH_3$

Key Term

- **Hydration of alkene (or alkyne)** is an addition of water in which H and OH add across a double (or triple) bond.

8.5 THE ALCOHOLS

The alcohols may be considered as derivatives of alkanes.

The replacement of one hydrogen atom in an alkane by a hydroxyl (OH) group gives the corresponding alcohol. Most of the common reactions of all alcohols are due to the functional group, OH.

They form a homologous series with the general formula $C_nH_{2n+1}OH$, (or) $C_nH_{2n+2}O$ where n is a number, equal to or greater than 1.

Ethanol is the most important member of the homologous series called the alcohols. Hence, in this section, the preparation and properties of ethanol will only be described. The ball-and-stick model of ethyl alcohol, CH_3CH_2OH, is illustrated in the given picture.

(a) Nomenclature of Alcohols

The common name of an alcohol combines the name of the alkyl group with the word *alcohol*.

For example, CH_3OH	methyl alcohol
$CH_3CH_2CH_2OH$	*n*-propyl alcohol
$CH_3CHOHCH_3$	*iso*-propyl alcohol

The IUPAC system: Alcohols are given their respective names by adding -ol instead of -e from alkane.

For example, CH_3OH	methanol
CH_3CH_2OH	ethanol

The chain is numbered from the end nearest the OH group. The chain with at least three carbon atoms is frequently numbered giving the location of the OH group. For example,

$$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2OH \quad \text{propan-1-ol} \quad \text{(or)} \quad \text{1-propanol}$$

$$\overset{3}{C}H_3\overset{2}{C}HOH\overset{1}{C}H_3 \quad \text{propan-2-ol} \quad \text{(or)} \quad \text{2-propanol}$$

(b) Isomers of Alcohols

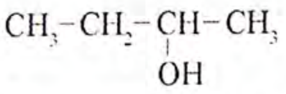
Alcohols containing at least three carbon atoms have more than one structure.

For example, there are four isomers of butanol.

$CH_3-CH_2-CH_2-CH_2-OH$

1-butanol/butan-1-ol

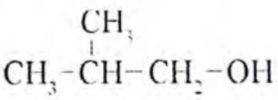
I



$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3$$

2-butanol/butan-2-ol

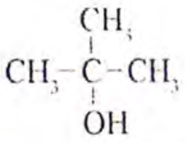
II



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_2-OH$$

2-methyl-1-propanol

III



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_3$$

2-methyl-2-propanol

IV

Alcohols form chain isomerism due to the different structures of C-skeleton in the longer chain. I and III or II and IV are chain isomers.

The basic carbon skeleton remains unchanged in the isomers, but a hydroxyl group (OH) can be located in different positions. So, I and II; III and IV are positional isomers.

(c) Methods of Preparation of Alcohols

(i) Hydration of ethene

Ethene, which is a gaseous by-product in the process of the cracking of petroleum molecules, is used as a basic material for starting the preparation of ethanol.

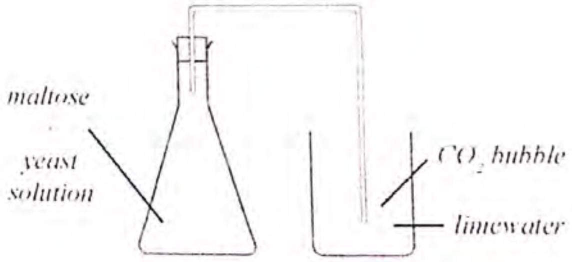
Ethene and steam are passed over a phosphoric acid catalyst at 570 °C and 60 – 70 atmospheric pressure to produce ethanol. This reaction is reversible. High pressure and a low temperature would give the best yield.

$$\underset{\text{ethene}}{CH_2=CH_2\,(g)} + H_2O\,(g) \underset{H_3PO_4}{\overset{570\ °C,\ 60-70\ atm}{\rightleftharpoons}} \underset{\text{ethanol}}{CH_3CH_2OH\,(l)}$$

(ii) Fermentation method

Starch is used as the raw material for the preparation of ethanol industrially. Potatoes, maize, rice and other starchy cereals may be used in the process.

The major steps may be summarised as follows: Starch is pressure-cooked to release the starch granules. The cooked starch is cooled and then treated with freshly germinated barley which is called malt for 1 hour at 60 °C. Malt contains the enzyme diastase. Starch breaks down into a sugar called maltose.



Preparation of ethanol by fermentation method

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n\,(s)} + \frac{n}{2}H_2O\,(l) \xrightarrow{\text{diastase}} \underset{\text{maltose}}{\frac{n}{2}C_{12}H_{22}O_{11}(aq)}$$

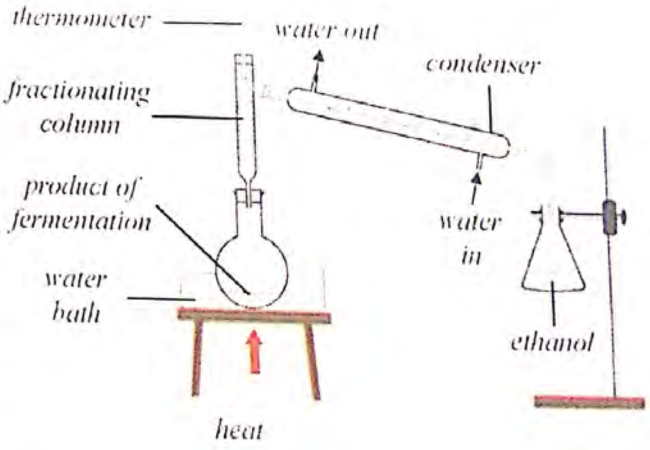
Yeast is added to maltose. The enzymes of the yeast catalyse the reaction. Yeast secretes two enzymes: (i) maltase which converts maltose into glucose and (ii) zymase which converts glucose into ethanol.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}\,(aq)} + H_2O\,(l) \xrightarrow[\text{(maltase)}]{\text{yeast}} \underset{\text{glucose}}{2C_6H_{12}O_6\,(aq)}$$

$$\underset{\text{glucose}}{C_6H_{12}O_6\,(aq)} \xrightarrow[\text{(zymase)}]{\text{yeast}} \underset{\text{ethanol}}{2CH_3CH_2OH\,(aq)} + 2CO_2\,(g)$$

The product contains about 11 % ethanol. It is fractionally distilled to yield the rectified spirit of commerce which contains about 95 % ethanol.

Cane sugar and fruit juices contain the sugar (sucrose, $C_{12}H_{22}O_{11}$). They may be used to manufacture the important industrial solvent, ethanol.



Fractional distillation of the fermented product

(d) Properties of Alcohols

(i) Physical properties

Alcohols from methanol, CH_3OH, to butanol, $CH_3CH_2CH_2CH_2OH$, are mobile liquids; those from $C_5H_{11}OH$ to $C_{11}H_{23}OH$ are oily liquids; above $C_{12}H_{25}OH$ they are usually solids. The first two members; methanol and ethanol are miscible with water in any proportion. The most toxic member is methanol.

(ii) Chemical properties

Reaction with metallic sodium

When a piece of sodium is added to ethanol, reaction occurs at room temperature, liberating hydrogen.

$$\underset{\text{ethanol}}{CH_3CH_2OH\ (l)} + Na\ (s) \longrightarrow \underset{\text{sodium ethoxide}}{CH_3CH_2ONa\ (aq)} + \frac{1}{2}H_2\ (g)$$

Methanol and most of the liquid alcohols also behave similarly.

Reaction with sulphuric acid

When ethanol is heated with an excess of concentrated sulphuric acid at 160 °C, ethene is produced. (see Section 8.3)

With a smaller proportion of concentrated sulphuric acid, diethyl ether is formed when the reaction temperature is kept at 140 °C.

$$\underset{\text{ethyl alcohol}}{2CH_3CH_2OH\ (l)} \xrightarrow[140\ ^\circ C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3\ (g)} + H_2O\ (g)$$

Formation of esters (Esterification)

Ethanoic acid (acetic acid) also reacts with ethanol when a small amount of concentrated sulphuric acid is added as catalyst.

$$\underset{\substack{\text{ethanoic acid}\\ \text{(acetic acid)}}}{CH_3COOH\ (l)} + \underset{\text{ethanol}}{CH_3CH_2OH\ (l)} \xrightarrow[H^+]{H_2SO_4} \underset{\substack{\text{ethyl ethanoate}\\ \text{(ethyl acetate)}}}{CH_3COOCH_2CH_3\ (l)} + H_2O\ (l)$$

Ethyl ethanoate is an ester. It has a pleasant fruity odour which is a characteristic of most esters.

Dehydrogenation

When ethanol vapour is passed over freshly reduced copper heated at 300 °C, removal of hydrogen occurs with formation of ethanal (also known as acetaldehyde)

$$\underset{\text{ethanol}}{CH_3CH_2OH\ (g)} \xrightarrow{Cu,\ 300\ ^\circ C} \underset{\text{ethanal (acetaldehyde)}}{CH_3CHO\ (l)} + H_2\ (g)$$

Oxidation

When ethanol is heated with acidified potassium dichromate solution, oxidation takes place in two stages to finally give ethanoic acid.

$$\underset{\text{ethanol}}{CH_3CH_2OH\,(l)} + [O] \xrightarrow[\Delta]{K_2Cr_2O_7,\,H^+} \underset{\substack{\text{ethanal}\\ + \\ H_2O\,(l)}}{CH_3CHO\,(l)} \xrightarrow[K_2Cr_2O_7,\,H^+\;\Delta]{[O]} \underset{\text{ethanoic acid (acetic acid)}}{CH_3COOH\,(l)}$$

REVIEW QUESTIONS

(1) Sugarcane is used to make ethanol. Name the process and catalyst used.

(2) In a reaction, the compound W with the molecular formula $C_4H_{10}O$ is converted to the compound X with the formula C_4H_8O. Explain whether the compound W is oxidised or reduced or dehydrated.

(3) Give the structures and the IUPAC names of the products obtained from the following reactions:
(a) oxidation of *n*-propyl alcohol (b) fermentation of glucose in the presence of yeast.

Key Terms

- **Fermentation** is a process in which ethanol is made from glucose using yeast in the absence of air.
- **Esterification** is a reaction of an alcohol with an acid to produce an ester and water.
- **Dehydrogenation** is a chemical reaction in which hydrogen is removed from a compound.

Chemistry in Society

- The hydrocarbons burn so that they are used as fuels. For example, methane is the main ingredient in natural gas, and butane is often used in lighters and portable cooking stoves.
- Liquid alkanes have various effects on the body, depending on the part exposed. On the skin, alkanes dissolve body oils. Repeated contact may cause dermatitis.

- Heavier liquid alkanes, when applied to the skin, act as emollients (skin softeners). Petroleum jelly (Vaseline is one brand) is a semisolid mixture of hydrocarbons that can be applied as an emollient or simply as a protective film.

- Alkenes occur widely in nature. Ripening fruits and vegetables give off ethene, which triggers further ripening. Food processors artificially introduce ethene to hasten the normal ripening process.
- Ethyne is used as the fuel for the oxyacetylene blow lamp used in cutting and welding metals.

- Ethanol can be found in medical wipes and the most common antibacterial hand sanitiser gels as an antiseptic.
- The largest use of ethanol is as an engine fuel and fuel additive. It has been used as rocket fuel and is currently used in lightweight rocket-powered racing aircraft.

EXERCISES

Q 1 to Q 9 (Understanding)

1. State TRUE or FALSE for each of the following. If FALSE, correct it.
   - (a) First four members of alkanes are gases.
   - (b) Saturated hydrocarbons undergo addition reactions.
   - (c) Colour of bromine solution may be discharged when alkane gas is passing through it.
   - (d) The second member of homologous series having general formula of C_nH_{2n} is ethene.
   - (e) The number of covalent bonds in the molecule of ethane is seven.
2. Fill in the blanks with a suitable word or phrase or numerical value with units as necessary.
   - (a) The IUPAC name of *iso*-butene is _____.
   - (b) Unsymmetrical alkenes give _____ products by the reaction with HBr.
   - (c) The next homologue of the molecule C_2H_4 is _____.
   - (d) The number of acidic hydrogen atoms in 1-butyne is _____.
   - (e) Ethanol has the formula C_2H_5OH and it contains a carbon–carbon _____ bond.
3. Choose the correct term or terms given in the brackets.
   - (a) Ethene can be produced from ethanol by (dehydrohalogenation, dehydrogenation, dehydration) with conc. H_2SO_4 at 160 °C.
   - (b) (Alkanes, Alkenes, Alkynes) contain a carbon-carbon double bond.
   - (c) (Alkanes, Alkenes, Alkynes) may undergo both substitution and addition reactions.
   - (d) The number of carbon atoms in 2,4-dimethyl-octan-1-ol is (8, 9, 10).
   - (e) Starch is hydrolysed by (diastase, maltase, zymase) to form maltose.
4. Match each of the items given in List A with the appropriate item in List B.

List A	List B
(a) ethyl ethanoate	(i) hydrogenation
(b) ethanol	(ii) 1,2-dichloroethane
(c) isomer of 1,1-dichloroethane	(iii) chlorination
(d) reaction of methane and chlorine under diffused sunlight	(iv) pleasant fruity odour
(e) reduction	(v) ethyl alcohol

5. Write the molecular formula and structural formula of the following, each of which contains five carbon atoms: (a) alkane (b) alkene (c) alkyne
6. Write the structures of the major products expected from the following reactions:
   - (a) dehydration of 1-propanol (b) hydrogenation of ethene
   - (c) hydroxylation of propene (d) fermentation of glucose
7. Write chemical equations for the following reactions:
   - (a) incomplete combustion of pentane, forming CO (gas)
   - (b) complete combustion of butane
   - (c) the esterification reaction between propanoic acid and methanol
8. Give the names and structures of the products of the following reactions:
   - (a) $CH_3CH_2CH=CH_2 + H_2$ over Ni catalyst
   - (b) $CH_3CH=CHCH_3 + Cl_2$
   - (c) $CH_3CH_2CH_2OH + Na$

9. Predict the major product of the reaction between 1-butene and hydrogen bromide. Give the reason for your answer.

Q 10 to Q 15 (Critical thinking)

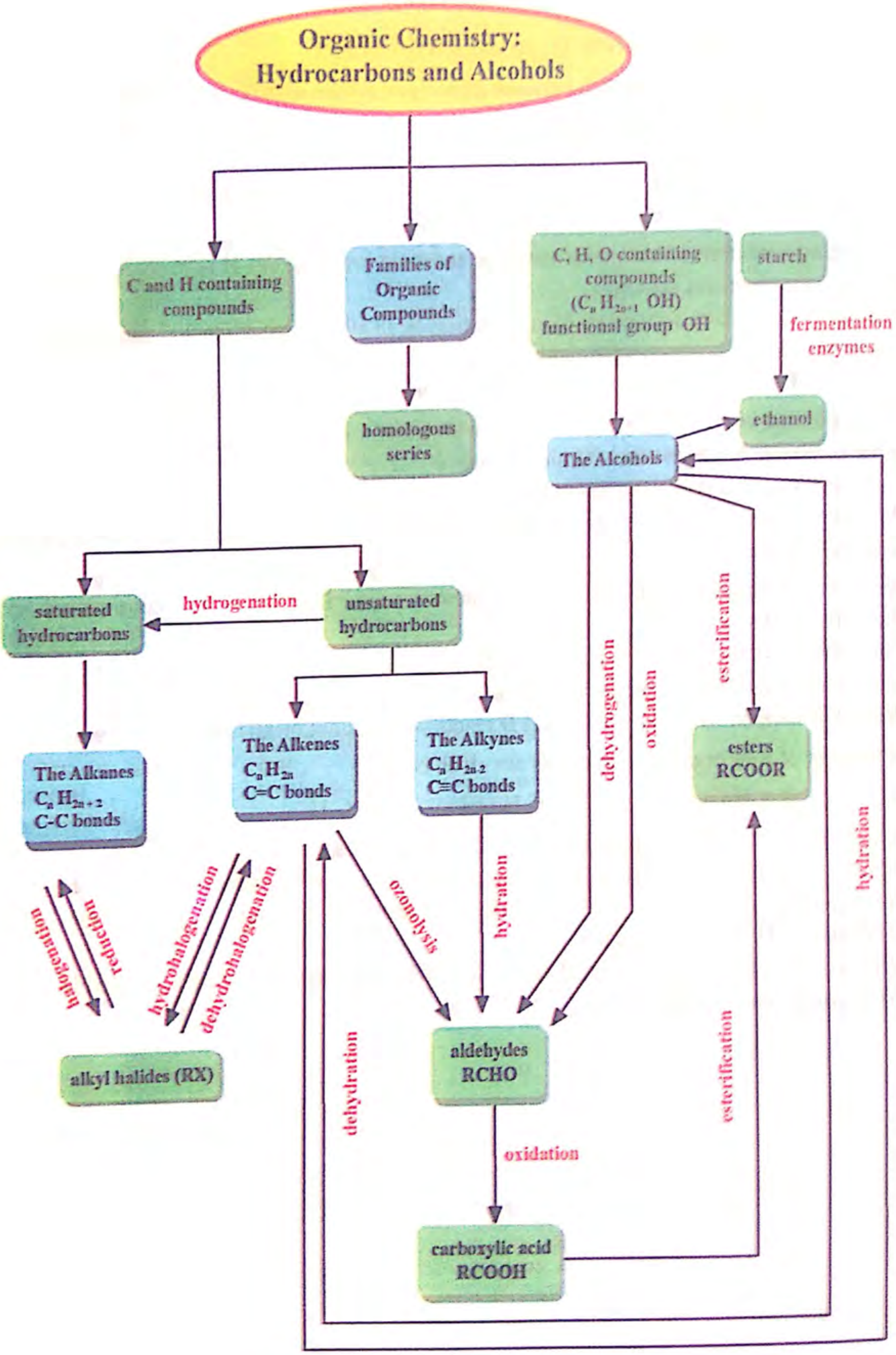
10. How would you convert carbon into: (a) ethane and (b) ethanol?
11. (a) Give a chemical test to distinguish between ethane and ethene with the relevant chemical equations.
    (b) Write the balanced chemical equation for the combustion of ethane in excess air. Name the products formed.
    (c) The carbon compound **Y** which on heating with concentrated sulphuric acid at 160 °C gives propene. Give the name of compound Y.
12. (a) By heating a mixture of sodium propanoate and soda lime, the gas **B** is evolved. What is the gas **B**? Write the chemical equation.
    (b) The gas **B** can also be formed by hydrogenation of an alkene using a nickel catalyst at 300 °C. Name the alkene. Write the chemical equation.
    (c) Is the gas **B** saturated or unsaturated hydrocarbon? Write the general formula.
13. Gas **X** is obtained by treating calcium carbide with water.
    (a) What is the gas **X**? Write the chemical equation.
    (b) Is the gas **X** a saturated or an unsaturated hydrocarbon?
    (c) What type of reaction can the gas **X** undergo (addition or substitution)? Give a chemical equation to support your answer.
14. (a) Write the chemical formula and name of the compound **D** which is the active ingredient of all alcoholic drinks.
    (b) The compound **D** can also be formed by the fermentation of glucose with enzyme (yeast). Name an enzyme and write the chemical equation.
    (c) What will happen when the compound **D** reacts with sodium metal? Write the chemical equation.
15. The formulae of four organic compounds are given below:

    I. C_2H_4 II. CH_3COOH III. C_2H_5OH IV. C_2H_6

    (a) Which one of the above compounds: I, II, III and IV is a saturated hydrocarbon?
    (b) Which compound (I, II, III or IV) gives ethene as a major product when it is heated in the presence of concentrated H_2SO_4? Write the chemical equation. What is the role of the concentrated H_2SO_4 in this reaction?
    (c) Write a chemical equation when II reacts with III in the presence of concentrated H_2SO_4. Name the major product formed.

CHAPTER REVIEW

(Concept Map)



GLOSSARY

Acid rain: the deposition of a mixture from wet (rain, snow, sleet, fog, cloud water and dew) and dry (acidifying particles and gases) acidic components

Addition reaction: the reaction in which two atoms or groups of atoms are added to a molecule, one on each side of a double or triple bond

Aerosols: the suspension of fine solid or liquid particles in gas (e.g., smoke, fog)

Air pollutants: any substances in the air that can, in high enough concentration, have adverse effects on humans and the environment

Air pollution: the presence of toxic chemicals, particulates, or biological materials in the air, at levels that cause discomfort, disease, or death to humans, damage other living organisms, or damage the natural environment

Alcohol: a hydrocarbon derivative in which a hydrogen atom attached to a carbon atom has been replaced by an OH group

Alkanes: hydrocarbons that contain only single bonds

Alkenes: unsaturated hydrocarbons that contain a carbon-carbon double bond

Alkynes: unsaturated hydrocarbons that contain a carbon-carbon triple bond

Alloy: a mixture of metals with other elements (usually metals but sometimes carbon), especially to give greater strength or resistance to corrosion

Anode: a positive electrode and accepts electrons

AQI: an index for reporting daily air quality index

Aqua regia: a mixture of concentrated hydrochloric acid and nitric acid in a volume ratio of 3:1

Atmosphere: the area of air and gas enveloping a celestial body in space, like stars and planets

Atmospheric pressure: the force exerted on a surface by the air above it as gravity pulls it to the Earth

Cathode: a negative electrode and donates electrons

Chain isomers: the isomers which are made up of two or more carbon or other compounds with the same molecular formula but different atomic arrangements, or branches

Chemical cell: a cell in which chemical energy is transformed into electrical energy by forcing the electrons to travel through a wire

Chlorination reaction: a chemical reaction in which a chlorine atom is introduced into a compound by substitution or by addition

Chlorofluorocarbons (CFCs): compounds of carbon, hydrogen, chlorine, and fluorine, typically gases used in refrigerants and aerosol propellants

Condensed structural formula: a formula which omits bonds where they can be assumed, and groups atoms together

Conductor: a substance which conducts or allows the passage of electricity

Corrosion: the deterioration of metals as a result of chemical reaction depending on the type of metal and the environmental conditions

Dehydration: the reaction in which H and OH are eliminated from adjacent carbon atoms to form water and a more unsaturated bond

Dehydrogenation: a chemical reaction in which hydrogen is removed from a compound

Dehydrohalogenation: a type of chemical reaction in which a hydrogen halide is removed from an alkyl halide with formation of a double bond

Denitrification: the process which is the opposite of nitrogen fixation

Diffusion: the process by which the gas molecules spread together until they form a uniform mixture

Ductility: the ability of a material to stretch under tensile stress

Effusion: the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening

Electrochemical series: an arrangement of cations and anions in the order of increasing readiness of discharge from solution on the passage of electricity

Electrode: an electrical conductor that emits or collects electrons in an electrolytic cell

Electrolysis: the decomposition of a compound, in solution or in the molten state, brought about by the passage of an electric current through it

Electrolyte: a substance in the molten state or as a solution in water, which allows the passage of electricity

Electrolytic cell: the cell in which electrical energy is transformed into chemical energy

Electromotive force (emf): the maximum potential difference between two electrodes of a galvanic or voltaic cell and it is measured in volt (V)

Electroplating: a process to coat one metal with a thin layer of another metal by electrolysis

End point: the point at which a titration is complete, usually marked by a change in colour of an indicator

Equivalence point: the point at which chemically equivalent quantities of reactants have been mixed

Esterification: a reaction of an alcohol with an acid to produce an ester and water

Eutrophication: the excessive richness of nutrients in a lake or other body of water, frequently due to run-off from the land, which causes a dense growth of plant life

Fermentation: a process in which ethanol is made from glucose using yeast in the absence of air

Flux: a substance added to the ores to promote fluidity and to remove mineral impurities

Frasch Process: an industrial method to extract sulphur from underground elemental deposits

Froth flotation: a process that selectively separates materials based upon whether they are water repelling (hydrophobic) or have an affinity for water (hydrophilic)

Full structural formula: a formula which shows every bond between every atom in the molecule

Functional group: a group of atoms that represents a potential reaction site in an organic compound

Gangue: the earthy impurities (sand, silt, gravel, etc.) associated with the ore

General formula: a type of empirical formula that represents the composition of any members of an entire class of compounds

Green building technology: the implementation of design in structures or buildings that are environmentally accountable and resource-efficient throughout the building's life cycle

Haber process: an industrial process of directly synthesising ammonia from hydrogen and nitrogen

Halogenation: a chemical reaction in which a halogen atom is introduced into a compound

Homologous series: a series of compounds in which each member differs from the next by a specific number and kind of atoms

Hydration of alkene (or alkyne): an addition of water in which H and OH add across a double (or triple) bond

Hydrocarbons: the compounds that contain only carbon and hydrogen

Hydrogenation: the reaction in which adding pairs of hydrogen atoms to a double or triple bond

Hydrohalogenation: the addition of hydrogen halides, such as HCl and HBr, to alkenes to yield corresponding haloalkanes

Hydroxylation: the reaction in which a hydroxyl group is introduced into an organic compound

Ideal gases: gases whose molecules occupy negligible space and have no interactions and which consequently obey the gas laws

Isomers: two or more compounds with the same molecular formula but different arrangements of atoms and have different properties

Laughing gas: a chemical compound with the formula N_2O, which is used as an anasesthetic

Law of Conservation of Mass: the law which states that the total mass of reactant(s) is equal to the total mass of the product(s)

Law of Definite Proportions: the law which states that every chemical compound contains fixed and constant proportions (by mass) of its constituent elements

Law of Multiple Proportions: the law which states that when two elements combine with each other to form more than one compound, the different masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers

Limiting reactant: the reactant in a chemical reaction that limits the amount of product because the reaction stops when the limiting reactant is completely consumed

Malleability: the ability of a material to be shaped under force or pressure is exerted on it

Mesopause: the thin transitional layer in the atmosphere, the boundary between the mesosphere and the thermosphere

Mesosphere: the layer of the atmosphere between the stratosphere and the thermosphere; its temperature decreases with altitude

Metallic lattice: a structure that consists of positively charged metal ions bound together by their inner electrons; however, their outer shell electrons are free to move around

Metallurgy: the process used for the extraction of pure metals from their ores

Molar solution: a solution which contains one mole of the compound in one cubic decimetre ($1\ dm^3$) of the solution

Molarity: the quantity in moles of the solute dissolved in one cubic decimetre of the solution

Molecular formula: a chemical formula that gives the actual number of atoms of each element in each molecule of a substance

Monoclinic sulphur: a needle-shaped crystalline allotrope of sulphur obtained by heating rhombic sulphur to 96 °C (369 K)

Negative oxidation number: the number of electrons added to a neutral atom

Nitrogen fertilisers: compounds that contain or produce nitrate or ammonium ions in the soil

Nitrogen fixation: the conversion of molecular nitrogen into nitrogen compounds by combining with other elements

Non-conductor (insulator): a solid substance which does not conduct electricity

Non-electrolyte: a substance in a solution that does not conduct electric current

One faraday: the quantity of electricity (96500 coloums) required to produce one mole of a univalent element

Ores: the minerals from which the metals can be extracted conveniently and economically

Oxidation: the removal of hydrogen (or electropositive element) from a substance; the addition of oxygen (or electronegative element) to a substance; the loss of electrons by an element, compound or ion, an increase in oxidation number

Oxidation number (oxidation state): the number of electrons lost or gained by an atom

Oxidising agent (oxidant): an acceptor of electrons and is reduced itself in a chemical reaction

Oxoacid: an acid that contains hydrogen, oxygen and at least one other element

Ozone depletion: the gradual thinning of the Earth's ozone layer in the stratosphere caused by the release of chemical compounds containing gaseous chlorine or bromine from industry and other human activities

Ozone layer: a layer in the stratosphere where ozone gas is more highly concentrated and absorbs the UV radiation from sunlight

Ozonolysis: the cleavage of an alkene or alkyne with ozone to form organic compounds, aldehydes or ketones

Particulate matter (PM): a mixture of tiny pieces of solid particles and liquid droplets in the air, and can consist of hundreds of different chemicals, including carbon, sulphur, nitrogen and metal compounds

Photochemical smog: the haze in the atmosphere accompanied by high levels of ozone and oxides of nitrogen, caused by the action of sunlight on pollutants

PM_{10}: the particles with a diameter of 10 µm, and they are also called the fine particles

$PM_{2.5}$: the atmospheric particulate matter that has a diameter of less than 2.5 µm, which is about 3 % of the diameter of human hair

Polarisation of the cell: the chemical reaction that occurs when a current is flowing causes hydrogen bubbles to form on the surface of the electrode preventing further reaction

Positional isomers: the isomers which have same carbon skeleton and the same functional groups but differ from each other in the location of the functional groups on or in the carbon chain

Positive oxidation number: the number of electrons removed from a neutral atom

Reactivity Series of metals: the arrangement of metals in the decreasing order of reactivity; the more reactive metals are easy to lose electrons and form positive ions

Real gases: gases whose molecules occupy spaces and have interactions; consequently, they only approach to the ideal gas law at high temperature and low pressure

Redox reactions: the chemical reactions which involve oxidation as well as reduction processes simultaneously

Reducing agent (reductant): a donor of electrons and is oxidised in a chemical reaction

Reduction: the removal of oxygen (or electronegative element) from a substance; the addition of hydrogen (or electropositive element) to a substance; the gain of electrons by an element, compound or ion; a decrease in oxidation number

Rhombic sulphur: an octahedral-shaped crystalline allotropic form of sulphur

Saturated hydrocarbons: hydrocarbons that contain only single bonds between carbon atoms

Sequential reactions: linked reactions in which the product of the first reaction becomes the reactant of the second reaction

Significant figures: digits that carry meaningful contribution to its measurement resolution

Slag: a fusible product formed when flux combined with gangue during the extraction of metals

Standard atmospheric pressure: the pressure exerted by a column of mercury 760 mm high at 0 °C at sea level

Standard solution: a solution of accurately known concentration that is used in titration

Steel: a mixture of the metal iron and the non-metal carbon

Stoichiometry: a part of chemistry which deals with the quantities of substances taking part in a chemical reaction

Stratopause: the thin transitional layer of the atmosphere between the stratosphere and the mesosphere

Stratosphere: the second layer of the atmosphere, where temperature increases with altitude due to the presence of ozone

Structural isomer: a type of isomer in which molecules have the same molecular formula but different arrangements of atoms within the molecule

Substitution reaction: a reaction in which an atom or a group of atoms attached to a carbon atom is replaced by another atom or group of atoms

Thermite reaction: a chemical reaction in which a lot of heat is released as a metal oxide is displaced by another metal which is more reactive than the metal in the metal oxide

Thermosphere: the fourth layer of the atmosphere where gases are extremely thinly distributed

Titration: the procedure in which a solution of a standard reagent (reactant) is added to a specific volume of a solution of unknown molarity

Titration error: the difference between end point and equivalence point of the titration

Tropopause: the interface between the troposphere and the stratosphere

Troposphere: the lowermost layer of the atmosphere

Ultraviolet radiation: a high energy radiation that comes from the Sun; there are three types of UV radiation: UVA, UVB and UVC

Unsaturated hydrocarbons: hydrocarbons that contain double or triple covalent bonds between adjacent carbon atoms

Volatile organic compounds (VOCs): organic chemicals that are emitted as gases from certain solids or liquids

Water of crystallisation: water that occurs as a constituent of crystalline substances in a definite stoichiometric ratio