

“शिक्षा मानव को बन्धनों से मुक्त करती है और आज के युग में तो यह लोकतंत्र की भावना का आधार भी है। जन्म तथा अन्य कारणों से उत्पन्न जाति एवं वर्गगत विषमताओं को दूर करते हुए मनुष्य को इन सबसे ऊपर उठाती है।”

— इन्दिरा गांधी

“Education is a liberating force, and in our age it is also a democratising force, cutting across the barriers of caste and class, smoothing out inequalities imposed by birth and other circumstances.”

— Indira Gandhi

ENVIRONMENTAL CHEMISTRY

**SCHOOL OF INTER-DISCIPLINARY AND TRANS-DISCIPLINARY
STUDIES (SOITS)
INDIRA GANDHI NATIONAL OPEN UNIVERSITY
MAIDAN GARHI, NEW DELHI-110068**

PROGRAMME DESIGN AND EXPERT COMMITTEE

Dr. Himanshu Pathak Director, ICAR-National Rice Research Institute Cuttack, Odisha	Prof. Nandini Sinha Kapoor SOITS, IGNOU
Prof. P.A. Azeez Director, SACON, Coimbatore	Prof. Shachi Shah Director, SOITS, IGNOU
Prof I.S. Thakur School of Environmental Sciences, JNU, New Delhi	Prof. B. Rupini SOITS, IGNOU
Prof Uma Melkania Dean, College of Basic Sciences and Humanities, GBPUAT, Pantnagar	Dr. Surendra Singh Suthar School of Environment & Natural Resources, Doon University, Dehradun
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Prof. S.K.Yadav SOA, IGNOU	Dr. V. Venkat Ramanan SOITS, IGNOU
	Dr. Deeksha Dave SOITS, IGNOU
	Dr. Y.S.C. Khuman SOITS, IGNOU

PROGRAMME COORDINATORS

Prof. Shachi Shah, Director, SOITS, IGNOU, Dr. V. Venkat Ramanan, SOITS, IGNOU,
Dr. Deeksha Dave, SOITS, IGNOU

BLOCK PREPARATION TEAM

BLOCK 1	BLOCK 2	BLOCK 3	BLOCK 4
Unit 1 Dr. Vivek Mishra, Department of Chemistry, Amity University, Noida	Unit-5 Dr. Anju Srivastava and Dr. Reena Jain, Department of Chemistry, Hindu College, University of Delhi	Unit-8 Dr. Anju Srivastava and Dr. Reena Jain, Department of Chemistry, Hindu College, University of Delhi	Unit-12 Prof. Lalita S. Kumar, School of Science, IGNOU, New Delhi

Unit-2 Dr. Kanika Solanki, Green Chemistry Network Centre, University of Delhi	Unit-6 Dr. Anju Srivastava and Dr. Reena Jain, Department of Chemistry, Hindu College, University of Delhi	Unit-9 Dr. Anju Srivastava and Dr. Reena Jain, Department of Chemistry, Hindu College, University of Delhi	Unit-13 Prof Sanjeev Kumar, School of Science, IGNOU, New Delhi
Unit-3 Dr. Deepti Rawat & Dr. Rahul Singhal, Green Chemistry Network Centre, University of Delhi	Unit-7 Dr. Anju Srivastava and Dr. Devanshi Magoo, Department of Chemistry Hindu College, University of Delhi	Unit-10 Dr. Reena Jain & Dr. Devanshi Magoo, Department of Chemistry, Hindu College, University of Delhi	Unit-14 Prof. Lalita S. Kumar, School of Science, IGNOU, New Delhi
Unit-4 Dr. Sriparna Dutta, Green Chemistry Network Centre, University of Delhi		Unit-11 Dr. Anju Srivastava and Dr. Reena Jain, Department of Chemistry, Hindu College, University of Delhi	Unit-15 Dr. M. Abdul Kareem, School of Science, IGNOU, New Delhi

COURSE COORDINATOR

Prof. B. Rupini, Environmental Studies, School of Interdisciplinary and Transdisciplinary Studies, Indira Gandhi National Open University, New Delhi

CONTENT EDITORS

Prof. R. K. Sharma, Department of Chemistry, University of Delhi, New Delhi &
Prof. B. Rupini, School of Interdisciplinary and Transdisciplinary Studies, Indira Gandhi National Open University, New Delhi

FORMAT EDITOR

Prof. B. Rupini, Environmental Studies, School of Interdisciplinary and Transdisciplinary Studies, Indira Gandhi National Open University, New Delhi

PRINT PRODUCTION

Mr. Y. N. Sharma
Assistant Registrar (Publication)
MPDD, IGNOU

Mr. Sudhir Kumar
Section Officer (Publication)
MPDD, IGNOU

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COURSE INTRODUCTION

Welcome to the MSc (Environmental Science) programme of IGNOU. The curriculum prepared for this programme is relevant and significant in the present-day scenario.

This core course is entitled “Environmental Chemistry (MEV-013)”. This course consists of 4 blocks comprising of 15 Units.

Block 1 deals with **Fundamentals of Environmental Chemistry**. In this block we tried to explain the fundamentals of environmental chemistry. The block also deals with the state of atmosphere in the Earth’s geological reservoirs. It provides a modern and concise introduction to environmental chemistry principles and the dynamic nature of environmental systems. It is this limited size that makes the atmosphere potentially so vulnerable to contamination. It explains how even the addition of a small amount of material can lead to significant changes in the way the atmosphere, and how the chemical species exist in equilibrium.

Block 2 deals with **Chemistry of Air, Water and Soil**. This block explains chemistry of air, water and soil, their composition. Distribution of chemical species in air and water, their properties, – Cation exchange capacity, pH, NPK in soils, soil organic matter, water soluble organic carbon and its significance, soil fertility have also been explained.

Block 3 deals with **Pollution Chemistry**. The block explains air, water, soil pollution and pollution parameters. The emphasis has been made on various organic and inorganic air pollutants, photochemical smog and their reactions, consequent health effects are addressed. It also elaborated parameters of water pollution, chemistry of hazardous substance and wastes.

Block 4 deals with **Analytical Techniques in Environmental Chemistry**. The block details on the classical methods of analysis required in environmental chemistry such as basic analytical techniques like titrimetry, gravimetry, spectrometry, chromatographic techniques and radio techniques. Finally, the block describes the application of these techniques in the environmental monitoring.

All these Blocks will provide you with sufficient knowledge about the pollutants, management, hazards, risk assessment, standards and laws pertaining to the industrial sector.

INTRODUCTION TO BLOCK 1

This block focuses on the fundamental principles of environmental chemistry. The block mainly deals with the state of atmosphere in the earth’s geological reservoirs. It provides a modern and concise introduction to environmental chemistry principles and the dynamic nature of environmental systems.

Unit 1 deals with the **Environmental Chemistry Part 1**. In this we discussed the concept and scope of environmental chemistry, Fundamentals of Elemental Stoichiometry, Chemical equilibrium, Chemical potential, Chemical Kinetics

- Simple reaction mechanisms, Order and molecularity of chemical reactions; Chemical reactions, Catalysis, Adsorption. The study of the chemical balance in natural systems and how the disturbance in this chemical balance happens by the anthropogenic activities by releasing of chemicals into the environment which change the natural ecosystem levels.

Unit 2 deals with the **Environmental Chemistry Part 2**. This unit deals with the chemical reactions that occur between an acid and base and result into formation of salt and water are generally called acid- base reactions. These reactions play a critical role in maintaining balance in our body as well as our environment. It explained how highly purified water also behaves like a weak electrolyte and shows conductivity and how it ionizes in hydrogen and hydroxyl ions but hydrogen ions do not exist in free form. It introduced to modern concept of oxidation and reduction reactions, by defining them as removal of electrons from a species is termed as oxidation whereas addition of electrons is called reduction. Almost all the elements and their compounds have tendency to undergo oxidation-reduction reactions. The unit also explained other redox chemical reactions of the environment like photosynthesis, respiration, corrosion that we experience in our day to day life.

Unit 3 deals with the **Environmental Chemistry Part 3**. This unit discussed about the concept of solubility, solubility product and solubility of gases governed by Henry's law. How carbonate cycle dominates pH control in most of aquatic system and regulation of various biogeochemical processes in environment. The role of Chemical speciation in assessing the toxicity associated with different forms of chemical element and their oxidation state illustrating it with arsenic Sources and toxicity of heavy metals such as Pb, Cd, As, Hg in the environment Different types of radionuclides and its effects. Impact of hydrocarbon (saturated and unsaturated) on environment. Mechanism, functions and classification of lubricants into lubricating oil, greases and solid lubricants. It concluded by explaining about degradation of biological waste into biogas.

Unit 4 deals with the **Developments in Environmental Chemistry**. The unit describes about the scientific methodologies/solutions showing phenomenal capability to protect human health and environment and these innovative solutions have been possible through green chemistry. We have had fantastic accomplishments as the solutions were at the molecular level since green chemistry preached the prevention of waste at source rather than treating it up after generation. So, quite a few of the existing processes were redesigned using the basic tenets of green chemistry. Progressively, industries also started adopting the path of green synthesis.

INTRODUCTION TO BLOCK 2

This block focuses on the sources and types of pollutants in air, water and soil. This block explains chemistry of air, water and soil, their composition. Distribution of chemical species in air and water, their properties, – Cation exchange capacity, pH, NPK in soils, soil organic matter, water soluble organic carbon and its significance. This block contains three units.

Unit 1 deals with **Atmospheric Chemistry**. It focusses on atmosphere, the gaseous envelope of the earth, nurtures life on earth and protects it from the harsh environment of the outer space. It serves as a source of oxygen for the sustenance of life on earth and carbon dioxide for plant's photosynthesis, provides nitrogen which is consumed by nitrogen fixing bacteria in producing nitrogen-based molecules, an essential component of life molecules. The emphasis was given on various chemical species, including oxides of nitrogen, carbon and sulphur as well as their particulate matter, present naturally and due to man's activities undergo photochemical reactions, and are responsible for several environmental episodes.

Unit 2 deals with the **Water Chemistry**. This chapter, highlighted the importance of water, distribution and unique properties of water. Apart from various other factors, the properties of water also depend on the salt content in it. Thus, the physical and chemical properties of fresh water differ from those of sea water. It also discussed the presence / addition of chemical species, gases, and organic matter in the water not only alters its physical properties such as colour, odour etc., but also changes its chemical and biological characteristics.

Unit 3 deals with the **Soil Chemistry**. In this unit we have elaborated upon the importance of soil, its nature, chemical properties and composition along with various processes that are involved in the formation of soil. The study of soil is based on two approaches, pedology that deals with studying soil as a natural body while edaphology deals with the study of soil properties with respect to plant production

INTRODUCTION TO BLOCK 3

This block focuses on the **Pollution Chemistry**. The block explains air, water, soil pollution and pollution parameters. The emphasis has been made on various organic and inorganic air pollutants, photochemical smog and their reactions, consequent health effects are addressed. This block contains four units.

Unit 1 deals with **Chemistry of Air Pollution – I**. It explained about gaseous inorganic air pollutants, Carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen oxides, ozone. You will be interested to know about detailed account of various effects of air pollution and the chemistry of acid rain.

Unit 2 deals with the **Chemistry of Air Pollution Part II**. It focusses on the classification of organic air pollutants and their sources. It described in detail about the ozone layer depletion and its impact on biosphere. This unit make you to understand the organic reactions that causing photochemical smog and it concluded by explaining the effects of photochemical smog in humans

Unit 3 deals with the **Parameters of Water Pollution**. It explained basic concept of physico chemical and biological parameters of that are responsible for the constituents found in water systems. This unit also elaborated about the significance of chelating agents in aqueous system, describe the properties of colloidal substance present in water bodies, and the ion exchange method of water management.

Unit 4 deals with the **Chemistry of Hazardous Substances and Wastes**. It explained about various physical and chemical hazards and the effects of physical

and chemical hazards. It provided the knowledge of identifying various types of combustible chemicals and make you to understand the effects of hazardous substance

INTRODUCTION TO BLOCK 4

This block focuses on the **Analytical Techniques in Environmental Chemistry**. In block 3 you have studied about chemistry of air, water and soil pollution. This block deals with the classical method of analysis. This block contains four units.

Unit 1 deals with **Basic Analytical Techniques**. The unit gives a detailed account of the various types of analytical techniques available and used by the analysts. The basic principles involved in the process of analysis will be explained. The unit also deals with the criteria for evaluating that includes sampling and measurement. A brief about evaluation of the analytical data would be given along with an introduction to the concepts of errors, accuracy, precision and significant figures. The unit ends with the ways of reporting the results of analysis. Optical methods based on absorption and emission are discussed in this unit.

Unit 2 deals with **Spectrophotometry**. In this introductory unit on spectrometry we have discussed about the principle and applications of three important analytical tools. Two of these, viz., UV-VIS spectrophotometry and IR spectrometry being techniques based on spectroscopy. We started the unit by defining spectroscopy as an important domain that concerns study of interaction of electromagnetic radiation with matter. It is also discussed the difference between spectroscopy, spectrometry and spectrophotometry before taking up UV-VIS spectrophotometry.

Unit 3 deals with **Chromatographic Techniques**. This unit mainly focused on chromatographic techniques which are used for the quantitative and qualitative analysis in various pharmaceuticals, food and dyes industries. Column chromatography has various disadvantages including manual setup, time consuming and accuracy. It explained various advanced techniques like gas liquid chromatography, HPLC Super critical liquid chromatography and their application which are being employed not only in industries but also for monitoring the environment, GLC is an advanced technique compared to conventional chromatography.

Unit 4 deals with **Radiochemical Techniques**. In this unit we have studied about the basics of radiochemical techniques like isotopes radioactive decay and various units used to measure the radioactivity. Apart from that we have discussed about the terminology that is frequently used while studying radioisotopes and the techniques associated with it. The concept of carbon dating is highlighted that is widely used by anthropologist and paleontologist to estimate the age of dead or decaying material obtained from fossils. At the end of this unit we have discussed about techniques that are popularly used to measure the radiation, principles and brief working mechanisms along with their applications with special reference to environment.

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BLOCK 1

**Fundamentals of
Environmental
Chemistry**

UNIT 1 : ENVIRONMENTAL CHEMISTRY-I

Structure

- 1.1 Introduction
- 1.2 Objectives
- 1.3 Concept and Scope of Environmental Chemistry
- 1.4 Fundamentals of Elemental Stoichiometry
- 1.5 Chemical Equilibrium
 - 1.5.1 Open and Closed System
 - 1.5.2 Reversible Reactions
- 1.6 Chemical Potential
- 1.7 Chemical Kinetics
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- 1.8 Simple Reaction Mechanisms
- 1.9 Order and Molecularity of chemical reactions
 - 1.9.1 Reaction Order
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- 1.10 Chemical Reactions
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 - 1.10.3 Oxidation
- 1.11. Catalysis
- 1.12. Adsorption in Catalysis
- 1.13 Let Us Sum Up
- 1.14 Key Words
- 1.15 References and Suggested Further Readings
- 1.16 Terminal Questions

1.1 INTRODUCTION

Environmental Chemistry is traditionally outlined as “*The study of the origin roots, reactions, impacts, transport, and fortunes of chemical species, in water, soil, and air environments, and the human activity influence on these*”. So according to this definition, the environmental chemistry is generally focusing on the pollutants in the various environments.

However, an updated definition would be “*The study of the chemical balance in natural systems and how the disturbance in this chemical balance happens by the anthropogenic activities by releasing of chemicals into the environment which change the natural ecosystem levels*”. Environmental chemistry encompasses all branches

of chemistry that are influenced on a regional basis by the loss of stratospheric ozone or global warming by urban air pollution or hazardous compounds that emerge from a chemical waste site, or on a global scale. Our courses concentrate on gaining a basic understanding of the nature of these chemical processes, so that the actions of humanity can be measured accurately.

1.2 OBJECTIVES

After studying this unit, you will be able to:

- Understand the concept and scope of environmental chemistry
- Explain chemical equilibrium
- Understand the concept of rate of reaction
- Explain chemical reactions involved in environments

1.3 CONCEPT AND SCOPE OF ENVIRONMENTAL CHEMISTRY

Environmental chemistry should never be synonymous with “green chemistry.” The **green chemistry** aim is to implement chemical processes that use smaller amounts of harmless chemicals as well as less energy use to reduce their impact on the environment. While, the goal of *environmental chemistry* is to understand the chemical reactions and processes that regulate the environmental systems and how the introduction of anthropogenic chemicals affects them. This approach allows environmental chemistry to be constructive instead of reactive.

Formerly, environmental chemistry has had a more reactive approach, to procure and recognizing problems after the occurrence of a tragedy or a clearly obvious impact on the environment with loss of life, damage to plants and animals, or radical changes in environmental conditions – such as the loss of visibility in air and water systems or the depletion of the stratospheric ozone layer. So, “Almost everything that happens in world around us could come under the general heading **Environmental Chemistry**”. Such as-

- Chemical reactions of all kind occur continuously in the atmosphere, in oceans, lakes and rivers, in all living things and even underneath the earth’s crust.
- These reactions take place quite independently of human activities. In order to understand environmental concerns, we need to have awareness not only about what products are intentionally released into the atmosphere, but also of the process under way.
- The normal concepts must be understood so that accurate assumptions can be made about the potential effects of new but related substances.

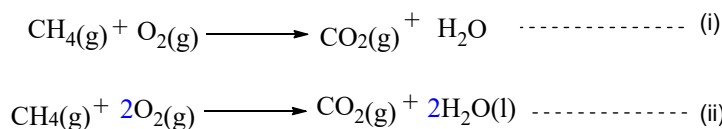
Indeed, although convenient to segment topics for study purposes, **Barry Commoner's first law of the environment** should always keep in mind: **"Everything is related everything else."**

Some topics that are rather distant from equations and reactions should be discussed. That is-

- Knowledge in biological, meteorological, oceanographic, and other fields is equally important to the overall understanding of the environment.
- Conservation of environmental resources along with biological diversity.
- Pollution prevention.
- The social problems associated to growth and environment.
- Design of a renewable energy network that is not polluting.
- Everybody, whatever profession, is impacted by environmental problems such as global warming, ozone depletion, declining forests, energy resources, global biodiversity loss, etc.
- It authorizes us to create a secure, balanced and clean natural environment.
- Large-scale heavy metal land pollution by factories. So this can be passed to waterways and taken up by living beings.
- It also discusses important issues such as safe and fresh clean water, hygienic living standards, fresh and clean air, soil quality, nutritious food and development.
- Nutrients draining from farmland into waterways can contribute to algae blooms and topsoil erosion
- Organometallic compounds
- As new career prospects for environmental protection and sustainability, sustainable environmental law, business administration, environmental health, sustainability and environmental engineering are emerging.
- During rainstorms metropolitan drainage of pollutants rinsing off resistant surfaces (streets, rooftops and parking lots). Typical contaminants include gasoline, motor oil, and other hydrocarbon, metals, chemicals, and soil.

1.4 FUNDAMENTALS OF ELEMENTAL STOICHIOMETRY

A chemical reaction written in form of equation provides the idea of both qualitative and quantitative features. Where qualitative is more a theoretical approach but quantitative is explicitly a practical approach summarizing basic principle of chemistry viz. principle of mass conversion to produce the resultant drawn in product side.



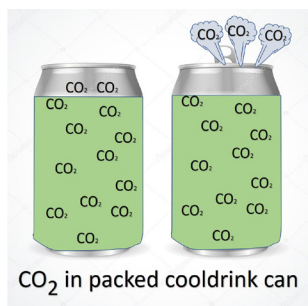
In equation (i) the reaction describes the formation of CO_2 and water from methane via the combustion process, but the quantity of elements in the reactant side and the product side are not equal, hence requires to poise the element proportion on the either side to determine the amount of each compound involved, which is defined as **Stoichiometry**.

Stoichiometrically balanced equation can be achieved via trial-and-error approach. As in the eqn. (i) **1 C-atom** approaches on the both side of the equation, but on the left side, there are **4H** atoms and only **2H** on the right, and to equalise the stoichiometry as in eqn. (ii), we have to double the number of water molecules so that we can get **4H** atoms in either sides. Now, while adjusting the elemental stoichiometry of hydrogen we by-chance changed the atom count for **oxygen** on left-hand side (LHS) and right-hand side (RHS) of the arrow. To normalize this issue, we can multiply the amount of molecular oxygen with 2 to get equal amount of oxygen atom on both the sides.

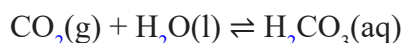
The **quantitative** idea of a balance equation is measured in either moles= Weighed Mass/ Molecular Weight (unit less quantity); Molarity = moles/volume (mol/L) and Weight by Volume (W/V): unit mg/L = Molarity (mol/L) \times Molecular weight (g/mol) $\times 10^{-3}$ (mg/g).

1.5 CHEMICAL EQUILIBRIUM

Chemical equilibrium defined as “A reaction is in chemical equilibrium if the forward reaction rate step equivalent to the reverse reaction rate step. a reaction exists in equilibrium, when the concentration of reactants and products are constant.”

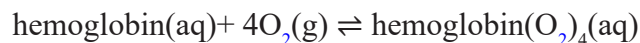


There are several examples of chemical equilibrium across us. One example is a fizzy cooldrink tin can or bottle. In the tin-can there is CO_2 thawed in the liquid. There is also CO_2 gas in the state between the liquid and the cap. There is a continual switch of CO_2 from liquid to gas phase, and from gas phase to liquid form. Though, if we glance at the tin can there does not seem to be any difference. The system is in equilibrium.

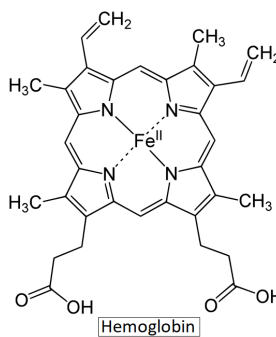


Without the chemical equilibrium it would not be possible to exist as we know it. Another sign of equilibrium in our daily lives occurs within our own bodies. Hemoglobin is a macromolecule which carries oxygen all over our bodies. We

wouldn't survive without it. The hemoglobin must be capable of consuming oxygen, while also releasing it, and this is managed by adjustments in the steadiness of this reaction in distinct locations within our bodies.



Hemoglobin binds with oxygen within the red blood cells of the lungs. This *oxyhemoglobin* flows through the blood stream to cells in the body along with the red blood cells.



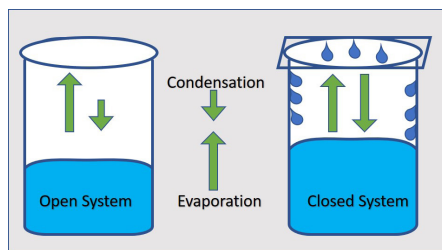
1.5.1 Open and Closed System

An **open system** allows the **energy** and **matter** to move within and outside of the system.

A **closed system** is one where only energy can travel inside and outside the system. Matter can't be obtained from the system or removed from it.

Liquid-gas phase equilibrium

Apparatus



2 beakers, glass sheet, water

Method

Fill two beakers with water in half, and in each case mark the water level.

One beaker covered with a glass sheet.

Leave the beakers for 2 -3 days, watch how the water levels in both beakers change.

Note: You could accelerate this experiment by putting the two beakers over a Bunsen burner, or by heating the water in direct sunlight.

Discussion

In the open beaker, due to evaporation, liquid water become vapors after heat, and the water level decreases. A small proportion of gas molecules may condense again, but condensation is far lower than evaporation, so, the vapors will escape to the atmosphere. The first beaker was an example of an open device in the liquid-gas demonstration, as the beaker could be heated or cooled (a variation in energy), and water vapor (the matter) would evaporate from the beaker.

Evaporation happens in the second beaker too. But at covered condition, the vapour reaches the glass cover sheet, where it cools where condenses again to become liquid water. It returns the water to the beaker. After start of condensation, the rate at which the water volume falls may begin to decrease. There will be no change in the water level at any stage, because the rate of evaporation will be equivalent to the rate of condensation. This represents **the closed System**. This can be indicated as-

Liquid \rightleftharpoons vapour

Observations

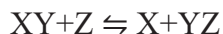
Evaporation is the phenomena when a liquified constituent goes from the liquid stage to the gaseous stage. Condensation is the phenomena when transition of gaseous substance occurs from gas to liquid phase

You will find that; the water level falls faster because of evaporation in the open beaker than in the covered beaker. There is an initial drop in the water volume in the closed beaker, but evaporation tends to stop after a while and the water level in this covered beaker is higher than that in the open one. The reaction in this example will go on in both directions. There is a transition of liquid to water vapor in the forward direction. There may also be a reverse transition, as vapor condenses again to form liquid.

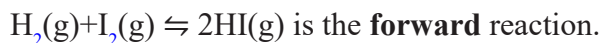
So, conclusion from above discussion is that, in a **closed system** it is apparent for reactions to be reversible and to reach at **equilibrium**.

1.5.2 Reversible Reactions

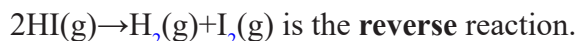
There are certain reactions which can occur in two directions. First direction is **forward reaction** in which reactants come together to shape the products, while other direction is **reversible direction** and vice versa in which the products again form the reactants. To display this form of reversible reaction, a special double-headed arrow (\rightleftharpoons) is used.



So, in reversible reaction-



The forward reaction always written **left to right** from the reaction.



The reverse reaction always written **right to left** of the given equation.

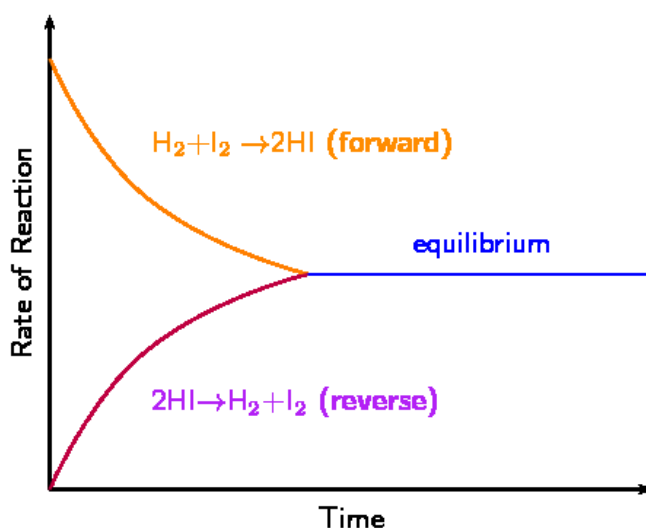


Figure 1.1 The change in rate of forward and reverse reactions in a closed system

In any reaction, the product is formed more slowly as reactant amount decreased. In a reversible reaction, the reactant is formed rapidly as the product quantity increases. Ultimately, forward reaction rate (reactants \rightarrow products) equals to reverse reaction rate (products \rightarrow reactants). at this moment, there are still reactants present, but no more progresses seem to be happening. The reaction is said to be in chemical equilibrium.

Although no macroscopic changes can always be detected, this doesn't mean the reaction has ended. The forward and reverse reactions tend to occur and so there are still microscopic changes in the system. This state is called **dynamic equilibrium**.

Reactions which are going to be completed are *irreversible*. However, in some reactions the reactants form products (in a forward reaction), and the products can change back into reactants (in a reverse reaction).

SAQ 1

What is the traditional definition of environmental chemistry?

1.6 CHEMICAL POTENTIAL

In the year 1875 J. Gibbs coined the word “chemical potential”. Chemical potential is a concept of thermodynamics, common to all, not only in the study of materials but also in physical, chemical engineering and biology background. It is a key concept because it is possible to achieve all the thermodynamically impressions of a substance at a given temperature and pressure from knowledge of its chemical potential. Chemical potential establishes the stability of materials under the constant pressure and temperature, such as chemical products, and solutions, and their capacity to react chemically to form new materials, to turn into another physical states, or to move from one space position to another.

There are few important points related to Chemical Potential. Such as-

- Chemical potential energy mainly depends on the strength of the bonds. Strong bonds have low energy and weak ones have high energy. Large quantities of heat and/or light energy can be released during strong bonds are forming. In other terms, chemical potential is correlated with the system's electronegativity.

Relation between chemical potential and electronegativity:

$$\mu = -\chi - (1)$$

where, μ = Chemical potential

χ = Electronegativity

- The stored energy in food molecules are preserved in form of **chemical potential energy**, that can-do work in the future. When our body breaks molecules for catabolism, the released energy can be used as work. But potential energy can't preserve only in food molecules.
- The value of the chemical potential of a substance depends upon both temperature and pressure. Additionally, the potential will increase when the pressure increase.
- Intensive properties are substance independent and depend entirely on material. Some intensive properties are like chemical potential temperature, density, refractive index, etc.
- Chemical energy is the capability of a chemicals to undergo a chemical reaction to turn it into other substances. Examples include food, batteries, fuel, etc. Breaking or creating of chemical bonds requires energy, which may be either evolved or absorbed from a chemical system.
- Chemical energy is a type of potential energy; however, kinetic energy is the energy in motion. Chemical energy deals with the energy stored in the bonds between atoms.
- Chemical potential increases with the density "n" of particles. Particles flow from high 'n' systems to low 'n' systems. The chemical potential of an ideal gas is always negative.

1.7 CHEMICAL KINETICS

Chemical kinetics is the evaluation of the rates and the mechanisms of chemical processes. This is of great practical importance. It is also important to know under what conditions a slow but valuable reaction can be made to proceed rapidly to produce a desired high yield product. For environmental chemistry, it has great predictive value.

By observing the kinetics and environmental reaction mechanisms, we can at least estimate approximately the residence times of both polluting and non-polluting

organisms. Our knowledge of various pollutants and atmospheric phenomena such as depletion of ozone, acid rain, photochemical smog etc. is focused primarily on the study of the kinetics of individual rate constants of thermal and photochemical reactions.

1.7.1 Kinetics of Reactions of Different Orders

Zero order reactions occur at a constant rate, and the magnitude of the rate does not change with time. The concentration plot against time is linear, and the slope of this line is equal to the zero-order rate constant. The differential of rate equation and its integrated forms is in Eq1.

$$-d[A]/dt = k = xt \text{ -(2)}$$

where k is the zero-order rate constant, and x is the amount reacted in time, t .

For a **first order reaction**, *the rate depends on the first power reactant concentration*. Consider the rate of a first order reaction, defined by Eq-3.

$$-d[A]/dt = k[A] \text{ -(3)}$$

On integrating Eq. 3, we obtain the following forms of rate law for a first order reaction.

- (i) $\log \{[A]_o/[A]_t\} = 2.303kt$
- (ii) $[A]_t = [A]_o e^{-kt}$
- (iii) $\log \{a/(a-x)\} = 2.303kt \text{ -(4)}$

where $[A]_o$ = initial concentration of the reactant, $A = a$ and $[A]_t$ = concentration at time $t = (a-x)$, and concentration of the reactant reacted in t time = x .

The unit of the first order rate constant is s^{-1} . It is independent of the unit of concentration used.

A **second order reaction** is one in which the rate depends on (i) *the concentration of one reactant raised to power two* or (ii) *on the concentrations of two reactants each raised to the first power* as shown in the rate laws (5) and (6).

$$\text{Rate} = k [A]^2 \text{ -(5)}$$

$$\text{Rate} = k[A][B] \text{ -(6)}$$

The Eq.6 changes into Eq. 5, if the initial concentrations of both A and B are taken equal. So when $[A] = [B]$, Eq. 6 becomes same as Eq. 5: $\text{rate} = k[A][A] = k[A]^2$.

On integrating Eq. 5, we get

$$k = (1/[A]_t - 1/[A]_o)$$

$$k = (1/t) \{ x/a(a-x) \} \text{ -(7)}$$

In Eq. 7, the symbols have same meaning as in case of first order reaction. The unit of a second order rate constant is $L.mol^{-1}.s^{-1}$.

In **third order reactions**, the rate expressions are of the type:

$$\text{Rate} = k [A]^3$$

$$\text{Rate} = k[A][B]^2 \text{ and}$$

$$\text{Rate} = k [A] [B] [C].$$

Under the condition, $[A] = [B] = [C]$, rate laws (ii) and (iii) will also reduce to rate law (i). The integrated form of the rate law: $\text{rate} = k [A]^3$ is Eq. 8.

$$k = (1/2t) (1/[A]t^2 - 1/[A]_0^2) \text{ -(8)}$$

The atmospheric oxidation of nitrous acid by O_2 ($2HNO_2 + O_2 \rightarrow 2HNO_3$) obeys the third order rate law: $-d[O_2]/dt = k [HNO_2][O_2]^2$. The unit of third order rate constant is $L^2 mol^{-2} s^{-1}$.

For **Pseudo-order reactions**, because of the experimental conditions used, the order of the chemical reaction tends to be less than the true order. Pseudo-orders arise when there is a significant excess of one or more reactants relative to others. For example, the atmospheric reaction: $NO + O_3 \rightarrow NO_2 + O_2$, obeyed the rate law:

$$-d[O_2]/dt = k [NO] [O_3] \text{ -(9)}$$

Under the condition $[O_3]$ in large excess (≥ 10 times) over $[NO]$, up to the end of reaction there would hardly be any significant change in $[O_3]$ and so $[O_3]$ would remain virtually constant. The kinetics will then obey the rate law:

$$-d[O_2]/dt = k_1 [NO] \text{ -(10)}$$

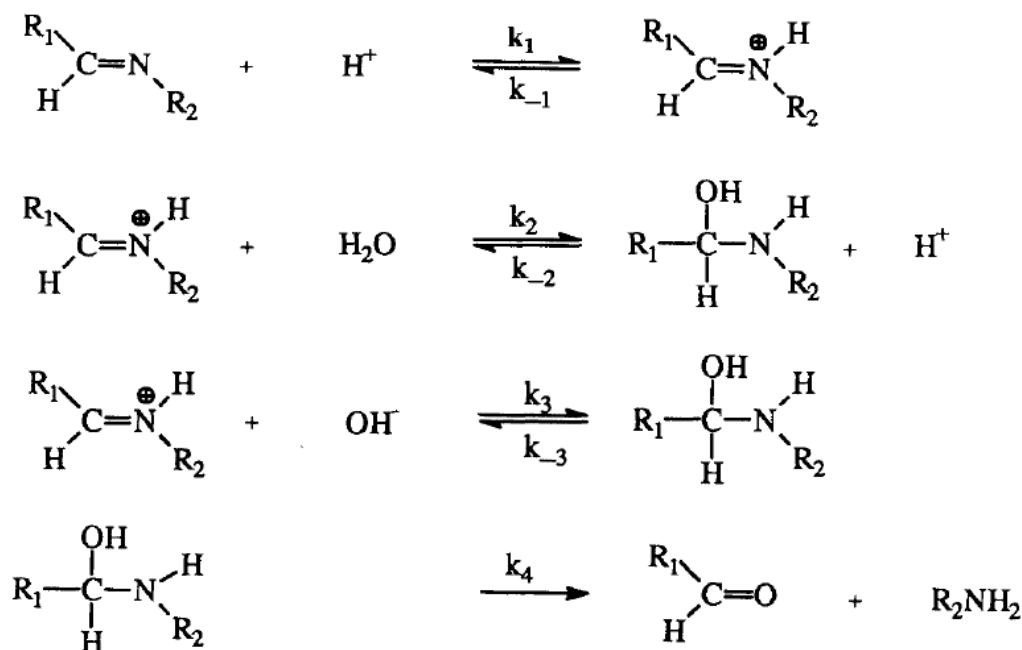
where $k_1 = k[O_3]$. So, the apparent order in O_3 during the reaction will be zero. The reaction will, therefore, follow a first order kinetics in $[NO]$.

1.8 SIMPLE REACTION MECHANISMS

The transformation of organic chemicals most often occurs in several molecular events referred to as **elementary reactions**. An elementary reaction is described as a process in which reacting chemical species pass via a single transition state without the intervention of an intermediate. A sequence of individual elementary reaction steps constitutes a **reaction mechanism**. For example, the overall reaction for the hydrolysis of a Schiff base is written:



The reaction mechanism for this seemingly simple reaction is in fact quite complex and is composed of four elementary reactions (Cordes and Jencks, 1963).



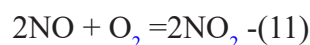
A reaction mechanism is a hypothesis or model that has been conceived from experimental evidence. As new experimental evidence is obtained, changes in the proposed reaction mechanism may be required. Chemical kinetics is probably the most powerful tool for the investigation and development of reaction mechanisms. The consistency of a reaction mechanism can be verified in the laboratory by determining the dependence of reaction rates on concentration.

It is useful to classify elementary reactions as per their molecularity and described as the sum of the exponents that appear for one single elementary reaction in a rate equation.

1.9 ORDER AND MOLECULARITY OF CHEMICAL REACTIONS

1.9.1 Reaction Order

The **reaction order relating to a chemical species** is defined as the order of the concentration in the differential form of that reactant species of the rate law, and **the order of a reaction** is defined as sum of the powers of all the concentration terms that occur in such a rate law. The experimental kinetics rate law for the important atmospheric reaction (11) is Eq. 8.



$$-d[\text{O}_2]/dt = k[\text{NO}]^2[\text{O}_2] \quad (12)$$

The Eq. 12 shows the order with respect to NO is two and with respect to O_2 is one, and the order of reaction to be three (i.e., the aggregate of the orders of NO and O_2).

Consider the aqueous phase atmospheric Fe^{3+} -catalyzed oxidation of dissolved sulfur dioxide, generally written as sulfur (IV), by O_2 . It obeys the rate law:

$$dS(IV)dt = k[\text{Fe(III)}][\text{S(IV)}] / [\text{H}^+]. \text{-(13)}$$

the reaction is first order in each of Fe(III) and S(IV) and of negative first order in $[\text{H}^+]$. So, order can be negative, and fractional also zero.

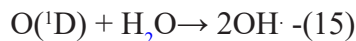
1.9.2 Molecularity of the Reaction

Reactions typically occur in more than one step, so each reaction is comprised of a series of elementary reactions. *The molecularity is the number of reactant molecules, ions, radicals or any other chemical species in an elementary step.* A reaction may have two or more steps and then the molecularity of each step would depend on the number of reactant molecules involved in that step.

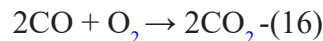
Unimolecular Reactions require only one molecule of reactants in the reaction. Example-The photodissociation of ozone in troposphere.



Bimolecular Reactions involve two reactant species. These are two-body reactions. Examples-The formation of the hydroxyl radical, (OH-radical is most important in atmospheric chemistry).



Termolecular (or Trimolecular) Reactions involve three reactants. The formation of carbon dioxide, formation of ozone in troposphere are classical examples of this type.



SAQ 2

What is the source of electrons in natural reducing environments?

.....

.....

What is the kinetic of chemical reaction in different orders?

.....

.....

1.10 CHEMICAL REACTIONS

There are several chemical reactions involved in environments. Among them, highly involved reactions are given below-

1.10.1 Hydrolysis

Hydrolysis is an example of nucleophilic displacement reactions in which a **nucleophile** (*an electron-rich species containing an unshared pair of electrons*) attacks an **electrophilic** atom (*an electron-deficient reaction center*).

Hydrolytic processes are not limited to the bodies of water such as rivers, streams, lakes, and oceans usually associated with the term aquatic ecosystems. Hydrolysis of organic chemicals also can occur in fog water, biological systems, groundwater systems, and the aqueous microenvironment associated with soils and sediments.

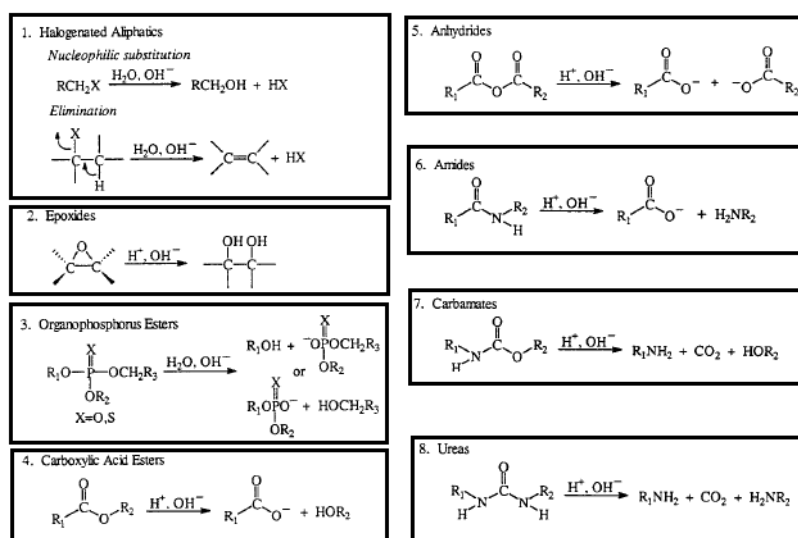


Figure 1.2 Hydrolysis reactions involved in our ecosystems

Hydrolysis is described as a chemical transition in which an organic molecule, RX, reacts with water, resulting in the forming of a new covalent bond with OH and a cleavage in the original molecule of the covalent bond with X (the leaving group). The resulting reaction is that X is substituted by OH~ (Harris, 1981; Mill and Mabey, 1988)



Hydrolysis Kinetics depends on-

1. Specific Acid and Base Catalysis
2. pH Dependence

1.10.2 Reduction

Reducing environments abound in nature (soils and waters, aquatic system, sewage sludge, hypolimnia of stratified lakes, and oxygen-free areas of eutrophic rivers);

until recently, however, very few investigations of organic reactions characteristic of these systems have been undertaken.

The realization that pollutants, which are normally considered persistent in aerobic environments, may not be nearly as persistent in a reducing environment has generated a great deal of interest in the behaviour of organic chemicals in anaerobic environments. The elucidation of reductive transformation pathways may lead to the development of remediation technologies for the removal of organic pollutants from contaminated ecosystems.

Reduction, defined as a gain of electrons, occurs when there is a transfer of electrons from an electron donor “or reductant” to an electron acceptor “or oxidant”. The oxidant in this case is the organic chemical or pollutant of interest. Reductive (and oxidative) transformations can be distinguished from other processes (e.g., hydrolysis) by determining if a change in the oxidation state of the atoms involved in the reaction process has occurred.

For example, the transformation of 1,1,2,2-tetrachloroethane can result in the formation of two reaction products, 1,1,2-trichloroethylene and 1,2-dichloroethylene. Although our understanding of reductive transformations in the environment has progressed to the point that we can identify the types of functional groups that will be susceptible to reduction in the environmental systems, our **limited** knowledge of reaction mechanisms for such transformations currently is a barrier to the prediction of absolute reduction rates, and how reaction rates will vary from one environmental system to the next.

The noticeable question arises here is, “**What is the source of electrons in natural reducing environments?**” The cumulative knowledge in this area suggests that naturally occurring reductants are not limited to two or three reactive species, as is the case for hydrolysis, but that a complex array of species is involved, ranging from chemical or “abiotic” reagents such as sulfide minerals, reduced metals, and natural organic matter, through extracellular biochemical reductants such as iron porphyrins, corrinoids, and bacterial transition-metal coenzymes, to biological systems such as microbial populations. Furthermore, the relationship between these various reductants in natural systems is most likely quite complex. For example, chemical species such as reduced metals and sulfide ion may be the direct result of microbial metabolism.

Reductive transformations are most suitably classified according to the type of functional group that is reduced. General schemes explaining the reductive transformations that are known to occur in natural reducing environments are summarized-

1.10.2.1 Reductive Dehalogenation

The reduction of halogenated aliphatic and aromatic compounds chemicals has been observed in a variety of environmental and laboratory systems, including anaerobic sediments, soils, anaerobic sewage sludge, groundwaters, aquifer materials, reduced iron porphyrin systems, bacterial transition-metal coenzymes, and mineral sulphides, and various chemical reducing agents. Reductive dehalogenation is a

detoxification process. The motivation to understand the reaction pathways of halogenated chemicals in these types of systems results from their widespread contamination of sediments, soils and groundwaters due to their frequent use as agrochemicals, solvents, and synthetic intermediates.

1.10.2.2 Nitroaromatic Reduction

The reduction of nitroaromatics in anaerobic systems has received considerable attention because of their importance as agrochemicals, munitions, textile dyes, and dye intermediates. The reaction products resulting from the reduction of nitroaromatic compounds are aromatic amines. The formation of aromatic amines occurs through a series of electron transfer reactions with nitroso compounds and hydroxylamines as even-electron intermediates. Pentachloronitrobenzene (PCNB) is another example of a nitroaromatic agrochemical that is known to undergo facile reduction in anaerobic systems. PCNB has been identified as a pollutant in river water and groundwater. The reduction of trifluralin has been observed in sediments and flooded soils. Reduction of nitroaromatics can occur through abiotic pathways. The reduction of TNT and DNT, as well as other polynitroaromatics, has been studied in some detail in anaerobic microbial enzyme systems. The reduction of 2-bromo-4,6-dinitroaniline, an important intermediate in the preparation of textile dyes that has been detected in river waters, in anaerobic sediment-water systems.

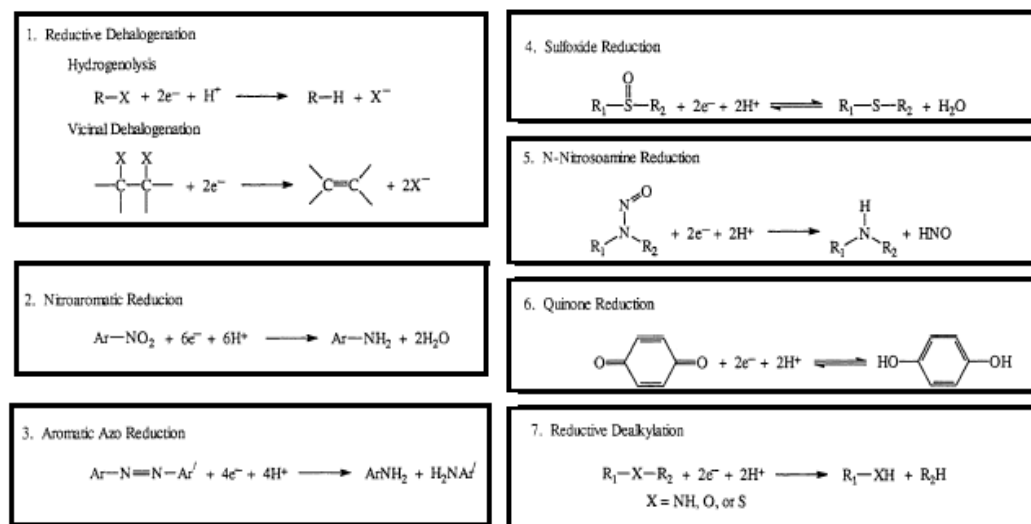


Table 3.1. Reductive Transformations Known to Occur in Natural Reducing Environments

Figure 1.3 Reduction reactions involved in environment systems

1.10.2.3 Aromatic Azo Reduction

Concern over the environmental status of aromatic azo compounds derives largely from their significance in the textile dye industry. Around 50 % of the dyes available on the market today are azo compounds. About 12 % of the synthetic fibre dyes produced each year are expected to be lost in waste streams by production and recycling processes, and 20 % of such losses would reach the atmosphere by wastewater treatment system effluents. The reductive cleavage of the azo linkage of the dyestuffs in aquatic ecosystems represents a possible pathway for the entry of aromatic amines into these systems. The aromatic amines are considered a hazardous class of compounds because of their mutagenic and carcinogenic properties.

1.10.2.4 *N*-Nitrosamine Reduction

The N-nitrosoamines are also a highly studied and important class of chemicals due to their mutagenic and carcinogenic properties. Much of this work has suggested that the formation of N-nitrosoamines may occur in crop soils and in foodstuffs that have been treated with agrochemicals containing secondary nitrogens (e.g, atrazine) and heavy applications of nitrogen fertilizers. Several N-nitrosoamines also have important uses in industrial processes. For example, N-nitrosodiphenylamine is extensively applied in the rubber industry to delay vulcanization.

1.10.2.5 Sulfoxide Reduction

The environmental significance of organic sulfoxides results primarily from their importance as agrochemicals; specifically, the organophosphorus and carbamate insecticides containing sulfoxide moieties. The reduction of sulfoxides is a two-electron transfer process that results in the formation of thioethers. Because the reduction of sulfoxides to thioethers is reversible, reoxidation of the thioether to the sulfoxide may occur in aerobic environments. Although oxidation of sulfoxides to sulfones (RSO_2R) has been observed in aerobic systems, no evidence exists that suggests reduction of the sulfone functional group to the sulfoxide moiety will occur in anaerobic systems. The chemical reduction of sulfones in the laboratory also is known to be quite difficult.

1.10.2.6 Quinone Reduction

Quinones are reduced by a one-electron transfer reaction to the radical. Transfer of the second electron results in formation of the hydroquinone. Because this reaction is readily reversible, the equilibrium between the quinone, semiquinone, and hydroquinone will be dependent on the reduction potential of the system of interest.

1.10.2.7 Reductive Dealkylation

Reductive dealkylation is the replacement of an alkyl group on a heteroatom with hydrogen. Although dealkylation may be considered a relatively minor structural change for many organic chemicals, the “unmasking” of a reactive functional group, such as an amino or hydroxyl group, can significantly alter a chemical’s behaviour in environmental systems. Dealkylation appears to be a common transformation pathway for agrochemicals with the requisite functionality.

1.10.3 OXIDATION

Oxidation is defined as a loss of electrons. Oxidizing agents gain electrons and are electrophiles. In organic chemistry, oxidation can either be associated with the introduction of oxygen into a molecule or the conversion of a molecule to a higher oxidation state. For example, in Equation 18.



The first step in the sequence is the incorporation of oxygen by a formal “oxygen atom donor,” whereas the second is formally a dehydrogenation, or oxidation of the carbon atom to a higher formal oxidation state. Almost all oxidations are kinetically second-order reactions rate is proportionate to the concentrations of both the oxidizing agent, Ox, and the substrate, A (Equation 19).

$$-dA/dt = k [Ox] [A] \text{ -(19)}$$

For reactions in water, there are few values for the rate constant, k , and few data on the concentrations of potential oxidants.

In environmental chemistry, there are many sources of oxidants whose importance is highly variable due to changes in concentration or reactivity as one moves from one region of the environment to another. A potent oxidant such as the hydroxyl radical, $\cdot OH$, that is of critical importance for organic transformations in the gaseous stage or during combustion, may not be important at all in another environmental compartment such as the soil. This could either be due to inadequate production rates for the species or to rapid side reactions that diminish its steady-state concentration. For the oxidation reaction, Oxygen is present as molecular oxygen (like autooxidation, superoxides, singlet oxygen, or in the form of ozone), Hydrogen peroxides decay products (like hydroxyl radical, peroxy radical, alkoxy and phenoxy radicals), clay and metal oxides, and thermal oxidation in the environments. These considerations will be addressed as each oxidizing species is discussed in turn for the remainder of the chapter.

- A. Molecular Oxygen
 - a. Autooxidation
 - b. Superoxide
 - c. Singlet oxygen
 - d. Ozone and Related Compounds: Photochemical Smog
- B. Hydrogen peroxide and its decay products
 - a. H_2O_2
 - b. Hydroxyl radical
 - c. Peroxy radical
 - d. Alkoxy and Phenoxy radical
- C. Surface Reactions
 - a. Clay
 - b. Silicon oxides
 - c. Aluminium oxides
 - d. Iron oxides
 - e. Manganese oxides
- D. Thermal Oxidations
 - a. Combustion
 - b. Incineration

REACTIONS WITH DISINFECTANTS

Water disinfection has been quite successful in practically eliminating many acute waterborne diseases from the countries where it has been widely practiced, but its possible roles in the development of chronic health disorders, such as cancer, have not been fully scrutinized. Potential biohazards arise during drinking water treatment and disinfecting agents are used for the treatment of industrial wastewaters to remove undesirable colors, odors, and toxic organic compounds as well as to

reduce the number of potentially harmful microorganisms in the effluent. Because of the higher concentrations of organic matter typically found in these waters, the likelihood of organic-disinfectant reactions occurring at significant rates is enhanced.

- A. Free aqueous chlorine (HOCl)
 - 1. Chlorine in Water
 - 2. Oxidation Reactions
 - 3. Substitution and Addition Reactions
 - 4. Enolizable Carbonyl Compounds: the Haloform Reaction
- B. Combined aqueous chlorine (chloramines)
- C. Ozone
- D. Chlorine dioxide

ENVIRONMENTAL PHOTOCHEMISTRY

The uptake of light energy (quanta) by organic compounds may cause subsequent photophysical or photochemical events to occur. Photophysical processes include emission of radiant energy (light or heat), whereas photochemical changes produce new compounds by transformations that include isomerization, bond cleavage, rearrangement, or intermolecular chemical reactions. In the environment, photochemical reactions have been reported to occur in the gas phase (troposphere, stratosphere), aqueous phase (atmospheric aerosols or droplets, surface waters, land-water interfaces) and in the solid phase (plant tissue exteriors, soil and mineral surfaces). All these possibilities need to be considered when fates of organic compounds in nature are considered. Although in many cases the contribution of photochemical processes is negligible, in others photolysis is by far the dominant pathway for loss of a chemical. There are several definitions to understand about photochemistry. Such as-

Internal conversion, thermal reversion of the excited singlet to the ground state with the release of heat to surrounding molecules such as the solvent. Because these two states are of like multiplicity, the transformation is allowed in terms of quantum theory and is often a very favourable process with a rate constant close to diffusion control.

Fluorescence, emission of visible or ultraviolet radiation. The emitted photon is always of a longer wavelength than the absorbed photon. This is also a quantum mechanically allowed process and usually occurs rapidly.

Intersystem crossing, a quantum-forbidden transition that produces a new excited state with unpaired electrons, a triplet. These transitions are usually 100 or more times slower than diffusion control. Triplet states have some degree of diradical character.

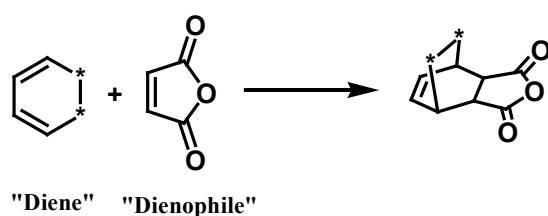
Quantum Yield: The quantum yield, of any photochemically induced process is defined as that fraction of the species converted to an excited state that undergoes a fate. Conversion of a triplet to the corresponding ground-state singlet (without the intervention of a quencher) is another quantum-mechanically forbidden and usually inefficient ISC process, called **phosphorescence** when it is accompanied

by emission of radiation. Phosphorescence and fluorescence are examples of luminescence phenomena.

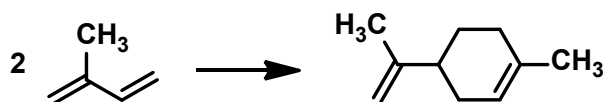
Chemical reaction involved. Because of the low instantaneous concentrations of most excited singlets, bimolecular chemical transformations involving them (such as reaction with a solvent) are not usually important unless they are kinetically very fast. Normally, one of the above processes predominates.

The Diels-Alder Reaction

The Diels-Alder reaction, a classic of synthetic organic chemistry, is theoretically a 4 + 2 cycloaddition in which a diene and a “dienophile” with very different electron abundances combine to form a new six-membered ring. The reaction has great synthetic usefulness and has attracted many researchers interested in its practical applications and mechanistic aspects.



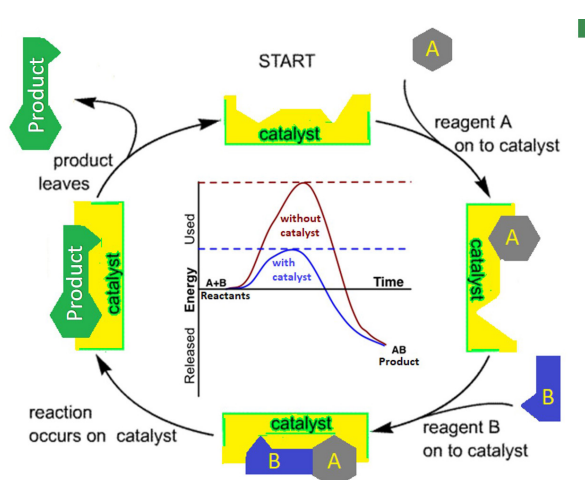
It is not at all certain whether any Diels-Alder reaction occurs under environmental conditions, although it has been suggested as a mechanism for the formation of *dl*-limonene from polyisoprene in the pyrolysis of waste rubber tire material (Equation 7.2; Pakdel et al., 1991).



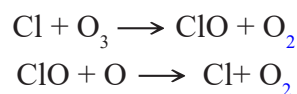
Berzelius coined the term “catalysis” as early as 1836 to describe different reactions to decomposition and transformation that involve the catalyst and its environmental aspects.

1.11 CATALYSIS

Catalysis is the process where a very little quantity of foreign material, called a catalyst, raises a chemical reaction rate without being absorbed by itself. Catalysis is environmentally beneficial and plays an essential role in the production of new and existing chemicals. In the catalysed reactions, less energy is needed for production, and higher efficiency is observed in



generating less by-products, co-products and other waste substances. Catalysts can be configured to be safe to the environment. Currently, a variety of catalysts are used in industrial manufacturing, and several have advantageous impacts. The green synthesis uses catalysts that can be recycled and reused to drive the reaction rather than the additional reagents used for the original process, which affected waste to accumulate at each stage. Any catalytic reaction that generates no waste will sustain the atoms. A catalyst allows the reaction rate to increase, and we can suggest that the catalyst speed up the chemical reaction. The catalysts are the substances that expedite a reaction process without being absorbed and undergoing any chemical changes. The catalysts though participate in the reaction and act by providing a route of lower activation energy. The catalysts are regenerated at the end of the reaction. For example, the stratospheric ozone depletion is due to catalytic action of species such as Cl, NO etc., as in the reactions:



In the above cycle, a single Cl can destroy thousands of O_3 molecules. Another important example is the iron-catalyzed oxidation of dissolved SO_2 in rainwater.

Another Example: When KClO_3 is heated at very high temperatures, the emitted oxygen gas will escape very gradually, but if MnO_2 is mixed up in tiny quantities then oxygen gas will be produced rapidly even at normal temperatures. In the first case Cl is serving as a catalyst and in another case MnO_2 is serving as a catalyst.

Types of catalysis

There are two types of catalysis:

- (i) **Homogeneous catalysis:** catalyst and reactants are in the same physical state
- (ii) **Heterogeneous catalysis:** catalyst and reactants both are in different physical states

Types of catalyst

There are various types of catalyst but usually, there are four types which are considerable and important-

- (i) **Positive catalyst:** The catalyst which stimulates the rate of reaction
- (ii) **Negative catalyst:** The catalyst which turn off the rate of reaction
- (iii) **Auto catalyst:** If any substance is produced during any chemical reaction, will work as catalyst for the *same* chemical reaction.
- (iv) **Induced catalyst:** If any substance is produced during any chemical reaction, will work as catalyst for *some other* chemical reaction.

Surface and Aqueous Catalysis

Clay Catalyzed Reactions or rearrangements:

Chemicals play an important role in contributing pollution; hence retrievable and reusable catalysts are prime demand where clays and zeolites are noteworthy. Clay were reintroduced in multiple reaction strategies like hydroalkoxylation in ether formation, esterification etc. Modified clays have also been used in oxidation and

formylation reactions. The divergence of clay catalyst was identified when they acted superbly with rearrangement reactions starting from pinacole -pinacolone, to isomerization, to Claisen rearrangement.

1.12 ADSORPTION IN CATALYSIS

A global environmental issue arises due to the toxic effects of chemicals, and heavy metal contamination. At varying concentrations these contaminants are found dissolved in water and wastewater. Because of the large quantities of coloring required in clothing, paper product, dyes are identified as one of the heavy pollutants of water bodies. paints and plastics. Potential risks in drinking water caused by heavy metals and other anions have raised public concern. Generally, the intake of metal ions and anions causes chronic effects, and humans can experience long-term exposure to such pollutants without knowing it.

Various physical and chemical approaches have been used to remove contaminants from polluted water. Adsorption was proposed as cheaper and more effective than chemical or physical techniques between all these approaches. Due to their reasonably easy design, activity, cost efficiency and energy savings these are favoured over other methods. Many components were effectively used in means of staining of water contaminants, such as microspheres, clays, composites clay-alginate, activated carbon chitosan, metal oxides, etc. The main classes of adsorbents include mesoporous silica, activated charcoal, bagasse, zeolite, metal oxides, alumina, carbon nanotubes, clay, activated carbon, and polymeric resin, etc.

These catalysts demonstrate the value of adsorption as catalytic properties. This type of catalysis is ecofriendly as it escalates the reaction rate without being utilized by itself and therefore the chemical and energy industries depend heavily on catalysis as a result. The popular Haber-Bosch method for ammonia generation uses metal-based catalyst for adsorption of Nitrogen and hydrogen gas and synthesis of ammonia industrially.



Figure 1.4 Different types of adsorbents

Classification of Adsorbent

Adsorbent can be categorized into three groups:

(a) Nonpolar solids:

Most of the molecular solids are non-polar. Such non-polar molecular solids do not dissolve in water. Where the adsorption is mainly physical e.g., activated charcoal.

(b) Polar solids:

These materials adsorb both polar and nonpolar molecules. However, they show preference with polar molecules. When the adsorption is chemical e.g. silica and aluminium oxides.

(c) Chemical Adsorbing surfaces which adsorb the molecules and subsequently release them after reaction, which may be either show catalytic approach by leaving the surface unchanged, or non-catalytic by replacing the surface atoms.

Adsorbent can also be classified as conventional or non-conventional adsorbents. Activated carbon, polymeric carbon, aluminous, silica gel, bauxite etc categorized as **Convention adsorbents**, while **Non-conventional adsorbents** include, hardwood, lignite, fly-ash, sawdust etc.

Mechanism of Adsorption

Adsorption is a simplistic process in which adsorptive molecules (gas or liquid) bind to a solid surface. In fact, adsorption is implemented as an operation in a column filled with porous sorbents, whether in batch or continuous mode. In these cases, the consequences of mass transfer are inevitable. The three common steps include: Film diffusion (external diffusion), Pore diffusion [intraparticle diffusion (IPD)] and Surface reaction.

Factors affecting adsorption

Some of the significant variable affecting adsorption are nature of the adsorbate and adsorbent, diffusion through the passage with in the catalyst particles (either macropores or micropores), surface area of adsorbent, Activation of adsorbent, rate of air flow, vapour concentration, humidity, temperature, degree of regeneration, contact time, processing method adopted etc. The slowest of these steps will determine the rate for the whole process and is called rate determining step.

Equilibrium Adsorption Isotherms

The equilibrium properties of a gas-solid system are defined by a curve of the concentration of adsorbed gas on the solid at constant temperature as a function of the equilibrium partial pressure of the gas. Such a curve is considered as an adsorption isotherm. Table shows the most well-known Isotherms which indicate the adsorption heat dependence on surface coverage implied by increasing isotherm. There are several more isotherms available according to individual requirements.

Isotherm	Isotherm equation	Uses
Henry's	$q_e = K_{HE} C_e$	One-Parameter Isotherm Simplest adsorption isotherm

Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}$ $R_L = \frac{1}{1 + k_L C_e}$	Homogeneous binding sites (same affinities), alike sorption energies, and no interactions between adsorbed species. RL is separation aspect which decides whether the adsorption is un-favorable when its value is >1, linear (=1), favourable (0 < RL < 1), and irreversible (RL = 0)
Freundlich	$q_e = k_f c_e^{1/n}$	Heterogeneous surfaces (varied affinities), 1/n (adsorption intensity) that specifies the energy and the heterogeneity of the adsorbent sites (1/n < 1 = Langmuir, 1/n > 1 cooperative adsorption)
Temkin	$q_e = \frac{RT}{b} (k_T c_e)$	Effective only for an intermediate range of adsorbate concentrations and gives information for adsorbate/adsorbate interactions, where b (J/mol) is Temkin isotherm constant k _T (L/g)—Temkin isotherm equilibrium binding constant
Flory - Huggins	$\ln\left(\frac{\theta}{C_e}\right) = n \ln(1 - \theta) + \ln k_{FH}$ $\Delta G^\circ = -RT \ln(k_{FH})$ $\ln\left(\frac{1000 * q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$	Account for the characteristic surface coverage of the adsorbed adsorbate on the adsorbent and the spontaneity of the process using ΔG ^o value obtained from K _{FH} , where, n is number of adsorbates occupying adsorption sites, and K _{FH} is Flory-Huggins equilibrium constant (L.mol ⁻¹)
Elovich	$\ln \frac{q_e}{c_e} = \ln k_E q_m - \frac{q_e}{q_m}$	Define the kinetics of chemisorption and Multilayer adsorption, where K _E is equilibrium constant (L.mg ⁻¹) and q _m is maximum adsorption capacity (mg.g ⁻¹)

SAQ- 3

What is the difference between adsorption and absorption? Explain with example?

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Explain the Catalytic cycle with figure.

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1.13 LET US SUM UP

Environmental chemistry focuses on the nature and effect of chemicals in groundwater, surface water and soil. We will learn in the Environmental Chemistry how chemicals-generally pollutants-pass through the environment. We are also studying the impacts of these pollutants on habitats, animals and human health. Environmental chemistry advises on the movement and effect of soil and groundwater pollutants, evaluate long-term threats to ecological and human health, apply for environmental permits to carry out corrective strategies, identify polluted soils as hazardous waste and control their disposal, and monitor on-site remediation. What type of reactions are happening during chemical processes and its effect on environment? After reading contents of this unit, we will observe how chemical reactions are involved in our surroundings. What type of reaction order and molecularity, chemical kinetics and potential are involved? Reactions are going on one direction or reversible.

1.14 KEY WORDS

Anthropogenic Pollution

It is defined as the introduction of harmful substances or the creation of harmful impacts in the environment that are directly tied to man's activities, including: agriculture, industry, and energy production and use.

Acid rain

Acid rain, or acid deposition, is a specific term that encompasses any type of precipitation of acidic elements, including rain, snow, fog, hail or even acidic particles, such as sulphuric or nitric acid dropping from the atmosphere onto the earth in wet or dry forms.

Ozone layer depletion

Ozone shield, carries high concentration of trioxxygen, in Earth's stratosphere is a special region that absorbs most of the UV radiation coming from Sun. **Ozone depletion**, steady diminishing of Earth's ozone layer in the stratosphere caused by the release of chemical gaseous chlorine or bromine from industry and other human activities.

Global warming

Global warming is a human caused phenomenon, in which average temperature of Earth climate increases. *Carbon dioxide* plays a vital role in elevating greenhouse gas concentration promoting severe illness to climate in form of global warming.

Nuclear explosion

Anything excess is a poison, the intense and rapid release of energy from a high-speed nuclear reaction or explosion more precisely cause a huge damage to the life. Apart from heat energy nuclear explosions can introduce radioactive particles in the stratosphere causing global fallout.

1.15 REFERENCES AND SUGGESTED FURTHER READINGS

1. Environmental chemistry Tenth edition. / Manahan, Stanley E | New York: CRC Press, [2017]; ISBN 9781498776936. (785 pages)
2. Reaction mechanisms in environmental organic chemistry, Richard A. Larson and Eric J. Weber [1994]; ISBN 0-87371-258-7, (448 pages)

1.16 TERMINAL QUESTIONS

1. Define the following
 - a. Chemical equilibrium
 - b. Dynamic equilibrium
 - c. Chemical potential
 - d. Order of reaction
2. What is the difference between Green chemistry and Environmental Chemistry?
3. Explain open and closed systems in equilibrium with suitable examples?
4. Explain the following in detail.
 - a. First order reaction
 - b. pseudo order reaction
5. Explain the mechanism of adsorption?
6. Explain the catalytic cycle in detail?

UNIT 2 : ENVIRONMENT CHEMISTRY-II

Structure

- 2.0 Introduction
- 2.1 Objectives
- 2.2 Acid-base Reactions
- 2.3 Ionic product of Water
- 2.4 pH and pOH
- 2.5 Hydrolysis
- 2.6 Buffer solutions
- 2.7 Common ion Effect
- 2.8 Oxidation and Reduction
- 2.9 Let Us Sum Up
- 2.10 Glossary
- 2.11 Suggested Readings
- 2.12 Terminal Questions

2.0 INTRODUCTION

Most of the chemical reactions take place in solutions, thus the study of such solutions forms an important branch of chemical sciences especially physical chemistry. If the solubility of solutes is analyzed in different solvents, we observe that the solutes follow the common principle of solubility which is '*like dissolves like*' means polar solvents dissolve polar solutes rapidly and to a great extent, while non-polar solutes are more soluble in non-polar solvents such as NaCl quickly dissolves in water while it remains insoluble in CCl₄ as water possesses high dielectric constant and polar properties that makes it suitable for most of ionic substances like sodium chloride. Depending upon the relative values of conductivities in aqueous solutions, the solutes may be categorized in following classes: (i) Strong electrolyte: highly conducting, (ii) Weak electrolyte: mildly conducting and (iii) Non electrolyte: non conducting but this classification also has a serious limitation i.e. a particular electrolyte might behave differently when it is dissolved in some other solvents. For instance:- if we dissolve acetic acid and sodium chloride in ammonia, both exhibit strong electrolytic behavior, whereas acetic acid ionizes slightly in water therefore, another classification is given which majorly focuses on the characteristics of solute rather than solvent. According to it, solutes can be classified as true and potential electrolytes. True electrolyte shows conductivity even in the pure liquid state while potential electrolyte does not display conductive behavior in pure liquid state but on dissolution in an ionic solvent it may provide conducting solution. When a weak electrolyte is dissolved in a polar solvent, equilibrium is established between its ions and unionized molecules and this phenomenon is known as ionic equilibrium. In order to get more information regarding this, we are going to discuss some important concepts in detail.

2.1 OBJECTIVES

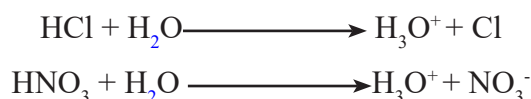
After studying this unit you will be able to

- Understand the concepts of acid-base and their reactions,
- Understand the ionization of water,
- Describe the theory of hydrolysis with examples of salt hydrolysis
- Discuss the origin of pH scale and pOH
- Define buffer solutions
- Define common ion effect and
- Explain fundamentals of oxidation- reduction with examples of redox reactions.

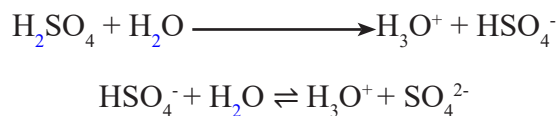
2.2 ACID-BASE REACTIONS

Acid

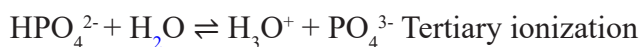
Acids are the substances that undergo dissociation when dissolved in water and form hydrogen ions as the only positive ion species but in aqueous solutions the hydrogen ions (H^+) or protons do not exist in free state. Every hydrogen ion readily combines with one water molecule to form hydronium ion (H_3O^+).



The driving force for this ionization is the great affinity of free hydrogen ions to combine with water molecules to form hydronium ions. The above two acids dissociate completely in aqueous solutions. Hydrochloric and nitric acids are the examples of monoprotic acids i.e. they liberate only one proton or hydrogen ion in water whereas sulphuric and phosphoric acids have two and three hydrogen atoms therefore they are called as diprotic and triprotic acids respectively.



Ionization of phosphoric acid

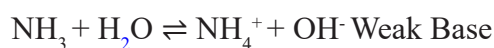
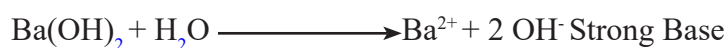


These ionization do not always occur to same extent. They follow the order of primary ionization > secondary > tertiary.

Some acids like carbonic acid, boric acid nitrous acid, ethanoic acid etc. do not ionize completely. Their extent of dissociation is comparatively less hence, known as weak acids while those which dissociate almost completely are called strong acids such as hydrochloric, hydrobromic, hydroiodic, nitric and perchloric acid.

Base

Originally, base is a substance which undergoes dissociation when dissolved in water and forms hydroxide ions (OH^-) as only negative ion species. Some bases like hydroxides of sodium potassium and certain bivalent metals dissociate almost completely in aqueous solution therefore, they are called strong bases, whereas those which produce small concentration of hydroxide in aqueous solution are termed as weak bases such as ammonia NH_3 .



The Bronsted-Lowry theory of acid and bases

A general theory of acids and bases was proposed in 1923 independently by J. N. Bronsted and T. M. Lowry that defines the concept of acid and base in all solvents. As described by these two scientists, a species that has the tendency to lose proton is called acid while bases possess characteristic feature to accept proton.

Acid = proton + conjugate base



According to this theory, a conjugate base is formed after donation of proton from a Bronsted-Lowry acid. Similarly, a conjugate acid is produced when a Bronsted-Lowry base receives a proton.

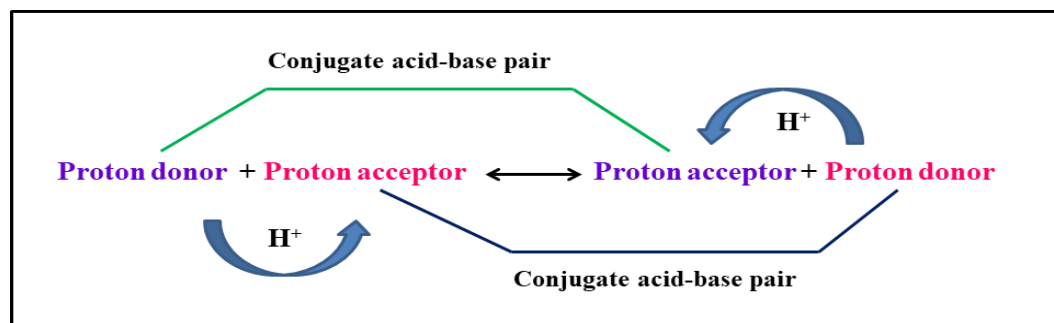
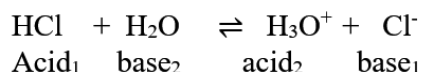
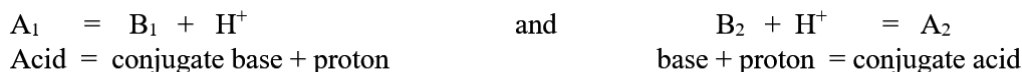
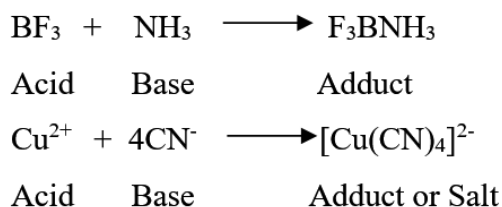


Figure 2.1: Representation of conjugate acid-base pair

It is also mentioned that strength of a conjugate base varies inversely as the strength of its respective acid. Further, the properties of an acid or base are significantly influenced by the solvent used.

Lewis Concept

In 1938, another definition of acids and bases was introduced by G.N. Lewis. Based on his investigations, he revealed that both acids and bases are capable of forming a covalent bond. During this phenomenon, an acid accepts a pair of electrons, whereas a base donates it. For example: BF_3 , AlCl_3 , SO_2 etc. have ability to attract an electron pair therefore termed as Lewis acids or electron acceptors. On the other hand, NH_3 , pyridine etc. possess a lone pair of electrons that can be donated easily hence called as Lewis base or electron donor.



Acid Base Reactions

Acid and base reaction is a type of chemical reaction wherein acid and base reacts together in stoichiometric ratio to neutralize each other as acid counteracts the base and vice versa. Therefore, this type of reactions is generally called as neutralization reaction.



In the above reaction, a proton is transferred to a water molecule to form hydronium ion H_3O^+ that further reacts with hydroxide ion OH^- to produce water and the positive portion of base combines with negative part of acid to yield salt.



These reactions can also be classified in the category of double displacement reactions. In the case of polyprotic acid, all the acidic hydrogen atoms of acid are replaced by the base if it is added in sufficient amount.

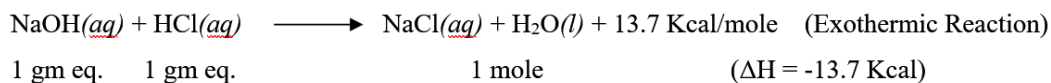


Similarly, reaction of a diacidic base with monobasic acid

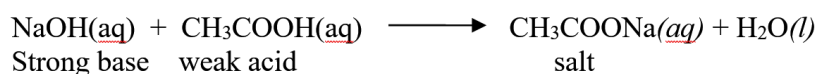
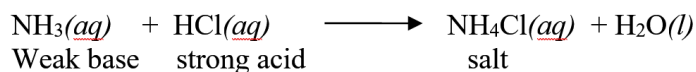
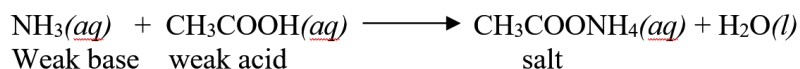


As we know when an acid reacts with a base they neutralize each other and during this process some amount of heat is liberated that depends on the nature of acid, base and their number of gram equivalents. The energy released when one gram

equivalent of acid reacts with one gram equivalent of base is known as enthalpy or heat of neutralization.

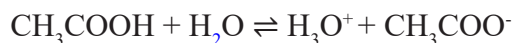


In the cases of weak acid- strong base, weak acid- weak base and strong acid-weak base, heat of neutralization will be lesser than 13.7 Kcal/mole as weak acids and bases do not dissociate completely. Some examples of weak acid-base reactions are given below:

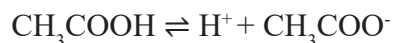


Acid-Base equilibria in water

To understand acid-base equilibrium in water, dissociation of a weak electrolyte i.e. ethanoic acid in dilute aqueous solution is given below:



In conventional manner the above can be written as:



Here, H^+ represents the hydrated hydrogen ion. On applying law of mass action:

$$K = \frac{[\text{CH}_3\text{COO}^-] [\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

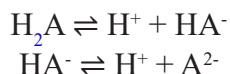
Here, K denotes equilibrium constant at a given temperature. It is also called ionization constant or dissociation constant of acid that can also be symbolized by K_a in aqueous solutions.

If V liters of a solution contain 1 mole of weak electrolyte ($V = 1/c$, where c indicates the concentration in mol L^{-1}) and suppose α represents degree of ionization at equilibrium, then α will be the amount of each ions and $(1 - \alpha)$ will be the amount of unionized electrolyte. In terms of concentration, $(1 - \alpha)/V$ and α/V show the concentration of unionized ethanoic acid and each of ions respectively. On putting these values in equilibrium equation:

$$K = \frac{\alpha^2}{(1-\alpha)V} \quad \text{or} \quad K = \frac{\alpha^2 c}{(1 - \alpha)}$$

This expression represents **Ostwald's dilution law**.

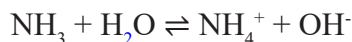
Similarly, for polyprotic acids dissociation constant can be given for each ionization as follows:



If acid is weak electrolyte then applying law of mass action on the above equations:

$$\begin{aligned} K_1 &= [\text{H}^+] [\text{HA}^-] / [\text{H}_2\text{A}] \\ K_2 &= [\text{H}^+] [\text{A}^{2-}] / [\text{HA}^-] \end{aligned}$$

Likewise, consider the dissociation of a weak base in aqueous media



On applying law of mass action

$$K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]}$$

Here, K_b is dissociation constant of a particular base that depends on temperature, nature of solvent.

Relative strength of weak acids and weak bases

According to Ostwald dilution law, dissociation constant of a weak acid

$$K_a = \frac{\alpha^2 c}{(1-\alpha)}$$

If degree of dissociation (α) is very less then we can neglect α in comparison to unity so finally we get

$$K_a = \alpha^2 c \text{ or } K_a = \alpha^2 / V$$

If dissociation constants of two different weak acids are K_{a1} and K_{a2} at a same concentration c then

$$\alpha_1 / \alpha_2 = \sqrt{K_{a1} / K_{a2}}$$

Here, α_1 and α_2 represent the respective degree of dissociation of two acids

Similar expression can be used for weak bases with the substitution of dissociation constant of acid with ionization constant of base i.e.

$$\alpha_1 / \alpha_2 = \sqrt{K_{b1} / K_{b2}}$$

In words it can be stated as, for any two slightly ionized electrolytes (weak acid or base) at equal dilution, the degrees of dissociation are directly proportional to the square roots of their dissociation constants.

Significance of Acid-Base reactions

Neutralization or acid-base reactions play a critical role in maintaining the necessary balance in our ecosystem as well as in our body. These reactions are especially very

useful in pharmaceutical, food and fertilizers manufacturing industries. Our day to day life is governed by these reactions such as digestion of food in our stomach. Similarly, use of an antacid to cure heartburn is also an example of neutralization reaction wherein stomach acid is neutralized either by $\text{Mg}(\text{OH})_2$ or by $\text{Al}(\text{OH})_3$ that are present in antacid. Besides, to resolve the problem of acidic water and soil in mining land some basic oxides or carbonates such as CaO , CaCO_3 or MgCO_3 are added to reduce their acidity.

SAQ 1

What are the fundamental theories to explain acidity and alkalinity of the substances and how they are different from one another?

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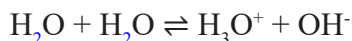
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2.3 IONIC PRODUCT OF WATER

Dissociation of water

In 1894, Kohlraush and Heyweiller observed that even highly purified water behaves like a very weak electrolyte and possesses definite conductivity. It ionizes in the following manner:



To simplify, it can be written as:



Applying law of mass action to the above equation on a particular temperature

$$K_i = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Here, K_i represents the ionization constant of water. As we know that degree of dissociation of water is very less, so the concentration of undissociated water molecules remain almost constant during this ionization process and this concentration can be combined with K_i (ionization constant of water) to give a new constant (K_w) that is known as **ionic product of water**.

$$K_w = K_i [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

In pure water, concentration of hydrogen ion $[\text{H}^+]$ will be equal to the concentration hydroxyl ion $[\text{OH}^-]$ i.e. $1 \times 10^{-7} \text{ M}$ at 25°C .

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) [\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

$$K_w = 1.0 \times 10^{-14}$$

The ionic product of water primarily depends upon temperature; it increases with increase in temperature.

$$[H^+] = K_w/[OH^-] \text{ and } [OH^-] = K_w/[H^+]$$

Acidic or alkaline nature of a solution relies upon the relative concentration of hydrogen ions to that of hydroxyl ions. When the concentration of hydrogen ions is exactly equal to the concentration of hydroxyl ions, the solution is called neutral solution. At ordinary temperatures, if the concentration of hydrogen ions $[H^+]$ is greater than $10^{-7} \text{ mol L}^{-1}$, solution will show acidic behavior and if less than $10^{-7} \text{ mol L}^{-1}$, alkaline nature will be exhibited. Similarly, if concentration of hydroxyl ions is greater than $10^{-7} \text{ mol L}^{-1}$, solution will be basic and if less than $10^{-7} \text{ mol L}^{-1}$ acidic properties will be displayed.

Neutral solution: $[H^+] = [OH^-] = 10^{-7}$

Acidic solution: $[H^+] > [OH^-]$ or $[H^+] > 10^{-7}$

Alkaline Solution: $[H^+] < [OH^-]$ or $[OH^-] > 10^{-7}$

SAQ 2

What do you understand by ionic product of water and explain its significance?

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2.4 pH and pOH

While dealing with dilute solutions, it is very difficult to represent the concentrations of hydrogen and hydroxide ions in terms of moles per liter (mol L^{-1}). Therefore; a very convenient method was introduced by S. P. L. Sorensen in 1909. He proposed a logarithmic scale to express hydrogen ion concentration as given below:

$$\text{pH} = \log_{10} 1/[H^+] = -\log_{10} [H^+] \text{ or } [H^+] = 10^{-\text{pH}}$$

Thus pH is the logarithm of hydrogen ions with negative sign. In this method, numbers between 0 to 14 are used to denote all the possible states of acidity and alkalinity from 1 mol L^{-1} hydrogen ions to 1 mol L^{-1} hydroxide ions.

As we know in neutral solution

$$[H^+] = [OH^-] = 10^{-7} \text{ therefore, } \text{pH} = 7$$

For acidic solution $\text{pH} < 7$ and $[H^+] > 10^{-7} \text{ mol L}^{-1}$

For alkaline solution $\text{pH} > 7$ and $[H^+] < 10^{-7} \text{ mol L}^{-1}$

The concentration of hydroxyl ions can be expressed in similar manner:

$$\text{pOH} = 1/\log_{10} [OH^-] = -\log_{10} [OH^-] \text{ or } [OH^-] = 10^{-\text{pOH}}$$

As we know

$$[H^+][OH^-] = K_w = 10^{-14}$$

Taking logs of both sides

$$\log [H^+] + \log [OH^-] = \log K_w = -14$$

$$\text{then } pH + pOH = pK_w = 14$$

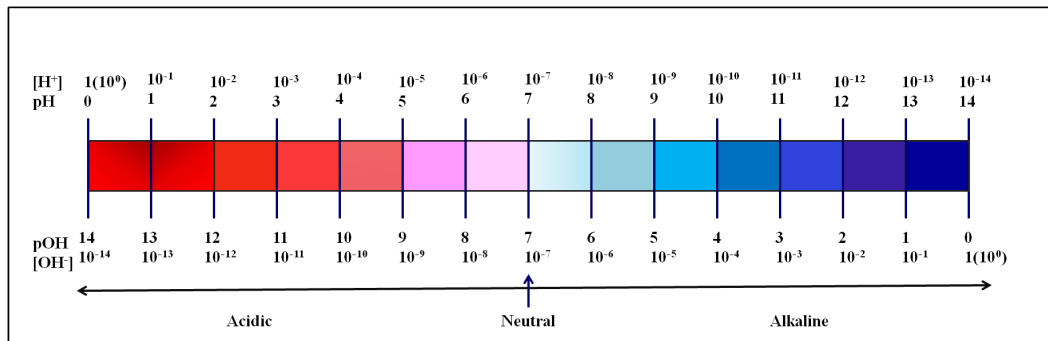


Figure 2.2 The pH scale

In quantitative analysis, small quantities are usually expressed in logarithmic or exponential form. Dissociation constants, ionic concentrations and solubility products may also be represented in this form for convenience.

SAQ 3

How pH and pOH are related to each other?

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2.5 HYDROLYSIS

The term hydrolysis is derived from ancient Greek words (Hydro-water+ Lysis-break down) and it means dissolution or destruction by water. Hydrolysis is a type of chemical reaction in which chemical bonds of a substance are decomposed by addition of water molecules. This phenomenon plays a quite significant role in biological systems as well as in chemical sciences. The process of hydrolysis is used to break down a variety of polymers such as carbohydrates, proteins, fats, nucleic acids etc. These decomposition reactions are usually catalyzed by acid, base or enzymes (hydrolases). Hydrolysis of salts is one of the most common examples of such reactions wherein the interaction between cations or anions of a salt and water takes place. During this process, a salt breaks down into its ions completely or partially depending upon its solubility factor and dissolution of salt into water may alter pH of solution that primarily relies upon its constituent ions. According

to the nature of their fragmentary ions, these salts are generally classified into four major categories:

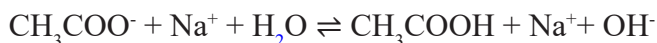
- (i) Salts of strong acids and strong bases, e.g. NaCl
- (ii) Salts of weak acids and strong bases, e.g. CH_3COONa
- (iii) Salts of strong acids and weak bases, e.g. NH_4Cl
- (iv) Salts of weak acids and weak bases, e.g. $\text{CH}_3\text{COONH}_4$

Dissolution of salts of strong acids and strong bases in water results in neutral solution as their cations and anions have no tendency to combine with hydrogen and hydroxyl ions of water therefore, the equilibrium hydrogen ions and hydroxyl ions remains undisturbed that maintains the neutrality of the solution whereas the salts of other three groups may interact with the ions of water and change their equilibrium and ultimately the pH of solution.

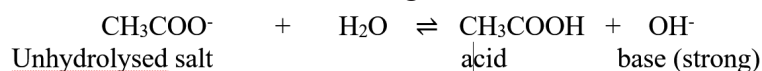
Degree of hydrolysis

Case 1: Salts of a weak acid and a strong base

The salts of this class give alkaline solutions on hydrolysis as the anionic part of a weak acid interacts with hydrogen ions of water to form weak acid which dissociates feebly. In order to maintain the constant value of ionic product (K_w), water further ionizes but hydrogen ions are again taken up by the negative charge bearing species of salt. Thus, the decrement in concentration of hydrogen ions with respect to hydroxyl ions is observed and due to high concentration of hydroxyl ions, solution becomes alkaline. Consider the hydrolysis of CH_3COONa :



As Na^+ ions are present on the both side of equation therefore, they may be left out and the equation can be written in following manner:



On applying law of mass action and considering the concentration of water as constant because it is present in excess, we obtain

$$K_h = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad \text{or} \quad K_h = \frac{[\text{base}][\text{acid}]}{[\text{Unhydrolysed salt}]}$$

Here, K_h is called hydrolysis constant. Since generated acid is weak in nature hence, it ionizes slightly while free strong base and unhydrolysed salt dissociate completely.

‘The fraction of each mole of anion (CH_3COO^-) that is hydrolysed at equilibrium is known as degree of hydrolysis.’

Assume 1 mole of salt is dissolved V litre of solution and x represents the degree of hydrolysis then the concentrations in mol L^{-1} are

$$[\text{CH}_3\text{COOH}] = [\text{OH}^-] = x/V \text{ and } [\text{CH}_3\text{COO}^-] = (1 - x)/V$$

Putting these values in the above equation

$$K_h = \frac{(x/V)(x/V)}{(1-x)/V} = \frac{x^2}{(1-x)/V}$$

It is evident from the above expression on increasing the dilution, the degree of hydrolysis x is also increased.

With hydrolytic equilibrium ($\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$), two equilibria must coexist i.e.



We know that

$$K_w = [\text{H}^+][\text{OH}^-], K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] \text{ and } K_h = [\text{OH}^-][\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-]$$

$$\text{But } \frac{K_w}{K_a} = \frac{[\text{H}^+][\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{H}^+][\text{CH}_3\text{COO}^-]} = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = K_h$$

$$\text{Thus, } K_h = K_w / K_a \text{ or } \text{p}K_h = \text{p}K_w / \text{p}K_a$$

The above expression shows the relationship between hydrolysis constant, ionic product of water and dissociation constant of water. As we know variation in temperature affects K_a slightly but K_w is significantly dependent on temperature therefore, the degree of hydrolysis will be majorly governed by temperature changes.

As a result of hydrolysis, the equal amounts of acid (CH_3COOH) and base (OH^-) will be produced. If the concentration of salt dissolved in water is $c \text{ mol L}^{-1}$ then

$$K_h = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{[\text{OH}^-]^2}{c} = \frac{K_w}{K_a}$$

$$\text{and } [\text{OH}^-] = \sqrt{c K_w / K_a}$$

since $[\text{H}^+] = K_w / [\text{OH}^-]$, substituting the values

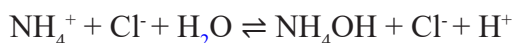
$$[\text{H}^+] = \sqrt{K_w K_a / c}$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c$$

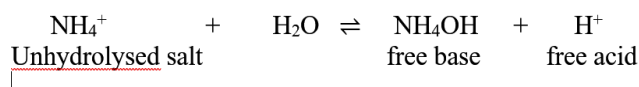
The above equation gives hydrogen ion concentration of hydrolyzed salt (weak acid and strong base) solution.

Case 2: Salts of a strong acid and a weak base

The salts of this category produce acidic solution on hydrolysis as cationic part of salt participates actively in hydrolysis and forms weak base which ionizes poorly therefore, concentration of hydrogen ions increases and solution exhibits acidic nature. Consider the dissociation of ammonium chloride:



Neglecting Cl^- ions as they are conjugate base of strong acid thus will not take part actively in hydrolysis



Applying law of mass action (Similar to case 1)

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{x^2}{(1-x)V}$$

Here, K_b represents dissociation constant of base and as we know the concentrations of formed base and acid are equal therefore, substituting values in the above equation

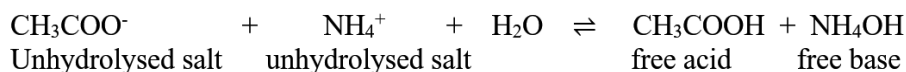
$$K_h = \frac{[H^+]^2}{c} = \frac{K_w}{K_b} \quad \text{and} \quad [H^+] = \sqrt{c K_w K_b}$$

or
$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b + \frac{1}{2} \log c$$

The above expression gives pH of hydrolysed salt of strong acid and weak base.

Case 3: Salts of a weak acid and weak base

The salts of this class may give acidic or alkaline or neutral solution on hydrolysis depending upon the strengths of their constituent acid and base e.g. ammonium acetate



In this case both cation and anion of salt interact with hydrogen and hydroxyl ions of water i.e. hydrolysed.

Applying law of mass action

$$K_h = \frac{[NH_4OH][CH_3COOH]}{[CH_3COO^-][NH_4^+]} = \frac{[\text{base}][\text{acid}]}{[\text{unhydrolysed salt}]^2}$$

We know that

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{and} \quad K_w = [H^+][OH^-]$$

$$K_h = \frac{K_w}{K_a \times K_b} \quad \text{or} \quad pK_h = pK_w - pK_a - pK_b$$

The individual concentrations can be represented as given below if 1 mol salt is dissolved in V L of solution and x denotes degree of hydrolysis

$$[CH_3COOH] = [NH_4OH] = x / V \quad \text{and} \quad [CH_3COO^-] = [NH_4^+] = (1 - x / V)$$

Substituting the values

$$K_h = \frac{(x/V)(x/V)}{\{(1-x/V)\}\{(1-x/V)\}} = \frac{x^2}{(1-x)^2}$$

It is evident from the above expression that degree of hydrolysis does not depend on the concentration of solution thus the pH of solution.

The concentration of hydrogen ions of hydrolysed salt solution can be calculated as given below

$$[H^+] = \frac{K_a [CH_3COOH]}{[CH_3COO^-]} = K_a \left\{ \frac{(x/V)}{(1-x)V} \right\} = K_a \left(\frac{x}{1-x} \right)$$

$$\text{Since } x/(1-x) = \sqrt{K_h} \text{ therefore } [H^+] = K_a \sqrt{K_h} = K_a \sqrt{K_w K_a / K_b}$$

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} pK_b$$

It is clear from the above equation if $K_a = K_b$ then solution will be neutral and if $K_a > K_b$ and $K_a < K_b$ then the solution will be acidic and alkaline respectively.

SAQ 4

What is degree of hydrolysis? Derive the expression for salts of weak acid and strong base.

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2.6 BUFFER SOLUTIONS

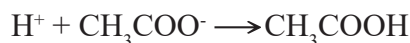
A particular pH is required for the proper functioning of various chemical, pharmaceutical, biological and biotechnological processes; therefore we need to have such solutions whose pH does not change appreciably even when small amounts of strong acid or strong base are added to them. These solutions are called buffer solutions. "Buffers are the chemical substances that resist changes in the concentration of hydrogen or hydroxyl ions and their resistance to change in pH upon introduction of small quantities of acid or alkali is known as buffer action."

Generally buffer solutions are comprised of a mixture of weak acid and its salt with strong base (usually sodium or potassium) or they can be a combination of weak base and its salt. In other words, buffers are the mixture of a weak acid and its conjugate base or weak base and its conjugate acid. The buffers have ability to reverse both acidity and alkalinity to some extent.

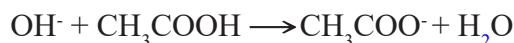
Case 1: A mixture of weak acid and its salt

A very common example of this class is a mixture acetic acid and its sodium salt. This buffer solution contains CH_3COOH molecules, CH_3COO^- and Na^+ ions as acetic acid dissociates feebly whereas sodium acetate ionizes almost completely. The buffer action of acetic acid- sodium acetate is given below:

On the addition of strong acid to this buffer solution, the introduced hydrogen ions will be immediately consumed by acetate ions to form acetic acid that dissociates in very slight amount.



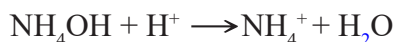
Thus the neutralization of added hydrogen ions takes place. Contrary to this when a strong base is introduced in to the solution, the hydroxyl ions are taken up by acetic acid to maintain the neutrality.



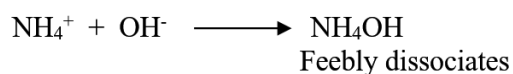
Case 2: A mixture of weak base and its salt

The most common example of this category is an equimolar mixture of aqueous solutions ammonium hydroxide and ammonium chloride. The buffer solution contains unionized NH_4OH , NH_4^+ and Cl^- ions. Let us consider the buffer action of this mixture:

When acid is added to this solution, the increased concentration of hydrogen ions are neutralized by ammonium hydroxide



On addition of strong base, the neutralization of excess amount of hydroxyl ions is attained by ammonium ions



Calculation for pH of buffer

The hydrogen ion concentration of weak acid and its salt can be expressed by following equation:

According to law of mass action $[\text{H}^+] = K_a [\text{acid}]/[\text{salt}]$
 or $\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

The above equation is called as Henderson-Hasselbalch equation that gives pH of buffer solution which is a mixture of weak acid and it's conjugate.

Similar expression can be given for weak base and its salt

$$[\text{OH}^-] = K_b [\text{base}]/[\text{salt}] \quad \text{or} \quad \text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

and pH can be calculated by following relationship

$$\text{pH} = \text{pK}_w - \text{pOH} \text{ or } \text{pH} = 14 - \text{pOH}$$

Buffer Capacity: The capacity of a buffer to withstand the change in pH is known as buffer capacity. A buffer solution that contains equimolar concentrations of acid or base and its salt exhibits the maximum buffer capacity.

SAQ 5:

What are buffers and how can we calculate the pH of buffer solution containing a weak base and its conjugate acid?

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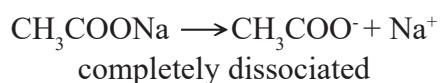
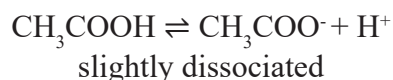
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2.7 COMMON ION EFFECT

If a strong electrolyte is introduced to a solution of feebly dissociated electrolyte that has at least an ion common with strong electrolyte, suppression in the ionization of weak electrolyte is observed and this phenomenon is known as common ion effect. E.g. reduction in dissociation of acetic acid (weak electrolyte) on addition of sodium acetate (strong electrolyte) in its solution



Introduction of sodium acetate to the solution of acetic acid increases concentration of CH_3COO^- in the medium and to overcome the addition of salt equilibrium shifts to backward direction hence, the degree of dissociation of CH_3COOH decreases.

In the same manner, ionization of weak base (NH_4OH) is suppressed in the presence of NH_4Cl (salt) or NaOH (strong base) as ammonium chloride supplies NH_4^+ ions, while NaOH furnishes OH^- ions and both ions cause reduction in the dissociation of ammonium hydroxide.

Common ion effect has prime importance in qualitative analysis wherein it has been used in salt as well as gravimetric analysis. The other applications of this effect include softening of water, purification of common salt and salting out of soap.

SAQ 6

Explain common ion effect with example and its applications.

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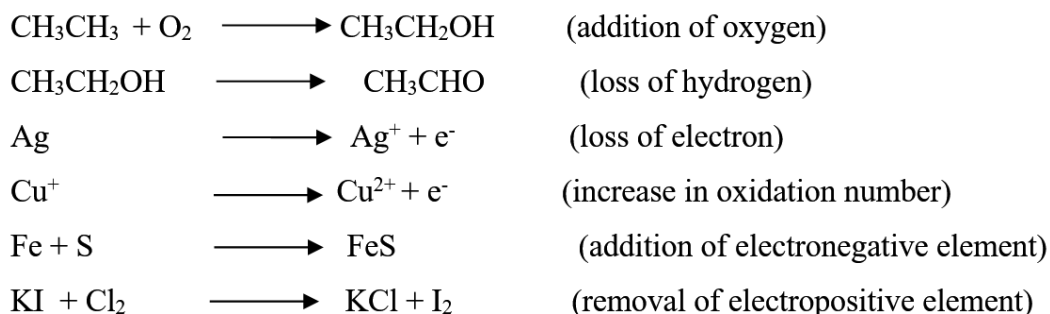
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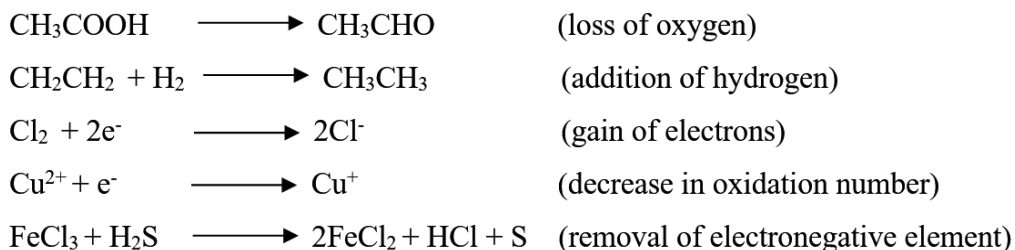
2.8 OXIDATION AND REDUCTION

Oxidation and reduction, these two fundamental terms have been used in chemistry since beginning. Oxidation includes gain of oxygen, loss of hydrogen or electron and increase in oxidation number or positive charge, whereas reduction deals with loss of oxygen, gain of electron or hydrogen and decrease in oxidation number or positive charge or increase in negative charge of any atom or molecule or species. The phenomena of oxidation and reduction are just opposite to each other and they must occur simultaneously. These processes are integral parts of chemical, physical, biological and biotechnological sciences.

Oxidation



Reduction



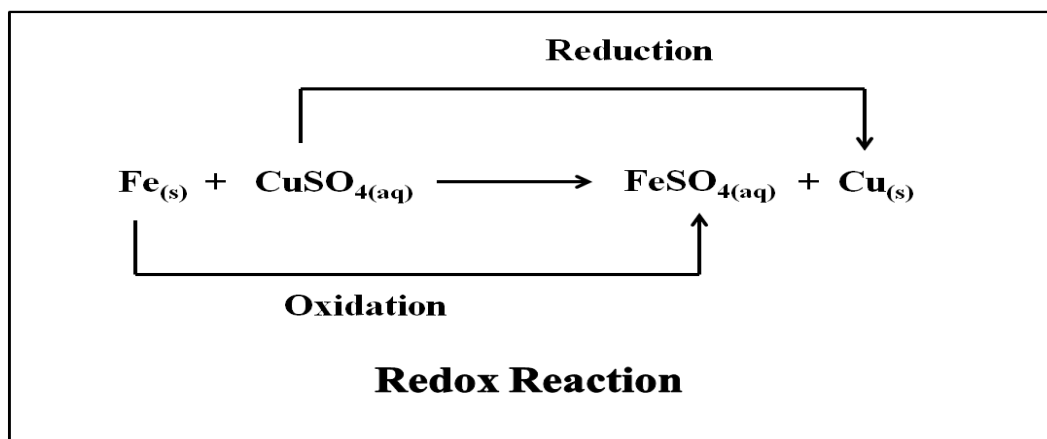
A substance (atom, ion or molecule) that has ability to oxidize other substances is called **oxidizing agent** and while oxidizing other species the substance itself gets reduced whereas **reducing agent** are those substances which have tendency to reduce other molecules or atom or element or species and during this process they

themselves get oxidized. In other words, oxidizing agents are known as electron acceptor while reducing agents are termed as electron donor.

As we mentioned earlier that oxidation and reduction take place concurrently therefore, these processes cannot be separated from each other and studied together.

Redox reactions

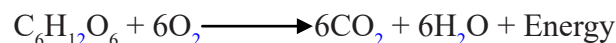
The chemical reactions in which the oxidation numbers of participating species (atoms, molecule or ions) are changed by the transfer of electrons from one species to another species are termed as redox reactions (**reduction/oxidation**).



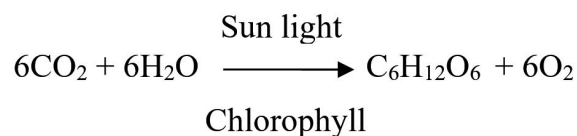
Here, oxidation state of iron changes from 0 to +2 while copper is converted from +2 to 0.

Redox reactions are prevalent in nature and almost one third reactions that have been taking place in our surrounding are oxidation reduction reactions. These reactions can occur abruptly, slowly or rapidly depending upon their environmental conditions. Few examples of redox reactions are given below:

1. Respiration: As we know that respiration is the ultimate energy yielding process in living organisms wherein consumed or stored food is transformed into energy through a series of redox reactions. During this process, oxidation of glucose and reduction of oxygen take place simultaneously.

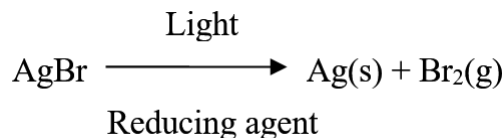


2. Photosynthesis: In this process green plant and certain micro-organisms convert light energy to chemical energy wherein carbon dioxide and water are transformed into energy rich organic compounds such as glucose or other sugars and oxygen in the presence of sunlight and some specific pigments like chlorophyll.

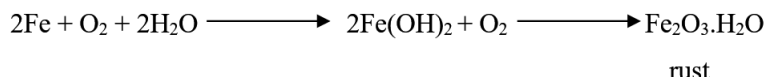


3. Photography: In classical approach, photographic films containing light sensitive silver halides are treated with solution of a reducing agent such as

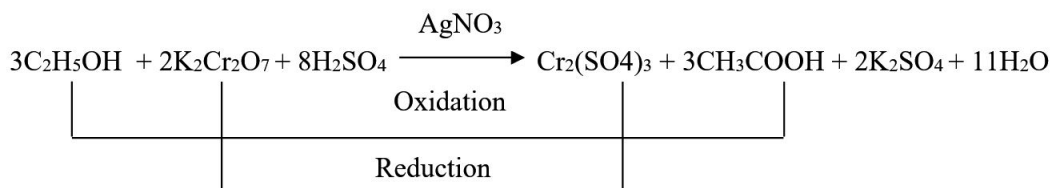
hydroquinone, *N*-methyl-*p*-aminophenol, ascorbic acid etc. which reduces silver halides to metallic silver. Besides, fixation of image is carried out by using the solution of sodium thiosulphate.



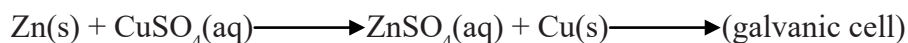
4. Corrosion: It is a natural galvanic process wherein deterioration of refined metals takes place through oxidation.



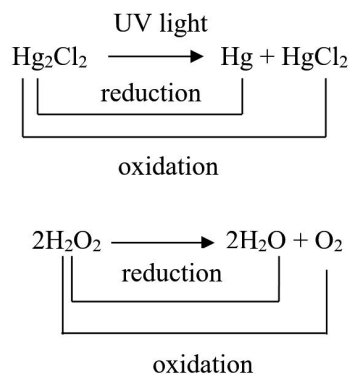
5. Breath analyzer: In a chamber of breath analyzer, an aqueous solution containing potassium dichromate, sulfuric acid and silver nitrate is filled. When an alcoholic breath sample is bubbled into this solution, sulfuric acid helps in transferring of ethanol from air to liquid where it reacts with potassium dichromate in presence of silver nitrate to yield acetic acid and chromium sulfate (green colour). This process is accelerated by AgNO_3 which acts as a catalyst for the above redox reaction.



6. Cells and batteries: Generally, in cell and batteries either chemical energy is converted into electric energy or electric energy is transformed into electrochemical energy through redox reactions.



Another type of redox reaction is disproportionation reaction that sometimes also called as dismutation in which a compound or molecule is converted into two or more dissimilar products through simultaneous oxidation and reduction of same species.



SAQ 7

What are oxidizing and reducing agents? Explain with suitable examples.

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2.9 LET US SUM UP

The brief description of some fundamental points of this unit is given below:

The chemical reactions that occur between an acid and base and result into formation of salt and water are generally called acid- base reactions. These reactions play a critical role in maintaining balance in our body as well as our environment.

Highly purified water also behaves like a weak electrolyte and shows conductivity. It ionizes in hydrogen and hydroxyl ions but hydrogen ions do not exist in free form. They are found in the form of hydronium ions $[H_3O^+]$. The product of active concentrations of hydronium ion and hydroxyl ions at a particular temperature is known as ionic product of water and its value at $25^\circ C$ is $K_w = 1 \times 10^{-14}$.

Basically, pH scale is used to express the acidity or alkalinity of a solution. Mathematically, it is defined as negative logarithm of hydrogen ion concentration at a given temperature. $pH > 7$ represents alkaline nature of solution whereas solutions having $pH < 7$ show acidic behavior and $pH = 7$ indicates neutrality of the solution.

The term hydrolysis is used to describe dissolution by water molecules. In simple words we say it includes chemical breakdown of a compound because of its reaction with water. In salt hydrolysis, reaction between salt and water takes place that results in to formation acidic, alkaline or neutral solution depending upon the salt used.

A buffer solution is an aqueous mixture of either weak acid and its conjugate base or weak base and its conjugate acid that resists in alteration of pH when small amounts of strong acid or base are added to it.

The common ion effect refers to decrease in dissociation of weak electrolyte when a strong electrolyte having a common ion is introduced to the solution of feebly ionized electrolyte. This effect has fundamental importance in quantitative analysis.

According to modern concept, removal of electrons from a species is termed as oxidation whereas addition of electrons is called reduction. Almost all the elements and their compounds have tendency to undergo oxidation-reduction reactions.

Photosynthesis, respiration, corrosion etc are some common examples of redox reactions that we experience in our day to day life.

2.10 GLOSSARY

Conductivity: A capacity of a substance to conduct electricity.

Electrolyte: A substance that conducts electricity in molten state or when dissolved in polar solvent.

Equilibrium: It is a state of a system when the rate of forward and backward reaction becomes equal and concentration of reactants and products remains constant.

Polyprotic acid: An acid which is capable of donating more than one hydrogen ion per molecule to aqueous solutions.

Solute: A substance (solid, liquid or gas) which is dissolved in solvent to form solution.

Solubility: It is the maximum amount of a solute that can be dissolved in a solvent at particular temperature.

2.11 SUGGESTED READINGS

1. J. Mendham, R. C. Denney, J.D. Barnes, JD and M.J.K. Thomas, 2006. Vogel's Textbook of Quantitative Chemical Analysis, 6th.
2. K. J. Laidler and J. H. Meiser, 2006, Physical Chemistry, 2nd.
3. B.R. Puri, L.R. Sharma and M.S. Pathania, 2008. Principles of Physical Chemistry, 7th.
4. K. L. Kapoor, 2009, A Text Book of Physical Chemistry, 3rd.
5. P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, 2010, Shriver and Atkins' Inorganic Chemistry, 5th.

2.12 TERMINAL QUESTIONS

1. Describe general theories of acids and bases.
2. What do you mean by hydrolysis? Explain salt hydrolysis by giving an example with equations.
3. What are buffers? Derive the formula for pH of mixture of weak acid and its salt type buffer.
4. Give detailed description of oxidation-reduction with suitable examples.

5. What are neutralization reactions? Illustrate the process of neutralization with examples.

ANSWERS

Self-Assessment Questions

1. Fundamental theories of acids and bases are given in section 2.2 Acid-Base reactions that include general principle (Arrhenius theory), Bronsted-Lowry and Lewis concept. These theories are different from each other at the basic level as they define the concept of acidity and alkalinity on liberation of hydrogen and hydroxyl ions, conjugate acid-base pair and donation as well as acceptance of electrons respectively.
2. The product of concentration of hydrogen ions and hydroxyl ions at a particular temperature is known as ionic product of water. As it remains constant at a given temperature and represents the neutrality of water therefore, it plays critical role in gathering information about reaction medium and conditions.
3. pH and pOH are inversely proportional to each other. Moreover, $\text{pH} + \text{pOH} = \text{pK}_w = 14$.
4. The fraction of each mole of anion or cation that hydrolysed at equilibrium is known as degree of hydrolysis. For the derivation of expression of salts of weak acid and strong base refer section 2.5 Hydrolysis (case 1: salts of weak acid and strong base).
5. Buffers are the chemical substances that resist changes in the concentration of hydrogen or hydroxyl ions when small quantities of acid or alkali are added to it. For calculation of pH of weak base and its conjugate acid visit section 2.6 Buffer solutions (Case 2: A mixture of weak base and its salt).
6. If a strong electrolyte is introduced to a solution of feebly dissociated electrolyte that has at least an ion common with strong electrolyte, suppression in the ionization of weak electrolyte is observed and this phenomenon is known as common ion effect. E.g. reduction in dissociation of acetic acid (weak electrolyte) on addition of sodium acetate (strong electrolyte) in its solution.
7. Common ion effect has prime importance in qualitative analysis wherein it has been used in salt as well as gravimetric analysis. The other applications of this effect include softening of water, purification of common salt and salting out of soap.
8. A substance (atom, ion or molecule) that has ability to oxidize other substances is called **oxidizing agent** and while oxidizing other species the substance itself gets reduced whereas **reducing agent** are those substances which have tendency to reduce other molecules or atom or element or species and during this process they themselves get oxidized. In other words, oxidizing agents are known as electron acceptor while reducing agents are termed as electron donor.

For the examples of oxidizing and reducing agents refer section 2.8 Oxidation and Reduction (Redox reactions).

Terminal Questions

1. General theories of acids and bases are described in section 2.2 Acid-Base reactions. Please refer this section for more information.
2. Hydrolysis is a type of chemical reaction in which chemical bonds of a substance are decomposed by addition of water molecules. This phenomenon plays a quite significant role in biological systems as well as in chemical sciences. For example of salt hydrolysis refer section 2.5 Hydrolysis.
3. The detailed description of buffers is provided in section 2.6 Buffer Solutions. Please refer that section for answer.
4. Oxidation and reduction is explained thoroughly in section 2.8 Oxidation and Reduction. Please visit that section for details.
5. Acid and base reaction is a type of chemical reaction wherein acid and base reacts together in stoichiometric ratio to neutralize each other as acid counteracts the base and vice versa. Therefore, this type of reactions generally called neutralization reaction. For example refer subsection Acid-base reactions in sectional heading 2.2 Acid-Base reactions.

UNIT 3 : ENVIRONMENTAL CHEMISTRY III

Structure

- 3.0 Introduction
- 3.1 Objective
- 3.2 Solubility and Solubility Product
- 3.3 Solubility of Gases
- 3.4 Carbonate System
- 3.5 Chemical Speciation
- 3.6 Chemistry of Heavy Metals
- 3.7 Radionuclides
- 3.8 Saturated and Unsaturated Hydrocarbons
- 3.9 Chemistry of Fuels
 - 3.9.1 Gasoline
 - 3.9.2 Chemistry of Gasoline Fuel additives
 - 3.9.3 Antiknock Agents
- 3.10 Lubricants
 - 3.10.1 Classification of Lubricants
 - 3.10.2 Properties of Lubricants
- 3.11 Biogas
- 3.12 Let Us Sum Up
- 3.13 Glossary
- 3.14 Suggested Readings
- 3.15 Terminal Questions

3.0 INTRODUCTION

Environment chemistry is an interdisciplinary field which encompasses the fundamental principles of chemistry, biochemistry, soil, toxicology and ecology. It deals with chemical composition, properties, reaction rate, transport, effects and ultimate fate of chemical species encountered in the environment. It is pertinent to identify and understand the problems associated in the environment and to find the mechanism by which it can be minimized or completely eliminated from the environment. The main objective behind environmental chemistry is to create awareness about its importance and need to restrain human activities which leads to indiscriminate release of pollutant into the environment.

3.1 OBJECTIVES

After studying this unit you will be able to

- describe concept of solubility and solubility product
- understand the aquatic chemistry of carbonate system

- explain about distribution, mobility and biological availability of chemical elements in natural system
- Classify atmospheric pollutants pertaining to heavy metals, radionuclides and saturated and unsaturated hydrocarbons encountered in the atmosphere
- Understand the chemistry of gasoline and additives used
- Explain the strategies to prevent knocking in gasoline
- Describe the mechanism, classification and properties of lubricants

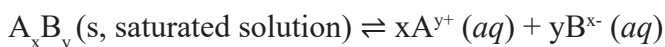
3.2 SOLUBILITY AND SOLUBILITY PRODUCT

Solubility product of the saturated solution of a sparingly soluble salt in water can be defined as the product of concentrations of ions raised to a power equal to number of times ions occur in the equation representing the dissociation of electrolyte.

When a saturated solution of an electrolyte is formed, a dynamic equilibrium is maintained between the excess of the solute and ions furnished by the already dissolved electrolyte.

Consider a sparingly soluble salt say, A_xB_y when added to water, a very small amount of it dissolves and rest of it remains in the water in the solid form. Here, the undissolved A_xB_y is in equilibrium with A and B ions formed in the solution.

This can be represented as:



According to the law of chemical equilibrium, equilibrium constant can be represented as:

$$K = \frac{a_{xA^{y+}} \times a_{yB^{x-}}}{a_{A_xB_y}}$$

where $a_{A^{y+}}$, $a_{B^{x-}}$ and $a_{A_xB_y}$ denote the activities of the furnished ions A^{y+} , B^{x-} and the undissolved electrolyte A_xB_y respectively. Now, the activity of solid is taken as 1 by convention. Therefore, the equation can be represented as:

$$K_{sp} = a_{xA^{y+}} \times a_{yB^{x-}}$$

Where, K_{sp} is known as the solubility product of electrolyte A_xB_y .

In common practice, concentration terms are more preferred as compared to the activities. In such a case, solubility product K_{sp} becomes concentration solubility product K'_{sp} and can be written as:

$$K'_{sp} = [A^{y+}]^x [B^{x-}]^y$$

In case of sparingly soluble salts, ionic concentration of the dissolved salts is very low so that the concentrations and activities can be taken as almost same indicating that solubility product is equal to the concentration solubility product. Therefore,

$$K_{sp} = K'_{sp}$$

Consequently,

Solubility product of a sparingly soluble salt A_xB_y can be represented in the equation form as:

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Interestingly, one can find the solubility of a sparingly soluble salt if its solubility product is known and vice-versa. Solubility and solubility product are correlated as follows. When a saturated solution of sparingly soluble salt AB is prepared, its solubility equilibrium can be represented as:



Let s denote the solubility of the salt. Then,

$$[A^+] = s \text{ mol L}^{-1} \text{ and similarly,}$$

$$[B^-] = s \text{ mol L}^{-1}$$

$$K_{sp} = [A^+] [B^-] = (s \text{ mol L}^{-1}) (s \text{ mol L}^{-1}) = s^2 \text{ mol}^2 \text{ L}^{-2}$$

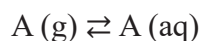
$$\text{Therefore, Solubility, } s = \sqrt{K_{sp}} \text{ mol L}^{-1}$$

Thus, molar solubility is defined as the number of moles of solute that can be dissolved in 1 litre of the solution.

The concept can be smartly employed to find out if a solution is saturated or not. If the ionic product $[A^{y+}]^x [B^{x-}]^y$ is found to be less than the solubility product, K_{sp} the solution is termed as unsaturated and it has the capacity to dissolve more of the electrolyte, whereas if the ionic product and the solubility product are found to be the same then the solution is perfectly saturated at that particular temperature.

3.3 SOLUBILITY OF GASES

Solubility of gases in water is governed by Henry's law. This law states that solubility of gas at constant temperature is directly proportional to partial pressure of gas in contact with the liquid. Consider



Where $A(aq)$ is aqueous concentration of gases in mol L^{-1} ; p_x is partial pressure of gas in atm; K is Henry's constant

$$\text{Units of } k = \text{mol L}^{-1} \text{ atm}^{-1}$$

Table illustrates the Henry's law constants for common dissolved gases in water at 25°C.

Gas	K(molL ⁻¹ atm ⁻¹)
O ₂	1.3 x10 ⁻³
CO ₂	3.4 x10 ⁻²
H ₂	7.8 x10 ⁻⁴
N ₂	6.5 x10 ⁻⁴
CH ₄	1.4 x10 ⁻³

In order to calculate gas solubility considering an example where concentration of O₂ in water is in equilibrium with air at 1 atmospheric pressure and temperature, a correction must be made for partial pressure of water by subtracting it from total pressure of gas (0.0313 atm) at 25 °C. Henry's constant for O₂=1.3 x10⁻³ molL⁻¹atm⁻¹ and considering that dry air is 20.95% by volume of O₂ yields the following equation"

$$P_{O_2} = (1.0000 \text{ atm} - 0.0313 \text{ atm}) \times 0.2095 = 0.2029 \text{ atm}$$

$$[O(aq)] = k P_{O_2} = 1.3 \times 10^{-3} \text{ molL}^{-1}\text{atm}^{-1} \times 0.2029 \text{ atm}$$

$$[O_2(aq)] = 2.6 \times 10^{-4} \text{ molL}^{-1}$$

Molar mass of oxygen is 32, so concentration of dissolved oxygen in water at 25°C is 8.3mgL⁻¹ or ppm.

The solubility of gases decrease with increasing temperature given by Clausius-Clapeyron equation:

$$\log \frac{c_1}{c_2} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

c₁ and c₂ denotes gas concentration at absolute temperatures of T₁ and T₂.

ΔH = heat of solution and its units are in cal mol⁻¹

R = gas constant where R = 1.987 cal degree⁻¹ mol⁻¹

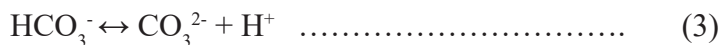
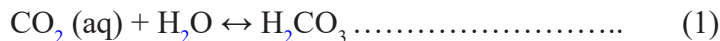
At high temperatures, decreased solubility of O₂ combined with increased respiration rates by aquatic organisms results in depletion of oxygen making survival difficult for aquatic species.

3.4 CARBONATE SYSTEM

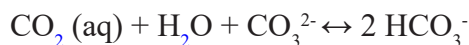
The major portion of carbon is present in the oceans in form of carbonate. The carbonate system is primarily responsible for controlling the pH and regulates various biogeochemical processes occurring in ocean. Carbon dioxide emitted through natural and anthropogenic sources are taken up by the oceans. This results in limiting the increase in CO₂ concentration and greenhouse warming but increasing acidification of sea water. Rapid exchange of CO₂ occurs between the atmosphere and aquatic system through equilibrium of CO₂(g) and dissolved CO₂



CO_2 rapidly reacts with water owing to its high solubility resulting in formation of carbonic acid.



Series of proton transfer reaction takes place resulting in bicarbonate and carbonate ion. Reactions 2 and 3 produces H^+ and lowers the pH of sea water. Dissolved CO_2 occurs in three inorganic forms: free aqueous CO_2 , HCO_3^- , and CO_3^{2-} which becomes an integral part of carbonate system. When CO_2 dissolves in sea water, it is not fully dissociated to CO_3^{2-} and number of H^+ are smaller due to natural buffering capacity of sea water as shown below



The sum of three aqueous carbonate species $[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ is defined as total CO_2 . Most of the surface water of ocean is approx. pH 8 where HCO_3^- is the dominant species and this represent 90% of DIC. A very small portion of H_2CO_3 is present hence concentration of $\text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3$ is combined and represented as $[\text{CO}_2(\text{aq})]$

Ocean acidification limits the coral life all marine organisms to properly synthesize their carbonate skeletal via the formation of biogenic calcium carbonate, CaCO_3 .

Due to increase in rate of anthropogenic emissions of CO_2 , calcification rate have declined and reduced the alkalinity of the oceans.

SAQ 1

Explain the role of carbonate system in oceans.

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3.5 CHEMICAL SPECIATION

The term chemical speciation refers to specific chemical forms of elements which may be inorganic, organic or organometallic species in the environment. It also refers to the oxidation state in which a particular element exists in the environment.

Metals are non-biodegradable in nature. When they enter in the environment they get partitioned into various physico-chemical forms such as colloidal, chelated, free

ionic combined with other chemical forms. The physical properties and chemical behaviour vary amongst different species in the environment. The phenomena such as chemical and biological transformation, metal mobility, bioavailability, toxicity and persistence in the environment depends on chemical form or speciation of a given metal ion. Example: Arsenic is extremely toxic in its inorganic form but arsenobetaine is non-toxic. Similarly elemental mercury is non-toxic but alkylmercurials are highly toxic.

The toxicity and mobility of metal ions depends upon:

- Concentration of metal ions which decreases on complexation.
- Redox environment. eg. toxicity associated with As(V) is low in oxidising environment while reduced form As(III) is highly poisonous.
- Oxidation number Cr(III) is essential element as glucose tolerance factor while Cr(VI) is highly toxic.

Because of the above reasons, the determination of the total concentration of a metal provides inadequate information. That is why speciation has gained considerable importance.

Speciation studies involves estimating individual physico-chemical forms of elements that make up the total concentration of a particular element in order to assess its impact on organism/environment.

But at times, the determination of specific concentration of species becomes quite a difficult task than determination of total element because of the following reasons:

1. Isolating the compound of particular interest from complex matrix is difficult.
2. Speciation techniques available disturb the equilibria existing between the various chemical species present in the system under study.
3. Determination of species at ultra-trace level requires analytical procedures of high degree of sensitivity.
4. Suitable standard reference materials are often unavailable.

The speciation analysis of metal ions can be performed by sequential extraction, whereby each of the fractions obtained shows a different form of association of the metal in the soil. The accepted modern procedure is:

Step I. Extraction of the acid soluble fraction (i.e., carbonates) with CH_3COOH

Step 2. Extraction of the reducible fraction (i.e., iron/manganese oxides) with hydroxylamine hydrochloride

Step 3. Extraction of the oxidizable fraction (i.e., organic matter and sulfides) by H_2O_2 oxidation followed by extraction with $\text{NH}_4(\text{CH}_3\text{COO})$

Chemistry of Cr(III) , Cr (VI) speciation

In natural water, chromium exhibits two common oxidation states +3 and +6 exhibiting different chemical behaviour, toxicity and bioavailability. Cr(III) is

associated with lesser toxicity because of limited solubility and strong complex formation. On the contrary, Cr(VI) is highly toxic and much more bioavailable to aquatic living organisms since it is easily transported into cells as sulphate analogues. It is also recognised as human carcinogen and mutagen.

Cr(III) speciation in sea water is dominated by Cr(III) hydrolysis products- $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_4^-$. $\text{Cr}(\text{OH})_3$ is dominant species in the pH range 7-11, while $\text{Cr}(\text{OH})_4^-$ becomes dominant above pH 11.3. Chromium is present as Cr(VI) under oxidizing conditions as anionic species- CrO_4^{2-} , HCrO_4^- , and dimer $\text{Cr}_2\text{O}_7^{2-}$.

In natural systems, Cr(III) does not migrate since its minerals precipitate in alkaline or neutral range. It remains as dissolved Cr(III) in low concentration. In slightly acidic conditions, it can be removed by adsorption. Phenomenon of precipitation and adsorption can be inhibited by complexation of Cr(III) with dissolved ligands. Dissolved Cr(III) concentration becomes higher and migrates when pH reaches around 5. Oxidants such as MnO_2 can solubilise Cr(III) in form of Cr(VI) compounds.

Cr(VI) enters in to aquatic system in two ways:

- reduction of Cr(VI) to Cr(III). Reduction is facilitated by Fe(II) which may be synthesized by photo-oxidation of organic matter in sea water surface.
- Removal of Cr(VI) by sorption process where there is high content of Mn or Fe oxide under oxidizing conditions. But sorption is not strong enough to keep moving Cr(VI) through soil or sediments under alkaline medium.

SAQ 2

What is meant by the term metal “speciation” and why is it important in aqueous systems?

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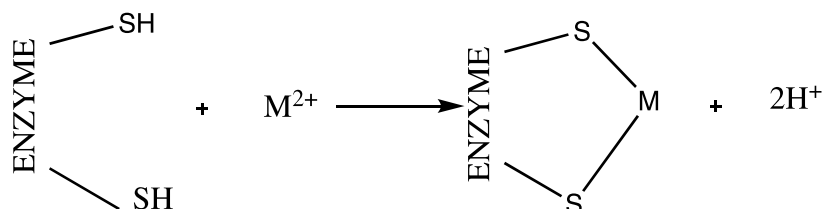
3.6 CHEMISTRY OF HEAVY METALS

The term heavy metal refers to those elements which have density greater than 6 gcm^{-3} .

Heavy metals occur naturally in soils, sedimentary deposits and water bodies. They find their way into the environment through soil, and sediments in form of dust, smoke and aerosol by anthropogenic sources. They are also added to the agricultural land by extensive uses of fertilizer and water bodies through industrial

wastes, sewage sludges. Mainly, four heavy metals such as lead, mercury, cadmium and arsenic are of greatest concern because of their extensive use, their toxicities and pervasiveness in the environment.

Heavy metals exert their toxic action by binding to the active site of the enzyme thereby inhibiting the enzymatic action. They have strong affinity for the sulfhydryl group (-SH) of the enzyme. Certain enzyme contains metal ions in their structures called metalloenzyme. Their action is inhibited when the essential metal ion of the enzyme is replaced by the toxic metal ion having same size or charge. Example: substitution of Zn by Cd in Zn^{2+} -containing metalloenzyme like carbonic anhydrase, carboxypeptidase, alcohol dehydrogenase.



Schematic representation of toxicity mechanism of heavy metals

Cadmium

Cadmium occurs in a very low concentration in the earth's crust. It is not an essential element and no biological function till date is reported in humans. It is used in industries to manufacture nickel cadmium batteries, control rods in nuclear power industry, pigments, semiconductor devices, stabilizers for PVC and other plastics. Other applications include electroplating metals for protection against corrosion and in non-ferrous alloys. A small amount of Cd occurs in form of impurity in zinc containing ores.

Cadmium in water arises mainly from industrial discharge and from waste mining. It is extremely dangerous to plants and animals because it absorbs efficiently and gets accumulated in the tissues. Rate of Cd absorption in humans increases particularly if they are on low Calcium diet. Majority of the cadmium ingested gets trapped in kidneys and is eliminated. A small portion gets bound to protein metallothionein present in kidneys. Effects of Cd poisoning in humans results in anemia, high blood pressure, damage to testicular tissues.

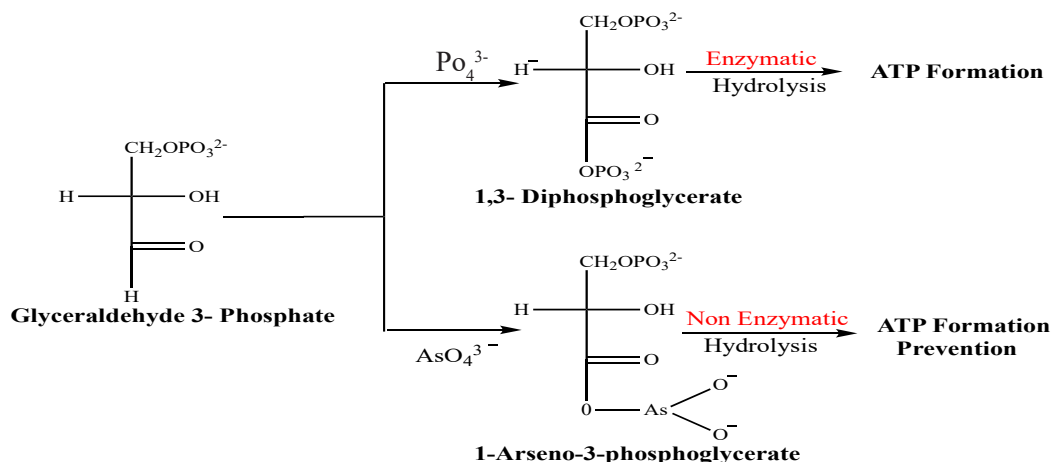
Cadmium poisoning caused itai-itai or ouch-ouch disease that was first recognized in the Jintzu river basin of Japan. Water in the Jintzu basin became contaminated with cadmium from mining activities. This contaminated water was used to irrigate rice fields, a staple food in that area. The bones of the victims become fragile and broke easily from loss of Ca. Many people suffered from abdominal pain, diarrhea, vomiting, liver damage and kidney failure.

Chemically, cadmium is similar to zinc since it occurs in association with zinc mineral and found in similar oxidation states (+2). It is proposed that Cd poisoning involves substitution of Zn by Cd in many metalloenzymes thereby altering the stereostructure of the enzyme and impairing the catalytic activity.

Arsenic

Arsenic is commonly used in pesticides (fungicide, insecticide, herbicide), alloys and in wood preservatives. Arsenic is a by-product used in the manufacture of some chemicals and mining operations. Many subsoils naturally contain arsenic compounds and seep into the groundwater and contaminate the source. In some parts of India and Bangladesh wells were dug up used for irrigation purpose have been epidemics of acute arsenic poisoning. Presence of arsenic in drinking water cause keratoses, skin discolouring which subsequently leads to cancer and damages liver and kidneys.

Arsenic exerts its toxic action by binding it strongly to the sulphhydryl groups on protein. The enzyme pyruvate dehydrogenase which generates cellular energy in citric acid cycle, is deactivated on complexation with As^{3+} thus preventing the formation of ATP. Arsenic is similar to phosphorus, so it is reduced from +5 to +3 oxidation state, so arsenic inhibits all biochemical reactions of phosphorus. Arsenic interferes in synthesis of ATP producing 1-arseno-3-phosphoglycerate instead of 1,3-diphosphoglycerate which on hydrolysis gives arsenate and 3-phosphoglycerate as shown in below diagram.



The three major biochemical effects of arsenic are :

1. Protein coagulation
2. Complexation with co-enzyme
3. Uncoupling of phosphorylation

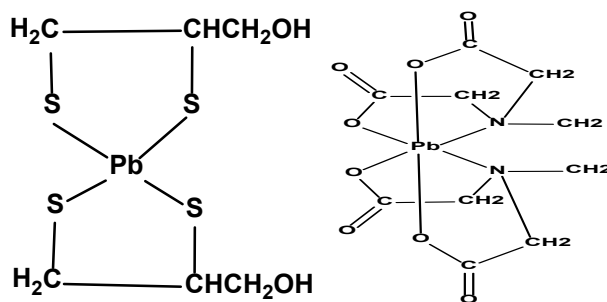
$\text{As(III)} [\text{AsO}_3^{3-}]$ is more toxic than $\text{As(V)} [\text{AsO}_4^{3-}]$ because it undergoes methylation by bacteria that produces species that are highly reactive and damages DNA. Antidotes for As poisoning includes chelating agents like British anti Lewsite (BAL) which possess -SH capable of binding strongly with As(III)

Lead

The sources of inorganic lead include industries, mining and from leaded gasoline. Lead is most abundant heavy metal in the atmosphere. The major source of atmospheric lead comes from Et_4Pb which is added to gasoline to inhibit knocking and improve fuel efficiency. Lead enters the human system by inhaling lead and swallowing lead salts. When it enters the blood stream as Pb^{2+} and it becomes biologically active highly and potentially more toxic.

Lead when present interferes in the heme synthesis which leads to hematological damage. Presence of lead disrupts heme synthesis by inhibiting the conversion of δ -aminolevulinic acid to prophobilinogen catalyzed by δ -aminolevulinic acid dehydrogenase. It does not permit utilization of oxygen and glucose for energy production. High levels of lead in blood results in anemia due to deficiency of hemoglobin. Chronic effects include causes kidney malfunction, increased blood pressure and interference in vitamin D metabolism. Lead exposure is highly dangerous to unborn and young children. It crosses the placenta barrier and causes premature births and mental impairments. Chemically, lead resemble calcium, so it accumulates in the body replacing calcium.

Lead poisoning can be treated by administering chelating agents which bind strongly to Pb^{2+} . Ca-EDTA complex is given to patients poisoned by lead, it displaces Ca^{2+} from chelated complex and resulting complex can be excreted in urine. Other chelating agents used to treat lead poisoning includes BAL, d-penicillamine.



BAL= 2,3-dimercaptopropanol Pb-BAL Chelate

Mercury

The main source of mercury is the principal ore cinnabar i.e. HgS . It is used industrially in three different forms: elemental mercury, organic mercury compounds and inorganic mercury. The greatest use of mercury is production of electrical apparatus. It forms amalgams with various metals like zinc, lead, tin, cadmium and widely used as fungicide. Mercury(II) chloride is used to make organo-metallic compounds, as a wood preservative, and as an antiseptic for sterilising surgical instruments. Mercury(II) sulphide is used in the red pigment, vermilion.

As a result, mercury and its compounds enter the natural bodies from manufacturing or sources where mercury is mined. The major sources of mercury emissions into the atmosphere is through burning of fossil fuels, electric power plants, waste incineration or weathering of rocks.

All forms of mercury are highly toxic but toxicities vary considerably. Elemental mercury is non-toxic but its vapours when inhaled are highly toxic because it can diffuse through lungs into the blood and then brain. Hg^{2+} is fairly toxic but does not cross the biological membrane though it has strong affinity for the sulphur containing amino acids and forms bonds with haemoglobin through sulphydryl groups. Hg^{1+} is non-toxic when ingested because it forms insoluble Hg_2Cl_2 in the stomach in acidic medium. Alkyl mercurial RHg^+ are highly toxic forms of mercury compounds, because they are highly soluble in fat and brain tissues. Hg-C bond is not easily disrupted stable and remains in tissue cell for prolonged period. They have the ability to easily cross the blood-brain and placental barrier.

Chemical species of mercury and their chemical and biochemical properties

Species	Chemical and biochemical properties
Hg	Non-toxic, but vapours when inhaled highly toxic
Hg_2^{2+}	Not very soluble, low toxicity
Hg^{2+}	Toxic but not transported across biological tissues
CH_3Hg	Highly toxic, highly liophilic i.e easily transported across biological membrane
$(\text{CH}_3)_2\text{Hg}$	Low toxicity but easily transformed to CH_3Hg

Biological methylation

The transformation of inorganic form of mercury(Hg^0 , Hg^{1+} , Hg^{2+}) to methyl and dimethyl derivatives by the action of anerobic bacteria in sediments and lakes is referred to as methylation. This transformation is mediated by methylcobalamin, Co(III) containing vitamin B_{12} co-enzyme. $-\text{CH}_3$ group bonded to co-enzyme is enzymatically transferred by methylcobalamin to Hg^{2+} giving CH_3Hg^+ or $(\text{CH}_3)_2\text{Hg}$.

Under acidic conditions, conversion of dimethylmercury to methylmercury occurs which is soluble in water. It is the methyl mercury form which enters into the food chain through phytoplankton. In this way concentration of mercury is build up at every level. In alkaline medium, methyl mercury can be converted to volatile dimethylmercury, $(\text{CH}_3)_2\text{Hg}$, may be formed which evaporates relatively quickly both from soils and water bodies.

The deleterious effects of the mercury came into limelight after the incidence of Minamata Bay in Japan during the period 1953-1960. The non-toxic inorganic mercury was discharged as effluent into the Bay by Minamata chemical plant manufacturing acetaldehyde using mercuric sulphate as catalyst . In the sediments, inorganic mercury was converted into methyl mercury which got accumulated into the fish which was eaten up by local inhabitants. This resulted in death of hundred people and thousands were permanently paralysed . Congenital defects were in new born babies whose mothers fed themselves with sea food contaminated by methyl mercury. Other effects includes impairment of vision, hearing and neurological damage. This was the first natural case of bioaccumulation (in fish) of a toxic species (methylmercury) which killed hundreds of people and caused genetical damage.

Chronic effects caused by mercury poisoning mercury includes neurological damage including increased excitability, irritability, chromosomal damage and birth defects and kidney problems.

SAQ 3

Explain the toxic effects of heavy metals on enzymes?

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SAQ 4

Explain the biochemical effects of Heavy Metals

a) Arsenic b) Lead c) Mercury with reference to their source , species, pathways in environment and impact on humans.

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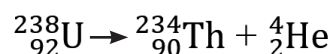
3.7 RADIONUCLIDES

Radionuclides are species of atoms that emit radiation when they undergo radioactive decay through emission of alpha particles, beta particles and gamma rays. Table provides the characteristics of defined decay processes:

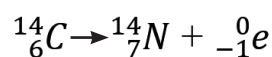
Radiation	Symbol	Charge	Transformation
Alpha (α)		+2	Mass number decrease by 4, atomic number decreases by 2
Beta (β)		-1	Atomic number increases by 1, mass remains unchanged
Gamma (γ)	${}^0\gamma_0$	0	No change in atomic number or mass

When α or β particles are emitted , the identity of elements is changed

e.g. decay of U-238 to Th-234,



In contrast to a emission, β decay results in increase in atomic number by 1, while mass number remains the same.



Gamma rays are highly energetic electromagnetic radiations similar to X-rays having no charge or mass.

${}^{238}\text{U}$ undergoes radioactive decay by forming chain of products through - variety of alpha and beta emissions ultimately leading to stable Lead-206 . The transformation of Ra-226 to Rn-222 is of particular environmental significance. Radon is a colorless, odorless, tasteless gas that naturally occurs in rocks, soil, water, and air. Radon in the ground, groundwater, or building materials invades working and living spaces and disintegrates into its decay products. It is second leading cause of lung liver cancer. Decay of radionuclides follow first order reaction

Radiation damages living organisms by initiating harmful chemical reactions in tissues. In case of acute radiation poisoning, bone marrow is destroyed and concentration of RBC is decreased. Radionuclides having very short life are highly dangerous but decay fast to affect the environment. In contrast radionuclides having very long half-life are quite persistent but may cause very little damage. But radionuclides having intermediate half-lives are highly dangerous and can pose threat. Sr-90 is the waste product of nuclear testing is interchangeable with Ra and K-40 are found in natural sources like water. Radionuclides are formed in large quantities as waste products in nuclear power plants. Artificially produced radionuclides find their widespread use in industrial and medical applications particularly as tracers.

SAQ 5

What characteristic features of radionuclides make them hazardous ?

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3.8 SATURATED AND UNSATURATED HYDROCARBONS

Majority of the hydrocarbons have their widespread use in fuels and therefore represents the most important organic pollutant of the atmosphere. The anthropogenic source of hydrocarbon pollutant encountered in atmosphere comes from incomplete combustion of gasoline (petroleum product). Hydrocarbons are broadly classified as

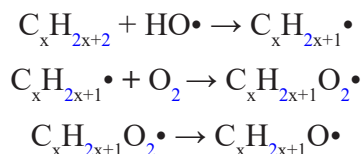
- **Saturated Hydrocarbon:** comprising of alkanes (also referred to as paraffins)
- **Unsaturated Hydrocarbons:** comprising of a. *alkenes* (olefinic compounds with double bonds between adjacent carbon atoms) b. *Alkynes* (compounds with triple bonds between adjacent carbon atoms) c. *aryl compounds* (aromatic)

Alkanes have single bond between the carbon atoms and represented by the general formula: C_nH_{2n+2} , Cyclic alkanes : C_nH_{2n} . examples include: methane, 2,2,3-trimethylbutane

The most stable hydrocarbons present in the atmosphere are alkanes. Straight chain alkanes with carbon atoms 1-30 and branched hydrocarbons with 6 carbon atoms are present in polluted atmosphere either as gas or as aerosol or may adsorbed to atmospheric particles.

The hydroxyl radicals present in atmosphere react with alkanes to form alkyl radical which then immediately picks up a molecule of oxygen leading to the formation of alkylperoxy radical. This radicals acts as oxidant by losing an atom of oxygen

to form alkoxy radical. These reactions of alkanes leads to the oxidized products that are precipitated from atmosphere with particulate matter and finally undergoes biodegradation in soil.



Alkenes have atleast one C=C double bond per molecule. The simplest alkene is ethylene. They are widely used to synthesize polymers for plastics (polyethylene, polypropylene, polystyrene), synthetic rubber (polybutadiene,) and various applications. They are emitted into the atmosphere through internal combustion engines, petroleum refinery, industrial applications.

Alkynes have triple bond between the carbon atoms and they are less commonly present in the atmosphere than alkenes. acetylene which is used as fuel for cutting and welding and butyne used in manufacture of synthetic rubber are sometimes found in traceable amounts in atmosphere. Chemically, alkenes are more reactive than alkanes since they possess electron available to form additional bonds with other atoms. In the presence of NO_x and sunlight, alkenes (e.g. propylene) react readily with OH radicals and subsequent addition of O_2 leads to formation of peroxy radical. These reactions are quite significant in the atmosphere as they participate in photochemical smog formation and contributes to atmospheric pollutants.

Aromatic (aryl)hydrocarbons consists of rings of six carbon atoms having alternative single and double bond. Aryl hydrocarbons find their widespread application as raw materials for the manufacture of monomers and plasticizers.

Simplest example is benzene. It is emitted from the exhaust engine of all petrol and diesel vehicles as well as from chemical industries. Aromatic compounds with multiple rings referred to as polycyclic aromatic hydrocarbons are of greatest concern. Most important example is benzo (∞) pyrene, compound that the body can metabolize to a carcinogenic form.

Features

- They are persistent organic pollutants because they do not break down easily.
- They are volatile making them highly mobile throughout the environment.
- These compounds are the most stable form of hydrocarbons having low hydrogen-to- carbon ratios They are formed by the combustion of petrol and diesel hydrocarbons under oxygen- deficient conditions.
- They are found deposited on surface of particulate matter present in smoke.

The most potent carcinogenic PAH's include : benzo- α -anthracene, dibenzo-a-anthracene and benzo- α -pyrene.

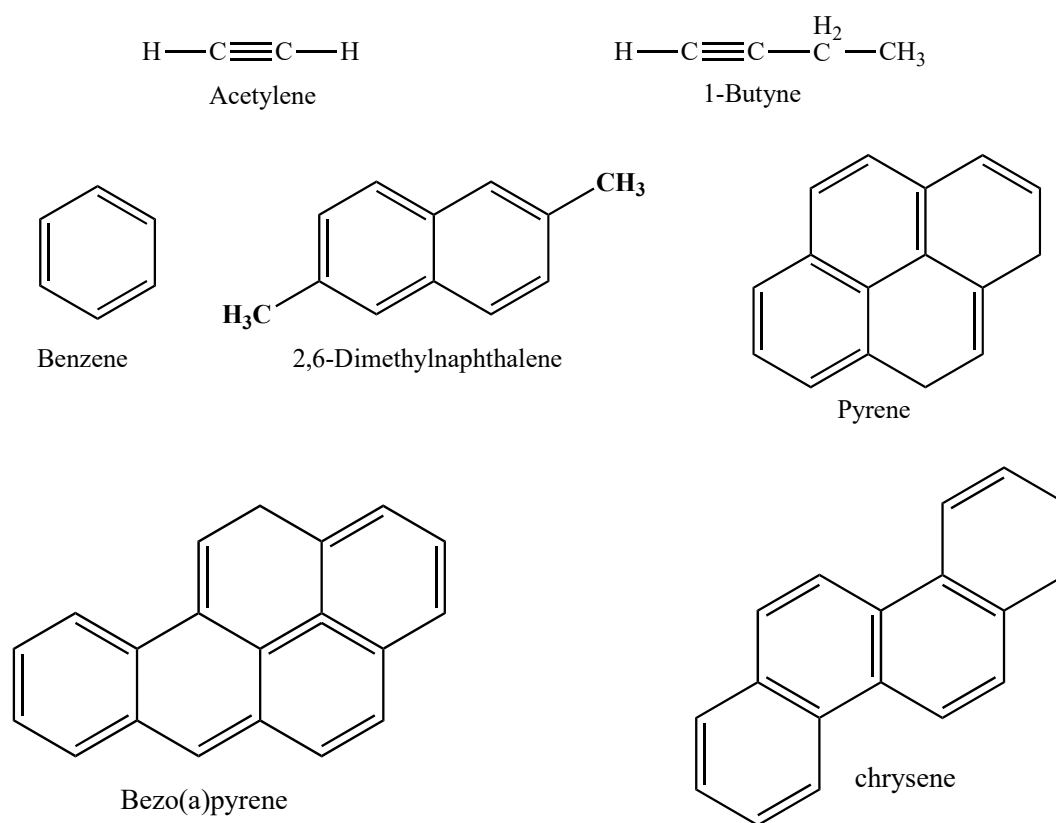


Figure 3.1 : Structural formulas of different types of hydrocarbon pollutants present in environment

SAQ 5

Explain how aromatic hydrocarbons act as environmental pollutants

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3.9 CHEMISTRY OF FUELS

Gasoline

The first product obtained in distillation of crude oil is gasoline. Generally, the boiling range of gasoline is 25-150°C. Gasoline are sometimes classified as motor gasoline for use in automobile and light trucks, aviation gasoline for use in piston engine aircrafts. Hydrocarbons having 3-8 carbon atoms condensed from natural gas are composed of natural gasoline. Natural gasoline does not provide good combustion performance desirable for automobile engine. Consequently, it is now used mainly as feedstock for petrochemical industry.

The gasoline produced from distillation of crude oil without any chemical treatments is straight run gasoline. It comprises primarily of straight chain hydrocarbons and is of limited value as automobile fuel. A high content of straight chain hydrocarbons causes fuel to begin burning before the spark plug ignites it. This pre-mature ignition produces an acoustic sound called knocking. Knocking is combustion phenomenon which takes place when air fuel mixture in the gasoline does not burn smoothly.

When the fuel in a gasoline engine is ignited by the spark plug, the flame tends to move away from the spark plug, and the heat and pressure is generated. Chemically, combustion is a multistage oxidation process where the organic hydroperoxides are generated initially. These decompose to form free radicals that start branch chain reactions. These chain reactions start local auto ignitions/detonations, ahead of the flame front in the unburned hydrocarbon air mixture due to the high temperature and pressure generated in the last portion of the fuel. This violent detonation creates pressure fluctuations and noise. This noise is called knock, and damages engine parts and the fuel efficiency of the engine is decreased.

The tendency of gasoline to cause knocking is rated according to a scale called octane number. It measures fuel's ability to avoid knocking. Branched hydrocarbon 2,2,4- trimethylpentane (isooctane) was found to be superior fuel that burned without causing knocking and is assigned an octane number of 100. Straight chain hydrocarbon n-heptane produced severe knocking and was assigned octane rating 0.

The octane rating of gasoline is determined by burning it in a special single- cylinder engine and comparing its anti-knocking properties with the standard mixtures of isooctane and heptane.

Table: Octane numbers of various hydrocarbons

Hydrocarbon	Formula	Octane Number
n-butane	C_4H_{10}	94
n-pentane	C_5H_{12}	62
2-methylbutane	C_5H_{12}	94
n-hexane	C_6H_{14}	25
2-methylpentane	C_6H_{14}	73
Heptane	C_7H_{16}	0
2-methylhexane	C_7H_{16}	42
2,3-dimethylpentane	C_7H_{16}	90
2-methylheptane	C_8H_{18}	22
2,3-dimethylhexane	C_8H_{18}	71
2,2,4-trimethylpentane	C_8H_{18}	100
Benzene	C_6H_6	106
Toluene	C_7H_8	118
o-xylene	C_8H_{10}	107
p-xylene	C_8H_{10}	116

From table, it is concluded that straight run gasoline has octane rating between 20-55 which is too, low to be used in automobile engine.

Octane number can be increased by three ways

- Cracking
- Catalytic reforming
- Anti-knocking compounds /octane boosters

Cracking is the process in which long chain hydrocarbons are converted to short chain hydrocarbon. The octane number of alkanes decreases as the carbon chain is lengthened but increases as chain branching increases. (Table)

Catalytic reforming is the process in which hydrocarbon vapours of straight chain gasoline are converted into branched or aromatic hydrocarbon in presence of catalyst to increase octane rating .

Chemistry of Gasoline Fuel Additive

The fuel additives in very small dosage are added to enhance the performance of the fuel which otherwise cannot be obtained through refining process.

Reasons for using additives in fuels include

- Reduction in emission from combustion of fuel
- Improve combustion properties of fuel
- Provides cleanliness and protection to engine
- Increases stability of fuel.

There are six types of gasoline fuel additive:

1. **Antioxidants:** During oxidation of gasoline, free radical chain reaction initiates which results in formation of hydroperoxides ultimately leading to the formation of insoluble gum as the end product. Anti-oxidants minimizes the oxidative degradation of gasoline fuel and prevents the gum forming tendency of the fuel. Antioxidants consists of hindered phenols, and aromatic diamines. Examples: 2,6-Di-tertiary butyl-para-cresol and 2,6-di-tertiary butyl phenol Phenylenediamine
2. **Metal deactivators/Passivators:** The presence of soluble metal salts in gasoline provides instability to fuel by catalysing oxidation reaction which forms gum and reduces fuel stability. Most commonly used metal deactivator is N,N-disalicylidene-1,2-propanediamine. This compounds can form chelate with copper metal in gasoline.
3. **Octane Booster:** It provides cost effective improvement in gasoline octane quality by reducing knocking. Examples : tetraethyl lead (TEL), methylcyclopentadienyl tricarbonyl (MMT)' oxygenate additives such as ethanol, methyl tertiary butyl ether (MTBE) considered as blending components rather than octane boosters.
4. **Anti-icing additive:** Anti-icing additives minimizes engine stalling and power loss due to formation of ice crystals which may restrict the flow of fuel to engine. It also provides protection against microbiological growth in fuel. It

comprises of freezing point depressants in particular glycol ethers example: ethylene glycol methyl ether.

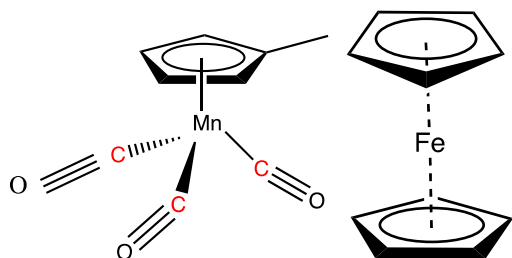
5. **Combustion improvers:** are used to heat the fuels and contains ash-less and metal additives. Examples: tertiary butyl acetate enhances antiknock characteristics of TEL; metal additives e.g. Compounds of boron and Phosphorus increase the ignition point of engine. Incomplete combustion leads to soot deposits in the combustion chambers, and impairs heat transfer and may result in unwanted fires. Combustion improver additives minimizes misfire and improves efficiency of the engine through reduced soot deposition,.
6. **Deposit control additives/detergent dispersants:** It consists of polar hydrophilic and non polar hydrophobic group in its structure. and which is derived from oxygen or nitrogen molecules and a which The nonpolar group enables enables fuel to be soluble in additive. The polar group attaches to the deposit particles and removes them from the metal surface through the detergent action. Control Additives controls the build up of soot deposit in carburettor and fuel injection equipment and inlet system by forming protective films. This will provide performance benefits such as reduced exhaust Emissions, improved fuel economy and reduced maintenance cost. Examples include amides, amines, polybutene succinimides, polyether amines, polyolefin amines and mannich amines.

Anti-knocking Agents

Knocking in the internal combustion engines affects the efficiency of the vehicle and fuel economy. It can be minimized by engine design and adjusting operating conditions or by using high octane gasoline. Most widely used additives to control knocking includes alkyl lead compounds such as tetraethyl lead (TEL) , tetramethyl lead (TML) and hence improves the performance of the engine. Addition of lead additives deactivates the chain branching reactions in the pre-ignition phase . When air-fuel mixture becomes compressed and heated, the weak bonds between the alkyl lead breaks releasing the free lead atom. This then reacts with free O₂ to form PbO and PbO₂ which tends to deposit in the combustion chamber This problem can be solved by using scavengers such as Ethylene dibromide and ethylene dichloride by converting non-volatile PbO₂ to volatile PbX₂. In this way lead is removed from the engine and released into the atmosphere. Gradually leaded gasoline was phased out by unleaded gasoline. The reason was that catalyst like Rh, Pt used in catalytic convertors were poisoned by lead and rendering them inactive. Several alternative antiknock agents were proposed and developed as substituent of lead-containing fuels, for example: methyl-cyclo-pentadienyl-manganese- tricarbony (MMT), ferrocene iron pentacarbonyl.

Methylcyclopentadienyl manganese tricarbonyl (MMT) an organometallic was used as an antiknock additive. This compound releases Mn atom which is then converted to Mn₃O₄ particles inside the combustion chamber which capture hydrocarbon radicals and inhibits knocking. Toxicity associated with Mn is low once it is released into the environment. But it was banned by USEPA because this additive was found to be toxic when ingested or inhaled. Secondly, fouling of spark plugs

and of on board sensors had been reported. Recently it has been permitted in US at level equivalent to 1/32 g of Mn gal⁻¹ of gasoline. MMT is suspected to be a strong neurotoxin and respiratory toxin. Additionally, MMT impairs the effectiveness of automobile emission control and increases pollution of vehicles. Knocking can be reduced by altering the composition of gasoline by reducing the fraction of low octane components and increasing the fraction of high octane components. In United Nations, removal of alkyl lead compounds was initially compensated by increasing the content of aromatic compounds particularly benzene, toluene, and xylene. Increasing the aromatic components in gasoline boosted octane rating.



Methylcyclopentadienyl manganese tricarbonyl (MMT) Ferrocene

The cause of BTX has decreased though it has high octane rating because

- Xylenes react with hydroxyl radicals and have greater potential to smog formation than alkanes
- Benzene is a carcinogen though having low photochemical activity.

This prompted the need to develop alternative fuel additives for improving octane rating of gasoline.

Focus has been laid on use of oxygenated compounds containing one or more oxygen atoms. These include ethanol, methanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) whose octane rating >100. MTBE is made by reacting methanol and isobutene in presence of acid catalyst.

It is synthesized in refineries in which isobutene is generated during catalytic cracking process. However, MTBE contaminates ground water storage tanks through gasoline leak. Its presence has unpleasant odour and is unacceptable in water supplies. Environment Protection Agency recommended reduction its use as gasoline oxygenate. Hence, ethanol and methanol emerged as gasoline oxygenate. Ethanol is added in amounts upto 10% of total volume to produce gasoline blends known as gasohol. This mixture has been used as fuel without any modification of automobile.

The advantage of using MTBE and ethanol is that they have low OH[•] reaction rates and vapour pressure. It is because of this reason that oxygenates in RFG was mandated upto level of 2% oxygen by weight according to 1990 Clean Air Act amendments which requires reduction in ozone forming VOC. Oxygenated fuels provide good combustion performance along with reduced emission of CO and NO_x.

Ethanol separates out from gasoline when in contact with water because of its extreme solubility. Vapour pressure of ethanol is twice than MTBE and requires special adjustments in gasoline components to lower volatile organic compounds. By removing lighter hydrocarbons from blend lowers gasoline volatility. In case of MTBE, vapour pressure requirements is met by removing butane fraction but replacing MTBE with ethanol requires removing pentane thereby increasing the cost. With introduction of RFG smog forming precursors has been reduced.

Disadvantages of alcohols, especially methanol, produce aldehydes as by-products during combustion. Since aldehydes are not major components of gasoline emissions, their emission from combustion sources is not regulated. Aldehydes can be highly irritating to the mucous membranes of the respiratory tract, and thus are undesirable in air. This problem can be remedied by using catalytic converters in the exhaust system to insure the complete oxidation of the aldehydes to carbon dioxide and water.

SAQ 6

Why lead components are added to gasoline and why was it removed with the advent of catalytic convertors ?

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SAQ 7

What advantages do oxygenates offer when added to gasoline in comparison to lead compounds.

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3.10 LUBRICANTS

Lubricant is as substance which is introduced between two sliding surfaces to reduce friction and wear rate. This process of reducing friction by application of lubricant is referred to as lubrication.

Functions of lubricants

- Reduces friction and wear and tear of surfaces
- Acts as coolant by dissipating heat
- Prevents entry of moisture

- Minimizes power loss in internal combustion engine
- Reduces maintenance cost

Mechanism of Lubrication

The phenomenon of lubrication can be explained by three types of mechanism :

1. **Thick Film Lubrication or hydrodynamic lubrication:** In hydrodynamic lubrication, the sliding surfaces are separated from each other by a thick fluid film of 1000A to avoid surface to surface contact. The thick film covers irregularities of the surfaces so that metal surfaces do not come in contact with each other which finally reduces the friction. The lubricant selected has minimum viscosity to reduce internal resistance and should remain in place and separate the surface. Hydrocarbon or mineral oils (having low molecular carbon atoms) are preferred lubricants for this type lubrication.
2. **Thin film or boundary Lubrication:** Boundary lubrication occurs when continuous fluid film cannot persist either due to low speed , high load or low viscosity of lubricating oil. The clearance space between the sliding surfaces is lubricated with a material that gets adsorbed on metallic surface by physical or chemical means which keeps the metal surfaces apart . Vegetable or animal oils and their soaps can be used for this type of lubrication. Though vegetable oils possess good adhesion property but they tend to break down at elevated temperatures.
3. **Extreme Pressure Lubrication:** When sliding surfaces are under high pressure and speed liquid lubricants fail to stick and decompose. To sustain such extreme pressure conditions, additives are added to mineral oils . These additives form strong films capable of sustaining high loads at elevated temperatures. The additives include organic compounds such as sulphur in sulphurized oils or phosphorus in tricresyl phosphate.

3.10.1 Classification of Lubricants:

Based on shear strength lubricants are classified into three types:

1. Lubricating oils or Liquid lubricants
2. Greases or semi-solid lubricants
3. Solid Lubricants
4. **Lubricating Oils or Liquid Lubricant:** They are classified into three categories:
 - i. **Animal and vegetable oils:** Vegetable oil is extracted from castor or rapeseed oil while animal oil extracted from animal fats such as fish comprising of fatty acids and alcohols. They have good sticking phenomenon and can withstand high loads at high temperatures and pressures. But they suffer from following drawbacks :
 - Expensive
 - Undergo oxidation to form gummy product
 - Hydrolyse easily in presence of moist air

- ii. **Mineral or Petroleum oil:** They are obtained by fractional distillation of petroleum comprising of lower molecular weight hydrocarbons having 12-50 carbon atoms. They are mostly used lubricants due to its high stability, abundance, and less costly. But oiliness of mineral oil is less, hence e higher molecular weight compounds such as oleic acid and stearic acid are added.
 - iii. **Blended Oils:** Vegetable/animal or mineral oil suffer from drawbacks, hence additives are added to such oil to increase their performance . Such additives added to lubricating oils are referred to as blended oil. Examples :stearic acid, palmitic acid, coconut or castor oil.
5. **Semi-Solid Lubricants or Grease:** A semi-solid lubricant obtained by combining lubricating oil of low viscosity which is thickened by addition of finely dispersed solids called thickeners. It consists of followings:
- **Base oil:** It is the principal component and can be either petroleum oil or a synthetic hydrocarbon of low to high viscosity.
 - **Additives:** are added to grease to increase their performance. Extreme pressure and friction modifiers are commonly used examples include: zinc alkyl dithiophosphate, dibenzyl sulphide
 - **Thickeners:** It comprises of two basic types: inorganic and organic thickeners. Organic thickeners are either soap based or non-soap based while inorganic thickeners are non-soap based. Simple soap based thickeners are formed by combing fatty acid or an ester with an alkali or alkaline earth metals like Na, K, Ca, by applying heat and pressure through process known as saponification. Non soap thickeners include synthetic polymers and silica gel etc.

Advantages of grease

- Reduces noise and vibration
- Water resistant and reduces oil vapour problem
- Prolong the life of worn parts
- Support much heavier load at lower speed.

Disadvantages

- Cannot effectively dissipate heat from the bearings, so work at relatively lower temperature
- Contaminants cannot be separated

6. **Solid Lubricants:** Solid lubricants are used in powder form or with binders so that they firmly stick to the metal surface. Also available in dispersion in non-volatile carriers such as soap, waxes, fats etc.

They are used under following conditions:

- Where high loads are required
- Operating temperatures and pressures are too high

- lubricating film cannot be protected by grease
- Contamination by grease

Classification of solid lubricants

- Inorganic lubricants with lamellar structure: The crystal lattice of these lubricants has layered structure with hexagonal rings that forms parallel layers. Each atom is bonded to another atom by weak Vander walls thus allowing sliding movements of plane. Examples include : **Graphite** is most commonly used solid lubricant in powder or suspension form. The high thermal and oxidation stabilities at temperature of 500-600° C makes it effective to be used at high temperatures and high sliding speeds. It has layered structure which enables the parallel layers to slide over one another thus making it an efficacious lubricant Also the layer of graphite has a tendency to absorb oil and to be wetted of it.
- Oxides: ZnO, MoO₂, Re₂O₇, B₂O₃ etc.
- Soft metals: Some soft metals possess lubrication properties due to low shear strength and high plasticity. Eg. Pb, Sn, Bi, Cd. They are used in pure form or as alloys and applied as coatings.
- Organic lubricants with chain structure of polymeric molecules: examples: polytetrafluoroethylene (PTFE) . The structure consists of long chain molecules parallel to each other held by weak forces so that they may slide past one another at low shear stress.
- Soaps: metal salts (Li, Na, K, Ca) of fatty acids.

3.10.2 Properties of Lubricants

1. Viscosity: It is defined as the resistance offered due to the motion of the forces between the fluid molecule. It is one of the most important property of lubricating oil. The formation of fluid film of lubricant between the metal surfaces depends upon the viscosity. High viscosity of lubricating oil results in excessive friction while because of low viscosity, film cannot be withstand between the sliding surfaces. Viscosity of liquid decreases with increasing temperature, hence as operating temperature rises, lubricating oil becomes thinner due to low viscosity. Viscosity of lubricating oil should such that it should not change with temperature changes.
2. Corrosion Stability: Steel or copper corrosion test are carried out to estimate the corrosive stability of lubricant. Corrosive substances like hydrogen sulphide , polysulphides are present in petroleum products which are removed by refining process. In copper corrosion test, a piece of copper strip is placed in lubricant for stipulated period of time and defined temperature to examine for tarnishing of strip. Steel corrosion test is carried out to determine the ability of oil to prevent corrosion of ferrous parts in water. Inhibitors like zinc dithiophosphate is added to prevent corrosion of lubricating oil.
3. Flash point and fire point: One of the important characteristic of good lubricant is that it should not volatilise under operating temperatures. Flash point is

defined as minimum temperature at which oil vapourizes to ignite momentarily when flame is brought near to it. Fire point is the minimum temperature at which lubricant oil burns continuously for atleast five seconds when flame is in contact with oil. The temperature of fire point is 10-40 C higher than flash point. The requirement for good lubricant is that it should have flash point above the operating temperature thus ensuring the safety against any fire hazards.

4. **Aniline Point:** Aniline point is defined as minimum equilibrium solution temperature for equal volumes of aniline and lubricant oil. It indicates deterioration of oil when in contact with rubbing sealings. Aromatic hydrocarbons have ability to dissolve natural and synthetic rubbers. A high value of aniline point indicates high paraffinic hydrocarbons and low percentage of aromatic hydrocarbons. Low content of aromatic hydrocarbon is preferred criteria for good lubricant oil. Aniline point is determined by mixing equal proportion of lubricating oil and aniline in a test tube and heating till a homogeneous solution is obtained. The test tube is then cooled till two phases separates. This temperature is recorded as aniline point.
5. **Cloud point and pour point:** Petroleum products are complex hydrocarbons and do not exhibit fixed freezing point. When they are cooled, they become solid due to congealing of hydrocarbons. Cloud point is the temperature at which crystallization of solids occur in form of haziness, while temperature at which oil just ceases to flow when cooled is called pour point. Cloud and pour point determines suitability of lubricant under cold environment. Examples include refrigerators plants and air craft engines which operates at sub-zero temperatures requires lubricants having low pour point which otherwise cause solidification of oil and jamming of machine parts.

SAQ 8

What are different types of mechanisms for lubrication?

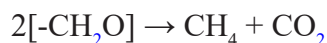
SAQ 9

What are important characteristics for a good lubricant?

3.11 BIOGAS

Increasing production of organic waste is one of the major environmental concerns of the present scenario. Sustainable waste management as well as waste prevention have become major goals to reduce pollution and greenhouse gas emissions to mitigate global climate changes. Uncontrolled waste dumping or incineration of organic waste are now a days not recommended practices for waste disposal from environmental point of view. This problem can be circumvented by production of biogas by degrading biological waste (manure, sewage, sludge, solid waste) in the presence of anaerobic bacteria.

Biochemical reaction of biomass can be represented as :



When micro-organisms have acted upon the biomass under anaerobic conditions, it results in formation of digestate and biogas. Digestate refers to decomposed substrate which is rich in nutrients and used as potent plant fertilizer.

Biogas is a combustible gas chiefly comprising of methane (50-70%) and carbon dioxide CO_2 (25-30%) as primary constituents while others include H_2 (0-1%), N_2 (0-10%), H_2S (0-3%) O_2 (0-2%).

Examples of biogas include :

- Natural gas produced by decaying animal and vegetable waste buried under the earth's surface.
- Gobar gas produced by anaerobic fermentation of cattle dung.
- Sewage gas-produced from municipal solid waste including human and animal faeces

The main advantage of using biogas through anaerobic digestion is that biodegradable waste is treated thus destroying disease causing pathogens and reducing the volume of the sludge generated. Secondly, value of the waste is conserved so that it serves as fertilizers for the crops.

Gobar Gas

Gobar gas is produced by degrading cow dung anaerobically. The plant consist of a digester covered with dome shaped roof made up of concrete fitted with a outlet pipe with a gas valve. There is a sloping inlet on one side and a outlet chamber on the other side. Manure along with wate slurry is directed to the digester through the inlet. In the presence of anaerobic bacteria, cattle dung undergoes fermentation resulting in the evolution of biogas. Pressure is built up on the slurry due to the evolution of biogas which forces the spent slurry to the overflow tank via outlet chamber. The residue (digestate) left after is withdrawn periodically and used as biofertilizer.

The digesters used are generally located in close proximity to dwellings or sources of the waste.

Biogas is widely used in villages owing to its simplicity in implementation and work up procedure and use of inexpensive raw material.

Advantages:

- It burns without smoke causing no pollution to the environment
- Possess high calorific value
- Cheap
- Clean and convenient
- Involves no storage problem

Disadvantages:

- Dependence on cattle dung from which it is produced through anaerobic fermentation
- Gas stove or burner should be in vicinity of 10 m of the plant.

SAQ10

Give reasons why production of biogas should be encouraged ?

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3.12 LET US SUM UP

This unit explained about

- Chemistry of the concept of solubility, solubility product and solubility of gases
- governed by Henry's law.
- How carbonate cycle dominates pH control in most of aquatic system and regulation of various biogeochemical processes in environment.
- Role of Chemical speciation in assessing the toxicity associated with different forms of chemical element and their oxidation state illustrating it with arsenic at
- Sources and toxicity of heavy metals such as Pb, Cd, As, Hg in the environment
- Different types of radionuclides and its effects.
- Impact of hydrocarbon (saturated and unsaturated) on environment.
- Chemistry of gasoline, additives added to gasoline to increase performance of engine, and how knocking can be averted by adding antiknock compounds.
- Mechanism, functions and classification of lubricants into lubricating oil, greases and solid lubricants.
- Degradation of biological waste into biogas.

3.13 GLOSSARY

Additive: The substance added to increase the performance properties

Antiknock: Resistance to pinging in sparked engines

Anti-knocking agent: Substance which is added to internal combustion engine to reduce knocking

Aniline point: Temperature above which equal proportion of petroleum products and aniline are miscible

Biogas: Combustible gas synthesized by decomposing biological waste under anaerobic conditions

Cloud Point: Temperature at which solid substance crystallises from the solution and imparts haziness

Cracking: Process to break down high molecular weight hydrocarbons to lighter ones

Octane number: Number which denotes antiknock characteristic of gasoline

PAH: Polyaromatic hydrocarbons comprises of two or more fused aromatic rings

Gasoline: Mixture of hydrocarbons with small amount of additives added to internal combustion engine.

Oxygenates: Oxygen containing compound used as gasoline blending agent eg. ETBE, MTBE, TAME

Pour Point: Lowest temperature at which oil flows when it is chilled under definite conditions

Solubility product: Equilibrium constant for a chemical reaction in which solid ionic compounds dissolves to yield its ions in solution

3.14 SUGGESTED READINGS

- A.K. De, Environmental Chemistry: New Age International Pvt., Ltd, New Delhi.
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- S.E. Manahan, Environmental Chemistry, CRC Press (2005).
- S. S. Dara: A Textbook of Engineering Chemistry, S. Chand & Company Ltd. New
- James Girad, Principles of Environmental Chemistry, Third Edition, Jones and Bartlett Publisher
- J.A. Kent: Riegel's Handbook of Industrial Chemistry, CBS Publisher, New Delhi

3.15 TERMINAL QUESTIONS

1. Define solubility product.
2. Name the predominate carbonate species in natural waters of oceans.
3. Name the antidotes that can be used for heavy metal poisoning.
4. For each of the following pairs of hydrocarbons, indicate which has the higher-octane rating.
 - a) Pentane or octane
 - b) 2-Methylpentane or 2,2-dimethylbutane
 - c) Octane or 2-methylheptane
5. List four compounds that are used as octane enhancers.
6. Why $\text{C}_2\text{H}_4\text{Br}$ is added to antiknocking agent tetraethyl lead?
7. Give two reasons why TEL was banned as a gasoline additive?
8. Name four solid lubricants.
9. What should be the flash point of good lubricant?
10. Explain how graphite acts as a lubricant.

UNIT 4 : DEVELOPMENTS IN ENVIRONMENTAL CHEMISTRY

Structure

- 4.0 Introduction
- 4.1 Objectives
- 4.2 Need for Emergence of Green Chemistry
 - 4.2.1 Bhopal Gas Tragedy
 - 4.2.2 Thalidomide Disaster
 - 4.2.3 Times Beach
 - 4.2.4 Love Canal Disaster
- 4.3 Some Important Laws for Environmental Protection
- 4.4 Green Chemistry and Sustainability
- 4.5 Concept of green chemistry
 - 4.5.1 Twelve Principles of Green Chemistry
- 4.6 Greener solvents
 - 4.6.1 Issues with the use of Traditional Solvents
 - 4.6.2 Green Solvents
 - 4.6.2.1 Water
 - 4.6.2.2 Supercritical Fluids (SCFs)
 - 4.6.2.3 Ionic Liquids
 - 4.6.2.4 Liquid Polymers
 - 4.6.2.5 Bio-Based Renewable Solvents
- 4.7 Earth friendly plastics
 - 4.7.1 Plastics-the Biggest Source of Pollution
 - 4.7.2 Greening of Plastics
- 4.8 Environmentally Benign Pesticides
 - 4.8.1 Effect of Synthetic Pesticides on Human Health and Environment
 - 4.8.2 Search for Environmentally Benign Pesticides
 - 4.8.3 Examples
 - 4.8.3.1 Microbial Pesticides
 - 4.8.3.2 Plant-pesticides
 - 4.8.3.3 Biochemical Pesticides
 - 4.8.3.2 Natural Home-made Solutions for Pest-control
- 4.9 Let Us Sum Up
- 4.10 Glossary
- 4.11 Suggested Further Readings
- 4.12 Terminal Questions

4.0 INTRODUCTION

Undeniably, the past few decades have witnessed an enormous improvement in scientific methodologies/solutions showing phenomenal capability to protect human health and environment and these innovative solutions have been possible through green chemistry. We have had fantastic accomplishments as the solutions

were at the molecular level since green chemistry preached the prevention of waste at source rather than treating it up after generation. So, quite a few of the existing processes were redesigned using the basic tenets of green chemistry. Progressively, industries also started adopting the path of green synthesis. In this unit we will learn the concept of green chemistry and their applications to prevent the environmental pollution.

4.1 OBJECTIVES

After studying this unit, you will be able to:

- Understand the significance of green chemistry, how it came into emergence and how it is playing a key role in improving human health and environment.
- Understand the basic concepts and various principles of green chemistry.
- Explain about green solvents.
- Discuss the problems associated with plastics and attempts being directed towards resolving plastic pollution through green chemistry.
- Explain about eco-friendly pesticides and their significant role in agrochemical sector.

4.2 NEED FOR EMERGENCE OF GREEN CHEMISTRY

If we reflect back on the past several decades, we find that chemistry has played an indispensable role in increasing the quality of life and overall growth and development of society besides sufficing our basic needs-right from clothes to food to medicines (**Figure 1**). As per the data provided by World Health Organization (WHO), life expectancy has increased over the years. Today, we have good pharmaceutical drugs to combat chronic diseases, improved transportation for energy efficiency, better nutrition, improved herbicides and pesticides for pest control, sophisticated medical devices etc.



Figure 4.1 Chemistry in everyday life.

However, the darker side of the massive production of chemicals and related goods with the industrial revolution has been the generation of waste that has negatively impacted both human health as well as environment. One thing is quite clear that none of the industries or manufacturers wished to harm the environment, but due to lack of fundamental understanding of the hazardous nature of many of the chemical products and poor handling, ended up releasing wastes continually into the environmental matrices. The awareness about the need to rethink chemical processes and designing began with the story of “Silent Spring” which was published in the form of book by Rachael Carlson way back in 1962. In this book, Carlson had written about how the bald eagle species became extinct because of excessive use of DDT. This was an extensively used pesticide that had entered the food chain, resulted in thinning of egg shells that failed to produce baby birds. Some of the other species such as ospreys and brown pelican also got affected by the use of DDT. The book was entitled silent spring with a much heavy heart by her as she feared that the birds who sang outside her window may become completely extinct. Thereafter, the awareness prompted the ban on this hazardous chemical pesticide.

A number of other incidences and disasters in the past triggered the need to adopt Green Chemistry, a few have been highlighted below:

4.2.1 Bhopal Gas Tragedy

On the night of 2nd-3rd December, 1984 the worst industrial disaster which is known as the Bhopal Gas Tragedy occurred at Union Carbide Company of India (a pesticide plant) due to leakage of methyl isocyanate gas. This gas spread rapidly within the radius of eight kilometres. More than 4000 people lost their lives and 2000 were almost injured. Studies carried out by ICMR (Indian Council of Medical Research) revealed that people died because of suffocation and toxins that had resulted in swelling in the brain and finally death

SAQ 1

What was the major factor that lead to the Bhopal Gas Tragedy?

4.2.2 Thalidomide Disaster

Thalidomide drug was introduced in Germany in 1957 as a sedative and hypnotic for treatment of morning sickness in pregnant women. It was one of the most sold drugs. However, a few years later it was found that approximately 10,000 children were born with phocomelia which resulted in limb malformation and this was a repercussion of the consumption of thalidomide drug by the mothers of the new born children. This is referred as the thalidomide disaster which had caused a great deal of fear in general public about the effects of synthetic chemicals and prompted many countries to tighten drug approval regulations.

SAQ 2

Give the structure of thalidomide drug.

4.2.3 Times Beach

Times Beach is a small town located in the St. Louis County, Missouri, United States, which became a permanent community of small homes and trailer parks. In 1982, the people residing in this town were forced to leave forever as the Environmental Protection Agency (EPA) had found high levels of a chemical called dioxin in the soil along the roads. The source of contamination was found to be dioxin-tainted waste oil that was sprayed on the roads almost a decade ago. The spray of this toxic chemical had led to deaths of various animals such as horses and birds in addition to the acute poisoning symptoms including intense stomach pain, headache, diarrhoea, nosebleeds, skin rashes etc. experienced by people living in and around Missouri town. The problem faced by the residents increased even more by a flood because of which 700 families had to leave their homes. Finally, the entire town has to be evacuated.

4.2.4 Love Canal Disaster

Another incidence that caught a lot of public attention was the love canal disaster. Love Canal was originally built by William T. Love in the eastern edge of Niagara Falls, New York with the vision to generate power economically to fuel the industry as well as homes of this model city. Love believed that this could be done by digging a short canal between the upper and lower Niagara Rivers. However, unfortunately this project failed to sustain the economy and transmit electricity over great distances by means of an alternating current. Even worse, the canal was turned into a municipal and industrial chemical dumpsite from 1930's to 1950's, the chemical dump continued. Years after, the chemical substances that had been dumped began to leak and the site got contaminated by atleast 82 chemicals many of which were suspected carcinogens including benzene, chlorinated hydrocarbons and dioxin. As a consequence of the massive exposure to these chemicals, many critical health issues including high birth defect, miscarriage rates, liver cancer, seizure, nervous diseases etc. were witnessed amongst the neighbourhood children.

4.3 SOME IMPORTANT LAWS FOR ENVIRONMENTAL PROTECTION

All these incidences are referred as unforeseen chemical consequences that resulted in tragedy, followed by public outrage which in turn necessitated some legislations (also called environmental laws and movements) to control the manufacture, use and disposal of substances. Some important laws are highlighted below:

- *1970 National Environmental Policy Act (NEPA)*: This law promotes the enhancement of environment by establishing the President's Council on Environmental Quality (CEQ).
- *1970 Clean Air Act*: To prevent air pollution, protect the ozone layer and promote public health.
- *1972 Pesticide Control Act*: For controlling the sale, distribution, and application of pesticides through an administrative registration process
- *1972 Clean Water Act*: To restore and maintain the chemical, physical, and biological integrity of the nation's waters.
- *1976 Toxic Substances Control Act*: Regulates the introduction of new or already existing chemicals.

However, these laws primarily focussed on dealing with pollution regulation. Soon the need was realized to prevent pollution at source rather than treating it after it was generated and thus, Green Chemistry was introduced.

4.4 GREEN CHEMISTRY AND SUSTAINABILITY

In the year 1990, Environmental Protection Agency (EPA) came with the first act called as the Pollution Prevention Act that focussed on pollution prevention at source which in turn lead to the emergence of Green Chemistry. This act states “Pollution Prevention is reducing or eliminating waste at the source by modifying the production process, promoting the use of non-toxic or less toxic substances, implementing conservation technique and reusing materials rather than putting them into the waste stream.” With the passing of this act, for the first time there was a change in the policy from pollution control to pollution prevention and the industries were motivated to undertake research that dealt with the production of no waste. Soon a year after, EPA started an alternative synthetic reaction programme that aimed at providing research grant for conducting chemical synthesis without causing pollution. Thereafter, Paul Anastas who was working at that time at the EPA office of Pollution Prevention and Toxics coined the term Green Chemistry. In the year 1998, Anastas along with John C. Warner gave the twelve principles of Green Chemistry and published the first book on Green Chemistry entitled “Green Chemistry: Theory and Practice.” These principles are encouraging scientists, chemists and industrialists to pursue chemistry in a greener way.

Green Chemistry is central to sustainable development or it can help in accomplishing sustainability. As per United Nations Brundtland Commission ‘Sustainable Development’ is defined as *“Meeting the needs of the present without compromising the ability of future generation to meet their own needs.”*

SAQ 3

What is Green Chemistry? What is the significance of the colour green?

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4.5 CONCEPT OF GREEN CHEMISTRY

The term green is often associated with the natural surroundings (for instance green is the colour of plants). According to the founders of Green Chemistry Anastas and Warner, “Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and/ or generation of hazardous substances.” It is also known as “clean or sustainable chemistry” or a chemistry that is “benign by design.” As per EPA “Green Chemistry prevents pollution at the molecular level, is a philosophy that applies to all areas of chemistry.” We cannot define it as a new branch of chemistry, but it is the way chemistry should be practiced i.e. dealing with chemicals and their manufacturing processes to minimize any negative

environmental effects. **Figure 2** highlights all the factors that green chemistry aims at reducing.



Figure 4.2 Approach of Green Chemistry.

4.5.1 Twelve Principles of Green Chemistry

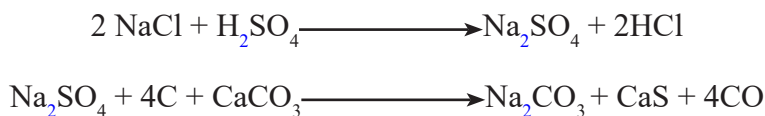
In this unit, we have described the twelve principles of Green Chemistry in a concise manner which will be helpful in understanding the basic concept involved.

Principle 1: Prevent Waste

According to this principle, it is better to prevent waste rather than clean up waste after it is formed. This is certainly one of the most effective principles which if followed well can eliminate problems of waste generation. Also, it can significantly reduce the costs involved in the manufacturing processes as there are huge expenses involved in the treatment and disposal.

To understand this principle, we must know what waste is? By the name itself waste means something undesirable or unwanted. It is a process or material that does not add value to goods or services. We may also interpret waste as material discharged or released into the environment in an amount of manner that may cause a disastrous effect. If we talk about chemical waste, it is simply the unwanted product generated during a manufacturing process or reagents which remain unutilized. For instance: in the Leblanc process employed largely by the textile industry in Lancashire in UK, huge amounts of waste were generated. This process dealt with the generation

of Na_2CO_3 from rock salt, limestone and sulphuric acid, HCl , CaS and CO are produced as waste as shown below:



The release of toxic HCl gas was reported to cause asthma and respiratory problems in South Lancashire where this process was carried out. Besides, the foul smelting CaS also lead to critical environmental issues. Roger Sheldon in 1992 gave a term called E-factor which is also known an environmental factor to measure waste. Larger the E-factor greater is the waste generated.

E-factor=kgs of by products (waste) produced/kg of desired product

Processes can be redesigned so that E-factor is minimized. There are successful examples which illustrate how the use of a selective catalyst helped in reducing E-Factor. For instance, Pzifer redesigned its Sertraline manufacturing process with the use of TiCl_4 as the catalyst that helped in minimizing the quantity of waste generated.

SAQ 4

Give an example to illustrate Principle 1.

Principle 2: Atom Economy

Principle 2 states that “Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.” The concept of atom economy developed by B.M. Trost is a consideration of “how much of the reactants end up in the final product.”

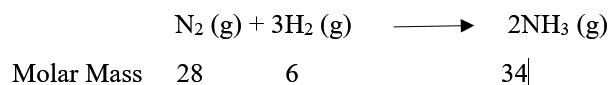
To understand how atom economy is different from the yield calculation, we need to understand what yield % is and how it is calculated.

$\% \text{ Yield} = (\text{Actual Quantity of desired product} / \text{Theoretical quantity of the desired product}) \times 100$

The biggest demerit with this calculation is that it does not consider waste or by-products formed because a 100% yield does not ensure whether waste is not generated. For instance: the very famous Wittig Reaction proceeds with 100% yield, but does not take into account the large amounts of by-products obtained. Any reaction can be considered green if there is maximum incorporation of the starting materials and reagents in the final product.

Examples of atom economical reaction:

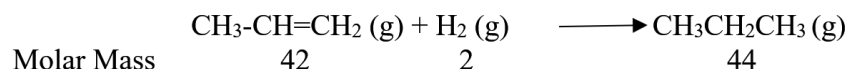
- (i) Generation of ammonia



Atom Economy = (Mass of atoms in the desired product ÷ Mass of the atoms of the reactants) × 100

$$\begin{aligned} &= \{34 \div (28+6)\} \times 100 \\ &= 100 \% \end{aligned}$$

(ii) Addition Reaction



$$\begin{aligned} \text{Atom Economy} &= (44 \div 44) \times 100 \\ &= 100 \% \end{aligned}$$

SAQ 5:

Give an example of a reaction comparing its atom economical and uneconomical pathways.

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Principle 3: Designing Less Hazardous Chemical Synthesis

As per principle 3, “Wherever practicable, synthetic methodologies should be designed to generate substances that possess little or no toxicity to human health and environment.” This principle motivates chemists to design products by avoiding reagents/starting materials that could be toxic. But, if we are not able to completely avoid the use of hazardous material, care must be taken towards minimizing its use. There are several examples to project how this principle is being implemented in industries due to increasing chemical consciousness with regard to hazard and exposure. For instance: Avalon Natural Products is a company that is based in California and has been a leader in making cosmetics has prohibited the use of chemicals banned under EU cosmetic derivative including perfluorinated compounds used in clothing, cookware, containers; bisphenol A-a carcinogen found in baby bottles; phthalates used in fragrances for long lasting effect and in nail polish to make it chip resistant, parabens employed for preventing cosmetics from deteriorating in bathrooms, sunlight and extreme conditions.

Also, there are examples of less hazardous chemical pathway employed. For instance: phosgene free route for the synthesis of polycarbonates using dimethyl carbonate which is much more greener than traditional pathway as it completely eliminates the use of HCl, CH_2Cl_2 , does not need crystallization, generates higher quality polycarbonates.

Principle 4: Designing Safer Products

According to this principle “Chemical products should be designed to preserve efficacy of function while reducing toxicity.” By safer chemical what we mean to say is a chemical that would cause minimum adverse effect on human health and environment. Examples of safer chemicals include structural analogues (i) methacrylonitrile which is a safer replacement of acrylonitrile (the probable human carcinogen) (ii) sodium salt of linear alkyl benzene sulphonic acid that readily biodegrades and is a greener alternative to branched alkyl benzene sulphonic acid.

Principle 5: Safer Solvents and Auxiliaries

This principle states “The use of auxiliary substances that do not directly contribute to the structure of the reaction product but are still necessary for the **chemical** reaction or process to occur should be made unnecessary wherever possible and innocuous when used.” The statement is self-explanatory and indicates that alternative greener replacements should be explored for toxic organic solvents which are major contributors to overall toxicity of a reaction. Many of the traditional solvents such as benzene, perchloroethylene used in dry cleaning, shoe polish, white correction fluid are known as human carcinogen and chlorinated hydrocarbons are known to persist in the atmosphere causing depletion of ozone layer. Thus, pharmaceutical and other industries are looking for replacements some of which include (i) Water (ii) Supercritical Fluids (iii) ionic liquids (iv) polyethylene glycol (v) fluorinated biphasic solvents (vi) biobased solvents (derived from renewable resources) (vi) no solvent is the best solvent. There are solvent selection guides available which enable scientists to use safer solvents in research.

SAQ 6:

Why do you think no solvent is the best solvent?

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Principle 6: Design for Energy Efficiency

Principle 6 states “Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.”

Thermal heating processes mostly employ fossil fuels reserves of which are limited and are soon going to exhaust. In addition, the energy supplied is not specific, which means it is not directed to the chemical bond of the molecule of the reactants. Besides, most of the energy is wasted in heating the container and the solvent, while some is also lost to the environment. The energy efficient alternatives have been lately been explored which include Microwave assisted, light induced photochemical reaction and ultrasound assisted irradiation.

How does microwave chemistry fall under the banner of green chemistry?

Principle 7: Renewable Resources

As per this principle “A raw material or feedstock should be renewable rather than depleting technically and economically practicable.”

All the forms of energy that we have been using with the advent of globalization and rapid industrialization are fossil fuel based, which are not only going to exhaust soon, but also have a serious effect on human health and environment. Hence, attention is now being devoted towards finding out alternative renewable resources which can work as excellent substitutes. The idea of making our future fuels, chemicals and materials from feedstocks that never deplete is certainly quite interesting. There are a few examples of alternative chemicals/products derived from natural resources including adipic acid from corn starch, biofuel production from microalgae, green plastics made from corn.

Principle 8: Reduce Derivatives

This principle states that “Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided wherever possible.

We often use protecting and deprotecting groups in organic synthesis in order to achieve desired chemoselectivity. To put it in simple words, whenever there are two reactive groups in a molecule and wish to use only one of the groups for the formation of desired product, the other group needs to be protected and subsequently deprotected. However, the incorporation of these groups require additional steps and reagents which also lead to an increase in waste generation. This principle advocates the reduction of using protecting groups and derivatives. The best alternative to avoid this is to use enzymes as they work under mild conditions and lead to chemo selectivity. They mostly react at the desired moiety and do not interfere with the rest of the molecular structure. The antibiotic synthesis of penicillin drug is the best example illustrating how the traditional protection deprotection method has been replaced with an enzymatic process and the enzyme used is penacylase.

Principle 9: Use of selective catalyst

According to Principle 9 “Catalytic reagents are superior to stoichiometric reagents.”

In comparison to the traditional stoichiometric processes that lead to enormous amount of waste generation, use of catalysts permit higher atom economy and lesser waste generation. Catalyst is a substance which expedites the rate of a reaction by providing an alternative pathway without itself undergoing any change and also enable a process to occur selectively. The catalytic oxidation of PHCH(OH)CH_3 using $\text{CrO}_4/\text{H}_2\text{SO}_4$ has an atom economy of about 42% while the same reaction when carried out in presence of a catalyst has an atom economy of 87%. Also, when the reduction of benzaldehyde is carried out in presence of stoichiometric reagents, atom economy is 81% but on the other hand catalytic reduction of benzaldehyde leads to 100% atom economy.

SAQ 8:

Give examples of catalysts that active, selective as well as reusable.

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Principle 10: Design for Degradation

This principle states “Chemical products should be so designed that at the end of their function, they do not persist in the environment and break down into innocuous degradation products.”

In order to understand this principle, we must understand what are persistent chemicals? These are chemicals which do not degrade easily and remain in the environment since long, thereby exhibiting toxic effects. In environment, degradation of the chemicals can occur via microbial activity and plants which is called biodegradation. However persistent chemicals do not degrade owing to lack of an appropriate enzyme or microbe. DDT is an example of organic pesticide that persists in the environment. Thus, now greener substitutes are being developed for DDT. Another very successful example is provided by the laundry industry. Detergents have found a lot of use over the past decades, however there was a problem due to its foaming which occurred because of non-biodegradability of alkyl benzenesulphonate in detergents. This problem was however resolved by using linear chain rather than branched chain on benzene sulphonate moiety, which showed better biodegradability.

Principle 11: Real Time Analysis for Pollution Prevention

As per this principle Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.” In other words, what this principle underpins is that if chemical reaction is monitored continually then, it can help prevent the release of hazardous and polluting substances due to accidents or unexpected reactions. Further, if effectively a reaction is monitored, then the warning signs can be spotted, and consequently, the reaction can be stopped or managed before such

an event occurs. Online monitoring has been possible with the help of analytical techniques such as GC-MS and LC-MS which help in seeing what is happening inside a reaction and to know when exactly it will be completed, thereby reducing waste, time and energy.

Principle 12: Inherently Safer Chemistry for Accident Prevention

According to this principle “substances and form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires”

Often, we have also heard of chemical releases due to either routine evolution of gases or accidental due to negligence of operator or operational malfunctioning. These releases have a detrimental effect on human health and environment. Therefore, there is a need to practice safer chemistry by designing chemical processes and products with specific aim to recognize and eliminate hazards from the manufacturing process.

4.6 GREENER SOLVENTS

Solvents have attracted a great deal of attention in the scientific community owing to the crucial role they play in agrochemicals, pharmaceuticals, paints, household and industrial cleaners etc. Not only do they provide a medium for the dissolution of a wide variety of substrates, but also accelerate many of the reactions. The largest user of solvents is the pharmaceutical sector.

4.6.1 Issues with the use of traditional solvents

Organic solvents are the major component of cleaning agents, adhesives, pharmaceuticals and cosmetics and have been used primarily for mass and heat transfer as well as separation of desired products from unreacted starting materials and by-products. Unfortunately, despite being useful one cannot ignore the flip side of the coin which has been toxicity, flammability, and environmental damage with the usage of copious amounts of solvents. We already are aware of the carcinogenic nature of hydrocarbon based solvents such as benzene. Also they are known to bioaccumulate because of their poor solubility in water. Besides, there are several other solvents (eg: carbon tetrachloride, and trichloroethylene) which may cause adverse health effects including eye irritation, headache, allergy, skin reactions etc. Therefore, efforts are being directed towards either reducing or completely eliminating the use of organic solvents.

Now we all talk about greener solvents which by definition are environmentally friendly solvents that are characterized by:

- Low toxicity
- Convenient Accessibility
- Greater Efficiency
- Enhanced reusability

- Increased Biodegradability

4.6.2 Alternative Green Solvents

In the subsequent sections, we shall be highlighting examples of alternative greener solvents that have made a way to large scale organic synthesis.

4.6.2.1 Water

Currently, water has gained prominence as a potentially benign solvent due to environmental benefits, safety, synthetic efficiency, low cost, high specific heat, natural abundance etc. One might be surprised to note that water had remained a poor solvent for organic transformations since long due to solubility reasons (poor solubility of organic compounds in water). Also removal of water was thought to be energy intensive; contaminated waste streams would be difficult to treat. Fortunately, these problems have been resolved gradually. Like for instance, the solubility issue was resolved using surfactants, phase transfer catalysts or by adding solubilizing groups such as sulphonates, phosphonates, oxalates etc. There are numerous examples which illustrate that reactions have been carried out “in water” as well as “on water” successfully with very high yield.

Now, what do we mean by in water and on water should be demarcated.

In-Water Reactions: When the reactants employed are soluble in water, it is an in water reaction. Quinoxaline synthesis is an example of in water reaction (**Figure 3**).

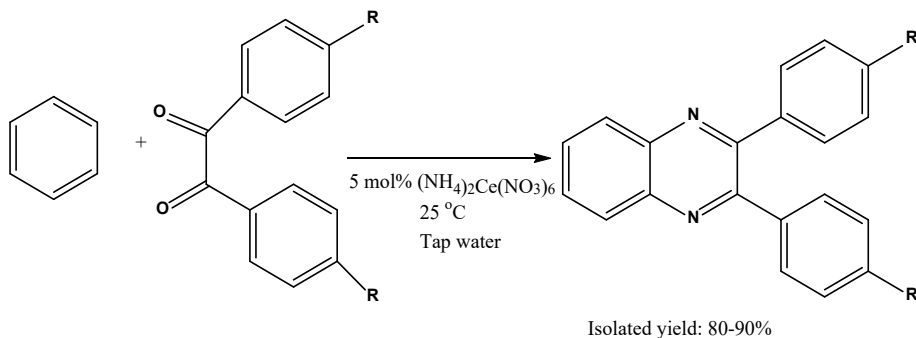


Figure 4.3 Schematic of quinoxaline synthesis accomplished in water.

On-Water Reactions: When reactants are insoluble in water (hydrophobic), they are simply suspended in water and remain in the form of aqueous emulsions or suspensions. Reactions also occur on water with good yield the reason for which remained unclear for long. However, in 1991 Breslow demonstrated that it could be due to hydrophobic effect (reactants tend to be away from water and accumulate together, which increases the probability of a reaction). **Figure 4** shows Diels Alder Reaction occurring on water. Breslow found that the rate of Diels Alder reaction increases drastically when carried out in water (**Table 1**).

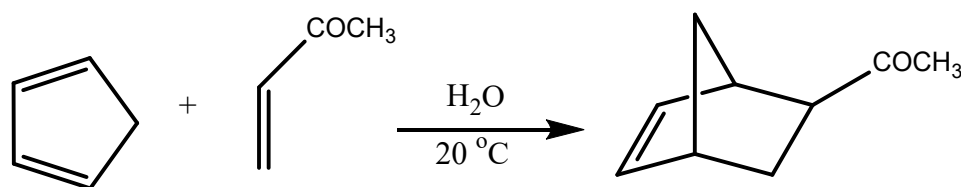


Figure 4.4 Diels Alder Reaction on water.

Table 1 Comparison of rate constant values of Diels Alder reaction

Solvent	Additional Component	Rate Constant $k_2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$
Isooctane	-	5.9
MeOH	-	75.5
Water	-	4,400.0
Water	LiCl (4.86 M)	10,800.0
Water	β -Cyclodextrin	10,900.0
Water	α -Cyclodextrin	2,610.0

4.6.2.2 Supercritical Fluids (SCFs)

Although supercritical fluids (SCFs) have been known since long, yet they got recognized as environmentally acceptable replacements for conventional solvents after the birth of green chemistry. So, what does the word supercritical mean? When any substance is subjected to a pressure and temperature greater than its critical point, it is said to be supercritical. A substance is characterized by its critical point that is obtained at specific conditions of temperature and pressure. In the supercritical region, the particular substance exhibits properties of both liquid as well as gas. The most commonly employed SCF includes supercritical carbon dioxide (scCO_2) which has $T_c=304 \text{ K}$ and $p_c=72.8 \text{ atm}$. scCO_2 has emerged as a green alternative solvent in a number of industrial reactions such as hydrogenation, hydroformylation, polymer production, C-C bond formation owing to myriad of advantages it offers including non-toxicity, abundance, tendency to get easily removed from the product. In **Figure 5**, we have shown an example of the hydrogenation reaction carried in scCO_2 which gives the desired product with 100% yield. It is also acquiring paramount significance as a solvent for extracting essential oils and other products from spices, aromatic herbs and medicinal plants. It is interesting to note that the decaffeination of coffee has also been accomplished using scCO_2 as solvent.

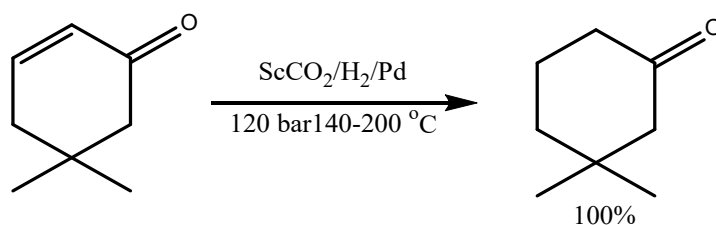


Figure 4.5 Example of use of scCO_2 in hydrogenation reaction.

SAQ 9 Extraction of an important compound from orange peel has been carried out using scCO_2 ? Can you name the compound?

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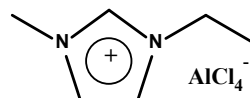
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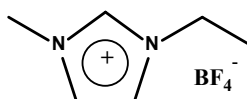
4.6.2.3 Ionic Liquids

Ionic liquids have emerged as a relatively new class of solvents that are primarily composed of complex organic salts comprising of cations and anions. These are essentially liquids at unusually lower temperature, as they have low vapour pressure. In technical terms, any salt, even NaCl above 800 °C can be designated as ionic liquid; however the most frequently used definition of ILs is “*Salts that exist in the liquid state below 100 °C and are liquid at room temperature.*” Owing to their complex interplay of coulumbic, hydrogen bonding and Van der Waals interactions of their ions, ILs have emerged as greener alternatives to volatile organic compounds (VOCs). Also, to add to their fascinating properties, ILs exhibit:

1. Non- Volatility (which allows for high temperature reactions without the requirement of a pressure vessel to contain the vapors) and Non-Flammability
2. Work as both catalysts as well as solvents
3. Robust
4. Tailor made, task specific solvents-Allow the tailoring as per requirement.



1-ethyl-3-methylimidazolium chloride ([emim]Cl) chloride ([emim]AlCl₄)



1-butyl-3-methylimidazolium fluoride-boron trifluoride ([bmim]BF₄)

Figure 4.6 Examples of room temperature ionic liquids.

Figure 6 shows examples of some of the common room temperature ionic liquids. Some well-known reactions conducted successfully in ILs include friedel crafts reaction, esterification, mannich reaction, regioselective alkylation, reduction of aldehydes, Fischer Tropsch Synthesis etc.

4.6.2.4 Liquid polymers

Similar to the ILs, liquid polymers having different molecular weights have also gained a lot of attention in organic synthesis since they possess low volatility, low

eco-toxicity, good thermal stability, non-flammability and most importantly rapid biodegradability. Amongst several liquid polymers, polyethylene glycol (PEG) has been utilized by both academic as well as industrial researchers in diverse areas including electroplating, cosmetics, personal care, dyes, paints etc. In **Figure 7**, it has been demonstrated how PEG-200 is used as a solvent in Diels Alder Reaction. PEG can also function as an excellent aqueous biphasic system (ABS) wherein two phases are formed when mixed with another water soluble polymer and such ABS are good for extracting toxic dyes that would otherwise be difficult to remove from the contaminated waste streams.

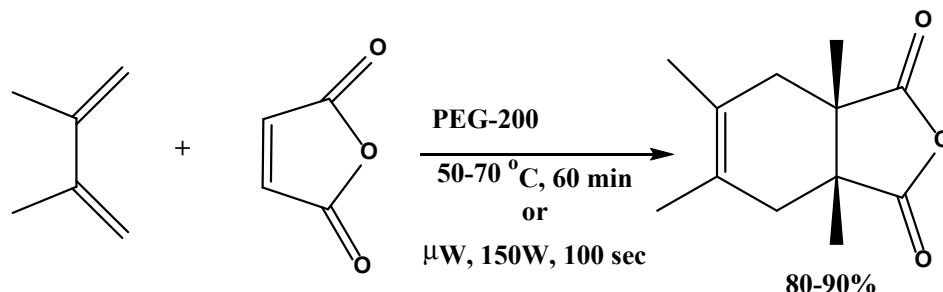


Figure 4.7 Example of Diels Alder Reaction in PEG-200.

4.6.2.5 Bio-Based Renewable Solvents

Solvents which are derived from renewable feedstocks that are bio-based have been classified as bio-based solvents. The sources generally include agricultural crops rich in carbohydrates including corn, wheat, beetroot etc. They offer several significant advantages including low VOC emission, low toxicity, biodegradability and environmentally friendliness. Some typical examples of bio-based solvents include bioethanol, glycerol and 2 Me-THF.

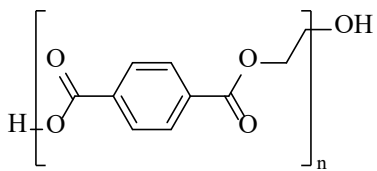
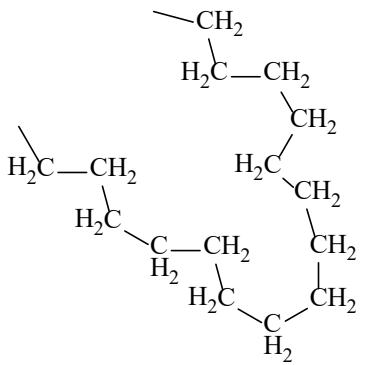
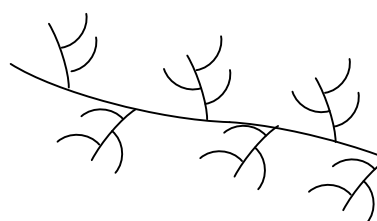
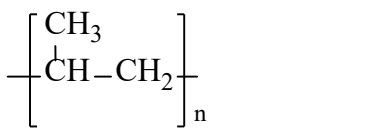
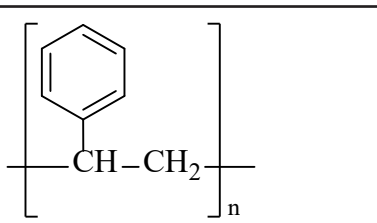
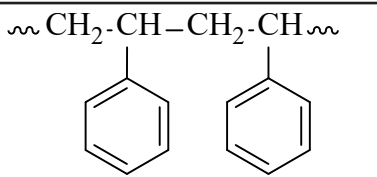
4.7 EARTH FRIENDLY PLASTICS

Plastics have turned out to be one of the biggest source of polluters today despite having innumerable valuable uses in daily life. While every minute, one million drinking plastic bottles are purchased, half or more than half of them are intended for one time use and thrown away as such which end up in either a landfill or natural environment, persisting for years and centuries. Not surprisingly, a staggering 8 million tonnes of plastic reaches the world's oceans every year and it is the ocean plastic which is known to kill millions of marine animals every year. Animals are killed via either entanglement in plastic objects or via ingestion of these wastes, or through the exposure to chemicals within the plastics that interfere with their physiology.

Before moving further, it is important to understand what do the plastic wastes comprise of and why are they so problematic?

Chemically, plastics are polymers of high molecular mass comprising of long chains of repeating molecular subunits called as monomers. **Table 2** provides data related to the variation in plastic polymers and their uses.

Table 2 Examples of polymers used as plastics with their structures and applications.

Sl. No	Polymer	Structure	Use/Application
1.	Polyethylene terephthalate (PET)		Water bottles, dispensing containers, biscuit trays
2.	High — density polyethylene (HDPE)		Shampoo bottles, milk bottles, freezer bags, ice cream containers
3.	Low — density polyethylene (LDPE)		Bags, trays, containers, food packaging film
4.	Polypropylene (PP)		Potato chip bags, microwave dishes, ice cream tubs, bottle caps
5.	Polystyrene (PS)		Cutlery, plates, cups
6.	Expanded polystyrene (EPS)		Protective packaging, hot drink cups

4.7.1 Primary issues with the synthetic plastics

They are produced from non-renewable sources including crude oil which are depleting.

Most of the synthetic plastics require the use destructive thermal treatment such as combustion or pyrolysis, which require high temperature

There has been increasing concerns due to the presence of toxic chemicals such as bisphenol A (BPA) and polystyrene (PS) that might leach into water. While BPA in particular is highly toxic and a known endocrine disruptor which can imitate body's hormones, interfering with the production, secretion, transport, action, function, and elimination of natural hormones often at times leading to fertility problems, male impotence, heart disease and other conditions; polystyrene has been declared a possible human carcinogen by the U.S. Environmental Protection Agency (EPA) and the International Agency for Research on Cancer.

Extremely small sized invisible plastics (mostly PS) called as microplastics are released from fibres, clothings when washed ultimately reach the oceans causing deleterious consequences to the marine species.

Considering the extreme toxicity and non-biodegradability associated with the conventional plastics, now attention is being directed towards the design of earth friendly or green plastics that are bio-degradable (decomposed by action of living organism into non-toxic simple molecules including carbon dioxide, water and biomass). These are essentially made from renewable materials such as plants, petrochemicals or microbes. The concept behind this is utilization of principles of green chemistry, especially principle 1 which aims at the prevention of pollution at source rather than treating up pollution after it has been caused and principle 7: utilization of renewable feedstocks whenever possible.

SAQ 10: Why do you think plastics have become a big issue today? What are the underlying problems?

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4.7.2 Greening of Plastics

Earth friendly plastics or bio-plastics commonly obtained from natural origins such as plants, animals or micro-organisms may be classified into the following types:

Polyhydroxyalkanoates (PHAs): Examples of bio-based plastics include Polyhydroxyalkanoates (PHAs) which are naturally produced by various micro-organisms eg: *Cuprividus necator*. Poly-3-hydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and polyhydroxyhexanoate (PHH) are specific examples of PHA based plastics.

Polylactic acid (PLA): PLA is a thermoplastic aliphatic polyester synthesized from renewable biomass, typically from fermented plant starch such as from corn, cassava, sugarcane or sugar beet pulp.

Cellulose-based Plastics: Cellulose esters such as cellulose acetate and nitrocellulose are utilized to prepare cellulose based plastics.

Lignin based Plastics: Lignin is commonly obtained as a by-product of polysaccharide extraction from various plant materials during the production of paper, ethanol etc. Lignin based plastics are bio-renewable natural aromatic polymers with biodegradable properties.

Green Chemistry Challenge Award for innovation of PLA

In the year 2002, Nature Works LLC received Greener Reaction Condition Awards for replacing petroleum based polymers with bio-based compostable and recyclable polylactic acid (PLA). This PLA based bioplastic is one of the most promising and popular materials as an alternative to synthetic polymer. The synthetic process via which it is manufactured eliminates the use of organic solvents and other hazardous materials and employed a catalyst that reduces energy usage (**Figure 8**). Furthermore, the approach to synthesis biodegradable or green plastics is a much better solution than disposing off the plastic waste to landfills or via incineration.

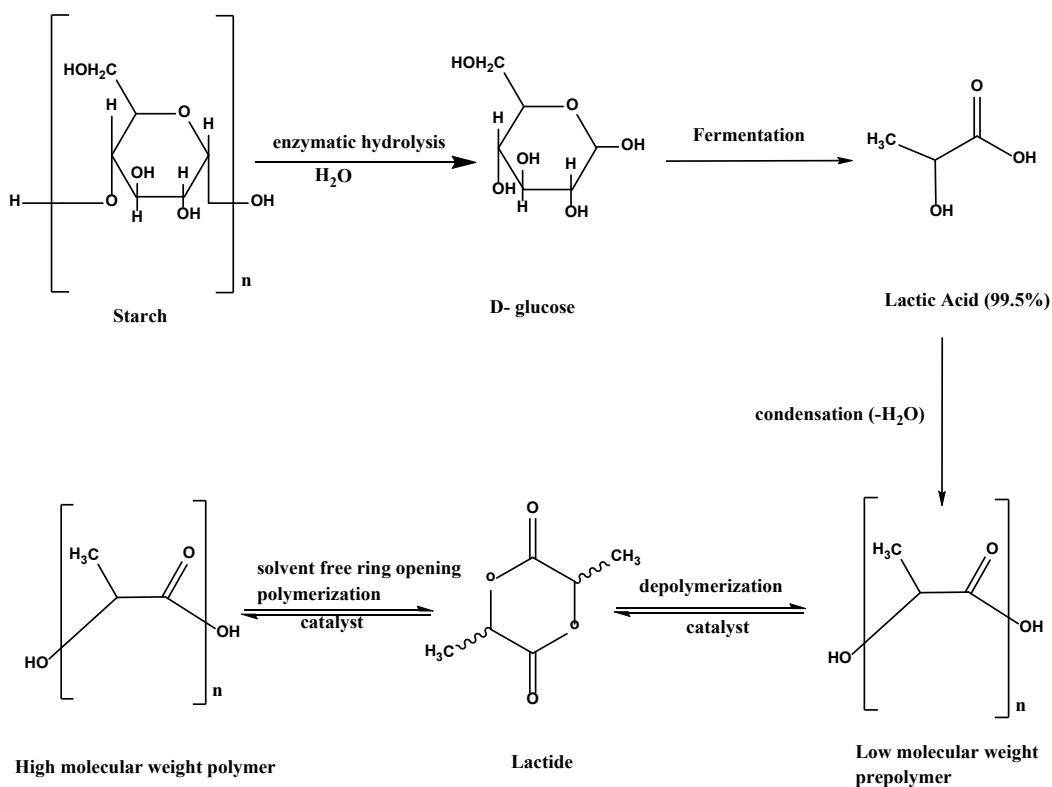


Figure 4.8 Synthesis of PLA by Nature works.

Conversion of plastic wastes into valuables

The most emerging green trend now is utilization of waste materials and converting them into valuables. This is a circular economy approach which primarily revolves around the concept of converting resources into waste and waste back into valuable resources which is greener and much more profitable as compared to the linear approach that only goes a one way path and leads to extensive waste generation. In view of pressing problems associated with plastic wastes, attempts are now being directed towards utilizing their untapped potential by converting them into

either fuels such as petrol, diesel and kerosene etc using catalytic degradation or transforming them into valuable catalytic materials. In India also, we are recycling plastic wastes extensively and the current Union government's focus is on plastic waste management via the Swachh Bharat Abhiyan programme.

ENVIRONMENTALLY BENIGN PESTICIDES

Over the past decades, the global agricultural sector has extensively relied on pesticides that have undoubtedly increased the crop yield and reduced post-harvest losses, but unfortunately their expanded use has polluted the environment whilst affecting human health considerably. As per estimates, barely 0.1% of the total agrochemicals utilized in crop protection succumbs to reach the target pest, while the remaining 99.9% is undeniably bound to enter the environment thus causing hazards to non-target organisms.

4.8.1 Effect of Synthetic pesticides on human health and environment

To understand fundamentally how the pesticides, cause massive destruction, we need to understand the basics. These are organic chemical substances that impart protection to plants from pests, weeds or diseases. Typically, the various forms of pesticides employed are insecticides, fungicides, herbicides, rodenticides and plant growth regulators. Some of the common classes of pesticides that have negatively impacted human health and environment include organochlorines, organophosphates, carbamates, pyrethroids, triazines, and neonicotinoids. As already mentioned previously, DDT was the first ever pesticide that had shown serious environmental consequences resulting in thinning of egg shells and bald eagle species becoming extinct.

Subsequently, there have been reports mentioning how harmful the other synthetic pesticides have proven to be. **Table 3** gives examples of the various pesticides that have exhibited toxicity. Exposure to these chemicals can occur through contact with either the skin or via ingestion or inhalation. In fact, residues of pesticides have often found in everyday food including cooked meals, water, wine, fruit juices, refreshments, animal feeds etc. The fate of the pesticides within human body is unpredictable; once inside, it may start getting metabolized, excreted, and stored or bioaccumulated in body fat leading to dermatological gastrointestinal, neurological, carcinogenic, respiratory, reproductive and endocrine effects.

Table 3 Rising toxicity of pesticides 1945-2003.

Pesticide	Brand Name	Use	LD50	Toxicity
DDT	Dinocide	Insecticide	27,000	1
Metiocarb	Mesurool	Insecticide	230	117
Carbofuran	Curater	Insecticide	160	69
Deltamethrin	Decis	Insecticide	10	2700
Fipronil	Regent	Insecticide	4.2	6429
Clothianidin	Pocncho	Insecticide	4.0	6750

Imidacloprid	gaucho	Insecticide	3.7	7297
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Source: Dr. J M Bonmatin, CNRS (France)

SAQ 11

Give examples of synthetic pesticides. In what way have they affected human health and environment?

.....

.....

.....

.....

Search for Environmentally benign pesticides

In view of the harmful effects caused by the synthetic pesticides, the scientific community has realized the need for implementation of sustainable practices. Consequently, environmentally benign pesticides are being developed that are making an important breakthrough in pest control. Most of the plant derived materials have emerged as green pesticides as they are safer and effective against diseases, nematodes and other organisms in addition to phytophagous insects.

4.8.3 Examples

4.8.3.1 Microbial pesticides

Naturally occurring or genetically altered bacteria, fungi, algae, protozoans or viruses have proven to be an attractive and greener alternative to chemical insecticides. These are called as the microbial pesticides and are pathogenic to the targeted pest. These are applied as the conventional insecticidal sprays, dusts or granules. The major advantages of using microbial pesticides include:

- (i) They are biodegradable.
- (ii) Cheaper, Renewable and can be handled safely.
- (iii) Residue-Free.
- (iv) Safe to natural enemies and higher organisms.
- (v) Difficult for insects to develop resistance against them.

4.8.3.2 Plant-pesticides

In nature, plants guard themselves against pests by evolved defence chemicals which alter the behaviour of selected pest. Such behaviour altering chemicals are defined as semiochemicals well known for their static mode of action, less persistence, and biodegradable nature. Plant pesticides are substances produced by plants from the genetic material that has been added to the plant. Among the plant

products, azadirachtin, pyrethrum, sabadilla, etc. are known to have a successful history in pest control.

4.8.3.3 Biochemical pesticides

These are the naturally occurring substances that successfully control the pests via non-toxic mechanisms. They interfere with growth or mating, such as plant growth regulators, or substances that repel or attract pests, such as pheromones.

4.8.3.4 Natural Home-made solutions for pest-control

1. Soap based insecticides

These soaps utilize the salts and fatty acids within them to target many soft-bodied pests including aphids, whiteflies, mealy bugs, earwigs, thrips, and the early stages of scale.

2. Neem Oil Insecticides

Insecticidal oils have also proven their efficacy in treating pests by suffocating them. One such classic example is the oil that is extracted from the seeds of neem tree which is biodegradable and natural fungicide. It acts as a hormone disruptor and an antifeedant for the insects that feed on leaves and other parts of plants. While applying to crops, 2 teaspoons neem oil and 1 teaspoon of mild liquid soap are mixed well with 1 quart of water, and immediately sprayed on the affected part of the plant foliage.

3. Diatomaceous earth

Diatomaceous earth made from sedimentary rocks by fossilized algae (diatoms) also works as a natural pesticide. This substance works in quite an interesting manner mechanistically by virtue of its abrasive qualities or tendency to absorb lipids a waxy substance obtained from insects' exoskeleton, which eventually dehydrates them to death.

4. Garlic Insecticide Spray

Garlic has a typical aroma which makes it work as an insect repellent and owing to its natural fungicidal and pesticidal properties, it has emerged as an excellent economical, non-toxic pesticide. Examples of pests that have been controlled using garlic include aphids, ants, termites, white flies, beetles, borers, caterpillars, slugs, army worms etc.

5. Tomato Leaf

Tomato leaves contain alkaloids-"tomatine," that has shown efficacy in controlling aphids and other insects.

As most of the synthetic pesticides are not safe and many have even proven to be cancerous to human beings, therefore these natural environmentally friendly pesticides emerged as cleaner alternatives in pest control.

SAQ 12

Environmentally friendly pesticides are making a breakthrough in pest control. How would you justify this statement?

4.9 LET US SUM UP

Undeniably, the past few decades have witnessed an enormous improvement in scientific methodologies/solutions showing phenomenal capability to protect human health and environment and these innovative solutions have been possible through green chemistry. We have had fantastic accomplishments as the solutions were at the molecular level since green chemistry preached the prevention of waste at source rather than treating it up after generation. So, quite a few of the existing processes were redesigned using the basic tenets of green chemistry. Progressively, industries also started adopting the path of green synthesis. Utilization of alternative greener solvents, catalysts and reagents, aiming at higher atom economy, relying on alternative renewable feedstocks have truly changed the landscape of synthesis pursued at academic as well as industrial level. Yet, despite accomplishing a lot as evident from the green chemistry challenge awards, a lot needs to be done as the number of challenges that lie ahead are far many. Population growth, energy, food supply, resource depletion, global climate change, water, toxics generation and dispersion remain the most pressing environmental issues facing the planet even today. Apart from this, there are research and implementation challenges in view of stringent laws. Nonetheless, green chemists foresee that all the barriers would be eventually resolved if there is effective preaching of green chemistry which requires educating our future chemists. Not just chemists, but since green chemistry is a powerful tool for safe and healthy environment for all including businessmen, economists, environmentalists etc. To be successful, green chemistry would require an interdisciplinary strategy in education, research and service.

4.10 GLOSSARY

Green Chemistry: Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and/ or generation of hazardous substances

Atom Economy: The atom economy of a reaction is a measure of the amount of starting materials that end up as useful products.

E-Factor: E-factor also known as environmental impact factor measures the waste generated in a process. Higher the E-factor greater is the waste generated.

Biodegradable Plastics: Plastics that can be decomposed readily by the action of living organisms, usually microbes, into non-toxic products.

Polylactic acid: PLA is a thermoplastic aliphatic polyester synthesized from renewable biomass, typically from fermented plant starch such as from corn, cassava, sugarcane or sugar beet pulp.

In-Water Reactions: When the reactants employed are soluble in water, it is an in water reaction.

On-Water Reactions: When reactants are insoluble in water (hydrophobic), they are simply suspended in water and remain in the form of aqueous emulsions or suspensions.

Supercritical Fluids: A fluid is defined as supercritical when its temperature and pressure exceed critical values (T_c and P_c respectively).

Green Chemistry Challenge Awards: In 1995, the U.S. Environmental Protection Agency (EPA) received support from President Bill Clinton to establish an annual awards program highlighting scientific innovations in academia and industry that advanced green chemistry. This created the annual Presidential Green Chemistry Challenge Awards, which have been a major platform for promoting awareness about green chemistry.

Ionic Liquids: These are green solvents primarily composed of complex organic salts. These are essentially liquids at unusually lower temperature, as they have low vapour pressure.

Pesticides: Substances that are meant to control pests, including weeds.

4.11 SUGGESTED READINGS

1. Anastas, P.T. Warner, J.C. (1998), Green Chemistry: Theory and Practice. Oxford University Press.
2. Lancaster, M. (2010). Green Chemistry: An introductory text, RSC Publishing, Cambridge, UK.
3. Sidhwani, I. Sharma, R. K. (2020). An introductory Text on Green Chemistry, Wiley Publications, USA.

4.12 TERMINAL QUESTIONS

Q.1 Explain the concept of atom economy using a suitable example.

Q.2 What do you understand by earth friendly plastics?

Q.3 How would you classify whether a solvent is green or not? What are the problems associated with traditional solvents?

Q.4 What are environmentally benign pesticides? Give examples of some explaining how they are a superior alternative to the synthetic ones.

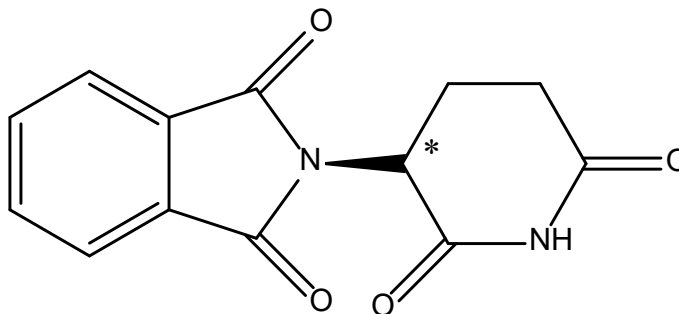
Q.5 Fundamentally highlight the differences between green chemistry and environmental chemistry.

Q.6 What are supercritical fluids? Give examples of reactions in which SCFs have been employed as green solvents?

Answers

Self-Assessment Questions

1. The accident had occurred due to non-functioning refrigeration unit, bulk storage of 42 tons methyl isocyanate (MIC) gas, non-functioning safety system, stashing staff and switch off of the warning system.

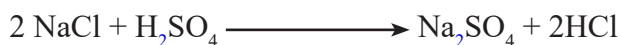


2. Chemistry is the design of chemical products and processes that reduce or eliminate the use and/ or generation of hazardous substances. According to EPA “*Green Chemistry prevents pollution at the molecular level, is a philosophy that applies to all areas of chemistry.*”

The colour green is associated with the natural surroundings. It is used for environmentally friendly and sustainable manufacturing processes.

3. Principle 1 states “It is better to prevent waste rather than to treat up after it is formed.”

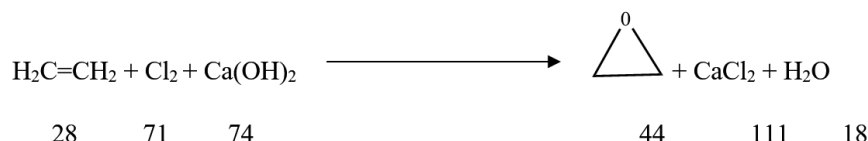
Example: In the Leblanc process employed largely by the textile industry in Lancashire in UK, huge amounts of waste were generated. This process dealt with the generation of Na_2CO_3 from rock salt, limestone and sulphuric acid, HCl, CaS and CO are produced as waste as shown below:



The release of toxic HCl gas was reported to cause asthma and respiratory problems in South Lancashire where this process was carried out. Besides, the foul smeling CaS also lead to critical environmental issues.

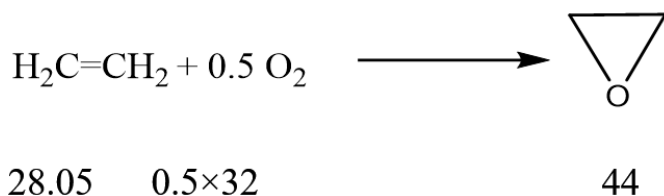
4. Oxirane synthesis has been carried out in two ways. The first approach is two-stepped (demonstrated here as one step) requiring $\text{Ca}(\text{OH})_2$. The second approach is single step that requires O_2 as oxidant. If we compare the atom economy of both the reactions, we find that the second approach is 100 % atom economical while the first one has a very low atom economy of about 25.6%.

Approach 1:



$$\% \text{ Atom economy} = \frac{44}{173} \times 100 = 25.4\%$$

Approach 2: Single Step Synthesis



$$\% \text{ Atom economy} = \frac{44}{44} \times 100 = 100\%$$

5. No solvent means performing reactions without using any solvent. This is certainly the best and greenest solution as it would not lead to any waste generation and maximize atom economy, because the reactants are the sole reagents utilized.
6. In conventional heating methods, oil bath or hot plate are used as a source of heat to a chemical reaction. Microwave irradiation is widely used as a source of heating in chemical synthesis. The basic mechanisms observed in microwave assisted synthesis are dipolar polarization and conduction. Microwave-assisted synthesis is greener on account of the following advantages (i) enhanced reaction rates (ii) higher yields (iii) greater selectivity (iv) more economic for the synthesis of a large number of organic molecules.
7. Examples of catalysts that suffice the three key goals of catalysis i.e. activity, selectivity and reusability are supported heterogeneous catalysts eg: Fe_3O_4 supported Cu nanocatalyst.
8. Extraction of D-Limonene from orange peels has been carried out efficiently using scCO_2 . This experiment is conducted in undergraduate laboratories.
9. Plastics have become a big issue today on account of the following reasons:
 - They are produced from non-renewable sources including crude oil which are depleting.

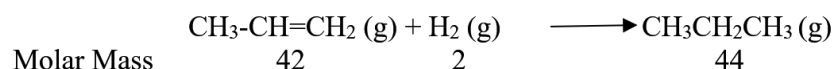
- Most of the synthetic plastics require the use destructive thermal treatment such as combustion or pyrolysis, which require high temperature
 - There has been increasing concerns due to the presence of toxic chemicals such as bisphenol A (BPA) and polystyrene (PS) that might leach into water. While BPA in particular is highly toxic and a known endocrine disruptor which can imitate body's hormones, interfering with the production, secretion, transport, action, function, and elimination of natural hormones often at times leading to fertility problems, male impotence, heart disease and other conditions; polystyrene has been declared a possible human carcinogen by the U.S. Environmental Protection Agency (EPA) and the International Agency for Research on Cancer.
 - Extremely small sized invisible plastics (mostly PS) called as microplastics are released from fibres, clothings when washed ultimately reach the oceans causing deleterious consequences to the marine species.
10. DDT, Metiocarb, Carbofuran, Deltamethrin, Fipronil and Clothianidin are examples of the synthetic pesticides employed. The organochlorine pesticides like DDT are extremely persistent and accumulate in fatty tissue. Through the process of bioaccumulation (lower amounts in the environment get magnified sequentially up the food chain), large amounts of organochlorines can accumulate in top species like humans; act as endocrine disruptors, interfering with hormonal function of estrogen, testosterone and other steroid hormones.
11. In view of the harmful effects caused by the synthetic pesticides, the scientific community has realized the need for implementation of sustainable practices. Consequently, environmentally benign pesticides are being developed that are making an important breakthrough in pest control. Most of the plant derived materials have emerged as green pesticides as they are safer and effective against diseases, nematodes and other organisms in addition to phytophagous insects. Examples of eco-friendly pesticides include include neem oil, garlic spray, tomato leaves etc.

Terminal Questions

1. The concept of atom economy developed by B.M. Trost is a consideration of "how much of the reactants end up in the final product."

Example to illustrate atom economy:

Addition Reaction



$$\begin{aligned} \text{Atom Economy} &= (44 \div 44) \times 100 \\ &= 100 \% \end{aligned}$$

2. Earth friendly plastics or bio-plastics commonly obtained from natural origins such as plants, animals or micro-organisms may be classified into the following types:

- (i) **Polyhydroxyalkanoates (PHAs):** Examples of bio-based plastics include Polyhydroxyalkanoates (PHAs) which are naturally produced by various micro-organisms eg: *Cuprividus necator*. Poly-3-hydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and polyhydroxyhexanoate (PHH) are specific examples of PHA based plastics.
- (ii) **Polylactic acid (PLA):** PLA is a thermoplastic aliphatic polyester synthesized from renewable biomass, typically from fermented plant starch such as from corn, cassava, sugarcane or sugar beet pulp.
- (iii) **Cellulose-based Plastics:** Cellulose esters such as cellulose acetate and nitrocellulose are utilized to prepare cellulose based plastics.
- (iv) **Lignin based Plastics:** Lignin commonly obtained as a by-product of polysaccharide extraction from various plant materials during the production of paper, ethanol etc.

By definition, green solvents are environmentally friendly solvents that are characterized by low toxicity, convenient accessibility, great efficiency and reusability. Through Life Cycle Assessment (LCA) a technique that quantifies environmental damage for each of the available solvents, one can decide which is greener.

Problems associated with the traditional solvents include:

Many of the traditional solvents are organic based and highly toxic. Besides, they may be volatile, flammable and also carcinogenic.

3. Environmentally benign pesticides are those which are:

- Biodegradable
- Cheaper, Renewable and can be handled safely
- Residue-Free
- Safe to natural enemies and higher organisms
- Difficult for insects to develop resistance against them.

4. The basic difference between green chemistry and environmental chemistry is that green chemistry focusses on the design of processes and products in an environmentally benign manner so that no waste is generate and toxicity is minimized whereas environmental chemistry aims at the chemistry to combat the environmental problems after they are created.

5. Supercritical fluids are those substances which when subjected to a pressure and temperature greater than their critical point (obtained at specific conditions of pressure and temperature), are said to be supercritical. In that region, the SCFs exhibit properties of both liquid as well as gas. The most

commonly employed SCF includes supercritical carbon dioxide (ScCO_2) which has $T_c=304$ K and $p_c=72.8$ atm. ScCO_2 has emerged as a green alternative solvent in a number of industrial reactions such as hydrogenation, hydroformylation, polymer production, C-C bond formation owing to myriad of advantages it offers including non-toxicity, abundance, non-renewable nature, tendency to get easily removed from the product.

BLOCK 2
**Chemistry of Air,
Water and Soil**

UNIT 5 : ATMOSPHERIC CHEMISTRY

Structure

- 5.0 Introduction
- 5.1 Objectives
- 5.2 Origin of Atmosphere
- 5.3 Composition of Atmosphere
- 5.4 Structure of Atmosphere
- 5.5 Atmospheric stability
 - 5.5.1 Atmospheric Lapse rate
 - 5.5.2 Types of Lapse Rates
 - 5.5.3 Lapse rates and Atmospheric Stability
 - 5.5.4 Importance of Understanding Atmospheric Stability
- 5.6 Chemical and Photochemical Reactions of Atmosphere
 - 5.6.1 Photochemistry of the Atmosphere
- 5.7 Distribution of Species in Atmosphere
 - 5.7.1 Ions in the Atmosphere
 - 5.7.2 Free Radicals in the Atmosphere
- 5.8 Reactions of Atmospheric Oxygen
- 5.9 Reactions of Atmospheric Ozone
- 5.10 Reactions of Nitrogen Oxides
- 5.11 Particles in the Atmosphere
 - 5.11.1 Characteristics of Particulates
 - 5.11.2 Chemical Reactions of Atmospheric Particles
 - 5.11.3 Aerosols
 - 5.11.4 Black Carbon
 - 5.11.5 Effects of Particulate Matter on Human Health
- 5.12 Let Us Sum Up
- 5.13 Key Words
- 5.14 References and Suggested Further Readings

5.0 INTRODUCTION

IMPORTANCE OF ATMOSPHERE

Atmosphere, the gaseous envelope of the earth, nurtures life on earth and protects it from the harsh environment of the outer space. It serves as a source of oxygen for the sustenance of life on earth and carbon dioxide for plant's photosynthesis, provides nitrogen which is consumed by nitrogen fixing bacteria in producing nitrogen-based molecules, an essential component of life molecules. As a basis of the hydrologic cycle, atmosphere provides a medium for the movement of water. The atmosphere plays an important role in absorbing cosmic rays from outer space and thus protects life from their adverse effects. By absorbing electromagnetic radiation below wavelength 300 nm, the atmosphere filters out damaging ultraviolet rays from the sun. Thus, atmosphere plays a significant role in stabilizing the Earth's

temperature, by reabsorbing infrared radiation given off by earth and remitting the absorbed solar energy back into space.

5.1 OBJECTIVES

After Studying this unit, you will be able to

- define atmosphere and describe its origin,
- classify atmosphere into various regions,
- describe the composition of atmosphere and its variation with height, latitude and season,
- explain the process and types of atmospheric reactions
- understand the distribution of chemical species in the atmosphere
- describe the ozone layer depletion and its impact on biosphere

5.2 ORIGIN OF ATMOSPHERE

Origin and development of the atmosphere can be correlated to the origin of Earth. Evolution of the atmosphere can be subdivided into three stages.

Stage I

Earth is believed to have formed about 4.5 billion years ago from a protoplanetary gas-dust cloud. Hydrogen and helium were the basic gaseous components of the cloud. Dust particles most likely contained metals and condensates of water, ammonia, methane and mixtures of formaldehyde, methylacetylene, acetonitrile and other compounds present in interstellar space. Due to gradual gravitational contraction of the gas dust cloud, as well as the action of radioactive decay of radionuclides, gravitational attraction of the simultaneously formed moon and other processes, the cloud became heated, resulting in its partial melting. The formation of the earth was an exothermic process. The large amounts of gases and vapours possessing high kinetic energy so released got scattered into cosmic space. Thus, a dense atmosphere so formed, about 3.5×10^9 years ago, contained hydrogen, water, ammonia, methane, noble gases and some sulphur compounds as its main components. At the initial stages, atmosphere was devoid of oxygen and thus was reducing in nature.

At the same time, a massive condensation of water vapours paved the way for gradual formation of the hydrosphere. This phenomenon affected the evolution of the atmosphere, by dissolving carbon dioxide in liquid water which followed the formation of the sedimentary rocks. On account of their low atomic masses, hydrogen and helium escaped into space and the atmosphere became rich in nitrogen.

Stage II

The second stage of evolution initiated at around 3.5×10^9 years ago lasted at about 2×10^9 years ago. During this period, volcanic eruptions resulted in the formation of large quantities of magma, saturated with dissolved gases. Later magma moved towards the surface of the earth and pushed iron present in the mantle. Atmosphere was still typically reducing in nature, due to the presence of high concentrations of reducing gases (H_2S , H_2 , CH_4) and was characterized by the absence of free oxygen.

Towards the later era of stage II, iron moved to the core and so the ejected gases did not get to interact with iron and so they were more oxidizing in nature. These included CO_2 , SO_2 and H_2O vapours. However, free oxygen was still absent and the atmosphere continued to be reducing, non oxidizing in nature. In due course of time, oxidising action of atmosphere resulted in the formation of iron oxides which incorporated into sediments, forming redbed.

Stage III

In the third stage, the present atmosphere, oxygen production began to exceed oxygen consumption *via* photochemical dissociation of water molecules. Water molecules, in the upper atmosphere, absorbed ultraviolet radiations and split into hydrogen and oxygen. Oxygen was majorly accumulated in the atmosphere through photosynthesis. Multi-cellular marine organisms appeared during this period. They consumed phytoplankton and floated on the water. With the decrease of phytoplankton, the number of heterotrophic bacteria also declined. This led to an increase in the oxygen in the atmosphere.

5.3 COMPOSITION OF ATMOSPHERE

The current atmosphere is a mixture of gases containing nitrogen (78.08% by volume), oxygen (21%), argon (about 0.93%) and carbon dioxide (0.03%) as the main components (Table 1). Except for water vapour whose atmospheric abundance varies from 0.1 to 4%, the proportions of other gases remain nearly uniform below an altitude of about 100 km. In addition, air contains trace amounts of gases like neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, sulphur dioxide, ozone, iodine, nitrogen dioxide, ammonia, and carbon monoxide, at levels below 0.002%. The mass of atmosphere at present is estimated to be about 5.6×10^{14} tonnes.

The atmospheric gases fall into three categories based on their abundance: major, minor, and trace. Nitrogen and oxygen, major components, together constitute approximately 99% of the atmosphere. Nitrogen accumulated over time as a result of its chemical inertness and high molar mass that prevented escape from the region of the earth's gravitation. It is believed that denitrifying bacteria in marine sediments serve as the major route for the return of nitrogen to the atmosphere. Oxygen is almost entirely of biological origin and **is exchanged** between the atmosphere and life through the processes of photosynthesis and respiration.

Carbon dioxide, ozone, methane and noble gases like neon, helium, argon, krypton and xenon are present in minor quantities. Argon gas originates from the decay of radioactive potassium K-40 in the mantle and crust. Other noble gases are very inert and do not generally engage in any chemical transformation within the atmosphere. Hydrogen is likewise present in trace quantities in the atmosphere, but since it is so light, after some time much of it has escaped Earth's gravitational pull to space. Ozone and carbon monoxide concentrations vary with time and location. Ozone is formed by the reaction of O_2 with oxygen atoms produced photochemically. The concentration of ozone varies with the time of day, the concentration of oxygen atoms from other sources (photochemical smog) and with altitude. The concentration of ozone reaches a maximum of 12 ppm at a height of 15-20 km. The concentration of carbon dioxide is increasing at a rate of 0.2-0.7% per year as a result of burning of fossil fuels. However, major amounts of CO_2 are of natural origin and represent the smallest part of the total carbonate reservoir that includes oceanic CO_2 , HCO_3^- , and carbonate sediments.

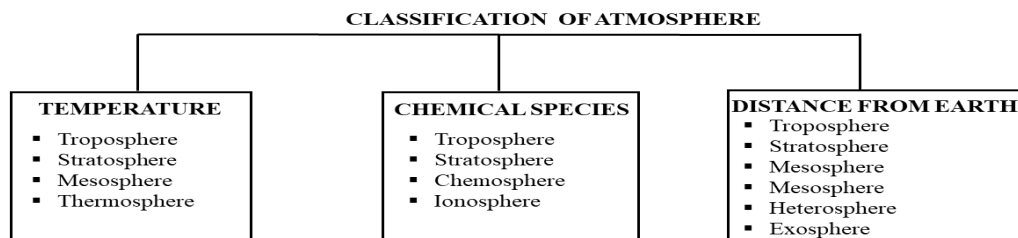
The most abundant gases in the troposphere include carbon dioxide, methane, nitrous oxide, water vapour and ozone which are involved in the Earth's natural greenhouse effect that keeps the planet warmer than it would be without an atmosphere. Through emissions of greenhouse gases however, mankind has enhanced the greenhouse effect which may now be leading to a warming of the Earth's temperatures.

Table 1. Composition of atmosphere

Constituent	Percent by volume	Concentration in Parts Per Million (ppm)
Nitrogen (N_2)	78.084	780,840.0
Oxygen (O_2)	20.946	209,460.0
Argon (Ar)	0.934	9,340.0
Carbon dioxide (CO_2)	0.036	360.0
Neon (Ne)	0.00182	18.2
Helium (He)	0.000524	5.24
Methane (CH_4)	0.00015	1.5
Krypton (Kr)	0.000114	1.14
Hydrogen (H_2)	0.00005	0.5

5.4 STRUCTURE OF ATMOSPHERE

Structure of the atmosphere is classified on various criteria



In this section, we shall discuss classification of atmosphere into four different layers based on its temperature profile. The temperature profile of atmosphere is controlled mainly by the degree of absorption of solar radiations in various regions. The vertical temperature profile of the atmosphere is shown in Figure 1. The table 2 gives the temperature range of various regions of the atmosphere. In general, the atmosphere is not heated by the sun's rays but rather heated from the warm Earth. Temperature thus decreases with increasing altitude and any change in this trend is due to the presence of species that absorb solar radiations directly.

Let us understand each region in detail for their composition and general behaviour.

Table 2. Temperature variations in different regions of atmosphere

Region	Altitude range (Km)	Temperature range (°C)
Troposphere	0 – 11	15 to -56
Stratosphere	11 – 50	-56 to -2
Mesosphere	50 – 85	-2 to -92
Thermosphere	85 - 500	-92 to 1200

1. Troposphere

The troposphere extends from sea level to a height of 11 km and includes the 1 km layer closest to the earth's surface in which life exists. The densest layer of the atmosphere, troposphere contains about 80% of the atmospheric mass, contributed by nitrogen, oxygen, carbon dioxide, argon, water vapours (0.1 to 5%) and traces of helium, neon, nitrous oxide, krypton, carbon monoxide, hydrogen, ozone and methane. Apart from these gases, the troposphere is also laden with particulate matter from several hundred/ cm³ (in pure air) to about a lakh/ cm³ (in polluted air). Size of these particles also varies from 0.1 to 10 Solid or liquid particles of dimensions less than 0.1 suspended in air are called Aitken particles.

The troposphere is characterized by the presence of thermally induced turbulent conditions which give rise to fluctuations in temperature and precipitation that is collectively referred to "weather." Tropo means change and almost all the changes we experience in our daily weather occur in this layer of the atmosphere. Radiations from the Earth heat the air near the ground level and as the altitude increases, there is a drop in temperature. In this context, a term called Lapse rate is used which is defined as the rate of change of temperature with altitude. For a dry ideal gas, the lapse rate, called dry Adiabatic Lapse rate, is -9.8 K/ km. Considering the presence

of water vapour that condenses to ice/ snow and release heat as rising air expand, the lapse rate in this region rises to -6.4 K/ Km . Essentially, the negative lapse rate indicates that temperature decreases with altitude in this region.

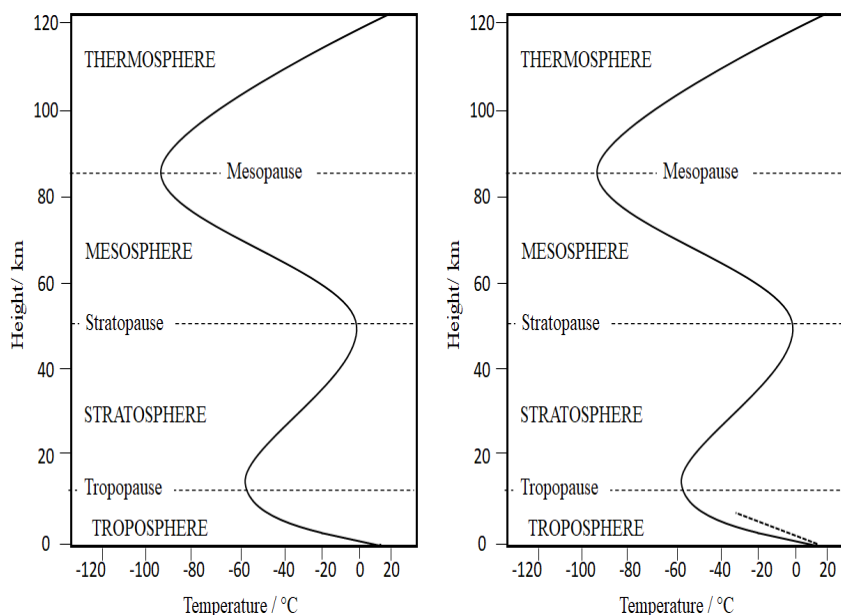


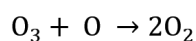
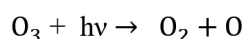
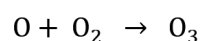
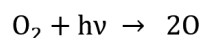
Figure 5.1 Variations in temperature of the atmosphere with altitude

The boundary between troposphere and stratosphere is called tropopause where the lowest temperature is reached. Tropopause marks temperature inversion and serves as a barrier causing water vapour to condense to ice, preventing it from reaching altitudes at which it would photo-dissociate through the action of high energy UV radiations. If this happened, hydrogen produced would escape into earth's atmosphere and get lost.

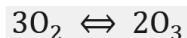
2. Stratosphere

The layer of the atmosphere above troposphere is called stratosphere, extending from about 11 km to about 50 km above the sea level. This layer is practically free from clouds and related weather phenomenon, making conditions perfect for flying planes. The most significant feature of this layer is that it shows a positive lapse rate with the temperature increasing to -2°C . The region is rich in ozone with a concentration range of 10-15 ppm, forming a layer at around 20 km altitude called ozonosphere. The warming up tendency of Stratosphere is due to ozone molecules absorbing solar UV radiations ($\lambda = 190\text{-}340 \text{ nm}$). These are the UV-B radiations which, if not absorbed by ozone, would reach the surface of Earth and cause harm to life. Hence, this thin layer of ozone is extremely important, acting as a protective shield from the toxic effects of UV-radiations on living beings on this planet.

Reactions for the formation of ozone and its absorption of UV-B radiation:



Thus, the formation of ozone and oxygen is a cyclic phenomenon.



The formation and destruction of ozone is a natural process, involving absorption of UV radiation and consequent release of heat. It is the heat that reduces the cooling effect and changes the lapse rate from negative to positive. Stratopause represents boundary between stratosphere and mesosphere, that depicts upper end of temperature inversion.

3. Mesosphere

The layer of atmosphere that follow stratosphere is known as mesosphere, extending from about 50 km above the sea level to about 85 km. This layer is characterized by the absence of radiation-absorbing species, resulting in a decrease in temperature to about -92 °C with increasing altitude. Apart from cold temperature, there is very low atmospheric pressure. *Mesopause* is the extremely cold, boundary between mesosphere and thermosphere which denotes the start of temperature inversion.

4. Thermosphere

The uppermost layer of the atmosphere, thermosphere, where artificial satellites orbit the earth. This layer is present at altitudes of several hundred km. It consists of minor concentrations of oxygen ions (O^+), molecular oxygen (O_2^+) and molecular nitrogen ions (N_2^+) which can effectively absorb UV-radiations. Hence with increasing altitude, temperatures as high as 1200 °C are observed by the absorption of electromagnetic radiation ($\lambda < 200 \text{ nm}$) by the gaseous species in this region.

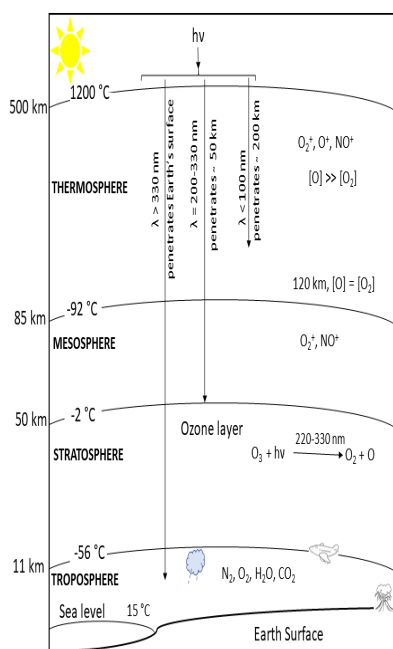


Figure 5.2 Major regions of the atmosphere

Check Your Progress I

Notes: (a) Write your answer in about 50 words

(b) Check your progress with possible answer at the end of the unit.

How was the present atmosphere formed. What factors were responsible for the atmosphere to become oxidizing in nature?

.....

.....

.....

.....

What is the present composition of the atmosphere

.....

.....

What do you understand about the temperature profile of the zones of the atmosphere

.....

.....

5.5 ATMOSPHERIC STABILITY

The temperature profile of atmosphere is of utmost importance in determining the stability and hence the degree of mixing of pollutants in various regions and atmosphere as a whole.

5.5.1 Atmospheric lapse rate

Imagine an insulated balloon, that doesn't exchange heat with the surroundings. As the balloon rises, it expands due to a decrease in atmospheric pressure. Expansion results in cooling of gas, so the temperature of air inside the balloon decreases. The layer of atmosphere closest to the earth surface is warm due to absorption of solar radiations. As warm air rises above cold air at the same pressure, it undergoes expansion owing to its lower density. Thus, it undergoes adiabatic expansion (no exchange of energy with surroundings) and becomes cooler. The rate of change in temperature of atmosphere with elevation is known as *Lapse rate*, denoted by the Greek capital letter Gamma (Γ). The lapse rate is taken negative when the temperature decreases with altitude, zero when the temperature is constant with altitude and positive when the temperature increases with altitude. Adiabatic Lapse Rate is the rate of fall in temperature of a rising air adiabatically and involves temperature changes due to the rising or sinking of an air parcel. Adiabatic lapse rates are usually categorized as dry or moist.

First law of thermodynamics

$$\partial E = \partial q - P\partial V$$

$$\partial q = 0 \text{ (Adiabatic)}$$

$$\therefore \partial E = -P\partial V \dots\dots\dots (i)$$

As $PV = RT$ (Ideal gas equation)

Upon differentiating,

$$P\partial V + V\partial P = R\partial T$$

$$\text{Or } P\partial V = R\partial T - V\partial P \dots\dots\dots (ii)$$

From (i) and (ii)

$$\partial E = -R\partial T + V\partial P$$

As $\partial E = C_v\partial T$, C_v : Heat capacity at constant volume

$$\therefore C_v\partial T = -R\partial T + V\partial P$$

$$(C_v + R)\partial T = V\partial P$$

$$C_p\partial T = V\partial P$$

$$C_p\partial T = -gPV\partial h \quad \left(\frac{\partial P}{\partial h} = -\rho g\right)$$

$$\text{Adiabatic Lapse rate} \longrightarrow \boxed{\frac{\partial T}{\partial h} = -\frac{gM}{C_p}}$$

5.5.2 Types of lapse rates

The lapse rates used to express the rate of temperature change with a change in altitude are follows:

- i. Dry adiabatic lapse rate
- ii. Wet adiabatic lapse rate

i. Dry adiabatic lapse rate

Earth's atmospheric air is rarely completely dry. It usually contains some amount of water vapour and when it contains as much water vapour as it is capable of, it is referred to as saturated air (i.e., a relative humidity of 100%). The dry adiabatic lapse rate (DALR) refers to the lapse rate of unsaturated air (i.e., air with a relative humidity of less than 100%). If there is no condensation of moisture from air, the cooling effect is about 10 °C per 1000 metres of altitude. For the earth's atmosphere, dry adiabatic lapse rate for the is 9.8 °C/km. It depends on the specific heat capacity of air at constant pressure, C_p and the acceleration due to gravity, g . Owing to low moisture content, it is mainly associated with stable conditions.

$$\Gamma_d =$$

Since g and C_p vary little with altitude, the dry adiabatic lapse rate is approximately constant in the troposphere.

ii. Wet adiabatic lapse rate

When there is sufficient moisture in rising air, water condenses out from it and releases latent heat. This offset the cooling effect of the expanding air, resulting in a *moist adiabatic lapse rate* (WALR). The moist adiabatic lapse rate is not constant and varies considerably due to presence of variable amounts of water vapour in the

air. The greater the amount of vapour, the smaller the adiabatic lapse rate because condensation process keeps on adding more latent heat of condensation. In the troposphere, the rate varies from about 4 °C / km in regions where the ambient temperature is about 25 °C to about 7 °C/km in middle of the troposphere. On average, it is taken as 6 °C/km. As air rises and cools, it may eventually lose its moisture through condensation, lapse rate then increases and approaches the dry adiabatic value. Wet Adiabatic Lapse rate is mainly associated with unstable conditions because of higher moisture content.

5.5.3 Lapse rates and atmospheric stability

Atmospheric gases move horizontally and/or vertically from regions of high atmospheric pressure to low atmospheric pressure. Air at one altitude would mix with air at another altitude. This phenomenon is known as *vertical mixing*. Atmospheric stability is the resistance of the atmosphere to the vertical mixing of air. The rate of change of atmospheric temperature with increasing altitude (temperature lapse rate) is important in understanding the atmospheric stability and degree of mixing in a particular atmospheric layer.

The atmospheric stability may be characterized as follows:

- A **very stable** atmosphere is one that has very little if any, vertical mixing of the air.
- A **stable** atmosphere is one that inhibits vertical mixing but does have some motion of the air.
- An **unstable** atmosphere is one that encourages continual vertical mixing of the air, upwards or downwards.
- A **neutral** atmosphere is one that neither discourages nor encourages vertical mixing of the air and is often referred to as conditionally stable.

The stability of atmosphere is determined by the relative numerical value of environmental lapse rate in comparison with either the dry or moist adiabatic lapse rates.

- Case I: $\Gamma > \Gamma_d$

When the temperature of the atmosphere decreases faster with altitude than the adiabatic lapse rate, then the atmosphere is turbulent in the atmosphere and the atmosphere is said to be unstable. It may also be referred to as being super-adiabatic. The air from one altitude mixes with the air from other altitudes. This feature is responsible for dispersal of pollutants (vertical mixing) and becomes desirable from viewpoint of controlling air pollution as pollutants will rapidly be dispersed throughout the atmosphere.

- Case II: $\Gamma < \Gamma_d$

When the temperature decreases less rapidly with altitude than the adiabatic lapse rate, the air is stable. It may also be referred to as being sub-adiabatic. Under these conditions, there is very little movement of air from one altitude to another so pollutants in the air will be restricted. Without vertical mixing, pollutants concentration rises rapidly.

- Case III: $\Gamma = \Gamma_d$

When the actual temperature gradient is same as that of adiabatic lapse rate, neutrally stable environment

Temperature inversion, the extreme case, occurs when the temperature increases with altitude resulting in a stable atmosphere. As shown in figure 3, the adiabatic lapse rate thus represents a boundary between atmospheric stability and instability.

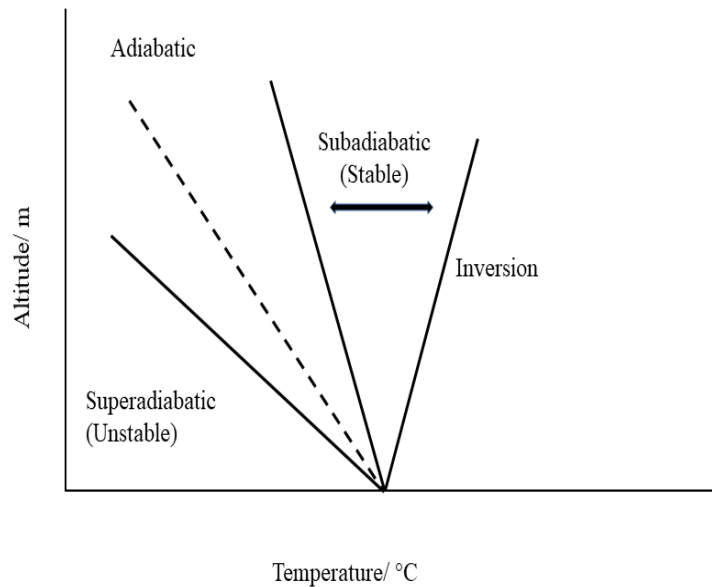


Figure 5.3 Adiabatic lapse representing a boundary between atmospheric stability and instability.

According to perfect gas law, $P = \rho RT$

P = pressure

ρ = density

R = gas constant

T = absolute temperature

Imagine an insulated balloon suspended in the atmosphere, the pressure of air inside the balloon-

$$P_b = \rho_b RT_b$$

And pressure of air outside the balloon, $P_a = \rho_a RT_a$

If balloon is at particular altitude, neglecting any effect caused by air resistance, then

$$P_a = P_b$$

$$\text{OR } \rho_b = \rho_a$$

Under stable atmospheric conditions, the balloon will remain suspended at a constant altitude and will resist any motion under influence of external forces.

At position 1, balloon having the same internal temperature and pressure as the surrounding atmosphere (Figure 4). When the balloon is raised to position 2, the pressure inside the balloon falls and balloon expands. Hence, balloon's temperature

drops. For $T_b < T_a$, we have $\rho_b > \rho_a$. Thus, the density of air inside balloon is greater than the surrounding air and balloon will therefore be pushed to its original position 1. Similarly, balloon is lowered from position 1 to position 3, when $T_b > T_a$ and $\rho_b < \rho_a$ i.e when air inside the balloon becomes less dense than the surrounding atmosphere.

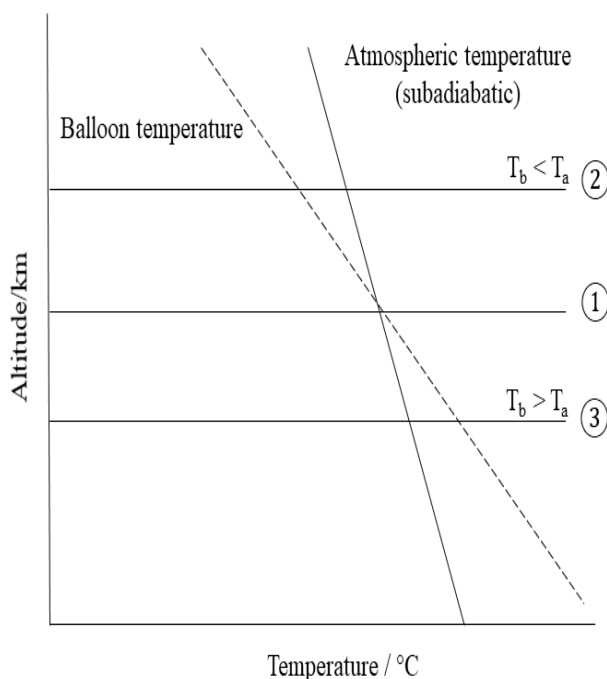


Figure 5.4 Raising the balloon from position 1 to position 2 causes the density inside greater than the density outside, so balloon returns to position 1. Lowering the balloon to position 3 causes the density of the balloon's air to be less than the density of atmosphere so it returns to position 1. This represents a stable atmosphere.

5.5.4 Importance of understanding atmospheric stability

The difference between the normal lapse rate and the dry and moist adiabatic lapse rates determines the vertical stability of the atmosphere. It also decides the movement of an air particle to return to its original position or to accelerate away from its original position once it is given a small vertical displacement. The lapse rate is of importance to meteorologists in forecasting cloud formations, thunderstorms, and the intensity of atmospheric turbulence.

Atmospheric turbulence and mixing play a major role in dispersal of air pollutants. The phenomenon of turbulence and mixing are dominant under unstable atmospheric conditions and promotes the dispersion of air pollutants. On the contrary, stable atmosphere represses turbulence and results in very poor dispersion of air pollutants. A stable atmosphere prevents rainfall, while an unstable atmosphere encourages thunderstorm and rainfall. A stable atmosphere also prevents forest fires; thus, an understanding of atmospheric stability is important in explaining forest fire behaviour.

5.6 CHEMICAL AND PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE

The study of atmospheric reactions is an important area in understanding the mechanistic details of chemical processes occurring in the air. The two most important parameters in atmospheric chemistry are the sun's radiation, predominantly in the ultraviolet region of the spectrum and the hydroxyl radical. The former acts a source of high energy to a single gas molecule to start a series of atmospheric reactions and latter serves as the most important reactive intermediate and reservoir of daytime atmospheric chemical phenomena.

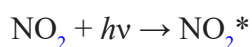
Gaseous atmospheric species can be classified as follows:

- Inorganic oxides- CO, CO₂, NO₂, SO₂
- Oxidants- O₃
- Reductants- CO, SO₂, H₂S
- Organics- CH₄, some alkenes and aryl compounds
- Photochemically active species- NO₂, formaldehyde
- Acids (H₂SO₄), Bases (NH₃), salts (NH₄HSO₄)
- Unstable reactive species- HO· radical, electronically excited NO₂,

In addition, both solid and liquid suspended particles play a significant role as source and sink for gas-phase species, as sites for surface reactions (solid particles) and as media for aqueous phase reactions (liquid droplets).

5.6.1 Photochemistry of the atmosphere

The most significant attribute of atmospheric chemistry is the occurrence of **photochemical reaction**, a chemical reaction initiated upon the absorption of light photons by the reactant molecules. The energy, E , of a photon of visible or ultraviolet light is given by the equation $E = h\nu$, where h is Planck's constant and ν is the frequency of light. As a consequence, energy associated with absorbed photons is sufficient to activate reactant molecules. The transient excited states of reactant molecules thus formed, differ in chemical and physical properties from the original molecules. The chemical species thus formed either transform to new molecules, combine among themselves or other molecules, or transfer electrons, hydrogen atoms, protons, or their energy to other molecules (Figure 5). The photochemical reactions play a crucial role in determining the nature and fate of chemical species in the atmosphere. Nitrogen dioxide, NO₂ is one of the most photochemically active species present in polluted air and a major contributor to smog formation. On absorption of light energy ($E = h\nu$) in the visible or UV region of the electromagnetic spectrum, NO₂ yields electronically excited molecule,



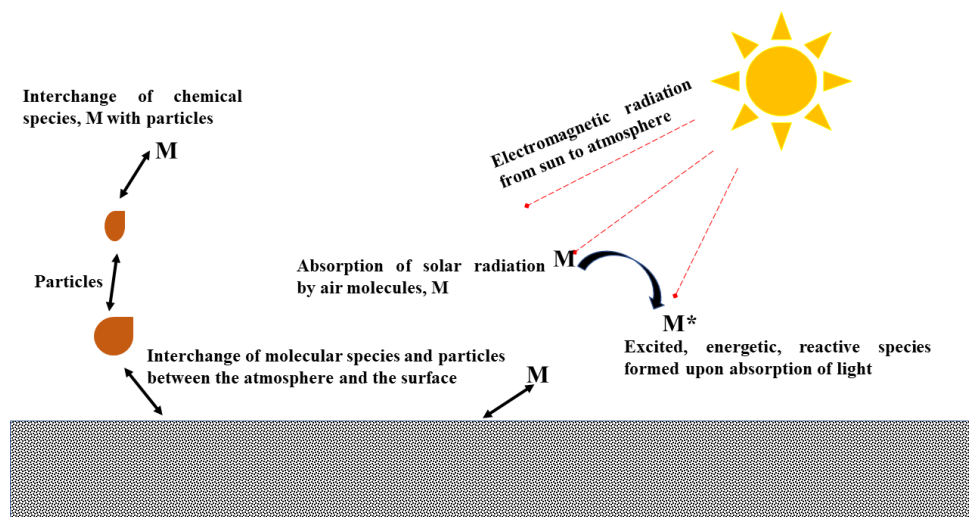
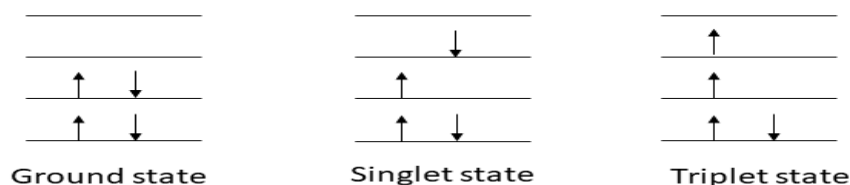


Figure 5.5 A schematic representation of atmospheric chemical processes.

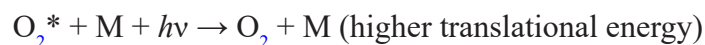
The nature of excited state may be understood by considering addition of electrons in a molecule. Most molecules contain even number of electrons. The electrons tend to occupy the orbitals, with maximum two electrons with opposite spins per orbital. On absorption of light of sufficient energy, one of these electrons may promote to high energy vacant orbital. In some cases, the promoted electron retains a spin opposite to that of its former partner, giving rise to an excited singlet state. While in some cases, the promoted electron experiences a spin reversal, such that it has same spin as that of its former partner, giving rise to excited triplet state.



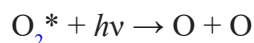
These energetic excited species are chemically reactive and are actively involved in atmospheric reactions which are discussed in detail in the following sections.

Following the light absorption, the electronically excited molecules lose their excess energies in either of the following reactions-

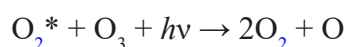
Energy loss to another atom or molecule by physical quenching and dissipation of energy as heat



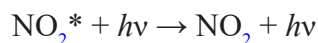
- *Dissociation* of the excited molecule



- *Direct reaction* with another species- The energy released during de-excitation is sufficient for the reaction to take place.



- *Luminescence* – loss of energy upon emission of electromagnetic radiation



The phenomena of luminescence with instantaneous re-emission of light is known as *Fluorescence*. In case, if it is significantly delayed, phosphorescence takes place. *Chemiluminescence* takes place when there is a formation of excited intermediate, which de-excites, releasing some of its energy in form of light.



- *Intermolecular energy transfer* wherein energy is transferred from excited species to other species, which then becomes excited.

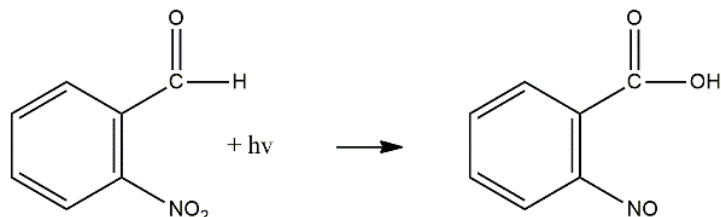


A photosensitized reaction may take place when the second species so generated participates in chemical transformations.

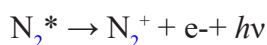
- *Intramolecular transfer*, wherein energy is transferred within the molecule itself.



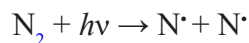
- *Spontaneous isomerization*, as seen in the conversion of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid, a reaction employed in chemical actinometers to measure exposure to electromagnetic radiation.



- Photoionization, depicts formation of ionic species with a loss of an electron



- Photodissociation – radicals are produced



Electromagnetic radiation absorbed in the infrared region are not sufficiently high in energy to be capable of breaking the chemical bonds. However, they provide sufficient vibrational and rotational energy to the receptor molecules. The energy absorbed as infrared radiation ultimately is dissipated as heat and raises the temperature of the whole atmosphere

5.7 DISTRIBUTION OF SPECIES IN ATMOSPHERE

Other than gaseous species, atmosphere also comprises of ions, free radicals and particulate matter. A detailed account of these species is discussed in the following sections.

5.7.1 IONS IN THE ATMOSPHERE

The layer of atmosphere extending from about 50 km above sea level constitutes the ionosphere. The importance of ionosphere is realised by the fact that it reflects and modifies radio waves used for communication and navigation. The height, concentration of ionized particles, and the existence of the different regions of the ionosphere varies with time. During the day, X-rays and ultraviolet radiation from the Sun provide sufficient energy to knock off electrons free from atoms and molecules, producing a continuous supply of ions and free electrons. The principal ions present in this region are N_2^+ , O_2^+ , NO^+ , N^+ and O^+ . At the same time, some of the ions and electrons collide and re-combine to form electrically neutral atoms and molecules. In dark, positive ions may recombine with free electrons. This phenomenon is rapid in lower regions of the ionosphere where the concentration of species is high. Thus, radio waves are bounced off by lower regions of the ionosphere and are transmitted over greater distances at night.

The ions do not escape from the ionosphere as they are strongly bound by Earth's magnetic field. One of manifestation of the influence of Earth's magnetic field on these ionizing particles is called Van allen belts. These belts are named after the scientist, Dr James Van Allen who is credited for their discovery. Van Allen Belts consists of a zone of high energy charged particles, held by the earth's magnetic field around the planet. If they are visualised as two doughnuts, then the axis of the earth's magnetic field extends through the holes in the doughnuts (Figure 6). The belt is divided into another two belts – outer and inner. The outer belt is formed by the electrons while the inner belt consisting of protons is formed as a result of cosmic ray collisions in the upper atmosphere.

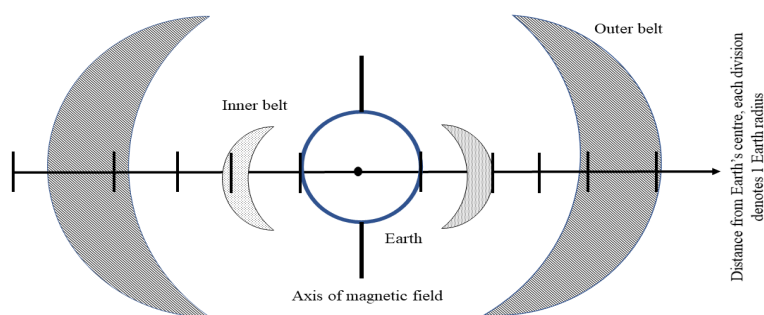
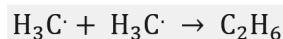


Figure 5.6 Cross section of the Van Allen Belts encircling the Earth.

5.7.2 Free radicals in the atmosphere

Atoms or groups of atoms with unpaired electrons called radicals are generated in the atmosphere by high energy electromagnetic radiations. Free radicals exhibit

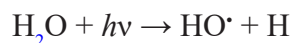
high reactivity by virtue of the strong pairing tendency of unpaired electrons. They participate in chain reactions wherein one of the products of each reaction is itself a radical. The termination of chain is marked by the reaction of a radical with another radical (chain-terminating reaction).



It is worthy to mention that free radicals and single atoms from diatomic gases are quite stable and may have half-lives of several minutes such that they persist under the rarefied conditions of the upper atmosphere. At high altitudes, these species travel long distances before colliding with other reactive species. On the other hand, electronically excited species are short-lived because their energy is lost through radiation, instead of reacting with another species. Some important radicals in atmosphere are hydroxyl ($\text{HO}\cdot$), Hydroperoxy ($\text{HOO}\cdot$) and alkylperoxy ($\text{H}_3\text{COO}\cdot$) radicals. In this section, the atmospheric chemistry of the most prevalent hydroxy ($\text{HO}\cdot$) and Hydroperoxy ($\text{HOO}\cdot$) radicals are discussed in detail.

• Hydroxyl and Hydroperoxyl radicals in the atmosphere

The hydroxyl radical $\text{OH}\cdot$, the most important reactive species in chemical reactions of the atmosphere. It is usually produced by photolysis of water at higher altitudes.



The production of $\text{HO}\cdot$ radical depends on the wavelength of light and availability of the substrate. Therefore, the concentration of $\text{HO}\cdot$ radical increases during summer and geographically tropical areas where the high humid conditions favour $\text{HO}\cdot$ formation. The diurnal plot of the variation of concentration of $\text{HO}\cdot$ radical with the daytime is shown in figure 7. The plot indicates that the concentration of $\text{HO}\cdot$ radical is maximum during afternoon and gradually decreases during night. Globally, the averaged diurnal and seasonal concentration of tropospheric $\text{HO}\cdot$ ranges from 2×10^5 to 1×10^6 radicals per cm^3 .

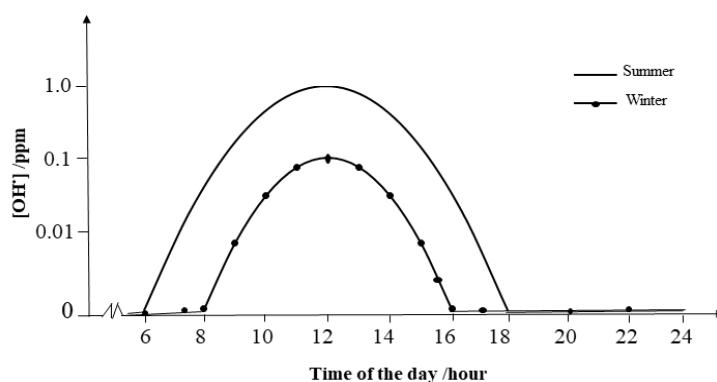
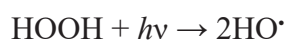
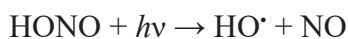
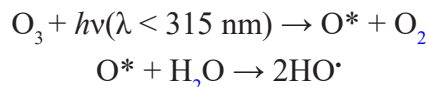


Figure 5.7 Average diurnal profiles of the hydroxyl radical

Under laboratory conditions, $\text{HO}\cdot$ radical is generated by the photolysis of nitrous acid vapour and hydrogen peroxide



The radical is also produced by photolysis of ozone, wherein the reaction proceeds with the formation of excited oxygen atoms that combine water molecules to yield hydroxyl radical.



It is also produced as an intermediate during the formation of photochemical smog, which will be discussed in detail in block III.

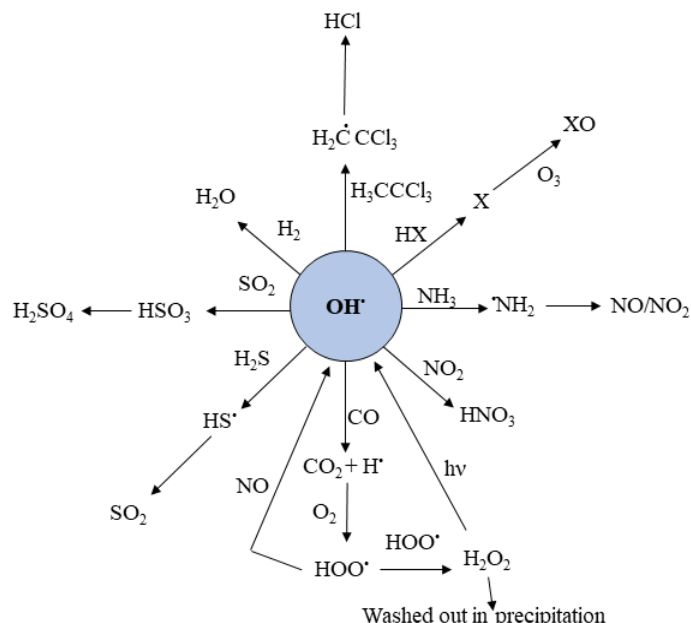
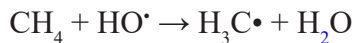


Figure 5.8 Central role of OH• radical in the troposphere.

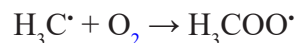
Hydroxyl radical bearing unpaired electron is highly unstable and extremely reactive. Therefore, it enters into several reactions with variety of species present in atmosphere. Some of the important reactions are summarised in figure 8.

Sinks for removal of Hydroxyl radical

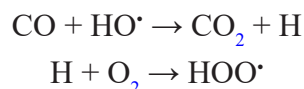
A sink refers to a medium that comprises of molecules that react with the species in question in order to make them potentially less harmful. For OH[•] radical, there are two sinks, methane or carbon monoxide, that eliminate it from the troposphere.



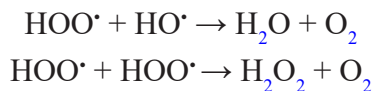
The methyl radical is highly reactive and forms methylperoxyl radical, $\text{H}_3\text{COO}^\bullet$ upon reaction with O_2 .



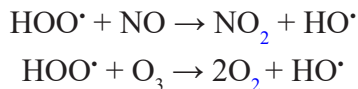
Similarly, reaction with carbon monoxide produces atomic hydrogen, which then reacts with O_2 and results in the formation of hydroperoxyl radical $HOO\cdot$:



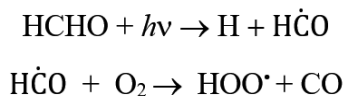
The hydroperoxyl radical undergoes series of chain termination reactions, either with radicals,



Or with neutral species that regenerate hydroxyl radicals.



The hydroperoxyl radical may be regenerated through reaction with formaldehyde, a major organic molecule present in atmosphere. Photolytic dissociation of formaldehyde furnishes formyl radical, as the reactive intermediate, that combines with atmospheric oxygen to produce hydroperoxyl radical.



The hydroperoxyl radical, $\text{HOO}\cdot$ serves as an important intermediate in variety of chemical reactions. However, hydroperoxyl radical reacts slowly with other species than hydroxy radical, $\text{OH}\cdot$. Thus, kinetic studies pertaining hydroperoxyl radical are difficult to study because these radicals hardly exist without hydroxyl radicals.

Check Your Progress II

Notes: (a) Write your answer in about 50 words

(b) Check your progress with possible answer at the end of the unit.

1. What is the relation between atmospheric stability and vertical mixing

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2. Differentiate between

Chemiluminescence and Luminescence

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Wet and dry adiabatic lapse rate

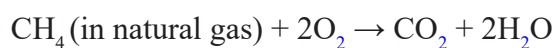
3. Discuss the importance of ionosphere.

4. Describe the mechanism for the production of OH• radicals in the troposphere. How would you expect increasing temperature to influence water vapour concentrations and hence the efficiency of OH• production?

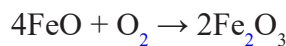
5. Which species are responsible for the removal of hydroxyl radical from the unpolluted troposphere?

5.8 REACTIONS OF ATMOSPHERIC OXYGEN

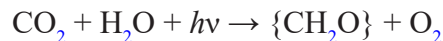
Oxygen in the atmosphere, especially in the troposphere, is crucial for survival of lifeforms. A schematic representation of the oxygen cycle depicting biogeochemical reactions of oxygen within atmosphere, lithosphere, hydrosphere and biosphere is shown in figure 9. Oxygen plays a dominant role in the processes occurring on the surface of earth. It drives the energy producing reactions, for example, the burning of fossil fuels.



Aerobic organisms rely on atmospheric oxygen for degrading organic matter. Oxygen also plays a crucial role in chemical weathering processes.



Oxygen is returned to the atmosphere through photosynthesis by green plants and planktons.



It can be shown that most of the carbon fixed by photosynthetic processes is dispersed in mineral formations as humic material, while only a small portion is deposited in fossil fuel beds. Thus, the oxygen production and consumption constitute a cyclic phenomenon, maintaining global oxygen levels constant.

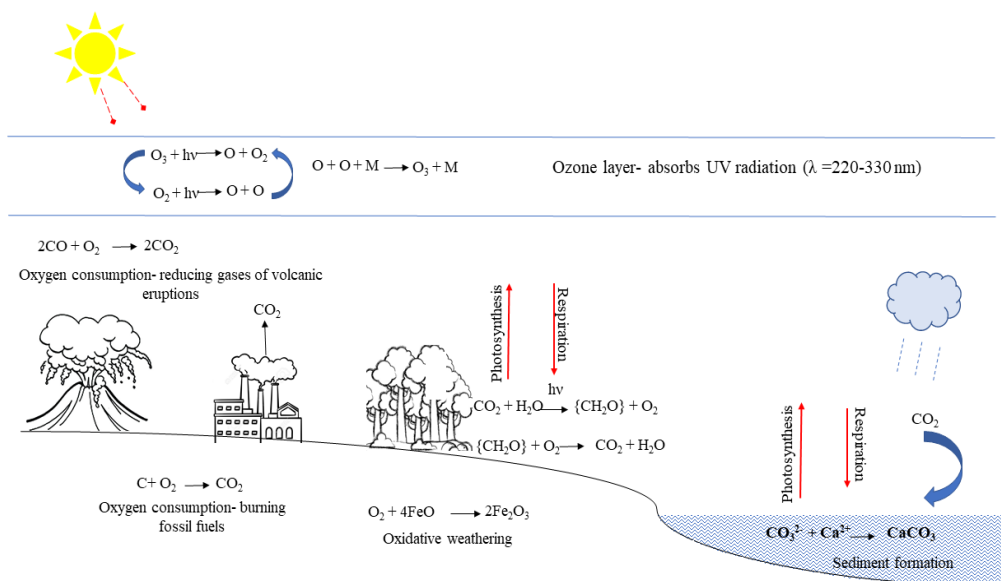
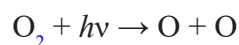


Figure 5.9 Oxygen exchange among the atmosphere, lithosphere, hydrosphere and biosphere.

Molecular oxygen displays unusual behaviour that its ground state is a triplet state with unpaired electron, denoted as $^3\text{O}_2$ which can be excited to singlet molecular oxygen, $^1\text{O}_2$. Singlet oxygen may also be produced by other processes such as direct photochemical excitation, transfer of energy from other electronically excited molecules, ozone photolysis and high-energy oxygen producing reactions.

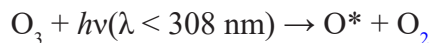
Under ionizing atmospheric conditions, elemental oxygen in the upper atmosphere exists in allotropic forms other than diatomic O_2 molecule. Thus, in addition to O_2 , the upper atmosphere contains oxygen atoms, O ; excited oxygen molecules, O_2^* and ozone, O_3 . Atomic oxygen is produced *via* photochemical reaction, as follows.



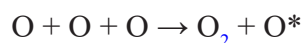
The energy of ultraviolet radiation in the wavelength regions 135-176 nm and 240-260 nm is sufficient to dissociate oxygen-oxygen bond in diatomic O_2 molecule (bond energy of $\text{O}_2 = 120 \text{ kcal/mol}$). Because of photodissociation, O_2 does not exist at very high altitudes and only less than 10% of the oxygen is present in its molecular form in the atmosphere at altitudes exceeding approximately 400

km. A manifestation of this phenomenon of high atomic oxygen concentration is realised by the fact the average molecular weight of air is lower than 28.97g/mole, observed at sea level at altitudes above 80 km.

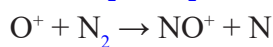
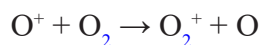
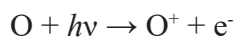
In the atmosphere, oxygen atoms exist in the ground state (O) as well as in excited states (O*) and are mainly produced through photolysis of ozone. The dissociation enthalpy required to dissociate oxygen-oxygen bond in a molecule of ozone is relatively low (26 kcal/mol) and thus facilitates the quick formation of excited oxygen atoms.



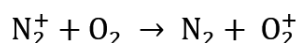
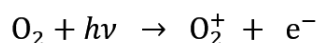
The highly energetic chemical reactions also allow for the formation of excited oxygen atoms that emit visible light at wavelengths 636 nm, 630 nm and 558 nm. The light so emitted is said to be partially responsible for airglow, luminescence of earth's upper atmosphere.



Oxygen ion, O⁺, may be produced by action of ultraviolet radiations on oxygen atoms. These are predominant species in some parts of ionosphere. Oxygen ion participates in reactions with neutral species like, N₂ or O₂, and releases other positive ions.

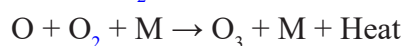
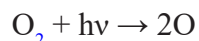


O₂⁺ ion may be produced in the intermediate regions of ionosphere upon absorption of light of wavelength 17-103 nm by O₂ molecule or from photochemical reaction of low energy X-rays.

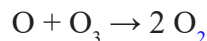


5.9 REACTIONS OF ATMOSPHERIC OZONE

Ozone forms a protective layer that envelops the earth surface by absorbing the sun's ultraviolet radiations (220-330 nm) which otherwise would potentially damage life forms on the earth. The presence of ozone in higher atmospheric layers is attributed to the photodissociation reactions of molecular oxygen. Upon absorption of ultraviolet radiation from the sun, oxygen molecule splits as follows:



Where M is the third body, such as a molecule of N₂, O₂ or Ar that allows formation of ozone by absorbing heat energy released during collision between atomic oxygen and oxygen. Some of the oxygen atoms react with intact ozone molecules to destroy them by converting to O₂.

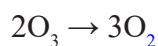


However, the above reaction is very slow because its activation energy is 18 kJmol^{-1} . To summarise, during daylight, ozone in the stratosphere is constantly being formed, decomposed and re-formed by a series of reactions. Ozone's concentration at any time of the day depends on the intensity of solar radiation and the altitude. The maximum ozone concentration of about 12 ppm is observed at altitude of 25-30 km in the stratosphere.

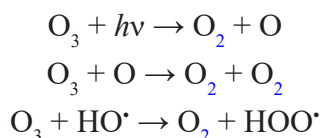
Oxygen and ozone filter out harmful ultraviolet radiation, such that incoming radiation in troposphere has wavelength $\geq 290 \text{ nm}$. This incoming light possess sufficient energy to allow photodissociation of key tropospheric species. The heat energy released in the above reaction is responsible for the increase in temperature with altitude in the stratosphere. As discussed in section 1.3, the air at a given altitude in stratosphere is cooler than air lying above it. Cooler air is denser than the hot air, therefore it doesn't rise spontaneously under influence of gravity. As a result, vertical mixing of the air in stratosphere is a very slow process as compared to that in the troposphere.

Catalytic process for ozone destruction

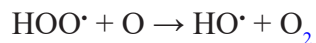
The decomposition reaction:



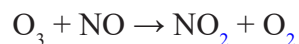
is thermodynamically favourable, indicates ozone is unstable. The reaction is catalysed by pollutant trace constituents, NO, NO₂, H, HO[•], HOO[•], ClO[•], Cl, Br, and BrO[•]. In addition, stratospheric ozone undergoes reaction with atomic oxygen, hydroxyl radical and NO.



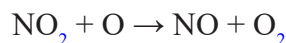
The following reaction regenerates HO[•] radical and further contributes to the decomposition of ozone.



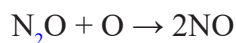
Similarly, nitric oxide, one of the key pollutants in troposphere is also held responsible for the destruction of ozone in stratosphere.



NO, so consumed during this reaction is recycled through the following reaction



Atmospheric N₂O also accounts for the release of nitric oxide in the atmosphere.

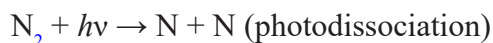


N₂O occurs naturally in the atmosphere and constitutes a major product of the denitrification process wherein fixed nitrogen is returned to the atmosphere in gaseous form.

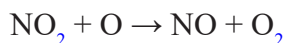
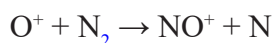
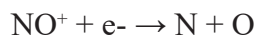
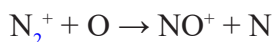
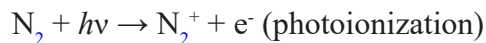
Despite its role as a protective shield in the stratosphere, tropospheric ozone is considered as an undesirable air pollutant and is harmful to human and ecosystem health. The details about its role as a pollutant will be discussed in detail in Block III.

5.10 REACTIONS OF NITROGEN OXIDES

Nitrogen constitutes about 78% by volume of the earth's atmosphere, representing an inexhaustible reservoir of the essential element. Due to high bond dissociation energy (945 kJmol⁻¹), N₂ molecule is chemically and photochemically unreactive. Thus, unlike oxygen which dissociates completely into oxygen atoms in the higher regions of thermosphere, nitrogen molecule does not dissociate upon absorption of ultraviolet radiation. However, atomic nitrogen is formed through photochemical reactions at high altitudes exceedingly approximately 100 km.



Other reactions producing atomic nitrogen are



In the above reactions, N₂⁺ is formed by photoionization when N₂ molecule absorbs a photon of light in the lower regions of the ionosphere, extending from about 50-85 km in altitude. In higher regions, the chief ionic species is NO⁺ generated from ionization of NO. NO is a colourless and odourless gas and is very reactive owing to its radical nature.

Of the eight known oxides of nitrogen, three oxides are present in appreciable amount in the atmosphere – Nitrous oxide, N₂O; nitric oxide, NO; nitrogen dioxide, NO₂. NO and NO₂ (collectively referred to as NO_x) are common air pollutants owing to their potential involvement in the stratospheric destruction of ozone layer, formation of photochemical smog and acid rain. The principal reactions of nitrogen oxides are outlined in figure 10.

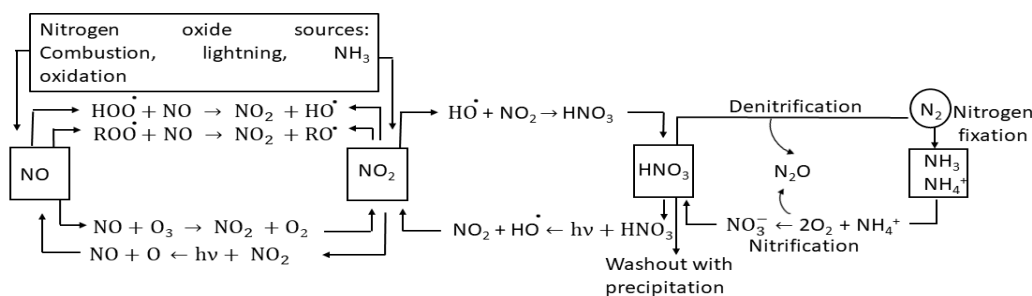
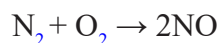
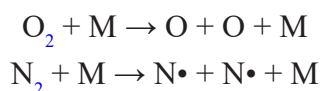


Figure 5.10 A schematic view of principal reactions among NO, NO₂ and HNO₃ in the atmosphere (ROO• denotes an organic peroxy radical)

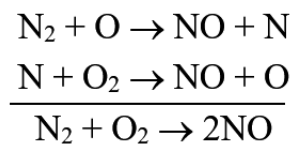
Nitric oxide, NO, through a series of photochemical reactions, enters the atmosphere from N₂O or NO₂ and oxygen atom. Other natural sources like lightning strikes, forest fires or volcanic eruptions also contribute to NO formation. The main anthropogenic sources of NO, contributing to 96% of total NO_x in atmosphere are the burning of fossil fuel in furnaces, factories and automobiles. At extremely high temperatures of these natural phenomena or inside the internal combustion engines, nitrogen and oxygen molecule react to give NO.



Elevated temperatures are favourable for a high equilibrium concentration as well as an increased rate of formation of NO. It is postulated that at high temperatures, the molecules of N₂ and O₂ dissociate to their respective atoms.



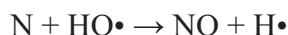
Where M represents a third body of high energy which itself does not react but provides energy sufficient for enabling the reaction. The atoms then react in a chain reaction to give NO.



In the combustion mixture, apart from N₂ there are hydrocarbon fragments (RH) which compete for highly reactive oxygen atoms.



The hydroxyl radical combines with atomic nitrogen which again leads to the formation of NO.



NO plays an important role in the ozone content of stratosphere. It removes O₃ by converting itself to NO₂. NO is regenerated upon reaction of NO₂ with atomic oxygen. The details about ozone depletion will be dealt with in Block III.



Nitrogen dioxide, NO_2 , is a brown gas, responsible for the colour of photochemical smog. It is produced by the oxidative decomposition of ammonia in the atmosphere. Like NO , its high reactivity is attributed to its radical nature. NO_2 is finally converted into either NO_2^- or NO_3^- in particulate matter. The particulates are then washed out by precipitation. The dissolution of nitrate in a water droplet results in the formation of nitric acid (HNO_3), thus contributes to acid rain damage to the ecosystem. Nitrogen dioxide participates in chemical reactions of volatile organic compounds (VOCs) producing PAN (Peroxyacetyl nitrate), component of smog. As shown in figure 11, acetaldehyde is oxidized and the resulting peroxyacetyl radical reacts with NO_2 to form peroxyacetic nitric anhydride. PAN is a very irritating molecule that is toxic to humans, animals, and plants.

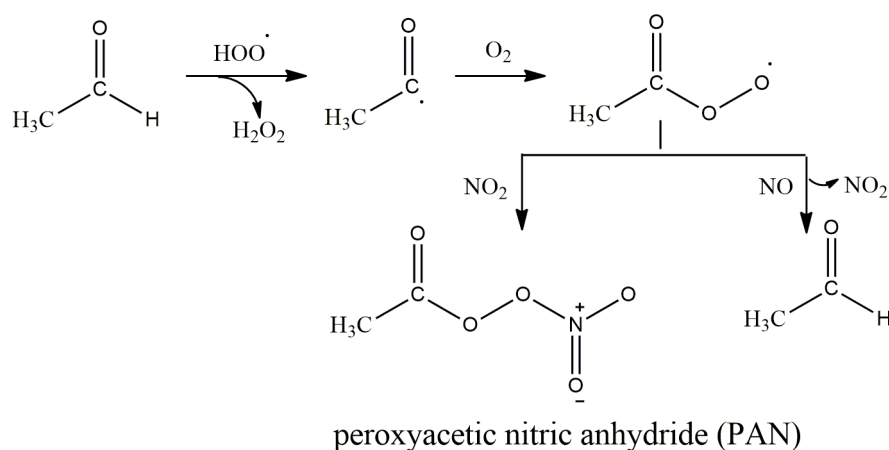
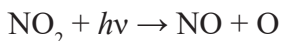
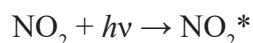


Figure 5.11 A schematic representation of peroxyacetic nitric anhydride (PAN) formation

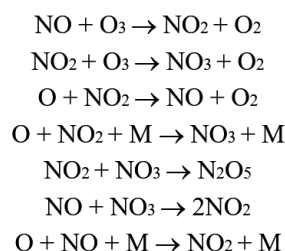
Nitrogen dioxide exists in equilibrium with its colourless dimer, Dinitrogen tetraoxide N_2O_4 . Its combination with water produces nitrous and nitric acids that oxidize many metals. Being very reactive, it is an important species in the atmosphere. It absorbs full range of ultraviolet and visible light entering the troposphere. At wavelengths below 398 nm, photodissociation takes place and generates ground state oxygen atoms as follows:



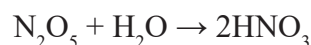
At wavelength > 430 nm, only excited species are formed,



At wavelengths between 398 nm and 430 nm, either process may take place. Under direct sunlight, the half-life of NO_2 is much shorter than that of any other common molecular atmospheric species, hence NO_2 shows high tendency to undergo photodissociation which may give rise to series of important reactions as summarised below. Small concentrations of NO_2 have also been detected in the lower stratosphere where the gas is produced by the oxidation of NO by ozone.



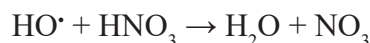
Nitrogen dioxide is removed from the atmosphere as nitric acid, nitrates, or as organic nitrogen (in atmospheres where photochemical smog is formed). Dinitrogen pentoxide formed in above reactions is the anhydride of nitric acid, which is formed when the combines with water



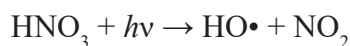
In the stratosphere, nitrogen dioxide combines with hydroxyl radicals and produces nitric acid:



Nitric acid is destroyed by hydroxyl radicals within stratosphere,

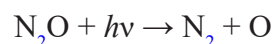


or by a photochemical reaction,

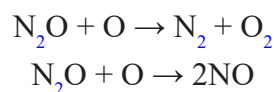


Thus, the above reactions elucidate that nitric acid serves as a temporary sink for stratospheric NO_2 . Nitric acid is then removed in form of precipitation, or upon reaction with bases (ammonia, particulate lime) forming particulate nitrates.

Nitrous oxide, N_2O , also called laughing gas, is present through natural sources in low amounts (0.3 ppm) in unpolluted atmosphere. The natural sources are microbial activity of the soil in tropical regions and the major part is released through activities in oceans. The gas is formed as a byproduct of denitrification reaction in aerobic atmosphere as well as nitrification reaction in anaerobic atmosphere. For the former, nitrogen in its highest oxidized form, i.e. NO_3^- is reduced to N_2 and N_2O is a by-product. For nitrification, the most reduced form of nitrogen, i.e. NH_4^+ is oxidized to NO_2^- and NO_3^- and N_2O is a by-product. N_2O is relatively unreactive in the troposphere and its concentration decreases with altitude in the stratosphere according to the photochemical reaction



and reaction with singlet atomic oxygen:



Increased fixation of nitrogen, together with increased microbial production of N_2O , contributes to depletion of ozone layer. Other neutral nitrogen oxides present in the atmosphere include N_2O_5 and N_2O_3 . Ammonia and other volatile organic amines, released upon decomposition of plant and animal materials, are readily oxidized to nitrogen oxides, N_2O , NO .

5.1 PARTICLES IN THE ATMOSPHERE

Several forms of particles, ranging from dust, smoke, soot, pollen, spores to micron sized aerosols are present in atmosphere. Particulate matter or simply particles constitute the most visible and apparent form of air pollution. It is a complex mixture of the solid particles and liquid droplets floating in the atmosphere. Very small, solid particles include black carbon, silver iodide, combustion nuclei, and sea-salt nuclei formed by the loss of water from droplets of seawater, while the larger particles comprise of cement dust, wind-blown soil dust, foundry dust, and pulverized coal. Mist, including raindrops, fog, and sulfuric acid droplets describe the liquid particulate matter. Other atmospheric particles of natural origin include bacteria, pollen grains, fog and volcanic ash. A brief description about various particles in the atmosphere is given in table 3.

Table 3. Terms describing atmospheric particles

Type	Description
Aerosol	Colloidal-sized atmospheric particle
Condensation aerosol	Formed by condensation of vapours or reactions of gases
Dispersion aerosol	Formed by grinding of solids, atomization of liquids or dispersion of dusts
Fog	high level of water droplets
Haze	Decreased visibility due to the presence of particles
Mists	Liquid particles
Smoke	Particles released by incomplete combustion of fuel

Chemically, the particulate matter comprises of a variety of components including acids (nitrates and sulphates), elemental carbon, metals (Mn, Cu, Zn, Cd, Cr, Fe, Ni, K, Ca, V, Ba, As, Se, Sr), soil, fugitive dust and sea spray.

5.11.1 Characteristics of particulates

Size- The size of the particles and droplets vary. Large *particles* can be seen as soot or smoke, while small particles like aerosols can only be detected with a microscope. The particle size varies from 2×10^{-4} to $500 \mu m$. Particles ranging from 0.001 to $10 \mu m$ in size are commonly suspended near the source of air pollution. The size of the particle is linked to its potential causing health problems. The smaller, more lethal is its effect. Two size ranges, $PM_{2.5}$ and PM_{10} are frequently been monitored at major emission sources and in air under ambient conditions. PM_{10} particles have aerodynamic diameter less than or equals to $10 \mu m$ and $PM_{2.5}$ corresponds to particles with aerodynamic diameters less than or equal to $2.5 \mu m$. These two

sets of particles differ in their behaviour in the atmosphere. $PM_{2.5}$ or fine particles tend to remain airborne for a longer time period and travel larger distances. On the contrary, PM_{10} or coarse particles, are too large to remain suspended in air and hence rapidly deposit on the earth's surface. Thus, particle size is a useful indicator about the amount of time a particle remains suspended in air.

- **Concentration-** It varies from several hundred/cm³ to 1,00,000/cm³ and above. The concentration at any time varies with the wind source, because the source of release may be very far from site at which the particles are formed.
- **Lifetime-** Particle's lifetime varies from few seconds to several years, that normally happen when the particles diffuse into stratosphere. Large size particulates have lower lifetime than small particles. The most common way of losing their existence is by settling down. Small particles coalesce, condense and settle down faster than larger particles.

Classification of particulates

Particulate matter is emitted directly or formed in the atmosphere. On the basis of their origin and size, the atmospheric particles are classified as primary and secondary particulate matter. Table 4 gives a comparison between primary and secondary particulate matter.

Table 4. A comparison between primary and secondary particulate matter

Primary particulate matter	Secondary particulate matter
Released directly into the atmosphere by wind, combustion processes, or human activities	Released as a result of chemical reactions of gaseous pollutants, initiated either by sunlight photochemically or with primary particulates that act as heterogenous reaction sites.
Belong to natural source of generation. Natural sources like forest fires, volcanic eruptions, dust storms, sand storms, ocean or sea sprays, biological sources-pollens, spores, microbes, meteorites.	Both natural and anthropogenic sources. Vehicular exhaust, combustion, construction, mining, metallurgical operations.
Include suspended dust, sea salt, organic carbon, elemental carbon, metals, small amount of sulphate and nitrate	Sulphates, nitrates, ammonia, volatile organic compounds
Coarse particles (PM_{10}) are composed of primary particulate matter	Fine particles ($PM_{2.5}$) contain secondary particulate matter

5.11.2 Chemical reactions of atmospheric particles

As discussed, secondary particulate matter is produced from chemical reactions in the atmosphere. Oxides of nitrogen, NO_2 and sulphur, SO_2 are the major species involved in the formation of the particulates. From troposphere, these particulates diffuse into stratosphere and remain suspended at a height of 20-27 km.

• Oxidation

Chemistry of sulphate formation- About half of SO_2 oxidation to sulphate occurs in the gas phase through the photochemical oxidation in the daytime. NO_x and hydrocarbon emission enhance the rate of oxidation. At least half of SO_2 oxidation takes place in cloud droplets. Within clouds, soluble SO_2 is scavenged by water droplets and rapidly oxidise to sulphate, forming small liquid droplets. Mechanistically, reaction involves the gas phase oxidation of $\text{SO}_2(\text{g})$ to $\text{H}_2\text{SO}_4(\text{g})$ followed by condensation of $\text{H}_2\text{SO}_4(\text{g})$. Dissolution of $\text{SO}_2(\text{g})$ in liquid water gives $\text{H}_2\text{SO}_3(\text{aq})$, followed by conversion of $\text{H}_2\text{SO}_3(\text{aq})$ to $\text{H}_2\text{SO}_4(\text{aq})$.

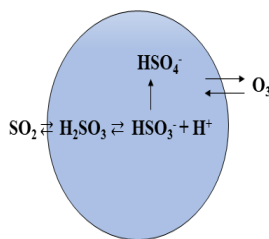
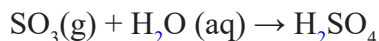
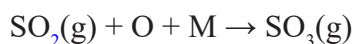
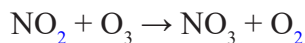


Figure 5.12 Oxidation of SO_2 inside water droplet

Sulphuric acid may also be formed through following reactions:

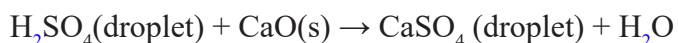
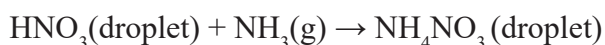
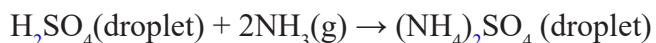


Chemistry of nitrate formation- NO_2 can be converted to nitric acid by reaction with hydroxyl radicals during the day. The reaction of OH^\bullet with NO_2 is about 10 times faster than with SO_2 . The peak daytime conversion rate of NO_2 to HNO_3 in the gas phase is about 10-50 % per hour. During night, NO_2 is converted to HNO_3 in the gas phase by a series of reactions involving ozone and the nitrate radical.



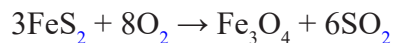
• Acid-base reaction

Both sulphuric and nitric acids droplets eventually combine with basic air pollutants like ammonia which is released during the biological decay processes at the ground level and lime. Acid-base reaction of these acids with ammonia affords ammonium salts as follows,



The formation of solid aerosol is affected when water evaporates from these droplets under low-humidity conditions.

Metal oxides, formed as a result of burning of fuels containing metals, represent a major class of inorganic particles in the atmosphere. For example, particulate iron oxide is formed during the combustion of pyrite-containing coal:



5.11.3 Aerosols

Atmospheric aerosols are colloidal sized solid or liquid particulates of diameter less than 100 μm , that are suspended in the air and are in equilibrium with the gaseous atmosphere. Particles of aerosol composed of carbonaceous material, oxides of metal, sulphates, nitrates, ammonium salts and silicon. The composition varies with the particle's size. Fine, small particles originating from pollutant gases, like SO_2 are acidic, while larger particles contain materials of mechanical origin, for example grinding of limestone and thus behave as base. Aerosol particles play a crucial role in major atmospheric phenomenon such as cloud formation, electrification and fog formation. In the lower atmosphere, aerosols modify the size and its distribution of the cloud droplets, thus influencing their ability to reflect and absorb sunlight. As a result, these particles can largely regulate the earth's energy budget. These particles have significant influence upon visibility in the atmosphere. Particles smaller than about 0.1 μm in diameter scatter light much like molecules, Rayleigh scattering. Their scattering of sunlight reduces visibility (haze) and redden sunrises and sunsets. Particles of the size ranging from 0.1 μm to 1 μm exhibit interference phenomena because they are about the same dimensions as the wavelength of visible light. In addition, aerosols have an outsized effect on the earth's climate. They help balancing the temperature of the planet by reflecting light. Very small particles called condensation nuclei serve as templates for condensation of atmospheric water vapor and thus play an important role in the formation of rain drops.

Aerosols can be pure compounds or complex mixtures, hydroscopic or hydrophobic. Aerosols can transport a wide variety of inorganic and organic pollutants significant distances if the sizes are in the submicron range. Owing to their active surface area, the particles act as reaction sites for heterogeneous atmospheric chemical reactions. One of the key reactions are responsible for destruction of stratospheric ozone. In the polar regions, the aerosols grow and form stratospheric clouds. The cloud's large surface areas provide active sites for chemical reactions to occur. Such reactions producing significant amounts of reactive chlorine pave the way for the destruction of ozone in stratosphere.

5.11.4 Black carbon

Black carbon, a component of particulate matter, is emitted from diesel engines, coal-fired power plants, and other sources burning fossil fuels. During incomplete combustion of fuel, CO_2 , carbon monoxide, volatile organic compounds, organic carbon and black carbon particles are formed. Particles of black carbon strongly absorb sunlight and give black colour to the soot which refers to the complex mixture of particulate matter released during incomplete combustion. It contributes to warming by converting absorbed solar radiation to heat.

Black carbon is a global environmental concern that severely affects human health and climate. Inhalation of black carbon causes respiratory and cardiovascular disease, cancer, and even birth defects. By absorbing solar radiation, black carbon is potent contributor to global warming and is responsible for climate change.

5.11.5 Effects of particulate matter on human health

Ultra-fine atmospheric particles can travel to respiratory tract, enter the bloodstream and release their fatal effects. Short and long-term exposure increases the risk of lung cancer, respiratory, cardiovascular, infectious and allergic diseases. $\text{PM}_{2.5}$ goes deep inside the body and cause greater damage to the health. Studies have indicated that each $10 \mu\text{g}/\text{m}^3$ increase in fine $\text{PM}_{2.5}$ long-term exposure has been associated with approximately 6% and 8% increased risk of cardiopulmonary and lung cancer mortality, respectively. Other effects include, irritation of eyes, nose and throat, severe asthma attacks, pre-term birth and low birth weight and premature death in people with heart and lung disease.

Check Your Progress III

Notes: (a) Write your answer in about 50 words

(b) Check your progress with possible answer at the end of the unit.

What are the principal forms of elemental oxygen and how are these generated.

What are the oxides of N in the atmosphere and their sinks?

What are the main sources and sinks for N_2O in the atmosphere?

What is the chemical composition of sulphate and nitrate aerosols? What is their fate in troposphere.

What do you understand by the term aerosols. Why are aerosols in the size range 0.1 to 1 μm effective in scattering light?

Differentiate between primary and secondary particles

5.12 LET US SUM UP

Earth's atmosphere is a thin envelope of gases surrounding the solid planet. The composition of the atmosphere consists largely of oxygen and nitrogen, as also water vapor, carbon dioxide, methane, noble gases and some other gases in trace amounts. The atmosphere absorbs heat from the Earth's surface and radiate it in all directions including back to the surface. Atmosphere has been classified into many layers or zones on the basis of several criteria. Various chemical species, including oxides of nitrogen, carbon and sulphur as well as their particulate matter, present naturally and due to man's activities undergo photochemical reactions, and are responsible for several environmental episodes.

5.13 KEY WORDS

Troposphere Lowest and densest layer of Earth's atmosphere extending from sea level to 11 km high, in which most weather changes occur and temperature generally decreases rapidly with altitude.

Stratosphere The part of the earth's atmosphere which extends from the top of the troposphere to about 50 Km above the surface and in which temperature increases gradually to about -2°C and clouds rarely form.

Mesosphere The part of the earth's atmosphere between the stratosphere and the thermosphere in which temperature decreases with altitude to the atmosphere's absolute minimum. Air in this region is very thin.

Thermosphere The region of the atmosphere above the mesosphere and below the height at which the atmosphere ceases to have the properties of a continuous medium. The thermosphere is characterized throughout by an increase in temperature with height

Ionosphere The layer of the earth's atmosphere which contains a high concentration of ions and free electrons and is able to reflect radio waves. It lies above the mesosphere and extends from about 80 to 1,000 km above the earth's surface.

Ozone A triatomic very reactive form of oxygen that is a bluish irritating gas of pungent odor, and a major air pollutant in the lower atmosphere but a beneficial component of the upper atmosphere, and that is used for oxidizing, bleaching, disinfecting, and deodorizing.

Adiabatic lapse rate The rate at which atmospheric temperature decreases with increasing altitude in conditions of thermal equilibrium.

Photochemical reaction A chemical reaction initiated by the absorption of energy in the form of light. The consequence of molecules' absorbing light is the creation of transient excited states whose chemical and physical properties differ greatly from the original molecules.

Free radicals An especially reactive atom or group of atoms that has one or more unpaired electrons

Photoionization The phenomenon in which the absorption of electromagnetic radiation by an atom in a gas induces the atom to emit a bound electron and thereby become ionized.

Photodissociation Photodissociation, photolysis, or photodecomposition is a chemical reaction in which a chemical compound is broken down by photons. It is defined as the interaction of one or more photons with one target molecule. Any photon with sufficient energy can affect the chemical bonds of a chemical compound.

5.14 REFERENCES AND SUGGESTED FURTHER READINGS

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- Environmental Chemistry, Colin Baird & Michael Cann, 5th edition WH Freeman and Company, New York, 1995
- Principles of Environment Chemistry, James E Girard, Second Edition, Jones and Bartlet Publishers, Sudbury MA, 2005
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- Introduction to Environmental Science and Technology, Gilbert M. Masters John Wiley & Sons, USA, 2003

ANSWERS TO CHECK YOUR PROGRESS

Check Your Progress I

1. Three stages of evolution. Cosmic dust that led to formation of Earth. Gravitational force holding the gases from escaping into outer space. Initial atmosphere was reducing. Volcanic eruptions and Iron moving to the core. Till stage II the nature of gases was reducing. In stage III, photodissociation of water vapours as well as photosynthesis led to oxygen accumulation.
2. Major gases are nitrogen and oxygen. Trace amounts of noble gases. Water vapours and carbon dioxide. Oxides of nitrogen, ozone, ammonia, methane, iodine.
3. Atmosphere does not get heated directly from Sun's rays. The atmosphere close to earth gets heated from the warm Earth. With increase in altitude, the atmosphere gets distant from the warm Earth and temperature decreases. Increase in temperature in any zone is due to presence of species.

Check Your Progress II

1. Atmospheric stability resists vertical mixing of air, which occurs due to pressure difference in different altitudes. Atmospheric stability in turn depends on the lapse rate. Accordingly, the stability varies from very stable to neutral to unstable, depending on the decrease in temperature of the atmosphere with altitude compared to the adiabatic lapse rate.
2. Conditions for temperature inversion. Perfect gas equation that explains the pressure inside an insulated balloon as compared to outside, which causes mixing or not.
 - (i) Instantaneous re-emission of absorbed light in case of Luminescence. Delayed remission in case of Chemiluminescence
 - (ii) Change of temperature with altitude for dry ideal gas. Inclusion of heat release due to presence of water vapour refers to wet adiabatic lapse rate
3. Layer of the Earth's atmosphere above 50Km, which is that ionized by solar and cosmic radiation. Atoms in this area have been stripped of one or more of their electrons, are "ionized," and are therefore positively charged. The ionized electrons behave as free particles. Region that reflects and modifies radio waves

used for communication and navigation. Responsible for formation of Van allen belts

4. It is produced by photolysis of water at higher altitudes. HO[•] radical is generated by the photolysis of nitrous acid vapour, hydrogen peroxide, ozone.

Production of HO[•] radical depends on the wavelength of light and availability of the substrate

Summers will increase OH concentration. Midday time also increases the photolysis to increase OH radical concentration.

5. OH radical is very reactive and enters into several reactions, most commonly H abstraction occurs. Major sinks of OH radical are CO and CH₄. But reacts with H₂S, SO₂, NH₃ and many more (Refer to fig. 8).

Check Your Progress III

1. In ground state O₂ in triplet state (³O₂), excited to singlet molecular oxygen (¹O₂). Singlet oxygen may also be produced by other processes such as direct photochemical excitation, transfer of energy from other electronically excited molecules, ozone photolysis and high-energy oxygen producing reactions.

Upper atmosphere- oxygen atoms, O; excited oxygen molecules, O₂^{*} and ozone, O₃, excited atoms, O^{*} Oxygen ion, O⁺, molecular ion O₂⁺.

Photoexcitation, photodissociation and other photochemical reactions.

2. Eight oxides of nitrogen, three are active and abundant – N₂O, NO, NO₂. Interchange and responsible for several reactions in atmosphere. Refer fig. 8
3. N₂O released from microbial activity, activities in oceans The natural sources are microbial activity of the soil in tropical regions and the major part is released through activities in oceans. Nitrification and denitrification process in anaerobic and aerobic conditions resp. Unreactive in troposphere. In stratosphere gets used up by converting to NO and N₂,
4. SO₂ reacts with OH, O to produce H₂SO₄. NO₂ reacts with OH and O to produce HNO₃. Both acids react with basic air pollutants like ammonia and lime. Acid-base reaction of these acids affords salts of Ca and ammonium ions.
5. Fine colloidal sized solid particles or liquid droplets of diameter less than 100 μm, suspended in the air. Examples- carbonaceous material, oxides of metal,. The composition varies with the particle's size. Play important role in cloud formation, electrification, fog formation. Influence visibility in the atmosphere. act as reaction sites for heterogeneous atmospheric chemical reactions.
Particles < 0.1 μm in diameter scatter light, Rayleigh scattering, reduces visibility (haze) and redden sunrises and sunsets.
6. Refer to table 4

UNIT 6 : WATER CHEMISTRY

Structure

- 6.0 Introduction
- 6.1 Objectives
- 6.2 Distribution of Water
- 6.3 Chemistry of Water-Structure and Polarity
- 6.4 Properties of Water
- 6.5 Hydrology
 - 6.5.1 Ground Water and Water Table
- 6.6 Sources and Uses of Water: The Hydrological Cycle
- 6.7 Physical and Chemical Properties of Fresh Water and Sea Water
 - 6.7.1 Physical Properties
 - 6.7.2 Chemical Properties
 - 6.7.3 Environmental Significance
- 6.8 Coagulation and Sedimentation
- 6.9 Water Quality
 - 6.9.1 Physical Characteristics
 - 6.9.2 Chemical Characteristics
 - 6.9.3 Biological Characteristics
- 6.10 Chemical Species in Water
 - 6.10.1 Organic Components in Water
 - 6.10.2 Inorganic Components in Water
- 6.11 Distribution of Gases in Water
 - 6.11.1 Oxygen in Water
 - 6.11.2 Carbon Dioxide in Water
- 6.12 Organic Matter and Dissolved Humic Substances in Water
- 6.13 Let Us Sum Up
- 6.14 Key Words
- 6.15 References and Suggested Further Readings
- 6.16 Terminal Questions

6.0 IMPORTANCE OF WATER

WATER IS LIFE. It's one of the most indispensable resources for all lifeforms on Earth, playing a prime role in maintaining various ecosystems on the planet by serving as a link between them. Water occurs in all spheres of the environment- a vast reservoir of saline water in oceans; in rivers, lakes etc. as surface water; in aquifers as groundwater; in polar ice caps as ice; in the atmosphere as water vapour along with several other segments of anthroposphere.

We consume several litres of freshwater daily to sustain life. As an essential nutrient, water plays a key role in the human body. In fact, about 70% of the human body is made up of water. One can survive up to multiple weeks without food, but only a couple of days without water. Every system of the body, starting from cells and tissues, to organs require water to function. Water serves as a medium for the transformation of complex biomolecules forming a foundation for life processes, ranging from respiration and digestion, to temperature regulation and waste removal. Industries also require water at various stages of their production. In agriculture, water is used for irrigation and livestock. Water stored in dams is utilized in producing hydroelectric power. However, freshwater is available in limited stock on Earth.

6.1. OBJECTIVES

After studying this unit, you will be able to

- Express the quantitative features of global water distribution,
- Discuss different stages and significance of hydrological cycle,
- Identify organic and inorganic chemical species in water,
- State the factors that decide the solubility of gases in water.

6.2 DISTRIBUTION OF WATER

The quality and quantity of available water is an important factor for the wellbeing of life. Nearly 71% of the Earth's surface is made up of water. In response to temperature variations and other factors, it exists in various forms in the environment. It may be classified as groundwater (present under earth's surface as an aquifer) and surface water (free-flowing water in the form of rivers, lakes etc.). As shown in figure 1, about 97% of the total available water is present in the oceans (marine water), while only 3% is fresh water. Ocean water is highly saline, making it unfit for drinking and agricultural purposes. Out of remaining 3% freshwater, 79% is stored in glaciers and polar ice caps, 20% is stored in aquifers or soil moisture, and only 1% is surface water (primarily lakes and rivers). The water stored in glaciers and polar ice caps as well as in aquifers or soil moisture is not available as drinking water. However, lakes and rivers are of the main sources of potable water, constituting even less than 0.01% of the total water supply.

Several civilizations have vanished due to the shortage of water. Due to climate change, numerous catastrophes have occurred from time to time in different parts of the globe, may be due to droughts or due to floods on other extremes. Waterborne diseases such as cholera and typhoid killed millions of people in the past and still cause great misery in less developed countries. Globally, issues related to quality and quantity of water supply are becoming more serious. These problems include increased water use due to population growth, contamination of drinking water by improperly discarded hazardous wastes and destruction of wildlife by water

pollution. An estimated 110,000 km³ of rain, snow, and ice falls annually on land surfaces and provides a mean to replenish freshwater resources.

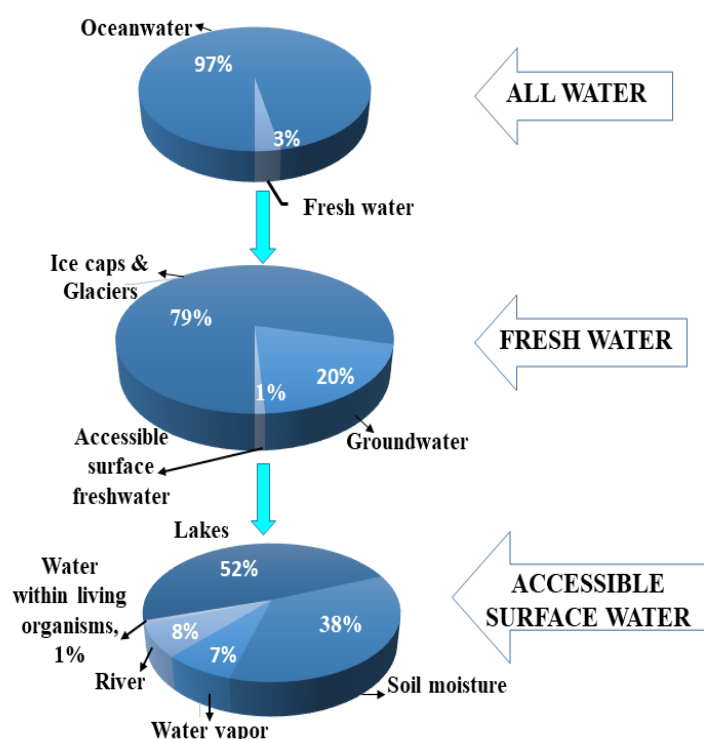


Figure 6.1 Distribution of water

6.3 CHEMISTRY OF WATER: STRUCTURE AND POLARITY

Water is an unusual molecule, consisting of covalently bonded two hydrogens and an oxygen atom. On account of the difference in electronegativities of the combining atoms, the molecule is polar in nature with an electrical dipole moment (Figure 2). This unique attribute is responsible for many of the special characteristics of water making it a universal solvent, with high ability to dissolve other substances. An important property of water is its ability to form Hydrogen bonds with itself and with other polar molecules. This property is responsible for strong attractive forces between molecules of water, and give rise to high surface tension and capillary forces. Hydrogen bonding plays a crucial role in retaining very small colloidal particles in water suspension. Not only this, it also accounts for the dissolution and transportation for several pollutants whose removal from water is often challenging.

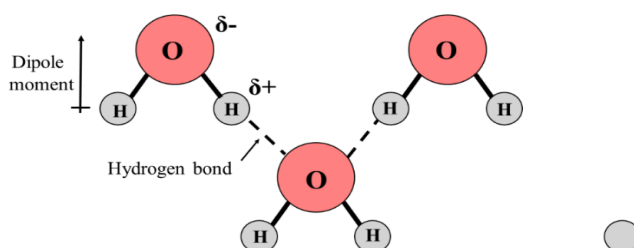


Figure 6.2 Hydrogen bonded water molecule

6.4 THE PROPERTIES OF WATER

Under natural conditions, water can exist in solid, liquid or gaseous state. A range of unique properties determine its environmental chemical behaviour and are essential to life.

Physical Properties of water

Water has many unique properties which are essential to life. Some of the special characteristics of water include its polar character, tendency to form hydrogen bonds, and high boiling point. These properties along with the respective consequences are listed below in table 1.

At optimum temperature and pressure, all three states (solid, liquid, and vapour) of water coexist and are in equilibrium with each other. This denotes the triple point, wherein an infinitesimally small changes in either temperature or pressure will cause water to be either a liquid, solid, or gas. The triple point of water is observed at temperature and pressure of 273.16 K (0.01°C) and 611.73 pascals (0.00603 atm), respectively. As shown in figure 3, a decrease in temperature and an increased pressure allows water to pass to solid directly from a gaseous phase. Water cannot exist as a liquid at pressures lower than the triple point and thus ice converts into vapour on increasing temperature (sublimation). At pressures higher than the triple point, increase in temperature forces ice to transform into liquid and finally vapour state.

Table 1. Important properties of water

Property	Effects and significance
Universal solvent	Dissolve a large number of chemical compounds. Allows transport of nutrients and waste matter, making biological processes conducive in an aqueous medium
Highest dielectric constant	High solubility of ionic substances and their ionization in solution
Melting point = 0 °C and boiling point = 100 °C	Exists as a liquid at room temperature
High surface tension	Formation of water droplets allows plants to transport water (and dissolved nutrients) from their roots to their leaves, and the movement of blood through vessels in the bodies of animals
Transparent to visible and longer wavelength portion of ultraviolet light	Colourless, thus aquatic plants survive beneath water because sunlight can reach them.

Maximum density at 4 °C.	Unique behaviour causes water to become less dense when cooled down to its solid form, ice. Ice floats and insulates deeper water; making the existence of life even possible at very low depths, vertical circulation restricted in a stratified water body.
Higher heat of evaporation (2260 J/g)- steam contains more energy than liquid water	Cooling effect determines the transport of heat between the atmosphere and water bodies. Allow moderation of the Earth's climate and regulation of body temperatures of living organisms, resulting in the cooling effect.
Higher latent heat of fusion (-334 J/g) than any other liquid except ammonia	Temperature stabilized at its freezing point. In high latitudes, permit heat to be stored by melting ice during summer and returned by freezing water to ice in winter without affecting temperature of polar ocean water.
Higher heat capacity (4.2 J/g °C) than other liquid except ammonia-water can contain a large amount of heat without undergoing much change in temperature	Absorbs sun's heat, allows moderation of the Earth's climate and regulation of body temperature more effectively. It is used as coolant.

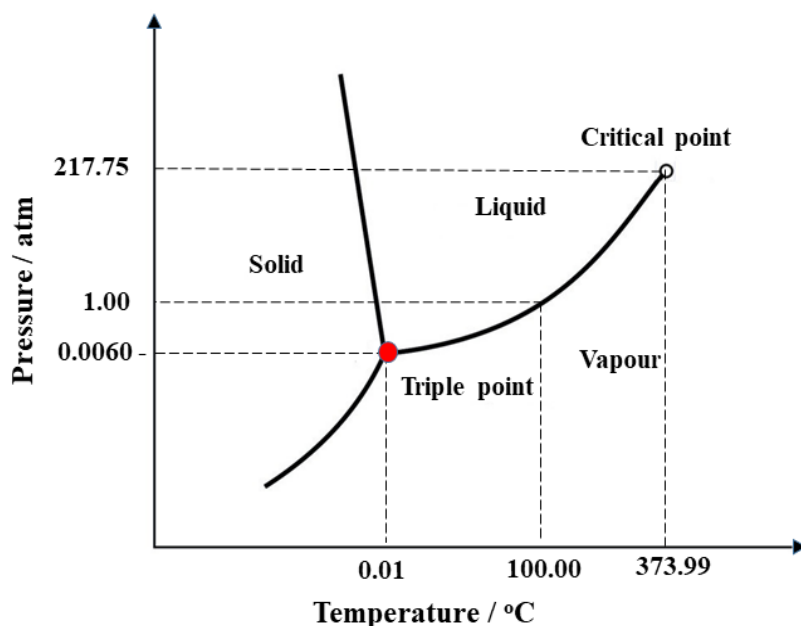


Figure 6.3 Phase diagram of the triple point of water

Check Your Progress – I

Q.1 How does polluted water responsible to disturb ecological balance?

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Q.2 Of all the water on our planet, approximately how much is fresh water, salt water, ice, ground water? How much is easily accessible?

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Q.3 Why is water a Universal Solvent ?

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.....

Q.4 Which among the following properties of water are greatly influenced by hydrogen bonding? (mark the correct answer amongst a, b, c and d)

- | | |
|---------------------------------------|------------------|
| 1. Absorption in the visible spectrum | 2. Boiling point |
| 2. Density near the freezing point | 4. Dipole moment |
| a) 1 and 2 | b) 1,2 and 3. |
| c) 3 and 4. Or | d) 2 and 4 |

6.5 HYDROLOGY

Hydrology is the branch of science dealing with the study of water on the Earth and beneath the surface of the Earth. It encompasses the natural distribution and movement of water, the [physical and chemical properties of water](#), and its relationship with the living and material components of the environment

It is classified into two broad sub-categories:

Limnology – The branch of science that deals with the characteristics of freshwater, including their biological as well as physical and chemical properties.

Oceanography- The branch of science dealing with the study of ocean and its physical, chemical and biological properties.

6.5.1 Groundwater and Water Table

Groundwater plays a crucial role in geochemical phenomena such as the formation of secondary minerals. The nature of rock formations strongly influences the quality and mobility of groundwater resources.

The top of the groundwater (saturated) region is called the water table. Lakes and streams are observed when the water table lies above the soil. However, the water table may be observed at the surface of the soil giving rise to swamps. Permeability of rocks largely impacts the flow of groundwater. For example, highly pervious porous rock allows water to pass through pores in such rocks and later water can also be extracted from such formation. This constitutes a permanent reservoir of groundwater or underground lake which may be understood as Aquifer or artificial wells (Figure 4).

Importance of groundwater can be realised by the facts that circulation of groundwater into rivers, prevents drying up of rivers and also sustains plant life. Earlier groundwater was regarded to be of the highest purity. However, on account of percolation of soil and its long residing time underground, groundwater contains natural organic matter in low concentrations and disease-causing microbes, which are otherwise present in lakes and rivers. Increasing urbanization and industrialization has led to groundwater pollution with continuous seeping of minerals and pollutants down into the surface.

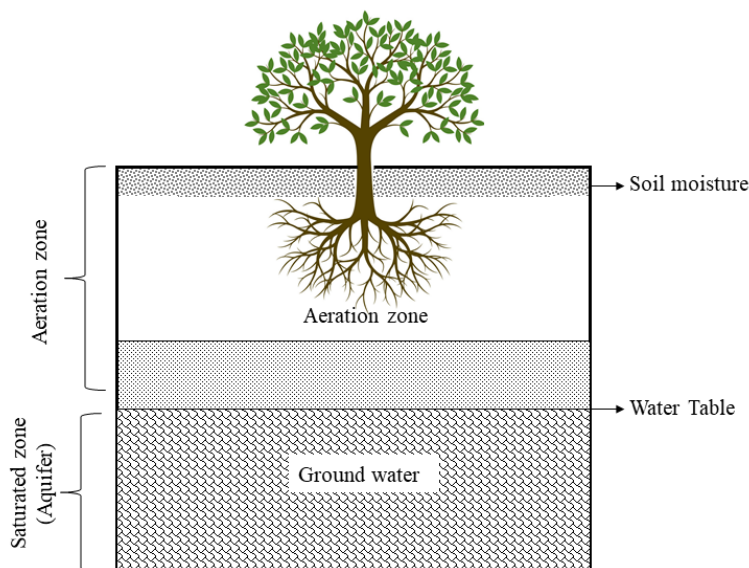


Figure 6.4 Water table

6.6 SOURCES AND USES OF WATER: THE HYDROLOGICAL CYCLE

The water cycle, or hydrologic cycle, is a continuous process *via* which water is purified by evaporation and recycled from the earth's surface (including the oceans) to the atmosphere and back to the land and oceans (Figure 5). On absorbing heat from the sun, water from various sources evaporates as water vapour. As this moist

air rises, it cools, condenses and returns to the Earth's surface as precipitation. Some precipitation penetrates the ground as groundwater, moving downward through the incisions, forming aquifers, while the unabsorbed groundwater returns to rivers, streams, and eventually to the oceans. This cycle repeats itself as water evaporates from the surface of water bodies and transpiration by plants returns the absorbed moisture into the atmosphere. Even though water regularly cycles through the ecosystem, a fine balance between various processes like evaporation, condensation and precipitation maintains the total water on Earth constant.

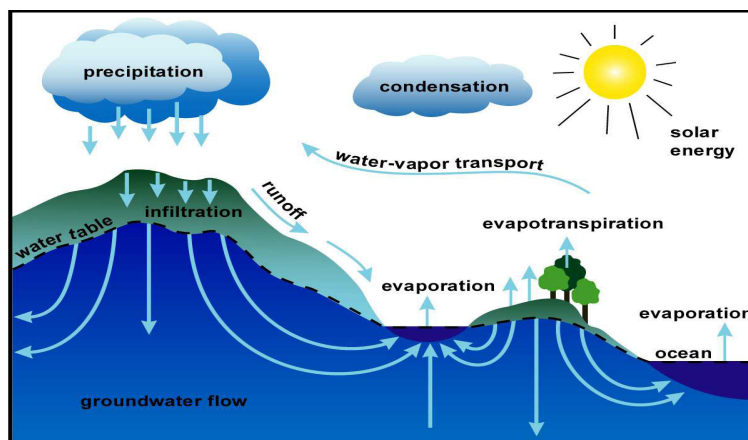


Figure 6.5 The Hydrological cycle

(Source: *Int. J. Sci. Res.*, 9(6), 2019, 320-331. DOI: 10.29322/IJSRP.9.06.2019.p 9051)

6.7 PHYSICAL AND CHEMICAL PROPERTIES OF FRESH WATER AND SEA WATER

As discussed earlier, about 97% of the total available water on Earth is present in the oceans (saltwater), while only 3% is freshwater. Seawater constitutes a rich source of various commercially important chemical elements. For example, much of the world's magnesium and bromine is recovered from seawater. Common salt (NaCl) is still obtained by evaporating sea water in some parts of the world. Also, sea water after desalination can supply a limitless supply of potable water. Many such desalination plants are operational in dry areas along the sea coast, such as Middle East Countries.

6.7.1 Physical Properties

The waters of the Ocean are different from fresh water in physical as well as chemical properties. The properties of seawater vary with latitude, depth, nearness to land, and input of fresh water. About 3.5% of sea water is composed of dissolved compounds while the remaining 96.5% is pure water. The chemical composition of sea water gives an idea about processes such as erosion of rocks and soil, volcanic activity, gaseous exchange with the atmosphere, metabolic and breakdown products of organisms and rain.

The salt content in seawater is denoted by salinity (S). Salinity is defined as the amount of salt in grams dissolved in one kilogram of seawater. It is expressed in parts per thousand (ppt) or practical salinity units (PSU). The average salinity of ocean water may range from 34 to 37 ppt or 34 to 37 psu. As shown in figure 6, the six most abundant ions of sea water, comprising about 99% of sea salts are chloride (Cl^-), sodium (Na^+), sulphate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+).

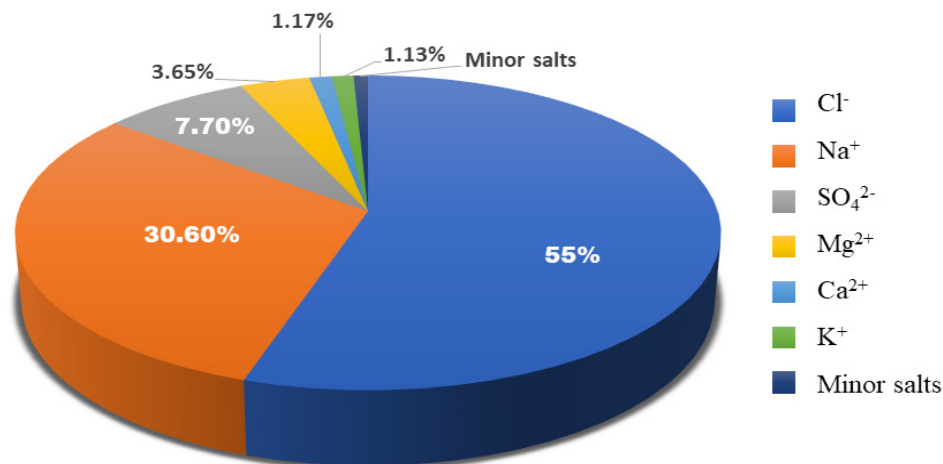


Figure 6.6. Relative proportions of dissolved salts in seawater.

Chloride makes up 55% of the salt in seawater. Inorganic carbon, boron, bromide, strontium and fluoride constitute the other major dissolved substances in sea water. Out of the several minor chemical constituents, inorganic phosphorus (HPO_4^{2-} and PO_4^{3-}) and inorganic nitrogen (NO_3^- , NO_2^- , and NH_4^+) are most notable, since they constitute essential nutrients for the growth of living organisms that inhabit the oceans and seas.

A variety of elements essential for the growth of marine organisms, include silicate (incorporated into the hard structural parts of some marine organisms), abundant in the upper ocean. Dissolved silicate concentrations range between less than 1 micromole/kg on the surface to 180 micromoles/kg at depth. The concentration of zinc ranges between approximately 0.05 nanomole/kg on the surface ocean to as much as 6 nanomoles/kg at depth. Several other elements including cadmium, iron, cobalt and copper show more complex behaviour. These elements get adsorbed on the surface of the sinking particles and hence moves from the surface to a greater depth.

Seawater also contains various dissolved atmospheric gases, mainly oxygen, nitrogen, argon and carbon dioxide. Some other components of seawater are dissolved organic substances, such as amino acids, organic rich particulates and carbohydrates. These materials are mainly present in the upper 100 m of the ocean, where the dissolved carbon is converted into organic matter *via* the process of photosynthesis.

Since oxygen is a reactive gas essential to life, oxygen concentrations in seawater that are not in direct equilibrium with the atmosphere is quite variable. Although oxygen is released by photosynthetic organisms at sunlit ocean depths, the concentration of gas in near-surface water is established mainly by exchange with the atmosphere. In the oceans, oxygen concentrations generally show minimum values at intermediate depths and comparatively high values in deep water.

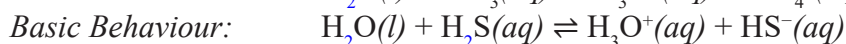
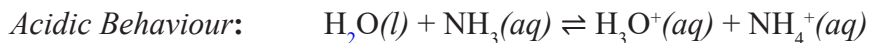
Freshwater contains less than 1% salt in comparison to almost 3% in sea water. When it comes to chemical composition beyond simple water and salt, seawater is very similar from place to place, whereas freshwater varies a lot depending on the type of soil and rock the water is in contact with. Some of the distinctive qualities of seawater are due to salt content. Due to the high salinity of sea water in comparison to the fresh water, the former has a higher viscosity, greater density, higher boiling point and lower freezing point than the latter. The various physical properties of fresh water and sea water are compared in table 2.

6.7.2 Chemical properties

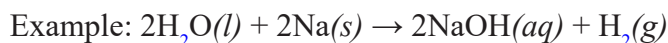
Water reacts with several substances to form different compounds. Some significant reactions are as follows:

- **Amphoteric nature** Water is amphoteric and can act as both acid and base.

Example:



Redox reactions: Any electropositive elements reduce water to hydrogen molecule.



Also, during the process of photosynthesis, water is oxidized to O_2 . As water can be oxidized as well as reduced, it is very useful in redox reactions.

- **Hydrolysis reaction**

Since water has a high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic and polar compounds easily. Some more reactions occur in sea water. The total concentration of CO_2 is very high in sea water, in comparison to atmosphere. It reacts with sea water to form carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}). About 90% of the total organic carbon is converted into HCO_3^- . During the conversion of CO_2 into HCO_3^- and CO_3^{2-} , hydrogen ions are also liberated. However, the relatively high concentrations of both total inorganic carbon and boron [as $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$] in seawater are sufficient to maintain the pH of seawater between 7.4 - 8.3, thus buffering the amount of hydrogen ion liberated. This buffering action is very important because the extent and rate of

Table 2. A Comparison between physical properties of fresh water and sea water

Property	Fresh water	Sea water
Salinity	Fresh water has very concentration of dissolved salts, about 0.05%.	Marine water is characterised by high salt content (3.5%) that arises due to leaching out of salt from the ocean floor and from rivers and streams.
Dissolved Ions	Freshwater contains similar elements as present in sea water, but much less of everything - fresh water is purer.	Seawater may contain hundreds of trace elements including metals like Pb and Hg, large quantities of Cl^- , and smaller quantities of Mg, S, Ca and K.
Electrical Conductivity	Fresh water has a lower value of electrical conductivity because of its low salt concentration.	Marine water has high electrical conductivity due to high salt content. for example, sea water due to dissolved salts conducts electricity about 100 times more than distilled water.
pH	Fresh Water is neutral.	Saltwater is more basic because they have higher salt content.
Density	Fresh water has less density than sea water. At 0°C , liquid water turns into ice, which has a density of approximately 917 kg/m^3 . Fresh water at the same temperature has a density of nearly $1,000 \text{ kg/m}^3$.	Due to dissolved salts, marine water is denser. A specific volume of salt water is heavier than the same volume of freshwater. The density of seawater usually increases with decrease in temperature, increase in salinity, and increasing depth in the ocean. The density of seawater at the surface of the ocean varies from $1,020 - 1,029 \text{ kg/m}^3$. Highest densities are observed with depth due to the overlying weight of water. In the deepest parts of the oceans, density of seawater can be as high as $1,050 \text{ kg/m}^3$.

Freezing point	The freezing point of Fresh water is 0.0°C.	Seawater freezes at a temperature lower than fresh water. The freezing temperature varies with the salt concentrations. More is the salt, lower is the initial freezing temperature. At a salinity of 35 ppt, seawater freezes at a temperature of -1.9°C. Hence sea water remains liquid at temperatures below 0°C, and salt is used on roads and sidewalks during the winters to prevent freezing of water on their surfaces.
Dissolved Oxygen	Oxygen dissolves in freshwater more easily than salt water, because water can flow fast in small rivers, stirring plenty of oxygen into itself. Fresh water contains 14-15 ppm of dissolved oxygen at 0°C	Salt water has less dissolved oxygen in comparison to fresh water. Seawater contains 10-11 ppm of dissolved oxygen at 0 °C.
Temperature Fluctuation	In smaller water bodies, which can sometimes be found in freshwater areas, temperature fluctuates more easily, affecting the aquatic life in that water body.	Large bodies of water, like salty seas, maintain the temperature more easily - they stay cooler in summer and warmer in winter. The temperature of the water has more to do with the depth of water.
Tonicity	Due to osmosis, water flows from solution of higher solute concentration to a lower concentration through a semipermeable membrane. Tonicity is important for the survival of aquatic life. Freshwater is hypotonic, thus living organisms do not require much water but excrete it regularly as water is absorbed to balance the salt concentration.	Marine water is hypertonic to plant and animal tissues; thus organisms tend to release water to their surroundings and require a regular uptake of water to eliminate salt.

many reactions in seawater are highly pH-dependent. Carbon dioxide produced by the combination of oxygen and organic carbon generally reduces the pH near

the depth of the oxygen minimum in seawater. In addition to exchange with the atmosphere and, through respiration, dissolved inorganic carbon concentrations in seawater are also influenced by the formation and dissolution of the calcareous shells (CaCO_3) of organisms mainly in the upper ocean. It has been estimated that dissolved Organic Carbon (DOC) near the surface of the open ocean range between 100 - 500 micromoles of C/ kg of seawater. In surface water, DOC mainly exists as carbohydrates, amino acids, lipids and humic substance. DOC concentrations in the deep ocean are 5 to 10 times lower than surface values, with much less amount of carbohydrates and amino acids, as compared to the surface water. DOC in the surface water participates actively in photochemical transformation, which is capable of greatly altering the bioavailability of essential trace nutrients, such as, Cu and Zn.

6.7.3 Environmental significance

A freshwater ecosystem comprises streams, wetlands, ponds, lakes, and rivers. It provides a natural habitat for animals and plants that are unable to survive under highly saline marine water. In contrast to freshwater ecosystem, marine ecosystem is more diverse. It consists of salt marshes, wetlands, estuaries, mangroves, and accommodate several different aquatic lifeforms. Some can use salt water but the majority of higher plants and most mammals must have access to fresh water to live. Freshwater and marine ecosystems occupying more than three-fourth of the Earth's surface, nurtures array of ecosystems by participating in various biogeochemical cycles and nutrient exchange, providing natural habitat to lifeforms, and also assist in degradation and dispersion of many environmental pollutants.

The main environmental significances of fresh and marine water life are as follows:

Habitat

Freshwater aquatic life thrives in streams, rivers and lakes, with very low saline content. Depending on the species, fishes can survive in temperatures that range from 5 and 24 °C. The aquatic life adapts well to changes in habitat viz, changes in water levels, oxygen and temperature. In comparison, marine life like saltwater fish, coral reef and seagrass bed, can only survive under high salt concentration. A marine animal's habitats include.

Physiology

The physiology refers to the physical conditions of the habitat in which an organism live in. under hypotonic conditions, freshwater fish retain more salt in their bodies than in their surrounding water. Thus, they can survive in fresh waters with very low salt content. On the other hand, marine water fish lose water to their surroundings via osmosis. This lifeform requires plenty of water to eliminate excess salt.

Species

Fresh and marine water are home for a variety of living species. For example, freshwater fish include cold water or tropical varieties. Pike, trout, shiner and goldfish are examples of cold varieties. Examples of tropical freshwater species are pacu, golden barb, red-tailed red eye puffer, catfish, guppy and angelfish. In comparison, marine fish are all cold-water fish, including seahorses, eels, jellyfish,

clownfish, sharks, common dolphin and tuna. Fishes in Antarctica can inhabit waters as cold as -2°C because of proteins in their blood that act as antifreeze. The body structure of marine organism also varies with depth. The body structure of the organisms that live on the surface of the water is in sharp contrast with the sleek, elongated shape of the animals that live deep inside the sea.

Effect of human activity

Although the oceans constitute a huge reservoir, human activities have begun to influence their composition. The addition of nutrients results in increased growth of phytoplanktons, decreased penetration of sunlight, high level of organic matter, and alteration of the community of bottom-dwelling organisms. Through industrialization, the concentration of pollutants such as Pb, Hg, toxic organic compounds, radioactive waste has increased tremendously in sea water finally resulting in their bioaccumulation. Another recent global problem is the increase of CO_2 levels in the atmosphere. It is thought that the oceans, as a great reservoir of carbon dioxide, will ameliorate this increase in CO_2 level, but actually, it is giving way to another problem of ocean acidification.

Check Your Progress – II

Q.1 Explain the process of hydrological cycle with suitable diagram. Also mention the environmental significance of it.

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Q.2 Differentiate between :

- (i) Fresh water ecosystem and marine ecosystem**
- (ii) Surface water and ground water**

(i)

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(ii)

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Surface water is usually associated with dissolved and suspended particles. The suspended matter enters the water body from land erosion, the dissolution of minerals, decay of vegetation and domestic and industrial waste discharges. It generally consists of suspended, dissolved organic and/or inorganic matter, as well as several biological organisms, such as bacteria, algae or viruses. Hence, this material has to be removed before water is put for drinking purposes, as deteriorates water quality by reducing its clarity (causing turbidity or colour) and carrying pathogens or toxic compounds, adsorbed on the surfaces of suspended matter. Thus, the effluent water requires appropriate treatment to remove disease-causing agents. The most commonly employed methods in water treatment include:

- i. Coagulation and Flocculation
- ii. Sedimentation
- iii. Filtration
- iv. Disinfection

Coagulation

The **aggregation** of colloidal particles is important to understand the number of processes, like industrial processes and aquatic chemical phenomena. The colloidal particles in minerals aggregate and separate from water is significant in the formation of mineral deposits. Aggregation of particles is a complex phenomenon and may be divided into two categories, namely coagulation and flocculation.

Colloidal particles are prevented from aggregation by electrostatic repulsive forces between electrical double layers. These repulsive forces can be minimised, allowing particles to aggregate together. For example, the addition of ions, such as Na^+ and Cl^- ions, from sodium chloride forces electrically charged colloidal particles to aggregate into larger-size particles and settle. These charged ions act by neutralising the electrical charges on the colloidal particles and forces them to clump together; this process is known as **coagulation** that removes colloidal solids from water and accelerate the sedimentation process. Salts such as aluminium sulphate, polyaluminium chloride (also known as PAC or liquid alum) and ferric sulphate are frequently used as coagulant in water treatment. For example, filter alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ when added to waste water, the hydrated aluminium ion which is acidic in nature, reacts with base to form gelatinous precipitate of aluminium hydroxide that carries suspended matter with it as it settles. Thus, the alkalinity of water is also reduced.



In some cases, colloidal particles are allowed to settle in presence of bridging compounds, that interact with colloidal particles through chemical bonds, join them *via* bridges and induce coagulation called *flocculants*. This process is called **flocculation**. Natural and synthetic polyelectrolytes are used as flocculants. Among the natural compounds so used are starch and cellulose derivatives, proteinaceous materials, and gums composed of polysaccharides. Synthetic polymers, including

neutral polymers and both anionic and cationic polyelectrolytes, are commonly used.

Sedimentation

Wastewater can be treated by several physical processes. For example, solids can be removed by sedimentation and filtration. Sedimentation involves physical pre-treatment of water before application of other purification treatments such as filtration and disinfection. It may be defined as the tendency of suspended solids (sand, silt and clay) in the suspension of water to settle out of the suspension under the influence of gravity. The particles that settle out from the suspension deposit as sediment or sludge at the bottom of sedimentation tank and are removed periodically.

Sedimentation is one of the most basic steps of purifying water. It may be used as a preliminary step in some water treatment methods. It offers the following advantages:

1. Effectively removes water turbidity.
2. Fewer chemicals are required for subsequent water treatment processes.
3. It makes any subsequent process easier.
4. Cost-effective

Hence, sedimentation of turbid water for household use is recommended as a pre-treatment method that disinfects water with solar radiation, chlorine or other chemical disinfectants. In water treatment, the process of sedimentation minimizes the concentration of particles in effluent water before the coagulation, to reduce the amount of coagulants required.

6.9 WATER QUALITY

Water quality refers to the physical, chemical and biological properties of water, governing its suitability for the survival of life. It usually varies with the respective usage of water. The characteristics of water can be classified into three broad categories:

- *Physical Characteristics*: temperature, colour, odour, turbidity and solids
- *Chemical Characteristics*: pH, conductivity, salinity, hardness, BOD
- *Biological Characteristics*: counts of specific organisms and groups of organisms

6.9.1 Physical Characteristics

Physical characteristics of water are influenced by senses of touch, sight, smell and taste.

Temperature: Temperature measures the average kinetic energy of water molecules in response to their thermal motion. It determines the suitability of water for various

aquatic life forms by controlling water quality parameters such as dissolved oxygen, rate of photosynthesis, etc.

Colour: Colour in water is primarily a concern of water quality for aesthetic reasons. Coloured water is considered unfit for drinking purposes. It indicates the presence of organic substances, such as algae, humic compounds, hazardous or toxic organic materials in water. Coloured water can be treated through techniques like coagulation, settling and filtration.

Taste and Odour: Taste and odour are perceptions to determine water quality. Odour arises due to production of gas upon decomposition of organic matter or other substances present in wastewater. For public supplies, the water should be free from any odour.

Turbidity: Turbidity is a measure of the light-transmitting properties of water and is expressed as the amount of suspended and colloidal material in mg/l or parts per million (ppm). The factors responsible for water turbidity include human activity, decaying plant matter, algal blooms, suspended sediments, and plant nutrients.

Solids: Total dissolved solids (TDS) refers to the inorganic salts and small amounts of organic matter present in water. It may be defined as the residue that remains after evaporation of water, followed by ignition and drying the residue to a constant weight. At high temperatures, gases are released upon combustion of volatile organic solids and the inorganic residue is left behind as inert ash. Solids are classified as settleable, suspended and filterable solids. Settleable solids (silt and heavy organic solids) tend to settle under gravity. Suspended solids and filterable solids are classified on the basis of particle size and their retention rates on standard glass-fibre filters. The solids featuring algal growths cause severe eutrophic conditions in a water body. This leads to a reduction in light penetrating in surface waters and thus interfere with aquatic plant life. Also, deposition of such solids on river bed creates to septic and offensive conditions.

6.9.2 Chemical Characteristics

Upon prolonged exposures, the presence of chemicals in drinking water supply severely affects human health and thus pose serious health concerns. The major chemical properties of the water are discussed as follows:

pH: pH is a measure of acidity or basicity of a water sample. It may be expressed as:

$$\text{pH} = -\log[\text{H}^+]$$

If $[\text{H}^+]$ increases, pH decreases and then it will be acidic.

If $[\text{H}^+]$ concentration decreases, pH increases and then it will be alkaline.

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

The pH scale varies from 0 (very acidic) to 14 (very alkaline). In fresh waters, pH ranges from 4.5, for acidic waters, to above 10.0 in water featuring intensive photosynthetic activity by algae. The allowed pH value for public water supplies may range between 6.6 to 8.4. It has been observed that any changes in pH may alter the

concentrations of other species in water to a more toxic form. Chlorine disinfection, ammonia toxicity, and heavy metal ion solubility in water are all subjective to pH changes.

Electrical Conductivity: Conductivity is the ability to conduct an electric current when dissolved solids ionize into constituent ions in water. Conductivity is a valuable tool to determine hardness, alkalinity and the dissolved solids content of the water. The conductivity is a relative term and its relation with the TDS concentration is unique for a given water sample. The conductivity increases with increasing concentration of TDS.

Salinity: Salinity increases with increasing concentration of dissolved salts in water. High saline content in some saline waters may be attributed to a combination of dissolved ions including sodium, chloride, carbonate and sulphate. The presence of high salt content may make water unfit for domestic, agricultural or industrial use.

Alkalinity: The capacity of water to accept H^+ ions is called alkalinity. Alkalinity plays an important role in water treatment and the chemistry and biology of natural waters. Highly alkaline water generally contains high concentrations of dissolved solids. It reflects buffer capacity of water and serves as a reservoir for inorganic carbon and thus helps in evaluating water's ability to support algal growth and other aquatic life.

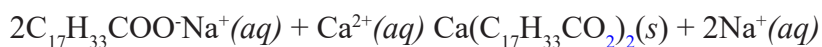
Acidity: It is defined as the ability of the water to neutralize OH^- . Presence of weak acids such as $H_2PO_4^-$, CO_2 , H_2S , proteins, fatty acids, and acidic metal ions, particularly Fe^{3+} are responsible for the acidic character of water body. Polluted water contains an appreciable concentration of free mineral acid. The term *free mineral acid* refers to strong acids such as H_2SO_4 and HCl in water.

For example, the action of hydrated metal ions with water may contribute to acidity,



Acidity of water is determined by titrating against a base using phenolphthalein as an indicator to detect endpoint (pH 8.2, where both strong and weak acids are neutralized), free mineral acid is determined by titration with a base to the methyl orange endpoint (pH 4.3, where only strong acids are neutralized).

Hardness: The hardness of water is essentially due to the presence of Ca^{2+} and Mg^{2+} minerals (mainly bicarbonate, sulphate and chloride) present naturally in water. A common manifestation of a hard water supply includes poor lathering of soap and scum accompanied by the formation of the curdy precipitate. The hardness can be of two types: temporary and permanent hardness.



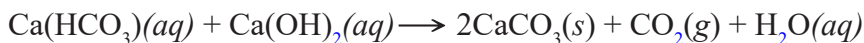
Soap Hard water Precipitate

Temporary hardness is due to the presence of bicarbonates of calcium and magnesium in water. It may be removed either by boiling the water or treating water with lime water.

By heating bicarbonate salts: High temperature causes decomposition of soluble bicarbonates into insoluble calcium carbonate precipitate which can then be removed from water using simple filtration technique.

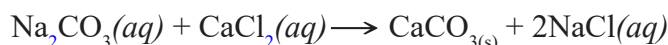


Treating hard water with lime water: Addition of calcium hydroxide to hard water precipitates out calcium carbonate which can be separated by filtration.

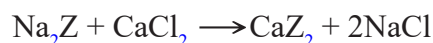


Permanent Hardness arises due to the presence of sulphates and chlorides of calcium and magnesium in water. It cannot be removed by simple boiling and hence requires special chemical treatment for softening. For example,

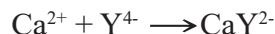
Treatment with washing soda - Addition of sodium carbonate (washing soda) to hard water converts soluble salts of calcium and magnesium into insoluble carbonate salts, which can further be separated by simple filtration.



Ion-Exchange - Ion exchange resins are organic polymers containing anionic functional groups to which the divalent cations (Ca^{2+}) bind more strongly than monovalent cations (Na^{+}). Inorganic materials called zeolites which are sodium aluminosilicate, $\text{Na}_3\text{Al}_2\text{SiO}_8$ or Na_2Z , (where $\text{Z} = \text{Al}_2\text{SiO}_8$) also exhibit ion-exchange properties. Zeolites possess high reactivity towards calcium and magnesium ions by forming insoluble calcium or magnesium zeolites. Thus, when hard water is passed through the resin, all the cations of soluble salts of calcium and magnesium responsible for hardness are retained with the resin and exchanged by sodium ions.



Sequestration- Sequestration is an effective method of softening water without removing Ca^{2+} and Mg^{2+} ions from the solution. The method involves the addition of a complexing agent, which forms a stable complex with calcium and magnesium ions and thus greatly reduces their concentrations in solution. For example, chelating calcium ions with excess EDTA ion (Y^{4-}), reduces the concentration of hydrated calcium ion and prevents the precipitation of calcium carbonate. EDTA, NTA (nitrilotriacetic acid), polyphosphate salts like sodium metaphosphate, $(\text{NaPO}_3)_n$ are the commonly used sequestering agents for water softening.



For streams and rivers, hardness varies between 1 to 1000 mg/L. Typical range include 47 mg/L to 74 mg/l CaCO_3 (Table 3).

Table 3. Relationship of Hardness and Classification of Natural water

Hardness as mg/L CaCO_3	Classification
0 - 60	Soft
61 - 120	Moderately hard
121 - 180	Hard

Biochemical Oxygen Demand (BOD)- It is the amount of dissolved oxygen required to degrade the organic matter from water by aerobic organisms at a given temperature over a specific period of time. It is widely used as an indication of the organic quality of water and thus indicates the pollution level. It is expressed in milligrams of oxygen consumed per litre of sample during 5 days (BOD 5) of incubation at 20 °C. When organic matter decomposes, microorganisms feed and oxidize the decaying material. Greater is the action of microbes, the more oxygen will be used up giving a high measure of BOD, leaving less oxygen for aquatic life in water.

6.9.3 Biological Characteristics

Microorganisms like bacteria, fungi, protozoa and algae are naturally present in water and act as living catalysts playing a significant role in a vast number of chemical processes in water and soil. Microorganism is responsible for formation of many sediments and mineral deposits, playing a significant role in secondary waste treatment.

Microbial contamination is one of the major concerns of water quality. Pathogenic microbes must be eliminated before water is used for domestic purposes. Total coliform bacteria are an entire group of bacterial species that are generally similar to and include the species *E. coli*, a thermotolerant coliform many of which are consistently present in very large numbers in the faeces of warm-blooded animals, including man. They can survive for a considerable time in water, making them a good indicator for the presence of other pathogenic bacteria. Untreated sewage, badly maintained septic systems, and farm animals with access to water bodies can cause high levels of fecal coliform bacteria to appear in and make the water unhealthy. Thus, the detection of *E. coli* in drinking water supplies provides strong evidence of fecal contamination. Hence, coliforms are considered as “indicator organisms” in an environmental sample to assess water quality before or in place of culturing other organisms. These bacteria help indicate measure of contamination levels.

Check Your Progress – III

Q.1 Explain why aluminium sulphate is used as a coagulant?

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Q.2 Discuss the application of zeolite in water treatment.

Water Chemistry

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Q.3 What is sedimentation ? What are the advantages of carrying out sedimentation process prior to the water treatment ?

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Q.4 Differentiate between permanent hardness and temporary hardness.

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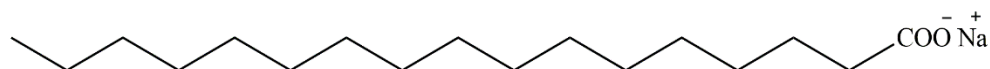
6.10 CHEMICAL SPECIES IN WATER

Water is a reservoir of a broad range of chemical species: organic and inorganic, largely dominate the quality of water. These include soaps, detergents, pesticides, oil, trace elements, organometallic compounds, inorganic anions.

6.10.1 Organic components in water

i. Soaps

Soaps are sodium or potassium salts of higher fatty acids such as sodium stearate, $C_{17}H_{35}COO^-Na^+$ produced from the hydrolysis of fats by saponification. They are good cleansers because of their ability to act as an emulsifying agent, lowering surface tension of water. The organic part of the soap is an ionic carboxyl head. Its hydrophilic nature allows soap to interact with water molecules *via* ion-dipole interactions and hydrogen bonding. The hydrophobic part of the soap is a long, non-polar hydrocarbon chain.



The hydrocarbon chains are attracted to each other by dispersion forces, forming cluster-like structures called micelles as shown in figure 7. In these micelles, the carboxylate end forms a negatively charged shell or micelle with the inner lying hydrocarbon chains. These negatively charged soap micelles repel each other and tend to remain dispersed in water. Oil and grease are non-polar hence remain insoluble in water.

Although soaps are good cleansers, they do have some disadvantages. Being salt of a weak acid, soaps are converted into free acids after attack by mineral acids.



These free fatty acids are less soluble and hence precipitate as soap scum, making the soap ineffective. Also, soaps form insoluble salts in hard water,

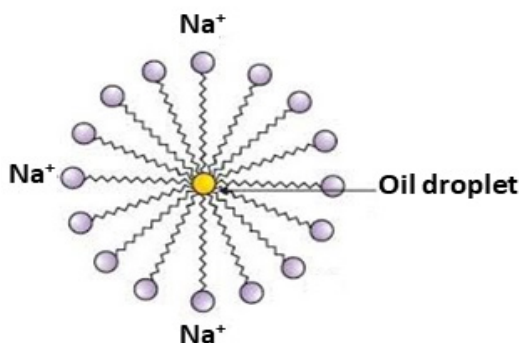
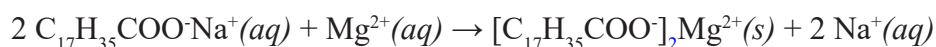
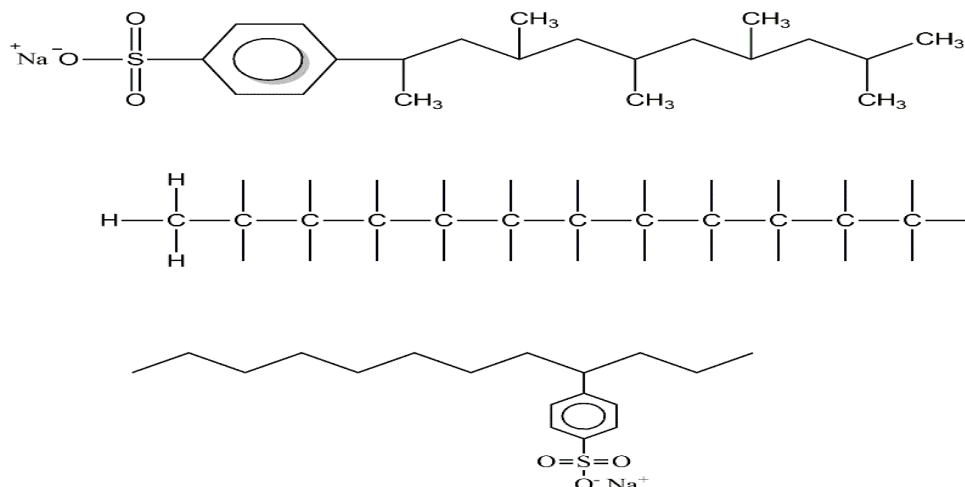


Figure 6.7. Structure of micelle

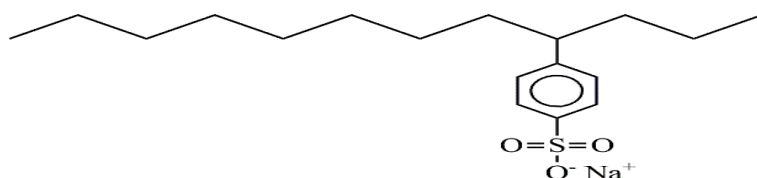
These insoluble salts of calcium and magnesium are ineffective cleansing agents. Hence, soaps are not regarded as potential cleansing agents for clothing, washing etc.

ii. Detergents

Unlike soaps, synthetic detergents are excellent cleansers as they neither form insoluble salts with hard water nor wash out of acidic waters. A molecule of detergent consists of two major components, surfactant and builder. Surfactant makes water “wetter” by lowering its surface tension. Owing to the amphiphilic structural attribute consisting of both hydrophilic group such as acid anion (SO_3^- , CO_3^{2-}) and a hydrophobic group (alkyl chain), surfactants break the interface between water and oil/dirt. For example,



Initially, alkylbenzene sulphonate (ABS) was used as the most common surfactant (e.g. Tetra propylene benzene sulphonate). However, due to a branched chain structure, ABS are non-biodegradable and are replaced by a biodegradable, linear alkyl sulphonate, LAS. The structure of LAS, α -benzenesulphonate is:



Most of the environmental problems associated with detergents are basically because of the second component i.e. builder. Polyphosphate like sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ is added as a builder that binds with calcium or magnesium ions. Thus, builders act as sequestering agents which render hardness causing calcium and magnesium ions inactive. Additionally, by imparting alkalinity to the detergent solution, builders further improve the cleansing qualities.

However, these phosphates-based builders are non-eco-friendly and often cause eutrophication in water bodies. An alternative to non-eco-friendly phosphates is nitrilotriacetic acid (NTA) which significantly reduces eutrophication. However, due to its toxic effects on aquatic life its usage is not recommended in synthetic detergents.

iii. Insecticides

Insecticide refers to chemicals, which are used to kill insects. Even though they are used indiscriminately in agriculture to improve productivity, they do lead to a serious environmental problem, especially water pollution. Being water soluble, they easily seep inside the ground and enter ground water aquifers. Contamination of a water body by insecticides drastically changes its physical, chemical and biological properties, making water toxic and unsuitable for uses. thereby They are classified into the following types:

1. Chlorinated hydrocarbons

Chlorinated hydrocarbon-based insecticides include DDT, aldrin, heptachlor, lindane, endrin, and toxaphene. The structures of these representative examples are shown in figure 8. These compounds have largely been ruled out because of their toxic nature and tendency to accumulate in food chains. For example, DDT, dichlorodiphenyltrichloroethane or is non-biodegradable. In the presence of air/moisture, it transforms to more toxic, DDD (Dichlorodiphenyldichloroethane). Also, it interferes with calcium metabolism process, especially in birds.

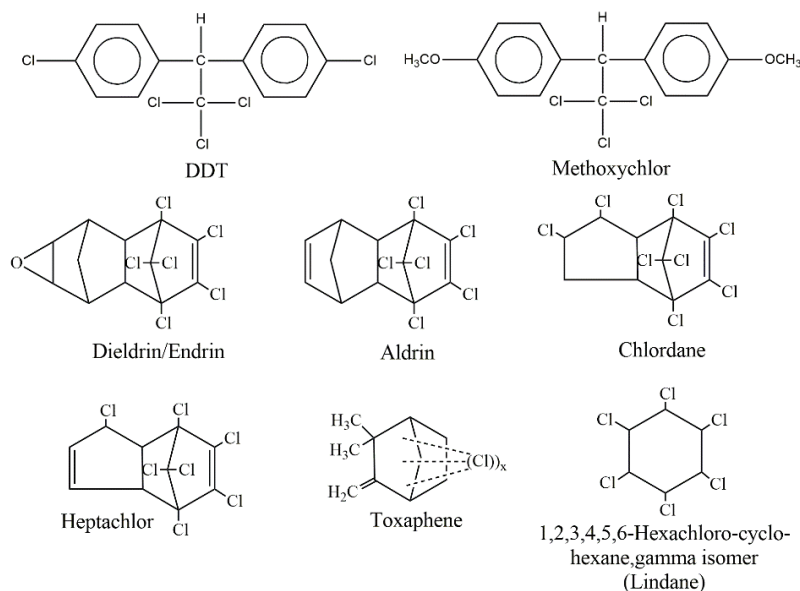


Figure 6.8 Some organochlorine insecticides

2. Organophosphate

Organophosphates are ester derivatives of phosphoric acid. For example, paraoxon, malathion, chlorpyrifos.

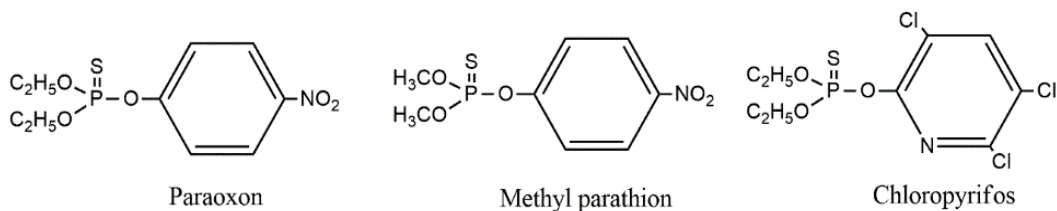
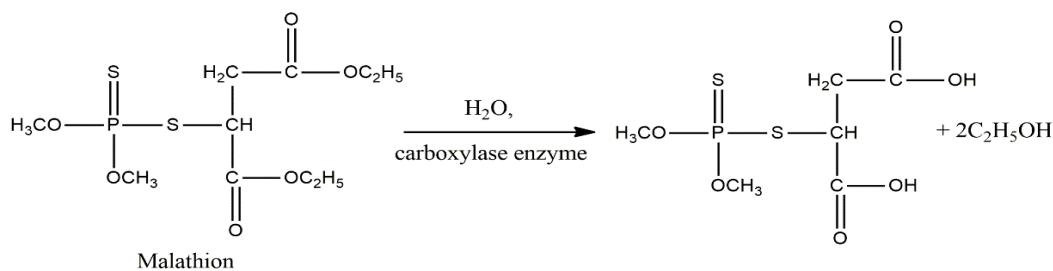


Figure 6.9 Some organophosphates insecticides

Although some organophosphorus compounds are highly toxic to humans, they are bio-degradable and usually break down in the environment and do not accumulate. For example, malathion is hydrolysed by carboxylase enzymes to relatively nontoxic products, as shown by the following reaction:



3. Carbamates

Organic derivatives of carbamic acid are known as carbamates. This group of insecticides include carbaryl, carbofuran, and pirimicarb (Figure 10).

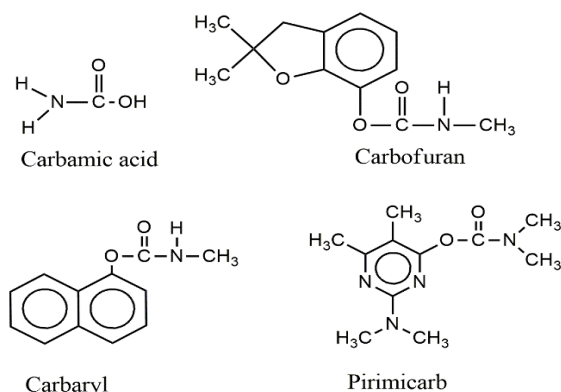
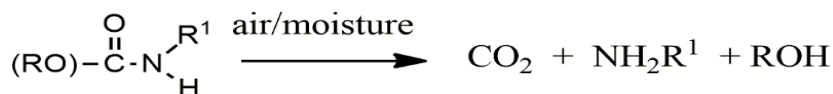


Figure 6.10 Carbamic acid and some insecticidal carbamates

They are widely used because of their high biodegradability than organochlorine pesticides and low toxicities than organophosphates pesticides.



Insecticides are weakly soluble in water than in oil(fat). They easily enter and attack the body of insect/pest. In addition, they have a high coefficient of bioaccumulation /biomagnification, which may be expressed as:

$$\text{Bioconcentration factor} = \frac{\text{Concentration of species inside body of organism}}{\text{Concentration of species in water/environment}}$$

Out of various categories of insecticides, chlorinated hydrocarbons especially DDT has a high coefficient of bioaccumulation

	Planktons	→ Insects	→ Birds
DDT (in ppm)	0.04	0.70	2.5 to 80

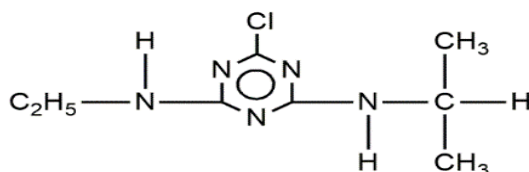
iv. Herbicides

Chemicals used to kill herbs, weeds, unwanted plants, without affecting the main crop. Initially, inorganic compounds such as NaAsO_3 , NaClO_3 , CuSO_4 were used.

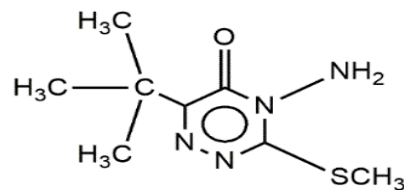
However, owing to their toxic and non-biodegradable behaviour, they were replaced by organic compounds. The organic herbicides are classified into follows:

1. Heterocyclic nitrogen compounds

These herbicides containing heterocyclic nitrogen atoms in ring structures and are termed as triazines which used to kill grassy weeds. They attack by blocking the stomata of unwanted herbs. Plants die due to lack of photosynthetic activity. For example, atrazine, metribuzin used to protect corn, soybean, sugarcane when discharged into water streams and pollute water significantly.



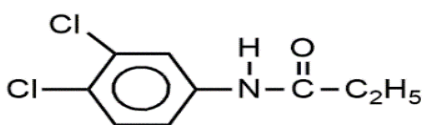
Atrazine



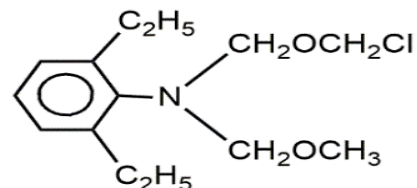
Metribuzin

2. Substituted amide derivatives

This group of herbicides consist of substituted amides. For example, propanil is used to kill grassy weeds in rice fields



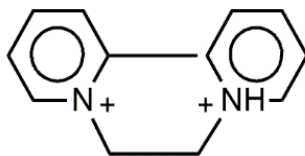
Propanil



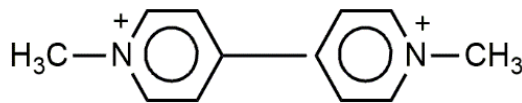
Alachlor

3. Bipyridilium Compounds

A molecule consists of two-pyridine rings. The two important pesticidal compounds of this category are diquat and paraquat, used to destroy crops of Marijuana



Diquat

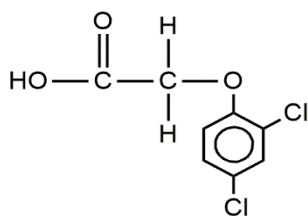


Paraquat

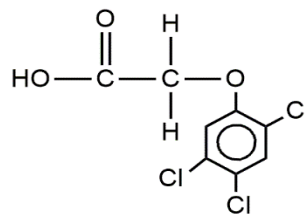
Quaternary amine groups acquire polar character, thus water soluble herbicide readily gets into the body of the plant along with water. Herbicides are not biodegradable; toxic; can cause diseases and even accidental death (case of paraquat); can be carried into rivers by rainwater or be leached to groundwater polluting these environments; some herbicides accumulate in the food chain and thus are toxic for animals, including man.

4. Chlorophenoxy compounds

This family of compounds include 2,4-Dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and are used for weed and brush control. They are even employed as military defoliants.



2,4- Dichlorophenoxyacetic acid



2,4,5 - Trichlorophenoxyacetic acid

v. Polychlorinated biphenyls

Polychlorinated biphenyls are present throughout the world in water, sediments, bird tissue and fish tissues. They are characterised by high chemical, thermal and biological stability, low vapour pressure, and high dielectric constants. As a result, they find applications as coolant insulation fluids in transformers and capacitors, for the impregnation of cotton and asbestos, as plasticizers and additives to epoxy paints. An extensive usage has resulted in their accumulation in the environment. These insoluble, dense, hydrophobic materials pose a serious concern to the water quality as a result of their bioaccumulation in fish.

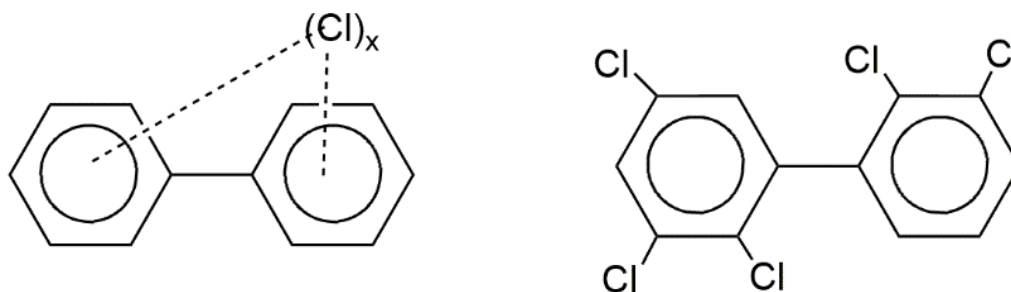


Figure 6.11 (a) General formula of polychlorinated biphenyls (left, where 'x' ranges from 1 to 10) and (b) a specific 5-chlorine congener

When the PCBs are discharged to the streams, the anaerobic bacteria degrade these PCBs to mono- and dichloro-derivatives by replacing Cl by H on the more highly chlorinated PCB molecules. The mono and dichloro-substituted PCBs are then degraded by aerobic bacteria which oxidise the PCB molecules and cleave the aromatic rings as shown in figure 12. Finally, the PCBs are degraded into inorganic chlorides, carbon dioxide and water.

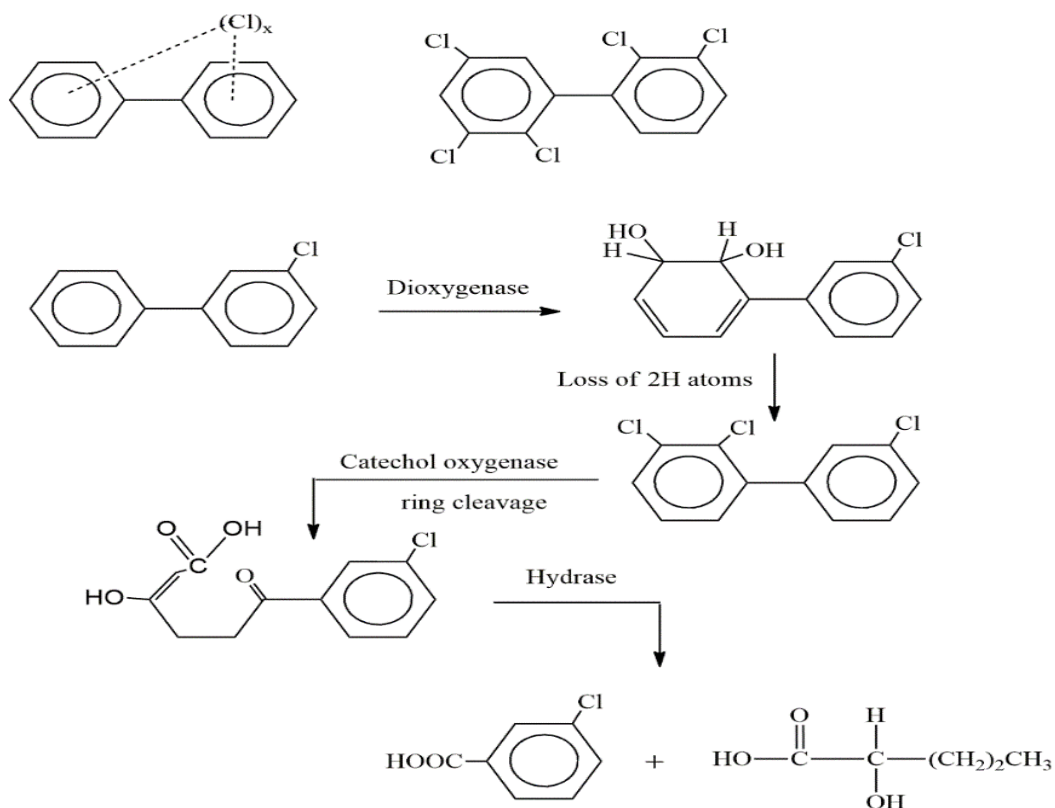


Figure 6.12 Enzymatic process involving attack of aerobic bacteria on mono-and dichloro-substituted PCBs

vi. Oil

Oil is a mixture of hydrocarbons containing paraffin, cycloparaffin, aromatic and heterocyclic compounds. Presence of oil and grease in surface water is toxic to aquatic life, especially in marine waters. It causes devastating physical effects, such as coating animals and plants with oil and suffocating them by oxygen depletion; form toxic products such as phenols, petroleum hydrocarbons, polyaromatic hydrocarbons, which are inhibitory to plant and animal growth, equally, mutagenic and carcinogenic to human beings.; destroy existing food supplies, breeding animals, and habitats; produce rancid odours; foul shorelines, clog water treatment plants, and form products that stay in the environment for many years. Other effects include deadly effects on fish by coating epithelial surfaces of gills, thus inhibits respiration and adversely impact the aesthetic value of shorelines and beaches. Even the thinnest layer of oil is highly impermeable to sunlight and oxygen, thus greatly hinders the photosynthesis by aquatic plants. Eventually, the concentration of dissolved oxygen in water body decrease leading to condition, Asphixiation.

6.10.2 Inorganic components in water

i. Metal ions and Trace elements

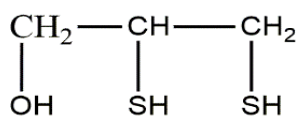
Trace elements are those elements that occur in water at concentrations of a few parts per million or even less. The important trace elements present in natural water are given in table 4. Of these, many are essential at low levels but toxic at high levels and tend to accumulate in food chains. Heavy metals are regarded as the most harmful of the elemental pollutants in the aquatic ecosystem because of their resistance to degradation under natural conditions. High concentrations of these

metals are released into the watercourses as a result of leaching from bedrocks, water drainage, runoff from riverbanks, and discharge of urban and industrial wastewaters.

Ca^{2+} is the most abundant cation in water and is responsible for hardness of water. It is essential human nutrition and a key element in the formation of teeth and bones. Sodium and potassium commonly exist as free ions. However, these cations are usually present in natural water in low concentrations. Other metal ions in natural water in a concentration of 1 mg/L or higher include aluminium, strontium, iron, manganese and zinc and non-essential metals like cadmium, mercury and lead which are toxic even in low concentrations. These metals possess high affinity towards sulphur, thus disrupt the functioning of sulphhydryl (containing -SH group) enzymes, controlling the speed of crucial metabolic processes in human body. As a result, metal bonded enzymes can no longer function normally and cause serious health concerns. They also bond to carboxylic acid and amino groups in proteins. The metal ions bind to cell membranes, hinder transport processes through cell wall.

Radionuclides also are trace elements and are formed in the environment by minerals present inside Earth's crust, atomic collisions by cosmic rays in the Earth's atmosphere, as well as by human activities. They also occur naturally in rocks and minerals and hence are frequently found in groundwater. The most common examples of radionuclides in groundwater are uranium, radium, and radon.

The heavy metal poisoning can be treated by administration of a compound that bonds to metal more strongly than the enzyme, such as British Anti-Lewisite (BAL), forming a combination which is soluble and hence can be easily excreted out of the body.



British Anti-Lewisite

Table 4. Important Trace Elements in Natural Water

Element	Maximum permissible limit (mg/L)	Sources	Effects and Significance
Beryllium	0.001	Coal, industrial waste	Toxic
Boron	5.0	Coal, detergents	Toxic
Chromium	0.1	Metal plating	Essential as Cr(IV), toxic as Cr(VI)
Copper	1.0	Metal plating, industrial and mining waste	Essential trace element, high concentrations toxic to plants

Fluorine (F ⁻)	0.05	Natural geological sources	Prevent tooth decay (0.05 mg/L), high concentrations cause fluorosis
Iodine (I ⁻)	0.02	Natural brine, industrial waste	Prevents goiter
Iron	0.3	Industrial waste, corrosion, acid-mine drainage	Essential nutrient, damages plumbing fixtures
Molybdenum	0.05	Industrial waste, natural sources like legumes	Toxic
Manganese	0.05	Industrial waste, acid-mine drainage	Toxic to plants, damage plumbing fixtures
Selenium	0.01	Natural sources: seafood, coal	Essential at low concentrations and toxic at high concentrations
Zinc	5.0	Industrial and mining waste, metal plating	Essential elements, boost immunity
Heavy metals			
Lead	0.01	Industrial and mining waste	Toxic
Mercury	0.001	Volcanic eruptions, fossil fuels like coal	Toxic, methylmercury toxic to lifeforms
Cadmium	0.005	Electroplating, pigment manufacturing	Toxic, damages kidney
Arsenic	0.05	Geothermal process, mining waste	Toxic, impairs respiration

The toxicities associated with common heavy metals are discussed as follows:

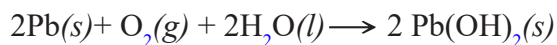
a. Cadmium

Cadmium is discharged in water body through industrial and mining wastes. Acute cadmium poisoning causes high blood pressure, kidney damage, destruction of testicular tissue and red blood cells. Its chemical similarity with zinc ions it replaces zinc ions in some enzymes, thus altering their stereo structures and impairing the catalytic activity. Excess cadmium causes anaemia, hypertension, development of tumours and bone marrow disorder. The best described incident relating to cadmium poisoning is the Ouch-Ouch disease among residents along the Jintsu River in Japan. It resulted in kidney failure and softening of bones accompanied by severe pain in bones and spine.

b. Lead

Lead is released from industrial and mining sources. Leaded gasoline is the major source of atmospheric and terrestrial lead, much of it enters the natural waters. In

addition, natural ore like galena (PbS) release lead to natural waters, where it exists as Pb^{2+} as $\text{Pb}(\text{OH})_2$

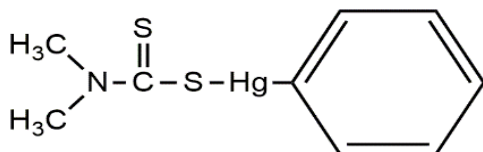


In excess concentrations, lead starts accumulating in body in body, displacing Ca^{2+} from bones resulting in weakening of bones and teeth. Being soft acid, it possesses a strong affinity towards -SH enzyme, thus hinders with their activity. Acute lead poisoning causes dysfunction in kidneys, reproductive system, liver and brain.

c. Mercury

Elemental mercury enters the environment through discharges from various natural (volcanic eruptions, forest fires) and anthropogenic sources such as industrial and mining activities, sewage waste, pharmaceutical products, amalgam dental fillings, discarded laboratory chemicals, batteries, broken thermometers, and many more. Elemental mercury vapour damages the nervous system when exposed at high concentrations. Inorganic mercury compounds such as HgS , $\text{Hg}(\text{NO}_3)_2$, HgCl_2 are rapidly accumulated in kidneys and damage them. Once deposited, microorganisms convert inorganic mercury into more toxic, organomercury compounds. These compounds rapidly bioaccumulate collect in organisms and 'biomagnify' as the concentrations increase up each level of the food chain.

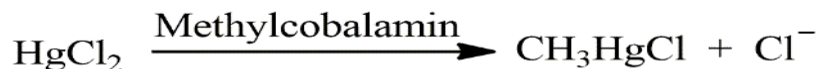
The organic mercury compounds, such as phenyl mercuric dimethyldithiocarbamate, are used commercially as pesticides. These alkyl mercury compounds are resistant to degradation, hence are potential environmental hazard than aryl or inorganic compounds.



Phenyl mercuric dimethyldithiocarbamate

Additionally, mobilization in methylated forms, $(\text{CH}_3)_2\text{Hg}$ and CH_3Hg in presence of specific bacteria pose a serious concern as heavy metal pollutants in water. These methylated forms are highly stable ($t_{1/2} = 70$ days), soluble in fat tissues and have a high coefficient of bioaccumulation. Other toxicological effects include strong affinity for sulfhydryl enzymes, potential to cross blood-brain and blood-placenta barrier. A strong manifestation of mercury poisoning was realised in Minamata disease (1953-1960) in the Minamata Bay area of Japan which had been contaminated with mercury waste (as HgCl_2) dumped from industries along the bay. More than 2000 people consumed mercury contaminated fish (total Hg concentrations > 5-20 ppm) and suffered from neurological disorders, paralysis, blindness, chromosome breakage, and birth effects. The major damage came due to the conversion of Hg^{2+} to more toxic CH_3Hg^+ in presence of acidic industrial wastewater.

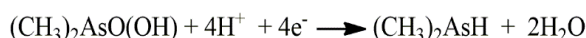
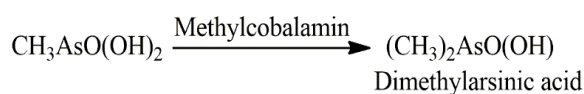
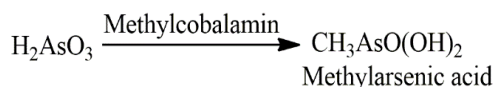
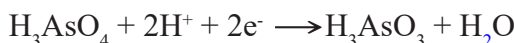
The methylating agent responsible for converting inorganic mercury to methylmercury compounds is an analogue of vitamin B₁₂, methylcobalamin, which is generated as an intermediate during the synthesis of methane by anaerobic bacteria. Under neutral or alkaline conditions, the formation of volatile dimethylmercury, (CH₃)₂Hg, is favoured.



d. Arsenic

Arsenic is released in the environment from natural sources like volcanic activities, weathered rocks, and forest fires or human activities such as combustion of fossil fuels, use of arsenical fungicides, herbicides and insecticides in agriculture, and wood preservatives. Arsenic from weathered rocks and soil percolates into the groundwater. In aquatic ecosystem, inorganic arsenic derived from rocks such as arsenic trioxide (As₂O₃) and orpiment (As₂S₃) are dominant. In groundwaters, arsenic exists primarily as oxy anions representing two oxidation states: As(III), H₂AsO₃⁻(aq) and As (V), H₂AsO₄⁻(aq), where the former is more toxic.

Acute poisoning results from the ingestion of more than about 100 mg of arsenic, while chronic exposure can cause arsenicosis, including skin lesions, blackfoot disease, peripheral vascular disease, and cancers. Like mercury, bacterial action also converts inorganic arsenic to more mobile and toxic organic forms, according to the following reactions:



Arsenic toxicity impairs cellular respiration by preventing ATP formation by various mitochondrial enzymes, and uncouple oxidative phosphorylation. Arsenate, AsO₄³⁻ ion acts as phosphate analogue and replaces phosphate in Glycolysis -ATP forming process, as shown in figure 13. The product of this reaction is 1-arseno-3-phosphoglycerate, which is unstable and spontaneously hydrolyses to form 3-phosphoglycerate and no ATP is produced.

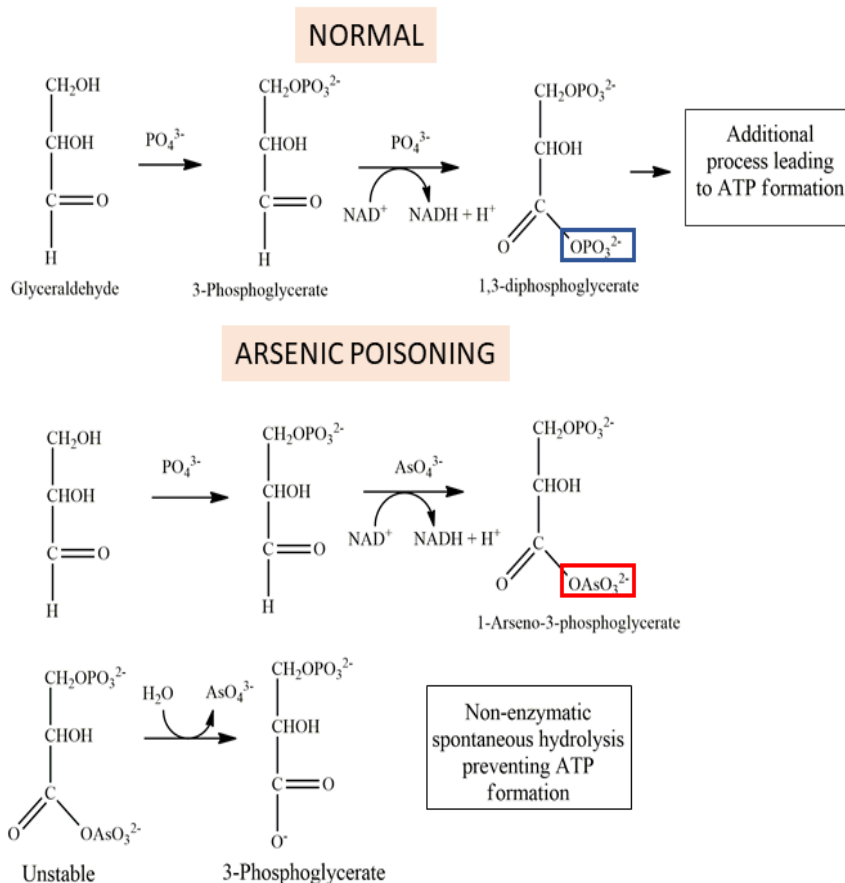


Figure 6.13 A schematic representation of arsenic poisoning and glycolysis

ii. Inorganic species

A variety of inorganic species including metals, neutral and anionic species are present in water under varying conditions.

a. Cyanide

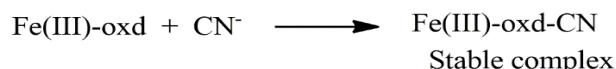
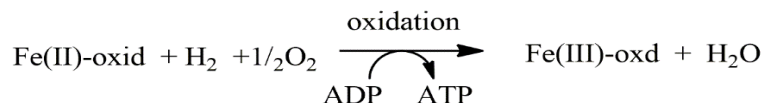
Cyanide is released from natural substances, for example seeds of apples, apricots, cherries etc. contain chemicals which metabolize to cyanide. The seeds contain amygdalin, a glycoside unit bonded to cyanide ion. Cyanide is released in air, water, and soil through natural processes and industrial activities.

The most toxic form of cyanide is free cyanide ion and hydrogen cyanide, HCN, either in a gaseous or aqueous state. The presence of cyanide ion in drinking water is a serious health concern. Once it enters the bloodstream, cyanide ion forms a stable complex with cytochrome oxidase, an enzyme that promotes the transfer of electrons in the mitochondria of cells during the synthesis of ATP. As a result, cells cannot utilize the oxygen present in the bloodstream, resulting in cytotoxic hypoxia or cellular asphyxiation. The lack of oxygen causes a shift from aerobic to anaerobic metabolism, leading to the accumulation of lactic acid in the blood. The combined effect of the hypoxia and lactate synthesis causes depression of the central nervous system that may result in respiratory arrest and death.

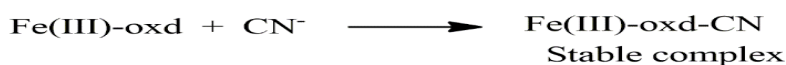
The physiological activity of cytochrome enzyme involves reversible oxidation-reduction of iron species, that cycle between ferric and ferrous states.



Once Fe(II)-oxidase is being formed, it oxidises back to Fe(III)-oxidase, the electron being released assists in conversion of ADP to ATP.



However, in presence of CN^- ion, a very stable complex with trivalent iron of cytochrome oxidase is formed. Hence, CN^- ion block the active site of ferricytochrome oxidase enzyme, thus inhibiting both cellular oxygen utilization and **ATP production**.



b. Sulphate (SO_4^{2-})

Sulphate is discharged into water from naturally occurring minerals contained in soils, aquifer rocks and sediments. Agricultural run-off, Industrial and mining processes releasing sulphur dioxide gas (falls as acid rain), also contributes to the sulphate content of surface waters. As such, sulphates are non-toxic to living organisms at normal concentrations. Problems arise due to their ability to form strong acids which change the pH. High levels of sulphate in water (above 250 ppm) may have a laxative effect, cause dehydration and are detrimental to the human health

c. Chloride (Cl^-)

Chloride enters surface water from sources like rocks containing chlorides, agricultural run-off, waste water from industries, oil well wastes, and effluent waste water from water treatment plants. Chlorides corrode metal, affecting the taste of food stored in metal containers. Fish and aquatic communities cannot survive in high level of chlorides. In humans, extracellular chloride is responsible for the osmotic activity of body fluids and maintains electrolytic balance in the body.

d. Fluoride (F^-)

Naturally, fluoride enters water through dissolution of minerals like fluorite (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). Optimum concentration in drinking water is vital for humans as it helps to avoid caries and prevent tooth decay. The maximum permissible limit of fluoride in drinking water is 1.5 ppm. Excess

fluoride contamination in water causes dental fluorosis and skeletal fluorosis, which cause bone and joint pain.

e. Nitrite (NO_2^-)

Nitrite ion is present in water with a relatively narrow pE range, rarely present in drinking water at levels over 0.1 mg/L. It is usually added as a corrosion inhibitor in some industrial process water. High concentrations of about 1.0 mg/l of nitrites can produce a serious condition in fish called “brown blood disease”. In humans, nitrites react directly with haemoglobin producing methaemoglobin. Methaemoglobin impairs oxygen carrying capacity of red blood cells and causes methemoglobinemia or “blue baby disease”.

f. Nitrate (NO_3^-) and Phosphate (PO_4^{3-})

Nitrate is essential for life and is found naturally in soil and water. It is formed during microbial decomposition of organic matter. Several nitrogenous fertilizers are applied to crops to improve productivity. Unfortunately, nitrogen is extremely soluble and can be leached into groundwater, from it enters the water streams. Ground water with a concentration of nitrate greater than 10mg/l is considered as hazardous as per EPA (Environmental Protection Agency). High nitrate concentrations in drinking water cause prostate and gastrointestinal cancer. It is hazardous to infants and pregnant women and causes methemoglobinemia or blue baby syndrome due to deficiency of oxygen in a foetus of a pregnant woman.

Similar to nitrate, an element vital for cellular growth and reproduction, phosphorus is one of the key elements in aquatic chemistry. The permissible limit phosphorous in drinking water is 5 mg/L, however, beyond that limit, it causes osteoporosis and kidney damage.

Phosphorus is discharged from point sources like sewage effluents and industrial discharges, and non-point sources including natural decomposition of rocks and minerals, agricultural runoff, erosion and sedimentation, animal waste, artificial fertilisers. Phosphorus exchange with sediments pave the way for the discharge of the element in watercourses, making phosphorous available for algae and therefore contributes to eutrophication.

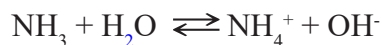
Eutrophication

It refers to the deteriorated condition of a water body with excess algal growth. The phenomenon involves the entry of plant nutrients, typically nitrates and phosphates which are the limiting nutrients for algal growth in many freshwater ecosystems. According to Liebig's Law of minima, “the growth of the plant is controlled by a limiting nutrient, the nutrient present in minimum quantity”. With the heavy application of fertilizers on agricultural lands, the excessive fertilisers are washed away by rains into river or lakes and the discharge of phosphate rich detergents and washing powders in sewage serves as a food source of phytoplankton, leading to eutrophication. It induces algal bloom where the water becomes densely populated with phytoplankton. A large number of floating phytoplankton produce oxygen during day time, however, the amount of dissolved oxygen will be greatly reduced

during night. This, in turn, affects photosynthesis by submerged vegetation. As a result, dissolved oxygen levels decrease dramatically. Besides this, growth of phytoplankton is followed by massive algal death due to exhaustion of nutrients. Eventually, dead biomass starts accumulating in the bottom of the lake where it decomposed aerobically by microorganisms and recycle nutrients carbon dioxide, phosphorus, nitrogen, and potassium needed for plant growth. The decomposition process further depletes the dissolved oxygen to such a level that most of aquatic life, especially fish die of suffocation and asphyxiation. Thus, an anoxic (oxygen-free) environment is created at the bottom of the lake, with a rise in organisms capable of surviving under anaerobic conditions. Eutrophication not only reduces gaseous exchange between water body and atmosphere, but is also responsible for pungent odour and undesirable colour of the water body.

g. Ammonia(NH₃)

Ammonia, soluble in water, is released naturally during biological degradation product of nitrogenous organic waste in water. Ammonia is sometimes added to drinking water, where it reacts with chlorine to provide residual chlorine that acts as a disinfectant. It also enters water body through discharge of industrial effluents containing ammonia and fertilizers. Under aqueous conditions, it is usually present as NH₄⁺



Although the ammonia is a nutrient required for life for formation of amino acids, excess ammonia may accumulate in the living organism and cause alteration of metabolism and is toxic to aquatic life at concentrations ranging from 0.53 to 22.8 mg/L. Toxicity increases with pH and temperature conditions. Under alkaline conditions, fish may suffer osmoregulatory and respiratory problems.

h. Hydrogen sulphide (H₂S)

Hydrogen sulphide gas is released in the environment through natural and industrial sources. The anaerobic decay of sulphur rich organic matter releases hydrogen sulphide in water. The objectionable rotten-eggs associated with this gas odour makes water unfit for drinking, household use, and industrial purposes. Under aqueous conditions, H₂S is a weak diprotic acid with pK_{a1} of 6.99 and pK_{a2} of 12.92. Thus, Sulphide ion does not exist as such in natural water and precipitates metal sulphides on interaction with heavy metal ions, releasing H₂S gas. The dissolved gas, in turn, corrode plumbing metals, such as iron, steel, copper and brass and exposed metal parts in washing machines and other water-using appliances and interferes with the effectiveness of water softeners.

Dissolved gases – oxygen for fish and carbon dioxide for photosynthetic algae are vital for the survival of aquatic life. Gases like nitrogen are undesirable as it causes fish death.

The solubility of gases in water can be quantitatively estimated by **Henry's Law**, which states that the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid.

$$X_g = H P_g$$

where:

P_g = partial pressure of gas

H = Henry's law constant

X_g = aqueous concentration of the gas

The Henry's law constant is a function of nature of gas or volatile organic compounds, temperature of the liquid and constituent of the liquid (water). The values of Henry's constant for various gases that are slightly soluble in water at 20 °C are shown in Table 5.

Table 5. Henry's Law Constants for gases in water at 25 °C

Gas	Henry's constant, KH (molL-1atm-1)
Oxygen (O ₂)	1.28 x 10 ⁻³
Nitrogen (N ₂)	6.48 x 10 ⁻⁴
Hydrogen (H ₂)	7.90 x 10 ⁻⁴
Carbon dioxide (CO ₂)	3.38 x10 ⁻²
Methane (CH ₄)	1.34 x 10 ⁻³
Nitric oxide (NO)	2.0 x 10 ⁻⁴

6.11.1 Oxygen in water-

Dissolved Oxygen: It refers to the amount of gaseous oxygen (O₂) dissolved in an aqueous solution. Oxygen enters water by diffusion from the surrounding air, by aeration (rapid movement), and as a waste product of photosynthesis of algae. The dissolved oxygen is crucial for the survival of aquatic life. The consumption of dissolved oxygen in degrading organic matter by microorganisms pose a serious threat to aquatic life. Many fishes die not from the toxicity of pollutants but from a deficiency of oxygen which is being consumed in the biodegradation of pollutants. The hypoxic condition in water body (DO< 3mg/L) leads to reduced cell functioning and disrupts circulatory fluid balance in an aquatic system, leading to death.

It is important to understand the effect of temperature on the solubility of gases in water. The solubility of oxygen in water decreases from 14.74 mg/L at 0°C to 7.03 mg/L at 35°C. At higher temperatures, the decreased solubility of oxygen is coupled with the increased respiration rate of aquatic organisms. This eventually gives rise to a condition wherein high oxygen demand accompanied by lower solubility of the gas in water results in severe oxygen depletion.

6.11.2 Carbon dioxide in water

Dissolved CO₂ in water is usually represented as H₂CO₃, a weak acid. The equilibrium constant for the reaction



Carbon dioxide enters water through the atmosphere and microbial decay of organic matter. Carbon dioxide, and its ionization products, bicarbonate ion (HCO₃⁻), and carbonate ion (CO₃²⁻) significantly influence the chemistry of water.

Algae in water body consume dissolved CO₂ in the synthesis of biomass. The following equilibrium have a strong buffering effect upon the pH of water, for example,

Equilibrium of dissolved CO₂ with gaseous carbon dioxide in the atmosphere,



Equilibrium of CO₃²⁻ ion between aquatic solution and solid carbonate minerals,



Carbon dioxide constitutes about 0.037% by volume of normal dry air. A reflection of its low concentration is realised in low alkalinity of water which exists in equilibrium with the atmosphere containing a very low level of carbon dioxide. Nevertheless, the formation of HCO₃⁻ and CO₃²⁻ greatly increases the solubility of carbon dioxide in water. High concentrations of free carbon dioxide in water may adversely affect respiration and gas exchange of aquatic animals and may even cause death. The concentration of free carbon dioxide should not exceed levels of 25 mg/L in water.

A large proportion of the carbon dioxide found in water result from the bacterial decomposition of organic matter. Even algae, consumers of CO₂ in photosynthesis, produce it *via* metabolic processes in the absence of light. Water seeping through layers of decaying organic matter while permeating through the ground, it dissolves CO₂ so released by the respiration of organisms in the soil. Later, it moves through limestone formations and dissolves calcium carbonate, contributing to the formation of limestone caves.



6.12 ORGANIC MATTER AND DISSOLVED HUMIC SUBSTANCES IN WATER

Organic matter is a complex mixture of organic compounds including aliphatic and aromatic hydrocarbons bearing functional groups such as amides, carboxyl, hydroxyl, and ketones and others in smaller amounts. On account of the interactions between the hydrological cycle and the biosphere and geosphere, water usually contains organic matter. The amount and property of organic matter vary with the origin of water. It also depends on the biogeochemical cycles of the surrounding environment. As a carrier of metals and other hydrophobic organic chemicals, the presence of organic matter in water is a major concern because it greatly affects the quality of water in terms of taste and odour, colour, and bacterial growth in the water distribution system

The natural sources like soil or anthropic sources like organic amendments (compost or biosolids) or spillage from sanitary landfills may release the organic matter. The organic matter may further be categorized as the abundant form, which is insoluble under normal soil conditions and the dissolved organic matter (DOM) which enters into water body. Dissolved organic matter (DOM) consists of soluble organic part derived from the partial decomposition of organic matter, including soil organic matter, plant residues, and soluble particles released by living organisms, including bacteria, algae, and plants. Depending on the nature of the components present in Dissolved organic matter, it can retain and/or mobilize organic and inorganic pollutants in the environment. The common route for the organic matter in soil and natural waters are humic substances which lend a yellowish- brown colour to a water body. These humic substances are produced by the decomposition of dead plant tissues, dead organisms, and excrement of living organisms by micro-organisms. Organic matter mostly consists of humic (humic acid (HA) and fulvic acid (FA)) and non-humic fractions, which are carbohydrates, amino acids, and proteins

The dissolved humic substances in surface and ground waters are present in concentrations ranging from less than 1 mg/L to greater than 100 mg/L. These compounds are even strong complexing agents for many trace metals present in water and also form stable soluble complexes with radionuclides. Formation of such water-soluble complexes is of particular interest because complexation increase concentrations of these metal ions in natural waters far greater than the concentrations that could be expected on the basis of the solubilities of inorganic species. The metals may be

transported in flowing groundwaters, followed by decomposition of the complex at elevated temperatures, and all this is believed to give rise the formation of ore deposits.

Check Your Progress – IV

Q.1 Though detergents can be used more effectively in hard water but their usage is discouraged. Why ?

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Q.2 Why is the use of DDT as insecticide banned ?

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Q.3 Discuss briefly the toxic effects of oil pollution.

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Q.4 Out of the several forms in which mercury occurs, which form is most toxic ? Give reasons.

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Q.5 Discuss the toxic effects of Arsenic in water

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.....

Q.6 Discuss toxic effects of cyanide on human health

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.....

Q.7 A large number of fish are suddenly found floating dead on a lake. There is no evidence of any dumping of the pollutant but there is an abundant growth of phytoplanktons. Suggest a reason for the death of the fishes.

.....

.....

Q.8 Write a short note on eutrophication

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.....

6.13 LET US SUM UP

In this chapter, highlighting the importance of water, we have discussed about the distribution and unique properties of water. Apart from various other factors, the properties of water also depend on the salt content in it. Thus, the physical and chemical properties of fresh water differs from those of sea water of. The presence / addition of chemical species, gases, and organic matter in the water not only alters its physical properties such as colour, odour etc., but also changes its chemical and biological characteristics.

6.14 KEY WORDS

Triple Point: The temperature and pressure at which the solid, liquid and vapour phases of a pure substance can coexist in equilibrium

Hydrological Cycle: The sequence of conditions through which water passes from vapor in the atmosphere through precipitation upon land or water surfaces and ultimately back into the atmosphere as a result of evaporation and transpiration.

Coagulation: The process of a liquid becoming viscous or thickened into a coherent mass

Sedimentation: The process of depositing or settling down of sediments

Flocculation : The process by which individual particles aggregate into clot like mass or precipitate into small lumps. Flocculation normally occurs as a result of a chemical reaction between the clay particles and another substance, usually salt water.

Micelles: A cluster of molecules that is formed in certain solution, such as soap solution

Eutrophication: Excessive richness of nutrients in a lake or other water body, frequently due to run-off from the land, which causes a dense growth of plant life, mainly the algae

Blue baby Syndrome : It is also known as infant methemoglobinemia, and is a condition where a baby's skin turns blue. This occurs due to a decreased amount of haemoglobin in the baby's blood. It is caused due to excessive consumption of nitrate in drinking water

Minamata disease : It is a chronic poisoning by alkyl mercury compounds from industrial waste, characterised by impairment of brain function such as speech, sight and muscular coordination.

Henry's Law : A law stating that the mass of a dissolved gas in a given volume of solvent at equilibrium is proportional to the partial pressure of gas.

Humic Substances : an organic residue of decaying matter

Humins : A black humic substance that is insoluble in water

6.15 REFERENCES AND SUGGESTED FURTHER READINGS

1. Environmental Chemistry, Colin Baird and Micheal Cann, Fifth Edition, W H Freemann & Company, New York, US, 1995.
2. Environmental Chemistry, Stanley E. Manahan, Seventh Edition, Boca Raton, FL, USA, CRC Press, 2000.
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6. Chemistry for Environmental Engineering and Science, Clair N Sawyer, Perry L McCarty and Gene F Perkin, Fifth Edition, Mc Graw Hill-Higher Education, 2003
7. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, Werner Stumm, James J. Morgan, Third Edition, Wiley-Blackwell, 2010.

ANSWERS TO CHECK YOUR PROGRESS

Check Your Progress – I

Ans 1. Because of water pollution, aquatic animals and plants die and this creates disturbance in ecological balance.

Ans 2. About 97% of the total available water is present in the oceans (marine water), while only 3% is fresh water. Out of remaining 3% freshwater, 79% is stored in glaciers and polar ice caps, 20% is stored in aquifers or soil moisture, and only 1% is surface water (primarily lakes and rivers).

Ans 3. Water is capable of dissolving a variety of different substances, which is why it is such a good solvent. And, water is called the “universal solvent” because it dissolves more substances than any other liquid.

It is water’s chemical composition and physical attributes that make it such an excellent solvent. Water molecules have a polar arrangement of the oxygen and hydrogen atoms—one side (hydrogen) has a positive electrical charge and the other side (oxygen) had a negative charge. This allows the water molecule to become attracted to many other different types of molecules. Water can become so heavily attracted to a different molecule, like salt (NaCl), that it can disrupt the attractive forces that hold the sodium and chloride in the salt molecule together and, thus, dissolve it.

Ans. 4. (b)

Check Your Progress – II

Ans. 1 Hydrological cycle is responsible for purification and redistribution of water on the Earth.

Ans 2 (i) Presence of excess amount of salt in sea water is responsible for differentiating fresh water ecosystem from marine ecosystem.

(ii) Ground water is an important source but can easily become contaminated and polluted. Pollutants such as oil, chemicals, pesticides, waste from landfills etc can move into the ground water through soil, making the groundwater polluted.

Check Your Progress – III

Ans.1 Aluminium sulphate is frequently used as coagulant in water treatment. Filter alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ when added to waste water, the hydrated aluminium ion which is acidic in nature, reacts with base to form gelatinous precipitate of aluminium hydroxide that carries suspended matter with it as it settles. Thus, the alkalinity of water is also reduced.

Ans.2 It is used as ion exchanger for softening hard water.

Ans.3 Sedimentation is one of the most basic steps of purifying water. It offers several advantages- it removes turbidity, makes the subsequent process easier, less number of chemicals are required for subsequent treatment and is cost effective.

Ans.4 Temporary hardness is due to the presence of bicarbonates of calcium and magnesium in water and it can be removed easily.

Permanent hardness is due to chlorides and sulphates of calcium and magnesium and is difficult to remove.

Check Your Progress – IV

Ans.1 Most of the environmental problems associated with detergents are basically because of an important component, builder. Polyphosphate like sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ is added as a builder that binds with calcium or magnesium ions. Thus, builders act as sequestering agents which render hardness causing calcium and magnesium ions inactive.

But, these phosphates-based builders are non-eco-friendly and often cause eutrophication in water bodies.

Ans.2 DDT is highly mobile with high coefficient of bioaccumulation. It gets converted into even more toxic compound, DDD, on exposure to air and moisture.

Ans. 3 Presence of oil and grease causes devastating physical effects, inhibition of plant and animal growth, produces rancid odour, clog the water treatment plant, non-biodegradable, hinders photosynthesis, causes asphyxiation.

Ans.4 CH_3Hg^+ is the most toxic form, as it able to cross the blood-brain as well as blood-placental barrier. It has a very high coefficient of bioaccumulation.

Ans.5 Arsenic toxicity impairs cellular respiration by preventing ATP formation. It may be further explained with equations

Ans. 6 CN^- ion block the active site of ferricytochrome oxidase enzyme, thus inhibiting both cellular oxygen utilization and ATP production. It may be further explained with equations

Ans.7 phytoplankton are decomposed by aerobic bacteria, resulting in DO drops

Ans.8 Excessive richness of nutrients, especially nitrates and phosphates, in a lake or other water body, which causes a dense growth of plant life, mainly the algae is known as eutrophication.

Terminal Questions

1. Explain physical properties of water?
2. Explain various ways in which the water bodies are affected by eutrophication?
3. Explain the toxic effects of the following ions present in water.
 - i. Cyanide ii. Arsenic iii. Mercury
4. Describe the equilibria involving carbonic acid, bicarbonate ion and carbonate ion?

UNIT 7 : SOIL CHEMISTRY

Structure

- 7.0 Introduction
- 7.1 Objectives
- 7.2 Origin and Nature
 - 7.2.1 Soil Composition
- 7.3 Soil Formation
 - 7.3.1 Soil Forming Process
- 7.4 Soil Chemical Properties
 - 7.4.1 Soil Acidity
 - 7.4.2 Ion Exchange Cation Exchange Capacity
- 7.5 Macro and Micronutrients in Soil
 - 3.5.1 Soil Macronutrients
 - 3.5.2 Soil Micronutrients
- 7.6. Soil Fertility
- 7.7. Let Us Sum Up
- 7.8. Key Words
- 7.9 References and Suggested Further Readings
- 7.10 Terminal Questions

7.0 INTRODUCTION

Derived from the Latin word ‘solum’, soil is a natural body of mineral and organic components that form the immediate surface of the earth. Formed as result of unabated modification of the earth’s crust by physical and biological agents, soil is a direct interface between atmosphere, lithosphere, hydrosphere and the biosphere that serves as a consolidated medium for further changes and developments in the constant evolution of the earth’s surface. A complex mixture of decaying organic matter, weathered mineral particles, water, gases and living organisms; soil is a natural incubating medium and habitat to not only plants but all terrestrial life forms. The physical characteristics and composition of soil largely depend upon climate, geographical location and composition of the parent material.

The study of soil is important as it is a vital natural source for food and renewable natural resources on which the society is largely dependent. In general, there are two approaches towards the scientific study of soil, pedology and edaphology. While pedology is the study of soil formation, classification and morphology; edaphology focuses on the influence of soil on living beings. Basically, considering soil as a natural habitat for plants, edaphology deals with study of soil productivity and conservation.

This unit has been designed to focus on the chemistry of soil. Soil composition, processes of soil formation and soil profile are discussed in this unit. Detailed overview of physical and chemical properties of soil and soil fertility has also been given.

7.1 OBJECTIVES

After reading this unit, you will be able to

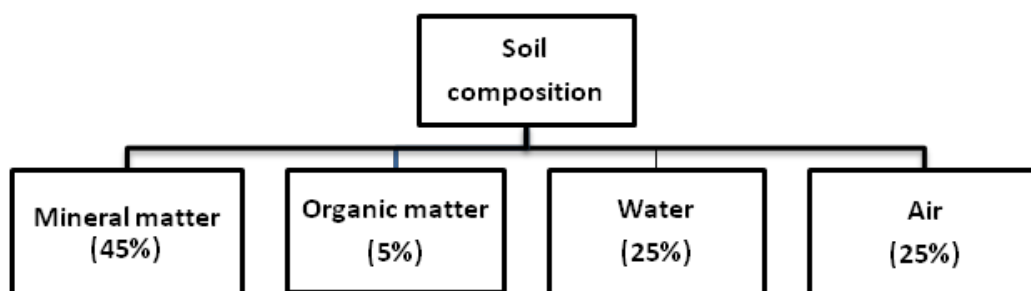
- understand the composition and profile of the soil,
- describe the properties of soil,
- explain the process of weathering,
- describe ion exchange properties of soil,
- explain the role of primary and secondary minerals,
- explain the role of pore spaces in soil, and
- explain various causes and the importance of soil pH.

7.2 ORIGIN AND NATURE

The formation of soil is initiated by physical and chemical weathering of rocks under the action of various atmospheric elements such as running water, wind, changes in temperature and living organisms. Perpetual modification of the earth's crust by these elements along with a myriad of complex processes involving interaction of rocks, flora and fauna, micro-organisms and production activities of man make the soil acquire characteristic colour, texture and pH etc.

7.2.1 Soil composition

The soil is a metre-deep layer with basic composition including mineral matter, organic matter, water and air along with micro-organisms. Typically, soil is constituted of 45% of inorganic or mineral matter; 5% organic matter; 25% water and 25% air.



Inorganic or Mineral matter:

The inorganic matter of the soil is a matrix of mineral particles obtained by decomposition and disintegration of the parent rocks by varying degrees producing particles of various shapes and sizes (Table 3.1).

Mineral Particle	Particle Size (mm)
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Clay	< 0.002
Silt	0.02 to 0.002
Sand	0.02 to 2.0
Gravel	2.0 and above

Table 1.1: Type and size of mineral particles in soil

In this context, the term soil mineralogy is used which is defined by the mineral composition of the soil. Minerals are naturally occurring compounds of inorganic nature that have definite crystalline structures and can be classified into primary and secondary minerals. Silicon, oxygen, aluminium, iron, calcium, potassium, sodium and magnesium are the most common elements present in the earth's crust and minerals constituting these elements hence dominate the soil environment.

Primary minerals: These are the minerals that are formed under elevated temperatures and inherit their properties from igneous and metamorphic rocks directly without much structural alteration. The sand and the silt fraction of soil consists mainly of primary minerals like silicates, phosphates and oxides of iron, titanium and zircon. Silicate minerals like quartz, mica, feldspars, pyroxenes etc. dominate the soil environment.

Secondary minerals: These are formed under low temperature reactions and assume their characteristics from sedimentary rocks mainly. Some typical secondary minerals present in soils include oxides, hydroxides, carbonates, sulphates and alumino-silicates. Montmorillonite, illite, kaolinite, calcite and gypsum are a few commonly found secondary silicate minerals in soil.

Minerals	Chemical formula
Primary minerals	
Silicates	
Quartz	SiO_2
Feldspars	KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$
Pyroxenes	MgSiO_3 , $\text{CaMg}(\text{Si}_2\text{O}_6)$
Phosphates	
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$
Oxides	
Iron	Fe_2O_3 , FeOOH
Titanium	TiO_2
Zirconium	ZrO_2
Secondary Minerals	
Alumino silicates	
Kaolinite	$\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$
Montmorillonite	$\text{M}(\text{Al}, \text{Fe}^{2+}, \text{Mg})_4\text{Si}_8\text{O}_{20}(\text{OH})_4$ M: interlayer metal cation
Sulphates	
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Carbonates	

Calcite	CaCO_3
Dolomite	$\text{CaMg}(\text{CO}_3)_2$

Table 3.1: Common primary and secondary soil minerals

Organic matter:

Perhaps the most important component of soil which is responsible for its productivity is the organic matter (Fig 1.2). Though contributing only to 5% of the total composition, organic matter is the source of nutrition for microorganisms and provides ion-exchange sites necessary for transportation to plants and influences the physical properties of soil. Through chemical reactions, organic matter also contributes to the weathering of mineral matter leading to soil formation. For example, some soil fungi produce citric acid and some other chelating organic acids that help in release of potassium and other metal ions from silicate minerals thereby speeding up the weathering process.

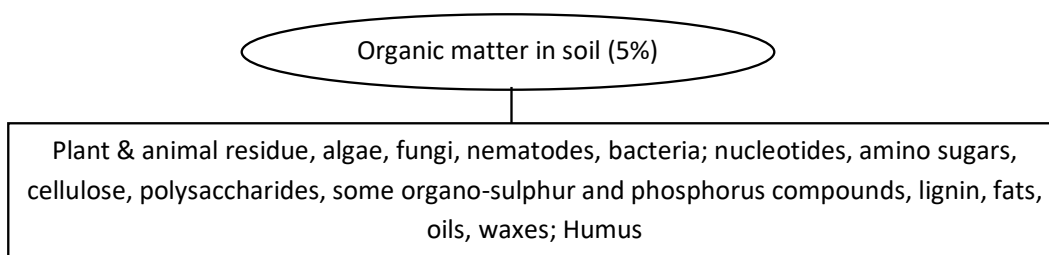


Fig. 3.2

The most significant ingredient that forms the bulk of the soil organic matter is humus. Humus is the residual matter produced by partial decay of plant matter by the action of bacteria and fungi, a process called humification. The process of humification increases the nitrogen:carbon ratio in the organic matter as the process of decay/biodegradation results in loss of carbon as CO_2 , while the nitrogen so produced is fixed by nitrogen-fixing bacteria and is incorporated in the humic residue. A water insoluble material, humus is composed of humic substances that are commonly classified on the basis of solubility as shown in Fig. 1.3. Humus is very beneficial for quality of soil and the incubation of life forms supported by it by means of the following properties:

- Humus increases the air and water circulation within the soil
- It provides good water holding capacity to the soil
- It enhances the aeration of soil thereby promoting penetration of roots
- Humus improves the physical texture of the soil by binding the soil particles together and reducing the pore size
- It acts as a source of food for a variety of soil organisms
- Humus helps in maintaining and replenishing the soil nutrients

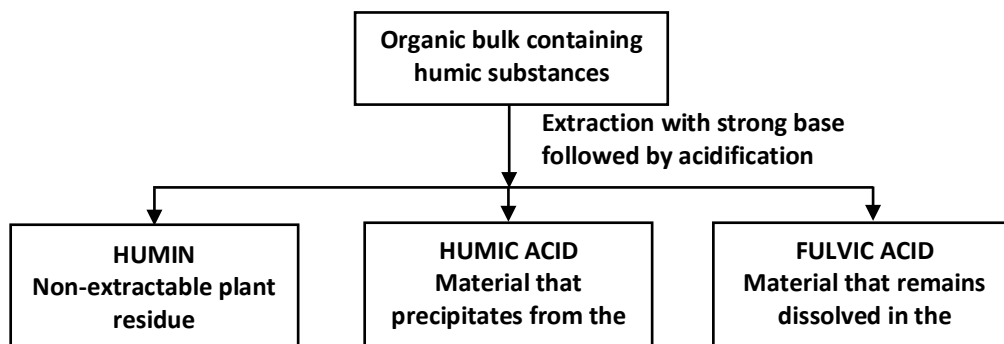


Fig. 3.3

Humic substances are natural chelating agents that are capable of interacting with metal oxides and hydroxides, metal ions and complex minerals to form metal-organic associations of various types. This interaction or binding can occur as chelation of metal, M with (a) a carboxyl group (b) carboxyl and phenolic groups or (c) two carboxyl groups (Fig 1.4).

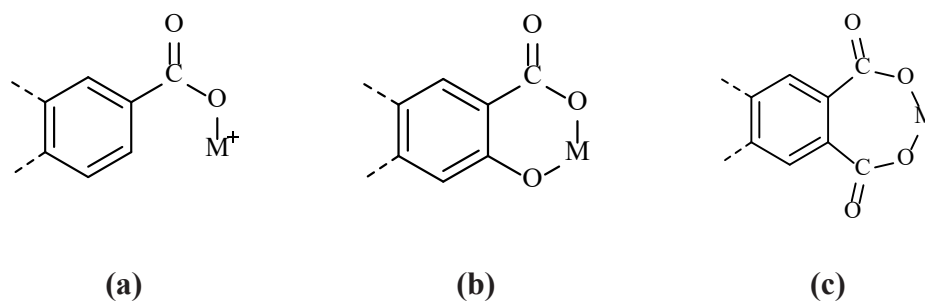
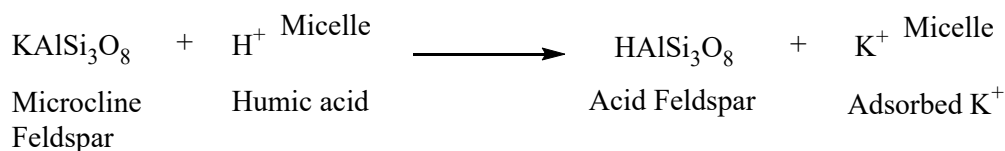


Fig. 3.4

Acid-base, complexing and sorptive properties of humic substances exert a strong effect on the properties of soil water. They enhance the mineral breakdown promoting nutrient availability to plants. Humic and humic acid remain insoluble in water and act through exchange of cations or organic materials. The following reaction shows the decomposition of microcline feldspar and release of potassium from a molecular state to an adsorbed state which is readily available for uptake by plants.



Fulvic acid (Fig 1.5) being the soluble species dissolves in water and exhibits its effect directly. The soluble fulvic acid-metal complexes are particularly involved in iron solubilisation and transport. The high affinity of humic and fulvic acids towards iron and the low crystal field stabilization energies of Fe^{3+} and Fe^{2+} ions make the minerals rich in iron more susceptible to attack by humic materials.

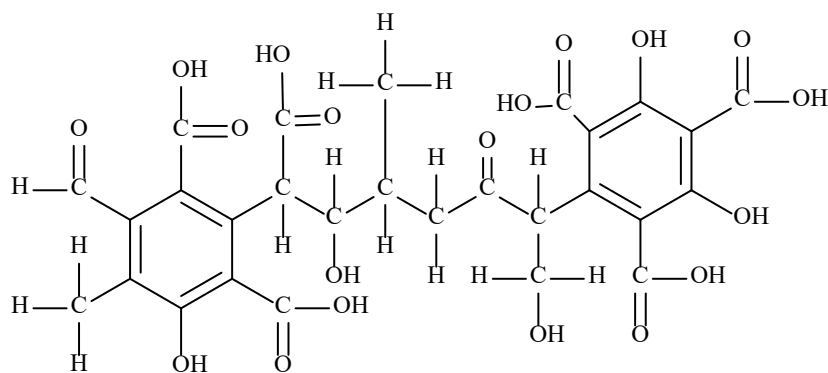
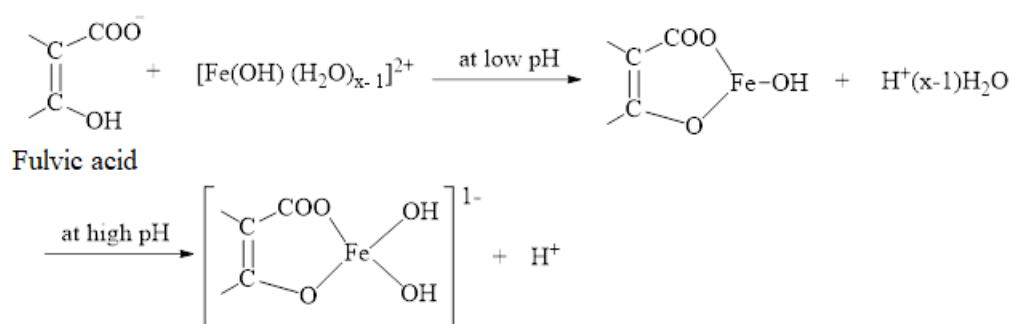


Fig. 3.5

Fulvic acids and polysachharides present in humus attract metal ions like Fe^{3+} , Zn^{2+} , Mn^{2+} and Cu^{2+} from their parent minerals and form stable organo-mineral complexes that can be taken up by plants or may take part in clay synthesis.



The humic materials i.e. humic and fulvic acids are thus capable of inducing decomposition of soil minerals by extracting metal ions and enabling their transport to soil environments where they can serve as nutrients. It has been observed that it is at a $\text{pH} > 6.5$ that the fulvic and the humic acids are able to effectively attack and degrade the soil minerals to form water soluble and water insoluble metal complexes. If the metal: humic acid (or fulvic acid) ratios are high, the organo-mineral complexes formed are water insoluble whereas a low metal: humic acid (or fulvic acid) ratio leads to water soluble complexes.

Water soluble organic carbon

The term water soluble organic carbon refers to the entire pool of organic carbon that is either dissolved in the interstitial pore water or is sorbed on the soil or sediment particles. Leaching of the water soluble organic carbon becomes a source of dissolved organic carbon (DOC) in natural waters. DOC is operationally defined as the organic content that passes through a filter of size $0.45\mu\text{m}$ and is the major form of carbon that gets transported with soil solution and in streams. Dissolved organic carbon leads to hydrological transport of carbon to different pools in the ecosystem mainly involving the transport from forest floor to the mineral soil. However, besides contributing to the global carbon cycle, the interaction of natural organic carbon in water with trace amount of pollutants has become a major environmental concern. DOC has been recognized as a major carrier of persistent organic contaminants and its potential for generating trihalomethanes and other

chlorinated products is often related to production of carcinogenic effects in test organisms.

Soil water:

Water is the liquid part of the solid-liquid-gas three phase system of soil environment. Soil water also known as the rhizic water affects the soil texture and aeration status while playing a pivotal role as a medium of nutrient transfer from soil to plants roots and other plant parts. The rhizic water is classified into gravitational water, capillary water and hygroscopic water.

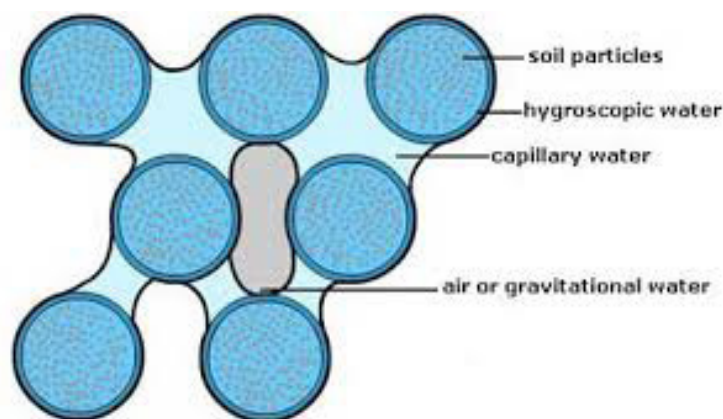


Fig. 3.6

The soil moisture available to plant roots is the one which is held by surface tension and cohesive forces in the soil is termed as capillary water. Thin films of water, hydrogen bonded to soil particles and inaccessible to plants is termed as the hygroscopic water while gravitational water is the excess water that percolates down to join the ground water reservoir. **Soil solution** is the aqueous phase that contains a wide range of suspended and dissolved organic and mineral matter along with some gaseous substances from various biochemical processes of the soil and from exchange with biosphere and hydrosphere. Gaseous compounds like CO_2 find their way to the soil water by means of certain chemical reactions or as a product of respiration of soil micro-organisms. They may enter from atmosphere by getting dissolved in the precipitation. The CO_2 concentration in the soil solution plays an important role in determining the soil pH. Dissolved CO_2 results in the formation of carbonic acid that releases H^+ ions contributing to acidity in soil:



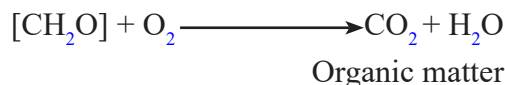
Other factors that contribute to the acidity of soil include, industrial and urban emissions, degradation of organic matter producing organic acids, nitrification processes involving conversion of NH_4^+ ions to NO_3^- ions and uptake of nutritive base cations by plants in exchange of H^+ ions. Dissolution of mineral substances contribute to the presence of mobile cations like K^+ , Na^+ , Ca^{2+} , NH_4^+ etc. along with chloride, nitrate and phosphate anions in the soil water. The ion concentration in the soil solution is decided by the soil pH to a large extent. Low values of soil pH reduce the metal adsorption capacities thereby increasing the metal concentrations in the soil solution. Acidic conditions lead to considerable increase in the concentration of iron and aluminium ions in the soil water.

A loam (almost equal proportions of sand: clay: silt) soil with humus containing approximately 60% water and close to 40% air is considered to be the best for the growth of majority of crops.

However, soils rich in clays tend to get water logged (water-saturated). As a result, such soils do not contain enough air required by most plant roots and hence become detrimental for plant growth.

Soil air:

The mixture of gases occupying the pore space between the soil particles not already occupied by soil water, in the aerated zone above the water table is termed as soil air. Atmospheric factors like pressure, temperature and moisture control the flow of soil air through the aerated zone. In comparison to the atmospheric composition of air; the soil air has 1-6% less oxygen and several times more carbon dioxide owing to the decay of organic matter that consumes O_2 and releases CO_2 . Increased levels of CO_2 reduce the soil pH thereby promoting weathering of carbonate minerals that in-turn leads to easy availability of mobile cations in soil water to be taken up by plants.



Apart from nitrogen, oxygen and carbon dioxide, trace amount of gases like carbon monoxide (CO) and carbon disulphide (CS_2) may occur in soil air due to miscellaneous organic and mineral processes and reactions occurring in the soil environment essentially depending on the geological composition of soil. Other gases that may be produced within the soil include methane (CH_4), hydrogen (H_2) and hydrogen sulphide (H_2S).

Check your progress 1

Notes: (a) Write your answers in about 50 words

(b) Check your progress with possible answers given at the end of the unit

How does the process of humification affect the nitrogen:carbon ratio in soil organic matter?

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What are primary and secondary minerals present in soil. Give examples.

Soil Chemistry

7.3 SOIL FORMATION

Soil forming processes

Soil formation is a complex and dynamic process involving decomposition and disintegration of rocks due to weathering forces resulting in the formation of a conglomerate of minerals in close association with interjacent organic matter. The entire process of soil formation involves two stages:

- (a) Weathering
- (b) Pedogenesis or soil development

(a) Weathering

Natural forces like wind, running water, changes in temperature along with the action of living organisms lead to breakdown of rocks into fine, smaller particles that initiate the process of soil formation. These processes are collectively termed as weathering by earth scientists. Weathering can be physical/mechanical, chemical or caused by biological agents.

Physical/ mechanical weathering:

When the dominant forces causing the disintegration of rocks are majorly mechanical in nature, such as erosion by the action of running water or abrasion and erosion by wind or severe changes/ fluctuations in temperature, then one can classify the weathering so caused to be physical or mechanical weathering. Differential thermal expansion under severe climatic conditions; expansion due freezing of interstitial water causing rupture; differential stress due to surface emergence of deep-seated rocks etc. are some of the prominent agents of physical weathering. Factors like gravity and abrasion by glacial ice further enhance the mechanical weathering. Disintegration brought into effect by such processes cause negligible change in the chemical or mineralogical composition of the resultant particles formed from the parent material.

Chemical weathering-Foundation for pedogenesis:

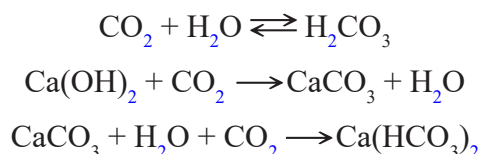
Mechanical weathering is largely a precursor to chemical weathering as physical disintegration of the solid of the rocky material to finer particles leads to initiation of favourable energetics for subsequent chemical alterations. The usual chemical processes involving acid-base reactions, hydrolysis, dissolution-precipitation and

redox reactions lead to an equilibrrious relation between rock-water-mineral system that forms the basis of soil development or pedogenesis.

Water plays a pivotal role in attainment of such an equilibrium as it tends to hold the weathering agents like H_2SO_4 , HNO_3 , HNO_2 , organic acids including humic and fulvic acids, CO_2 and O_2 , in the solution and facilitates their transport to chemically active sites allowing a molecular and ionic level interaction. Thus, it is evident that chemical weathering is ineffective in desert areas due to intrinsic lack moisture. As a result of chemical weathering the parent mineral materials are transformed into newer mineral materials through varied processes predominantly involving the following reactions:

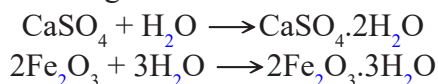
1. Carbonation

It is the formation of carbonic acid by combination of carbon dioxide and water. The carbonic acid so formed reacts with the hydroxides of calcium, magnesium and other rock minerals leading to formation of carbonates and bicarbonates.



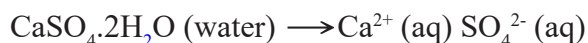
2. Hydration

Hydration makes the mineral materials combine with water molecules thereby increasing the volume and making the resultant material soft and prone to weathering.



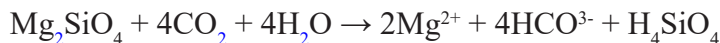
3. Dissolution

Water soluble minerals like limestone and gypsum under the solvent action of water increase the availability of ions in the solution form.



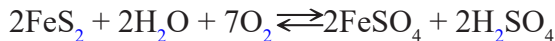
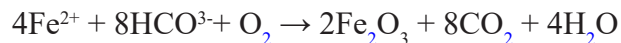
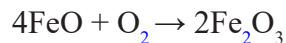
4. Hydrolysis

Hydrolysis is the chemical action of water assisted by the presence of CO_2 . Silicates majorly undergo weathering by means of hydrolysis as shown in the following reactions:



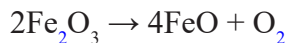
5. Oxidation

Oxidation of minerals results in the formation of their oxides. Dissolution of such oxides in soil water weakens the rocks and assists in the weathering process. Well aerated and drained soils promote oxidation as presence of oxygen, water and dissolved gases under such conditions leads to dominance of oxidation reactions. Iron, manganese and sulphur are the most commonly effected minerals by the oxidation process.



6. Reduction

Reduction mainly occurs in the deep-seated areas of the earth's crust that are poorly aerated.



Weathering by biological agents:

Though the dominant processes of weathering may be physical or chemical, they are always accompanied by biological agents that play an indispensable role in the formation and evolution of soil. The intruding action of plant roots and the physical action of rodents, worms and other organisms act as mechanical forces for the disintegration of rock in the upper surface environment. The release of organic acids by micro-organisms like bacteria, fungi, algae and humic matter produced by the degradation of vegetable matter transforms the weathered mineral matter into a dynamic system that stores energy and synthesises organic matter. This action of organic acids primarily helps in the formation of secondary minerals like clay and further assists in supporting miniature ecosystems and growth of plants thus indicating the formation of embryonic soil. Ranging from simple dissolution reactions in the acidic environment near the tips of plant roots to complex biochemical processes, the role of chemical dimension of weathering by biological agents is essential to the process of soil formation.

(b) Pedogenesis or soil development

The thin upper layer constituting of an unconsolidated mixture of disintegrated mineral matter and organic matter undergoes modifications under topographic, climatic and biological effects leading to development of distinct layers in soil that are categorized downwards and are called the soil horizons forming the basis of soil profile.

Factors affecting soil formation

Climatic / active factors: Rainfall, temperature, humidity are some of the climatic factors that have a profound effect on the process of soil formation.

Topographic/ passive factors: The chemical composition, aeration status and soil texture are mainly decided by the nature of the parent rock material and topography which act as the passive factors in soil development.

Biospheric factors: Living organisms play a significant role in soil formation as their mechanical and biological activities promote and modify the physico-chemical processes involved in soil development.

SOIL PROFILE

Weathering of the parent material over a period of time leads to formation of layers of soil stacked one above the other. These horizontal layers or horizons differ in thickness, structure, texture and composition. The structured organization of soil layers is indicative of progressive levels of maturity of soil. A vertical section displays of the soil components denoting its various zones from surface level to the bed rock is called soil profile (Fig. 1.7). Generally, the soil horizons are categorized into: organic or O horizon and mineral horizons, A, E, B and C.

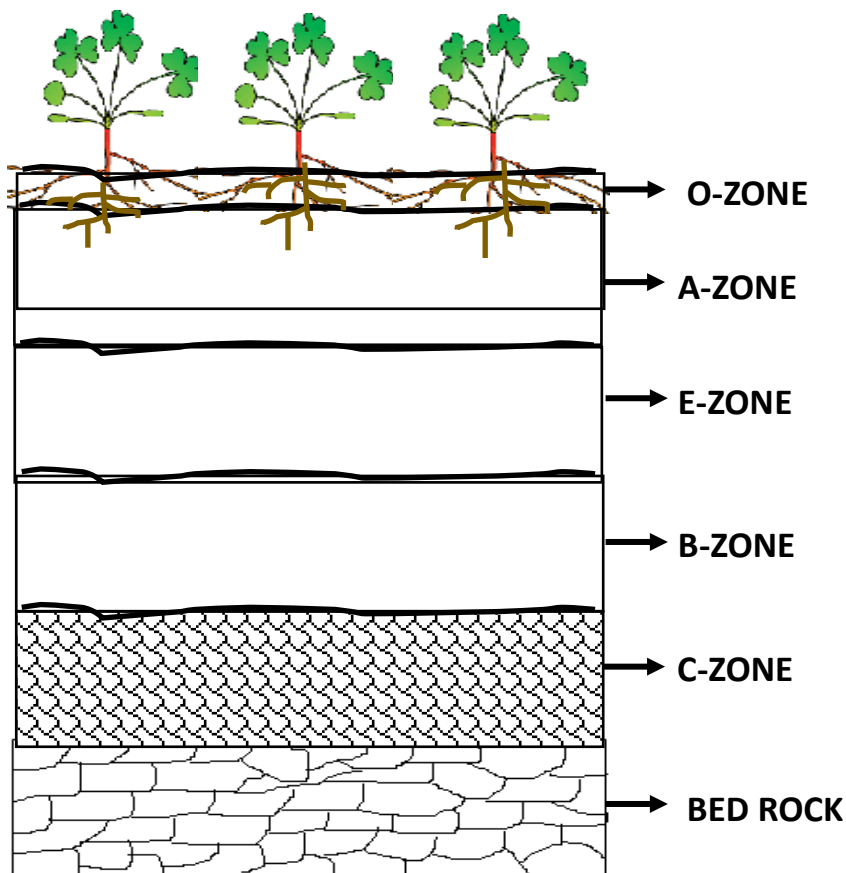


Fig. 3.7: Soil Profile

O-Horizon: It is the uppermost horizon of the soil profile also known as the litter zone. This layer is generally found in forests and is not present in desert or cultivated fields.

A-Horizon: The A Horizon also called the top soil is several inches thick and contains most of the soil organic matter ranging from undecomposed to completely decomposed humus. The plant roots are also present in this layer which has the maximum biological activity and is essential for plant productivity.

E-Horizon: This is the layer of elution of clay and oxides of iron and aluminium by weathering or leaching leaving a concentration of sand and silt particles

B-Horizon: This layer forms the subsoil or the zone of accumulation. The material dissolved from horizon A makes its way to this zone and gets re-deposited.

The water percolating downwards from horizon A is rich in organic acids and complexing agents and thus leaches out minerals in the form of metal oxides which get precipitated in this region along with organic matter and colloidal material through the process of eluviation which thereby enriches the B zone of soil.

C-Horizon: This soil zone lacks organic matter and is largely composed of the weathered material from the parent rock. Beneath the C horizon is the bed rock, parent material and even older sediments from past pedological cycles.

Check your progress 2

Notes: (a) Write your answers in about 50 words

(b) Check your progress with possible answers given at the end of the unit

1) What are the two main stages of soil formation?

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2) Explain with the help of reactions, how water assists the process of chemical weathering.

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7.4 SOIL CHEMICAL PROPERTIES

Soils exhibit characteristic chemical properties depending upon their chemical composition and also the degree of agricultural exploitation. These soil features act as relevant indicators of its origin and plant nutrition potential and hence the land use value. Soil acidity (pH), ion exchange and cation adsorption capacities are some of the important factors that decide the nature of soil environment.

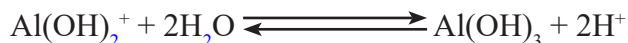
7.4.1 Soil acidity (pH)

The acidity of soil is directly related to the soil mineralogy and organic content of the soil. Soil pH also has a direct effect on the solubility of metal ions and hence their availability and chelation capacity. Acidity of soil (pH) is usually measured in a dilute (0.01M) solution of calcium chloride or in a 1:2.5 (weight to volume) suspension of soil in water. The acidic soils are generally rich in the mineral ions of

calcium and magnesium as their precipitation as carbonates increases the buffering capacity of the solution.



Aluminium ions (Al^{3+}) also play an important role in soil buffering as exhibited in the following hydrolysis reaction generally prevalent in humid and clay rich soils.



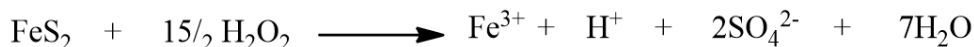
Depending upon the availability and saturation of ions like Mg^{2+} , Na^+ , K^+ and Ca^{2+} , the soil pH may keep changing over time. The concentration of these base cations is largely affected by atmospheric agents like weathering, precipitation and agricultural exploitation by use of fertilizers which in turn leads to fluctuations in the soil pH value. Some of the factors that contribute to lowering of soil pH are listed below:

- Production of organic acids by soil microorganisms
- High organic matter content in soil
- Loss of basic cations through plant harvest and leaching
- Addition of acids in the soil environment by atmospheric agents
- Greater uptake of cations than anions by plants
- Production of mineral acids in soil:

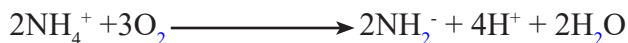
Pyrite (FeS_2) containing minerals present in soil are prone to aerial oxidation leading to the formation of acid-sulphate soils called 'cat-clays' that may have pH as low as 3.0.



Potential acid-sulphate formation can be tested in the soils by performing a peroxide test, which involves oxidizing the FeS_2 in soil with 30% H_2O_2 followed by testing for acidity and sulphate. A pH value lower than 3.0 and appreciable levels of sulphate indicate the potential to form acid-sulphate soils.



Addition of acid forming chemicals by means of inorganic fertilizers:



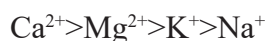
Soils of humid regions generally associate with low values of pH as the content of mineral acids and organic acids remains subject to recharge by rainfall. The attack of these acids on minerals further adds to the acidity of the soil. Whereas under arid conditions, such as in deserts, the soil tends to have higher values of pH due to dominance of minerals that are salts of weak acids and strong bases. Further, the addition of carbonates by atmospheric agents, hydrolysis of exchangeable sodium ions and greater uptake of anions by plants also contribute to soil alkalinity.

7.4.2 Ion exchange in soil and cation exchange capacity

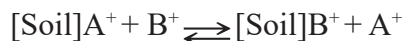
One of the most important chemical functions of the soil is exchange of cations and the ability to do so is defined in terms of **cation exchange capacity (CEC)**. The CEC is a measure of the potential of cation adsorption and also a measure of surface negative charge. The cation exchange capacity of soils is measured by the cation yield of the soil through extraction with a solution of ammonium acetate and is expressed in milli equivalents of monovalent ion per 100g of soil.

Exchangeable cations are those that are held on the surface of clay and organic particles or clay-humus complex and also between the layers of clay minerals, thus cation exchange is prevalent at both the mineral and the organic portions of the soil. The clay minerals are able to exchange cations due to the availability of negatively charged sites on the mineral surface that are formed when atoms of lower oxidation number (Mg^{2+}) are exchanged for the ones with higher oxidation number (Al^{3+}). The surplus negative charge enables the mineral to act as a cation exchanger. Presence of carboxylic and phenolic groups in the organic component of the soil make it possible for it to exchange cations. The value of CEC, therefore has a dependence upon the organic and clay content of the soil apart from clay mineralogy and soil acidity (pH).

There is preferential take up of certain cations by the cation exchange sites and one of the controlling factors for adsorption and replacement of ions is the valency. Cations possessing high valency have a high energy of adsorption and are preferentially adsorbed over cations with a lower valency. This fact also explains the relative concentration of the ions in soil composition in accordance with the given sequence. These cations will be less readily replaced and hence the order. Further, the cations lying close to negatively charged exchange sites are more strongly attracted thereby leading to preferential adsorption of cations with a smaller radius of hydration.



Given the exchange reaction for the ions A^+ and B^+ is:



At chemical equilibrium we have:

$$K_{AB} = \frac{[S_B][A^+]}{[S_A][B^+]}$$

Where S_A and S_B represent ionic fraction of A^+ and B^+ bound to the soil; $[A^+]$ and $[B^+]$ represent the ions present in the surrounding solution and K_{AB} is the exchange constant for the reaction which expresses the relative tendency of soil to retain A^+ and B^+ . Then for a soil with all exchange sites occupied by A^+ , the value of S_A is 1.0 while with half of the sites occupied by A^+ , the value of S_A will be 0.5 and so on.

Cation exchange in soil is directly related to increase in the soil acidity. This can be explained by the fact that elements like K, Mg, Ca and other essential metals

are made available to the plants through cation exchange. During this process, hydrogen ions are exchanged for the uptake of metal ions by the plant roots, thereby contributing to decrease in soil pH value. However, soil tends to resist the change in pH and the buffering capacity depends on the type of soil.



Like CEC, the anion exchange capacity (AEC) of soils represents the total amount of exchangeable anions that can be adsorbed by the soil. While cation exchange process dominates the soil environment, exchange of anions is rare owing to the fact that as acid radicals, the anions in the presence of hydrogen lead to the dissociation of adsorbent surfaces like the clay minerals. However tropical soils have been observed to possess appreciable AEC in comparison to temperate soils.

The oxide surface in the mineral portion of the soil may act as a seat for anion exchange. At low values of pH the metal oxide surface acquires a net positive charge thereby holding anions like halides by electrostatic attraction (Fig 1.8).

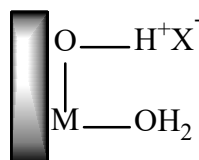


Fig. 1.8

At higher values of pH, the metal surface loses H^+ ions from water molecules bound to its surface thereby forming OH^- ions and hence a net negative charge on the surface (Fig. 1.9 a). Under such circumstance anion exchange between OH^- on the metal surface and anions like HPO_4^{2-} in the surrounding soil water becomes possible (Fig. 1.9 b).

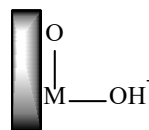


Fig. 1.9 a

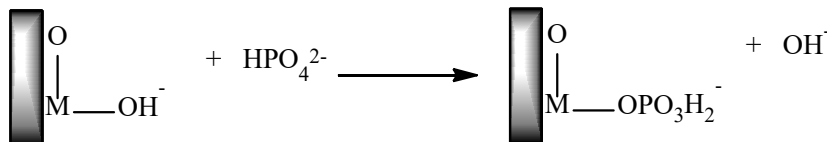


Fig. 1.9 b

Check your progress 3

Notes: (a) Write your answers in about 50 words

(b) Check your progress with possible answers given at the end of the unit

How is soil acidity measured? What term is used to describe the ability of soil to exchange cations?

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What are cat-clays and how can they be tested? Give the reactions involved.

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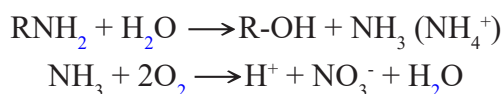
7.5 MACRO AND MICRONUTRIENTS IN SOIL

7.5.1 Soil Macronutrients

Plants thrive on the nutrients provided by the soil and hence supporting plant growth by supplying various nutrients is one of the primary functions of the soil. Carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, magnesium, calcium and sulfur are considered to be essential plant macronutrients. Among the macronutrients essential for the growth of plants, carbon, hydrogen and oxygen are taken up from the atmosphere while nitrogen, phosphorus, potassium and others are taken up directly from soil. These nutrients are commonly added in the form of fertilizers to make up their deficiency in the soil.

Nitrogen

Nitrogen is not a substantial product of mineral weathering and is rather sourced through the organic component of the soil i.e. the biodegradation of dead plants, animals and soil microorganism activities. The amino nitrogen so obtained is hydrolysed to the NH_4^+ form which is further oxidised by soil bacteria to the nitrate form (NO_3^-).



However, the *in-situ* production of these utilizable forms of nitrogen does not meet the requirement of nitrogen demand. Also, the nitrogen supplements added in the form of fertilizers and through rain are often leached away. The organic nitrogen bound to soil humus serves as a reserve for uptake by plants and plays an important role in maintaining the soil fertility as the rate of nitrogen release through the gradual decay process parallels the plant growth rate thus providing a sustainable

nutrient source. Most plants thrive on NO_3^- form of nitrogen while few like rice take up ammonium.

Nitrogen forms an essential component of proteins and living matter and crop produced on nitrogen rich soils are therefore significantly richer in protein and more nutritious. An important source contributing to the soil nitrogen content is atmospheric nitrogen fixation by leguminous plants like clover and soyabean that contain the nitrogen fixing bacteria of the *Rhizobium* species present in their root nodules. Sustainable nitrogen content and soil fertility can be maintained by crop rotation between legumes and nitrogen consuming plants. Figure 1.10 gives a comprehensive outlay for the sources and sinks of nitrogen.

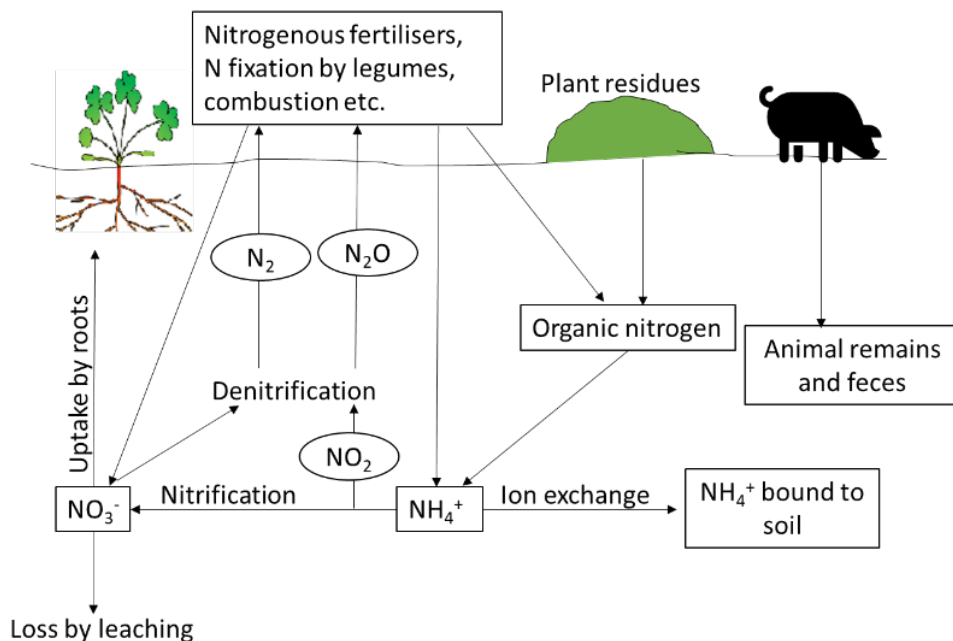


Fig 3.10

Phosphorus

Phosphorus as phosphates may get incorporated in the soil environment as a product of mineral weathering. Phosphorus is taken up by the plants in the form of inorganic orthophosphate species like H_2PO_4^- and HPO_4^{2-} that are available in the soil at a near neutral pH. At lower pH values the orthophosphate ions get precipitated by species of Fe^{3+} and Al^{3+} while under alkaline conditions, they may react with calcium carbonate to form the insoluble hydroxyapatite form.



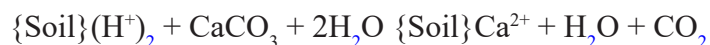
Potassium

Potassium is available to the plants in the form of exchangeable K^+ held by clay minerals. Potassium is one of the most abundant elements of the earth's crust (2.6%) and is important for activation of certain enzymes and carbohydrate transformations that are essential to the growth of plants apart from maintaining water balance in plants. Growing plants consume significant levels of potassium and potassium deficiency adversely affects crop yields. Soils heavily fertilized with other nutrients

face enhanced removal of potassium making it a limiting nutrient. For example, addition of nitrogen fertilizers to soil in turn increases potassium removal.

Calcium

Normally soils are rich in calcium but calcium deficiency may arise due to plant uptake and leaching by carbonic acid. Also, presence of high levels of potassium, magnesium and sodium sometimes lead to calcium deficiency owing to the competition among ions for uptake by plants. Treatment of acidic soils by liming or application of calcium carbonate makes up for the calcium deficiency if any.



Magnesium

Most of the magnesium in the earth's crust is strongly bound in the form of minerals, while the exchangeable Mg^{2+} ions on the exchange sites of organic or clay component of the soil is available for uptake by plants. Excessive levels of sodium or potassium in soil and high calcium/magnesium ratio may result in magnesium deficiency.

Sulfur

Sulfur is a constituent element of some essential amino acids like thiamine and biotin and is taken up by the plants in the form of sulphate ions (SO_4^{2-}) that are usually present as soluble salts in soil water or as immobilized sulphate minerals that are insoluble. Sulfur deficient soils do not support healthy plant growth and deficiency can be made up in the form of sulfur containing fertilizers. Sulfur present in the form of FeS_2 in soil may react with acid in acid-sulphate soils to release H_2S that is hazardous to plants and soil microorganisms.

7.5.2 Soil Micronutrients

These elements are required by the plants in trace amounts and may prove to be toxic at elevated concentrations. Chlorine, iron, manganese, boron, copper, molybdenum and zinc are recognized as essential plant micronutrients. These mineral elements enter the soil environment mainly through weathering and are important for functioning of some essential enzymes. Iron, chlorine, manganese and zinc may be involved in the photosynthesis.

7.6 SOIL FERTILITY

Soil fertility is defined as the ability of soil to provide all the essential nutrients in utilizable form for uptake by plants in a balanced proportion. It is recognized as a combined effect of the three interacting components, physical, chemical and biological characteristics of the soil. It is different from soil productivity in the sense that fertility indicates the status of available plant nutrients in soil whereas productivity is a result of various factors that affect crop production including fertility.

A fertile soil would contain all the macro nutrients required for basic plant nutrition such as N, P, K along with the nutrients required in minor quantities. A fertile soil is also characterized by a near neutral pH with the presence of sufficient amount of soil organic matter that helps improve soil structure for optimal retention of moisture and nutrient elements. However, not all soils have optimum conditions for plant growth and all essential nutrients in adequate quantities. Soil fertility and crop production can thus be improved by using fertilizers.

Common soil fertilizers contain nitrogen, phosphorus and potassium as major components, while magnesium, sulphate and a few micro nutrients may also be added. These fertilizers are designated by numbers that represent the percentage composition of the fertilizer. For example, a fertilizer numbered as 6-8-12 is indicative of a composition of N-6%, P as P_2O_5 -8% and K as K_2O -12%. Organic fertilizers like manure usually correspond to a 0.5-0.24-0.5 composition and need to undergo biodegradation to release the nutrients in form of nitrates, phosphates and exchangeable potassium that can be readily assimilated by plants.

Check your progress 4

Notes: (a) Write your answers in about 50 words

(b) Check your progress with possible answers given at the end of the unit

What nutrients are added to soil in the form of fertilizers to make up their deficiency?

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What does a fertilizer numbered as 5-10-10 indicate?

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7.7 LET US SUM UP

In this unit we have elaborated upon the importance of soil, its nature, chemical properties and composition along with various processes that are involved in the formation of soil. The study of soil is based on two approaches, pedology that deals with studying soil as a natural body while edaphology deals with the study of soil properties with respect to plant production. The formation of soil basically embodies two stages. The genesis is initiated by weathering of rocks by physical, chemical

and biological agents while the second stage is pedogenesis which involves an interplay of several factors and complex processes before a consolidated medium for proliferation of life can be formed. Thus, soil formation is a continued process witnessing changes, developments and evolution. As a result of constant evolution, the soil develops a profile in the form of various layers stacked over one another, differing in structure, texture, thickness and composition. Miner matter is the major constituent of soil (45%), while organic matter which majorly influences productivity of soil, stands at 5%. The rest 50% is air and water in equal ratios. Depending upon the chemical composition, soil exhibits typical chemical properties. The nature of soil environment and hence its plant nutrition potential is decided by some key properties like acidity, ion exchange and cation adsorption capacities. Soil supports plant growth and providing various plant nutrients is the primary function of soil thereby making soil fertility an important aspect of studying soil.

7.8 KEY WORDS

Humus :	Humus constitutes the bulk of the soil organic matter. It is produced by the process of humification which is partial decay of plant matter by the action of bacteria and fungi.
Rhizic water :	Soil water is also called rhizic water. It is the liquid part of the soil environment and plays an important role in transfer of nutrients from soil to plants
Weathering :	The processes that collectively lead to breakdown of rocks into smaller fine particles by the action of natural forces like wind, water, temperature change etc. are called weathering. It forms the basis of soil formation
Pedogenesis :	Development of soil and its different layers under the influence of various topographic, climatic and biological effects
Soil profile :	Sectional display of soil components in a vertical fashion denoting various zones from surface to the bed rock.
Cation exchange capacity :	A measure of the total capacity of soil to hold exchangeable cations. It is a useful indicator of soil fertility. Expressed in milli equivalents of monovalent ion per 100g of soil

7.9 REFERENCES AND SUGGESTED FURTHER READINGS

1. Manahan, S.E. (2010). Environmental Chemistry. CRC Press. Taylor & Francis Group.
2. Mirsal, I.A. (2008). Soil Pollution: Origin, monitoring and Remediation. Springer.
3. Wright, R.T., Boorse, D.F. (2017). Environmental Science: Toward a Sustainable Future. Pearson
4. Bohn, H.L., O'Connor, G.A., Mc Neal, B.L. (2001). Soil Chemistry. John Wiley & Sons, Inc.

ANSWERS TO CHECK YOUR PROGRESS

Check Your Progress 1

The nitrogen:carbon ratio in the organic matter increases by the process of humification. This is so because humification involves decay or biodegradation of plant material during which carbon is evolved and lost as CO₂, while the nitrogen so produced is fixed by nitrogen-fixing bacteria and is incorporated in the humic residue.

Primary minerals: These are the minerals that are formed under elevated temperatures and inherit their properties from igneous and metamorphic rocks directly without much structural alteration. Examples: Quartz, feldspars, pyroxenes

Secondary minerals: These minerals are formed under low temperature reactions and assume their characteristics mainly from sedimentary rocks. Examples: kaolinite, calcite, gypsum.

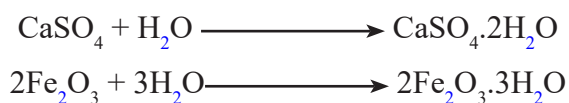
Check Your progress 2

(a) Weathering (b) Pedogenesis or soil development

One means by which chemical weathering comes into effect is by the chemical action of water which can happen in the following ways:

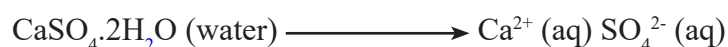
a. Hydration

Hydration makes the mineral materials combine with water molecules thereby increasing the volume and making the resultant material soft and prone to weathering.



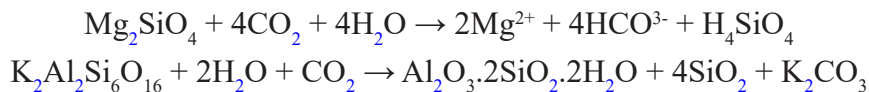
b. Dissolution

Water soluble minerals like limestone and gypsum under the solvent action of water increase the availability of ions in the solution form.



c. Hydrolysis

Hydrolysis is the chemical action of water assisted by the presence of CO_2 . Silicates majorly undergo weathering by means of hydrolysis as shown in the following reactions:

**Check Your Progress 3**

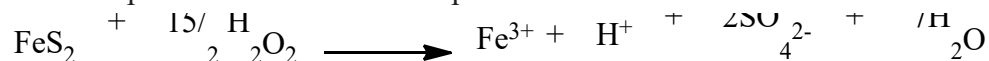
- 1) Acidity of soil (pH) is usually measured in a dilute (0.01M) solution of calcium chloride or in a 1:2.5 (weight to volume) suspension of soil in water.

CEC: Cation Exchange Capacity

- 2) Pyrite (FeS_2) containing minerals present in soil are prone to aerial oxidation leading to the formation of acid-sulphate soils called 'cat-clays' that may have pH as low as 3.0.



Potential acid-sulphate formation can be tested in the soils by performing a peroxide test, which involves oxidizing the FeS_2 in soil with 30% H_2O_2 followed by testing for acidity and sulphate. A pH value lower than 3.0 and appreciable levels of sulphate indicate the potential to form acid-sulphate soils.

**Check Your Progress 4**

- 1) Nitrogen, Phosphorus and Potassium
- 2) A fertilizer numbered as 5-10-10 is indicative of a composition of N-5%, P as P_2O_5 -10% and K as K_2O -10%.

7.10 TERMINAL QUESTIONS

1. List out the main weathering agents involved in chemical process of weathering?
2. Distinguish between micro and macronutrients and give suitable examples each?
3. Describe the soil horizons and explain their importance in determining the soil properties?
4. Describe ion exchange process in the soil?

BLOCK 3

Pollution Chemistry

UNIT 8 : CHEMISTRY OF AIR POLLUTION-I

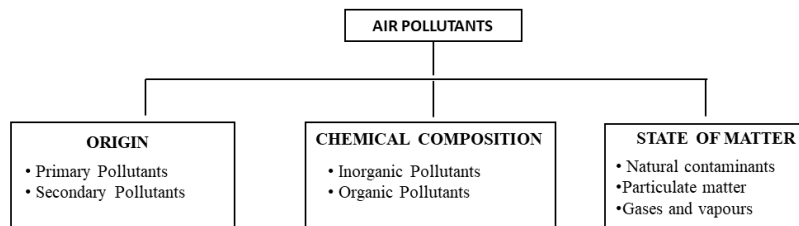
- 8.0** Introduction
- 8.1** Objectives
- 8.2** Carbon Monoxide
 - 8.2.1** Harmful Effects of Carbon Monoxide
 - 8.2.2** Control of Carbon Monoxide Emissions
 - 8.2.3** Sinks of Carbon Monoxide
- 8.3** Carbon Dioxide
 - 8.3.1** Global Warming
 - 8.3.2** Effects of Global Warming
- 8.4** Oxide of Nitrogen
 - 8.4.1** Harmful Effects of Nitrogen Oxides
 - 8.4.2** Control of Nitrogen Oxides
- 8.5** Sulphur Dioxide
 - 8.5.1** Sulphur Dioxide Reactions in the Atmosphere
 - 8.5.2** Effects of Sulphur Dioxide
 - 8.5.3** Removal of Sulphur Dioxide
- 8.6** Ozone
 - 8.6.1** Harmful Effects of Ozone
- 8.7** Acid Rain
 - 8.7.1** Harmful Effects of Acid Rain
- 8.8** Let's Sum Up
- 8.9** Glossary
- 8.10** References and Suggested Further Readings
- 8.11** Terminal Questions

8.0 INTRODUCTION

Undeniably, with increasing industrialisation and urbanisation, human activities release certain substances into the air, which have detrimental effects on health of man and his environment. Air pollution refers to the atmospheric condition in which substances are present in concentrations that may have devastating effects on life and planet as a whole. It is a major environmental problem that impairs the resources needed for long-term sustainable development of the planet. The sources of air pollution are natural like volcanic eruptions, forest fires, pollen grains and anthropogenic such as industrial processes; burning of fossil fuels, power generation, agricultural and other activities. They release oxides of carbon, nitrogen and sulphur, hydrocarbons, particulate matter (smoke, dust, fumes, aerosols), radioactive materials in the air. Most of these substances occur naturally

in atmosphere and are usually considered to be innocuous when present in lower concentrations. However, a substance is considered as an air pollutant only when its concentration is relatively high in comparison to optimum values and may lead to severe health effects.

The air pollutants are classified on three broad categories:



A. According to Origin:

- Primary pollutants are released directly into the atmosphere. They include oxides of carbon, nitrogen and sulphur, particulate matter, radioactive compounds
- Secondary pollutants are released from photochemical reactions of primary pollutants. For example, ground level ozone, formaldehyde, photochemical smog, peroxy acetyl nitrate (PAN).

B. According to Chemical composition:

- Inorganic pollutants include oxides of carbon, sulphur and nitrogen, ozone.
- Organic pollutants include volatile organic compounds (VOCs) comprising of hydrocarbons, aldehydes and ketones, alcohols, organo-sulphur compounds.

C. According to states of matter:

- Natural contaminants include pollutants which are produced from natural sources like pollen grains (size: 10-50 μm) from weeds, grasses and trees.
- Particulate matter refers to aggregates of liquid or solid particles with size less than 500 μm . This includes dust, fog, smoke, mist, spray, ash, fumes etc.
- Gases and vapours-based pollutants are oxides of carbon, nitrogen, sulphur, hydrocarbons, ozone, hydrogen sulphide, chlorine and hydrogen chloride.

8.1 OBJECTIVES

After studying this unit, you should be able to

- Define green house gases and their effect,
- Describe the ozone layer depletion and its impacts on biosphere,
- Classify various pollutants on the basis of their nature and sources,
- Explain the effects of air pollutants on human health and
- Explain air pollution control measures.

8.2 CARBON MONOXIDE

Carbon monoxide (CO), is the most abundant air pollutant found in the atmosphere. More than 90% of the total CO emitted from burning of fossil fuels is derived from vehicular emissions. The natural concentration of carbon monoxide in atmosphere is about 0.1 ppm, with residence time of about four months. Majorly, it is released as an intermediate during the oxidation of methane by hydroxyl radical. It is pertinent to mention that methane level in the atmosphere is about 1.6 ppm, 10 times greater the concentration of CO. As a result, any oxidative phenomena involving methane significantly contributes to the overall carbon monoxide burden, about two-thirds of the total CO. Incomplete combustion of fuels contribute to CO emissions in high concentrations of about 50-100 ppm in urban atmosphere. It enters the atmosphere through natural as well as anthropogenic sources.

- Natural sources- Volcanic eruptions, seed germination, electric discharges, degradation of chlorophyll, contributing to about 20% of the total release
- Anthropogenic sources, accounts for about 6% of CO emissions. Major contribution comes from automobiles (60%) wherein the gas is released as by-product of incomplete combustion of fossil fuels. Industries and agricultural burning contribute about 20% and 10% respectively.

The remaining atmospheric CO comes from unknown sources which include some plants and marine organisms known as siphonophores, an order of Hydrozoans. Carbon monoxide is also produced by decay of plant matter other than chlorophyll.

8.2.1 Harmful effects of Carbon monoxide

Carbon monoxide constitutes the single largest pollutant in the urban atmosphere, fatal in even relatively low concentrations. This is because of its strong affinity to generate a stable complex with haemoglobin in blood stream, forming carboxyhaemoglobin (COHb). This impairs oxygen carrying capacity of haemoglobin to body cells (Figure 1). At concentration of 100 ppm, an individual experiences dizziness and headache (Table 1). Cigarette smoke contributes to about 400-450 ppm of CO exposure. On an average, non-smokers have about 1% of their

haemoglobin present as complex with CO (carboxyhaemoglobin), while the value is double for smokers. The cigarette smoke contains 2% of CO, out of which 0.04% is inhaled and the rest 1.6% is inhaled by a passive smoker. A pack of cigarette contributes to about 3-6% of COHb level in the blood, however the amount of COHb in blood of cigarette smokers increases with increase in smoking. Exposures to very high concentrations (750 ppm) of CO, causes headache, fatigue, unconsciousness and even death. In lungs, heavy concentrations of CO lead to *Pulmonary edema*.

CO does not poison plants because it rapidly oxidises to CO₂ which is used for photosynthesis. However, CO has damaging effects on plants when exposed for longer period of time. For example, at high concentration of about 100-1000 ppm, CO affects plants. Some visible effects include curling of leaves, reduced leaf size, premature ageing and interference with cellular respiration. Exposures to 2000 ppm of CO for 38 hours, inhibit nitrogen-fixing of bacteria.

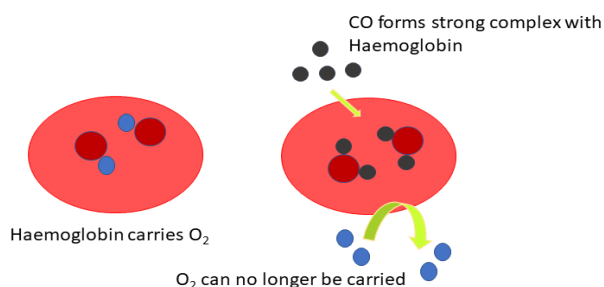


Figure 8.1 A schematic representation of reaction of CO with haemoglobin in red blood cells

Table 1. Exposure levels and the related symptoms of CO exposure in humans

Exposure level in ppm	Symptoms
10	Visual perception and judgement problem
100	Headache, dizziness and fatigue
250	Unconsciousness, reduced mental activity
300	Throbbing headache
500	Vomiting, collapse
750	Death after few hours
1000	Immediate death, Hypoxia

8.2.2 Control of Carbon monoxide emissions

Internal Combustion engine is the chief source, contributing about 60-70% of pollutant carbon monoxide emissions. Gasoline, a low boiling fraction of distillation of petrol, is primarily made up of hydrocarbons. A mixture of gasoline and air serves as the automobile fuel. Gasoline-powered internal combustion engine takes air from the atmosphere and gasoline, and then releases the energy stored in the fuel to propel a vehicle. Modern engines compress the mixture of gasoline and air to the extent of 1/7 or 1/8 of the original volume. As the compression ratio is increased, a point is reached where knocking is observed. The fuel does not burn smoothly or burns explosively giving a metallic rattle sound called knocking. To overcome this problem, anti-knocking agents like tetraethyl lead, ethylene dibromide have

been employed for smooth burning of the fuel. Tetraethyl lead converts into PbO that acts as free radical scavenger and itself gets converted to Pb(s), the latter gets deposit in the engine. Therefore, lead-gasoline is usually not preferred.

Fuel and air mixture govern the composition of exhaust gases coming from the vehicle. The gases include CO₂, H₂O, hydrocarbons, NO_x, CO. High operational temperatures of engine are responsible for the release of NO_x while CO emissions result from incomplete combustion of fuel.

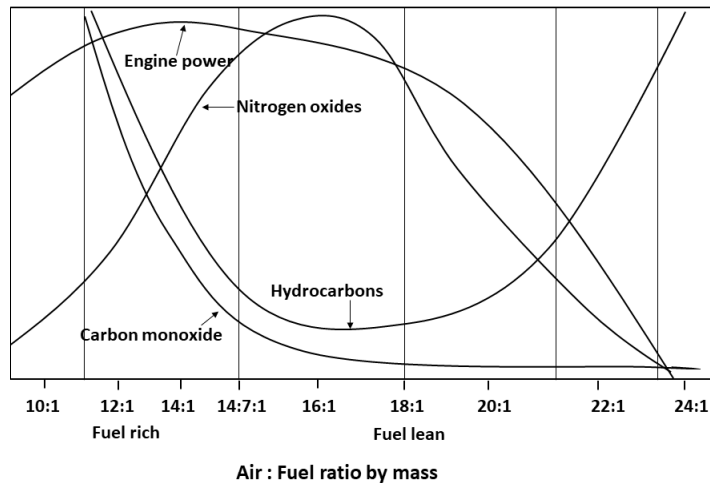


Figure 8.2 Effect of air : fuel ratio on gasoline vehicle emissions

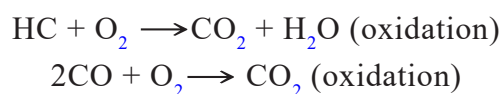
Control measures have been adopted by employing the use of leaner air-fuel mixture, meaning the one in which the ratio of air to fuel is relatively high. At air: fuel ratio greater than 16:1, the carbon monoxide emissions are practically eliminated from an internal combustion engine. As shown in figure 2, the extreme left of the graph corresponds to low air : fuel ratio area and high air fuel ratio is observed above 18:1. Lesser the air, low is the combustion rate and hence more is the CO and hydrocarbons production. An air mixture, rich in air and results in low CO and hydrocarbon production is called as Leaner mixture, when there is more air than required to burn the fuel. But leaner mixture will surprisingly not give low hydrocarbons.

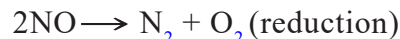
Modern day engines work on two air-fuel ratios:

- Stoichiometric ratio- 14.6:1
- Leaner mixture- 20:1

The environmental drawback to higher air : fuel ratios is that lean burn engines produce nitrogen oxides at high temperatures.

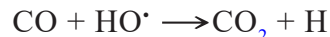
Modern day automobiles use catalytic exhaust reactors to control carbon monoxide emissions. The excess air is passed through the exhaust gas and the mixture is passed through the catalytic convertor in the exhaust system, affords oxidation of CO to CO₂.



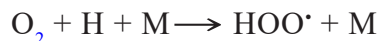


8.2.3 Sinks of Carbon monoxide

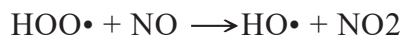
The removal of carbon dioxide from atmosphere is affected by the reaction with hydroxy radicals HO• as follows:



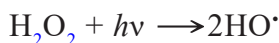
This eventually releases hydroperoxyl radical as the by-product,



Further HO• regenerates from HOO• according to the following reactions:

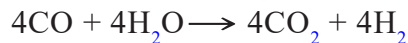


The photochemical dissociation of H₂O₂ to regenerates back HO• as follows:

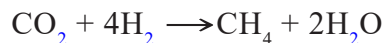


Another possible mode for removal of atmospheric CO is soil. In presence of moisture, certain anaerobic soil microorganisms like *Methanosarcina Barkerii* and *Methanobacterium formicum*, remove CO from the atmosphere by oxidising and converting into methane in the presence of moisture.

CO reacts with water in two phases:



Subsequently, CO₂ and H₂ react together producing methane

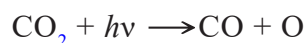


Thus, soil serve as a sink for the removal of atmospheric carbon monoxide.

8.3 CARBON DIOXIDE

A minor but an essential component of the atmosphere, carbon dioxide is released from multiple natural sources like volcanic eruptions, the combustion of organic matter, respiration by living organisms, fermentation by microorganisms and through human activities like burning of fossil fuels, deforestation and land use changes. Plants consume carbon dioxide and convert it into carbohydrates during photosynthesis. The oxygen so released is subsequently used for respiration by heterotrophic organisms. This is a cyclic phenomenon which carbon dioxide is interconverted in the environment through a series of processes.

Chemically as well as photochemically, carbon dioxide is a relatively insignificant in terms of its low concentrations and low photochemical reactivity. However, it undergoes an important photochemical reaction, a photodissociation by high energy solar ultraviolet radiations in the stratosphere. This reaction serves as a major source of CO at higher altitudes,



Carbon dioxide is a potential greenhouse gas that traps heat energy from the sun, and contributes significantly in maintaining global temperatures habitable for

humans and millions of other species. Other than CO_2 , other principal greenhouse gases in Earth's atmosphere are water vapor, methane, nitrous oxide and ozone. In absence of these gases, the average global temperatures would be about -18°C (0°F), in contrast to the actually present temperature of 15°C (59°F). However, with increasing industrialization, deforestation, conversions of forestlands, wetlands to agriculture, the atmospheric balance of carbon dioxide is disturbed and threatens to change drastically in the coming years. Unfortunately, this has slowly propelled a rise in average global temperatures. Atmospheric levels of carbon dioxide and other infrared-absorbing "greenhouse gases" have increased substantially and are at the highest levels ever recorded. The gases contribute to global warming, by allowing incoming heat energy from the sun to penetrate to the Earth's surface, while reabsorbing infrared radiation emanating from it, thus trapping the heat into the lower atmosphere. This phenomenon of trapping of heat inside earth's atmosphere is known as the greenhouse effect. Methane is about 20–30 times more effective in trapping heat than is CO_2 . Other trace gases like chlorofluorocarbons and N_2O are also contribute to the greenhouse effect. A brief description about the sources of these gases is given below:

- Methane- Decomposition of organic matter in landfills, swamps and by anaerobic biodegradation of organic wastes in rice paddies release methane in the atmosphere. It is also produced during bacterial action in the digestive tracts of ruminant animals
- Nitrous oxide- Agricultural and industrial activities, combustion of fossil fuels and solid waste contribute significantly to nitrous oxide emissions.
- Fluorinated gases: Hydrofluorocarbons, perfluorocarbons, sulphur hexafluoride, and nitrogen trifluoride are released from a variety of industrial processes. Fluorinated gases are also responsible for depletion of stratospheric ozone.

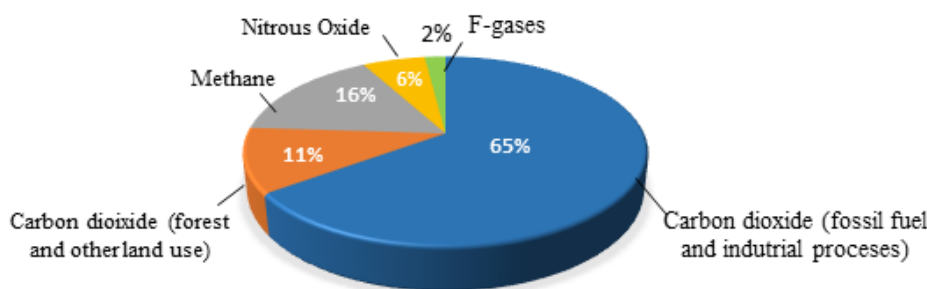


Figure 8.3 Major Greenhouse gases (F-gases: Fluorinated gases)

Of all the greenhouse gases as shown in figure 3, carbon dioxide accounts for the largest share, it is responsible for about half of the atmospheric heat retained by trace gases. The origin of the greenhouse effect concept lies in the 19th century, when French mathematician Joseph Fourier speculated in 1824 that the Earth would be much colder if it had no atmosphere. In 1896, Swedish scientist Svante Arrhenius, first person to correlate the rise in carbon dioxide levels from burning fossil fuels to a warming of the planet. Later, American climate scientist James E. Hansen declared that "The greenhouse effect has been detected and is affecting earth's weather and climate patterns." Climate change not only describe the rising

average temperatures referred to as global warming but also extreme weather events, shifting wildlife populations and habitats, rising seas, and many more. A schematic representation of greenhouse effect is shown in figure 4.

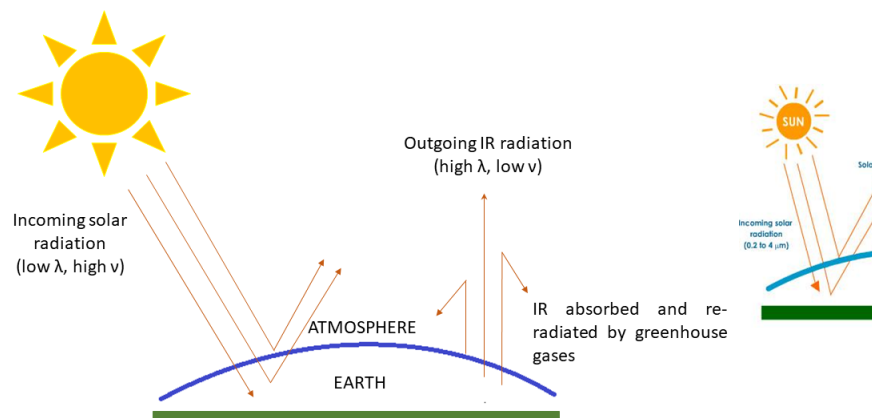


Figure 8.4 A schematic representation of greenhouse effect in Earth's atmosphere

Radiations from sun reaching the Earth's surface are cut down upto 40-50% due to absorption or reflection back by the species like ozone, particulate matter, aerosols in the upper region of atmosphere. Out of this, remaining 50% is visible light and IR radiation. This low wavelength and high frequency light reaching earth surface and like any other solid body, earth absorbs these radiations incident on it. Absorption is followed by emission of radiations. The radiations emitted from the surface are low frequency and high wavelength falling in the IR region and cause heating effect or warm the earth's climate. The frequency match of these IR radiations matches with those of CO_2 , H_2O , CH_4 , N_2O , ozone (to some extent) and CFCs. These gases absorb thermal IR radiations and subsequently re-emit them. Part of it is escaped into upper atmosphere and the remaining part is redirected back to earth's surface, where it is again absorbed by the Earth. It is this redirection of thermal IR radiations which cause trapping of sunlight and results in heating up of the earth. This is imaginary occurrence phenomenon and is responsible for average temperature of earth to be around 15°C . The same phenomenon is seen in glasshouse for growing plants in temperate regions. Due to cold, dry conditions do not process enough sunlight for plants to grow on their own, keeping them in glass house allows little available sunlight to remain trapped inside, because glass is made up of silicates and Si-O-Si-O- bonds play same role as CO_2 in the atmosphere. This creates effect of creating a house for greening of plants is called greenhouse effect, coined by Joseph Fourier.

8.3.1 Global warming

Global warming is a consequence of greenhouse effect. With increasing concentration of thermal IR absorbing species in atmosphere, sun's radiations remain trapped in the atmosphere and consequently the greenhouse effect is accelerated. This accelerated Greenhouse effect is called Global warming.

A steady increase in global carbon dioxide levels is shown in figure 5. Concentrations of CO_2 vary with seasonal changes, with maximum values occur in April and minimum values in late September or October. These alternations arise to the

“photosynthetic pulse,” influenced by forests in middle latitudes. Forests largely influence than any other vegetation because photosynthesis by trees occur at a large level. Additionally, forests store readily oxidizable carbon in the form of wood and humus that influence atmospheric CO_2 content. Thus, during the summers, trees carry out enough photosynthesis thereby reducing the atmospheric carbon dioxide content. However, during winters, metabolic activities like bacterial decomposition of humus, releases a substantial amount of CO_2 . At present, worldwide destruction of forests and conversion of forest lands to agricultural uses is largely responsible for the overall increase in atmospheric CO_2 levels.

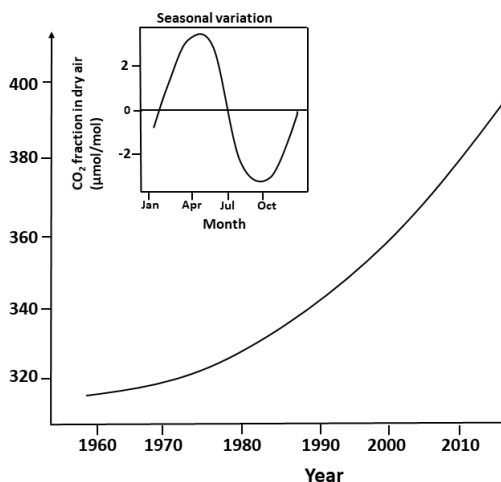


Figure 8.5 Increase in CO_2 concentrations in recent years. The inset figure reveals seasonal variations in northern hemisphere.

Radiative forcing refers to the reduction in infrared radiation penetrating outward through the atmosphere per unit increase in the level of gas in the atmosphere. Radiative forcing of methane is about 25 times greater than that of CO_2 . Increasing concentration of greenhouse gases forces retention infrared radiations because their absorption spectra fill gaps in the overall spectrum of outgoing radiation. CO_2 (IR active molecule) absorbs greater fraction of infrared radiation, thus increase in CO_2 concentrations have a small effect, whereas an increase in concentration of methane, chlorofluorocarbons or other greenhouse gases have much larger effect.

The mechanisms underlying the rate of building up of carbon dioxide and methane in atmosphere may be understood by both positive and negative feedback. Studies reveal that rise in CO_2 concentrations results in accelerated uptake of this gas by plants during photosynthesis, which tends to slow building up of the atmospheric CO_2 . In warm climatic conditions with adequate rainfall, plants would grow faster and hence would take up more CO_2 . Thus, forests have an important contribution with high CO_2 fixing ability. However, with continuous increase in CO_2 concentrations, it is likely that the forests would lag behind in their ability to fix additional CO_2 . Similarly, higher atmospheric CO_2 levels would lead to increased sorption of the gas by oceans. The dissolved CO_2 content in the oceans is about 60 times greater than the amount of atmospheric CO_2 . Nevertheless, the time required to transfer carbon dioxide from the atmosphere to the top layers of the ocean is of the order of years. As a result of low mixing rates, the time for transferring carbon dioxide from the topmost layer of ocean to ocean depths is much longer, of the order of decades. Therefore, like the absorption of CO_2 by forests, increased uptake of CO_2 by oceans

will also lag behind the atmospheric CO₂ emissions. Severe drought conditions that are arising due to climatic warming could lead to a substantial fall in uptake of CO₂ by plants. Warmer conditions would result in increased production of both CO₂ and CH₄ by microbial decomposition of organic matter. Thus, global warming is largely responsible for the surge in rate at which biodegradation release these gases into the atmosphere.

It is anticipated that carbon dioxide levels will continue to increase substantially. With conceivable projections of CO₂ production and a reasonable estimate that half of that amount will stay in the atmosphere, it is estimated that sometime during the middle of the next century the concentration of this gas will reach 600 ppm in the atmosphere. Clouds reflect the incoming light radiation and absorb outgoing infrared radiation. Several factors like degree of cloud cover, brightness, altitude, and thickness determine the intensity of climatic changes. Warming promotes cloud formation, which reflect more incoming radiations. The computational studies predict global warming of at least 3.0°C and as much as 5.5°C occurring over a period of just a few decades.

8.3.2 Effect of Global Warming

One of the most immediate and obvious effects of global warming is the increase in global temperatures. The rate at which average global temperature is increasing, it is predicted that it would rise by 3.5 to 4 °C in the next 50 years. Rise in temperature would lead to following:

Melting of glaciers

Increased global temperature would result in melting of glaciers and ice caps all over the world, causing sea-level to rise, threatening low-lying islands, coastal areas. Global sea levels are rising at a rate of 0.13 inches (3.2 mm) a year, and the rise is occurring at a faster rate in recent years. If this continues, oceans could be ice free by 2050.

Climate change

Drought is the most serious problem that could arise from climatic changes as a result of global warming. A 3-degree warming accompanied by 10% a decrease in precipitation would lead to increased rates of evaporation and decreased rainfall (irregular weather pattern). Rising temperatures would adversely affect wildlife and their habitats. Populations of species like Adélie penguin in Antarctica, have collapsed by 90 percent. More than a million species worldwide could get extinct by 2050.

More frequent and extreme weather events

Weather events like cyclones, forest fires, droughts, floods become more frequent and intense as a result of global warming. This would result in loss of human life, damage to property and the environment.

Acidification of oceans

Oceans absorb extra heat and CO_2 than atmosphere. Warming would make them more acidic. Warming ocean waters are bleaching coral reefs and paving way for stronger storms. Rise in acidity threaten shellfish, without which marine food chain would collapse.

Impairs human health

Warm temperatures affect human health. With increasing rainfall, the probability of water-borne diseases like malaria are likely to spread. Higher the temperatures, more is resistance of pests -weeds, insects, rodents towards control measures and their adaptability increases. This would result in increase in number of infectious diseases and greater threat to epidemics.

Agriculture

The increasing temperatures will probably offset the benefits of atmospheric carbon dioxide on crop plants. Climate changes influence the productivity of agriculture significantly. Increase in temperatures would result in a situation with decreased run-off, decline in water availability for agricultural, municipal, and industrial usages. Water scarcity would severely affect irrigation and production of lower quality, higher salinity runoff water and wastewater.

Know your progress I

Q1. How are air pollutants classified on the basis of their origin?

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Q2. What are the ill effects of CO on human health and plants?

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Q3. Explain air/fuel ratio.

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Q4. What is global warming? How is it different from greenhouse effect? What are the environmental outcomes of global warming?

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Q5. Which parameters affect the radiative balance of the earth / atmosphere with the sun?

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8.4 OXIDES OF NITROGEN

The oxides of nitrogen commonly encountered in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Nitrous oxide is a greenhouse gas and contributes to global warming. The other oxides, nitric oxide (NO) and nitrogen dioxide (NO_2) are of major concern as pollutants and commonly referred to as NO_x .

A detailed atmospheric chemistry of nitrogen oxides has already been discussed in Unit I of Block II. The following section deals with the harmful effects associated with nitrogen oxide emissions and their control.

8.4.1 Harmful Effects of Nitrogen Oxides

The oxides of nitrogen, which have adverse effects on human health, are nitric oxide (NO) and more toxic nitrogen dioxide (NO_2). NO interacts with haemoglobin and greatly impairs its oxygen carrying efficiency similar to CO . However, under polluted atmospheric conditions, nitric oxide levels are much lower than carbon monoxide, so it doesn't interact the haemoglobin to much extent.

Acute exposure to NO_2 leads to serious health problems. NO_2 is relatively insoluble, when inhaled it interacts with the moisture in the alveoli of the lungs and is converted to nitrous and nitric acids, causing inflammation of inner lining of the lungs. This reduces immunity against lung infections. Exposures to a level of 150-200 ppm of NO_2 causes *bronchiolitis fibrosa obliterans*, that proves fatal within 3-5 weeks after exposure. Death usually occurs within 2-10 days of exposure to high concentration of 500 ppm or more. Another example of NO_2 poisoning is

the “Silo-filler’s disease,” which is caused by NO_2 released from fermentation of ensilage containing nitrate. A number of deaths have occurred due to the inhalation of NO_2 -containing gases released from burning celluloid and nitrocellulose film, as well as from discharge of NO_2 oxidant (used with liquid hydrazine fuel) from missile rocket motors.

Other health problems associated with inhalation of very high levels of NO_2 are-

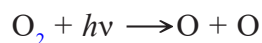
- Harm to a developing foetus
- Decreased female fertility
- Spasms
- Swelling of the throat
- Rapid pulse
- Dilated heart

Prolonged exposures to NO_2 cause heavy damage to plant life as well. This results from secondary products of nitrogen oxides, for example PAN formation in smog. Laboratory studies indicate that exposing the plants to several parts per million of NO_2 results in leaf spotting and breakdown of plant tissue. Also, a reversible fall in the rate of photosynthesis results from exposure to a level of 10 ppm of NO .

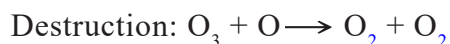
The oxide of nitrogen (NO_x) have been known to create problems for textile industries. Long term exposures often cause fading of dyes and inks used in textiles. Major damage occurs due to action of particulate nitrates and nitric acid so produced from NO_x .

Nitrogen oxides cause environmental health hazards upon reacting with other chemicals in presence of sunlight to form photochemical smog. Nitrogen oxides and sulphur dioxide react with moisture in the air to form acid rain. It is feared that NO_x emanating from supersonic transport planes could catalyse the partial destruction of the stratospheric ozone layer that absorbs and prevents from damaging effects of short-wavelength ($\lambda = 240\text{-}300\text{ nm}$) ultraviolet radiation.

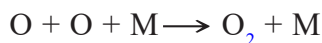
In the upper stratosphere and in the mesosphere, molecular oxygen undergoes photodissociation by action of ultraviolet light of wavelength less than 242 nm,



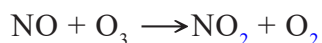
In the presence of third body that absorbs energy, the formation and destruction of ozone can be understood as follows:

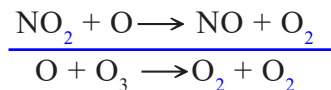


Finally, O_3 formation can be prevented by recombination of oxygen atoms:

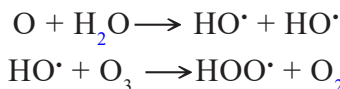


The reaction of nitric oxide with ozone is also said to be responsible for destruction of ozone layer as follows:

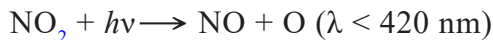




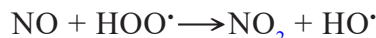
In addition to NO_x, water vapour released in the atmosphere from aircraft exhausts further accelerate depletion of ozone layer according to the following reactions:



Again, atomic oxygen responsible for regeneration of ozone is formed as follows:



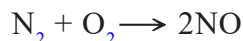
A photochemical reaction of HOO[•] competes for NO, and assist in removing NO from atmosphere,



8.4.2 Control of Nitrogen Oxides

The stationary sources such as power plant furnaces account for 50-1000 ppm concentrations of NO_x emissions. Both kinetic and thermodynamic factors like concentrations of O₂ and temperatures, respectively control NO formation, which is favoured under high oxygen concentrations and high temperatures. Thus, in lowering NO emissions from stationary sources, these factors must be taken into account. For example, reduction in flame temperature is achieved by addition of recirculated exhaust gas, cool air, or inert gases. However, this lowers the efficiency of energy conversion as calculated by the Carnot equation.

Low-excess-air firing reduces NO_x emissions during the combustion of fossil fuels. The term refers to the use of minimum amount of excess O₂ needed for oxidation of the fuel, such that less oxygen is available in the high temperature region of the flame.



The low excess firing is normally associated with incomplete combustion of fuel and results in the emission of hydrocarbons, soot, and CO. This problem may be overcome by a two-stage combustion process that comprises of the following steps:

1. The initial stage involves firing of fuel at relatively high temperatures in presence of sub-stoichiometric amount of air, (90-95% of the stoichiometric requirement). Thus, formation of NO is limited by the absence of excess oxygen.
2. At second stage, burning of fuel is accomplished in excess air at a relatively low temperature. The low temperature prevents formation of NO.

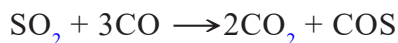
In some power plants, the two-stage combustion process has led to reduction in NO_x emissions by about 90%.

A variety of methods like catalytic decomposition of nitrogen oxides, catalytic reduction of nitrogen oxides, and sorption of NO_x by liquids or solids, have been developed for efficient removal of NO_x from stack gas (gas passing through smoke *stack*). The reaction is accelerated upon oxidation of NO to more water-soluble species like NO₂, N₂O₄, N₂O₃, HNO₂, and HNO₃.

A representative example of catalytic reduction of NO in stack gas involving methane is shown as follows:



However, a major concern associated with these processes is the release of undesirable by-products. For example, sulphur dioxide reacts with carbon monoxide that is used to reduce NO emissions, produces toxic carbonyl sulphide, COS as follows:

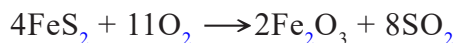


A majority of sorption processes are employed for the simultaneous removal of oxides of both nitrogen and sulphur. In this method, sulfuric acid or alkaline scrubbing solutions $[\text{Ca}(\text{OH})_2 \text{ or } \text{Mg}(\text{OH})_2]$ may be used as sorbents. For example, the use of NO_2 in conjunction with the flue gas regulates NO emissions (primary product of combustion) by producing N_2O_3 , which is most efficiently absorbed.

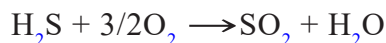


8.5 SULPHUR DIOXIDE

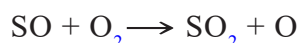
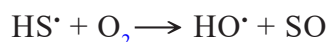
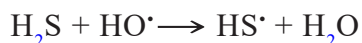
A group of oxides of sulphur, SO_2 and SO_3 are collectively as SO_x . Of greatest concern is the sulphur dioxide (SO_2), a colourless gas with a characteristic odour of burning sulphur. It enters the atmosphere from a variety of natural and anthropogenic sources. The primary anthropogenic sources include combustion of coal and residual fuel oil. Approximately half of the sulphur in coal is present as pyrites, FeS_2 and the remaining half consists of organic sulphur. The combustion of pyrite releases SO_2 in accordance with the following reaction:



Natural sources in form of geothermal activities like volcanoes, hot springs introduce sulphur largely as SO_2 and H_2S . In addition, biological decay of organic matter and reduction of sulphates release sulphur in the form of $(\text{CH}_3)_2\text{S}$ and H_2S . H_2S entering into the atmosphere is converted to SO_2 by the following reaction:



It is a multi-step phenomenon wherein the initial reaction starts with abstraction of hydrogen ion by hydroxyl radical, followed by two other reactions that produce SO_2



The single largest source *via* which natural sulphur discharges to the atmosphere is believed to be biogenic dimethyl sulphide, $(\text{CH}_3)_2\text{S}$, from marine sources.

8.5.1 Sulphur dioxide reactions in the atmosphere

Like nitrogen dioxide, sulphur dioxide participates in complex reactions in the atmosphere forming secondary pollutants like sulphate aerosols, particulate matter and acid rain. Generally, high level of air pollution is indicated by a substantial

increase in aerosol particles, accompanied by reduction in visibility. These chemical reactions are affected by changes in temperature, light intensity, humidity, atmospheric transport, and surface characteristics of particulate matter.

Sulphur dioxide reacts with other species in the atmosphere through following processes:

1. Photochemical reactions
2. Photochemical and chemical reactions in the presence of oxides of nitrogen and/or hydrocarbons, mainly alkenes
3. Chemical processes in water droplets containing ammonia and metal salts
4. Reactions on surface of atmospheric solid particles

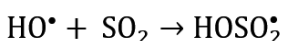
Owing to the dynamic nature of the atmosphere with varying temperature, humidity, composition, humidity, and intensity of sunlight, different processes may prevail under different atmospheric conditions.

Photochemical reactions drive the key reaction pathways involving oxidation of SO_2 . Direct photochemical reactions in the troposphere are insignificant because energy associated with light, $\lambda > 218 \text{ nm}$ is not sufficient enough to cause the photodissociation of SO_2 molecule. In an unpolluted atmospheric condition, the oxidation of sulphur dioxide is a rather slow. Thus, the participation of other pollutant species is required in the atmospheric reactions with SO_2 .

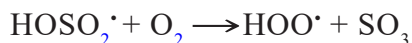
Thus, under polluted atmosphere, SO_2 reacts photochemically with other compounds in atmosphere and is oxidized, forming sulphur trioxide, sulphuric acid and salts of sulphuric acid, sulphates, particularly ammonium sulphate and ammonium hydrogen sulphate. Sulphur trioxide (SO_3) is normally released with SO_2 at concentration of about 1 - 5 % of the SO_2 . Its combination with moisture in the air produces sulphuric acid. Both SO_2 and SO_3 tend to be washed as acid rain (see section 1.6) or settle as aerosols.

Oxidation of atmospheric SO_2 : Homogenous gas-phase mechanism

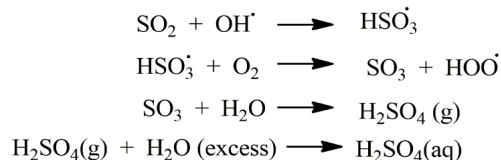
Under clear sky conditions, the predominant route for the oxidation of SO_2 to H_2SO_4 is a homogeneous gas-phase reaction. The presence of hydrocarbons and oxides of nitrogen markedly increases the rate of oxidation atmospheric SO_2 . Various oxidising species (photochemical oxidants) like HO^\bullet , HOO^\bullet , O , O_3 , NO_3 , N_2O_5 , ROO^\bullet , and RO^\bullet can effectively oxidize SO_2 . The most significant gas-phase reaction resulting in the oxidation of SO_2 is the addition of HO^\bullet radical. Since SO_2 molecule contains multiple bonds but no hydrogen, it is likely that HO^\bullet radical will add to the sulphur atom in the molecule, forming rather unstable HOSO_2^\bullet which converts to a form of sulphate.



A stable molecule of SO_3 can be formed from this radical upon removal of hydrogen atom in presence of O_2 gas.



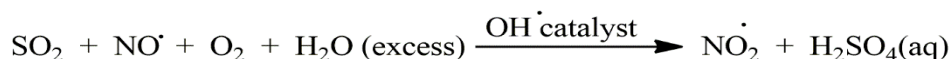
The sulphur trioxide combines with gaseous water forming sulphuric acid, which then combines with water either in form of water vapour or mist, to form an aerosol of droplets, which are chemically an aqueous solution of sulphuric acid. The sequence of reactions is summarized below:



The overall reaction is:



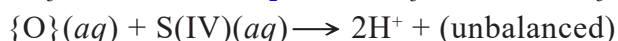
On including return of HOO^\bullet to HO^\bullet *via* reaction with NO^\bullet , the overall reaction is HO^\bullet catalysed co-oxidation of SO_2 and NO^\bullet



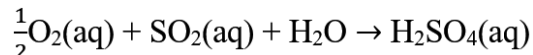
The rate of reaction depends on the concentration of HO^\bullet . Thus, under relatively clean atmospheric conditions, only a small portion of SO_2 is oxidized. However, the reaction rate increases with increasing concentrations of HO^\bullet , specifically under atmosphere with photochemical smog reactions. In actual, only minor portion of SO_2 is oxidised in air, the rest is removed through dry deposition before the above reaction has time to occur.

Aqueous phase oxidation of sulphur dioxide

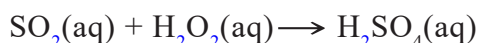
Under moist atmospheric conditions, with heavy mist, fog or cloud, fraction of SO_2 exists in dissolved aqueous form. Majorly oxidation of SO_2 to sulphuric acid predominates in aqueous medium rather than in the gas phase. Even though SO_2 is moderately soluble in water (solubility is 11.3 g/100 ml), the overall process of oxidation of sulphur dioxide under aqueous conditions is a rather complicated one, involving series of steps, *viz* transport of gaseous SO_2 and oxidant to the aqueous phase, diffusion of species in the aqueous droplet, followed by hydrolysis and ionization of SO_2 and eventually oxidation of SO_2 in presence of oxidizing agent, like H_2O_2 , HO^\bullet , or O_3 and S(IV) is $\text{SO}_2(\text{aq})$, $\text{HSO}_3^-(\text{aq})$, and $\text{SO}_3^{2-}(\text{aq})$.



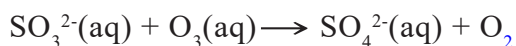
In the absence of catalytic species, the reaction with dissolved O_2 , is very slow to be of any relevance.



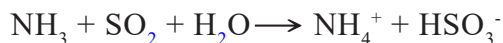
In presence of oxidizing agent like hydrogen peroxide, sulphur dioxide oxidizes to form sulphuric acid as follows:



Ozone, O_3 , too oxidizes sulphur dioxide under aqueous medium. The reaction is relatively fast with sulphite ion.



The rate of oxidation of SO_2 by ozone increases with increasing pH. For example, the oxidation of sulphur dioxide in aqueous medium is accelerated in the presence of ammonia. The reaction affords the formation of bisulphite ion and sulphite ion in solution:



Dissolved solutes in water also catalyse the oxidation of aqueous SO_2 . For example, salts of iron(III) and Mn(II) actively catalyse the oxidation process. Dissolved nitrogen species, NO_2 and HNO_2 , also effectively oxidize aqueous sulphur dioxide under laboratory conditions. This may be attributed to the fact that nitrite dissolved in water droplets may react *via* photochemical reaction producing radical, HO^\bullet , which in turn oxidizes the dissolved sulphite.

Heterogeneous reactions that occur on surface of solid particles effectively remove sulphur dioxide from the atmosphere as rain or settle as aerosol. The particles acting as nucleation centres, grow in size by accumulating reaction products, i.e., aerosols. For example, under polluted atmospheres, particles of soot so released during the incomplete combustion of carbonaceous fuels, catalyse the oxidation of sulphur dioxide to sulphate. Moreover, oxides of metals like aluminium, calcium, iron, chromium, iron, vanadium or lead, play a catalytic role by adsorbing SO_2 in the heterogenous oxidation of the gas. Because the oxide based particulate matter offers a low surface area with low degree of adsorption, so fraction of SO_2 oxidized on metal oxide surfaces is relatively small.

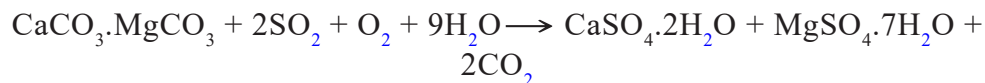
8.5.2 Effect of atmospheric Sulphur dioxide

Sulphur dioxide mainly affects the respiratory tract and causes irritation. Studies have shown that SO_2 aggravates existing respiratory problems, especially in sensitized asthmatics. Even healthy man experiences broncho-constriction when exposed to a level of 1.6 ppm of SO_2 . The main danger of SO_2 pollution, arises from its reaction products, H_2SO_4 and sulphate aerosols. The sulphate particles enter deep inside the lungs, causing even more severe health problems. SO_2 adsorbs on small particulates such as salts of iron, manganese and vanadium present in the atmosphere and thus makes the way to the alveoli of the lungs, wherein the presence of moist air, it oxidizes to sulphuric acid aerosols.

Atmospheric sulphur dioxide is also deleterious to plants, acute exposure to high levels of the gas kills leaf tissue, a condition known as leaf necrosis. Prolonged exposures cause chlorosis, a bleaching or yellowing of the green portions of the leaf. Long-term, low level exposure to sulphur dioxide is also known to reduce yields of crops such as wheat or barley.

Sulphur dioxide pollution is also known to corrode and damage buildings, monuments etc. Limestone, marble, and dolomite, which are carbonates of calcium and/or magnesium, on being attacked by atmospheric sulphur dioxide form products that are either water-soluble or deposit as solid crusts on the rock's surface. This adversely affects the appearance, structural integrity, and life of the building, a phenomenon commonly referred as stone leprosy.

Although both SO_2 and NO_x attack these minerals, chemical analysis indicates predominant formation of sulphate salts. For example, Dolomite, a calcium/magnesium carbonate mineral, reacts with atmospheric sulphur dioxide as follows:



8.5.3 Removal of sulphur dioxide

With technological advancement, a number of processes have been developed to remove sulphur and its oxides from fuel before combustion and from stack gas after combustion. Physical separation techniques may be employed to remove discrete particles of sulphur from coal, chief source of sulphur dioxide pollution. Chemical methods such as fluidized bed combustion of coal involves burning of coal in bed of finely divided limestone or dolomite. The process called as Limestone scrubbing (Calsox) can be summarised by the following equations:

Strong heating results in calcination of limestone and produces lime, CaO that effectively absorbs SO_2 . Thus, the method prevents release of SO_2 in the atmosphere.

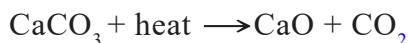
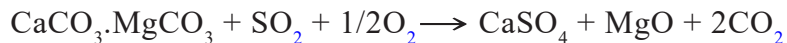


Table 2. Major Stack gas Scrubbing systems

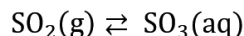
Process	Chemical Reactions	Major Advantages or disadvantages
Lime slurry scrubbing	$\text{Ca}(\text{OH})_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$	Upto 200 kg of lime per metric ton of coal are required, large quantities of waste produced
Limestone slurry scrubbing (Calsox)	$\text{CaCO}_3 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{CO}_2$	Low efficiency
Magnesium oxide scrubbing	$\text{Mg}(\text{OH})_2 + \text{SO}_2 \rightarrow \text{MgSO}_4 + \text{H}_2\text{O}$	Sorbent can be regenerated
Sodium-base scrubbing	$\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2 \rightarrow 2\text{NaHSO}_3$ $2\text{NaHSO}_3 + \text{heat} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2$	Costly
Double alkali	$2\text{NaOH} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$ (regeneration) $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{SO}_3 \rightarrow \text{CaSO}_3(\text{s}) + 2\text{NaOH}$	Solution of sodium alkali can be regenerated

Table 2 summarizes major stack gas scrubbing methodologies for effective removal of sulphur dioxide gas. These methods comprise of throwaway and recovery systems as well as dry and wet systems. A throwaway system involves an injection of dry limestone or dolomite into the boiler. The solid sulphate and oxide so produced are then removed by electrostatic precipitation or cyclone separators. The process removes sulphur dioxide with an efficiency of about 50% efficient or less. The overall reaction is:



Except for catalytic oxidation, all other processes involve acid-base reactions, relying upon absorption of sulphur dioxide.

For example, limestone slurry scrubbing is an acid-base reaction with SO_2 . On dissolution of SO_2 in water, the following equilibrium is established



In accordance with Henry's law, the equilibrium concentration of SO_2 (aq)

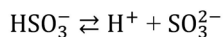
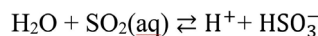
$$\text{SO}_2(\text{aq}) = K \times P_{\text{SO}_2}$$

Where : concentration of dissolved sulphur dioxide

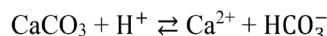
K: Henry's law constant

P_{SO_2} : partial pressure of SO_2

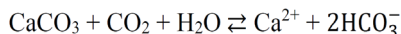
In presence of a base, the above equilibrium shifts to the right in accordance with the following reactions,



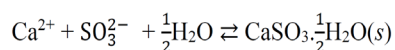
In presence of calcium carbonate, H^+ ion so released is consumed by the reaction as follows:



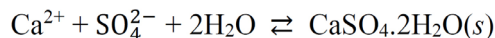
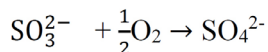
While carbon dioxide from stack gas is effectively absorbed by limestone as follows:



Finally, the reaction between sulphite and calcium ions results in the formation of an insoluble calcium sulphite hemihydrate which can be removed later on.



In addition, aerial oxidation of sulphite yields gypsum in accordance with the following reactions:



However, gypsum's formation is undesirable because it causes scaling and corrodes the scrubber equipment.

Lime slurry scrubbing employing the use of lime, $\text{Ca}(\text{OH})_2$ (in place of limestone), OH^- ions directly neutralise H^+ ions,



The reactions involving sulphur-based species in lime slurry scrubber are essentially the same as discussed for limestone slurry scrubbing process. However, owing to

higher pH of lime in comparison to limestone, the former effectively absorbs carbon dioxide and converts into soluble bicarbonates.



The process of limestone or lime slurry scrubbing are highly effective in removing in sulphur dioxide with an efficiency of over 90%.

Know your progress-II

Q1. Explain the limestone scrubbing for control of SO_x .

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Q2. Discuss the effect of NO_x on human health and vegetation.

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Q3. What is the source and sink for sulphur oxide?

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Q4. Discuss the sorption method for control of NO_x emissions.

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Q5. A power plant consumes 10000 tons of coal per day. The coal has 2% sulphur. If the sulphur oxides released are confined during one day to a volume of 10^{11} m^3 . Calculate the concentration of SO_2 in the air surrounding the power plant.

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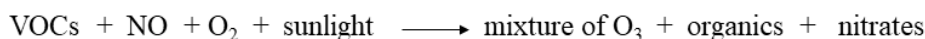
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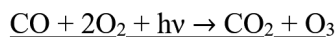
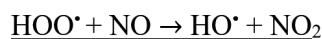
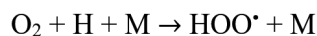
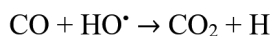
8.6 OZONE

Ozone occurs both in Earth's upper atmosphere and ground level. Majorly, it is found naturally in stratosphere (11-50 km from earth surface) at altitude of 17 to 25 km at a concentration of about **10-15 ppm**, forming 3mm thick layer, called ozonosphere. However, this thin layer is thick enough to protect life on earth. Stratospheric ozone absorbs sun's ultraviolet radiation in the region 220-330 nm, and serves as the natural shield that protects the living beings from devastating effects of such radiations. However, due to man-made chemicals such as chlorofluorocarbons, ozone layer is depleting at a fast rate. A detailed description on the chemistry of chlorofluorocarbons and their deleterious effects on stratospheric ozone is being dealt in the subsequent chapter (Unit 2, Block III).

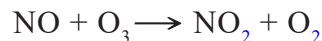
In contrast to life-saving stratospheric ozone, the tropospheric or ground-level ozone is one of the important air pollutants and a greenhouse gas. It is a secondary pollutant which is not emitted directly into the air from anthropogenic sources, rather released as a result of various chemical reactions between NO_x and volatile organic compounds (VOCs) in presence of sunlight. Emissions from industries, vehicular exhausts, power plants, refineries etc. are the major source for the entry of oxides of nitrogen and VOCs in the lower-atmosphere. Motor vehicle exhaust fumes release as much as 70% of the nitrogen oxides and 50% of the organic chemicals forming ozone. Typically, this combination of reactants in the presence of sunlight constitute a mixture that causes unpleasant atmospheric pollution referred as Photochemical smog, which is discussed in depth in the next unit (Unit II, Block III).



Also, a reaction between CO and HO[•] radical affords ozone, as follows:



Ozone, once formed is scavenged by NO such that it attains steady state concentration from a balance between its production and destruction.



However, presence of CO and VOCs disturbs this balance by producing peroxy radicals and give rise to increased concentration of ozone.

As a result of worldwide increase in the burning of fossil fuels, the concentrations of atmospheric CO₂ and ground level ozone are increasing at rate of approximately 0.5% and 0.32% respectively, annually. High concentrations of ozone have also been observed in winters, due to high levels of NO_x and VOCs emissions.

8.6.1. Harmful effects of ozone

Ozone, at ground-level is a secondary pollutant. In contrast to sulphur dioxide, its effect on a healthy individual is as serious as on the one with pre-existing respiratory

problem. Harmful effects of inhalation of ozone include headache and irritation in eyes, upper respiratory system, and lungs causing shortness of breath and chest pain while breathing. Acute conditions include fatal *pulmonary edema* which refers to abnormal accumulation of fluid in lung tissues and results in destruction of lung tissue.

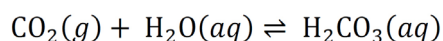
Long exposure to ozone has also been known to cause chromosomal damage. In body tissues, ozone produces highly reactive free radicals which can cause lipid peroxidation, oxidation of sulfhydryl (–SH) groups, and other destructive oxidation processes.

In addition to its effects on human health, ozone adversely affects vegetation and decreases crop productivity. Other damages include cracking of rubber, fading of dyes, paints, coatings and many more. Attack of ozone on the polymeric material proceeds with cleavage of bonds, resulting in deterioration of the polymer.

8.7 ACID RAIN

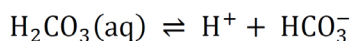
Acid rain or acid deposition is a broad term covering a variety of phenomena, including acid fog, dew and acid snow, corresponding to precipitation of excess amounts of acid in atmosphere. In general, acid deposition refers to deposition of aqueous acids, acidic gases and acidic salts (NH_4HSO_4). Deposition in solution form refers to acid precipitation while dry deposition is the deposition of dry gases and compounds. The phenomenon of acid rain was first discovered by Angus Smith in mid-1800s.

Under natural unpolluted conditions, rain is considered to be mildly acidic owing to the formation of carbonic acid from dissolved carbon dioxide gas in air,



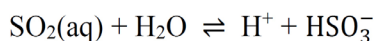
Carbonic acid

Partial ionization of H_2CO_3 release H^+ , enhancing the acidity of the system



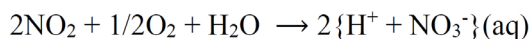
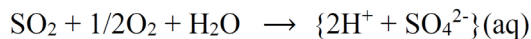
The above reaction corroborates pH value 5.6 of the unpolluted rain. The rain, significantly more acidic, with pH less than 5.6 is considered to be acid rain. The two important acids in acid rain are sulphuric acid, H_2SO_4 and nitric acid, HNO_3 . These acids result from the emission of SO_2 and NO_x in the atmosphere, their reaction with water and oxygen and finally their falling on the ground with rain.

Due to high solubility in water, atmospheric SO_2 is more acidic than CO_2 . This is evident from Henry's law constant (K_H) values of $1.2 \text{ molL}^{-1}\text{atm}^{-1}$ (for SO_2) in comparison to $3.38 \times 10^{-2} \text{ molL}^{-1}\text{atm}^{-1}$ (for CO_2). Also, the value of equilibrium constant, K for the reaction of SO_2 with water is higher than the value of 4.45×10^{-7} for CO_2 .



$$K_a = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{SO}_2]} = 1.7 \times 10^{-2}$$

Even though, direct emissions of strong acids like hydrochloric acid (gas arising from hydrogen chloride emissions) or sulphuric acid mist contributes to acid rain, the secondary air pollutants released upon atmospheric oxidation of SO₂ and NO_x are the major contributors according to the following equations



These reactions largely affect the chemical (acidity) and physical (volatility, solubility) properties of acidic atmospheric pollutants. For example, HNO₃ is highly water soluble, strongly acidic, highly reactive and badly affects plants, corrodes materials in contrast to NO₂ which is relatively weak in its action. Thus, primary pollutants NO_x and SO₂ are not at large responsible for acid rain. Indeed, a major damage comes from the secondary pollutants, H₂SO₄ and HNO₃ being formed over a period of time.

In addition to acid-precipitation, dry deposition also contributes to acid rain. It involves deposition of non-aqueous chemicals on solid and liquid surfaces. At ground level, air enriched with these chemicals passes over the surfaces and deposit them as pollutants (particulates and aerosols). Winds can blow acidic species over areas as far as several hundred to several thousand kilometers away from the area of release. Thus, Acid rain is a wider problem. It is usually classified as a regional air pollution problem, in contrast to a local air pollution problem of smog and a global one for ozone-depleting chlorofluorocarbons and greenhouse gases.

Table 3 depicts major cations and anions in acid precipitation corresponding to pH 4.25. Although, the actual values vary with time and location, the table however, presents some major characteristics of ionic solutes in precipitation. Apparently, the high concentration of sulphate ion is suggestive of major contribution of sulphuric acid towards acid precipitation. Nitric and hydrochloric acid contributes to a less extent.

Table 3. Typical values of ion concentration in Acidic precipitation

Cations		Anion	
Ion	Concentration Equivalents / L X 10 ⁶	Ion	Concentration Equivalents/ L X 10 ⁶
H ⁺	56		51
NH ₄ ⁺	10		20
Ca ²⁺	7	Cl ⁻	12
Na ⁺	5		
Mg ²⁺	3		
K ⁺	2		

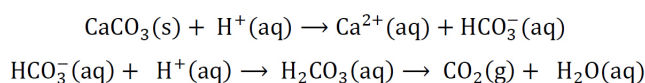
Another aspect in study of acid rain and sulphur pollution is the comparison of primary sulphate pollutants (released directly from point sources) and secondary sulphate pollutants (formed from reactions of gaseous sulphur compounds, majorly by atmospheric oxidation of SO₂). A low primary- sulphate content indicates transport of pollutants from certain distances whereas high primary sulphate content

refers to local emissions. This becomes important in understanding the efficacy of measures adopted in controlling SO_2 pollution by reducing atmospheric sulphates. Primary and secondary sulphates can also be measured by determining O^{18} isotopic content in sulphates. Studies report higher O^{18} content in sulphate emissions from power plant than those released from oxidation of SO_2 . The method is significant in view of the information it provides on the origin and control of acid rain.

8.7.1 Effects of Acid Rain

The damaging effects of acid rain are as follows:

- The damaging effects of acid rain are as follows:
- Acid rain affects biological life depending on composition of soil and bedrock in the region. Granite and quartz bedrock are worst affected because of soil's weak capacity to neutralise the acids.
- It deteriorates exposed limestone and marble-based structures, a phenomenon referred to as stone-leprosy. This is due to the neutralising action of H^+ on calcium carbonate., as evident from the following equations:



- Acidity retards the growth of some plants including those in freshwater systems. This is because of decrease in productivity in lakes and streams that feed them, the amount of dissolved organic carbon (DOC) declines rapidly in surface waters. The DOC also includes UV light absorbing molecules, thus decline in DOC allows entry of UV light into lower layer of the lake.
- Acidity from precipitation also has a deleterious effect on soil quality. When pH of the soil decreases, essential plant nutrients like potassium, calcium, and magnesium are leached from it.
- Acidification of lakes results in elevated levels of dissolved aluminium Al^{3+} , which is leached from rocks by H^+ under neutral pH conditions. Scientists believe that both acidity and high levels of aluminium are responsible for the devastating decrease in fish population in acidified water systems.
- Other effects include destruction of sensitive forests and reduction in crop productivity; leaching of nutrient cations and heavy metals from soils, rocks, and the sediments of lakes and streams; dissolution of metals such as lead and copper from water distribution pipes; corrosion of exposed metal surfaces.
- Acid rain limits global warming. This may be understood by the fact that sulphur dioxide is oxidised to sulphuric acid and sulphates aerosols. This sulphate based colloidal suspension of particles suspended in air serve as condensation nuclei upon which water vapours condense out. By modifying the properties of clouds, the aerosol particles reflect sunlight back into space. This tends to offset greenhouse warming.
- In addition, precipitation rich in ammonium, nitrate and sulphate ions in association with atmospheric acid is known as acid rime. It features frozen cloudwater, which condense on snowflakes or exposed surfaces. Acid rime

makes up 60% of the snowpack in mountainous regions. The acid deposition by rime may pave the way for the transfer of acidic components in atmosphere to the surface of earth.

Know your progress-III

Q1. Explain the circumstances leading to acid rain? How does acid rain affect us?

Q2. What is acid deposition, and what are its major components and causes? What areas tend to be affected by acid deposition?

Q3. Why does rain water normally have a pH of about 5.6? When does it become acid rain?

Q4. Differentiate between “good ozone” and “bad ozone”.

Q5. Describe the mechanism of ozone formation in the lower troposphere.

8.8 LET US SUM UP

Air pollution is one the main environmental challenges of the current times all over the world. With increasing industrialisation and human activities, the release of air pollutants in large concentrations is responsible for deterioration of air quality and serious health problems. Air pollution has reached such a critical stage where it has disturbed the heat balance of the atmosphere by letting more harmful radiations from the sun. As a result, our polluted atmosphere has turned into an insulator, thus preventing heat energy from escaping back into the space. This global rise in temperature, Global warming is responsible for the present-day climate changes. Due to serious danger caused to health of human and his environment, it becomes important to understand the chemistry of air pollution. In this context, the chapter presents an overview of major inorganic pollutants present in the air we breathe. These include oxides of carbon, nitrogen and sulphur. The sources, harmful effects and strategies adopted to control the emissions of these noxious gases have been discussed in detail. In addition, the chapter also provides a discussion on the chemistry of tropospheric ozone, and the acid rain.

8.9 KEYWORDS

Primary pollutant	An air pollutant emitted from a source directly into the atmosphere. The source can be either a natural process such as sandstorms and volcanic eruptions or anthropogenic (influenced by humans) such as industrial and vehicle emissions.
Secondary pollutant	Air pollutant, not emitted directly from a source, but formed in the atmosphere as a result of chemical or physical interactions between primary pollutants or with other components of the atmosphere. Most important <i>secondary air pollutants</i> are <i>Ground Level Ozone</i> , <i>Smog</i> , <i>PAN</i> .
Carboxyhaemoglobin	Carboxyhaemoglobin (COHb) is a stable complex of carbon monoxide and haemoglobin (Hb) formed in red blood cells upon contact with carbon monoxide (CO), resulting in oxygen deficiency in the body.
Pulmonary edema	A gaseous compound in the atmosphere, capable of absorbing infrared radiation, thereby trapping and holding heat in the atmosphere. Some examples are carbon dioxide, water vapor, halogenated fluorocarbons, methane, hydrofluorocarbons, nitrous oxide, CFCs and ozone.
Greenhouse gas	
Global Warming	The rise in global temperatures due mainly to the increasing concentrations of heat-trapping greenhouse gases in the atmosphere.

Visible light	Form of electromagnetic radiation, <i>visible</i> to human eyes and having wavelengths in the range of 400–700 nm.
Infrared radiation	Form of electromagnetic radiation, having wavelength 750 nm–1mm, with energy in between visible light and microwave radiation. The IR radiation is invisible to the eye and can be detected as a sensation of warmth on the skin.
Bronchiolitis fibrosa obliterans	An inflammatory condition that affects the lung's smallest airways, the bronchioles. Symptoms include a dry cough, shortness of breath, wheezing and feeling tired.
Leaf necrosis	Distress in plants, commonly observed as dark watery spots on leaves. The morphological changes arise due to degeneration or death of plant tissues. Symptom include dark watery spots on leaves or fruits, that may be tan or black.
Silo-filler disease	Condition associated majorly with farm laborers, resulting from exposure to silo gas, a combination of nitrogen dioxide (NO ₂) and carbon dioxide (CO ₂), produced from the oxidation of plants or from nitrogen rich soil. The nitrogen dioxide combines with water in the lungs to form highly corrosive nitric acid. Inhaling even a small amount can result in serious, permanent, or fatal lung injury.
Stone leprosy	Damage and disfigurement of sandstone/marble buildings caused by acid rain.
Acid rime	Condensed fog containing ammonium, sulphate and nitrate associated with atmospheric acid, freezing onto exposed surface of the objects in the winter.

8.10 REFERENCES AND SUGGESTED FURTHER READINGS

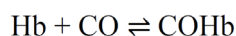
1. Colin Baird and Micheal Cann, *Environmental Chemistry*, Fifth Edition, W. H. Freeman & Company, New York, US, 2012.
2. Stanley E. Manahan, *Environmental Chemistry*, Tenth Edition, CRC Press, Taylor and Francis Group, US, 2017.
3. Stanley E. Manahan, *Fundamentals of Environmental Chemistry*, Third Edition, CRC Press, Taylor and Francis Group, US, 2001.
4. Gary W. vanLoon and Stephen J. Duffy, *Environmental Chemistry - A global perspective*, Fourth Edition, Oxford University Press, 2018.
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Answers to know your progress

Know your progress-I

Ans 1. Based on origin, pollutants are classified as primary and secondary pollutants. Primary pollutant refers to an air pollutant that is directly released into the atmosphere as a result of natural or man-made activities. For example, CO, NO_x, SO₂, etc. Whereas the secondary pollutant is produced in the atmosphere as a result of chemical reactions between primary gaseous pollutants within the atmosphere. For example, ground-level ozone, photochemical smog, acid rain and peroxy acetyl nitrate (PAN).

Ans 2. In humans, increased levels of carbon monoxide result in decreased oxygen carrying capacity of red blood cells. This is due to a formation of carboxyhaemoglobin (COHb), a stable complex of carbon monoxide and haemoglobin (Hb), that restricts the transport of oxygen from lungs to the cells. In plants, high CO levels impair plant growth. Some of the visible changes include curling of leaves, reduced leaf size and chlorophyll with premature ageing.



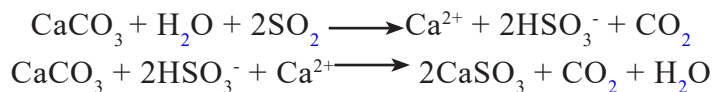
Ans 3. The Combustion of fuel is the source of energy that propels the vehicle. Air : fuel ratio refers to the mass ratio of air to fuel present in an internal combustion engine. For example, for gasoline fuel, the stoichiometric air: fuel ratio is 14.7:1 i.e. for every one gram of fuel, 14.7 g of air are required.

Ans 4. Gases present in the earth's atmosphere trap heat from the sun close to the surface, warming the Earth's surface and maintaining a stable average temperature and hence stable climate. This natural phenomenon is called the Greenhouse effect that allows life to exist. However, increasing industrialisation and human activities release CO₂, CH₄, CFCs and other pollutants in very high concentrations and have resulted in a gradual increase of the earth's temperature. This unbalanced and enhanced warming of the planet is known as Global warming. Major consequences of the global warming include melting of glaciers and polar ice caps, warming of oceans, killing coral and many species of fish, rising ocean levels that threaten population in coastal areas resulting in complete disappearance of many pacific island nations. Other effects include the unpredictable nature of weather with increased probability of occurrence of hurricanes, floods and droughts.

Ans 5. The global average equilibrium temperature of the Earth is determined by a balance between the energy absorbed by incoming solar radiation and the energy lost to space by the emission of thermal infrared radiation. The amount of solar energy absorbed depends on energy and wavelength of the incoming irradianations as well as Earth's reflective properties. Both natural and human activities contribute to changes in Earth's energy balance. Factors such as composition of atmosphere (greenhouse gases and aerosols), the reflectivity of Earth's atmosphere (albedo), cloud cover and vegetation and land use patterns largely affect the Earth energy budget.

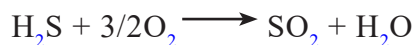
Know your progress-II

Ans 1. The Limestone scrubbing method involves the spraying of a wet slurry of limestone into a large chamber where the calcium in the limestone reacts with the SO_2 present in the exhaust of coal-fired power plants. The reaction enables the SO_2 to be removed before it's released into the atmosphere.



Ans 2. In humans, high levels of nitrogen dioxide cause inflammation of the inner lining of the lungs, and it can reduce immunity to lung infections. This can cause problems such as wheezing, coughing, colds, flu and bronchitis. Long-term exposure to high levels of nitrogen dioxide can cause chronic lung disease. High levels of NO_x have a negative effect on vegetation, including leaf damage and reduced growth, making vegetation more prone to diseases. NO_x also reacts with other pollutants in the presence of sunlight to form ozone which can damage vegetation at high concentrations.

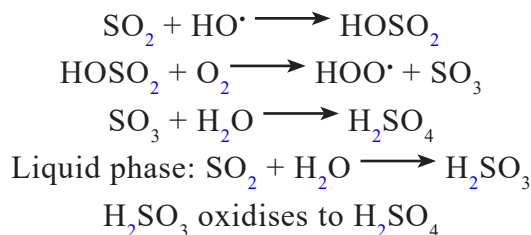
Ans 3. Natural sources are geothermal activities like volcanoes, hot springs that introduce sulphur largely as SO_2 and H_2S . In addition, biological decay of organic matter and reduction of sulphates release sulphur in the form of $(\text{CH}_3)_2\text{S}$ and H_2S . H_2S entering into the atmosphere is converted to SO_2 by the following reaction:



The major anthropogenic source is the combustion of sulfur-containing fossil fuels such as coal and crude petroleum.

Sulphur dioxide is removed from the atmosphere by both dry and wet deposition processes. A major sink process for SO_2 is its gas-phase oxidation to H_2SO_4 in presence of HO^\bullet radical and subsequent aerosol formation by nucleation or condensation.

Gas phase- Reaction with HO^\bullet



Ans 4. Sorption of NO_x by liquids or solids has been developed for efficient removal of NO_x from stack gas (gas passing through smoke *stack*). In this method, sulfuric acid or alkaline scrubbing solutions [$\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$] may be used as sorbents. For example, the use of NO_2 in conjunction with the flue gas regulates NO emissions (primary product of combustion) by producing N_2O_3 , which is most efficiently absorbed.



The reaction is accelerated upon oxidation of NO to more water-soluble species like NO₂, N₂O₄, N₂O₃, HNO₂, and HNO₃.

Ans 5. The amount of SO₂ released is

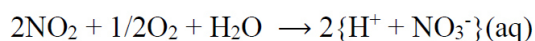
$$\frac{64 \text{ tons of SO}_2}{32 \text{ tons S}} \times \frac{2 \text{ tons of S}}{100 \text{ tons of coal}} \times \frac{10,000 \text{ tons of coal}}{\text{day}} = 400 \frac{\text{tons of SO}_2}{\text{day}}$$

If the volume over which this gas is dispersed is 10¹¹ cubic metre, then:

$$\text{Concentration of SO}_2 = 400 \frac{\text{tons of SO}_2}{\text{day}} \times \frac{1 \text{ day}}{10^{11} \text{ m}^3} \times \frac{10^{12} \mu\text{g}}{1 \text{ ton}} = 4000 \mu\text{g/m}^3$$

Check your progress-III

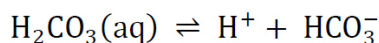
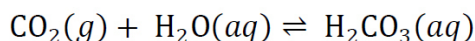
Ans 1. Harmful gases like sulphur dioxide and nitrogen dioxide, react with the water vapour present in the atmosphere to form sulphuric acid and nitric acid. The acids then fall on the surface as acid rain.



Acid rain corrodes bridges and buildings. It adversely affects forests, freshwater and soil. Acidity kills aquatic life and reduces the fertility of the soil, ultimately affecting growth and productivity of plant crops.

Ans 2. Acid rain or acid deposition, refers to any form of precipitation with acidic components, such as sulfuric or nitric acid that fall to the ground from the atmosphere in wet or dry forms. This can include rain, snow, fog, hail or even dust that is acidic. It can damage freshwater lake and stream ecosystems by lowering the pH of the water. Few fish species can survive extreme changes in pH, and affected lakes could become completely devoid of fish life.

Ans 3. Normally rain has pH of about 5.6 due to dissolution of CO₂ of the atmosphere into it.



When the pH of rain falls below 5.6, it becomes acid rain.

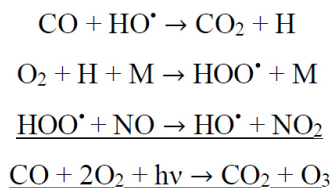
Ans 4. Ozone can be good or bad, depending on where it is found. Good ozone occurs naturally in the stratosphere, where it forms a protective layer that shields us from the sun's harmful ultraviolet rays. However, this protective shield (ozone layer) is gradually being destroyed by manmade chemicals. Bad Ozone refers to tropospheric, or ground level ozone, which does not occur naturally rather is produced as a result of chemical reactions between oxides of nitrogen (NO_x) and volatile organic compounds (VOC) in the presence of sunlight. It is a harmful air pollutant that affects plants and human health. It damages crops, trees and other

vegetation. In humans, ground level ozone causes difficulty in breathing. In high levels, it causes serious damage to the lungs.

Ans 5. Ground-level or bad ozone is not emitted directly into the atmosphere, but is produced from chemical reactions between NO_x and VOCs in the presence of sunlight



Also, a reaction between CO and HO[•] radical affords ozone, as follows:



Ground level ozone is a harmful air pollutant. The main health concern of exposure to ground-level ozone is its effect on the respiratory system, especially on lungs. It causes shortening of breath, coughing and sore or scratchy throat. High levels of ozone may aggravate chronic lung diseases such as emphysema and bronchitis with reduced immunity to fight bacterial infections in the respiratory system

8.11 TERMINAL QUESTIONS

1. What is global warming? How is it different from greenhouse effect? What are the environmental outcomes of global warming?
2. What is the main characteristic feature of greenhouse gases?
3. List the gases responsible for creating ozone at lower atmosphere. Explain?
4. What are major sinks of carbon dioxide?
5. What is the major source of methane emissions?
6. What is acid deposition, and what are its major components and causes? What areas tend to be affected by acid deposition?
7. Describe the mechanism of ozone formation in the lower troposphere?

UNIT 9 : CHEMISTRY OF AIR POLLUTION-II

Structure

9.0 Introduction

9.1 Objectives

9.2 Sources of Organic Air Pollutants

9.2.1 Hydrocarbons as Pollutants

9.2.2 Oxygen Containing Organic Pollutants

9.2.3 Organohalide Compounds

9.2.4 Organosulphur and Organonitrogen Compounds

9.3 Reactions of Organic Compounds in Atmosphere: Photochemical Smog

9.3.1 Understanding Reactions During Photochemical Smog

9.3.2 Reactions of Hydrocarbons with O/ O₃/ HO•

9.3.3 Chain Terminating Reactions

9.3.4 Compounds That Readily Undergo Photodissociation in Atmosphere

9.3.5 Aerosols in Atmospheric Smog

9.3.6 Effects of Photochemical Smog

9.4 Ozone Layer and its Depletion

9.4.1 Chlorine and Bromine Radicals as Catalysts

9.4.2 Antarctic Ozone Hole

9.4.3 Ozone Destruction in Arctic Region

9.4.4 Ozone Destruction in Non-Polar Regions

9.5 Let Us Sum Up

9.6 Key Words

9.7 References and Suggested Further Readings

9.8 Terminal Questions

9.0 INTRODUCTION

Apart from carbon monoxide and carbon dioxide, atmosphere contains carbon-based pollutants, which are called organic pollutants. These pollutants range from gaseous molecules to particulates and pose detrimental effect on the quality of the atmosphere. Some have a direct effect and are called primary pollutants whereas others exert their effect when get converted into some other species upon photochemical reactions in atmosphere and are called secondary pollutants. In this section we shall be studying the details of these compounds and the major serious environmental episodes they are responsible for.

9.1 OBJECTIVES

After studying this unit, you should be able to

- Classify organic air pollutants and their sources
- describe the ozone layer depletion and its impact on biosphere.

- Understand the organic reactions that causing photochemical smog
- Explain the effects of photochemical smog in humans

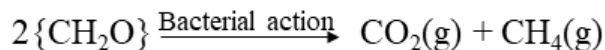
9.2 SOURCES OF ORGANIC AIR POLLUTANTS

9.2.1 Hydrocarbons as Pollutants

i. Natural Sources

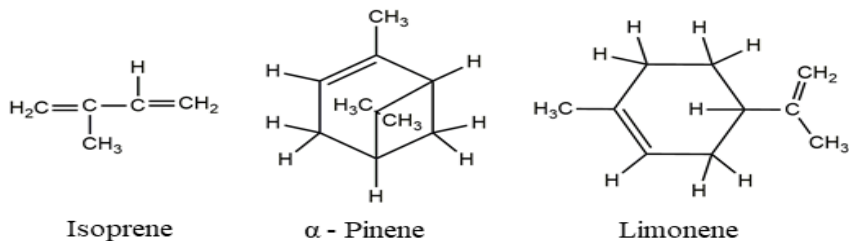
The most widely found organic compounds in the atmosphere through natural sources are hydrocarbons. Contributing to approx. 86% of the total hydrocarbons present in the atmosphere, natural sources include vegetation, forest fires, volcanoes, wastes of animals and other living organisms, microorganisms.

Amongst the hydrocarbons, methane is present in the largest quantity, and is released into the troposphere by organic matter decomposition by anaerobic bacteria in water and soil.



Ethylene is the next common hydrocarbon in the atmosphere and is very reactive in the atmosphere due to its double bond.

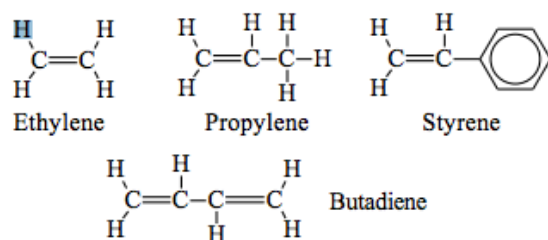
As such, there are nearly 367 organic compounds known to be released from forests and other vegetation. Plants release, into the atmosphere, a class of compounds called terpenes found in essential oils, which are themselves plant extracts that impart flavor or essence. The common terpenes known are -pinene, -pinene, limonene, isoprene. The common structural feature of these compounds is the presence of one or more olefinic bonds, which makes them very reactive and hence susceptible to reaction with reactive species in the atmosphere such as HO• and O₃. Some of these terpenes react to produce particles or aerosols which scatter light and are responsible for the blue haze that is commonly seen above thick vegetation, farms and forests.



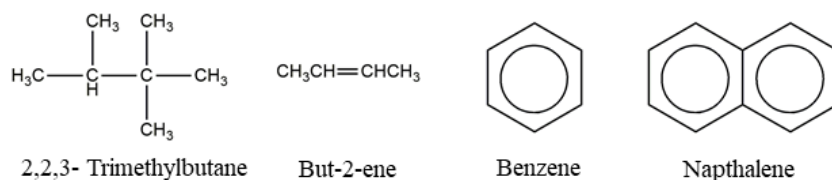
ii. Anthropogenic Sources

Several hydrocarbons are released in the atmosphere due to anthropogenic activities such as production of fuels, petroleum refining, solvent applications, emissions from internal combustion engines and other parts in automobiles and turbines.

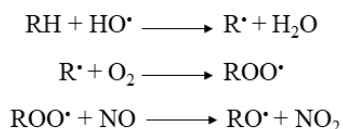
Some alkenes are produced on large scale as monomers for manufacturing a wide range of polymers.



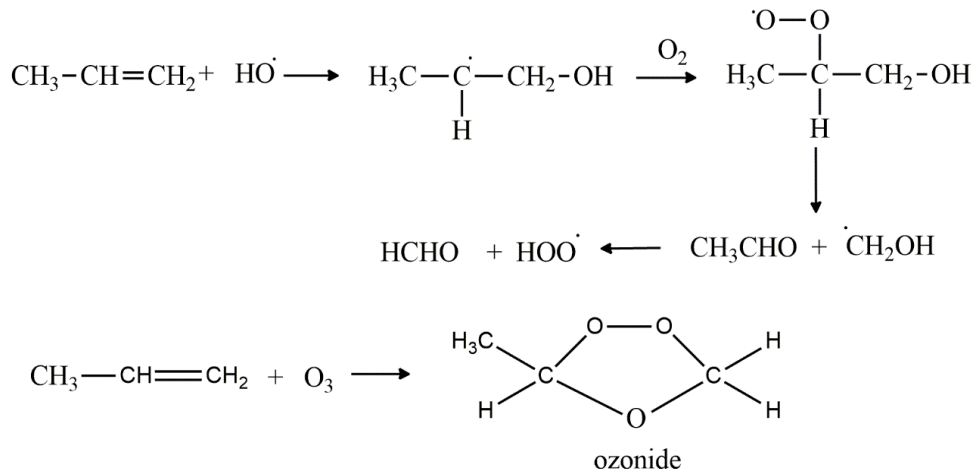
Gasoline and other petroleum products are the source of most of the anthropogenic hydrocarbon pollutants. Some of them are released directly and some as byproducts of combustion of hydrocarbons. These include alkanes, alkenes and arenes.



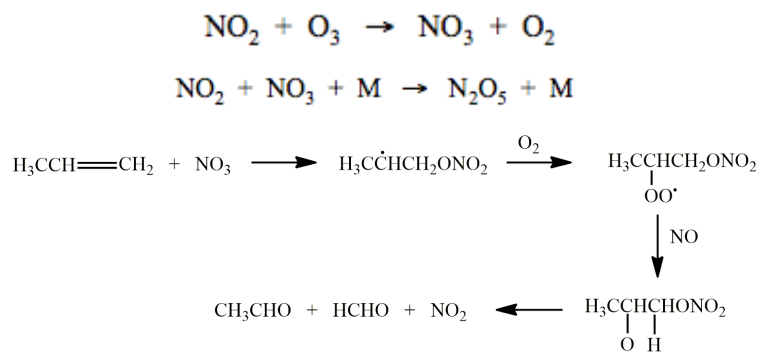
Hydrocarbons are attacked by $\text{HO}\cdot$ radicals present in the atmosphere when the latter abstracts H from alkanes to generate the corresponding alkyl radical. Alkyl radical reacts with oxygen to produce alkylperoxy which itself loses an oxygen atom to generate alkoxy radical. Usually, NO_2 takes up this oxygen atom. As a result of these and subsequent reactions, lower-molecular-mass alkanes are eventually oxidized to species that can be precipitated from the atmosphere with particulate matter to ultimately undergo biodegradation in soil.



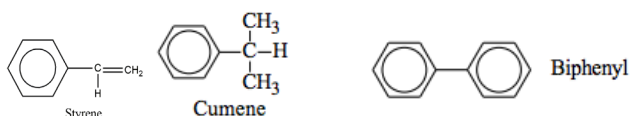
Alkenes are much more reactive than alkanes owing to their double bonds, which is attacked by $\text{OH}\cdot$, and/ or ozone to produce carbonyl compounds.



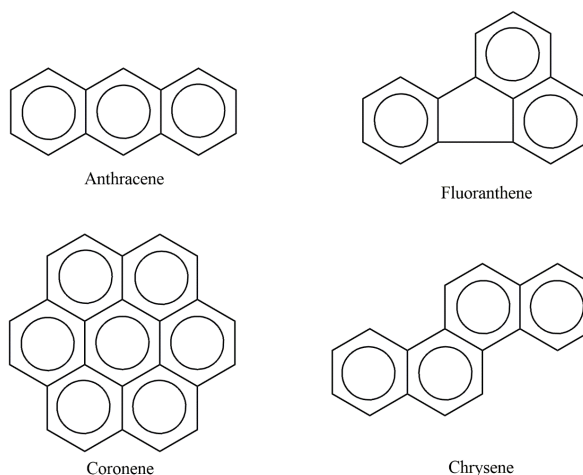
The reactivity of alkenes is further enhanced in the presence of NO_x and sunlight. In the night time, NO₃ concentrations are higher than OH• and so the following reaction is seen.



Aryl hydrocarbons range from single benzene ring containing compounds to those having multiple rings fused with each other. Benzene and related hydrocarbons are petrochemical products used as solvents, monomers, diesel and gasoline additives. They are the by-products of combustion and hence are atmospheric pollutants.



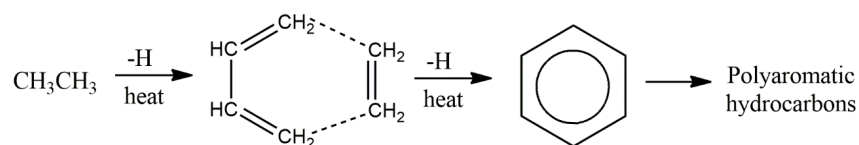
The multiple fused ring systems constitute a class of organic compounds called polycyclic aromatic hydrocarbons (PAHs).



PAHs are formed mainly as a result of partial combustion of coal or gasoline in the internal combustion engine, when the supply of oxygen is insufficient. These exist as solids and so are present as particulates in the atmosphere. Because of their carcinogenic effects, their release into the atmosphere is a cause of serious concern. Some examples are shown below. These have a severely condensed structure, which implies that their C to H is very high, or H content is very low. Due to their very low vapour pressure, they are present as aerosols in the atmosphere.

Lower hydrocarbons such as methane and ethane undergo series of dehydrogenation and addition reactions at very high temperatures of more than 5000 C (of the engines

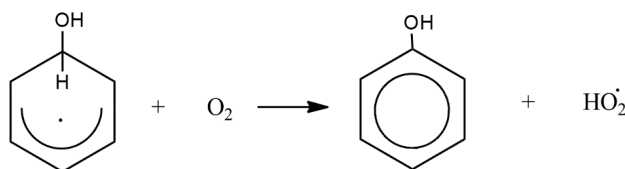
and thermal plants) to form PAHs. The reactions involve free radical, breaking and combination of bonds to result in condensed aryl structures.



The ease of formation of PAHs is parallel to the decreasing H content in the precursor molecule, i.e. arenes > alkenes > alkanes.

Yet another form of particulates is soot, which is itself a highly condensed structure of PAH, with H content as low as 1-3% and O content 5%. PAHs are adsorbed on soot.

In the atmosphere, $\text{OH}\cdot$ attacks the benzene ring and further reacts with oxygen to produce phenols and hydroperoxy radical.



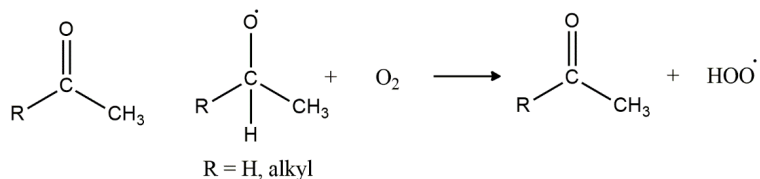
Alternately, similar to H abstraction in alkanes, $\text{OH}\cdot$ reacts with alkyl chain on the benzene ring and then with O_2 to form peroxy radical that can further undergo chain reactions.

In the night time, when NO_3 concentration is far more than $\text{OH}\cdot$, addition on aryl double bonds occurs to give secondary pollutants. The extent of such reactions is not very high.

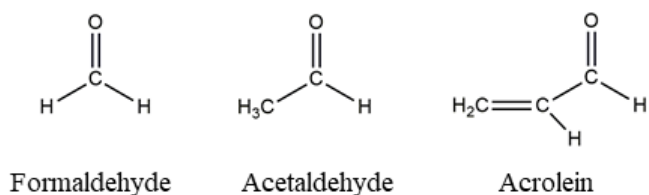
9.2.2 Oxygen Containing Organic Pollutantss

These include aldehydes and ketones, esters, alcohols, phenols.

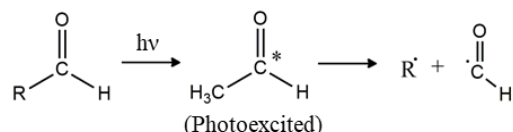
Hydrocarbons, most commonly oxidize photochemically to aldehydes and ketones as the stable species upon reaction with OH , O_3 , O . A typical such reaction is shown below:



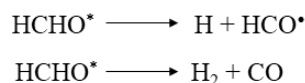
Lower aldehydes and ketones, such as formaldehyde, acetaldehyde and 2-butanone, are produced at industrial scale for the manufacture of resins, polymers, dyes, paints, adhesives, solvents in addition to being released naturally from bacterial action on vegetation.



The reactive C-O double bond, called carbonyl group, readily absorbs solar radiation (near UV region) and the resulting photoexcited molecule dissociates into alkyl and carbonyl radical. With an additional methyl, acrolein, is even more reactive.



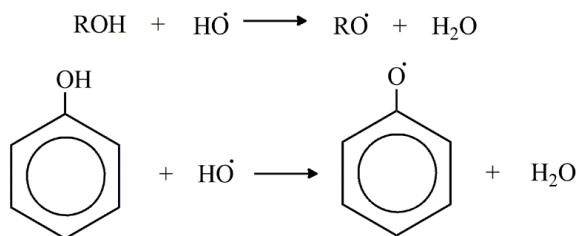
Formaldehyde, being the first member of the aldehyde family and having no alkyl group, proceeds differently. The photolytically excited formaldehyde molecule reacts in two possible ways:



A very significant reaction pathway for the aldehydes and ketones is their reaction with OH radical and then with O₂ to give the acyl peroxy radical, which in turn reacts with NO₂ present in abundance in a polluted atmosphere to produce strong oxidant nitrates as secondary pollutants. The mechanism and conditions of production of such molecules will be dealt with in section 2.3.

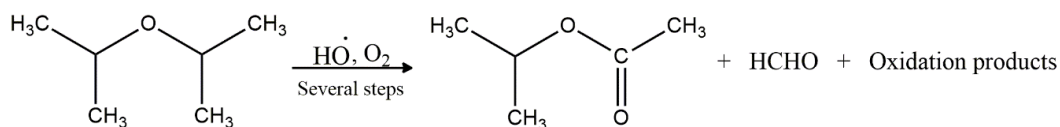
Lower alcohols, found abundantly in the atmosphere, containing up to four carbons are extensively used as solvents and as starting materials for several commercially important aldehydes, acids, esters and other compounds. Methanol and ethanol are used as anti-freeze agents and can be used as fuel for vehicles. Phenols are most commonly used in manufacture of polymers and resins and are themselves produced from burning of coke. These aromatic systems are seen more to be contaminating water than air.

Both alcohols and phenols are very reactive towards radicals such as OH[•], and themselves form alkoxy and phenoxy radicals by abstraction of the acidic H. Amongst these and as expected, the alcohols with alkenyl groups are more reactive due to the vulnerable double bonds.



Several cyclic ethers, used as industrial solvents, and lower ethers are also seen in the atmosphere. Methyl tertiary butyl ether has replaced harmful tetraethyl lead in

gasoline. Diisopropyl ether is used to increase octane number. All of these ethers react with HO• radical.



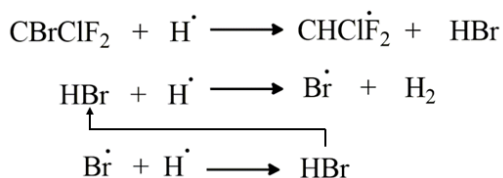
Carboxylic acids seen in the atmosphere are generally the end result of photochemical oxidations of other functional groups in air. Some specific examples of acids released directly are from natural sources such as -pinene giving pinonic acid.

9.2.3 Organohalide Compounds

A range of members in this class of compounds include substitution of one or two H to all Hs by halogens. Of these, the most abundantly found halides in the atmosphere are chloromethane, chloroform, carbon tetrachloride, vinyl chloride. These compounds are used as solvents, raw material for manufacture of polymers, resins and other compounds. Aromatic halides, e.g. chloro/ bromo benzenes, polychlorinated biphenyls, used for their high chemical and thermal stability as heat transfer liquids, hydraulic fluids, are found in the atmosphere.

In this class of organic halides are the manmade chlorofluorocarbons, popularly called CFCs or Freons, in which the first few members are volatile. These synthetic compounds have certain exceptional properties for which they have various applications. Their properties, like high stability, chemical inertness, non-toxicity make them find use as coolants, refrigerants, propellants and foaming agents. Some examples include CCl₃F (CFC-11), CCl₂F₂ (CFC-12), C₂Cl₃F₃ (CFC-113).

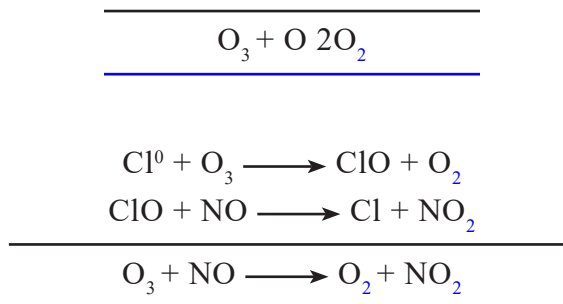
Halons, which contain bromine, such as CBrClF₂ (Halon-1211) are used as fire extinguishers, because they destroy H which is responsible for combustion.



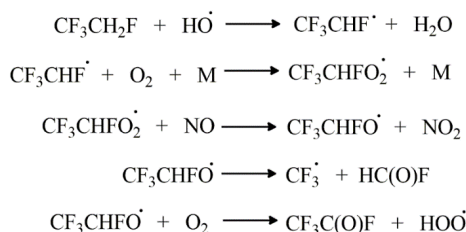
The chemical inertness of CFCs posed a serious environment threat. The volatile CFCs diffuse into the stratosphere since they have no sinks in the troposphere, where it was discovered in 1974 that they catalyze depletion of the protective ozone layer.

Chlorine radical is responsible for this destruction and is itself generated by absorbing high energy UV radiations. Only these radiations cleave the strong C-Cl bond. Cl radical knocks off oxygen atom from ozone resulting in formation of reactive ClO radical. The latter react with oxygen atom (resulting from UV absorption of ozone) or NO in the atmosphere. The scheme of reactions responsible for the depletion are:



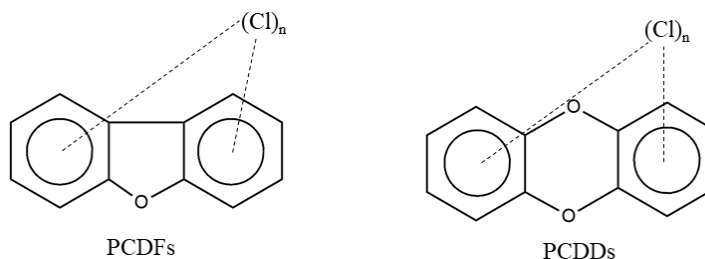


The use of CFC is the single major reason for the depletion of ozone, posing a big threat to life on this planet. The details of ozone depletion are dealt with in section 2.4. The 1987 international treaty called Montreal Protocol, designed to protect depletion of ozone, banned the manufacture and use of CFCs. However, the useful properties of these compounds were too beneficial to have discarded them completely. Hence, research and development led to new substitutes of CFCs, while eliminating the site for release of ozone depleting chlorine radical. The new compounds, called hydrochlorofluoro carbons and hydrofluoro carbons, had weaker C-H bonds which gets scavenged in the troposphere by OH radicals easily, thereby preventing the molecules from reaching stratosphere.



Another class of compounds are the completely fluorinated compounds called perfluorocarbons, such carbon tetrafluoride and hexafluoro ethane, which are used in electronic industry extensively. The C-F bond is extremely stable and does not get destroyed even in the stratosphere. The only concern for these is that they may act as potential Greenhouse gas since they absorb infrared radiations in the upper atmosphere.

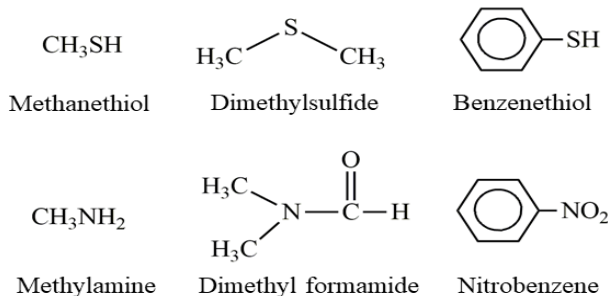
Extremely toxic polychlorinated dibenzo dioxins (PCDD) and polychlorinated dibenzo furans (PCDF) are generated from incomplete combustion in automobile engines, power plants, steel and other metal industries and municipal sewage incinerators. They are present in low amounts but are associated with particulate matter in the atmosphere.



9.2.4 Organosulphur and Organonitrogen Compounds

Hydrogen sulphide, H_2S and their alkyl substitutions, thiols or mercaptans, as well as sulphides, R_2S , are released in the atmosphere from microbial activities, plants and vegetation, human and animal excreta, sewage treatment, starch and wood pulp processing. Their most striking feature is their extremely undesirable garlic like strong odour. For this purpose, methyl mercaptan is even added to gas fuels and in petroleum refining to detect gas leakage. Alkyl sulphides, with S-C-S linkage are moderately toxic if ingested. These strongly odorous compounds cause atmospheric pollution at a local level and like other organic compounds, are attacked by $\text{HO}\cdot$ radical for H abstraction or $\text{HS}\cdot$ radical formation by direct reaction with O atom. Thiol and sulphides release sulphur in the atmosphere as SO_2 through the photochemical reactions, which goes on to oxidize to sulphites and sulphates and dissolves in water droplets to cause acid rain.

The common N containing organic compounds in the atmosphere are amines, amides, nitro compounds. Amines have a characteristic odour which makes them undesirable pollutants, even when present in small amounts. These are found in decaying matter especially protein matter, packaging waste, sewage treatment plants. Aniline, which is used commonly in manufacture of dyes, in printing, drugs, photography material, pesticides are also known carcinogens. When in atmosphere, these have their H attacked by OH radical and the resulting radical goes on to react further.



Check Your Progress I

Notes: (a) Write your answer in about 50 words

(b) Check your progress with possible answer at the end of the unit.

1. What will be the effect (direct or secondary) of mercaptans, alkanes and alkenes in the atmosphere?

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2. Why is the reaction with hydroxyl radical different for alkenes and alkanes. Which of the two is more reactive.

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3. Consider the oxidation of hydrocarbons in the atmosphere. What is the first stable class of compounds generally produced?

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Why are hydrofluorocarbons not a potential threat for ozone depletion while are the main reason for its destruction?

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9.3 REACTIONS OF ORGANIC COMPOUNDS IN ATMOSPHERE: PHOTOCHEMICAL SMOG

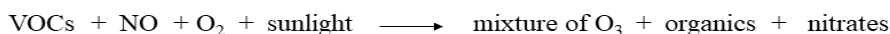
The unpleasant environmental phenomenon known today as Photochemical smog was first observed in Los Angeles in early 1940s. The problem is seen in urban areas with many industries, and heavy vehicular traffic, although natural sources such as, -pinene and isoprene from trees contribute significantly. These sources produce relatively high levels of ground level ozone -an undesirable constituent of air if present at low altitudes-via light induced reactions of pollutants. The phenomenon is therefore, also called ‘ozone layer in the wrong place’, to contrast it with stratospheric ozone which is most desirable and whose depletion is a growing concern. Apart from ozone, several oxidation products of hydrocarbons are also produced during this phenomenon. The role of sunlight and photochemical reactions was identified in 1950s.

Smog, as the name suggests, is a combination of smoke and fog and is formed as a consequence of several hundreds of reactions in the atmosphere taking place simultaneously. To start with, the original reactants for photochemical smog are nitric oxide, hydrocarbons and sunlight. The former two are primary pollutants and in the presence of sunlight they undergo several reactions resulting in harmful secondary pollutants. NO and hydrocarbons, are released as exhausts from vehicles,

from low vapour pressure solvents, liquid fuels, chimneys of plants and industries as well as from biogenic sources. Such hydrocarbons with low boiling points are termed as volatile organic compounds (VOCs). So, the essential conditions for photochemical smog to occur is to have these compounds and sunlight. Also, the air movement should be very low, in order that dilution of these reactants does not take place and the required components are in close proximity to eventually react photochemically. The photo chemical reactions of the primary pollutants result in the formation of secondary pollutants, in which the main components are O_3 and peroxyacetyl nitrate.

The final composition of photochemical smog is:

- Inorganic gases such as O_3 , NO_x
- Partially oxidized (and sometimes nitrated) organic compounds, such as peroxy acetylnitrate, peroxy benzoynitrate, acetyl peroxide etc.



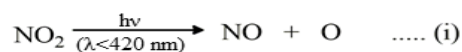
Due to this composition, we also call it oxidizing smog.

Photochemical smog is characterized by reduced visibility, severe irritation in eyes, cracking of rubber tyres, deterioration of materials.

9.3.1 Understanding Reactions during Photochemical Smog

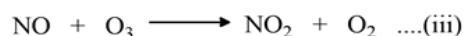
Internal combustion engines in automobiles, heavy vehicles and certain terpenes from trees release reactive hydrocarbons (alkenes etc) and oxides of nitrogen which are the main chemicals involved in smog formation. Hydrocarbons which on their own are not very harmful, are transformed into their oxidation products which may (or may not) combine with N oxides, together constituting a mixture of noxious secondary pollutants. Apart from gaseous products, particulates and aerosols are also present in this mixture.

Formation of photochemical smog initiates with the absorption of visible light by the brownish gas NO_2 . NO_2 captures the energy required to drive the O_3 - NO_x cycle where oxygen atoms are generated and further react with molecular oxygen to produce O_3 . This is the primary reaction for producing O atoms.



($M = O_2 / N_2$ which absorbs excess energy while not changing chemically)

NO_2 is regenerated when thermal (dark) reactions recreate NO_2 and O_2 and destroying O_3 .



During the sunlight exposure of atmosphere, O_3 levels in troposphere increase until the rate of ozone destruction equals its photochemical production. During the dark

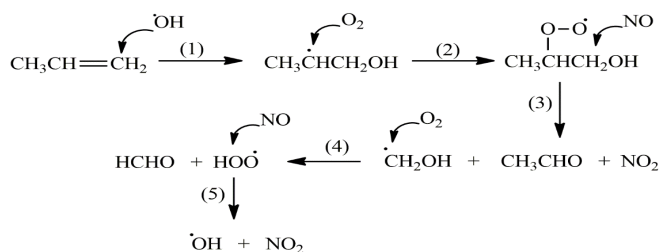
or night time, ozone levels decrease due to reaction (iii). Since a molecule of O_3 is produced only from consumption of a molecule of NO_2 , the levels of O_3 will always be lower than the initial amount of NO_2 present in air.

Accordingly, reaction (ii) is called the titration reaction and is responsible for limiting the concentration of O_3 .

However, in polluted urban areas, levels of ozone can greatly exceed concentrations predicted in eqns.(i) – (iii). This happens due to a second set of processes which involve hydrocarbons, i.e. in which the oxidation products of hydrocarbons reoxidise NO to NO_2 , without consuming O_3 . This is detailed in the subsequent section.

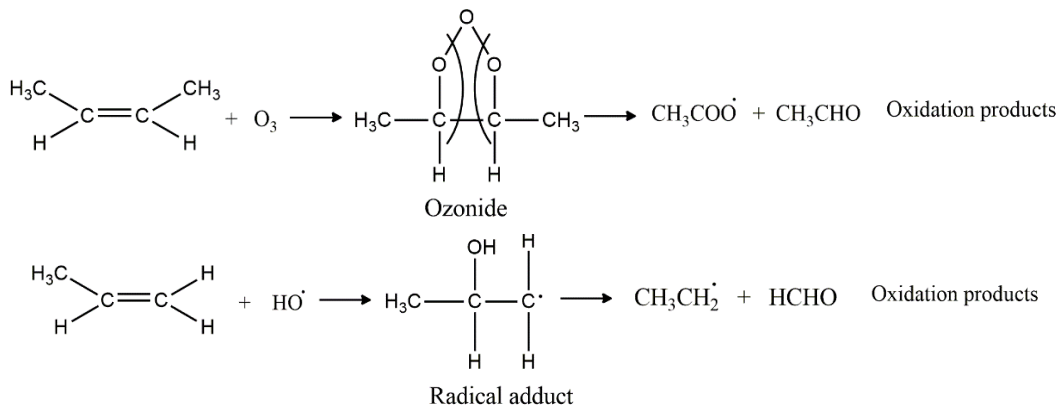
9.3.2 Reactions of hydrocarbons with O / O_3 / HO^\bullet

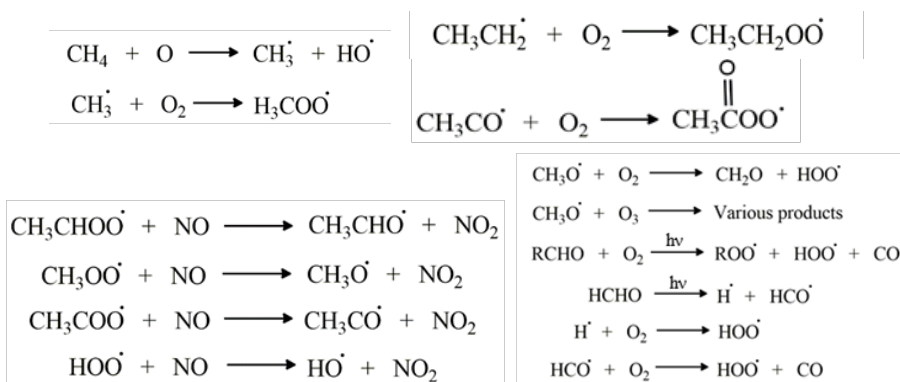
Species like O , 0OH , O_3 react with hydrocarbons, particularly olefins, to form free radicals that lead to several oxidation products. These chain of reactions also produce reactive oxidant radicals such as alkyl peroxy radical, RO_2^\bullet or hydroperoxy radical, HO_2^\bullet which can oxidise NO , while themselves getting further converted to another radical (alkyloxy RO^\bullet or hydroxyl HO^\bullet radical resp.) The alkyloxy or hydroxyl radicals, in turn, can start another series of such reactions with hydrocarbons, incorporating O_2 and regenerating RO_2^\bullet and HO_2^\bullet . One such pathway is shown:



(1) OH^\bullet radical attacks alkene molecule to form a new radical, (2) new radical reacts with O_2 to form alkyl peroxy radical (ROO^\bullet), (3) Reaction of NO_2 with alkyl peroxy radical results in the formation of NO_2 , acetaldehyde and a new organic radical, (4) Organic radical reacts with O_2 to form formaldehyde and hydroxyperoxy radical (HOO^\bullet) and (5) Oxidation of NO molecule to NO_2 by hydroxyperoxy radical (HOO^\bullet) results in regeneration of OH^\bullet radical.

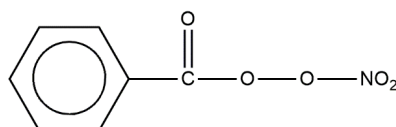
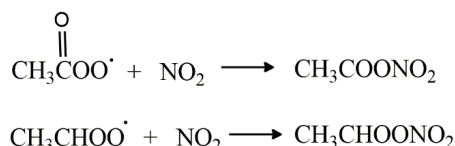
Some more pathways are depicted in the following schemes.



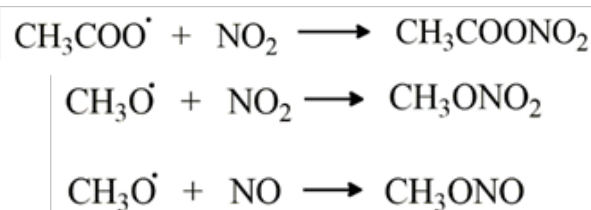


9.3.3 Chain terminating reactions

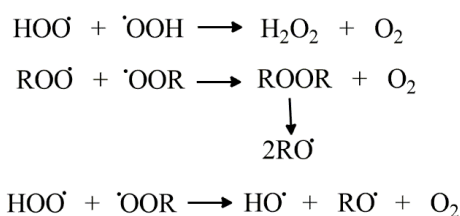
While the ultimate fate of hydrocarbons is the breakdown to CO_2 , there are a number of volatile products that result from the complex web of photochemical reactions under the smog conditions. Two radicals combine to terminate the chain reaction. Thus formaldehyde, acetaldehyde are seen in such atmospheres. The acylperoxy radicals and alkyl peroxy radicals further react with nitrogen dioxide (stable radical) giving peroxyacylnitrate and peroxy alkyl nitrate, respectively, with $-(\text{CO})\text{OONO}_2$ moiety, which cause severe irritation in eyes, and are called lachrymators. One such peroxy nitrate is peroxyacetyl nitrate, PAN, formed by the combination of acetylperoxy radical and NO_2 . Similarly, Peroxybenzoylnitrate (PB_zN) is formed when aryl hydrocarbons undergo similar reactions.



Another set of compounds, called acyloxy nitrates (RCO_2NO_2), are formed by the reaction of nitrogen dioxide with carboxyl free radicals



Other chain terminating reactions



As seen from the latter two reactions, termination is very difficult due to weak peroxy linkages that eventually break to generate more radicals.

Another way the radicals are used up is that they may get adsorbed on particulate matter and increase the size and cluster of aerosols.

Photochemical smog follows a cyclic pattern over a 24-hour period, the main steps being:

- Emission of NO_x and hydrocarbons into the atmosphere. NO_x absorbs solar energy to initiate reactions with hydrocarbons
- Consumption of NO_x and simultaneous buildup of oxidants- O , O_3 , peroxides.
- Oxidation of hydrocarbons to produce a wide variety of products including aerosols and eye irritants.

In a typical PC smog day, NO and hydrocarbons accumulated before sunrise start getting consumed as morning rush hours begin once sun rises. Therefore, shortly after sunrise there is a sharp decrease in concentrations of NO and simultaneous increase in NO_2 concentrations. During noon time there is decrease of NO_2 concentration (as well as NO) when the oxidation product and oxidant level rises and peaks itself. Hydrocarbon concentrations also decrease during the day. The pattern of these species during the day is shown in figure 1.

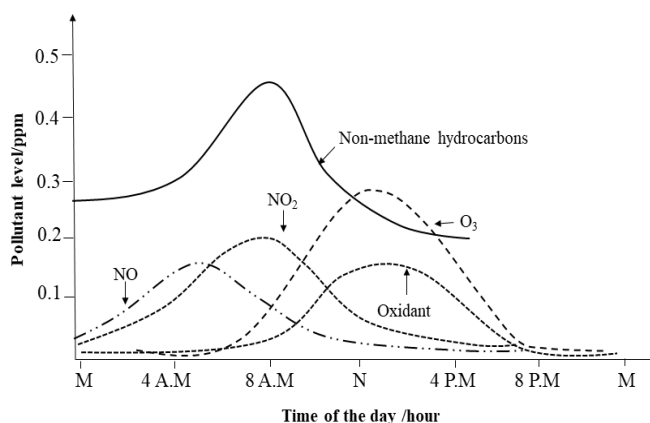


Figure 9.1 Generalized plot of atmospheric concentrations of species involved in smog formation as a function of time of day

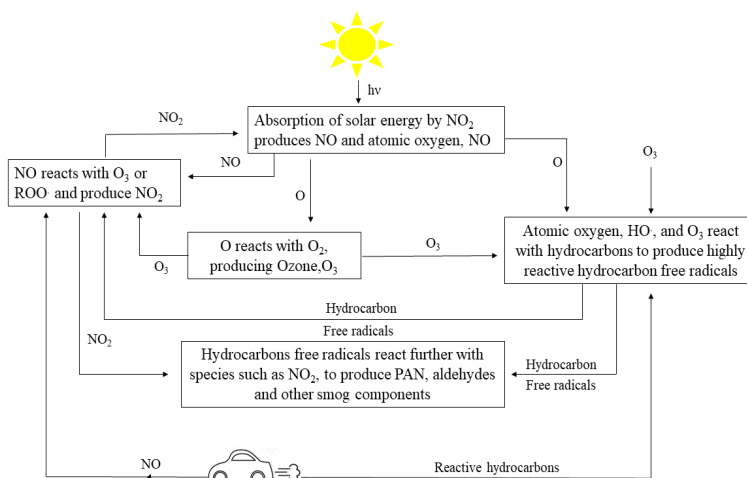
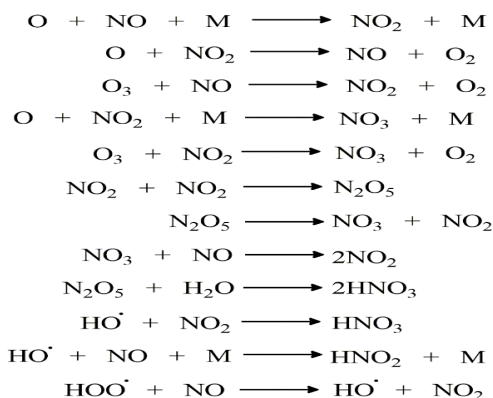


Figure 9.2 Overall summary of photochemical reactions taking place during formation of photochemical smog

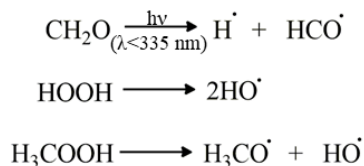
Some significant photochemical reactions involving nitrogen oxides are



9.3.4 Compounds that readily undergo Photodissociation in Atmosphere

Earlier in this section, we discussed how NO_2 readily undergoes photodissociation and is responsible for initiating the smog related reactions.

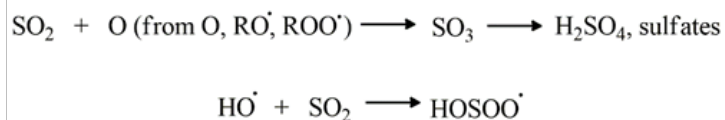
Other compounds, especially in polluted conditions, that are readily photolyzable include formaldehyde and hydrogen peroxide and organic peroxides. All of these are either directly released in the atmosphere or are first produced and then dissociate.



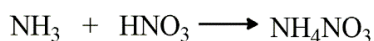
9.3.5 Aerosols in atmospheric smog

Since the level of oxidants in a smoggy atmosphere is very high, the otherwise slowly oxidizable compounds in clean atmosphere get very readily oxidized.

Thus, sulphur dioxide gets oxidized to sulphates by the oxidants like O, O_3 , NO_3 , N_2O_5 , HO^\bullet radical.



Similarly, as shown before, nitric acid is formed in large amounts in the presence of oxidants, which leads to formation of nitrate salts on the surface of aerosol droplets.



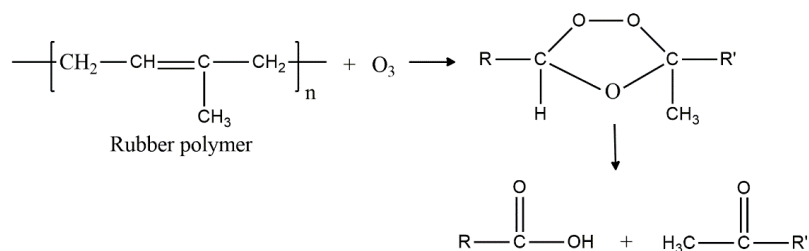
Presence of inorganic acids in the atmosphere causes corrosion and hence damage to materials. Sulphate and nitrate salts constitute urban aerosols and because of their sizes being very small ($< 2\mu\text{m}$) they scatter light very efficiently and reduce

the visibility markedly. In the areas above seas and oceans, NaCl reacts with acids to give Na_2SO_4 and NaNO_3 particles. Particles of polycyclic aromatic hydrocarbons, carbon and condensed gases are also components of this aerosol mixture.

9.3.6 Effects of Photochemical Smog

O_3 , PAN and aldehydes in Photochemical smog atmosphere cause adverse effects to the health of humans, damage to materials and toxicity to plants and vegetation. These compounds cause irritation in eyes and in the respiratory mucous lining. O_3 is a pungent smelling gas causes breathing problems. Ozone causes reduction in plant growth and crop yield.

The most striking characteristic of photochemical smog is that O_3 present attacks the double bond of rubber and adds to it to form ozonide. Other materials that have double bonds in their structure are attacked similarly. This causes cracking of rubber, deteriorates their mechanical strength severely making them brittle.



Check Your Progress II

Notes: (a) Write your answer in about 50 words

(b) Check your progress with possible answer at the end of the unit.

What are UV-A, UV-B, and UV-C radiation. What is the danger posed if UV-B is not absorbed by ozone in stratosphere.

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1. In a laboratory a mixture of benzaldehyde and NO_2 was irradiated with ultraviolet light, when people doing this experiment started experiencing irritation in their eyes. What possible product is responsible for this discomfort. Explain with reaction scheme.

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2. As a smog-forming day advances what is the trend in the levels of NO, oxidants, hydrocarbons, NO₂? Which species is the last in attaining its peak value ?

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3. The beginning of photodissociation is responsible for rapid oxidation of NO to NO₂ in a smoggy atmosphere? Justify.

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4. Why is photochemical smog also referred to as ‘ ozone layer in the wrong place’.

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9.4 OZONE LAYER AND ITS DEPLETION

Ozone is a minor component of the atmosphere (present in concentration range 0.02 – 0.1 ppm present at altitude range 17-25Km), yet it plays a key role in sustaining life on our planet. Stratospheric ozone serves as a protective shield against UV radiations that are harmful for life on this planet. Ozone in stratosphere absorbs UV radiation in the wavelength range 220 –320 nm. Therefore, it is effective in filtering out harmful UV-B radiations (280-320 nm). UV-A radiations (320-400 nm) are less harmful and UV-C radiations ($\lambda < 280$ nm) do not reach the troposphere.

Sydney Chapman, a British scientist, gave a theory for the origin of this ozone layer in 1930, which is known as the Chapman cycle (figure 3). The theory is well accepted as the basis for current understanding of stratospheric ozone. Ozone is continuously being formed during day time in the stratosphere by the combination of oxygen molecule and oxygen atom, and is also being continuously destructed by splitting into molecular and atomic oxygen on absorption of UV radiations. This continuous replenishment and destruction keeps it at a steady state concentration. For the production of O₃, UV-C radiations, that reach stratosphere, split O₂ to oxygen atoms which in turn collide with O₂ to form O₃. Ozone absorbs UV-B and

UV-C but in the process is destroyed temporarily (or sometimes reacts with O atom to give two oxygen molecules).

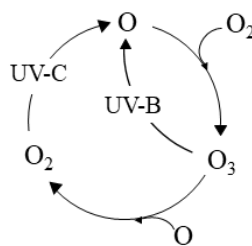


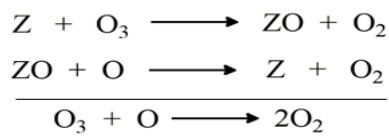
Figure 9.3 Schematic summary of the production and non-catalytic destruction reactions for stratospheric ozone (The Chapman cycle)

If all molecules of O_3 are forced into a layer they make only a 3 mm thin layer at 273 K and 1 atm pressure. The 3 mm ozone layer in the stratosphere is thick enough to act as a protective shield against harmful high energy UV radiations for plant and animal life on this planet. Exposure to life forms to UV B radiations can cause damage to eyes as seen in increasing occurrence of cataracts in humans, skin cancer. Fair and light skinned people have a stronger absorption of UV B radiations because of low content of protective melanin. The absorbed radiations cause alteration in DNA function and distorts genetic code translation. Cell division increases abnormally leading to skin cancer (squamous cell carcinoma). A substantial reduction in the concentration of ozone can harm the immune system and pose a threat to the very existence of life. UV B damages crop and microscopic aquatic plants, thereby disturbing the critical links in food chain and hence the productivity of seas.

Scientists have observed and confirmed through measurements that ozone levels in the stratosphere have been dropping gradually and while ozone is being depleted in the air worldwide, severe depletion in its amounts, was first seen in the Antarctica region in 1980s, which is referred to as ozone hole. This environment crisis was discovered by Dr J C Farman in 1980s based on data collected over decades. He saw a gradual decrease in ozone layer concentrations in the months of September-November (Spring season) in South Pole every year, which converted into a sharper decline in 1970s and reached its minimum low to 50% of the total amount in mid 1980s. Every year, from then, the amounts of ozone in Antarctica go down to this level during Spring time. This extreme thinning of stratospheric ozone in the Antarctic region has been given the name of 'hole', which appears every year for these two-three months. As years have passed, the area of this hole gradually increased, assuming the size of the Antarctica continent, and became a cause of serious concern.

The chemistry of ozone depletion has been a subject of much research and discussion, owing to its extreme environment and health significance. In fact, the 1995 Nobel Prize in Chemistry was awarded to three scientists who revealed the role of "man-made" chemicals, chlorofluorocarbons, or CFCs, in the ozone depletion process. The depletion in ozone layer was being caused largely by the presence of Cl_2 molecules or to be precise, Cl radicals, in the stratosphere.

Apart from the mechanism discussed above for the destruction of O_3 , which involves only oxygen species, there are quite a number of molecules and atoms that can cause its destruction by knocking off an oxygen atom from O_3 . The general mechanism (referred as scheme I) of involvement of such non-oxygen species (shown as Z) is :

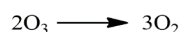


From the net reaction, it can be seen that the species Z acts as a catalyst in the destruction of ozone. In regions of stratosphere, where oxygen atom concentration is reasonable, ZO reacts with O to give and regenerate Z, which starts another cycle of destruction of ozone. So, whereas the reaction between oxygen atom and ozone, causing depletion of latter, can take place on its own, the environment concern is the enhancement of this depletion by the increase in stratospheric concentration of Z catalysts due to human activities.

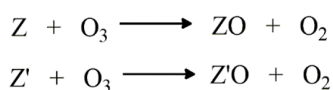
Species Z is a free radical atom or molecule, i.e. chlorine, bromine, nitric oxide hydroxyl radicals, which catalyse ozone destruction in the middle and upper stratosphere. This way, several thousands of molecules of O_3 get destroyed by a single unit of Z.

NO is present even in clean atmosphere in the upper and middle stratosphere, though in small amounts, because of a very short half life to make it in stratosphere. The precursor for NO production is N_2O (N_2O in turn diffuses into stratosphere from troposphere and has a life time of 150 years), which reacts with excited oxygen to produce mainly N_2 and O_2 . Thus, NO catalyses the destruction of ozone to a small extent. But it is the HO^\bullet radical in high stratosphere altitudes (>45 km) which is mainly responsible for ozone destruction in this region.

If we look into scheme I of catalytic destruction of ozone, it can be seen that the availability of oxygen atom is necessary in order that Z acts as a catalyst. However, it is in the lower stratosphere (17-25 Km) that maximum number of ozone molecules are found whereas the oxygen atoms are not present in substantial amounts. The low concentration of oxygen atoms in this region is because the UV C radiations are not able to reach to such low altitudes and secondly, O_2 molecules are in high concentration in this region causing whatever little oxygen atoms present to combine to produce ozone. Thus, this route (i.e. scheme I), where the catalyst action occurs only with the presence of oxygen atoms, is not preferred. Instead, destruction of ozone in the lower stratosphere happens via the overall reaction as:



There is another route (referred as scheme II) for the catalytic destruction of ozone in the lower stratosphere in the presence of high concentrations of Z catalysts.



Z and Z' represent catalysts that are chemically different but similar in nature. ZO and Z'O so formed, react amongst themselves to produce an unstable intermediate that gets dissociated by heat or light to regenerate the catalysts Z, Z' along with O₂

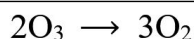
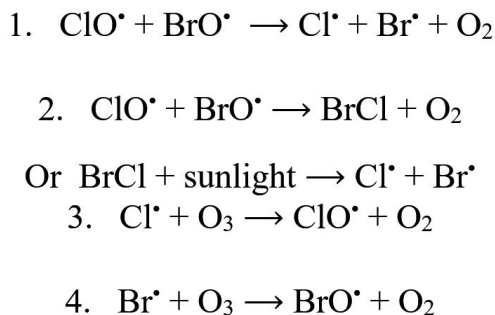
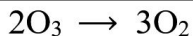
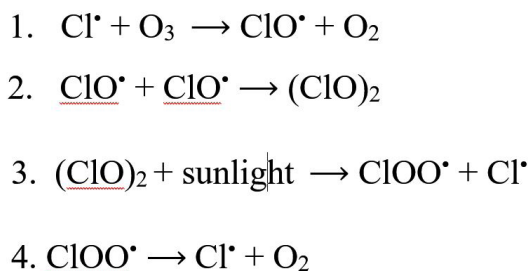


9.4.1 Chlorine and Bromine radicals as Z catalysts

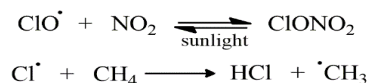
Methyl chloride is a Cl containing compound released naturally from decaying vegetation in oceans, which gets mostly decomposed in troposphere and some of it diffuses into stratosphere.

In 1928, several chlorine-based compounds with outstanding properties were developed that found applications in a variety of fields. This class of compounds is called ChoroFluoro carbons (CFCs), wherein one or more hydrogens of the parent hydrocarbons were replaced by halogens to achieve properties like non toxicity, non-flammability, thermal stability and non-reactivity. Several compounds were developed in this category for commercial purposes. The first amongst these was CFC-12 developed by DuPont, with one carbon, two chlorines and two fluorines. In the 1980s, 1000Kg per CFC was released into the atmosphere annually. While their properties made CFCs very useful in applications like coolants, refrigerants, propellants etc. their non reactivity and insolubility in water (rain) eventually led to a heavy price to be paid by mankind itself. They have lifetimes of 50-200+ years and have no sinks in troposphere, which makes them diffuse into stratosphere. They absorb UV radiations to undergo photolysis of C-Cl bond. Cl radical so generated knocks off O from O₃ and catalyses the destruction of O₃. Catalytic destruction of ozone also involves Br radical as catalyst.

Mechanism of destruction by CFC in polar regions follows scheme II as shown below:



From the above scheme of reactions, one CFC molecule is capable of destroying 100,000 molecule of ozone. At a given time under normal conditions of the atmosphere, the active forms of chlorine- Cl^\bullet and ClO^\bullet , however, are found locked in two major inactive forms, viz. HCl and ClONO_2 . The two forms are thus like 'reservoirs' of the active Cl^\bullet radical.



ClONO_2 decomposes into the active ClO^\bullet by sunlight and HCl gets decomposed by $\text{}^\bullet\text{OH}$ radical present in the region.



Similarly, bromine is present in the troposphere from the synthetically produced Halons as well as in the form of methyl bromide through natural sources, which diffuse into the stratosphere and have a fate similar to Cl containing compounds. However, the difference here is that Br^\bullet and BrO^\bullet radical remain as they are and are not in their inactive form. The latter is because the inactive forms are not stable and get dissociated efficiently.



9.4.2 Antarctic Ozone hole

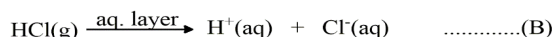
Extensive research work in 1980s enabled the understanding of ozone hole in the Antarctic region. Unusual chemical reactions in unusual weather conditions are responsible for this phenomenon.

It is obvious that CFCs are released in regions where they are used, i.e. in cities and urban areas, and so they should be mostly found in the atmospheres of these regions. In fact, higher amounts of CFCs are released in the Northern Hemisphere. These gases undergo mixing with other air components in the troposphere within a year or two, following which they rise into the stratosphere, mainly in tropical latitudes. Winds sweep this air towards north pole and south pole from the tropics, which makes the distribution of CFCs nearly uniform throughout the global stratosphere. Thus, although polar regions have no or negligible release of these chlorine containing compounds, these are the regions which get the most severe brunt of their destructive action which effects the entire globe.

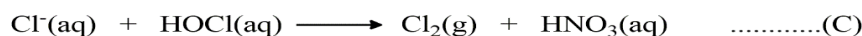
The Antarctic region witnesses winter months (March–September) without sun and hence the region is severely cold with temperatures dropping to below -80°C (July and August witness -90°C in a typical year). These polar winter conditions cause the formation of special type of clouds in the lower stratosphere, called Polar Stratospheric Clouds or PSCs (note that in normal conditions, stratosphere is devoid of clouds). The PSCs are of two types- PSC Type I clouds which are clouds made up of solid crystals of nitric acid trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$) formed around -77°C , and PSC Type II clouds which are larger ice crystals formed at around -85°C , from the condensation of whatever little amount of water vapours is present in

the region. The other important feature of this region is that low temperatures are accompanied with low pressures and together with earth's rotation, these conditions produce an endlessly circling whirlpool of winds (wind speeds > 300 Km/h) called Polar Vortex which insulates the air from the outside for several months (till well into spring time).

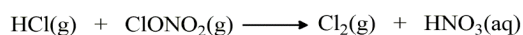
The frozen crystals of the polar stratospheric clouds provide a surface for the following important heterogeneous phase reactions (which ultimately release chlorine atoms):



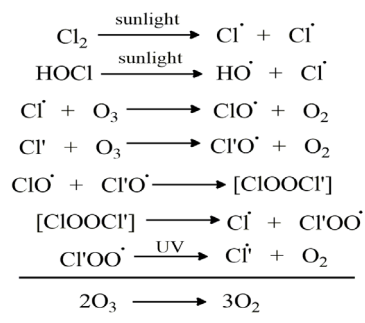
The two forms of dissolved chlorine formed in reaction A and reaction B, further react to produce molecular chlorine that escapes into gas phase.



Overall reaction of (A) (B) and (C)



The above reactions show how an important reservoir of chlorine atoms is transformed into hypochlorous acid and molecular chlorine.



This way, molecular chlorine gets accumulated in the dark winter months and becomes the predominant chlorine containing gas in the lower stratosphere. As soon as sunlight appears in the Antarctica in spring time (early September), Cl_2 dissociates into atomic chlorine and starts destructing O_3 molecules in plenty. Smaller levels of gaseous HOCl undergoes similar dissociation in presence of sunlight.

The heterogeneous phase reactions also lock the gaseous NO_2 in condensed form of HNO_3 and hence in the Type I cloud, thereby making it unavailable for ClO^\cdot to be scavenged. ClO^\cdot is therefore free to destroy several thousands of O_3 molecules. Thus, polar stratospheric clouds reactivate chlorine radicals from an inactive reservoir and remove the scavenger of chlorine monoxide, both paths leading to propagation of ozone depletion. Such conditions of catalytic destruction of ozone are not created in any other part of the planet, except to some extent in Arctic region.

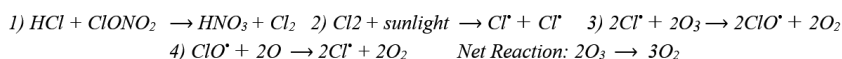
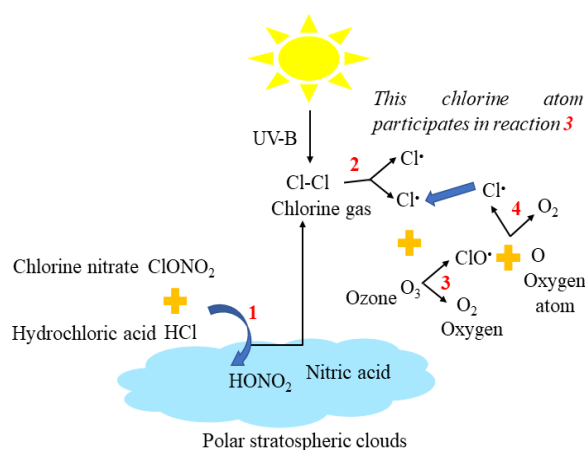


Figure 9.4 Schematic representation of production of molecular chlorine from inactive forms of chlorine in the winter and spring stratosphere in polar regions.

The catalytic destruction of ozone continues through spring (early September – late October), since the temperatures above Antarctica are very low (-80°C) even in early spring which keeps the PSC intact for months. In addition, Polar vortex is still stable and does not allow the entry and mixing of zone rich air from outside (non-polar regions) to ‘fill up’ the ozone hole. Polar vortex is stable throughout spring, thereafter sunlight intensity increases and breaks the vortex (early November). At this stage when both PSC and Polar vortex vanish, ozone rich and NO_2 rich air from non-polar regions gushes into the Antarctica atmosphere to convert the active chlorine atoms back to inactive form, like in any other region of the atmosphere. The catalytic destruction cycle of ozone ceases operation, ozone concentration builds back to normal, and the ozone hole closes for another year till the next spring.

9.4.3 Ozone Destruction in Arctic Region

Arctic region also witnesses ozone depletion, though to much less an extent as compared to Antarctic region. This is because of the region being warmer (or milder winter) than Antarctic region. Antarctica is surrounded by oceans which drops its temperatures to even below -85°C , in fact to -90°C in winters. On the other hand, Arctic region has more of inhabited land mass which does not keep temperatures as low. As a result, PSC Type I clouds are formed but not PSC Type II clouds. Surface for heterogeneous phase reactions does not exist and so active chlorine atoms required for catalytic destruction of ozone are much lesser. Secondly, polar vortex encircling the Arctic atmosphere is very weak and begins to break very early in spring, even before catalytic destruction of ozone by active Cl atoms begins. Air from temperate region starts mixing with Arctic region. This air brings with it, ozone as well as oxides of nitrogen which scavenge the ozone depleting chlorine monoxide. Hence ozone hole is filled up even before it assumes high level of depletion.

9.4.4 Ozone Destruction in Non-Polar Regions

The key reactions for the destruction of ozone are the heterogeneous phase reactions (A & B in section 2.4.2), occurring on the surface of the polar stratospheric clouds, which enable the mass scale conversion of Cl in its active form from the inactive reservoirs. In non polar regions, due to non availability of such surfaces, these reactions and hence ozone destruction does not take place. However, sulfate aerosols in the stratosphere are found, to provide such surfaces for heterogeneous reactions, that lead to destruction of ozone in the non polar regions. This is the reason why in the period 1979-91, Canada and Russia in Northern Hemisphere and Chile and Argentina in Southern Hemisphere witnessed severe ozone depletion. Two major volcanic eruptions around this time released a large amount of Sulphur in the atmosphere, which subsequently oxidized to sulphate aerosols and led to ozone depletion.

Check Your Progress III

Notes: (a) Write your answer in about 50 words

(b) Check your progress with possible answer at the end of the unit.

1. What are UV-A, UV-B, and UV-C radiation. What is the danger posed if UV-B is not absorbed by ozone in stratosphere.

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Explain the role of extreme cold temperature in the formation of Antarctic ozone hole.

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3. Why is ozone hole not seen in non polar regions

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9.5 LET US SUM UP

Various pollutants which are organic in nature are dealt with in this unit. Organic species necessarily have carbon and hydrogen, with and without hetero atom like oxygen, Sulphur, halogens, nitrogen. Hydrocarbons in the atmosphere include alkanes, alkenes and arenes which are released from natural sources, and significantly from anthropogenic sources as vehicular exhausts and from factories and industries. These are primary pollutants. Oxygen containing compounds are, especially carbonyl compounds are present in the atmosphere from the photochemical reactions with primary pollutants. Halogen containing organic molecules are majorly synthetic.

These organic species result in some important pollution phenomena that also influence inorganic species. Some of their most important effects are manifested in phenomenon like photochemical smog and ozone hole. Photochemical smog is attributed to urban areas where excessive release of NO and hydrocarbons is seen and in the presence of intense sunlight, several photochemical reactions occur that produce ozone, peroxy compounds, peroxy nitrates and other oxidants. These cause reduced visibility, severe eye irritation and destruction of materials such as rubber tyres etc. Ozone hole is an annual phenomenon seen in the Antarctica region, mainly due to the presence of Cl radicals that catalyse the destruction of stratospheric ozone layer.

9.6 KEY WORDS

Mercaptans	organic components of hydrocarbons with sulfur having a characteristic ultragarlic odour.
Aldehydes	organic compound containing a carbonyl functional group with the structure $-\text{CHO}$, i.e. f a carbonyl center with the carbon atom also bonded to hydrogen and to an R group, which is any generic alkyl or side chain.
Alkoxy radical	a monovalent free radical species containing alkyl group united to oxygen atom
Smog	a mixture of smoke and fog in air, that represents a kind of air pollution.
Polar stratospheric cloud	clouds formed in the stratosphere in the polar regions at altitudes of 15 to 25 Km. These are formed only at very cold temperatures, less than -77°C . Two types of such clouds are known- PSC Type I formed at -77°C and PSC Type II formed at even lower temperatures of -85°C . these clouds are now understood as the sites of harmful destruction of ozone in stratosphere.
Polar vortex	swirling mass of air blowing in counter clockwise direction and created due to low pressures in the polar region, especially North pole.

VOCs	Volatile organic compounds, which are organic compounds with low boiling points that makes possible their evaporation at normal atmospheric conditions of temperature and pressure. They participate in atmospheric photochemical reactions because of which they have become pollutants of serious concern.
PAN	Peroxyacetyl nitrate, a secondary pollutant that is formed in the photochemical reaction between organic peroxy radicals by the oxidation of VOCs, or by aldehydes oxidized in the presence of oxides of nitrogen. The compound is a lachrymator or an eye irritant and toxic.
Freons	These are fluorinated hydrocarbons that have at least one C-Cl or C-Br bond. This class of compounds includes chlorofluorocarbons as well as hydrochlorofluorocarbons, They are colorless, odourless, non flammable non toxic gases that are extensively used as anti freeze agents, refrigerants and propellants one C-Cl bond. Amongst these chlorofluorocarbons are infamous for being the main reason for ozone destruction in stratosphere.

9.7 REFERENCES AND SUGGESTED FURTHER READINGS

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- Environmental Chemistry, Colin Baird & Michael Cann, 5th edition WH Freeman and Company, New York, 1995
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- Living in the Environment: Principles, Connections, and Solutions, Miller. G.T.Brooks Cole 2012
- Introduction to Environmental Science and Technology, Gilbert M. Masters
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- *Introduction to Environmental Science and Technology*, G M Masters, John Wiley & Sons, 1974.

Check your Progress I

1. Mercaptans have reactive acidic H. Alkanes are non polar and so stable. Alkenes structural feature is double bond, which is very prone to attack by radicals.
2. Alkenes have C=C in their structure. π -electrons are loosely held and so susceptible to electron seeking species in the atmosphere- OH, O, O_3 . They add to the double bond. Alkanes have no such reactive sites. They have C-C and C-H sigma bonds. No polarity, hence reactions are of H abstraction. Hence, different mechanisms. Refer to text for mechanism (section 2.2.1)
3. Aldehydes and ketones are the first stable products of oxidation of alkanes and alkenes/. Alkylloxy radicals formed after H abstraction by OH, then addition of O_2 , followed by loss of O by alkyl peroxy radicals. The latter further loses H to O_2 to give carbonyl compounds. For equations refer to text in section 2.2.2. Alkenes have addition of OH, O or O_3 to give aldehydes and ketones.
4. C-Cl bond is very strong and requires a lot of energy to get cleaved. No sinks in troposphere, so diffuse to stratosphere. Here UV radiations $< 400\text{ nm}$ break the bond to release Cl^0 radicals, responsible for ozone destruction.
Presence of even one H in the molecule enables the cleavage of C-H bond in troposphere and so the sink remains in this layer of atmosphere. For reactions, refer section 2.2.3.

Check Your Progress II

1. The experiment between NO_2 , benzaldehyde and UV radiation is a recipe for PC smog. Benzaldehyde on irradiation gets photoexcited and oxidized to give benzoyl peroxy radical which combines with NO_2 to give a stable product peroxy benzoyl nitrate. This compound is the eye irritant. Reaction in section 2.3.3.
2. Before sunrise NO and hydrocarbons are in plenty, but as sun shines the consumption of these two rapidly increases and brings down their concentration. NO_2 concentration simultaneously increases.
3. Hydrocarbons see a sharp increase in the early morning and because of rapid oxidation, the concentration drops rapidly too during rest of the daytime. By 12 noon, ozone and oxidized hydrocarbon levels build up significantly. Refer fig. 3. Taking methane as example, its reaction with oxygen atoms generates OH radical and methyl radical. OH radical can abstract H from methane molecule or other hydrocarbons to generate corresponding alkyl radical. Methyl/ alkyl radical react with O_2 to give peroxy radical that further reacts with NO to give NO_2 . Reaction of OH radical with CO (from vehicular exhausts) also causes formation of HOO radical that oxidized NO to NO_2 . Similarly O_3 produced during these conditions converts NO to NO_2 .

4. Presence of NO, hydrocarbons and intense sunlight are the conditions required for photochemical smog. Such conditions lead to formation of oxidants including ozone, H_2O_2 , organic peroxides (ROOR'), organic hydroperoxides (ROOH), and peroxyacyl nitrates such as peroxyacetyl nitrate (PAN). Amongst these, ozone is a primary pollutant and causes harmful effects. Hence the term

Check Your Progress III

5. UV-A radiation, 320 nm-400 nm; 290 nm-320 nm; UV-C radiation, < 290 nm. If UV B is not absorbed in stratosphere it will penetrate into troposphere and cause a lot of harm to the exposed life forms on the planet. Damage to crop, aquatic plants that are the food of marine life, Humans can have increased incidence of eye problems- cataracts. Light skinned people absorb UV B rxPSC I and PSC II are formed at temperatures around -770C and -850 C resp. Such low temperatures also cause the formation of stable polar vortex that insulates the inside air from outside. PSCs provide the surface for heterogeneous phase reactions which enable formation of molecular Cl_2 and HOCl from inactive sinks. The two active Cl forms on getting irradiated by sunlight releases Cl radical and severely deplete ozone with its catalytic action.
6. Heterogeneous phase reactions are key to ozone depletion, because these release active chlorine atoms from the inactive sinks. For these reactions, PSC are required, which is enabled by extremely low temperatures, at least less than -800C. In the absence of such low temperatures in non polar regions, ozone hole is not seen.

9.8 TERMINAL QUESTIONS

1. What is UV-A, UV-B, and UV-C radiation? What is the danger posed if UV-B is not absorbed by ozone in stratosphere?
2. Explain the sources of the following organic air pollutants?
 - a. Organohalides
 - b. Organo nitrogen compounds
3. What are the alternative organic compounds for CFCs? Explain?

UNIT 10 : PARAMETERS OF WATER POLLUTION

Structure

- 10.0 Introduction
- 10.1 Objectives
- 10.2 Aquatic System
- 10.3 Dissolved Oxygen
 - 10.3.1 Oxygen Sag Curve
- 10.4 Biochemical Oxygen Demand (BOD)
- 10.5 Chemical Oxygen Demand (COD)
- 10.6 Acidity
- 10.7 Alkalinity
 - 3.7.1 Alkalinity and Ph
- 10.8 Acid-Base Chemistry in Natural Water: The Carbonate System
- 10.9 Complexation and Chelation
 - 10.9.1 Natural and Waste Water
 - 10.9.2 Occurrence and Importance of Chelating Agents in Aqueous System
 - 10.9.3 Colloidal Particles in Water
 - 10.9.4 Formation of Colloidal Particles
 - 10.9.5 Properties of Colloidal Substances
 - 10.9.6 Classification of Colloidal Particles
 - 10.9.7 Stability of Colloidal Particles
 - 10.9.8 Colloidal Properties of Clays
 - 10.9.9 Aggregation of Colloidal Particles
 - 10.9.10 Flocculation of Colloids by Polyelectrolytes
 - 10.9.11 Flocculation of Bacteria by Polymeric Materials
 - 10.9.12 Environmental Significance of Colloids
- 10.10 Ion Exchange with Bottom Sediments
 - 10.10.1 Metals in Suspended Matter and Sediments
 - 10.10.2 Method for Determination of CEC.
 - 10.10.3 Method for Determination of ECS
- 10.11 Organic Compounds in Sediments and Suspended Matter
- 10.12 Let Us Sum Up
- 10.13 Key Words
- 10.14 References and Suggested Further Readings
- 10.15 Terminal Questions

10.0 INTRODUCTION

All forms of life on Earth are dependent upon water and every human being needs several litres of water every day to sustain life. Unfortunately, in many areas of the world, it is not always possible to have a ready source of potable water. This problem of availability of pure drinking water is increasing with increase in industrialization

and modernization. There are several possible ways of chemical contamination in water including heavy metal contaminations from metal processing industry, insecticides, pesticides, herbicides and salinity in the runoff water from agricultural lands; chlorinated hydrocarbon wastes from industrial chemical production and many other types of industrial discharges polluting the surface water. At present, toxic chemicals pose the greatest threat to the safety of water supply in industrialised nations. Also, the human civilization is facing even a more serious threat in the form of groundwater pollution, which is caused by dumping of waste chemicals in landfills, storage lagoons, heating ponds and various other facilities. Thus, it is imperative to understand the sources, interactions and effects of water pollutants and thus to control the pollutants in an environmentally safe and economically viable manner. Water pollution and measures to control it may be studied much more effectively only with a strong background of aquatic environment chemistry. The chapter covers certain basic parameters of water pollution.

10.1 OBJECTIVES

After studying this unit, you will be able to

- discuss the physical, chemical and biological characteristics of water systems,
- explain the natural, human and biological factors that are responsible for the constituents found in water systems
- explain the significance of chelating agents in aqueous system,
- describe the properties of colloidal substance present in water bodies,
- explain the ion exchange method of water management.

10.2 AQUATIC ECOSYSTEM

Before discussing about various parameters of water pollution, it is important to understand the aquatic ecosystem (Figure1). The large plants and algae (phytoplankton) are the main producers and liberate oxygen during photosynthesis. The zooplanktons and benthos are the primary consumers. Fish, insects, frog, man etc. are other consumers, along with detritivores which live off organic debris. The decay organisms, bacteria, fungi etc. recycle the nutrients back into the ecosystem. The water remains clean and healthy as long as the ecosystem remains balanced. However as and when the ecosystem loses balance, it stops functioning properly, resulting in water pollution.

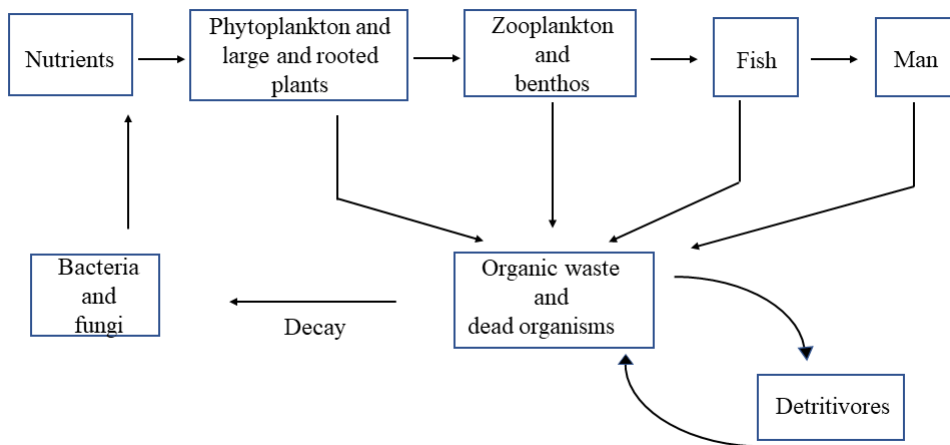
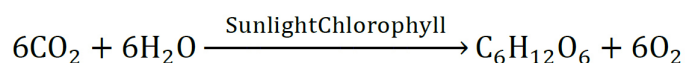


Figure 10.1 An aquatic ecosystem

10.3 DISSOLVED OXYGEN (DO)

Natural waters contain dissolved gasses. The solubility of gas in water is inversely proportional to temperature and total dissolved solid content. For example, atmospheric carbon dioxide dissolved in water contributes to the total dissolved carbon content in water, primarily as bicarbonate (HCO_3^{2-}). Oxygen is also an important species in water. In fact, it is the only significant oxidizing agent present in natural water. The amount of dissolved oxygen (DO) is an important parameter of water quality. There are four processes which affect the amount of dissolved oxygen in water:

- i. **Photosynthesis** – During photosynthesis, the chlorophyll containing cells of green plants in presence of sunlight are able to convert carbon dioxide and water into glucose and oxygen.



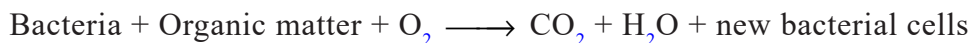
Photosynthesis occurs only during day time (6 am – 6 pm) and results in increasing the DO level in water

- ii. **Respiration** – Respiration is almost opposite of photosynthesis, in which an organism derives its energy by combustion of organic matter in presence of oxygen.

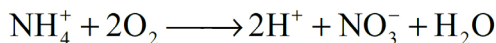


Respiration is a continuous 24-hour process and removes oxygen from water.

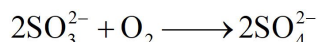
- iii. **Oxidation of various wastes** - The various wastes present in water gets oxidized on consumption of dissolved oxygen and hence results in decrease in oxygen level in water



In addition to the microorganism mediated oxidation of organic waste, oxygen is also consumed in the bio-oxidation of nitrogenous material,



and also, in the chemical or biochemical oxidation of various reducing agents present in water



- iv. **Reaeration** – Reaeration is a process in which oxygen enters the water body through the contact that water surface makes with atmosphere. The solubility of oxygen in fresh water is low (14.7 ppm at 0 °C at 1 atm pressure) and it further decreases with increase in temperature (7.0 ppm at 35 °C at 1 atm pressure). The variation of solubility of oxygen in water with increasing temperature, at 1 atm is given in Figure 2.

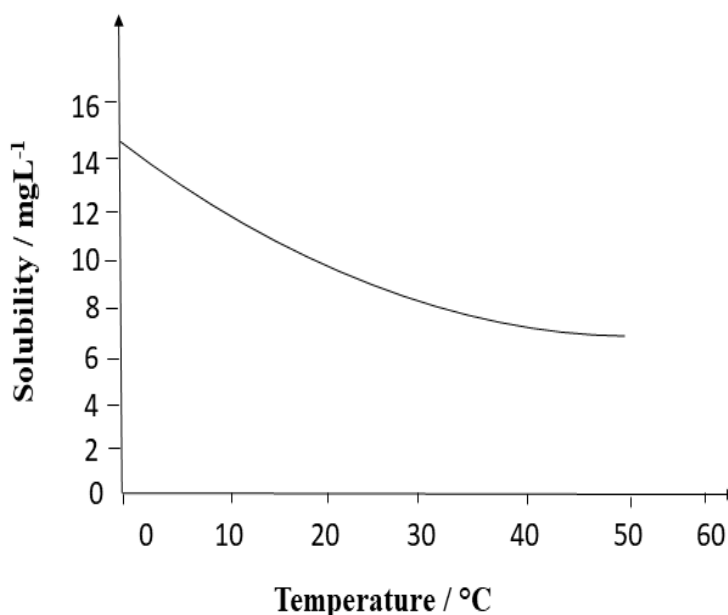


Figure 10.2 Solubility of oxygen in fresh water exposed to water saturated with air at 1 atm pressure (American public health association 1971)

When the actual amount of oxygen is less than the saturation level, the atmospheric oxygen passes into the water at a rate which is proportional to the deficit and the surface area of water in contact with atmosphere. Thus, reaeration is also responsible for replenishing the water with dissolved oxygen. However, if at any point of time, the water is supersaturated, the oxygen diffuses out of the water. The combined effect of photosynthesis, reaeration and respiration results in a diurnal variation of dissolved oxygen with time, as shown in figure 3.

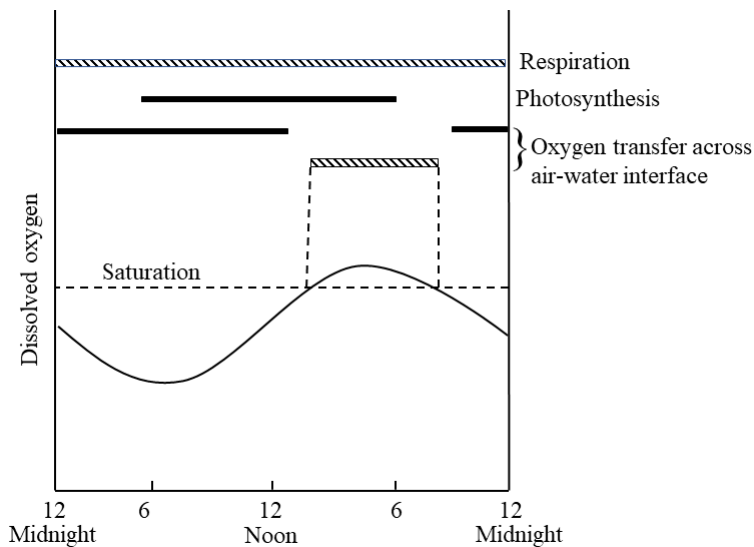


Figure 10.3 Diurnal variation of DO assuming photosynthesis from 6 am to 6 pm

10.3.1 Oxygen sag curve

Whenever waste is discharged in a water body, the amount of dissolved oxygen decreases, due to the oxidation of the waste by micro-organisms, mainly bacteria. Initially the rate of oxidation of waste is very high. Hence the rate of decrease of DO is higher than the rate of reaeration. Thus, the DO level drops drastically. However, when DO reaches a minimum level, the rate of reaeration becomes equal in the rate of consumption of oxygen. Beyond that point the rate of reaeration exceeds the rate of consumption of oxygen and hence the DO level eventually returns to normal. This sequence is also known as self-purification ability of water. This phenomena of deoxygenation and reaeration, occurring simultaneously in a water body results in oxygen sag curve, as shown in figure 4.

The x -axis of the plot may be either distance or time. If the entire waste is released together at one time, then x -axis will be time. However, if there is continuous discharge of waste into the water body, then DO is plotted against distance downstream from the point of discharge. The drop in dissolved oxygen content in a water body not only reflects the quality of water but also govern the biota in the water body.

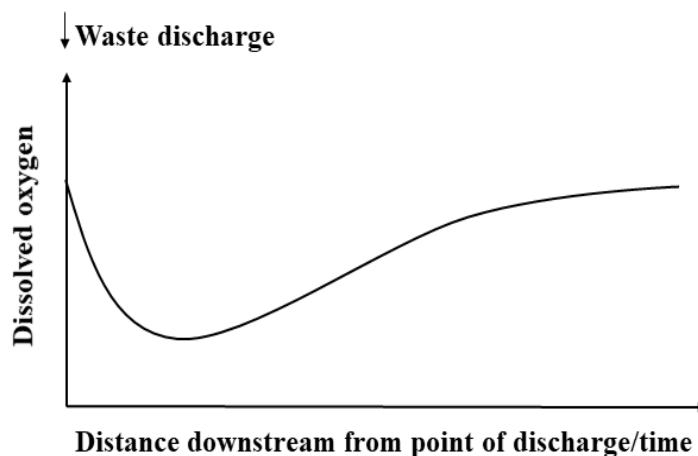


Figure 10.4 The oxygen sag curve

Table 1. Variation of water quality with DO

DO in ppm (at 20°C, 1 atm pressure)	Water quality
8 – 9	Good
6.7 – 8.1	Slightly polluted
4.5 – 6.7	Moderately polluted
4 – 4.5	Heavily polluted
> 4.5	Grossly polluted

With drop in DO, the normal genre fish will be replaced by fishes and organisms which are tolerant of low oxygen condition or which are able to attain oxygen from the surface.

10.4 BIOCHEMICAL OXYGEN DEMAND (BOD)

The capacity of organic matter to consume oxygen in a water body is known as biochemical (or biological) oxygen demand and is a measure of amount of oxygen required to aerobically oxidize the organic waste in the water body.

A plot of BOD remaining versus time (Figure 5) indicates that the amount of BOD remaining is proportional to the organic material remaining unoxidized and decreases exponentially with time (t).

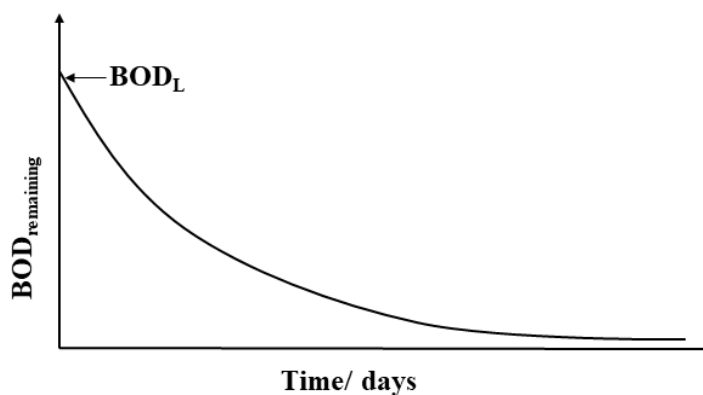


Figure 10.5 BOD remaining as function of time with initial BOD_L

To avoid any confusion, it is always better to study the plot of BOD utilized. Figure 6 is a plot between BOD utilized and time in which BOD utilized is proportional to the amount of organic matter oxidized. A standard way to measure BOD is to determine the total amount of dissolved oxygen needed by aerobic decomposers to break down the organic matter in a given volume of water over a 5-day incubation period at 20 °C. This is known as a 5-day BOD or $BOD_{5 \text{ days}}$ (as shown in figure 6).

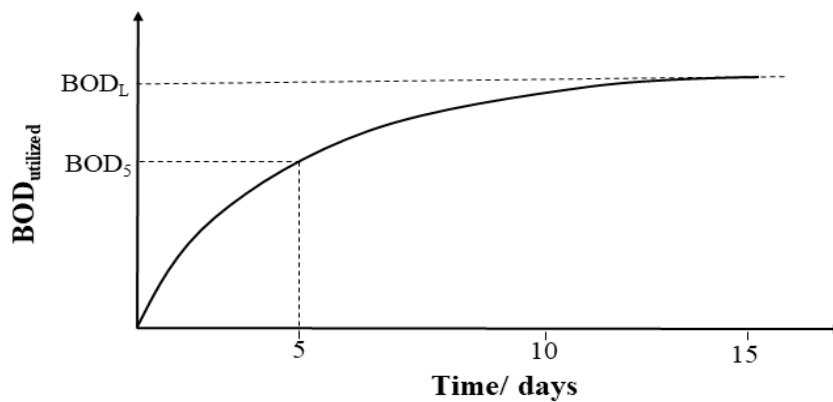


Figure 10.6 This is the usual curve for BOD and is actually BOD utilized. It also represents the 5-day BOD.

Ultimate BOD or BOD_L or L_0 is the initial value of BOD, which is equal to the total amount of dissolved oxygen required for complete decomposition of organic matter. The decomposition of organic waste follows 1st order kinetics

\therefore Rate of reaction \propto amount of organic matter remaining undecomposed

$$\frac{-dL}{dt} \propto L_t$$

When L_t = BOD remaining at time 't'

$$\text{or } \frac{-dL}{dt} \propto KL_t$$

K = reaction rate constant = 0.22/day

$$\text{or } \frac{L_t}{L_0} = e^{-Kt}$$

$$\text{or } L_t = L_0 e^{-Kt}$$

$$\therefore \text{BOD utilized} = \text{BOD Ultimate} - \text{BOD remaining}$$

$$\text{or } (\text{BOD})_{\text{utilized}} = L_0 - L_t$$

$$\text{or } (\text{BOD})_{\text{utilized}} = L_0 - L_0 e^{-Kt}$$

$$\text{or } (\text{BOD})_{\text{utilized}} = L_0(1 - e^{-Kt})$$

It may be noted that 5-day BOD is considerably lower than the ultimate BOD.

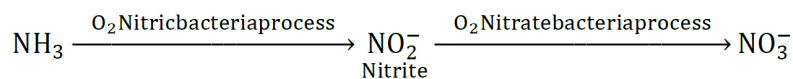
$$(\text{BOD})_{5\text{days}} = L_0(1 - e^{-0.22 \times 5})$$

For example, if for a given water sample, 5-day BOD is 200 mg/L, then ultimate BOD can be calculated

$$L_0 = (\text{BOD})_{\text{ultimate}} = \frac{200}{(1 - e^{-0.22 \times 5})} = 300 \text{ mg/L}$$

The 5-day BOD of domestic sewage (about 200 mg/L) is normally much lower than that of industrial sewage, which may even vary to several thousands of mg/L. This is then compared with the saturation level of dissolved oxygen in water at 20°C (~9.2 mg/L). On comparison, it is easy to anticipate the quick depletion of oxygen which may even convert the aerobic water into anaerobic, unless the dilution factor is high. When the dissolved oxygen gets depleted, the normal fishes are killed.

Further, after 8 – 10 days there is a secondary effect, in the form of oxidation of ammonia, which also consumes oxygen



Hence, the process of nitrification also consumes oxygen, along with the regular oxidation of organic compounds (carbonaceous process). Figure 7 represents the complete BOD curve.

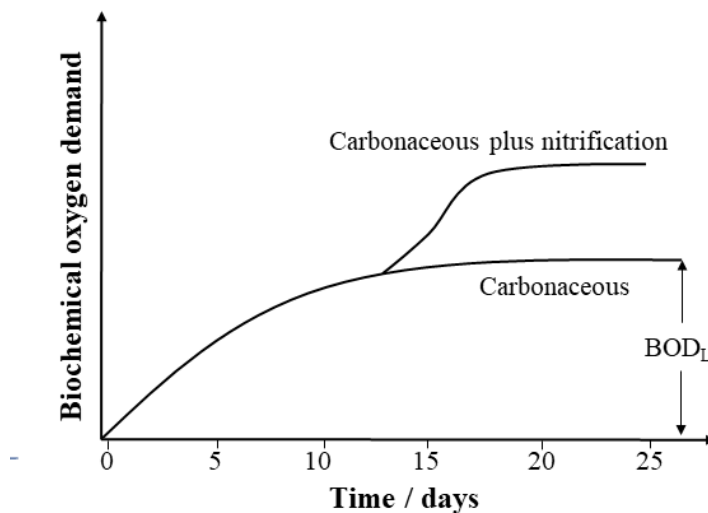
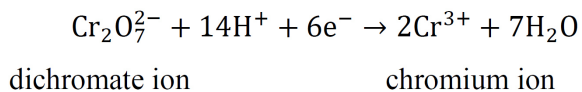


Figure 10.7 The complete BOD curve includes the carbonaceous and nitrification demands

10.5 CHEMICAL OXYGEN DEMAND (COD)

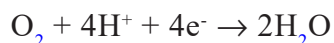
Evaluation of chemical oxygen demand is done by using a strong oxidizing agent, such as potassium dichromate in H_2SO_4 rather than by using O_2 to oxidize the organic waste.

The reduction half reaction when $\text{Cr}_2\text{O}_7^{2-}$ is used in acidic medium to oxidize organic matter is:



Hence one mole of dichromate ion accepts 6 electrons.

The reduction half reaction when oxygen is used to oxidize the organic matter is:



This one mole of oxygen accepts only 4 electrons.

Therefore, the number of moles of O_2 consumed by organic matter = 6/4 times number of moles of $Cr_2O_7^{2-}$ used.

The COD evaluation makes a faster determination of oxygen demand. The difficulty with COD index as a measure of oxygen demand is that acidified dichromate is such a strong oxidizing agent that it even oxidizes those substances which are not oxidized by oxygen in the determination of BOD. Since acidified dichromate solution oxidizes all stable organic matter into CO_2 ; Cl^- to Cl_2 , COD value is greater than that of BOD value. However, neither of the two method of oxidation could oxidize aromatic hydrocarbon and alkanes, which resist degradation in natural water.

Know you progress I

Q.1 Define DO and give its value that is to be maintained in aquatic ecosystem. Explain in details the oxygen sag curve.

Q.2 What factors influence the dissolved oxygen recovery? As water temperature increases, what happens to the amount of dissolved oxygen?

Q.3 Explain the diurnal plot for variation of DO with time

Q.4 What does Biochemical Oxygen Demand, (BOD) value less than 5 ppm indicate?

Q.5 The 2-day and 4-day BOD values of a sewage sample are 100 mg/L and 155 mg/L, respectively. Calculate the value of BOD rate constant per day.

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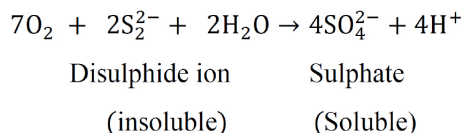
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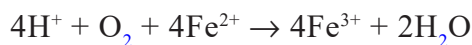
10.6 ACIDITY

Aquatic biota is sensitive to extremes of pH, however there is a range of pH in which organisms live. Acidity is defined as the capacity of water to neutralize OH^- . Acidity generally results from the presence of weak acids such as CO_2 , H_2S , fatty acids, acidic metal ions, such as Fe^{2+} , mineral acid such as H_2SO_4 which enters the water body mainly due to microbial oxidation of pyrite and other sulfide minerals from the drainage coming out of acid mine.

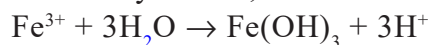
Acid Mine Drainage – Normally iron pyrites FeS_2 , also known as “fool’s gold”, in absence of air is a stable and insoluble component of underground rocks. However, as a result of mining, when it is exposed to air, it becomes partially solubilized.



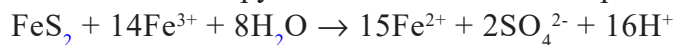
Thus, insoluble FeS_2 is converted into soluble FeSO_4 and a large amount of H_2SO_4 is also released. Some of the acid released is used in the oxidation of Fe^{2+} into Fe^{3+} ion.



The ferric iron precipitates ferric hydroxide,



Hence, Fe^{3+} ion further dissolves pyrites and oxidizes it to sulphates as follows:



Thus, the oxidation of iron pyrite results in the production of soluble iron (II) sulphate and sulphuric acid. Due to the production of H_2SO_4 , the value of pH in acid-polluted water may even fall below 3, proving fatal to most of the aquatic life. In case where the water does not have contact with a basic mineral, such as limestone, the pH may become dangerously low. Unfortunately, the concentrated acid can also liberate some more toxic heavy metals from their ores in the mine, further adding to the pollution. Also, once the drainage from the highly acidic mine water gets diluted and its pH increases, soluble $\text{Fe}_2(\text{SO}_4)_3$ is converted into yellowish brown precipitate of $\text{Fe}(\text{OH})_3$. Thus, the drainage from acid mine is characterized by acidified water and a rust colored solid. Apart from the mines, even the industrial wastes frequently

contribute strong acid to water decreasing its pH. Some hydrated ions may also contribute to acidity. For example, the pressure of hydrated aluminum ion results in generation of H_3O^+ ions and hence lower down the pH.

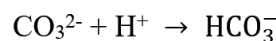
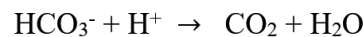


Since the permissible pH value for water used for public supply may range between 6.6 – 8.4, it is important to determine the total acidity of the water body. The total acidity is determined by titration with base to phenolphthalein endpoint (pH ~ 8.1), however free mineral acid is determined by titration with base to methyl orange endpoint (pH ~ 4.3). Once the acidity is known, the amount of time or other chemicals needed to neutralize the acid may be calculated to make the water fit for public supply.

10.7 ALKALINITY

The capacity of water to accept H^+ ions is known as alkalinity. Excess alkalinity is accompanied with high pH value and high amount of dissolved solids. Generally human activity does not introduce high alkalinity directly into water. However, activities like strip mining or geographical location of an area with alkaline soil and high mineral strata may lead to high alkalinity of a water body. Excess alkalinity is indicated by a characteristic fringe of white salts at the edges of water body or on the banks of a stream. The species responsible for alkalinity are mainly bicarbonate ion, carbonate ion, hydroxide ion, ammonia and conjugate bases of phosphoric, boric, silicic and organic acids.

It is often used by biologists as a measure of water fertility.



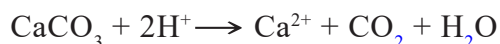
Alkalinity protects aquatic life by resisting change in pH. Higher alkalinity in surface water provide buffering action against the acid rain and other acidic wastes. Factors affecting alkalinity in water body include presence of salts, rocks and soils, plant activities, and industrial wastewater discharges. Total alkalinity in a medium where the main contributors are only HCO_3^- , CO_3^{2-} and OH^- may be represented as:

$$\text{Total alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

The contribution of HCO_3^- , CO_3^{2-} and OH^- towards alkalinity of water is dependent on the pH of the solution. At pH 7, the concentration of OH^- is very low and $[\text{HCO}_3^-] > [\text{CO}_3^{2-}]$. Hence, the HCO_3^- is the major contributor of alkalinity at pH 7. Further, at this pH, the concentration of CO_2 is very high, even higher than its concentration when water is in equilibrium with atmosphere. This is due to large amount of CO_2 released in water because of bacterial decay in water and sediments. At pH =10, however both CO_3^{2-} and OH^- are present in higher concentration than HCO_3^- , though the major contributor towards alkalinity is CO_3^{2-} . Hence the dissolved inorganic carbon concentration remains only about half that at pH 7. The

lower inorganic carbon concentration at pH 10 indicates that the aquatic system can donate dissolved inorganic carbon for use in photosynthesis resulting in the change in pH but not the alkalinity. Thus, at pH 10, more biomass (higher rate of photosynthesis) is produced, for the same change in pH, in comparison to less biomass at pH 7. Hence, alkalinity is also a measure of water fertility. It may further be shown that the solubility of carbon dioxide in water increases with increase in alkalinity.

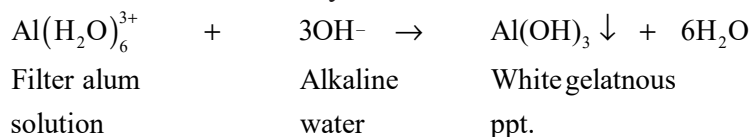
Alkalinity frequently is expressed in units of equivalents/L of CaCO_3 , based upon the following acid-neutralizing reaction:



10.7.1 Alkalinity and pH

Alkalinity is the capacity to accept H^+ and hence a capacity factor whereas pH is an intensively factor. For example, let us compare a solution of 1.00×10^{-2} M NaOH with a solution of 0.100 M HCO_3^- . The pH of NaOH solution is 12 but that of sodium bicarbonate is much lower and is just 8.34. However, 1.0 L of NaOH can neutralize only 1.00×10^{-2} mole of acid, whereas 1.0 L of NaHCO_3 solution will neutralize 0.100 mole of acid. Thus, the alkalinity of NaHCO_3 is 100 times than that of NaOH, despite the fact that former has a lower pH than

Acidic substances like filter alum, $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$, which also acts as coagulant is added to water to remove its alkalinity.



10.8 ACID-BASE CHEMISTRY IN NATURAL WATER: THE CARBONATE SYSTEM

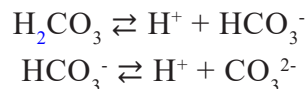
Natural water contains significant quantities of dissolved carbon dioxide as well as Mg^{2+} and Ca^{2+} ions. In this section, the natural processes producing these substances are discussed:

The CO_2 -carbonate system:

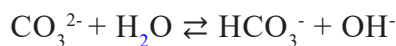
The acid-base chemistry of natural water system is governed by the interaction of the carbonate anion, a moderately strong base with a weak acid, H_2CO_3 , carbonic acid. The latter is produced from the dissolution of atmospheric carbon dioxide gas in water and from the decomposition of organic matter in the water. The equilibrium is then established between the dissolved carbon dioxide and carbonic acid. The pure water in equilibrium with atmospheric carbon dioxide is slightly acidic on account of interaction of water with carbon dioxide and carbonic acid.



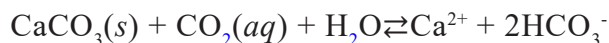
In aqueous medium, carbonic acid is also in equilibrium with a bicarbonate ion, HCO_3^- and hydrogen ion,



The dissolved carbonate ion acts as a base because it increases the concentrations of bicarbonate ion and hydroxide ion in the water.



The predominant source of the carbonate ion is limestone rocks, made up of calcium carbonate, CaCO_3 . The concentration of CO_2 in water determines degree of dissolution of calcium carbonate as water containing a high level of carbon dioxide readily dissolves calcium from its carbonate minerals (Figure 8). The natural water on exposure to limestone, is referred as calcareous waters. In addition, several aquatic organisms, such as corals and shelled creatures such as clams, oysters, and scallops convert the carbon dioxide in water into calcium carbonate. The phenomenon of respiration of microorganisms degrades organic matter in water, sediments, and soil, affords the high levels of CO_2 required to dissolve CaCO_3 in water. This represents an important factor in aquatic chemical processes and geochemical transformations.



When the above reaction is reversed, CO_2 is lost and calcium carbonate deposits are formed.

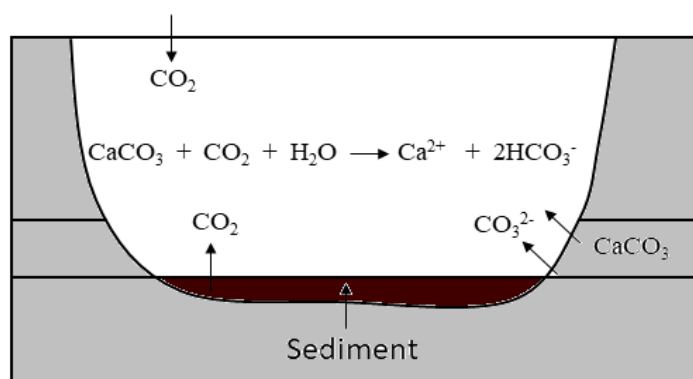


Figure 10.8 Carbon dioxide-calcium carbonate equilibria.

10.9 COMPLEXATION AND CHELATION

As we are aware, the metal ions in aqueous medium occurs in the hydrated form, $[\text{M}(\text{H}_2\text{O})_6]^{n+}$. This hydrated metal ion may further bond to an ion or a molecule which can contribute a lone pair of electron. Such ion or molecule which donate a pair of electrons and it is bonded to the metal ion through a coordinate bond is known as ligand and it results in the formation of a complex or coordination

compound or ion. These complexes have different properties in comparison to its constituent ions or molecules.

Ligands such as ammonia, which donates only one lone pair and is bonded to metal ion through one site are known as unidentate ligands. Complexes of metal ions with unidentate ligands relatively play less role in the chemistry of water.

The ligands which can form bond with metal ion through more than one atom are known as multidentate or polydentate or a chelating ligand. The bonding of metal ion with a chelating ligand results in the formation of a ring structure, known as chelate. Some examples of chelating agents are:

i. Ethylene diaminetetraacetate (EDTA)

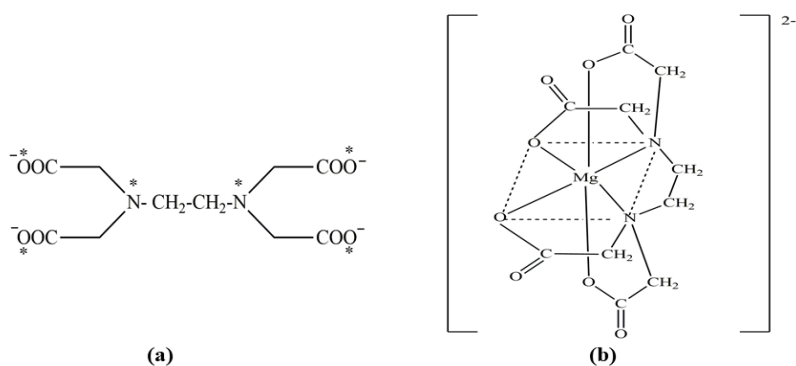


Figure 10.9 (a) EDTA ligand and (b) EDTA-Metal complex, where M is a divalent metal ion.

As shown in figure 9 (a), it is a hexadentate ligand, bonding to the metal through six sites giving an octahedral complex. A specimen example of EDTA complex is given with magnesium ion is shown in figure 9 (b).

II. NTA- Nitrilotriacetate:

NTA a chelating agent with four bonding sites [marked as astrik mark*, shown in figure 10 (a)] may simultaneously bond to a metal ion forming a tetrahedral structure with three rings as shown in figure 10 (b).

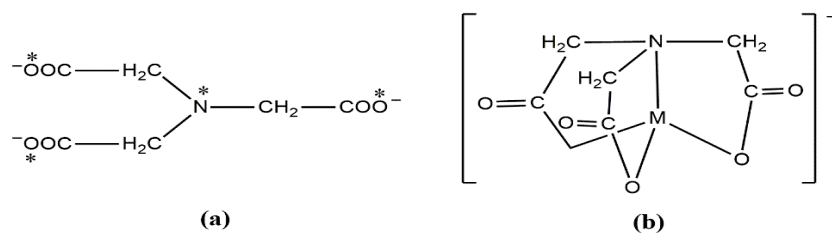


Figure 10.10 (a) NTA ligand and (b) NTA-Metal complex, where M is a divalent metal ion.

Chelates are more stable than complexes involving unidentate ligands, due to a greater number of bonding sites in the chelating agent and its high entropy factor. Further, the stability increases with increase in the number of chelating sites available on the ligand.

10.9.1 Natural and Waste water

Ligands present in waste and natural waters contains a variety of functional groups, which can donate a lone pair of electron and hence are capable of forming a co-ordinate bond with the metal ion. Some of the common functional groups present in the ligands are-carboxylate, phenoxide, aliphatic amines, aromatic amines and phosphate. Most of the metal ions found in natural water and biological systems includes Mg^{2+} , Ca^{2+} , Fe^{2+} , Zn^{2+} . However, the polluted water may also contain heavy metal ions such as Co^{2+} , Ni^{2+} , Sr^{2+} and Cd^{2+} etc.

When a metal reacts with a ligand to form a complex, both the metal and the ligand gets affected. Complexation may change the oxidation state of the metal, may convert insoluble metal compound into a soluble complex or vice-versa. Thus, the complexes have different properties in comparison to the metal ion or the ligand taken separately. For example, an aqueous solution of nickel chloride contains Ni^{2+} ions. This cationic metal ion, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, is soluble in the water, remains strongly bonded and is immobilized by ion exchange process in soil and thus is less hazardous. However, on reaction with a ligand like CN^- , the cationic metal ion is converted into an anionic species.



This anionic species is loosely held by soil, is highly mobile and hence is more hazardous.

10.9.2 Occurrence and Importance of Chelating Agents in aqueous System

Naturally occurring chelating agent such as amino acids, proteins, porphyrins, humic substances and many more are found in water and soil. Porphyrin chelate of iron (i.e., hemoglobin) and that of magnesium (i.e., chlorophyll) are essential for life processes. Similarly, presence of some of the humic substances are essential for cultivation and soil fertility. Chelating agent such as BAL (British Anti Lewisite), $(\text{SH})\text{CH}_2\text{-CH}(\text{SH})\text{-CH}_2(\text{OH})$ is used for the treatment of heavy metal poisoning, especially caused by Hg^{2+} , Pb^{2+} and Cd^{2+} . Insoluble chelating agents like chelating resins converts the soluble metal ion into insoluble chelates, which can be filtered out and separated easily. This principle of converting soluble metal ions into insoluble chelates finds application in waste water treatment for removing heavy metal ions from the solution.

Several synthetics chelating agents such as EDTA, NTA, tripolyphosphate, sodium citrate are synthesized in large quantities for use in metal plating industries, detergent industries, food processing industries etc. Small quantities of these chelating agents and metal chelates enter into water easily through industrial discharge and act as water pollutants. These chelating agents normally converts a metal cation into a negatively charged chelate, which is less strongly sorbed by mineral matter and is more mobile and thus forcing greater environmental hazard. For example, metal chelates with NTA is highly mobile and hazardous in nature. Also chelates formed by strong chelating agents such as EDTA have been shown to increase the migration rates of radioactive ^{60}Co from pits used for disposal of intermediate level

radioactive waste, posing severe threat to the environment. Hence, complexation not only increases the mobility of metal ions but also increases the leaching of heavy metals from waste disposal sites and reduce the efficiency with which heavy metals are removed with sludge in the traditional municipal water treatment process.

Another important class of naturally occurring complexing agents is of humic substances. Humic substances are formed during the decomposition of vegetation and are degradation resistant. These humic substances are high molecular weight polyelectrolytic macromolecules which effect the properties of water due to their acid-base sorptive and complexing properties. The molecular weight of fulvic acid ranges in few hundreds in comparison to the molecular weight of humin and humic acid which varies in tens of thousands.

These humic substances binds with the metal ion to form a chelate and this type of chelate formation is one of its most important environmental quality. The most common binding sites in humic substances are the phenolic hydroxyl group and carboxylic sites. Generally, the metal ion forms a chelate between a carboxylic group and a phenolic group or a chelate between two carboxylic group or may just for a complex either with the carboxylic group or a phenolic hydroxyl group.

Since, fulvic acid is soluble in water, it plays an important role in solubilizing the metal complexes in water. It keeps some of the biologically important transition metal ions, especially iron, in solution and hence also helps in their transportation. These soluble fulvic acid- type compounds also impart colour to water. For example, Gelbstoffe, a yellow material is generally found in water bodies in association with soluble iron.

Humic acid and humin remain insoluble in water and affect the water quality through exchange of cations, or organic materials with water. Hence these materials may accumulate large quantities of metal ions. For example, lignite coal, a humic acid material is effectively able to remove metal ion from water.

Presence of excess humic substances in water is harmful. When water is disinfected by chlorination, the humic substances present in it gets converted into trihalomethanes (THMs) which are carcinogenic in nature. The formation of THMs can be reduced by removing as much as humic substances as possible from the water, prior to chlorination.

Know You Progress II

Q.1 Under what conditions will the carbonate hardness equal to alkalinity?

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Q.2 With respect to the constituents causing alkalinity in water, why can't HCO_3^- and OH^- exist together ? Explain.

Q.3 What is the disadvantage of using high alkaline water?

Q.4 Why does rain water normally have a pH of about 5-6? When does it become acidic?

10.10 COLLOIDAL PARTICLES IN WATER

There are certain molecules like common salt which when put in water, readily dissolves in it, making up a solution. Such particles have size as small as 1mm. On other extreme, if we add sand into water, the sand initially will be seen dispersed in water but after some time it settles down, giving a clear solution. Such particles are known as suspended particles and results in suspensions. These particles have size range in thousands nanometer.

In between these two extremes are particles which are much smaller than suspended particles but larger than individual molecules. Such substances are known as colloidal particles. These particles range in size from 1 to 1000 nanometer and results in formation of colloidal suspensions in water. Unlike sand particles, these particles don't settle down by gravity alone. Colloidal particles may exist in solid, liquid or gases but particles of most environmental importance are those that occur in liquids or gases. As per table 2, eight classes of colloidal dispersion are known.

Table 2. Types of colloidal dispersion

Dispersed phase	Dispersion medium	Common name
Solid	Solid	
Liquid	Solid	
Gas	Solid	
Solid	Liquid	Sol
Liquid	Liquid	Emulsion
Gas	Liquid	Foam
Solid	Gas	Smoke
Liquid	Gas	Fog

There are no hard and fast boundaries between molecular, colloidal or suspended particles. Some even consider particles with dimensions ranging from 1000-10,000 nm as colloids in water.

10.10.1 Formation of Colloidal Particles

Colloidal particles may be obtained by grinding of coarse material using a special device known as colloidal mill or by aggregation of molecules into a small size cluster which cannot settle on its own. Natural phenomena such as weathering of rocks and minerals also results in formation of colloids. Some micro-organisms such as bacteria, fungi, virus etc., when not clamped together also form colloidal dispersion. Certain substances such as soaps, starch, agar-agar etc. which are considered to be soluble in water, also forms colloidal dispersions. Similarly, milk, mayonnaise, paints are all colloidal suspensions.

10.10.2 Properties of Colloidal Substances

These colloidal particles which have size in between that of the particles in solution and in suspended form, have the characteristics of both these species. But, in general, these particles exhibit unique properties and behavior due to their small size, small mass and high surface area. In fact, due to their large surface area, the surface phenomena predominate and control the behavior of these particles. Also, due to their extremely small mass, the gravitational effects are unimportant.

- i. **Tyndall Effect:** Size of some of the colloidal particles is greater or similar to the wavelength of light. So, these particles interfere with the passage of light and hence scatter the light. Such scattering of light by colloidal particles is known as Tyndall effect and the scattered light can easily be scanned by an observer standing near the right angles to the beam of the light. Sometimes, rays of sunlight piercing between the clouds is seen when the atmosphere is having colloidal dust particles. Students often see this effect in their classrooms when the chalk or other dust is present in the air in colloidal form. Tyndall effect is used as an important basis of determining turbidity in water.
- ii. **Electrical Properties:** All colloidal particles are electrically charged-may be negatively or positively, depending upon their nature. Since like charges repel each other, they do not come close enough to agglomerate into larger

particles. When they are placed in electric field, they migrate towards an oppositely charged pole. This phenomenon is known as electrophoresis and is extensively useful to determine the nature of the charge on these particles. Further, the charge on the surface is pH dependent. At pH around 7, most of the colloidal particles in neutral water are negatively charged. For example, bacterial cells, proteins etc.

- iii. **Brownian Movement:** Brownian movement is a random, uncontrolled zig-zag movement of particles in a colloidal solution, as they constantly collide with each other and with the walls of the container. This movement was initially associated only with living matter but later on it has been observed that even non-living material exhibit this phenomenon.
- iv. **Adsorption:** Due to the large surface area, the colloidal particles have great adsorptive powers. This adsorption is selective in nature, yielding charge and high stability to the colloidal dispersion. This adsorptive power of the colloidal solution helps them to adsorb environmentally significant ions and molecules.
- v. **Dialysis:** Due to larger size of colloidal particles in comparison to the molecules and ions forming the solution, they are not able to pass through ordinary semipermeable membranes. This helps in separation of colloidal particles from soluble molecules and ions.

10.10.3 Classification of colloidal particles

Colloidal particles may be classified into three categories: Hydrophilic colloids, hydrophobic colloids and Association colloids.

- (a) **Hydrophilic colloids:** These types of colloids generally consist of macromolecules like proteins and synthetic polymers. Hence, hydrophilic colloids are solutions of very large molecules or ions. Such colloids interact very strongly with water, resulting in the immediate formation of colloidal solution on coming in contact with water. Such suspensions are less affected by the addition of salts in water.
- (b) **Hydrophobic colloids:** Such colloids interact to a lesser extent with water. They are however, stabilized due to their charges. For example, a negatively charged hydrophobic colloidal particle is surrounded by their positively charged counter-ions in solution, resulting in the formation of an electrical double layer, which is responsible for the repulsion amongst the particles (Figure 11). Such colloids are highly affected by the addition of salts in water and even tends to settle down in the presence of salts. Gold particles of small size, clay particles and petroleum droplets are examples of hydrophobic colloids.

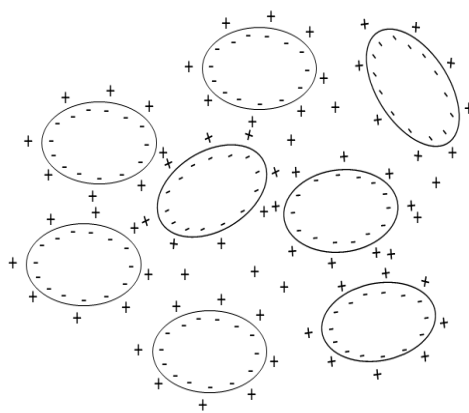


Figure 10.11 Representation of negatively charged hydrophobic colloidal particles surrounded in solution by positively charged counter-ions, forming an electrical double layer.

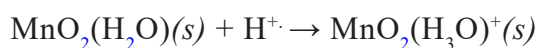
- (c) **Association colloids:** Such colloids, consist of special aggregates of molecules and ions called micelles. For sodium stearate, $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$, which is a typical soap, has two parts - a long hydrophobic tail made up of hydrocarbon part i.e $\text{CH}_3(\text{CH}_2)_{16}-$ and a hydrophilic $-\text{COO}^-$ head. When the soap is rubbed on a dirt, the long hydrophobic tail of the soap holds the dirt molecule on the cloth whereas the hydrophilic part holds the water. On rubbing, the hydrophobic part pulls the dirt and forms a micelle. The micelle is a shell of the soap compound with dirt in its center.

10.10.4 Stability of Colloidal Particles

Since colloidal particles are significant for the environment, their stability is of prime importance. The two main phenomena that contribute towards the stability of colloids are

- i. Hydration and
 - ii. Surface charge
- i. **Hydration:** A layer of water is formed over the surface of the colloids, preventing the particles to come closer to each other and form larger units. Thus, the stability of colloids is retained.
- ii. **Surface charge:** The surface charge on colloidal particles may prevent aggregation, as like-charged particles repel each other. There are three different ways in which particle may acquire a surface charge:
- Chemical reaction at the particle surface-This phenomenon, is shown by oxides and hydroxides and is pH dependent. For example, the surface charge on manganese oxide changes depending on the pH.

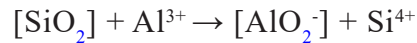
In acidic medium, the particles get positive charge on the surface



However, in basic medium, the colloidal particles get negative charge.



- Ion absorption- In this phenomenon, the ions get attached onto the surface of the colloidal particles *via* hydrogen bonding or Van der Waals forces.
- Ion replacement –This phenomenon usually occurs in clay. For example, Some of the Si^{4+} are replaced by the Al^{3+} in the basic SiO_2 unit in crystalline lattice of clay, resulting in a net negative charge on the colloidal particles.



10.10.5 Colloidal Properties of Clays

Clay constitute one of the most important class of common minerals occurring as colloidal matter in water. Clays are mainly hydrated aluminum and silicon oxide, formed by weathering of rocks and are considered as secondary minerals. Examples of some common clays are-

- Kaoliite- $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$
- Hydrous Mica- $\text{KAl}_2(\text{OH})_2(\text{AlSi}_3)\text{O}_{10}$

Clays may differ from each other by general chemical formula, structure, chemical and physical properties. Clays have layered structure with sheets of aluminum oxide and silicon oxide, arranged alternating to each other.

As discussed earlier, the clay may attain negative charge on the surface by ion replacement method i.e., by the replacement of Si^{4+} and Al^{3+} ions by metal ions of similar size but smaller charge. The negative charge, thus acquired, is compensated by association of a cation on the surface. These cations don't have to fit specifically on the sites in the lattice of the clay, they may even be of larger size, such as K^+ , Na^+ or NH_4^+ . Such cations can exchange for other cations in water and hence are called as exchangeable cations. The amount of exchangeable cations is known as cation-exchange capacity (CEC) and is expressed as milliequivalents of the monovalent cation per 100g of dry clay. This cation exchange capacity is an important characteristic of colloids and sediments.

10.10.6 Aggregation of Colloidal Particles

The process by which colloidal particles aggregate and precipitate from the colloidal solution is very important in aquatic environment. For example, the biomass during the biological waste treatment settles down due to the aggregation of bacterial cells. Similarly, the bottom sediments are also formed due to the aggregation of colloidal particles. The process of aggregation of colloids is also important for clarification of turbid water to obtain purified water for domestic and industrial use. Even the crude oil that comes out of ground is in the form of colloidal suspension in water; the colloidal particles of hydrocarbons must be separated from the water before the crude oil is refined. The aggregation of colloidal particles may be done by two methods-coagulation and flocculation.

- Coagulation:** In coagulation, the electrostatic repulsion between the colloidal particles of same charge is reduced, allowing these particles to come closer and hence aggregate. This is done by adding a salt, like NaCl , into the suspension of colloidal particles. The Na^+ and Cl^- ions tend to neutralize the

electrical charges on the colloidal particles and allow them to come together and aggregate. Hydrophobic colloids are often readily coagulated by this method. Since in this method, a double layer of electrical charge (one layer of adsorbed ions and other of counter-ions) is surrounding a charged particle, this aggregation mechanism is also known as double-layer compression. This happens in estuaries where sediment-laden fresh water flows into the sea and is largely responsible for delta formation where large rivers enter oceans.

- An important point that may be noted is that initially aggregation results when negatively charged colloidal particles are made to react with positive ion. However, as more and more of positive ions are added, their sorption results in the formation of positive colloidal particles (Figure 12).
- ii. **Flocculation:** When colloidal particles are made to settle by virtue of bridging groups, called flocculants, it results in aggregation of colloidal particles. This phenomenon is known as flocculation.

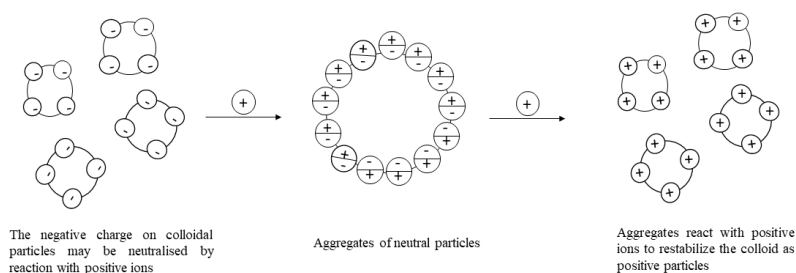


Figure 10.12 Aggregation of negatively charged colloidal particles by reaction with positive ions, followed by re stabilization as a positively charged colloid.

10.10.7 Flocculation of colloids by Polyelectrolytes

Polyelectrolyte are natural or synthetic polymers with high formula weight containing ionizable functional groups. Negatively charged functional groups such as SO_3^- , COO^- are present in anionic polyelectrolyte, whereas positively charged functional group such as NH_4^+ are present in cationic polyelectrolyte. A positively charged metal ion serves as a bridge between the anionic polyelectrolyte and the negatively charged colloidal particles, thus causing aggregation of the colloid.

10.10.8 Flocculation of Bacteria by Polymeric Materials

Aggregation, settling and separation of microbes is a significant process in aquatic systems and is essential in biological waste treatment processes, mainly the activated sludge process, in which the microorganisms reduces the carbonaceous solutes in water by converting them into biomass. Part of the carbon, converted into CO_2 by the metabolic process of bacteria, slowly evolves out from the water. However, a significant fraction of carbon is converted into bacterial floc, which has the aggregates of bacterial cells and hence settles down easily to be removed later on. This bacterial flocculation occurs with the help of polyelectrolytes formed by the bacteria. These bacterial cells are hydrophilic in nature and involves a bridging species to get aggregated.

10.10.9 Environmental Significance of Colloids

As already discussed, an important role of colloids has been the removal of turbidity from domestic and industrial water and the dewatering of sludges produced during water and waste water treatment. Colloids such as clay minerals may effectively immobilize dissolved chemicals in water and exert a purifying action. Due to their structure and high surface area, clays can strongly sorb the chemical species from water, thus playing an important role in the transportation and reaction of biological wastes, organic chemicals, gases and other pollutants present in water. Sometimes, clay can also be used for the sorption of organic compounds to inhibit degradation.

A recent focus is on the role of colloids in transformation and transportation of pollutants in aqueous environment. Colloids may adsorb pollutants such as metals and other ions, a wide variety of toxic organic compound and radionuclides. Oxidation, reduction and other transformation reactions can be catalyzed by colloids. Due to their high surface area, colloids may be used even to transport the contaminants, mainly the immobilized contaminants on aquifer solids, to relatively longer distance from their origin. Colloidal nanoparticles (5-200nm diameter) are nowadays used for catalytic destruction of environmental pollutants.

10.11 ION EXCHANGE WITH BOTTOM SEDIMENTS

Bottom sediments are important sources of both inorganic and organic matter in streams, fresh-water impoundments, estuaries and oceans. These bottom sediments are different from ordinary wet soil. The wet soil is aerobic, i.e., in oxidizing conditions as it is in contact with atmosphere, contains less amount of organic matter and do not undergo continuous leaching. On contrary, the bottom sediments are anaerobic, reducing conditions, have very high level of organic matter with high rate of leaching.

One of the most important characteristics of bottom sediments is their ability to exchange cations with surrounding water, as they are important repositories of metal ions. Cations Exchange Capacity (CEC) is the capacity of these sediments to sorb cation. Another parameter which is important for sediments is the Exchangeable Cation Status (ECS) which refers to the amount of specific ions which is bonded to a given amount of sediments. Both, CEC and ECS are expressed a milliequivalents per 100g of solid. These bottom sediments also have a capacity to sorb and release hydrogen ions and hence have an important buffering effect in some waters. The average value of CEC for fresh water sediments is 20 -30 milliequivalent per 100 gram. The ECS value of individual cation may typically range from less than 1 to 10-20 milliequivalent per 100g.

10.11.1 Metals in Suspended Matter and Sediments

Metal such as iron, zinc, sodium, potassium, calcium, magnesium and trace metals such as chromium, cadmium, copper, molybdenum, nickel, cobalt and manganese

are present in sediments as well as suspended matter. Depending on the pE values, these metals may be present as discrete compounds, ions held by cation-exchanging clay, bound to the hydrated oxides of iron or manganese or chelated by insoluble humic substances. Complexing agents such as amino acids, histidine, tyrosine, chloride (in sea water) are responsible for solubilization of these metal ions present in sediments or suspended matter.

These metals when present in suspension are more accessible than those in sediments. The toxicity associated with heavy metals in sediments and their availability to organisms plays an important role in determining the environmental effects of these metals in aquatic systems. Since sediments are anaerobic, so the microbial reduction reactions are predominant. For example, sulfates are reduced to metal sulfides (metal sulfides have very low solubility), hence restricting bioavailability of metals. However, when these sediments are exposed to air, metals are again converted into more soluble sulfates, responsible for the release of metals such as zinc, mercury, copper and lead in the aquatic ecosystem.

For evaluation of CEC and ECS, the bottom sediments are selected and then studied accordingly. However, it is very important to seal and freeze these sediments as soon as they are collected, because certain exchangeable ions like Fe^{2+} and Mn^{2+} present in anaerobic sediments may get exposed to air and get converted into non-exchangeable oxides, Fe_2O_3 and MnO_2 .

10.11.2 Method for determination of CEC

The following steps are involved in the determination of CEC-

- i. The sediments are treated with a solution of ammonium salt, so that all exchangeable sites are occupied by NH_4^+ ion.
- ii. The NH_4^+ ions are then displaced by treatment with aqueous solution of NaCl.
- iii. The quantity of displaced NH_4^+ is evaluated in the dried sample.
- iv. The CEC values may be expressed as the number of milliequivalents of ammonium ion exchanged per 100 g of dried sample.

10.11.3 Method for determination of ECS

The following steps are involved in the method for determination of ECS-

- i. All exchangeable ions, such as Fe^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} are made to leach out from the sediments by treatment with ammonium acetate solution.
- ii. These metal ions are then estimated individually in the leachate.
- iii. Exchangeable H^+ cannot be determined by direct methods, but is estimated only by indirect methods.

Total CEC – Sum of ECS of all exchangeable cations (except H^+) = ECS for H^+ ion

Apart from metal ions, some water receiving heavy loads of domestic and industrial wastes, may be heavily loaded with inorganic polyphosphates (from detergents or run off from fields having polyphosphate fertilizers). The polyphosphates may be sorbed on sediments and their exchange with sediments plays a vital role in making phosphorous available for algae, thus contributing towards eutrophication.

10.12 ORGANIC COMPOUNDS IN SEDIMENTS AND SUSPENDED MATTER

Several organic compounds interact with suspended material and sediments in a water body. When the suspended material containing sorbed organic matter settles down, it carries these organic compounds into the sediments also. For example, run off water from agriculture land may carry herbicides and pesticides with it into sediments.

The most common type of sediments that binds with organic matter are clays, humic (organic) substances and complexes between clay and humic substances. Both humic substances and clays act as cation exchangers and sorb cationic organic compounds through ion exchange, greatly reducing the mobility and biological activity of these compounds. Actually, when these organic compounds are sorbed by clay, they are held between the layers of the clay mineral, virtually reducing the biological activity of these compound to almost zero. Further, the degree of sorption of this organic matter is inversely proportional to their water solubility. Hence the more insoluble compounds are sorbed strongly by lipophilic sediments, such as humic substances, and the organic compounds with high vapor pressure are lost from water or solids by evaporation. When this happens, photochemical processes can play an important role in their degradation. However, sorption of comparatively non-volatile hydrocarbon removes them and also retard their biodegradation.

Since most of the sediments do not have anion exchange sites, negatively charged organic compounds are not held strongly at all. Hence, these compounds remain relatively mobile and biodegradable in water, despite the presence of sediments.

The sorption of neutral species like petroleum cannot be explained by ion-exchange mechanism. This may happen due to hydrogen bonding, Van der Waals forces, charge transfer, complexation, and hydrophobic interactions.

Hence, the organic matter in solution or in suspended form undergoes chemical degradation and biodegradation at four different rates and via different pathways in comparison to sorbed organic matter by the sediments.

In some cases, pollutant compounds get covalently bonded as bound residues to humic substances in soil or even sediments. This kind of bonding is assumed to be *via* the action of extracellular enzymes, present in some organisms. These enzymes act as oxidoreductase which catalyse oxidation-reduction reaction, cause polymerization of the aromatic compounds (Figure 13). Hence it becomes difficult to remove such residues from humic substances thermally, biochemically or by exposure to acid or base. Release of organic matter which is sorbed by the sediments, is slowed down. Similarly, its biodegradation is also slowed down appreciably, resulting in very high bioaccumulation of these matter in the sediments. For example, herbicides are highly toxic in water and their biodegradation is further slowed down by their sorption over solids or sediments. Hence in extensively farmed areas, there is high accumulation of these herbicides in the sediments of the nearby stream, lake, reservoir etc.

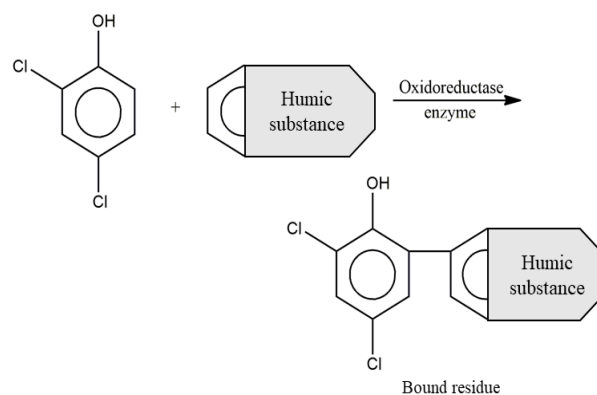


Figure 10.13 Enzyme-catalysed coupling of pollutant 2,4-dichlorophenol ring on molecule of humic substance.

Herbicides. 2, 4 -D (2, 4- dichlorphenoxyaceticacid) has been exclusively studied in regard to sorption reaction. The studies have been carried out in a place where there is strong clay – fulvic acid complex component. The sorption is described using Freundlich isotherm type:

$$X = KC^n$$

Where X= amount sorbed per unit weight of solid

C= concentration of 2, 4 -D in water solution at equilibrium

n and K are constants and their values can be calculated by plotting log X versus log C, to give a linear plot with slope = n and intercept = log K.

The study of sorption of 2, 4 -D on organoclay complex, at 5 °C gives the value of n as 0.76 and logK as 0.85. However, at 25 °C, the value of n increased to 0.83 and that of logK decreased to 0.716.

Know your progress-III

Q.1 Which phenomenon of colloids involves the formation of a delta?

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Q.2 A small amount of electrolyte is needed for the formation of sol white large amount is required for coagulation of sol comment.

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.....

Q.3 Why do we add alum to purify water?

Parameters of
Water pollution

Q.4 In determination of CEC, NH_4^+ is used to replace the exchangeable cations originally present in the soil. Can other cations be used?

Q.5 What factors determine the amount and type of cations on the exchange complex?

10.13 LET US SUM UP

Currently, the availability of potable water is a major threat to the human civilization. With increasing industrialization, rate of contamination of water with pollutants such as heavy metal ions, organic waste, pesticides, herbicides, chemicals and various types of industrial discharges, is constantly increasing. Additionally, when the polluted water percolates down, it pollutes the ground water reservoir as well. For a sustainable development, it is imperative understand the sources, interactions and effects of water pollutants, in order to control these pollutants. For this, it is important to understand and discuss the various parameters of water pollution.

10.14 KEYWORDS

Oxygen Sag Curve - The curve obtained when the concentration of dissolved oxygen in a river into which sewage or some other pollutant has been discharged is plotted against the distance downstream from the sewage outlet.

Biological Oxygen Demand – It is the amount of dissolved oxygen needed (i.e. demanded) by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific time period. It is abbreviated as BOD.

Chemical Oxygen Demand – It is an indicative measure of the amount of oxygen that can be consumed by reactions in a measured solution. It is commonly expressed in mass of oxygen consumed over volume of solution which in SI units is mg/L. It is abbreviated as COD.

Hydrophilic – Hydrophilic molecule or portion of a molecule is one whose interactions with water and other polar substances are more thermodynamically favourable. They are typically charge-polarized and capable of hydrogen bonding.

Hydrophobic –Hydrophobic literally means “the fear of water”. Hydrophobic molecules and surfaces repel water. Hydrophobic liquids, such as oil, will separate from water. These molecules are usually nonpolar, meaning the atoms that make the molecule do not produce a static electric field.

Chelate complex - A complex where a metal ion is bound to two or more atoms of the chelating agent, resulting in the formation of one or more rings.

Cations Exchange Capacity (CEC)- It is a measure of how many cations can be retained on soil particle surfaces. Negative charges on the surfaces of soil particles bind positively-charged atoms or molecules (cations), but allow these to exchange with other positively charged particles in the surrounding soil water. It is abbreviated as CEC.

Exchangeable Cation Status (ECS) - Exchangeable cations are those that can be exchanged by a cation of an added salt solution. In many cases, the definition of an exchangeable cation is entirely straightforward, that is, any added cation will exchange the soil cation. In other cases, the definition is less sure. It is abbreviated as ECS.

10.15 REFERENCES AND SUGGESTED FURTHER READINGS

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Answers to check your Progress

Know Your Progress I

Ans. 1 The amount of oxygen dissolved in water at a given temperature is known as DO. At 20 °C, The DO should be close to 9 ppm. The DO is an indication of pollution in water. The phenomena of deoxygenation and reaeration, occurring simultaneously in a water body results in oxygen sag.

Ans. 2 Four factors which influence the DO in water are- reaeration, photosynthesis, decomposition and respiration. The DO decreases with increase in the temperature.

Ans. 3 We know,

$$(\text{BOD})_{5 \text{ days}} = \frac{(\text{DO}_0 - \text{DO}_5)}{V_w} \times (V_w + V_d) = \frac{(8.5-5)}{6} \times (300) = 175 \text{ mg/l}$$

$$(\text{BOD})_{5 \text{ days}} = L_o(1 - e^{-0.22 \times 5})$$

at any particular temperature

$$L_o = (\text{BOD})_{\text{ultimate}} = \frac{175}{(1 - e^{-0.22 \times 5})} = 256 \text{ mg/L}$$

Ans. 5 The combined effect of photosynthesis, reaeration and respiration results in a diurnal variation of dissolved oxygen with time.

Ans. 6 BOD is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to rich in dissolved oxygen.

Ans. 7 Assuming the temperature to be the same and taking the BOD rate constant as K,

$$(\text{BOD})_{2 \text{ days}} = L_o(1 - e^{-2K})$$

$$(\text{BOD})_{4 \text{ days}} = L_o(1 - e^{-4K})$$

Dividing the above two equations,

$$\frac{\text{BOD}_2}{\text{BOD}_4} = \frac{L_o(1 - e^{-2K})}{L_o(1 - e^{-4K})} = \frac{100}{155} = \frac{(1 - e^{-2K})}{(1 - e^{-4K})}$$

Solving above, gives $K = 0.298 \sim 0.3$ per day

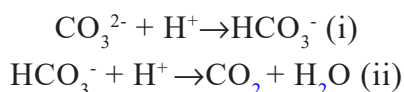
Know Your Progress II

Ans. 1 When Cl^- , SO_4^{2-} are present but NaHCO_3 and Na_2CO_3 are absent in water.

Ans. 2 HCO_3^- and OH^- together combines to form CO_3^{2-} ions. Therefore, this situation never arises.

Ans. 3 High alkaline water leads to caustic embrittlement and deposition of precipitates and sludges in boiler tubes and pipes.

Ans. 4 Water Alkalinity is mainly due to carbonate and bicarbonate salts in a water sample. The carbonate ion has two end points, one from carbonate to bicarbonate and another from bicarbonate to carbon dioxide.



Both the steps are indicated by methyl orange indicator but only step (i) is indicated by phenolphthalein indicator. Step (ii) cannot be indicated by phenolphthalein indicator, because the pH drops to around 6, due to the formation of carbonic acid in step (ii), whereas the colour change range for phenolphthalein is 8.3-10.

Ans. 5 Due to the dissolution of CO_2 of the atmosphere. If pH drops below 5, it becomes acid rain

Know Your Progress III

Ans. 1 Coagulation or flocculation is involved in the formation of the delta. The river contains clay particle when combined with seawater with electrolyte due to the presence of opposite ions clay particle gets coagulated and forms delta.

Ans. 2 A freshly formed precipitate is converted into a sol by the addition of a small amount of electrolyte as a peptizing agent that helps in the formation of sol. However, when a large amount of electrolyte is added, the oppositely charged ions neutralize the charge of sol particles and the sol particle gets coagulated.

Ans. 3 The Colloidal impurities present in water gets coagulated by adding alum, thus making water potable. When added to water, Al^{3+} ions hydrolyze rapidly and form a range of metal hydrolysis species. These cationic species adsorb onto the negatively charged particles and neutralize the charge during coagulation.

Ans. 4 Yes, other cations can be used. They are K^+ , Na^+ , Ca^{2+} , etc. Though the ionic radius of Na^+ (97), K^+ (133), Ca^{++} (99), Mg^{++} (90), Li^+ (68) is smaller than NH_4^+ (143), the ionic radius of hydrated cation of Na^+ (300), K^+ (450), Ca^{++} (600), Mg^{++} (800), Li^+ (600) is much higher than NH_4^+ (250) in pm. Among the ions of same valence, the ion with smallest hydrated radius is preferred.

Ans 5. The *factors* that *determine the amount and type of cations on the exchange complex* are the charge and concentration of *cations*, pH of the reaction.

Ans 6. Since we have 100 g of soil, simply adding the milliequivalents of exchangeable cations equals the CEC as follows: $1 + 5 + 6 + 2 + 1 + 1 = 16$. So, the CEC is 16 meq/100 g soil.

H⁺ and Al³⁺ are acid-forming cations which total 6 meq. Ca²⁺, Mg²⁺, K⁺ and Na⁺ are basic-forming cations which total 10 meq.

$$\begin{aligned}\% \text{ base saturation} &= \frac{\text{Amount of exchangeable bases}}{\text{CEC}} \times 100\% \\ &= \frac{10 \text{ meq}/100 \text{ g}}{16 \text{ meq}/100 \text{ g}} \times 100 \% = 62.5\%\end{aligned}$$

Ans 7. $\text{CEC} = \frac{33.8 \text{ meq}}{87.2 \text{ g}} \times 100 = 38.8 \text{ meq}/100 \text{ g}.$

Ans 8. Some main such measures are as follows:

1. Direct dispatch of waste into the water body should be avoided
2. Penalty should be imposed on the industries that dispose of wastes into natural water.
3. Proper methods to protect the rivers, lakes, and seas should be followed
4. People should be made aware of the adverse impact of water pollution.
5. People should be educated about creating a culture of responsibility to minimize the disposal of wastes.

10.12 TERMINAL QUESTIONS

1. Differentiate between BOD and COD. Derive the following relation for BOD, where the symbols have usual meaning

$$(\text{BOD})_{5\text{days}} = L_o (1 - e^{-0.22 \times 5})$$

2. With respect to the constituents causing alkalinity in water, why can't HCO₃⁻ and OH⁻ exist together ? Explain.
3. 6.0 mL of wastewater is diluted to 300 mL distilled water in standard BOD bottle. Initial DO in the bottle is determined to be 8.5 mg/L. DO after 5 days at 20 °C is found to be 5 mg/L. Determine BOD_{5-days} of wastewater and compute the ultimate BOD.
4. Why can't the alkalinity of a water sample caused by bicarbonate ions be indicated by phenolphthalein as indicator?
5. 100 g of a soil has the following cations on the exchange sites:
1 meq H⁺, 6 meq Ca²⁺, 1 meq Na⁺, 5 meq Al³⁺, 2 meq Mg²⁺, 1 meq Na⁺.

What is the CEC of this soil in meq/100 g soil? What is the percentage base saturation of the soil?

6. A sediment sample was equilibrated with a solution of NH₄⁺ ion and the NH₄⁺ was later displaced by Na⁺ for analysis. A total of 33.8 milliequivalents of NH₄⁺ were bound to the sediment and later displaced by Na⁺. After drying, the sediment weighed 87.2 g. What was its CEC in milliequivalents/100 g?
7. What are some major Preventive Measures to Control the water pollution?

UNIT 11 : CHEMISTRY OF HAZARDOUS SUBSTANCES AND WASTES

STRUCTURE

- 11.0 Introduction
- 11.1 Objectives
- 11.2 Classification of Hazardous Substances and Wastes
- 11.3 Combustible Waste: Physical and Chemical Properties
 - 11.3.1. Dust Explosions and Combustion of Finely Divided Particles
 - 11.3.2. Toxic Products of Combustion
- 11.4 Reactive Substances: Physical and Chemical Properties
- 11.5 Corrosive Substances: Physical and Chemical Properties
- 11.6 Toxic Substances: Physical and Chemical Properties
 - 11.6.1. Type of Toxic Substances
 - 11.6.2. Risks of Using Toxic Substances
- 11.7 Let's Sum Up
- 11.8 Glossary
- 11.9 References and Suggested Further Readings

11.0 INTRODUCTION

While studying the various aspects of the environment, it is pertinent to understand yet another aspect, which is hazardous waste in whatever physical state, its nature and its harmful effects.

Waste generation has been known even in the Roman times, when metals extracted from ores were subjected to smelting operations. Industrial revolution saw major pollution arising out of production of materials and chemicals. Being generally non-hazardous, this waste did not pose a threat. However, it was during World war II and later, when a sudden escalation in the production of wastes, particularly hazardous wastes, occurred. In the present times, there are more than 50,000 hazardous waste sites and 300,000 underground storage tanks in the US alone, indicating the volume of waste generation and the scale at which this waste production needs mitigation.

By definition, hazardous waste is any substance that poses danger to the environment, living organisms, or materials by acting toxic to organisms, by explosion, or fire hazards or by any other detrimental effect. Alternately, any substance, which due to its corrosive, reactive, toxic and infectious characteristics causes irreparable damage to the environment or human health is a hazardous substance.

Industrial activities, medical sector, commercial centres, agriculture and agro-industries, household and the informal sector, small competitive and labour intensive businesses are the major source of hazardous waste. Amongst these, the industrial hazardous waste poses greater risks in developing countries, than in developed countries, because of use of obsolete and poor management technologies. Some

of the multinational companies from the developed countries even exploit the developing countries and use the technologies banned in their parent country in these developing nations. The Bhopal Gas Tragedy that happened in December 1984 is a living example of this situation, in which the plant was set up in Bhopal by Union Carbide of USA. Developing countries have faced yet another serious problem by becoming the dumping ground for wastes generated in developed nations, which would ship the thousands of tonnes of wastes generated as a result of their multiple activities and not dumping them in their nation due to heavy surcharges. To address this problem of Crossing national boundaries for dumping hazardous waste in developing countries, Basel Convention on the “Control of Transboundary Movement of Hazardous Wastes and their Disposal” was held in Basel, Switzerland in 1989. In a span of ten years, the treaty was signed by more than 100 countries, including India. As a result, India is obliged to regulate and minimize the import of hazardous waste or other wastes for disposal or recycling and also to minimize generation of hazardous waste in the country considering social, technological and economic aspects.

11.1 OBJECTIVES

After studying this unit, you will be able to:

- Define various physical and chemical hazards
- Explain the effects of physical and chemical hazards
- Identify various types of combustible chemicals and
- Understand the effects of hazardous substance

11.2 CLASSIFICATION OF HAZARDOUS SUBSTANCES AND WASTES

Several criteria are used to classify hazardous wastes, as listed below:

I. Characteristics

In 2003, the United Nations adopted the Global Harmonized System (GHS) for Hazard Communication, which includes important criteria regarding the classification of hazardous substances. Based on their characteristics, hazardous substances can be broadly classified into following categories:

- (a) **Explosives** - All those substances, which have the tendency to undergo violent chemical changes or detonate rapidly can be classified under this category. The waste resulting from ordnance manufacturing and some industrial gases comes under the category of explosive waste. Such wastes may exist in solid, liquid or gases forms and have a high potential for hazards in storage, collection and disposal. For example, fireworks, ammunition, airbag inflators etc . Wastes such as organic solvents, oil etc., which are flammable and pose

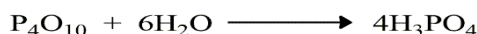
problems in collection, storage and disposal also fall in this category of hazardous substance.

- (b) **Gases** - Substances with a vapour pressure of 300 kPa or higher at 50 °C and exist in gaseous state at standard temperature and pressure fall into this category. These substances include several common items such as aerosols, compressed gases, fire extinguishers etc.
- (c) **Ignitable substances**- All those substances which catch fire easily may be classified as ignitable hazardous substances. Such substances may further be divided into two categories:
 - (i) **Flammable Liquids** - Liquids with a flashpoint of 60-65 °C falls in this category. Such low boiling liquids catch fire in presence of an ignition source. Common examples include adhesives, paint, alcohol, diesel, kerosene etc.
 - (ii) **Flammable Solids** - This class of hazardous material includes readily combustible solids, such as sodium metal, matches, sodium batteries etc which may catch fire from friction or on contact with water. Self-reactive substances that may undergo violent exothermic reactions, pyrophoric substances like white phosphorus which catch fire spontaneously in air also fall under this category.
- (d) **Oxidizing substances, organic peroxides**- Substances such as nitrates, nitrites, that cause combustion by yielding oxygen as a result of a chemical reaction are known as oxidizers and are hazardous in nature. Organic peroxides and hydrogen peroxides also fall under this category of hazardous substances.
- (e) **Toxic and Infectious substances** - All those substances which release toxic material during their extraction/ procedure or chemical analysis falls in this category of hazardous substances. such substances can further be divided into two broad categories:
 - (i) Substances which cause chronic toxicity - Repeated exposure of small doses of such substances, spread over a long period of time, manifests the symptoms of toxicity. For example, exposure of lead salts results in chronic toxicity and hence acts as slow poison.
 - (ii) Substances which cause acute toxicity- A single dose of such substances is enough to manifest the symptoms of ill effects and toxicity. For methyl isocyanate, released during Bhopal Gas tragedy.

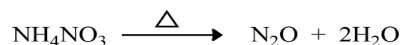
Infectious substances containing pathogens, such as viruses, bacteria and other microbes that can cause disease in humans and animals are also hazardous in nature. Biomedical wastes produced from hospitals and biological research facilities, such as discarded malignant tissues during surgical procedures, infected and contaminated material bandages, hypodermic needles etc. are also classified in this category. Such waste may produce toxins and infect other living organisms.

- (f) **Radioactive Material**- Substances that emit ionising radiation are radioactive. Such substances are hazardous to living organisms and the environment, as they persist in the environment for a long period and have a long half-life. For example, uranium, plutonium, etc.
- (g) **Corrosives**- Any substance which has the tendency to corrode steel or exhibit extreme acidity or basicity, can be classified as corrosive hazardous substance. For example, strong acids like sulphuric acid, strong alkalis like sodium hydroxide, strong oxidants like oxygen difluoride, protein denaturing agents like nitric acid, etc.
- (h) **Reactive Substances**- All those substances which react violently with water, CN^- / S^{2-} bearing waste, etc., and which have the tendency to undergo violent chemical changes, can be classified under this category.

Phosphorus pentoxide reacts spontaneously and/or vigorously with water hence falls into this category.



Substances like ammonium nitrate which generate toxic fumes of nitrous oxide also falls in this category:



Some of the reactive substances have both the oxidizing and reducing components within the same molecule, which undergo reaction, in a violent and explosive manner, e.g. TNT and nitroglycerin.

Several organic compounds have very covalently bonded atoms in comparison to the bonds in the products that form due to their decomposition. Such highly exothermic reactions typically have one of the following weak bond types:

- O-O bonds - a single bond is half the strength of a double bond. For example, peroxides, hydroperoxides
- N=N - double bond weaker than triple bond. For example, azo compounds, triazenes, nitrous oxide
- C=C bond in allenes and polyenes
- X-X, X-N, X-O bonds in interhalogen compounds, nitrogen trihalides, halogen oxides

- (i) **Miscellaneous Hazardous Materials**- All those hazardous substances that do not fall in the above eight categories are covered in this category. Such substances include environmentally hazardous substances, genetically modified organisms and substances that are stored and transported at high temperatures. Some of the common examples include dry ice, and fuel cell engines. With modernization and rise of technology, e-waste such as batteries found in mobiles, laptops and tablets, computers, monitors, DVD players, cables, is also being generated in large quantities. These wastes, known

as e-wastes, are all hazardous to the environment and public health, if not disposed of properly.

The characteristics, source and possible impact of hazardous waste are discussed in Table 4.1

Table 4.1. Source, characteristics and impact of hazardous waste in India

Classification of Hazard	Source	Characteristics	Impact on Human Health/ Environment	Example
Explosive / Flammable	Nuclear power plants, biomedical research laboratories, college and university laboratories	The waste has a flash point of less than 60°C, Produces harmful gases, results in increase in temperature and pressure, causes fire hazards	Causes air pollution, explosions and fire	Fireworks, Ammunition
Oxidizing	Chemical Units, laboratories, Power Plants, etc	They may yield oxygen and thereby cause or contribute to the combustion of other materials.	Severe Water Pollution, resulting in loss of crop and effects on aquatic life, etc	Bleach, medical oxygen
Eco-toxic	R & D Units, etc	May bioaccumulate	Effect the biotic system by causing genetic mutations, Physical deformations, Birth defects, etc	Diethyl phthalate, pesticides
Toxic (Delayed or Chronic)	Chemical and Pharma Units, Fertilizers Units, Tanneries, etc	Such waste is likely to leach dangerous concentrations of toxic chemicals into groundwater. They may cause delayed or chronic effects, including carcinogenicity	Effect the fertility of soil and lead to soil contamination, etc	Pesticides, biocides
Peroxide waste	Plastic and Rubber Industries, etc	These are organic waste containing -O-O- structure and may undergo exothermic self-accelerating decomposition.	Water Pollution, etc.	Methyl ethyl ketone peroxide (MEKP)
Poisonous	Radioactive and Nuclear Units, Chemical Industries, etc	They have serious impact on human health and at times may even prove fatal	Behaviour abnormalities, Cancer, Physiological malfunctions	mercury, arsenic salts, cadmium

Infectious Substances	R and D and health care Units, Drugs manufacturing units, etc	These waste contain microorganisms and their toxins, which may result in diseases in animals or humans.	Contagious diseases, Soil and water pollution	Discarded sharps, unwanted microbiological cultures, human or animal tissues
Corrosives	General Manufacturing Units	Such waste has pH <2 or pH >12.5. These wastes are chemically active and may cause severe damage to the flora and fauna, or materials by direct contact with them.	Water contamination, etc	sulphuric acid, nitric acid

II. Process generating waste, as identified by the Government - EPA has listed more than 450 wastes as hazardous. Each such substance is assigned an EPA hazardous waste number, denoted by a letter followed by 3 numerals. This type of waste has been explicitly classified by various government organizations as hazardous. Every year after collating data from non-specific and specific sources, several materials are included into this classification. Strictly governed by different regulations and legislations, this type of waste needs to be handled properly. The letter assigned to each such substance, is any one letter from list of four letters, given below:

- **F-type wastes from nonspecific sources:** It includes the hazardous waste generated in various industrial processes. Spent solvent wastes, dioxin bearing wastes, chlorinated aliphatic hydrocarbons production, wood preserving wastes etc. all fall into this category. These types of waste are also known as non-specific source waste as multiple industries produce them. For example F012 is used to denote the sludge generated in the wastewater treatment process using cyanide ions. F007 is used to denote spent plating-bath solutions from electroplating
- **K-type wastes from specific sources:** It includes the waste generated by specific industrial processes. EPA has determined a total of 13 categories that define the K list, All these wastes generate specific types of wastewater and sludge. Several types of waste including waste from pesticide manufacturing units, petroleum refining units, explosive manufacturing units, organic chemicals manufacturing units etc. fall in this category. K019 is used for heavy waste generated during the production of ethylene dichloride. Similarly, K067 represents electrolytic anode slimes/sludges produced from primary zinc production
- **P-type acute hazardous wastes:** The list includes commercial pure grades of chemicals that are produced and marketed. All those substances which are fatal to humans in low doses, or capable of causing irreversible illness comes in this category. For example, P027 is used for 3-chloropropane nitrile.
- **U-Type miscellaneous hazardous wastes:** These are specific compounds such as calcium chromate (U032) or phthalic anhydride (U190).

Know your progress I

Q.1 Discuss the broad basis on which the hazardous substances have been categorized.

Q.2 Discuss briefly the ignitable substances.

Q.3 Distinguish between K-type and F-type of waste.

Q.4 What letter is assigned to describe the waste including commercial pure grade of chemicals.

11.3 COMBUSTIBLE WASTE: PHYSICAL AND CHEMICAL PROPERTIES

A combustible substance is something that can burn in air. Combustible waste readily gets evaporated to give vapours which are denser than air and ignite easily. The temperature at which the mixture of vapor and air ignites at the liquid's surface, on exposure to a flame is known as **flash point**. Flammable materials are those combustible substances which ignite easily on exposure to flame.

To study combustible substances, it is important to study the concept of flammability limit and flammability range. **Lower flammability limit (LFL)** is that value of

vapour : air ratio below which ignition cannot occur due to insufficient fuel. **Upper flammability limit (UFL)** is that value of vapour: air ratio above which ignition cannot occur, due to insufficient air. The difference between LFL and UFL at a specified temperature is known as **Flammability range**. Based on the flash point and the combustibility, the combustible materials may be divided into following categories:

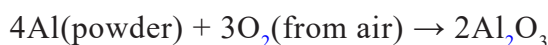
- (a) **Flammable and combustible solid** – Solids which may ignite from friction or due to heat remaining in its manufacture leading to serious hazards, can be classified in this category. For example, alkali metal, metal hydrides etc.
- (b) **Flammable Liquid** – Any liquid having a flash point less than 60.5 °C is considered as flammable liquid. When a flammable liquid is heated in an enclosed vessel, it may lead to an explosion due to the building up of pressure inside the container. This is known as Boiling Liquid Expanding Vapour Explosion (BLEVE) and may be highly disastrous in nature. On the basis of the flash point and the boiling point of the liquid, the hazard statement of the liquids can be defined as per Table 11.2

Table 11.2: Flash point and boiling point of liquids

Flash Point*	Boiling Point	Hazard Statement
< 23 °C	≤ 35 °C**	Extremely flammable
< 23 °C	> 35 °C	Highly flammable
23 to 60 °C	> 35 °C	Flammable
> 60 to 93 °C	NA	Combustible

* closed-cup method

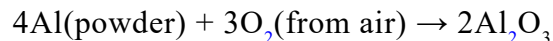
** TDG regulations currently indicate “Any” flash point



- (c) **Combustible liquid**- All those liquids which have a flash point between 60.5 °C and 93.3 °C comes under this category of combustible substances.
- (d) **Flammable Compressed Gas**- Any substance which exists in gaseous phase at 1 atm and 0 °C and meets the specified criteria for lower flammability limit, flammability range and flame projection is a flammable compressed gas.
- (e) **Catalyst ignition** – Catalysts such as Raney nickel, platinum etc., when recovered from hydrogenation reactions, may get saturated with hydrogen and catch fire.
- (f) **Flammable aerosols** – Flammable liquid may rupture and get aerosolized when stored under pressure. Such aerosols, when exposed to heat, may explode.

11.3.1. Dust Explosions and Combustion of Finely Divided Particles

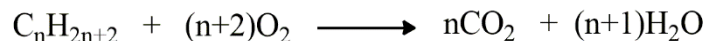
Certain solids when grinded into a finely divided powder may lead to dust explosion. For example, dust of magnesium and its alloys, zirconium, titanium and aluminium may explode in air.



Explosions due to coal dust are common in coal mines. Finely divided particles of combustible materials, such as spray of hydrocarbon liquid, may ignite at a temperature below the flash point of the liquid. This happens because oxygen in such cases is able to come to intimate contact with the liquid particles, just as in vapours, and ignite easily. At times even the dust of polymers, such as polyethylene and polystyrene can be explosive.

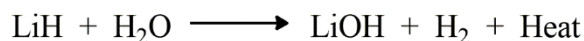
Oxidizers

The combustible substances, which are reducing in nature, react with oxidizing agents, such as air, nitric acid, halogens etc., to liberate heat. For example, combustion of a mixture of organic compounds containing C, H and O results in liberation of heat. In some cases, along with heat, exhaust gases may also contain hazardous air pollutants, such as nitrogen oxides, acidic gases, trace metals (e.g., Be, Cd) etc.



Spontaneous Ignition

Certain substances catch fire spontaneously in air without any source of ignition. Such substances are known as pyrophoric substances. Spontaneous ignition may occur due to the presence of moisture in air or even due to bacterial fermentation. For example, lithium hydride reacts with water from the moist air to liberate heat, which is sufficient to ignite the hydride itself. Hence lithium hydride starts burning in air.



Ignition of lithium hydride in air:

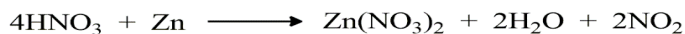


Sometimes, even the mixture of combustible substance with an oxidising agent may catch fire spontaneously. Such a mixture is known as **hypergolic mixtures**. For example, a mixture of nitric acid and phenol.

11.3.2. Toxic Products of Combustion

As a result of combustion, sometimes toxic products or by-products are generated, which are an even bigger threat to mankind and the environment. For example,

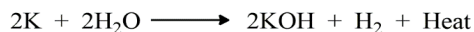
the reaction of concentrated HNO_3 with zinc metal, gives toxic NO_2 gas as a by-product.



Similarly, the combustion of carbon compounds under oxygen-deficient conditions results in the formation of highly noxious carbon monoxide. In the presence of carbon monoxide, haemoglobin in the blood forms carboxyhaemoglobin, which is not able to carry oxygen to the body tissue, and may cause serious illness or may even prove out to be fatal. Some of these by products may even act as pre-carcinogens and may yield cancer producing metabolites in the body.

11.4 REACTIVE SUBSTANCES: PHYSICAL AND CHEMICAL PROPERTIES

Substances which undergo rapid or violent reactions under certain conditions or produce toxic gases on reaction with water, acids or bases, are known as reactive substances. Substances which react violently or form potential explosive mixtures with water are also considered to be reactive in nature. For example, metals like sodium and potassium react so violently with water, that the heat produced may even ignite the metal and hydrogen.

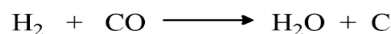
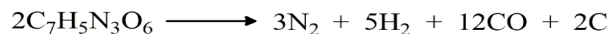


Factors on which reactivity of a substance depends upon:

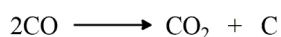
- (i) **Temperature**—Rate of reaction increases sharply with increase in temperature.
- (ii) **Heat** – Heating also increases the rate of reaction. Reactions in which the reactant needs activation to get started are affected by heating to a greater extent.
- (iii) **Physical form of reactant** – Smaller is the particle size of the reactant, higher is its reactivity. A finely divided metal reacts more explosively in comparison to a single piece of metal.
- (iv) **Degree of mixing of reactants** – Higher is the efficiency of mixing of the reactants, more explosive the reaction is.
- (v) **Degree of dilution with nonreactive media** – Dilution of the reaction mixture with a nonreactive media results in decreased rate of reaction.
- (vi) **Catalyst** – Addition of a catalyst further increases the rate of reaction.
- (vii) **Pressure** – Application of pressure on the reaction mixture increases the rate of reaction.

Compounds such as nitroglycerin, trinitrotoluene (TNT), are inherently stable but explode on using a detonating device. Trinitrotoluene (TNT) is 2,4,6-trinitrotoluene

with a chemical formula $C_6H_2(NO_2)_3CH_3$. TNT is an example of redox compound, in which both oxidising and reducing functions are present in the same molecule. It has less amount of oxygen than what is required for complete oxidation of all components, and hence has a negative balance of oxygen. It is known as an easy to handle explosive material. Upon detonation, TNT undergoes following decomposition reactions:



and



The reaction is highly exothermic in nature and the explosion has a sooty appearance due to the production of carbon. Since TNT is rich in carbon, its mixture with oxygen rich compounds can yield more energy per kg than TNT alone. During the 20th century, amatol, a mixture of TNT with ammonium nitrate was a widely used military explosive.

Similarly, even inorganic salts such as ammonium nitrate and ammonium chromate are explosive and toxic. Ammonium dichromate is also known as *Vesuvian Fire*, as it has been commonly used in demonstrations of table top volcanoes. However, now due to its carcinogenic nature, its use is discouraged. It has the exact amount of oxygen needed for complete oxidation of all its components and hence has a zero balance of oxygen. A small ignition on the pile of ammonium dichromate initiates a highly exothermic reaction.



Ammonium nitrate, though is used as a fertilizer, but gets exploded violently on coming in contact with any source of ignition. On ignition, it decomposes into nitrous oxide and water vapour, resulting in an explosion.

Know your progress II

Q.1 Discuss the significance of Lower flammability limit, Upper flammability limit, and flammability range in determining the flammability hazards of organic liquids.

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Q2. What are substances called that catch fire spontaneously in air without an ignition source?

Q3. Differentiate between flammable liquids and combustible liquids.

11.5 CORROSIVE SUBSTANCES: PHYSICAL AND CHEMICAL PROPERTIES

Substances which can dissolve metals, oxidise the surface of the metal and in general deteriorate the materials including the living tissue, are known as corrosive substances. Contact with corrosive material results in immediate death of the living cells at the site of contact. Corrosion is generally followed by the degeneration of the dead cell and this process is known as necrosis. However, an irritant material does not result in the direct death of the cell, but just damages the cell, leading to inflammations.

The corrosive substances may broadly belong to any one of the following four categories:

(i) Strong acids, (ii) strong bases, (iii) oxidants and (iv) dehydrating agents.

Naturally, the more acidic or more alkaline a substance is, the greater would be its corrosive action. The effect of the corrosive substance also depends of its physical state as shown in Table 11.3.

Table 11.3: Physical state of corrosive substances and their effects

Physical State of Corrosive substance	Effects
Solid	Substances such as phenol cause irritation and burning sensation to the skin and eyes. Inhalation of dust from corrosive solids results in irritation in the respiratory tract. Substances such as KOH, in which the dissolution process is exothermic liberates heat on dissolution in water.

Liquid	Splash of liquids such as H_2SO_4 , NaOH , adversely effects the skin, eyes and human tissues.
Gases and Vapours	Corrosive gases and vapours are also extremely hazardous and cause severe irritation and bodily injury especially to eyes and respiratory tract. Highly soluble gases such as HCl , NH_3 , cause severe irritation in nose and throat. Less soluble gases, such as SO_2 , NO_2 etc can even penetrate deep into the lungs.

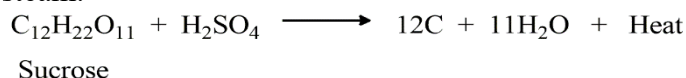
Usually, a corrosive chemical attacks human skin and denatures proteins or performs amide hydrolysis of ester hydrolysis. Amide hydrolysis results in the damage to proteins containing amide bonds, whereas lipids containing ester bonds are attacked by ester hydrolysis. Sometimes, the corrosive agent even gets involved in a chemical reaction, involving dehydration of skin and even production of heat, which in turn cause thermal / chemical burn. Most of these corrosive substances even attack the metal surfaces, causing its rapid oxidation. Some of the commonly used corrosive chemicals have been discussed below.

Hydrochloric acid

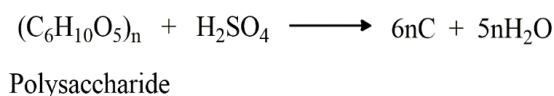
Hydrochloric acid, (HCl) at 38% concentration has a pH level of 1.1. The acid is commonly used in batteries, fireworks, leather and building materials, but is so strong that it immediately starts dissolving the skin tissues, on coming in contact to the skin. HCl gas, inhaled, can damage the respiratory tract tissues. Though it is also produced in our stomach to assist the digestive system, but in very small concentration.

Sulfuric acid

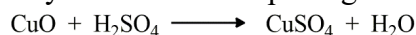
Sulphuric acid (H_2SO_4), also called as oil of vitriol, is one of the most important industrial chemicals and plays an important role in the manufacture of number of chemicals, ranging from fertilizers such as superphosphates, sulphates to dyes, paints, fabric pigments, explosives and lubricants. It has a pH of 0.5 at a concentration of 33.5%. Concentrated sulphuric acid can be used as a dehydrating and oxidising agent. It is such a powerful dehydrating property that it is able to remove water from various chemical compounds, including carbohydrates, producing carbon black, heat and steam.



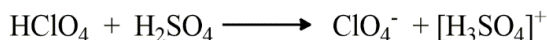
It reacts with cellulose present in paper and fabric, to give a burnt appearance, due to the formation of carbon black.



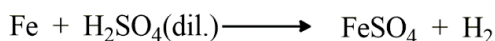
As an acid, sulphuric acid reacts with bases to give the corresponding sulphate. For example, on reaction with copper(II)oxide, it gives blue coloured copper(II) sulphate, which is commonly used for electroplating and as fungicide.



When combined with nitric acid, sulphuric acid not only act as a dehydrating agent but also as an acid, forming nitronium ion, NO_2^+ , which is used as an electrophile in nitration reaction. With super acids, such as HF and HClO_4 , it acts as a base, resulting in the formation of $[\text{H}_3\text{SO}_4]^+$.



Dilute sulphuric acid reacts with reactive metals such as Fe, Al, Zn, Ni etc., to liberate hydrogen.



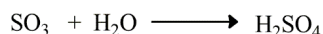
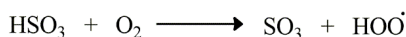
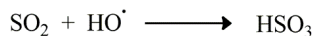
Concentrated sulphuric acid is a strong oxidising agent and reacts with metal (even with non-active metals such as Cu), to liberate sulphur dioxide and water.



However, lead and tungsten are resistant to concentrated sulphuric acid. Hot concentrated sulphuric acid oxidises non-metals such as carbon.



In the stratosphere, sulphuric acid is formed by the oxidation of volcanic sulphur dioxide by the hydroxyl radical.



Sulphuric acid reaches supersaturation in the stratosphere and can nucleate aerosol particles by providing a surface for the growth of aerosols via condensation and coagulation. This results in the formation of stratospheric aerosol layer. Sulphuric acid is also formed in the upper atmosphere of Venus by the Sun's photochemical action on carbon, sulphur dioxide and water vapour.

It also readily absorbs water vapour from the air and hence is also hygroscopic in nature. The reaction between sulphuric acid and water is highly exothermic in nature. It causes severe **skin burns**, even secondary thermal burns, irritation in the nose and **throat** and cause difficulties in breathing if inhaled. Preparation of diluted sulphuric acid is difficult from its concentrated counterpart due to the heat released in its dilution process. To avoid splattering, the concentrated acid is always added to water with simultaneous cooling

Apart from this, it results in phenomena, such as acid rain, thus adversely affecting the environment.

Nitric Acid

Like sulphuric acid, nitric acid (HNO_3) is a powerful oxidising agent and a highly corrosive mineral acid. Commercially available nitric acid is colourless and is an azeotrope in water with a concentration of 68% in water. Fuming nitric acid contains more than 86% of the acid, with high concentration of nitrogen dioxide.

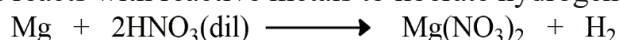
The pure compound is colourless, but older samples acquire yellow colour due to its decomposition into oxides of nitrogen and water. Thus, it is stored in brown glass bottles.



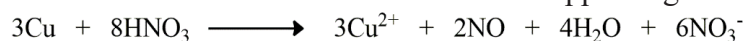
With sulphuric acid, it acts as a base, resulting in the production of nitronium ion which is an active reagent in aromatic nitration reaction.



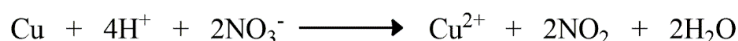
Dilute nitric acid reacts with reactive metals to liberate hydrogen.



Dilute nitric acid reacts with non-active metals such as copper to give nitric oxide.

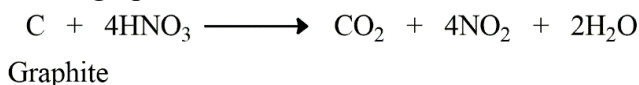


The nitric oxide produced may react with atmospheric oxygen to give brown fumes of nitrogen dioxide. However, with concentrated nitric acid, copper directly produces brown fumes of nitrogen dioxide.



Most of the metals upon reaction with nitric acid form respective nitrates. Some metalloids and metals are oxidized to the respective oxides, for example Sn forms SnO_2 , Ti forms TiO_2 . The precious metals such as Au, Pt do not react with nitric acid. However, on combination with HCl, it forms aqua regia.

Nitric acid oxidises the non-metals, such as C (graphite), I_2 , to their highest oxidation state. It can react with graphite but not with diamond.



If used in high concentrations, nitric acid may even cause severe burns, ulceration and dermatitis. It reacts with protein in skin tissues to form xanthoproteic acid, resulting in the yellow staining on the skin.

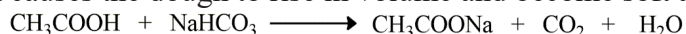
It is also an industrially important compound, used in production of several chemicals, such as ammonium nitrate (fertilizer), plastics, dyes and TNT. It is also used in medical industry, mainly to remove warts. It is used in various forms as the oxidizer in liquid-fuelled rockets. Nitric acid is also used as a chemical doping agent for organic semiconductors and in the purification of carbon nanotubes (raw).

Chromic Acid

Chromic acid (H_2CrO_4) is a strong oxidising agent and is mainly used in the manufacturing of coloured glass and chromium plating. Solution of chromic acid in sulphuric acid is a powerful oxidising agent and hence is used to clean laboratory glassware. Due to its ability to brighten raw brass, it was widely used in the instrument repair industry. But since it adversely affects human health and the environment, its general use is now being discouraged. Like other acids, it also causes severe burns on the skin.

Acetic acid

Acetic acid (CH_3COOH), if undiluted, is known as glacial acetic acid. 4% acetic acid solution in water is commonly known as vinegar. It is a weak monoprotic acid. Acetic acid has a pH of 2.4 at 5% dilution and is extensively used in food industry. In bakeries, baking soda and vinegar combination results in the production of carbon dioxide, which causes the dough to rise in volume and become soft and fluffy.



It is widely used in the production of vinyl acetate monomer, which is further polymerised to polyvinyl acetate or other polymers which are important component of paints and adhesives. It is equally important in the medical industry for the treatment of ear infections and even a disease as big as cancer. Though a mild acid, yet it can be considerably harmful to human health and the environment, if used in concentrated amounts. Prolonged exposure to the vapours of acetic acid can produce some irritation of eyes, nose and throat.

Hydrofluoric acid

Hydrofluoric acid, HF, is highly corrosive acid, which not only attacks glass, concrete and several metals but also the natural carbonaceous materials such as wood, leather etc. It is widely used in semiconductor industry for cleaning silicon wafers and is also used for etching glass by treatment with silicon dioxide, forming gaseous or water-soluble silicon fluorides. Since it reacts with glass to form fluorosilicate ions, it is stored in copper bottles, instead of glass bottles.



5% to 9 % hydrofluoric acid gel is commonly used to etch the ceramic restorations and hence is an important component of household rust stain remover in car washes.

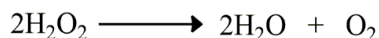
Exposure of concentrated acid causes severe skin burn; however, dilute solution of hydrofluoric acid deeply penetrates into the skin before dissociating, thus causing delayed injury. It is however used to make most fluorine containing compounds, such as antidepressants and materials such as Teflon.

Hydrogen Peroxide

Hydrogen peroxide, H_2O_2 , is used as a propellant in rocketry, as an oxidiser, antiseptic and bleaching agent. A mixture solution of hydrogen peroxide and sulphuric acid is known as Piranha solution, and is used for cleaning the laboratory glassware. In acidic medium, hydrogen peroxide acts as an oxidising agent, whereas in basic

medium it is a good reducing agent. It is used in certain waste water treatment processes, such as Fenton's process, to oxidise organic pollutants.

It is unstable and decomposes in the presence of sunlight, due to which it is stored with a stabilizer, in a dark coloured bottle, in a weakly acidic solution.



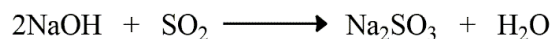
Though, as a result of biochemical processes, it is formed as a short-lived product in humans and other animals, it is toxic to cells. In high concentrations, it is an aggressive oxidizer and results in corrosion of several materials, including human skin. It results in severe burns even if present in low concentrations. It reacts violently with reducing agents.

Ammonium hydroxide

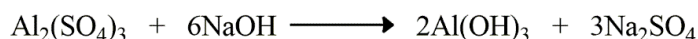
Ammonium hydroxide (NH_4OH) is a weak base, with a pH of 10.09. It is an industrially important chemical, used as a glass cleaning agent and as a refrigerant. It is an extensively used chemical in the production of soaps, ceramics, pharmaceuticals, inks and explosives. At times it is even used as an additive in food items to maintain the correct level of acidity. However, it causes extensive damage to the tissues, if exposed to the skin.

Sodium hydroxide

Strong bases, such as sodium or potassium hydroxide find extensive industrial applications, mainly in paper, detergent and soap industry. Sodium hydroxide, being a base neutralises the acids and acidic oxides, and hence is used to scrub the harmful acidic gases like SO_2 , etc.



NaOH on reaction with aluminium sulphate produces a gelatinous flocculant, $\text{Al}(\text{OH})_3$, which in turn is used to filter out particulate matter in water treatment.

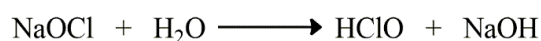


They can corrode metals such as lead, aluminium and can cause severe burns on coming in contact with skin.

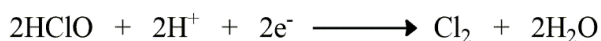
Sodium Hypochlorite

Sodium hypochlorite (NaOCl) is a base with a pH of close to 13 at 10-15% concentration. It is a very useful compound extensively used as a pesticide, as an antiseptic, as a bleach as well as disinfectant. However, it is corrosive in nature and may produce toxic fumes when mixed with other cleaning products. 1% freshly prepared Sodium hypochlorite solution is extensively used

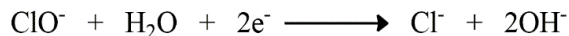
Solutions of sodium hypochlorite are basic in nature, as it undergoes hydrolysis to form sodium hydroxide.



Hypochlorous acid thus formed is a strong oxidising agent and, in the process, gets reduced to chlorine gas.



The hypochlorite ion, however, is a weaker oxidizing agent that is usually reduced to the chloride ion

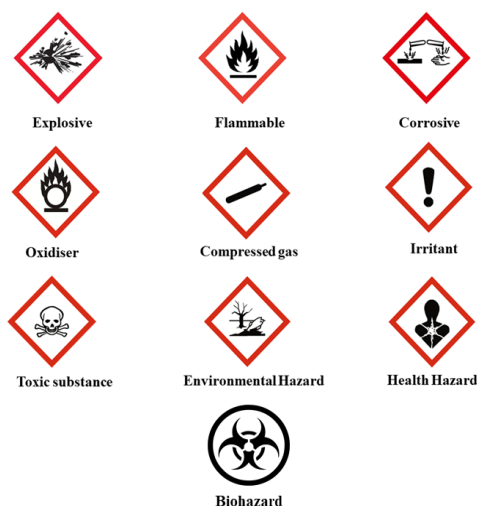


It is this oxidizing (bleaching and bactericidal) power that renders sodium hypochlorite useful as a disinfectant for mopping and spraying in these difficult times of COVID 19.

Apart from some of the compound discussed above, several other compounds, such as Interhalogens (example: ClF , BrF_3), halogen oxides (such as OF_2 , Cl_2O , Cl_2O_7), elemental fluorine, chlorine, bromine (F_2 , Cl_2 , Br_2) etc. demonstrate their corrosive properties. Such compounds are corrosive irritants that not only acidify, but also oxidize and dehydrate tissue cells, at times are corrosive to mucous membranes.

Safe Storage

Mineral acids, including hydrochloric, nitric, sulfuric, and perchloric acid can be stored in non-metallic special cabinets designed for them. These cabinets have acid resistant coating. Volatile acids, such as fuming nitric acid, should be stored in a vented cabinet, such as the fume hood, especially after opening their bottle. Organic acids such as acetic acid should be stored separately from mineral acids. Chemicals which can form explosive salts by reacting with metals, or by itself should be stored carefully and separately. Depending upon the corrosive / toxic/ oxidising/explosive nature, certain symbols have been devised and may be put on the bottles of the said chemical (Scheme 1).



Scheme 1. Hazard symbols

11.6 TOXIC SUBSTANCES: PHYSICAL AND

Toxic substances are the chemicals which cause harm to human health on entering into the body. Once any toxic substance is released into the environment, it gets absorbed with water and nutrients, finally reaching the leaves and the stem and entering the human body. Animals, including humans, take up environmental toxic substances by eating (ingestion), drinking, breathing (inhalation), absorbing them through the skin (skin absorption), or by direct transmission from mother to egg or foetus. There are thousands and thousands of natural and artificial toxic substances, found in solid, liquid or gaseous forms. These substances, commonly known as toxins, damage the organ or at times the tissues, by interfering with their specific functions. At times, it even causes cells to mutate, usually resulting in serious injury or harm to human health and may even be fatal at times. Most of us encounter a number of these substances inside our homes only, almost on a daily basis. Everyday products like household cleaning chemicals, medicines, pesticides and cosmetics. Even the vehicular emission contains toxic substances.

In order to minimise the risks that these toxic substances pose to human health, it is important to first understand their properties and work in a direction to minimise the risk.

11.6.1. Type of toxic substances

We are exposed to several toxic substances, both anthropogenic and natural, in our homes as well as the workplace, almost on a daily basis. Anthropogenic materials that are produced in large quantities for industrial and domestic use are highly toxic and dangerous, because most of them are organic and thus bond readily with body tissues and also their production and distribution occur rapidly but is poorly controlled. Moreover, hundreds of chemicals and substances are developed every year, only few are tested for their toxicity and at times even their disposal is not monitored properly.

Toxins such as heavy metals, toxic solvents, VOCs and high-risk pesticides act as neurological, behavioural, developmental and reproductive toxins. Chlorinated hydrocarbons, including DDT (dichlorobiphenyl trichloroethane) was a commonly used pesticide in agriculture and other chemical industries. However, due to the damage that it was causing to the environment, and its high coefficient of bioaccumulation, its use has now been banned. PCB (polychlorinated biphenyl), another anthropogenic fire-resistant toxic substance, was initially used as a lubricant and heat-transfer fluid, has again been banned due to its toxic nature and its high resistance to decomposition in water bodies and soil. A number of petroleum products, used in oil refining, plastics manufacturing, industrial solvents, and household cleaning agents are also highly toxic in nature. Methylene chloride is a common industrial solvent, mainly used in the paint industry as a thinner or paint stripper. Exposure to methylene chloride may lead to irritation in eyes and skin, headache, nausea, dizziness. It may even harm the central nervous system, affecting the body coordination. High exposure to this toxic chemical may even prove out to be fatal. Isopropyl alcohol is a commonly used disinfectant, widely used in hospitals, cleanrooms, pharmaceutical companies, laboratories and medical

device manufacturing units. Generally, 70% isopropyl alcohol acts rapidly against bacteria, viruses and fungi because water present in it plays a key role in denaturing protein. The alcohol solution penetrates the cell wall more effectively, coagulating the protein inside, finally proving to be fatal for the microorganism. Branded hand sanitizer contains 70-90% isopropyl alcohol. It may be further noted that if the alcohol concentration drops below 50%, the usefulness of disinfectant drops drastically. Similar to methylene chloride, exposure to the vapours of isopropyl alcohol leads to irritation in eyes and respiratory tract. Hydrogen peroxide is commonly used as a bleaching agent, oxidiser and antiseptic, but at the same time it is also toxic in nature. Inhalation of vapours of hydrogen peroxide, causes severe pulmonary irritation. If ingested, it may induce vomiting, stomach ache and gastric distension. It may be fatal, if ingested in high concentration. Heavy metals such as mercury, lead, cadmium, chromium etc., are highly toxic, as they are mainly non-biodegradable and have a high coefficient of bioaccumulation. Similarly, radioactive substances such as uranium and plutonium are also highly toxic agents, resulting in both chemical and radiological toxicity. The toxicity is mainly caused by breathing air containing uranium dust, or by eating substances containing uranium. Hence, the air enters the bloodstream, leading to acute kidney failure or death. Since all isotopes of uranium emit alpha particles, the workers handling and processing uranium, have a very high probability of developing radiation-induced cancer.

Apart from synthetic toxins, natural toxic materials also occur everywhere and most of them are extremely toxic in nature. For example, mushrooms and moulds contain innumerable toxic substances that can be lethal to human beings even in minute quantities. Similarly, castor beans contain a highly toxic substance, ricin. Certain vegetables such as potatoes, peppers and tomatoes contain alkaloid solanine, which also demonstrate their toxic effects at times. Except for toxic minerals and heavy metals released by mining and agriculture, most people rarely worry much about naturally occurring toxic substances.

11.6.2. Risk of using toxic substances

The toxicity of these substances depends upon several factors, such as the way the toxic substance moves through the environment and finally enter into the body, the way the toxins move through our bodies, dosage of toxin in our body, solubility of toxic substances in water as well as in fatty tissues and its molecular shape.

- (a) Chemicals entering into the body through skin absorption – Organic solvents and organic pesticides are absorbed by the skin and enter the bloodstream.
- (b) Chemicals entering into the body through inhalation – Inhalation is the most common form of exposure to toxic substances and occurs on coming into contact with airborne toxic substances. Intoxication caused by inhalation of such substances may lead to both acute and chronic effects. Acute effects, such as irritation in the throat, lungs and lining of the nose are experienced immediately upon exposure to toxic substances. Diseases like lung infection and cancer result from long term chronic effects which are experienced months and years after the initial exposure to these chemicals. For example,

exposure to benzene causes cancer, which can remain dormant for several years and is only detected at later stages.

- (c) Chemicals entering into the body through ingestion – Ingestion is the least common form of exposure, which mainly occurs when people eat, drink or smoke immediately after handling toxic substances, without taking any precautions.
- (d) Metabolism of Toxic substances in the body- Another important factor which determines the toxicity of a substance is the way the substance moves through the environment and finally through the body. Most of the minerals and chemicals move effectively in dissolved form, either in water or in oil-based liquid. Compounds of mineral substances such as Cu, Zn, Na, K, Se, Pb and Cd, dissolve best in water. Organic compounds, including benzene, chlorinated hydrocarbons, chloroform and others dissolve readily in oily solvents and fatty tissues of our body. Most of these substances, mainly through agriculture, or mining activities or due to natural spill, move with the runoff into groundwater or surface water systems and are taken up by plants and animals. Organic chemicals also move into the environment, from where animals ingest or inhale these compounds to store and distribute them in their bodies. Once a toxic substance enters into the body, all the fat-soluble compounds are taken up and stored by fatty tissue of lipids in our cells. Proteins and enzymes in our blood or bone or organ tissues, recognise and form bonds with those toxic molecules whose shape fits into them. Most of the chemicals on entering the body are metabolized to result into some other compound, irrespective of their original nature-toxic or innocuous. When a toxic substance enters the body, it may be metabolized to a less or a more toxic compound. As a result, it can cause a poisoning effect in the body. If the compound gets transformed to a more toxic substance and the rate of this metabolism is high then the poisoning effect in the body will be very quick and vice versa. There is another class of toxic substances which do not have any metabolic activity in the body.

The metabolism of toxic substances, as with other substances, is carried out with enzymes in two phases. The first phase of enzymatic reactions includes reductions, oxidations and hydrolyses introducing groups like $-OH$, $-NH_2$, $COOH$ into the foreign substance. These groups enable the second phase of reactions referred to as syntheses. If the foreign substance possesses these reactive groups originally, it enters into phase II reactions directly. Some foreign compounds would complete their metabolism with phase I reactions, because their structure or properties do not allow further conjugation.

Benzene, as a foreign substance, is a good example to illustrate the two-phase metabolism inside the human body. In its metabolism, benzene undergoes oxidation to phenol, which enters into second phase reactions, to produce phenyl glucuronide and phenyl hydrogen sulphate. A reactive intermediate in the phase I reaction is benzene epoxide, which has toxic effects. If phenol is taken in directly, only phase II reactions occur. Cyanide, when administered,

undergoes phase II reaction to form relatively non-toxic thiocyanate. Ethanol gets oxidized via phase I reactions to mainly form carbon dioxide, with acetaldehyde and acetic acid as intermediates in this pathway. It is acetic acid which, despite having the functional group suitable for conjugation, gets completely oxidized to carbon dioxide by enzymatic action. These simpler compounds, formed as a result of metabolism are later on excreted out either in urine or faeces or saliva or sweat.

However, certain persistent toxins, such as DDT, are not metabolized easily and hence, continue to accumulate in the tissues, proving to be fatal, if their toxic dosages are reached. The body parts that are most easily damaged by exposure to such toxins are those areas where cells and tissues are reproducing and growing, such as brain cells, bones, innings of lungs and intestine.

Dosage is another very important factor that governs the toxicity of a substance. All chemical substances can become toxic in high concentration but even a highly toxic substance may demonstrate no toxicity at very low concentrations. For example, consumption of very large dose of common salt (NaCl) or baking powder (NaHCO_3), will have severe effect on the human body and at times may even prove out to be fatal, but the consumption of these chemicals, especially NaCl in moderate doses is essential for the human body. Similarly, a trace element like selenium is essential for the body in extremely minute quantities, as it helps in making a special protein, called antioxidant enzyme, which plays an important role in preventing cell damage. But, high concentrations of selenium have been observed to cause severe birth defects and are carcinogenic as well.

Green Chemistry aims to eliminate the usage and generation of hazardous and toxic substances by designing better manufacturing processes for the chemical products. Thus, green chemistry has the potential to not only protect the environment but also to benefit the mankind and society by minimising or even completely eliminating the toxic and hazardous chemicals.

Know your Progress III

Q.1 Match the following kinds of hazardous substances on the left with a specific example of each from the right, below:

1.Explosives	(a) Uranium
2.Compressed gases	(b) White phosphorus
3.Radioactive materials	(c) CNG
4.Flammable solids	(d) Sulphuric acid, sodium hydroxide
5.Oxidizing materials	(e) Nitroglycerin
6.Corrosive materials	(f) Hydrogen peroxide

Q2. How is stratospheric aerosol layer formed?

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Q3. Why is HF stored in copper bottles and not glass bottles?

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Q4. Why is sodium hypochlorite used as a disinfectant?

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Q5. Explain the dehydrating and oxidising properties of sulphuric acid.

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Q6. Write a short note on naturally occurring toxic substances.

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Q7. Match the corrosive substance from the column on the left, below, with one of its major properties from the right column:

1. Alkali metal hydroxides	(a) Reacts with protein in tissue to form yellow xanthoproteic acid
2. Hydrogen peroxide	(b) Strong bases
3. Hydrofluoric acid, HF	(c) Oxidizer
4. Nitric acid, HNO ₃	(d) Dissolves glass

11.7 LET'S SUM UP

Any substance, which causes irreparable damage to the environment or human health, due to its corrosive, reactive, toxic and infectious characteristics is a hazardous substance. Industrial activities, medical sector, commercial centres, agriculture and agro-industries, household and the informal sector, small competitive and labour-intensive businesses are the major source of hazardous waste. This chapter deals with an insight to various categories of hazardous substances, such as combustible, corrosive, reactive and toxic, which are released into the environment, causing an irreparable damage to the environment and human health.

11.8 GLOSSARY

Hazardous waste	Any substance that has substantial or potential threats to public health or the environment or materials.
Flash point	It is the lowest temperature at which a liquid can give off its vapor to form an ignitable mixture in air near the surface of the liquid. The lower the flash point, the easier it is to ignite the material.
Flammability Limit	It is the range in which a flammable substance can produce a fire or explosion when an ignition source is present. It applies generally to vapors.
Corrosive substance	Corrosive substances include those with a low (< pH 2.5) and high (pH >12.5) pH value. They can cause irreparable damage to skin and eyes
Green Chemistry	Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

11.9 REFERENCES AND SUGGESTED FURTHER READINGS

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4. Eugene Meyer, *Chemistry of Hazardous Materials*, Sixth Edition, Pearson, 2014.
- P. A. Carson, *Hazardous Chemicals Handbook*, Second Edition, Elsevier, 2002.

Know your Progress I

Ans 1. Hazardous waste has been categorised on the basis of their characteristics and on the basis of the process generating the waste.

Ans 2. Ignitable substances- Substances which catch fire easily may be classified as ignitable hazardous substances. Such substances may further be divided into two categories: **Flammable Liquids** and **Flammable Solids**.

Ans 3. F-type waste - such waste is known as non-specific source waste and is produced by multiple industries.

K-type wastes- Such waste is generated by specific industrial processes.

Ans 4. P-type acute hazardous wastes.

Know your Progress II

Ans 1. To study combustible substances, it is important to study the concept of flammability limit and flammability range. **Lower flammability limit (LFL)** is that value of vapour: air ratio below which ignition cannot occur, due to insufficient fuel. **Upper flammability limit (UFL)** is that value of vapour: air ratio above which ignition cannot occur, due to insufficient air. The difference between LFL and UFL at a specified temperature is known as **Flammability range**.

Ans 2. Such substances are known as pyrophoric substances. Spontaneous ignition may occur due to the presence of moisture in air or even due to bacterial fermentation.

Ans 3. Flammable Liquid-Any liquid having a flash point less than 60.5 °C is considered as flammable liquid.

Combustible liquid- All those liquids which have a flash point between 60.5 °C and 93.3 °C comes under this category of combustible substances.

Know your Progress III

Ans 1. 1-e, 2 -c, 3- a, 4 -b, 5-f, 6-d

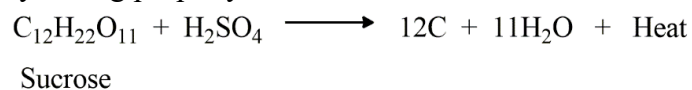
Ans 2. Sulphuric acid reaches supersaturation in the stratosphere and can nucleate aerosol particles by providing a surface for the growth of aerosols via condensation and coagulation. This results in the formation of stratospheric aerosol layer.

Ans 3. Since HF reacts with glass to form fluorosilicate ions, it is stored in copper bottles, instead of glass bottles.



Ans 4. Sodium hypochlorite exhibits this oxidizing (bleaching and bactericidal) power that renders it useful as a disinfectant for mopping and spraying.

Ans 5. (a) Dehydrating property



(b) Oxidising property



Ans 6. Natural toxic materials such as mushrooms and moulds contain innumerable toxic substances that can be lethal to human beings even in minute quantities. Similarly, castor beans contain a highly toxic substance, ricin. Certain vegetables such as potatoes, peppers and tomatoes contain alkaloid solanine, which also demonstrate their toxic effects at times. Except for toxic minerals and heavy metals released by mining and agriculture, most people rarely worry much about naturally occurring toxic substances.

Ans 7. 1- b, 2- c, 3- d 4-a.

BLOCK 4

**Analytical Techniques
in Environmental
Chemistry**

UNIT 12 : BASIC ANALYTICAL TECHNIQUES

Structure

- 12.0 Introduction
- 12.1 Objectives
- 12.2 Analytical Techniques: Importance
- 12.3 Classification of Analytical Techniques
 - 12.3.1 Chemical Methods of Analysis
 - 12.3.2 Electrical Methods of Analysis
 - 12.3.3 Optical Methods of Analysis
 - 12.3.4 Nuclear Methods
 - 12.3.5 Thermal Methods of Analysis
- 12.4 Criteria for Evaluating
- 12.5 Evaluation of Analytical Data
 - 12.5.1 Errors and Detection of Errors
 - 12.5.2 Accuracy and Precision
- 12.6 Reporting of Results
 - 12.6.1 Chemical Expression of Results
 - 12.6.2 Numerical Expression of Results
 - 12.6.3 Significant Figures
- 12.7 Let Us Sum Up
- 12.8 Terminal Questions

12.0 INTRODUCTION

The environmental scientists are generally concerned with the identification, characterization and quantification of materials present in the environment, both polluting and non-polluting. In other words, we can say that the important task for an environmental analyst in this context is finding out what and how much of the materials present in the environment. You might know that this task is accomplished by chemical and instrumental analysis done using a number of analytical techniques. In view of the objective of learning the use and significance of analytical techniques generally related to the environment, in the first unit of this course you will be introduced to the various types of analytical techniques available and used by the analysts. The basic principles involved in the process of analysis will be explained. The unit also deals with the criteria for evaluating that includes sampling and measurement. A brief about evaluation of the analytical data would be given along with an introduction to the concepts of errors, accuracy, precision and significant figures. The unit ends with the ways of reporting the results of analysis.

12.1 OBJECTIVES

After studying this unit, you should be able to:

- enlist and explain the analytical techniques used by the environmental scientists for the analysis of polluting and non-polluting components,
- describe in brief the principles involved in the analytical techniques,
- explain the procedure of sampling of environmental materials,
- describe the method of measurement during environmental analysis,
- explain the concept of errors, accuracy, precision and significant figures,
- differentiate between accuracy and precision, and
- state the procedure of reporting the analytical results.

12.2 ANALYTICAL TECHNIQUES: IMPORTANCE

You would agree with the fact that chemicals are part and parcel of our day-to-day life. These include the food we eat, the clothes we wear, the medicines we take, the radiations produced and the wide variety of facilities in the form of latest machines that we use. All of us know that the use of chemicals in excess and without proper knowledge has been responsible for the contamination of our environment in various ways. This has led to various types of pollution and all of us are the victims in some or the other ways. The need of the hour is to assess the levels of pollution and take precautionary measures to combat it.

Sample: A sample is the part of the material, which is examined during analysis.

An environmental analyst analyses the type of chemical and the amount of the chemical present as a pollutant or otherwise in the given **sample**. The constituents to be analysed may be elements, ions, radicals, functional groups or compounds. The methods or the techniques for chemical analysis are developed by analytical scientists or analysts to accomplish this task and are called **analytical techniques**. In the process of developing these techniques the analysts try to use the principles from many fields of science viz. chemistry, physics, biology, biochemistry, geology, engineering and computers, etc. The development of new and improved analytical techniques permits separation, detection, structure elucidation and quantification of much lower levels of chemical species, multi-component analysis and a much short duration for analysis.

A substance can be determined by a number of techniques, and the analytical chemist has to select the most advantageous technique available in the laboratory. For choosing a suitable technique, the analyst has to keep in mind the following objectives:

- **Type** of samples to be analysed
- **Information** sought
- **Purpose** of the analysis
- **Accuracy, sensitivity and selectivity** of the instrument

The performance of an analysis will depend on the following:

- **Experience** of the analyst

- **Availability** of the equipment
- **Preparation** of the sample for analysis
- **Time** and **Cost** involved in the analysis

While choosing an instrumental technique one should be aware of the fact that most instrumental methods are relative methods. Therefore, these must be calibrated with standards. Usually an analytical calibration curve of instrument response versus concentration or amount of the substance is prepared prior to analysis of unknowns.

Let us understand the way the analytical techniques are classified.

12.3 CLASSIFICATION OF ANALYTICAL TECHNIQUES

A method to be called as an analytical technique should be based on the measurement of a property, which is related to either the nature or the amount of the substance under examination. The property, which depends on the nature of the substance is helpful in **qualitative** analysis, whereas the property which depends on the amount of the substance is useful in **quantitative** analysis. You will read about both the types in the subsections coming ahead.

As mentioned above the analytical methods depend on the measurement of some physical property. Various physical properties, which are characteristics of a particular substance or its constituent, can be made the basis of an analytical technique. In the broader sense the analytical techniques can be classified on the basis of type of properties in the following way.

- i) Chemical methods of analysis
- ii) Electrical methods of analysis
- iii) Optical methods of analysis
- iv) Nuclear radiation methods of analysis
- v) Thermal methods of analysis
- vi) Separation methods

These methods can further be classified into different techniques depending on the measurement of a characteristic property based on either the nature or the amount of the desired constituent of the sample. We will briefly outline the principles involved in the important and relevant methods under each type in the following subsections. For the sake of an overview the classification is given in Fig. 1.1. The basic principle of the techniques is given in brief thereafter as you would be studying the details in the other units of this course dealing with the specific technique.

Potentiometry:
derived from the
word “potential”, the
half cell potential
(electrode potential)
obtained by measuring
voltage across an
electrochemical cell
with the help of a
standard electrode.

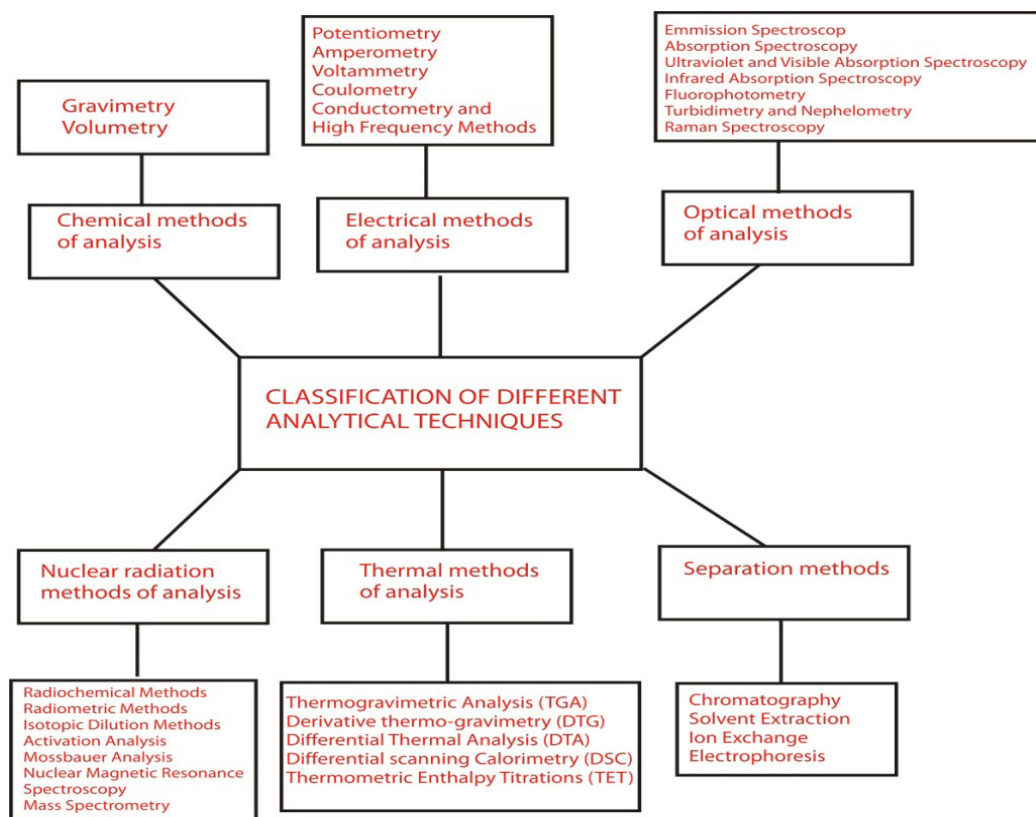


Fig. 1.1: An overview of Classification of Analytical Techniques

1.3.1 Chemical Methods of Analysis

The chemical methods of analysis belong to the broad type of analysis called the quantitative analysis. As mentioned earlier, these methods are based on the measurement of quantity. In one case it is the mass of the substance while in the other the volume is taken into consideration. The corresponding methods are known as **gravimetry** and **volumetry**. Both of these being developed at early stages are also known as **classical methods of analysis**.

i) Gravimetry

Gravimetry is an accurate macro-analysis procedure which mainly depends upon precipitation of an ionic or molecular substance on the basis of a chemical reaction. In gravimetric analysis, the component to be estimated is converted into an insoluble precipitate, which is filtered, dried, ignited and weighed accurately. Knowing the stoichiometry of the chemical reaction involved in precipitation the mass of the precipitate is used to determine the amount of the component in the substance. At undergraduate level you might have estimated barium as barium sulphate following gravimetric analysis.

ii) Volumetry

The amount of the analyte can also be determined by measurement of the **volume**. The method based on accurate measurement of volume of a reagent solution of accurately known concentration, taken for a reaction is known as **volumetric analysis**. The measurement of volume saves time to a considerable extent. The greater speed of volumetric analysis is an important advantage over gravimetry.

The volumetric analysis is characterized by a titration; hence the method is also known as **titrimetry**.

You will be learning these chemical techniques while performing the experiments included in the course.

1.3.2 Electrical Methods of Analysis

An electrical method of analysis also known as electroanalytical method can be defined as one, in which an electrochemical property of a solution is measured. The electrical quantities, such as, potential, current, quantity of current, resistance and dielectric constant are considered under this class. These methods have been categorised into following briefly explained five types.

Analytical method based on the measurement of potential difference across an electrochemical cell is called **potentiometry**. The result of the analysis can be computed directly from the voltage of the cell, or the equivalence point of a titration known as **potentiometric titration**. In potentiometric titrations we discuss redox titration curves based on half-cell potentials.

A special class of potentiometry where the potential of an indicator electrode is measured as a function of hydrogen ion concentration is called **pH metry**. By suitably modifying the common voltmeter to high impedance mV meter and usually making use of a glass electrode as a hydrogen ion indicator electrode suitable pHmeters can be designed to measure pH instantaneously.

In voltammetry current is measured at varied potentials.

Amperometry involves current measurements. The term amperometry is derived from the word “ampere” which is the unit of current. Amperometry methods are generally applied to the detection of equivalence point of titration and method is known as **amperometric titration**.

In amperometry the current is measured at a fixed potential.

i) Voltammetry

In voltammetry an electroactive species is consumed (oxidized or reduced) only at the surface layer of the indicator electrode in an electrolytic cell. The resulting current, due to electron transfer process, is measured as a function of applied potential. The current versus potential curves are plotted. In voltammetry we study the relationship between the current and electrode potential and its application to chemical analysis.

In coulometry the current is used to oxidize or reduce only the analyte.

ii) Coulometry

Analytical methods based on the measurement of the quantity of electricity are designated by the term **coulometry**. The term is derived from “coulomb”, which is one of the units used for quantity of current. A fundamental requirement of all coulometric methods is that the species determined interacts with 100% current efficiency.

iii) Conductometry

The measurement of conductance (the reciprocal of the resistance) can sometimes be useful in chemical analysis. Methods based on electrical conductance measurements are grouped under the term **conductometry**. The analysis can be computed directly

Turbidimetry and **nephelometry** frequently give erratic results, therefore these are applied only when the results need not to be very accurate and other precise methods are not available.

from conductance measurements or by the determination of equivalence point of titrations (**conductometric titrations**).

1.3.3 Optical Methods of Analysis

The optical methods are called as spectroscopic methods of analysis. These are based on the interaction of electromagnetic radiation (emr) with the quantised energy states of the matter. Here we study the measurement of a quantity based on emission, absorption, scattering or change in some property of electromagnetic radiation depending on the nature or the amount of the constituents of the sample. The classification may be based on either the type of effect (emission, absorption or scattering) or the type of the emr (x-ray, uv-vis, IR etc.) used. The important spectroscopic methods are mentioned below.

i) Emission Spectroscopy

These methods depend on the electromagnetic radiation produced when the analyte is excited by thermal, electrical or radiant energy. Each element has a characteristic emission spectrum, this is applied to qualitative analysis. Quantitative determinations are also possible, as during the burning of the sample under controlled conditions the energy emitted for a given spectral line of an element is proportional to the number of atoms that are excited and consequently to the concentration of element in the sample.

ii) Absorption Spectrometry

This method is based on the measurement of the absorption of electromagnetic radiation by matter. Absorption refers to a process by which a chemical species in a transparent medium selectively absorbs the photons of certain electromagnetic radiation. The absorption varies with the wavelength of incident radiation. Absorbance is easily measured in each spectral region and is of great utility in analytical studies.

iii) Ultraviolet and Visible Absorption Spectroscopy

Analytical method, which involves the measurement of absorption of ultraviolet and visible radiation (wavelength range from 180 to 780 nm) by an atomic, ionic or molecular species, is known as **ultraviolet** and **visible** spectroscopic method (UV-VIS). UV and visible spectroscopy involve transitions between electronic levels of absorbing chemical species. These methods find application in qualitative as well as quantitative analysis.

iv) Infrared Absorption Spectroscopy

Infrared absorption spectroscopy (IR) involves the absorption of infrared radiation (wavelength range from 0.78 to 1000 μm) depending on increasing the energy of vibration or rotation associated with a covalent bond, provided that such an increase results in a change in the dipole moment of the molecule. IR spectroscopy finds widespread application in qualitative and quantitative analyses. However, its most important use has been for the functional group identification of organic compounds.

v) Fluorophotometry

The energy of the photons of incident radiation absorbed and changes the absorbing species to excited state. Certain chemical substances (known as photoluminescent) after excitation can re-emit radiation. Re-emission of radiation can be immediately ($< 10^{-8}$ sec) after the absorption and is known as **fluorescence**. The fluorescence intensity is practically proportional to the concentration of fluorescent substance. The measurement of the intensity of fluorescence serves useful analytical purposes and the technique is known as **fluorophotometry**.

When re-emission of radiation takes longer time (minutes, hours or days) the phenomenon is known as **phosphorescence** and the related technique as **phosphorimetry**.

vi) Turbidimetry and Nephelometry

Analytical methods where determinations are made by measuring opacity of suspension of small particles with the help of measuring intensity of transmitted light is known as **turbidimetry**.

The analytical method, which is based upon the measurement of intensity of light scattered by a suspension of small particles, is designated as **nephelometry**.

vii) Raman Spectroscopy

Raman spectroscopy involves the scattering of electromagnetic radiation by a liquid (solution) following **Raman effect** (scattering with change of wavelength). Raman and infrared techniques concern vibrational energy change and they are complimentary to each other. An important advantage of Raman spectra over IR spectra lies in the fact that water does not interfere in Raman spectroscopy and aqueous solutions can be handled very well.

Some other optical methods, namely, flame photometry, refractometry and polarimetry find applications in analytical laboratory but are not considered due to their less importance.

1.3.4 Nuclear Methods

These methods can provide analytical information based on nuclear properties. Some of the types of the nuclear methods are given below.

- i) Radiochemical Methods
- ii) Mossbauer Spectroscopy
- iii) Nuclear Magnetic Resonance Spectroscopy
- iv) Mass Spectrometry

Table 1.1 lists these methods along with the property measured and the mechanism involved.

Table 1.1: Nuclear methods of analysis with the property measured and the mechanism involved

S.N	Name of the method	Property measured	Mechanism involved
1.	Radiochemical methods	Radioactivity	Radioactive disintegration of radioisotopes can be measured with high sensitivity and specificity.
2.	Mossbauer spectroscopy	Resonance absorption of γ -rays	Resonance fluorescence of γ -rays and involves intranuclear energy levels.
3.	Nuclear magnetic resonance spectroscopy	Position of signals (chemical shift) and their intensity in NMR spectrum	Interaction of quantized nuclear spin with an applied magnetic field
4.	Mass spectrometry	Position and intensity of signals of mass spectrum	Mass to charge ratio of ionized atoms or molecules

1.3.5 Thermal Methods of Analysis

In thermal methods of analysis some property of the system is measured as a function of temperature. In some of these methods the temperature is used as an independent variable while in some others as a dependent variable say time. The recorded curves are helpful in interpreting the thermal behaviour of the sample.

Thermal methods are classed into nearly a dozen varieties. Out of these some commonly used methods are:

- i) Thermogravimetric Analysis (TGA)
- ii) Derivative Thermogravimetry (DTG)
- iii) Differential Thermal Analysis (DTA)
- iv) Differential Scanning Calorimetry (DSC)
- v) Thermometric Enthalpy Titrations (TET)

Property measured and instrument used for these methods are given in Table 1.2.

Table 1.2: Thermal Methods

S.N	Name of the method	Property measured	As a function of	Instrument
1.	Thermogravimetric Analysis (TGA)	Change in weight	Temp.	Thermobalance
2.	Derivative thermogravimetry (DTG)	Rate of change in weight	Temp.	Thermobalance
3.	Differential Thermal Analysis (DTA)	Heat absorbed or evolved	Temp.	DTA apparatus

4.	Differential Scanning Calorimetry (DSC)	Thermal Transition	Temp. change	DSC cell
5.	Thermometric Enthalpy Titrations (TET)	Temp. change	Volume of titrant	Titration calorimeter

1.3.6 Separation Methods

In the previous subsections 1.3.1 – 1.3.5 you have learnt that the determination of a substance which is free from interfering substances can be accurately made by the direct application of the suitable technique. However, in natural samples because of the complex nature there is always a presence of interfering substances. Extremely few methods may be specific or even selective and accuracy by most methods is affected by the interfering substances. It is, therefore, frequently necessary to perform quantitative separations with the objective either for isolation of the analyte or to remove the interfering substances. Therefore, separation is a prerequisite procedure for such determinations. Though separation is not a purely analytical technique but it is commonly required prior to many analyses.

You will know about some methods of separations in this subsection. In separations, in general by appropriate reactions, the desired constituent is brought into one phase and interfering elements are brought into another and the phases being separated by physical processes. Some methods of separation are the following:

A. Classical methods

- i) Precipitation
- ii) Distillation
- iii) Sublimation
- iv) Formation of complexes

B. Modern methods

- i) Chromatography
- ii) Solvent extraction
- iii) Ion-Exchange
- iv) Electrophoresis

You are well aware about the classical methods and only the modern methods will be defined here briefly and you will learn these methods in details in other unit.

i) Chromatography

Chromatography is a multistage separation process in which the sample is applied on a stationary phase over which a mobile phase is percolated. Various solutes present in the sample are separated on the basis of differential migration. Chromatography can be classified into various kinds depending on the nature of stationary and mobile phases and the mechanism of distribution involved. These kinds are named as paper chromatography, thin-layer chromatography, liquid chromatography, high performance liquid chromatography, gas chromatography, gel chromatography, partition chromatography, adsorption chromatography, ion exchange chromatography, electrochromatography etc.

Chromatography has been used with remarkable success in the separations of inorganic, organic and biochemical substances. The separations of vitamins, hormones, natural pigments, fission products of uranium and steroids etc. are some good examples of its scope and success.

ii) **Solvent Extraction**

In *solvent extraction*, a desired solute can be isolated/extracted by distributing it between two immiscible liquids. It exploits the differential solubility of a given solute in two immiscible solvents to separate it from the given mixture. Solvent extraction can be applied as a single stage procedure or a multistage procedure (counter current extraction).

iii) **Ion Exchange**

Ion exchange is a stoichiometric process in which a solid (insoluble) material, known as ion exchanger, when comes in contact with an electrolyte solution takes either positive or negative ions (known as counter ions) and releases the ions of like charge (to maintain the stoichiometry) to the solution. The solid materials having cations as exchangeable ions are known as *cation exchangers* and having anions as exchangeable ions are known as *anion exchangers*. Ion exchange is a reversible process. The exchanged ions can be replaced by other ions of like charge. Ion exchangers find great utility in separating the ionic species of similar nature. Some separations of common interest are of rare earth elements and of amino acids.

iv) **Electrophoresis**

The movement of charged particles in the influence of an electric field, in general, is known as *electrophoresis*. If the components of a mixture have different velocities under the influence of the electric field, it is possible to separate them. This method has been used with remarkable success for the separation and characterization of polysaccharides, nucleic acids, haemoglobins and other high molecular weight compounds. Small organic and inorganic ions can also be separated with the help of this technique (known as *ionophoresis*).

SAQ 1

What is the essential feature of a method to be called as an analytical technique?

SAQ 2

Name the methods that are now known as classical methods.

SAQ 3

Define polarography.

SAQ 4

Is chromatography a single stage or a multistage separation process?

Often beginners carry out usually steps iii), iv) and v) for the sake of convenience.

12.4 CRITERIA FOR EVALUATING

Analytical chemistry is of enormous importance in science and industry. It deals with the development of methods for chemical analysis which are utilized in detection, determination and separation of chemical constituents and structure elucidation

of chemical compounds. For example, the chemical formula of an unknown substance is ascertained from the percentage contents of its constituents found by analysis. Today, with the help of newer techniques, such as mass spectrometry, NMR spectroscopy, high performance liquid chromatography, etc., the structure elucidation has become more perfect.

Utility of analytical techniques is to be found in various fields as the key to the solution of a variety of scientific problems and of industrial problems. It is a chemical discipline with interdisciplinary character providing valuable information in many branches of science and technology. All fundamental laws are based on analysis. Mechanisms in so many chemical reactions are developed as a result of analysis. Much of what is known of the mechanisms by which chemical reactions occur has been learned through kinetic studies employing quantitative measurements of the rates at which reactants are consumed or products are formed. You understand the importance of rates in an industrial process to decide the cost of the products coming out of an industry.

The results of a typical quantitative analysis are based upon two series of measurements, one of which is related to the amount of sample taken, and the second to the relative amount of the desired constituent present in the sample. On the basis of the amount of the sample taken the methods are named as macro, meso, micro, and ultramicro methods. On the basis of the relative amount of the desired constituent the results take the form of numerical data in suitable units such as percent, parts per million, parts per billion or some other form.

In order to understand the criteria for evaluating the utility of the analytical techniques, it is useful to identify the several steps in performing quantitative analyses. A complete analysis actually consists of the following main steps:

- i) Sampling
- ii) Dissolution of the sample
- iii) Separation of interfering substances
- iv) Measurement
- v) Interpretation of the measurements

Sampling

The heart of the quantitative analysis is to carry a sample with great care through a number of manipulations without accidental losses and without introducing foreign material, since the sample is representative of all components and their amounts as contained in the bulk material. Conclusions will be drawn about the composition of the bulk material from the analysis of a very small portion of the material. Knowledge of statistics is of considerable importance as an aid to establishing sampling programmes so that data obtained may be subjected to statistical treatment when necessary.

Sampling techniques may be quite different in different cases. Each type of material has its own special sampling instructions, which take into account the specific characteristics of the material, the quantity taken, its purpose, etc.

Dissolution of the Sample

Most analyses are performed on solutions of the sample. Therefore, suitable solvent is required to dissolve the sample rapidly and under conditions in which there is no loss of the analyte. The dissolution process depends on the nature of the sample material.

Two most common methods employed in dissolving inorganic sample are (1) treatment with hydrochloric acid, nitric acid, mixture of hydrochloric and nitric acids, sulphuric acid or perchloric acid, and (2) fusion with an acidic or basic flux followed by treatment with water or an acid.

Organic solvents are preferentially taken to dissolve the samples of organic nature. However, special methods are to be developed to dissolve a silicate material, a high molecular weight polymer or a specimen of animal tissue.

Separation of Interfering Substances

The interfering substances are the compounds or elements that prevent the direct measurement of the species being determined. Therefore, before an analytical measurement can be made it is usually necessary to solve the problem of interferences by their separation from the analyte.

There may be two ways in general to achieve separation (i) by isolating the desired constituent in a measurable form or (ii) by removing the interfering substances from the desired constituent.

In most of the separation techniques the substance of interest is transferred from one phase to another. Therefore the separation procedures can be classified depending on the type of phases involved in these procedures. There may be four such combinations: solid-liquid, liquid-liquid, solid-gas and liquid-gas.

Measurement

The way of measurement depends upon the type of analytical technique being used. A gravimetric method involves the measurement of weight of a suitable form of the analyte. In a volumetric method the measurement is of the volume of a solution of known concentration which is required to react with the analyte. A characteristic feature of most instrumental methods is the necessity for finding empirically the value of the intensity factor corresponding to the mass or concentration of a given constituent. The majority of these methods therefore, require calibration by the use of a standard containing a known amount of constituent, which serves as a basis for comparison in the measurement.

The established procedure must be followed carefully in individual quantitative determinations. Equal care must be taken in the choice of suitable technique for the desired determination. The success or failure of an analysis is often critically dependent upon the proper selection of method.

The analytical chemistry can save much time and improve the accuracy of results by a critical comparison of the various methods on the basis of certain criteria.

Although no simple rule can be prescribed but some essential characteristics of a method which must always be considered are the following:

- a) The complexity of the materials to be analysed
- b) The probable concentration of the species of interest
- c) Accuracy
- d) Sensitivity and detection limit
- e) Selectivity
- f) Duration of an analysis
- g) Cost of equipment

Interpretation of the Measurement

The result of an analytical measurement after proper calculation is usually reported in relative terms, that is, in some way that expresses the quantity of the analyte present per unit weight or volume of the sample. Thus the results take the form of numerical data in suitable units such as percent, parts per million or some other.

The methods of statistics are commonly used and are especially useful in expressing the analytical results. You should remember that the analytical results can be reliable only if all the conditions for which the particular method was developed and verified are strictly obeyed. Any deviation from these conditions leads to error and loss in accuracy.

SAQ 5

Name any two criteria helpful in comparing the analytical methods.

12.5 EVALUATION OF ANALYTICAL DATA

A chemical analysis is usually more than a simple measurement. In a measurement the operator mainly takes care of three components: the system, some property being measured, and the instrument. Errors originate in all three components and need to be considered in a measurement. It is a real fact that no single physical measurement is perfectly accurate. The question of accuracy must, in general, receive attention both before and after an analysis. The aspect which can answer the quality assurance is the evaluation of analytical data.

The purpose of this unit is to provide sufficient information to the student to enable him to examine the factors affecting the reliability of results and understand the contributions of errors, their types, their minimization for accuracy and precision of the measurement and the proper use of significant figures.

1.5.1 Errors and detection of Errors

The data obtained by a physical measurement should always raise the question of errors and their nature. Various types of errors are caused in quantitative chemical

analysis. It is, therefore, worthwhile to account for these errors. Now first understand what are error and its types.

Error

The error is an inverse measure of the accuracy of a result. Less the error, more accurate the result is. Error is mathematically defined as the difference between the observed value and the true value:

$$E = O - T \dots (2.1)$$

where E is the error (absolute error), O is the observed value of a measurement, and T is the true value. It is with regard to sign, and it is reported in the same units as the measurements. Let us consider, for example, for the capacity of a measuring flask whose true value, as given by standard measurements, is 250 ml. For a series of 5 measurements done by an analyst the error is represented in Table 1.3.

Table 1.3: Expression of Error in Measurements in Volume of a Flask

Serial Number of observations	Observed value (ml)	True value (ml)	Error (E) (ml)
1	249	250	- 1
2	247	250	- 3
3	250	250	0
4	248	250	- 2
5	251	250	+ 1
		Total	- 5 ml
		Average	- 1 ml

The error represented in the above table is the absolute error and the average

$$\text{Error} = \frac{\text{Total error}}{\text{Number of Observations}} = \frac{-5 \text{ ml}}{5} = -1 \text{ ml}$$

However, the absolute error is of little practical significance for a quantitative analysis. It is the relative error, that is, the error relative to the true value (E/T) expressed in suitable units, is of the practical importance as a measure of inaccuracy (or as an inverse measure of accuracy). It is convenient to express relative error in terms of percentage (parts per hundred), or parts per thousand (ppt), preferably.

To understand the importance of relative error let us consider the measurement of the capacities of three standard flasks of 10, 100 and 1000 ml by three analysts A, B and C respectively represented as follows:

Analyst	A	B	C
T =	10 ml	100 ml	1000 ml
O =	11 ml	101 ml	1001 ml
E =	1 ml	1 ml	1 ml
Relative Error = E/T	1/10 = 0.1	1/100 = 0.01	1/1000 = 0.001
% R.E. = (E×100)/T	10%	1%	0.1%

You see that the absolute error in all the three cases is the same (1 ml), but the comparison of the relative errors tells that the error (inaccuracy) in case of the analyst C is the least and hence his result is the most reliable out of all the three.

However, for a finite measurement the true value is, usually, not known and the scatter is measured in terms of *deviation* which is the difference between the observed value and the mean of the given set of data. You will study about the deviation in detail in the next unit (Unit 3) of this block.

Types of Errors

For a practical point of view, it is useful to classify errors into two categories: (i) determinate errors, and (ii) indeterminate errors.

i) Determinate Errors

As the name implies, determinate errors are those whose magnitude can be determined after assigning a definite cause and thereby they can be corrected for. For example, weighing of a hygroscopic salt like calcium chloride. Its weight will vary according to water absorbed by it from atmosphere if it were weighed in open. The error caused due to absorption of water by the salt can be corrected for if the salt were weighed after drying and keeping in a desiccator.

The determinate errors may be constant or variable. When the determinate error possessed the same value from one measurement to another under a variety of conditions, is called a *constant error*, for example, error due to uncalibrated weights. On the other hand, in certain cases the determinate errors may vary in magnitude with conditions, for example, the errors caused due to expansion or contraction of volumetric solutions with a change in temperature. The magnitude of the change in volume can be determined by noting the temperature. These *variable determinate errors* are sometimes called *systematic errors*. Commonly people do not use this designation of systematic error only for variable errors but frequently call both types of determinate errors (constant or variable) as systematic errors and we shall also follow the same nomenclature.

Indeterminate Errors

Indeterminate errors are the errors for those no exact cause can be assigned, hence they cannot be corrected. The sources of these errors may be similar to those for the determinate errors but no definite causes out of these can be assigned for indeterminate errors. Even after applying every correction for the possible determinate errors the replicate observations may vary. Such a variation in observations is due to the indeterminate errors. These errors follow the rules of chance or the laws of probability and are also known as *Random Errors*. These errors, which accompany every determination, are quite irregular and generally small.

Indeterminate errors cannot be prevented or eliminated by corrections. However, they can be considerably reduced by increased care in work, and increase of the number of replicate determinations. Their pattern of occurrence can be analysed by the techniques of statistics in order to secure a worthwhile insight into their magnitudes, frequencies of occurrence, and effects on the final expression of

results. A plot of the normal distribution of occurrence of indeterminate errors can be prepared.

Sources of Determinate Errors

Determinate errors may be caused by numerous sources. It is not needed to enumerate them all but more important ones are given as follows:

- Errors due to reagents: The quality of the reagents is very important in the quantitative analysis. Certain reagents may possess impurities that will interfere in a particular quantitative analysis. Errors are also caused by the use of incorrectly standardized solutions for titration.
 - a) **Personal errors:** These errors are caused due to constitutional inability of an analyst to make certain observations accurately, that is, they are caused due to some natural weakness of the analyst. For example, some persons always detect the end point a little past in titration because their inability to judge colour changes exactly. Personal errors also include the so called psychological errors, due to certain bias often met within students, for example, some students often tend to choose in a burette reading the division which is closer to the previous determination or even to those found by his fellow students rather than the actual one. Obviously, this makes the results less accurate.
 - b) **Operational errors:** The operational errors are associated with the operation of an analysis. These errors are independent of the instrument and the apparatus employed, also these errors are not related to the chemical properties of the system in hand. Their magnitude depends more upon the analyst himself than on any other factor. They are mainly caused by carelessness of the operator in a quantitative work, for example, loss in bumping of uncovered solution while heating, failure to remove precipitate quantitatively from vessels, underwashing or overwashing of precipitate, etc.
 - c) **Methodic errors:** Sometimes a particular method for the determination of a particular constituent in the given sample may not be accurate because of improper selection of the procedure in the required range and will give the inaccurate result. For example, in the determination of iron (present in traces) in water, the gravimetric method will not give the correct result, and a method suitable for trace contents, say, a spectrophotometric method should be selected. The methodic errors are inherent in the method, and cannot be corrected unless the correct method is applied.

SAQ 6

In an analysis the observed value is 5.24 g compared with the accepted (true) value of 5.28 g. What is the relative error in parts per thousand?

1.5.2 Accuracy and Precision

You have experienced that a single measurement cannot be taken as an accurate result. A single result could be in error of one kind or the other. Our confidence in an analytical result is increased by increasing the number of parallel determinations (replicate determinations). When assessing the final results it is necessary to judge (i) their accuracy, and (ii) their precision. It will be worth while to understand the meanings of these two terms while evaluating the analytical data.

Accuracy

The term accuracy is defined as the nearness of a measurement to its true value (or accepted value). It is expressed in terms of error. Error (defined in section 2.2) is an inverse measure of accuracy. Less the error greater is the accuracy. Thus, after knowing the relative error the loss in accuracy can be estimated.

There are various ways and units to express the accuracy of a measurement. The most common being either in terms of percent relative error or in terms of relative accuracy in percentage. Consider the illustration.

Example 2.1

A sample was analyzed for desired constituent having 2.62 g as the true value. The results of three measurements were 2.50 g, 2.54 g, and 2.52 g. Find the error of the mean (mean error), the percent relative error and the relative accuracy of the mean of the measurements.

Solution

Measurement (O)	True Value (T)	Error (O-T)
2.50 g	2.62 g	- 0.12 g
2.54 g	2.62 g	- 0.08 g
2.52 g	2.62 g	- 0.10 g
Total 7.56		Total - 0.30 g
Mean $7.56/3 = 2.52\text{g}$		Mean Error = -0.10g

$$\% \text{ Relative Error} = \frac{\text{Mean Error}}{\text{True Value}} \times 100 = \frac{-0.10}{2.62} \times 100 = -3.8\%$$

$$\text{Relative Accuracy (\%)} = \frac{\text{Mean}}{\text{True Value}} \times 100 = \frac{2.52}{2.62} \times 100 = 96.2\%$$

Also it can be calculated from % R.E. as $100 - 3.8 = 96.2\%$

Precision

Precision is defined as the reproducibility of measurements. It tells an agreement between the numerical values of replicate measurements. The magnitude of random errors determines the precision of the analytical results. It follows that the closer the results of replicate determinations are to each other, the more precise is the analysis considered to be. Precision in a common way is expressed in terms of deviation. Less the deviation more precise the result is. *Deviation or apparent error* is defined as the difference between the measured value and the mean (average) of the series of measurements.

The deviation bears a relationship to the mean value of a series similar to that which exists between the absolute error and the true value. Mathematically,

$$d = X - \bar{x} \dots (2.2)$$

where, d is the deviation, x_i is the observation, and \bar{x} is the mean of series

of measurements, $\bar{x} = \frac{x_1 + x_2 + \dots + x_n}{n} = \frac{\sum x_i}{n}$ where symbol \sum represents summation (add all). Deviation is, generally, taken without regard to sign.

It is more informative to express the precision in terms of relative deviation which is deviation relative to the mean expressed in suitable units.

$$\text{Thus, average deviation (a.d.)} = \frac{d_1 + d_2 + d_n}{n} = \frac{\sum (x_i - \bar{x})}{n}$$

$$\text{and \% a.d.} = \frac{\text{a.d.}}{\bar{x}} \times 100$$

The most important measures of precision are the standard deviation and the variance. The standard deviation s of a measurement is theoretically given by:

$$s = \sqrt{\frac{d_1^2 + d_2^2 + \dots + d_n^2}{n-1}} \dots (2.3)$$

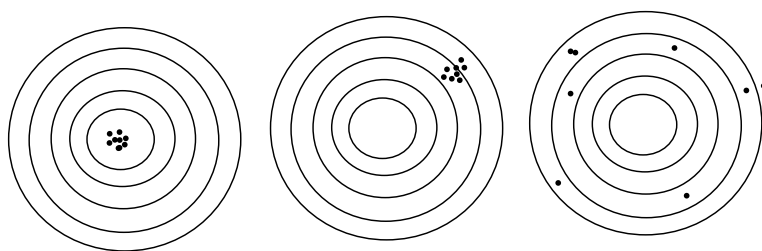
where, n is the number of observations and $(n - 1)$ is known as the degree of freedom.

Variance V is the square of the standard deviation,

$$V = s^2 = \frac{\sum d^2}{n-1} \dots (2.4)$$

Distinction between Accuracy and Precision

The accuracy should not be confused with the precision. Good agreement in parallel determinations signifies that the determinations have been made under closely similar conditions, it does not guarantee the accuracy of the results. A method may be precise but may not be accurate if a large systematic error is made. On the other hand it is nearly impossible to have accuracy without good precision. The difference of the terms accuracy and precision can be illustrated by considering the shooting of series of bullets on the targets by three riflemen (A, B, C), shown in Figure 2.1



A	B	C
Both Accurate and Precise	Precise but not accurate	Neither precise nor accurate

Fig. 1.2: Shooting by three Riflemen.

Rifleman A has the ideal marksmanship. His all hits are in centre. His results are both accurate and precise. The shooting by rifleman B shows a good grouping of hits which indicate that the marksman is undoubtedly consistent, but in this target the grouping is centered at 3 O'clock hence cannot be considered as representing accurate shooting. His results agree well mutually means precise, but the final result (obtained as their mean value) differs somewhat from the actual value, therefore not accurate. This illustrates the effect of a constant error such as poorly adjusted sights and, since precise marksmanship is evidenced, it is reasonable to assume that if the source of error can be located and corrected, accurate shooting should be forthcoming.

The shooting by rifleman C shows that the hits are spotted all over the face of the target in a display of poor reproducibility. It seems that the rifleman has no experience of shooting, his hits result only as an accident. We say that the mean value is of low reliability. Hence, these results are neither precise nor accurate. Also we see that good precision is needed for good accuracy.

Of course the most favourable methods are those which give precise and at the same time accurate results. In practice results that are precise but subject to small systematic error are often more useful than results with an accurate mean value but low precision, since in first case we can actually find out how much they differ from the true value, while in the second case we know nothing but that the mean value is of low reliability. In the following example you can see the difference of accuracy and precision for the results of burette reading of a titration.

Example 2.2

The burette readings of titrations carried out by three students A, B and C are given below. Compare the accuracy and precision of the three students, if the true reading is 22.22 ml.

Student	A	B	C
Burette readings	ml	ml	ml
	22.22	22.28	22.38
	22.24	22.27	22.12
	22.23	22.29	22.32
	22.21	22.28	22.30

	22.20	22.28	22.18
Mean value	22.22	22.28	22.18

You can understand from the observed values and calculated mean values of titrations of three students that the results of student A are reproducible and the mean value resembles the true value. Hence the results of student A are both *precise* and *accurate*. A look of the titration results of student B shows that his results are reproducible but the mean value is slightly on the higher side than the true value. May be he might be taking the end point (colour change) on the higher side. Therefore, the results of student B are precise but not accurate. The readings of students C are spread in a wide range with a poor reproducibility. Hence his results are neither precise nor accurate.

SAQ 7

Define accuracy and precision.

12.6 REPORTING OF RESULTS

An analytical result is reported in two parts: (i) chemical, and (ii) numerical.

1.6.1 Chemical Expression of Results

As far as possible, the result of the element determined should be reported in the chemical form in which it is present in the sample analyzed. For example, in reporting the result of a determination of nitrogen, it should be reported as nitrate, nitrite or ammonia depending upon the chemical form in which the element (nitrogen) is present. The analysis of a solution of electrolytes is generally expressed in terms of the ions present (as Fe^{3+} , Ca^{2+} , Cl^- , CO_3^{2-} , etc.).

However, when the actual form is not known or some other specific purpose is to be solved, the expression may be modified. Often the purpose for the analysis decides the form in which the constituents are reported. For example, when limestone is used for the purpose of manufacture of lime, its calcium content is expressed as calcium oxide. The hardness of water is usually expressed in terms of calcium carbonate (although a number of ions other than calcium are present in water).

1.6.2 Numerical Expression of Results

In most of the analyses, it is the relative amount of the constituent in a sample that is of importance. Therefore, the numerical expression represents the amount of the desired constituent as parts of the amount of the sample in suitable units. Thus, if W_i is the amount of the constituent of interest, W_s is the amount of the sample, and C is a factor required to express the results in suitable units, the expression

$$\frac{W_i}{W_s} \times C$$

is useful for the numerical expression of results of an analysis.

For example, if W_i and W_s are in grams and C is 100, the result is given in percent (%) by weight of the constituent in the sample. If C is set equal to 1000 and W_i and W_s in same units, the answer is in parts per thousand (ppt) by weight of the constituent in the sample. And if C is set equal to 1,000,000 the answer is in parts per million (ppm) by weight of the constituent in the sample, and so on. The quantities W_i and W_s may also be expressed in volume units. Way of numerical expression of the results also depends on the physical state (solid, liquid, or gas) of the constituent and of the sample.

Solids

In case of the solid sample, usually, the weight constituent of interest and that of sample are taken in the same weight units and the result is expressed as percentage by weight (weight of constituent \times 100/ weight of sample) to give the number of parts of analyte in 100 parts of the sample.

Liquids

The percentage in liquid samples is expressed in three ways:

- i) *Weight percentage*: It is expressed in the same way as in solids and $\frac{\text{Weight of constituent} \times 100}{\text{Weight of sample}}$ gives the number of parts of the desired constituent in 100 parts of the sample. Both weights are taken in same units.
- ii) *Weight-volume percentage*: $\frac{\text{Weight of constituent in g} \times 100}{\text{Volume of sample in mL}}$ gives the number of parts by weight of constituent in 100 parts by volume of the sample. The temperature should be mentioned.
- iii) *Volume percentage*: $\frac{\text{Volume of constituent}}{\text{Volume of sample}} \times 100$ gives the number of parts of volume of desired constituent in 100 volumes of the sample. Both the volumes should be taken in the same units and the temperature should be specified.

Gases

The composition of a gaseous mixture is usually expressed in percentage by volume, that is, $\frac{\text{Volume of constituent}}{\text{Volume of sample}} \times 100$. Both the volumes should be taken in the same units and the temperature should be specified.

The percentage representation is very common, but it is useful mainly for major constituents. When the constituent is in traces, it is advantageous to express in parts per million by weight or volume. For further lower amounts, parts per billion or parts per trillion may also be used.

1.6.3 Significant Figures

In the preceding section you learnt how to report the results of measurements of an analysis. In this section you will learn about the use of correct number of significant figures. The correct number of significant figures in measurement and calculations is critical in giving the proper significance to an analysis.

You know that a *number* is a mathematical expression of a quantity. A *figure*, or *digit*, is any one of the characters 0, 1, 2,..., 9 which, alone or in combination, serves to express a number. *The digits of a number which are needed to express the precision of the measurement from which the number was derived are known as significant figures.*

Digits from 1 to 9 are always a part of significant figures, while 0 may or may not be a significant figure. A digit signifies the amount of the quantity in the place in which it stands. In case of the number 542, the figures signify that there are five hundreds, four tens, and two units and are therefore all significant.

The character zero (0) is used in two ways, it may be used as a significant figure or it may be used merely to locate the decimal place. When zero is the part of the measurement it is significant. For example, the weight of a crucible is found to be 12.610 g. The terminal zero is significant meaning that the weight can be measured correctly upto third place of decimal. The zero after 1 is significant because this is the part of the measurement. Similarly, expressing the concentration of a copper sulphate solution as 0.1000 N, the three zeros after 1 are all significant.

Consider the number 107.2 cm. The zero between 1 and 7 is significant because zero placed between two significant figures is significant. This number has four significant figures regardless of where the decimal point is placed, say 1072 mm, 10.72 dm, 1.072 m and 0.001072 km all have four significant figures, they simply represent the result in different units. In the last number 0.001072 km, the zeros before 1 are just to locate the decimal point and therefore are not significant.

To write a result with some degree of certainty the correct use of significant figures must be made, which depends on various rules for computation. The student should be familiar about these (the rules have got the limited validity), i.e.

- i) Observed quantities should be recorded with one uncertain figure retained. That is, there must be as many significant figures in a result or in any data as will give only one uncertain figure. Thus, in most analyses represent the last retained significant figure by ± 1 . For example, a value 22.6 ml represented as 22.6 ± 1 means that this is known to be between 22.5 ml and 22.7 ml.
- ii) *In rounding off* quantities to desired number of significant figures by dropping the superfluous figures, increase the last retained figure by one if the following figure (which is dropped) is greater than 5. For example, the number 46.2368 rounded off to four significant figures becomes 46.24.

If the dropped digit is exactly 5 (not ... 51, 524, etc. which are treated as greater than 5), the last retained figure is rounded off to the nearest even digit.

Thus,

3.55 is rounded off to two significant figures = 3.6

3.65 is rounded off to two significant figures also = 3.6

14.75 rounded off to one decimal place = 14.8

2.652 rounded off to one decimal place = 2.7

If the dropped figure is less than 5 the last retained figure is not changed.

Thus,

26.4332 rounded off to four significant figures = 26.43.

- iii) *In addition or subtraction* the answer is rounded off to the significant figures in terms of the least significant unit. It is mainly for decimal places in the numbers and the number having the fewest decimals is thus the least significant unit. Thus, the result of sum or difference should have the number of decimals equal to the number of decimals present in the least significant unit (means the number having the fewest decimals). Although, all numbers being added or subtracted can be rounded off to the least significant unit. But again for the consistency in the answer in practice we keep an extra figure during stepwise calculations and then the final result is rounded off to one less figure. For example, summing the numbers: $26.234 + 3.223 + 143.4 + 2.2260$, the third number 143.4 is the least significant unit which contains only one decimal place. Therefore, all other numbers are rounded off to two decimal places and the final result is then rounded off to one decimal place (equal to the number having least decimal places).

26.234 is rounded off to 26.23

3.223 is rounded off to 3.22

143.4 is retained as 143.4

2.2260 is rounded off to 2.23

Sum = 175.08

Finally rounded to one decimal place the sum = 175.1 Answer

In multiplication or division you can retain in each factor one more significant figure than that of a factor having the least significant figures (that is significant figures contained in the least precise factor). After calculations the answer is rounded off to the number of significant figures contained in the least precise factor. For example, in the multiplication

$$7.0783 \times 0.00305 \times 6.602$$

the middle factor has got the least (=3) significant figures hence the values will be written as

$$7.078 \times 0.00305 \times 6.602 = 0.1425233$$

The answer rounded off to 3 significant figures is = 0.143

- iv) If a calculation involves addition / subtraction and multiplication /division then the individual steps must be treated separately. As good practice one extra figure may be retained in the intermediate calculations and the final result is then rounded off by dropping the superfluous figures.
- v) When a *calculator* or computer is used, insert all available digits in the calculation. The final result is rounded off as desired.
- vi) One extra figure may be included in the average.

- vii) In *logarithm* calculations as you understand a logarithm of a given number is composed of two parts (i) the *characteristic* which is a whole number and is indicative of the position of the decimal in the given number and hence is not a significant figure, (ii) the *mantissa* which is a decimal fraction and is the same regardless of the position of decimal in the given number. For example, to express properly the logarithm of 2.4×10^4 , characteristic is 4 and mantissa is 0.3802 and the logarithm is 4.3802. The result is rounded to 4.38 since the given number (2.4×10^4) has only two significant figures.

Example

Calculate the pH of a 4.0×10^{-3} M solution of hydrochloric acid.

Solution

$$\text{pH} = -\log [\text{H}^+] = -\log 4.0 \times 10^{-3}$$

The -3 is the characteristic (from 10^{-3}). The mantissa is 0.6010 (from the logarithm of 4.0). But the concentration is known only upto two significant figures, hence

$$\text{pH} = -(-3 + 0.6010) = 3 - 0.60 = 2.40 \text{ Answer.}$$

SAQ 8

List the proper number of significant figures in the following numbers

- i) 0.162 ii) 10.06 iii) 200.0 iv) 0.0260

12.7 LET US SUM UP

Let us summarise the key points dealt in this unit.

The classical as well as instrumental analytical techniques are very important to an environmental analyst; the reason being the increasing levels of many types of pollutants day by day across the globe. This helps in monitoring of various pollutants and hence in applying some of the corrective measures.

In a broad sense the analytical techniques can be grouped into qualitative and quantitative types. The classification of these techniques is based also on the physical properties of the analytes. On the basis of these properties the types are divided into chemical, electrical, optical, nuclear radiation, thermal and separation methods. All the methods are further divided into many types. Thus chemical methods are divided into gravimetric and volumetric analysis. Electrical methods have potentiometry, voltammetry coulometry, amperimetry and conductometry. Emission, absorption, ultraviolet-visible absorption, IR absorption, fluorophotometry, turbidimetry and nephelometry and Raman spectroscopy are the parts of optical methods. Nuclear methods include radiochemical spectroscopy, Mossbauer spectroscopy, nuclear magnetic resonance spectroscopy and mass spectrometry. Thermal methods are thermogravimetric analysis, derivative thermogravimetry, differential thermal analysis, differential scanning calorimetry and thermometric enthalpy titrations. Separation methods have classical and modern methods wherein chromatography and electrophoresis are parts of the latter one.

A complete analysis actually consists of the many steps. These include sampling, dissolution of the sample, separation of interfering substances, measurement and interpretation of the measurements. Evaluation of analytical data includes errors, detection of errors and the concept of accuracy and precision. There are chemical and numerical methods of reporting the results where the concept of significant figures is very important.

12.8 TERMINAL QUESTIONS

1. What is the essential feature of a method to be called as an analytical technique?
2. Name the methods that are now known as classical methods.
3. Define accuracy and precision with suitable examples.

UNIT 13 : SPECTROMETRY

Structure

13.0 Introduction

13.1 Objectives

13.2 UV-Vis Spectrophotometry

13.2.1 Origin and Nature of Spectrum

13.2.2 Beer-Lambert's Law

13.2.3 Basic Instrumentation for UV-VIS Spectrophotometry

13.2.4 Environmental Applications of UV-VIS Spectrophotometry

13.3 IR Spectrometry

13.3.1 Origin and Nature of Spectrum

13.3.1 Basic Instrumentation for IR Spectrometry

13.3.1 Environmental Applications of Infrared Spectrometry

13.4 Mass Spectrometry

13.4.2. Principle

13.4.3. Instrumentation for Mass Spectrometry

13.4.4. Hyphenation of MS with Other Techniques (ICP-MS)

13.4.5. Environmental Applications of Mass Spectrometry

13.5 Summary

13.6 Terminal Questions

13.7 Answers

13.0 INTRODUCTION

You know that spectroscopy is the study of interaction of electromagnetic (EM) radiation with matter. We get different types of spectra as a consequence of the interaction of different types of electromagnetic radiation with matter. For example, the interaction of radiation in the UV-VIS region with certain types of species gives rise to UV-VIS spectra whereas; the interaction of EM radiation from the IR region with the sample gives IR spectra and so on. In this unit you would learn about UV-VIS spectrophotometry and IR spectrometry as important spectroscopic techniques in terms of their principle and environmental applications.

In addition, you would also learn about another important technique called mass spectrometry. This is not a spectroscopic method *per say* as it does not involve the interaction of EM radiation and matter. However, it is an important instrumental technique having wide range of applications in diverse domains and is generally clubbed with spectrometric methods. In the next unit you would learn about chromatography – another important set of methods with wide ranging applications.

13.1 Objectives

After studying this unit, you should be able to:

- differentiate between the terms-spectroscopy, spectrometry and spectrophotometry;
- explain the origin and the characteristics of UV-VIS spectrum;
- explain Beer-Lambert's law;
- describe the principle of UV-VIS spectrophotometry;
- draw a schematic diagram of UV-VIS spectrophotometer;
- enlist environmental applications of UV-VIS spectrophotometry;
- explain the origin of IR spectrum;
- draw a schematic diagram of IR spectrometer;
- list and explain some environmental applications of IR spectrometry;
- explain the principle of mass spectrometry;
- define and explain the terms like base peak, molecular ion, fragments, etc. in the context of mass spectrometry;
- draw a block diagram of mass spectrometer;
- discuss some environmental applications of mass spectrometry.

13.2 UV-VIS SPECTROPHOTOMETRY

The UV-VIS spectrophotometry is one of the oldest spectroscopic methods having wide ranging applications in diverse domains. It is based on the interaction of electromagnetic radiation in the UV-VIS region with molecules, ions or complexes. You would have noticed that we have used three terms, viz., spectroscopy, spectrometry and spectrophotometry in the introduction above. These are used interchangeably however; there is a fine line of distinction between them. It is worthwhile to learn about the difference between these terms before we move ahead.

Spectroscopy is a very broad term that encompasses the domain of study of interaction of electromagnetic radiation with matter whereas spectrometry refers to the measurement of consequence of such an interaction. On the other hand, spectrophotometry, refers to the measurement of interaction of the electromagnetic radiation in visible (and UV also) range with matter. Here, we are going to take up spectrophotometry. Let us now learn about the origin and nature of the UV-VIS spectrum.

13.2.1 Origin and nature of UV-VIS spectrum

The UV-VIS region of electromagnetic spectrum extends from about 200 nm to about 760 nm. Of this, the UV range extends from about 200 nm to 380 nm and visible range spans from about 380 nm to 760 nm, Fig. (2.1). The radiation below 200 nm falls in the far UV region and is used in special cases as it requires special instruments. The energies of UV-VIS radiation vary from about 600 kJ mol⁻¹ to 160

kJ mol^{-1} . These energies of UV-VIS radiation are comparable to the difference in electronic energy levels of the atoms molecules / ions and complexes etc. Therefore, when the UV-VIS radiation interacts with these species it causes transitions amongst their electronic energy levels. Accordingly, the UV-VIS spectroscopy is also called as **electronic spectroscopy**.

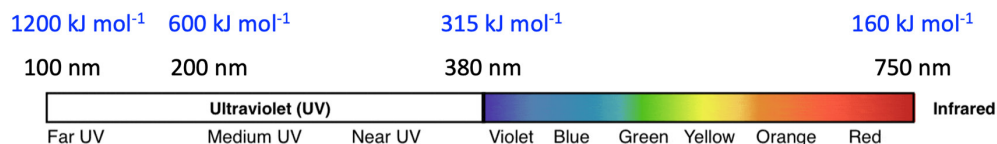


Fig. 2.1: Ultraviolet (UV) and Visible ranges of radiation and their approximate energies

Let's take the example of organic molecules to understand the origin of UV-VIS spectrum. You would recall from your earlier knowledge of bonding in organic molecules that according to molecular orbital theory, the atomic orbitals of constituent atoms combine to give different bonding and anti-bonding molecular orbitals. In addition to these molecular orbitals there are nonbonding electrons on the atoms like, N, O, S and halogens etc., that stay in non-bonding molecular orbitals. A generalised molecular orbital energy level diagram for organic molecules and the possible transitions amongst these molecular orbitals (electronic energy levels) is given in Fig. (2.2).

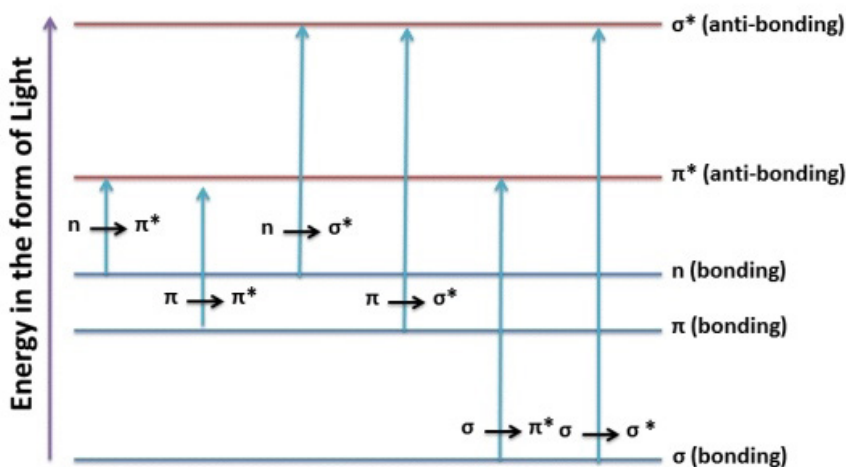


Fig. 2.2: Generalised molecular orbital energy level diagram and possible transitions for organic molecules

The Fig. 2.2 shows that a number of transitions amongst the electronic energy levels of organic molecules are possible. However according to the selection rules only some of these transitions are observed in a given molecule. The two commonly observed and prominent transitions in organic molecules are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Of these, $\pi \rightarrow \pi^*$ transitions are generally intense while $n \rightarrow \pi^*$ transitions are weak.

In order to obtain a UV-VIS spectrum the electromagnetic radiation spread over a range of wavelengths (in the UV-VIS range) is passed through the sample solution taken in a container called a **cuvette**. The intensity of the radiation decreases (if the

species absorbs it) after passing through the sample as schematically shown in Fig. 2.3.

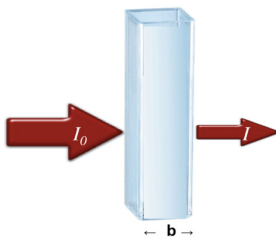


Fig. 2.3: Schematic diagram showing the decrease in the intensity of radiation after passing through an absorbing species taken in a cuvette

The amount of the radiation absorbed at each wavelength is measured and plotted against the wavelength of radiation to obtain the UV-VIS spectrum. Thus, a typical UV-VIS spectrum is a plot of wavelength versus the intensity of absorption and consists of a number of signals called **absorption bands**. A typical UV spectrum is given in Fig 2.4 (a). The abscissa (x-axis) indicates the wavelengths absorbed and the ordinate (y-axis) represents the intensity of absorption.

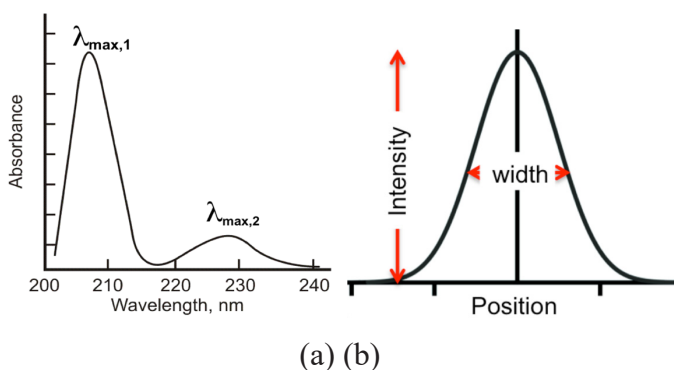


Fig. 2.4: (a) A representative UV spectrum and (b) Characteristics of a UV-VIS absorption band

Having learnt about the origin of UV-VIS spectrum as a consequence of the interaction of EM radiation in the UV-VIS range with the absorbing species, let us now learn about the nature of UV-VIS spectrum. The UV-VIS spectral bands are characterised by three parameters as shown in Fig. 2.4 (b). These are:

- position of absorption maximum, λ_{\max} ,
- intensity of the absorption band
- width of the absorption band

The wavelength corresponding to the maximum absorptions is typically called λ_{\max} (lambda max). It is a measure of the difference in the electronic energy levels involved in the most intense transition. The intensity of the absorption band depends mainly on two factors. These are, the probability of transition and the concentration of the absorbing species. The width of the absorption band, on the other hand, is partly due to the instrumentation used and partly due to the nature of absorbing species. The relationship between the intensity of absorption and the concentration forms the basis for quantitative applications of UV-VIS spectrometry. We would talk about it in the next subsection.

13.2.2 Beer-Lambert's Law

When a monochromatic radiation of certain intensity is made to fall on a absorbing sample taken in a cuvette, a part of the radiation is reflected, another part is absorbed, and the remaining part is transmitted. The decrease in the intensity of incident radiation depends on the thickness of the absorbing medium as well as the concentration of the absorbing species. This dependence can be expressed in terms of Beer-Lambert's law. This law in fact is a combination of two laws, namely the Lambert's law and the Beer's law. Let's learn about these laws.

Lambert's law

According to Lambert's law the amount of monochromatic radiation absorbed by a substance is proportional to the intensity of the incident radiation and the thickness of the absorbing medium (Refer Fig. 2.3 again). The mathematical expression for the Lambert law is

$$\log \frac{I}{I_0} = -\frac{k}{2.303} b \dots (2.1)$$

Where, I_0 represents the intensity of incident light falling on the absorbing medium (cuvette) of thickness b ; I is the intensity of the transmitted radiation, and k is the proportionality constant. The negative sign implies that the intensity of the radiation decreases after passing through the absorbing medium. The significance of the Eq. 2.1 is that, *"The intensity of the transmitted light decreases exponentially when the thickness of the substance, through which the light is passing, increases linearly"*.

Beer's law

According to Beer's law the amount of monochromatic radiation absorbed by a substance is proportional to the intensity of the incident radiation and the concentration of the absorbing medium. The mathematical expression for the Beer's law is

$$\log \frac{I}{I_0} = -\frac{k'}{2.303} c \dots (2.2)$$

Where, I_0 represents the intensity of incident radiation falling on the absorbing substance of concentration c , I is the intensity of the transmitted radiation, and k' is the proportionality constant. The negative sign implies that the intensity of the radiation decreases after passing through the absorbing medium. Eq. 2.2 signifies that, *"The intensity of the transmitted radiation decreases exponentially when the concentration of the substance, through which the radiation is passing, increases linearly"*. You may note here that the relation between intensity of the transmitted light and concentration is similar to the one for the intensity of the transmitted light and the thickness of the absorbing medium.

The two laws can be combined to give Beer-Lambert's law, which can be stated as, *"the amount of monochromatic radiation absorbed by a substance is proportional*

to the intensity of the incident radiation, the thickness and the concentration of the absorbing medium". The mathematical expression being,

$$\log \frac{I}{I_0} = -\frac{k.k'}{2.303} bc \dots (2.3)$$

Rearranging, we get

$$\Rightarrow \log \frac{I_0}{I} = \frac{k.k'}{2.303} bc = abc \quad \text{where } a = \frac{k.k'}{2.303} \dots (2.4)$$

The constant 'a' in this expression is called **absorptivity** (earlier called extinction coefficient) whose value depends on unit of concentration used and is a function of wavelength of the monochromatic radiation. The concentration is generally expressed in terms of g per dm³ and b in cm. Therefore; absorptivity has units of cm⁻¹g⁻¹ dm³. However, if the concentration of the solution is expressed as mol dm⁻³ and b in cm then the constant is called **molar absorptivity** (earlier called as molar extinction coefficient) and is expressed as e. It's units then become cm⁻¹ mol⁻¹dm³. In such a case, we can write Beer-Lambert's law expression as,

$$\log \frac{I_0}{I} = \epsilon bc \dots (2.5)$$

The term $\log \frac{I_0}{I}$ is called absorbance and is represented as 'A'.

$$\log \frac{I_0}{I} = A \dots (2.6)$$

The expressions for Beer-Lambert's law then becomes,

$$\log \frac{I_0}{I} = A = abc \text{ or } \epsilon bc \dots (2.7)$$

The absorbance, A is related to another important term called transmittance which is defined as the fraction of the incident radiation transmitted by the absorbing medium. Mathematically,

$$\text{Transmittance, } T = \frac{I}{I_0} \dots (2.8)$$

It is generally expressed as a percentage and is expressed as,

$$\text{Percentage transmittance, } \%T = \frac{I}{I_0} \times 100\% \dots (2.9)$$

$$\text{The transmittance and absorbance are related as, } A = -\log T \dots (2.10)$$

It is desirable that you get acquainted with the expressions related to the Beer-Lambert's law and learn to use them. Let us take some examples to illustrate the application of these expressions..

Absorbance is defined as the logarithm of the ratio of the intensities of the incident and transmitted radiations.

Eq. 2.7: use 'a' if concentration is expressed in g dm⁻³ and path length in cm and 'ε' if the concentration in mol dm⁻³ and b in cm.

Example 1

The molar absorptivity of a substance is $1.2 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$. Calculate the absorbance of $1.6 \times 10^{-4} \text{ M}$ solution of the substance taken in a cuvette having a path length of 1.0 cm.

Solution

As per the Beer- Lambert's law, absorbance, $A = \epsilon c b$

We are given:

$$\epsilon = 1.2 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3, c = 1.6 \times 10^{-4} \text{ mol dm}^{-3} \text{ and } b = 1.0 \text{ cm}$$

Substituting the values in the expression for absorbance we get,

$$A = 1.2 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 \times 1.6 \times 10^{-4} \text{ mol dm}^{-3} \times 1.0 \text{ cm} = 1.92$$

Thus, the absorbance of the given solution would be: **1.92**.

You may note here that though transmittance and absorbance are equivalent expressions which can be interconverted, it is the absorbance which is directly proportional to the absorbed fraction of the radiation.

Example 2

A solution containing 4.4002 g of copper sulphate per 250 cm^3 of aqueous solution when taken in a cuvette having a path length of 1 cm gave an absorbance of 0.26 at 635 nm. Calculate the molar absorptivity of copper sulphate.

Solution

We are given: Absorbance, $A = 0.26$ Path length, $b = 1.0 \text{ cm}$

$$\text{Molar concentration, } c = \frac{4.4 \times 1000}{159.6 \times 250} = 0.1103 \text{ M}$$

We know that according to Beer-Lambert's Law

$$A = \epsilon c b$$

Rearranging we get,

$$\epsilon = A / c b$$

$$\text{Substituting the values, we get } \epsilon = \frac{0.26}{0.1103 \text{ mol dm}^{-3} \times 1.0 \text{ cm}} = 2.357 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3. \text{ On the}$$

basis of given data the molar absorption coefficient for copper sulphate is found to be $2.357 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$.

Having learnt about the origin, nature and principle of UV-VIS spectrometry we can now take up the applications of UV-VIS spectrometry. However, before moving ahead why don't you answer the following SAQs to assess your understanding of the concepts dealt so far?

SAQ 1

An aqueous solution of copper sulphate taken in a cuvette having a path length of 2 cm showed an absorbance of 0.47. Determine the concentration of the solution. (You may use any required data from example 2 given above)

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.....

.....

SAQ 2

15.7 mg of benzene ($M_m = 78.11 \text{ g mol}^{-1}$) was dissolved in hexane to prepare 100.0 cm^3 of solution. The solution taken in a cuvette of 1 cm gave an absorbance of 0.40 at 256 nm. Find the molar absorptivity of benzene at this wavelength.

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13.2.3 Basic Instrumentation for UV-VIS Spectrophotometry

UV-VIS spectrophotometry has found increasing applications in numerous fields. In order to meet this demand, UV/Vis spectrophotometers with a wide range of features have become available. These range from simple instruments for routine work to highly sophisticated instruments for advance work. However, the basic principle in these instruments remains the same. In a typical spectrophotometer the radiation emanating from the UV or VIS source is passed through a suitable monochromator to get a monochromatic radiation. This is then split into two equivalent beams with the help of a beam splitter and are passed through the reference and the sample cell simultaneously. The transmitted radiations obtained after the interaction with the sample / reference are sent to the detectors. The difference in the transmitted signal is suitably processed, amplified and sent to the recorder. A schematic diagram for a double beam spectrophotometer is given in Fig. 2.5.

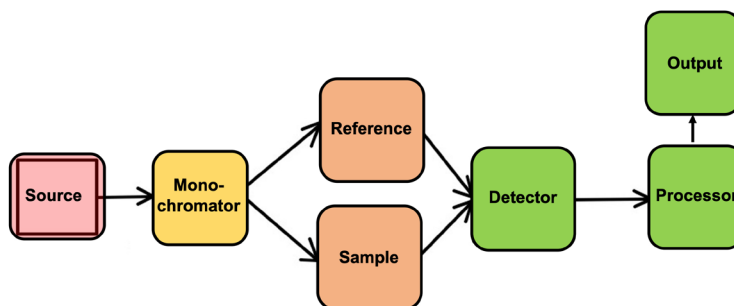


Fig 2.5: A schematic diagram of a dispersive IR spectrometer

13.2.4 Environmental Applications of UV-VIS Spectrophotometry

UV-VIS spectrometry is highly adaptable, and versatile technique that provides an affordable and reliable method of analysis. It finds applications in most of the areas of environmental concern viz., air, water and soil. A number of important UV/Vis methodologies have been developed for the determination of organic, inorganic and complex ionic structure in various environmental matrices. Some of the general and specific applications of UV-VIS spectrometry are listed below.

- Determination of heavy metals by coloured complex formation with selected ligands.
- Identification of petroleum products in marine environment; useful in cases of oil spills. Detection of bacteria in water samples by monitoring the change in transmittance as a function of time.
- Determination of pesticide residues in soil samples by suitable complexation followed by absorbance measurement.
- Determination of fluoride content in water samples using Alizarin red method. In this method, the water sample is treated with the reagent and the complex is extracted with pentanol and the absorbance is measured at 430 nm.
- Determination of nitrite in water and soil samples by reacting with p-nitroaniline in acid medium to form diazonium ion followed by treatment with ethylcyanoacetate in basic medium to form an azo dye. The dye is then monitored by measuring absorbance at 465 nm.
- Determination of sodium dodecyl sulfate (SDS)-a component of non-biodegradable surfactants in wastewater by forming a yellow colored complex with acridine orange. The complex is then extracted using toluene and the concentration is obtained by measuring absorbance at 467 nm.
- Determination of ozone in ambient air by passing it in a solution of indigo disulfonate (IDS) in a special double sintered disc absorber and following the reduction in the concentration of IDS by measuring absorbance at 610 nm.

13.3 IR SPECTROMETRY

The infrared (IR) spectrometry is a common spectroscopic technique used for structure elucidation and identification of a large variety of organic, inorganic and biological samples. It involves the interaction of electromagnetic radiation in the IR region with the substances being investigated and causes transitions amongst the quantized vibrational energy levels of the system. Accordingly, IR spectrometry is also called vibrational spectrometry. IR spectrometry finds applications in quite diverse areas like drugs and pharmaceuticals, chemical industry, polymer industry, forensic determinations, air pollution monitoring, agriculture, semiconductor microelectronics, clinical and biomedical determinations etc. The identification

of molecular structures and the determination of their concentration of different species in a sample is an essential part of environmental analysis.

The IR spectrometry involves the measurement of the amount of IR radiation absorbed or emitted by a sample as a function of the wavelength and its correlation with the structure and amount of the species being analysed. In order to understand the basic theory behind IR spectrometry, let us first learn about the vibration motion of the molecules and the origin of IR spectrum.

2.3.1 Origin and nature of spectrum

The bonds in molecules can be considered as flexible springs holding two balls (atoms) together. The bonded atoms are in constant state of motion around their mean position as shown schematically in Fig. 2.5. These are said to be executing vibrational motion within the molecule. The vibration motion of a bond in the molecule can be visualised by keeping one atom fixed and pulling the second atom by a certain distance from its mean position (Fig. 2.6) and leaving it. The restoring force of the bond pulls the atom back; the atom comes back to the equilibrium position and then contracts. The process continues and the molecule keeps vibrating. However, in reality both the atoms move around their mean position. The motion of the two atoms may be in unison or out of phase.

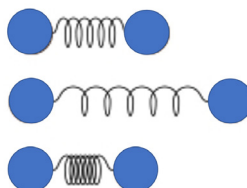


Fig. 2.6: Schematic representation of molecular vibration in a diatomic molecule

The frequency of vibration of a bond in a molecule is called vibrational frequency. The vibrational frequency of a diatomic molecule is given by the following formula.

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \quad ; \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots (2.11)$$

Where, k is the force constant (a measure of strength of the bond) and μ is the reduced mass, Eq. 2.11. You may note that the oscillation or vibrational frequency of the molecule is directly proportional to the square root of the force constant implying that a stronger bond has a higher vibrational frequency. The vibration frequencies of different bonds between two carbon atoms, given below, substantiate it.

$\text{C}\equiv\text{C}$	$\text{C}=\text{C}$	$\text{C}-\text{C}$
2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

Similarly, the oscillation or vibration frequency is inversely proportional to the square root of the reduced mass; the vibration frequency decreases with increase in the reduced mass.

C-H	C-C	C-O	C-Cl	C-Br
3000 cm ⁻¹	1200 cm ⁻¹	1100 cm ⁻¹	750 cm ⁻¹	600 cm ⁻¹

In this example, as the mass of atom bonded to carbon atom increases, the reduced mass of the bond increases and the vibration frequency decreases. Further, like the electronic energy, the vibrational motion is also quantized meaning thereby that the vibrating molecule (or bond) can take up only certain energies. The quantised vibrational energy levels are given by the following expression

$$\epsilon_v = \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e \text{ cm}^{-1} \quad (v = 0, 1, 2, \dots) \quad \dots (2.12)$$

Where, v is vibrational quantum number that can have values of 0, 1, 2, 3..., upto infinity. A schematic energy level diagram for a vibrating diatomic molecule is given in Fig. 2.6. The vibrational energy level having vibrational quantum number, $v=0$ is called the **ground state** and has the lowest energy called as **zero-point energy**.

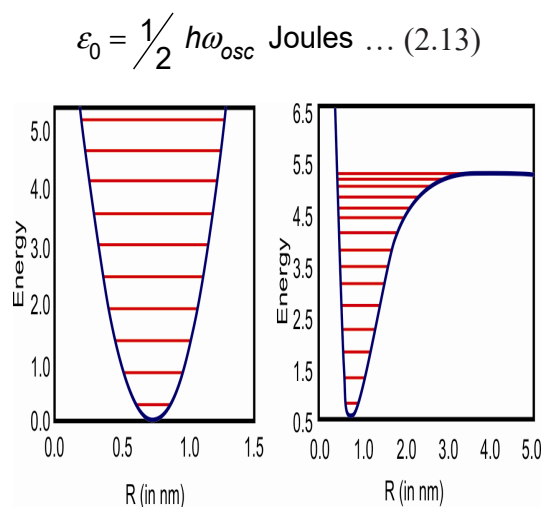


Fig. 2.7: Schematic energy level diagram for a vibrating diatomic molecule. (https://en.wikipedia.org/wiki/File:Anharmonic_oscillator.gif)

It is important to note that in a higher energy vibrational level the atoms have a larger deviation from their mean position however the vibration frequency of the bond does not change. The difference of energies between vibrational energy levels is much smaller than that of the electronic energy levels, about a thousand times smaller. The transitions between the quantised vibrational energy levels can be brought out by radiation in the IR range to give an IR spectrum. The wavelength of IR ranges from about 0.8 to 100 μm (12 500–100 cm⁻¹ in wavenumbers) and is divided into a near-infrared (NIR) (12 000–4000 cm⁻¹) and a mid-IR (mid-infrared) (4000–100 cm⁻¹) part. It is the mid-IR region that is of interest for routine measurements.

When the radiation in the mid-IR region interacts with an absorbing species, it causes transitions amongst different vibrational levels. Let us see what kind of spectrum we expect from such an interaction. You may be thinking that as there are a large number of vibrational energy levels in case of vibrating molecule, we may

have a very large number of signals in the spectrum of all the molecules. You are partly correct. Let us see what all transitions are observed in the IR spectrum of a molecule.

First and foremost, we have to understand that all molecules do not show an IR spectrum. For an IR spectrum to be observed, the vibrating bond must be associated with a fluctuating or oscillating dipole moment. In the absence of such a fluctuating dipole moment the IR radiation cannot interact with the molecule and we say that the vibration in the molecule is IR inactive. For example, a homonuclear diatomic molecule like H_2 would not give an IR spectrum because it does not have a dipole moment and also it does not generate a fluctuating dipole moment on vibration. On the other hand, HBr gas has a dipole moment and it does absorb in the IR region.

Now, if a molecule has a fluctuating dipole moment, which transitions would we observe? For this we need to know about the **selection rule**. According to the selection rule governing vibrational transitions the transitions in which $\Delta v = \pm 1, \pm 2, \pm 3 \dots$ etc. are allowed. This means that the molecule may go over from any vibrational level to any other level. However, for all practical purposes, to begin with most of the vibrating molecules are in their ground state. Which implies that only the transitions originating from $v=0$ level are possible. This reduces the number of possible transitions drastically. Further, the transition probability of the transitions for Δv more than 3 is insignificant, i.e., the transitions with $\Delta v > 3$ may occur but the signal would be so small that we would not observe it.

In nutshell this means that for a vibrating diatomic molecule there would be a maximum of three signals. First would be an intense signal due to transition from ground state ($v = 0$) to the first ($v = 1$) excited vibrational level; this is called **fundamental vibration**. The second signal is due to the transition from ($v = 0$) to ($v = 2$) vibrational level. This is relatively a weak signal and is called **first overtone**. It will be observed at a frequency slightly lesser than that of the double of the fundamental transition. The third signal is due to the transition from ($v = 0$) to ($v = 3$) level. It is the weakest signal and is called the **second overtone**. This will be observed at a frequency lesser than that the triple of the fundamental transition. The origin of fundamental vibration and the overtones is given in Fig. 2.8.

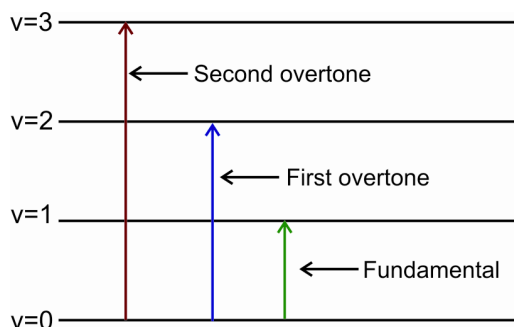


Fig. 2.8: The origin of fundamental vibration and the overtones

A diatomic molecule by default is linear and has only one possible way of executing vibrational motion. If a vibrating diatomic molecule shows oscillating dipole moment, then we expect three signals in the IR spectrum. How many signals would

be there for a polyatomic molecule? A linear polyatomic molecule has $(3N - 5)$ different modes of vibration where N is the number of atoms in the molecule. A non-linear molecule on the other hand has $(3N - 6)$ different modes of vibration. For example, CO_2 – a linear triatomic molecule shows 4 different modes of vibration whereas H_2O – a nonlinear triatomic molecule shows only 3 different modes of vibration. The different modes of vibration for carbon dioxide molecule are given in Fig. 2.9. Which of these modes of vibrations for carbon dioxide would be IR active?

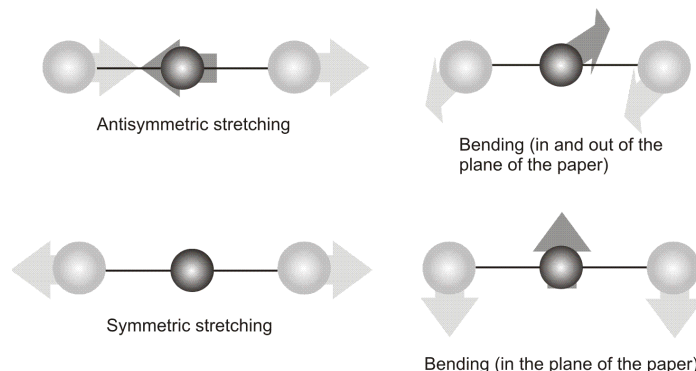


Fig. 2.9: Different modes of vibration for carbon dioxide molecule

If you guessed that all the modes of vibration other than the symmetric stretching vibration would be IR active, then you are quite right. In all the stages of symmetric stretching vibration mode the dipole moment of the molecule remains zero. You would recall from above that for a vibrational mode to be IR active it must be accompanied by oscillatory dipole moment. So, the IR spectrum of carbon dioxide molecule is expected to show a signal each for the fundamental vibrations and the corresponding overtones for all the IR active modes. However, in addition, we may also have weak bands due to combination of two fundamentals vibrations called **combination bands** or difference of two fundamentals called **difference bands** etc. Thus, the spectrum for CO_2 is expected to have a number of signals. This is for a small molecule with just three atoms, you can very well visualise that for larger molecules the IR spectrum would be quite complex. A typical IR spectrum is given in Fig. 2.10.

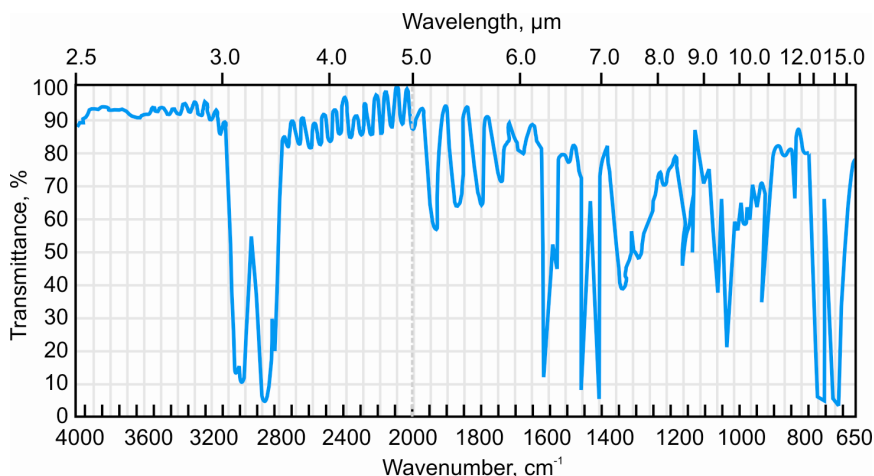


Fig. 2.10: A representative IR spectrum for a polyatomic molecule

In an IR spectrum, on X-axis the position of the signal is given either in wavenumber or wavelength whereas the Y-axis represents percent transmittance. The wavenumber unit (in cm^{-1}) however is preferred over wavelength (in μm , micrometers).

SAQ 3

Calculate the number of modes of vibrational motion for methane, CH_4 which has a tetrahedral shape.

SAQ 4

List the advantages of IR spectrometry over UV-VIS spectrometry.

13.3.2 Basic Instrumentation for IR spectrometry

The technique of IR spectrometry is used extensively, and its instrumentation has also advanced over time. There are three types of instruments commonly used. These are

- Dispersive infrared spectrometers
- Non-dispersive infrared spectrometers, and
- Fourier-transform infrared spectrometers

However, we would briefly describe a dispersive IR spectrometer-the simplest of the three types. A dispersive IR spectrometer typically consists of three basic components: radiation source, monochromator, and detector besides sample compartment and processing devices. A schematic diagram of a typical dispersive spectrometer is shown in Fig. 2.11.

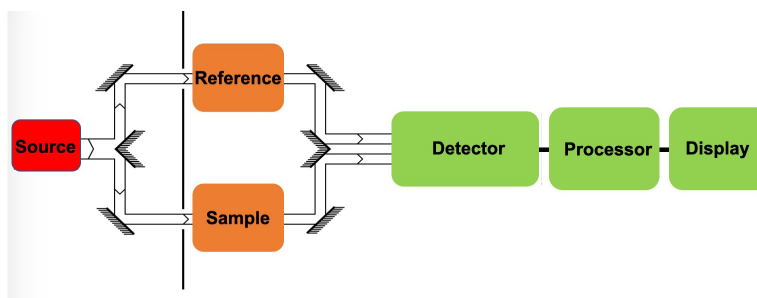


Fig 2.11: A schematic diagram of a dispersive IR spectrometer

In a typical dispersive IR spectrometer, radiation from an IR source is split into two parts. These equivalent beams pass through the sample and reference chambers respectively. The radiation coming out of these is then dispersed by monochromators into their component frequencies. These beams then are made to fall on the detector, that generates an electrical signal that is sent to the processor unit and results in a recorder response.

13.3.3 Environmental application of IR spectrometry

The identification of molecular structures of wide range of organic, and inorganic species and the determination of their concentration in an environmental sample is an essential part of environmental analysis. The bands in the IR spectrum of the sample occur at discrete frequencies and are related to the molecular structure of a sample. This makes the IR spectrum an important analytical tool. These absorption frequencies in the IR spectrum help in the identification of the chemical nature of the sample whereas the intensity of the signals can be used for quantitative determination of its concentration. The quantitative determinations by IR spectrometry rely on the Beer's Law which you have learnt above.

The major advantage of IR spectrometry over other techniques is that practically most of the species of environmental importance can be analyzed quantitatively as well as qualitatively. The added advantage of the technique is that it is nondestructive i.e., the sample is not damaged and also it allows for in situ and remote measurement of samples in different physical states. IR methods for air emission monitoring and analysis have been in use for over past 60 years, however its usage has dramatically increased in the past 2-3 decades due to the developments in instrumentation.

Let us outline some of the environmental applications of IR spectrometry.

- Routine identification and quantification of gaseous pollutants like SO_2 , NO_2 , NH_3 , and O_3 in the atmosphere by continuous air pollutants analyzer. The available instruments can measure these pollutants simultaneously by using different sensors.
- The measurement and the monitoring of the atmospheric gases. In these applications the air is made to enter the absorption cell that is in the optical path of the instrument. The species of interest are identified by the absorption of predetermined frequencies specific for the species.
- Determination of volatile organic compounds (VOC) emitted into the environment from industrial and biogenic sources.
- The technique can be used in waste management by getting the information about the stage of organic matter decomposition and also for monitoring of landfill remediation.
- Determination of the soil organic matter, SOM and nitrate in soil samples and monitoring of bioremediation processes of polluted soils by microbial strains.
- The versatility of the technique can be gauged from the fact that it allows remote detection and identification of pollutant clouds in the atmosphere.

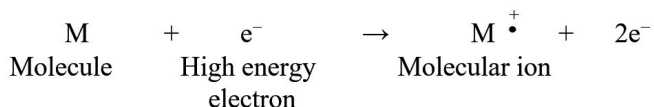
- Determination of toxic and carcinogenic contaminants like chlorinated aliphatic hydrocarbons and chlorinated aromatic hydrocarbons (CHCs) in water samples.

13.4 MASS SPECTROMETRY

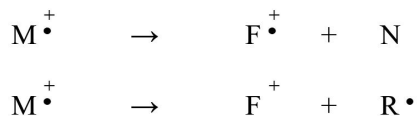
You would recall from the introduction above that mass spectrometry is not a spectroscopic method in true sense, as it does not involve interaction of electromagnetic radiation with matter. However, it is generally clubbed with the spectrometric methods due to its importance in structure determination and quantification. So, what is mass spectrometry and what is its principle? Let's learn about the principle of mass spectrometry.

13.4.1 Principle of mass spectrometry

In mass spectrometry we study the consequences of bombardment of the species to be determined taken in vapour phase, with high energy (~ 70 eV) electrons. This leads to the ionisation of the species by knocking off an electron from it to give a positively charged ion called **molecular ion**, M^+ . As the molecular ion carries a charge as well as a free electron it is more appropriately called a **radical ion** or **radical cation**.



The excess energy of the impacting electrons causes the molecular ions to carry a large amount of energy. This energy is much more than that required for breaking the bonds in the molecular ion. As a consequence, the highly energetic molecular ions break down to give fragments, which in turn undergo further fragmentation to yield still smaller fragments. The molecular ion fragments from the vulnerable places and depending on the nature of the molecular ion there are a number of ways in which the fragmentation can take place. This results into a pool of fragments of the molecule being analysed. In one of the ways of fragmentation, the molecular ions may dissociate into smaller fragment ions (F^+) and a neutral molecule. Alternatively, the odd-electron radical cation may break down to give an ion and a radical as fragments as shown below.



These ions are then separated and detected according to their mass to charge (m/z) ratio using magnetic and/or electrostatic fields. The identified fragments are then put together to determine the structure of the molecule being analysed i.e., the fragments provide clue to the structure of the molecule.

A typical mass spectrum is a graphical representation of the m/z values of the identified fragments against their relative amounts or intensities. The x-axis represents the m/z values of the detected ions, and the y-axis represents the relative abundance of each of the detected fragment ion. For this purpose, the most abundant fragment is arbitrarily assigned an intensity value of 100 and is called the **base peak**. The abundances of all other fragments are represented as the percentage of the base peak. It is important to note that the base peak need not necessarily be the molecular ion peak. Further, since in most of the cases the value of z equals 1, the x-axis effectively represents the formula mass of the detected fragment ions.

Let's take the mass spectrum of methanol as an example, The mass spectrum of methanol (molar mass = 32 g mol^{-1}) is shown as a typical mass spectrum in Fig. 2.12. You may note that the molecular ion peak is at m/z of 32 whereas the peak at m/z of 31 is the base peak (i.e., of highest intensity, arbitrarily given a value of 100).

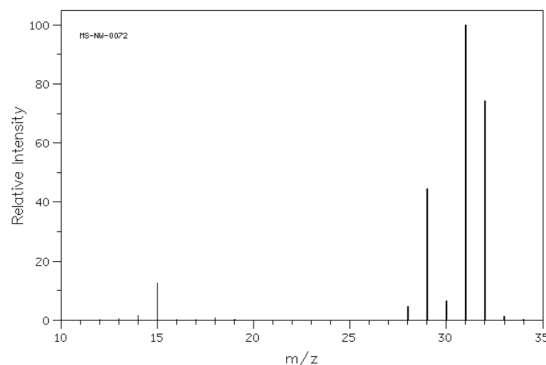
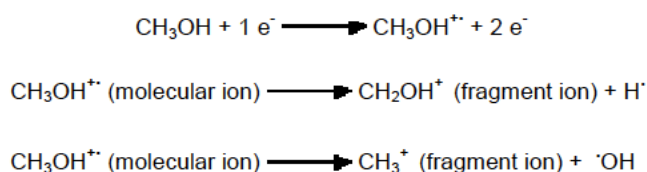


Fig. 2.12: Mass spectrum of methanol (CH_3OH)

The presence and the intensity of peaks at values greater than that of the molecular ion can provide important information about the elemental composition of the molecule.

If you look closely at the spectrum, you will find that in addition to the molecular ion and the fragment ion peaks there is a small signal at $m/z=33$ and is the $[\text{M}+1]^+$ peak. You may be wondering where does this peak come from? The origin of this peak can be explained by taking the natural abundance of the isotopes of constituent atoms of a molecule into account. Let's understand this.

There are three types of atoms in the methanol molecule i.e., C, H and O and each of these has more than one isotope. To understand the $\text{M}+1$ peak in methanol let's just consider the isotopes of Carbon. There are two stable isotopes of carbon i.e., ^{12}C and ^{13}C with the natural abundance of 98.9 % and 1.1 % respectively. This means that if we have 1000 molecules of methanol, 989 of them would contain ^{12}C isotope whereas 11 molecules would have ^{13}C ; in other words, 989 molecules would have a molecular mass of 32 whereas 11 would have a mass of 33. These 11 molecules with a mass of 33 are responsible for the $\text{M}+1$ peak and the peak is called an **isotopic peak**. The oxygen isotope ^{18}O would contribute to the origin of $\text{M}+2$ peak whereas deuterium, the isotope of hydrogen would add to $\text{M}+1$ peak though

the contribution is much smaller. Having learnt about the basic principle of mass spectrometry and origin of mass spectrum let us learn about the instrumentation required to obtain mass spectrum. However, before that answer the following simple question to assess your understanding of the basics of mass spectrometry.

SAQ 5

Define the following terms:

- i. Molecular ion
 - ii. fragments
 - iii. Base peak
 - iv. Isotopic peak
-
-
-
-

13.4.2 Instrumentation for mass spectrometry

You have learnt that in mass spectrometry the substance to be analysed is ionized with high energy electron beam and the resulting fragments are sorted and detected. Accordingly, there are two main components of a mass spectrometer; the ionization chamber where the substance is ionized and the fragments are produced, and the analyzer in which the fragments are sorted and detected. In addition, we need to have sample inlet, a detector and a data processing unit. The block diagram of a mass spectrometer is given in Fig. 2.13.

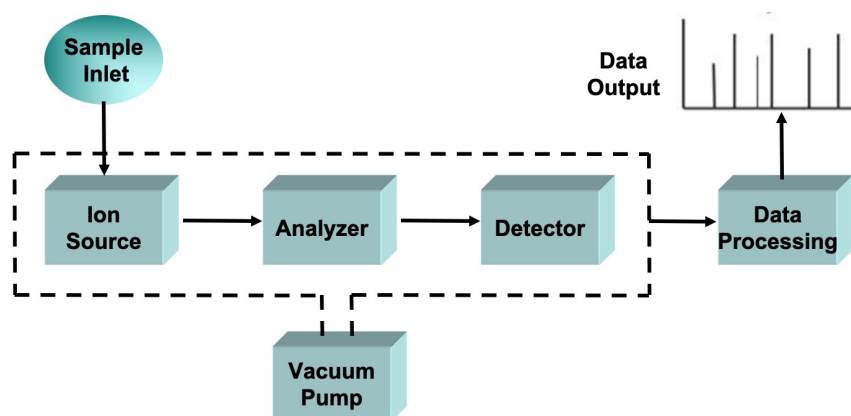


Fig. 2.13: A schematic block diagram for a mass spectrometer

There are different ways of ionisation and also for sorting and detection of fragments. As a consequence, we have a wide variety of mass spectrometers employing different ionisation and detecting techniques. However, we would give a brief account of a simple mass spectrometer using electron ionisation, EI for ionisation and magnetic sector for sorting of fragments. Let's first learn about electron ionisation-a commonly used method of generating ions in mass spectrometer.

Electron ionisation, EI (earlier called electron impact) is oldest and one of the commonly used methods for ionisation of the substance to be analysed. In this method, a beam of electrons having energy of 10-150 eV, typically ~70 eV is made to pass through the sample in the gas-phase. These electrons knock off an electron from the molecule and generate a positively charged ion as discussed above. The process for simple molecule like methanol can be represented as



The ions so obtained are accelerated to have same kinetic energy and are passed through a magnetic analyser so as to separate the fragment ions.

Magnetic sector analyser: it consists of a curved and evacuated metallic tube through which the fragment ions from the ionisation chamber are made to pass through as they travel to the detector. An electromagnet or a permanent magnet is fixed perpendicular to the tube to provide a stable and uniform magnetic field. The ions entering the analyser have approximately the same kinetic energy, but different masses. As a consequence, they have different velocities; heavier ions are slower.

In order to separate different ions on the basis of their m/z values the field strength of the electromagnet is varied. At a given magnetic field strength, only the fragments of a certain m/z value would be able to pass through the circular path without hitting the analyser tube; rest of the ions having larger or smaller m/z values would hit the tube and get destroyed. By continuously increasing the strength of the electromagnet, the fragment ions of increasing m/z values are able to pass through the analyser and get detected at the detector. The ions are generally detected by suitable electron multipliers, which quickly provide a proportional electrical signal that can be processed, stored or suitably displayed as a mass spectrum. This job is done by a signal processing and output unit.

The process described above for generation of fragments is one of the commonly used methods. With the advancement in instrumentation and varied nature of the samples to be analysed a wide array of methods are available. Similarly, for separation of fragments also a number of techniques are available. The combination of ionisation methods and techniques of separation and detection of fragments different types of mass spectrometers are available.

13.4.3 Hyphenation of MS with other techniques

Mass spectrometry is an important technique for the identification of substances of diverse types. However, many a times the substance to be determined is not available as a pure sample. It is part of a matrix say a pollutant in water or soil. In such cases the analytical procedure involves the separation or isolation of the substance of interest and then its determination. Further, many a times we may have a mixture of closely related substances to be determined, say a number of amino acids in a protein hydrolysate. In such and many other cases it becomes useful to couple a separation technique like, GC or LC with one of the suitable variants of mass spectrometry. In certain other cases where metal ions are to be analysed an atomic spectrometric method is integrated with mass spectrometry. This integration of two methods is termed hyphenation and is indicated by a hyphen (-) for example,

Gas Chromatography-Mass Spectrometry (GC-MS), Liquid Chromatography-Mass Spectrometry (LC-MS), Inductive Coupled Plasma spectrometry – Mass Spectrometry (ICP-MS) etc. The hyphenation exploits the benefits of both the techniques.

GC-MS is one of the most popular hyphenated techniques involving mass spectrometry. Compounds that are small, volatile, and stable in high temperature prevalent in GC conditions can be easily analyzed by GC-MS. In a typical GC-MS setup, a sample injected into the GC device, is vaporized, separated in the GC column and fed into a mass spectrometer. The GC separates the components of a mixture in time and the mass spectrometer provides information that helps in the structural identification of each component. A schematic diagram showing the arrangement of different instrumental components is given in Fig. (2.14)

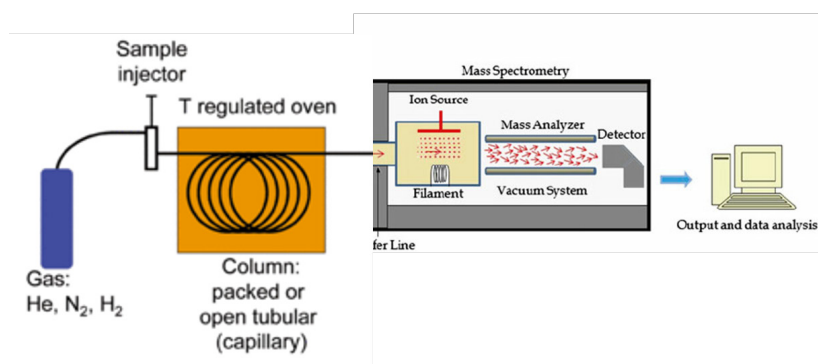


Fig. 2.14: A schematic diagram for a GC-MS instrumental setup

13.4.4 Environmental applications of mass spectrometry

Environmental pollution is undoubtedly one of the most prominent areas of current scientific endeavor. Its detection, mitigation as well as its minimization are all crucial. Mass spectrometry is extensively used to analyse the effects of natural and man-made substances on the environment. There is a dire need to precisely monitor these effects. Mass spectrometry can be used for detecting and analysing pollutants like heavy metals, pesticides, industrial wastes, explosives toxins and many more. As these substances are generally present in very low amounts, mass spectrometry becomes a technique of choice. Some of the environmental applications of mass spectrometry are given as under:

- Detection of heavy metals like lead and mercury in environmental samples at a concentration of the order of ng g⁻¹
- Determination of the concentrations of heavy metals like chromium (Cr) in soil and water samples using ICP-MS
- The characterisation and quantitation of organic pesticides using GC coupled mass spectrometers
- Evaluation of fate of newly developed pesticide in the environment in terms of its transport properties and degradation products etc.

13.5 SUMMARY

In this introductory unit on spectrometry we have discussed about the principle and applications of three important analytical tools. Two of these, viz., UV-VIS spectrophotometry and IR spectrometry being techniques based on spectroscopy. We started the unit by defining spectroscopy as an important domain that concerns study of interaction of electromagnetic radiation with matter. We then went on to clarify the difference between spectroscopy, spectrometry and spectrophotometry before taking up UV-VIS spectrophotometry.

In UV-VIS spectrophotometry you have learnt that it is one of the oldest spectroscopic based on the interaction of electromagnetic radiation in the UV-VIS region with molecules, ions or complexes. The electromagnetic radiation in the UV-VIS region causes transitions amongst the electronic energy levels of the species with which it interacts. The UV-VIS spectrum obtained as a consequence of the interaction is a plot of wavelength versus the intensity of absorption and consists of a number of signals called absorption bands. These bands are characterised by three parameters viz., the position, intensity and the width of the absorption band. The relationship between the intensity of absorption and the concentration forms the basis for quantitative applications of UV-VIS spectrometry. This relationship has been established in terms of Beer-Lambert's law and its application clarified with the help of examples. the applications of UV-VIS spectrophotometry in environmental analysis have also been enumerated. These are primarily quantitative in nature.

The IR spectrometry is based on interaction of electromagnetic radiation in the IR region with different species. The interaction is manifested in terms of transitions amongst the quantized vibrational energy levels. The origin of different signals in the resulting spectrum have been explained. The applications of IR spectrometry spread over wide areas of environmental concern. These span over both the quantitative as well as qualitative analysis of environmental samples.

The third tool we took up was mass spectrometry. In mass spectrometry the sample being analysed is ionised by a suitable technique and the molecular ion and its fragments are then separated and analysed. The m/z ratio of the fragments and their intensities are then used to decipher the structure of the sample. Mass spectrometry has wide ranging applications in environmental science and these have also been outlined.

13.6 TERMINAL QUESTIONS

1. Differentiate between the terms spectroscopy and spectrometry.
2. Draw a schematic diagram of a UV-VIS spectrum and list the characteristics of such a spectrum.
3. A 5.00×10^{-4} M solution of an analyte is placed in a sample cell having a path length of 1.00 cm. When measured at a wavelength of 490 nm, the absorbance

of the solution is found to be 0.338. What is the molar absorptivity of the analyte at this wavelength?

4. Draw a schematic energy level diagram and explain the types of transitions observed in organic compounds.
5. Discuss the origin of isotopic peak in the mass spectrum of a molecule.
6. Is mass spectrometry a spectroscopic method? Justify your answer.
7. What is a hyphenated technique? What are its advantages?

13.7 ANSWERS

Self-Assessment Questions

1. We know that according to Beer-Lambert's Law
 $A = \epsilon c b$

Rearranging we get,
 $c = A / \epsilon b$

Given: $A = 0.47$ $b = 2$ cm and $\epsilon = 2.357 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ (from example 2)
Substituting the values,
 $c = 0.47 / 2 \text{ cm} \times 2.357 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3 = 9.97 \times 10^{-2} \text{ mol dm}^{-3}$
2. We are given: Absorbance, $A = 0.40$ path length, $b = 1.0$ cm
We need to first find concentration of benzene:
Given mass of benzene = 15.7 mg = 0.0157 g; volume of solution = 100 cm^3
Molar mass = 78.11 g mol^{-1}
Molar concentration of benzene, $c = \frac{0.0157 \times 1000}{78.11 \text{ g mol}^{-1} \times 100} = 0.02 \text{ M}$

We know that according to Beer-Lambert's Law
 $A = \epsilon c b$

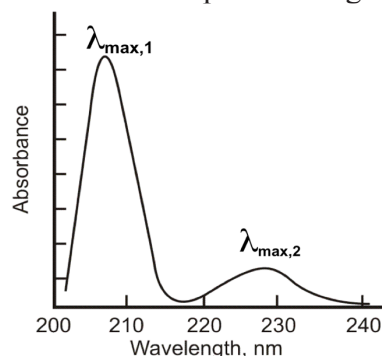
Rearranging we get,
 $\epsilon = A / c b$

Substituting the values, we get $\epsilon = \frac{0.40}{0.02 \text{ mol dm}^{-3} \times 1 \text{ cm}} = 20 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$
3. We know that the number of vibrational modes possible for a non linear polyatomic molecule = $3N - 6$. (Where N is the number of atoms in the molecule)
Here $N = 5$
The number of vibrational modes = $(3 \times 5) - 6 = 9$

4. The major advantage of IR spectrometry over other techniques are as under:
 - i. Most of the species of environmental importance can analyzed quantitatively as well as qualitatively.
 - ii. The technique is nondestructive i.e., the sample is not damaged
 - iii. It allows for in situ and remote measurement of samples in different physical states.
5. The definitions of the given terms are as under
 - a. **Molecular ion:** It is the radical ion or radical cation obtained by the ionisation of the molecule in mass spectrometer. The high energy electrons knock off an electron from the molecule being analysed to give a positively charged ion called molecular ion. It is denoted as .
 - b. **Fragments:** The molecular ions obtained during ionisation in mass spectrometer carry a large amount of energy. As a consequence, these highly energetic molecular ions break down to give smaller species called fragments.
 - c. **Base peak :** In a mass spectrum the peak corresponding to the most abundant fragment is called base peak and is arbitrarily assigned an intensity of 100
 - d. **Isotopic peak:** In mass spectrum certain peaks are observed at m/z values greater than that of the molecular ion. These arise due the molecules having heavier isotope in natural abundance and are called isotopic peaks. Their intensities are governed by relative isotopic abundance of different atoms present in the molecule.

Terminal Questions

1. Spectroscopy refers to the study of interaction of electromagnetic radiation with matter whereas spectrometry refers to the measurement of consequence of such an interaction.
2. A schematic diagram of a UV-VIS spectrum is given below



The UV-VIS spectrum has the following characteristics

- Position
- Intensity and
- Width

3. We know that according to Beer-Lambert's Law

$$A = \epsilon c b$$

Rearranging we get,

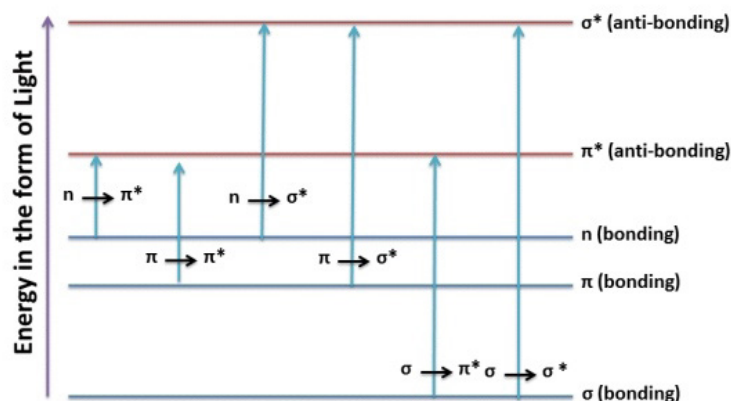
$$\epsilon = A / c b$$

Given: $A = 0.338$ $b = 1 \text{ cm}$ and $c = 5.00 \times 10^{-4} \text{ mol dm}^{-3}$

Substituting the values, we get

$$\epsilon = 0.338 / 5.00 \times 10^{-4} \text{ mol dm}^{-3} \times 1 \text{ cm} = 676 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$$

4. A schematic generalised electronic energy level diagram for organic molecules is given below



Different possible transitions are indicated on the diagram. However, of these two transitions namely $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ are the significant ones.

5. The origin of isotopic peak lies in the existence of isotopes of different atoms. In a given sample under investigation, a certain number of molecules have the presence of heavier isotope of an atom. This adds to the molecular mass and the molecular ion obtained from such a molecule has a higher molecular mass and hence m/z value. These show up as isotopic peak in the mass spectrum and the intensity of such a peak depends on the relative natural abundance of the isotopes of the atom.
6. No, mass spectrometry is not a spectroscopic method because it does not involve the interaction of electromagnetic radiation with the sample.
7. A Hyphenated technique is combination or coupling of two different analytical techniques. This involves a suitable interface and exploits the potential of both the techniques. Generally, one of these techniques happens to be a separation method and the second is a spectrometric method. For example, in GC-MS the analytical sample is separated by gas chromatography and the separated components are analysed by mass spectrometry.

UNIT 14 : CHROMATOGRAPHY TECHNIQUES

Structure

- 14.0 Introduction
- 14.1 Objectives
- 14.2 Gas Liquid Chromatography
 - 14.2.1 Principle
 - 14.2.2 Instrumentation
 - 14.2.3 Application of GLC
- 14.3 High-Performance Liquid Chromatography
 - 14.3.1 Principle
 - 14.3.2 Instrumentation
 - 14.3.3 Types of HPLC
 - 14.3.4 Application of HPLC
- 14.4 Supercritical Fluid Chromatography
- 14.5 Application of Chromatographic Techniques in Environmental Monitoring
- 14.6 Let Us Sum Up
- 14.7 Glossary
- 14.8 Terminal Questions

14.0 INTRODUCTION

Analytical science in recent years has progressed enormously with the discovery of pioneering separation methods. The subject has full-fledged into a separate unit called “separation science”. Numerous journals have been dedicated solely to this field. Limited instrumental methods can be directly used for the quantitative study on account of the presence of interfering substances and ions. These interfering elements must be separated before analysis. These separations are mainly based upon the formation of a second phase with a different concentration of desired constituent and based on physical or chemical properties of the components need to be separated.

The methods usually depend on differences in properties such as mobility, volatility, solubility, exchange equilibrium, surface activity, partition ratio, molecular geometry and kinetic energy. Various chromatographic methods based upon these differences are discussed in the following chapters.

Some chromatographic techniques require some modification, expertise and are time consuming. It requires constant care while performing the experiment. To overcome this problem, nowadays various advanced techniques such as Gas Chromatography (GC) , Gas Liquid Chromatography (GLC), High Power Liquid Chromatography (HPLC), Ultra Performance Liquid Chromatography (UPLC) and Ultra Performance Convergence Chromatography (UPCC) are used by pharmaceutical and research industries. In this unit, we shall study the modern aided chromatography such as GLC, high-performance liquid chromatography (HPLC)

and supercritical fluid chromatography. And also, we shall state the application of these chromatographic techniques in monitoring the environment.

14.1 OBJECTIVES

After studying this unit, you should be able to understand:

- Advanced chromatographic techniques
- Gas-liquid chromatography
- High-performance liquid chromatography
- Supercritical fluid chromatography
- Application of chromatographic techniques in environmental monitoring

14.2 GAS-LIQUID CHROMATOGRAPHY

Gas-liquid chromatography (GLC) is a technique employed for the separation of two phases in a mixture where one is a stationary phase and other is a mobile phase. Stationary phase is a non-volatile liquid coated on a solid surface and mobile phase is a carrier gas which is inert in nature *i.e.* unreactive gas such as Neon, Helium and Argon. Gas-liquid chromatography is a type of partition chromatography. Therefore, it is also known as gas-liquid partition chromatography (GLPC) or vapor phase chromatography (VPC). The instrument used for gas liquid chromatography technique is known as gas chromatograph.

HISTORY

In most of the chromatographic techniques, the mobile phase used was liquid but in 1950, Dr. Martin with his young colleague A.T. James demonstrated a chromatographic technique at the October meeting of 'Biochemical Society' and in that chromatographic technique the stationary phase was liquid and mobile phase was a gas. Thus, that technique was named as Gas-Liquid chromatography or GLC.

14.2.1 PRINCIPLE OF GLC

GLC is based on the partition of stationary phase and mobile phase. Stationary phase is a liquid and it is selected on the basis of polarity by the rule of "like dissolves like". The selected liquid solution is a polar liquid which is able to interact with the solute particles. The sample mixture after passing through the stationary phase and mobile phase will separate on the basis of partition coefficient.

Partition coefficient (K_g) = Conc. of solute in liquid / Conc. of solute in gas

Partition coefficient is directly proportional to the concentration of solute in liquid solution, if the partition coefficient is less than the elution of component is fast and vice-versa. More volatile substances having low boiling point and high vapor

pressure will have more concentration in mobile phase and therefore, will elute faster. Branched chain compounds and compounds having lower number of carbon atoms have low boiling point and are more volatile and therefore, will elute faster than the compounds having higher number of carbon atoms. Similarly, less polar compounds have lower boiling point and will elute faster than the compounds having more polarity. In conclusion, more polar compounds are retained for a longer period in the column.

Retention Time: The time taken by a compound to travel through the column to the detector is called as its retention time and it depends on the following factors:

- **Boiling point:** If the boiling point of compound is low, then its retention time will be less as compared to the compounds having higher boiling point.
- **Solubility in liquid phase:** More solubility in liquid phase implies high retention time.

Temperature of column: Higher the temperature of column, more readily all the solute particles in a column will evaporate. The solute which elutes faster will have lesser retention time.

14.2.2 Instrumentation:

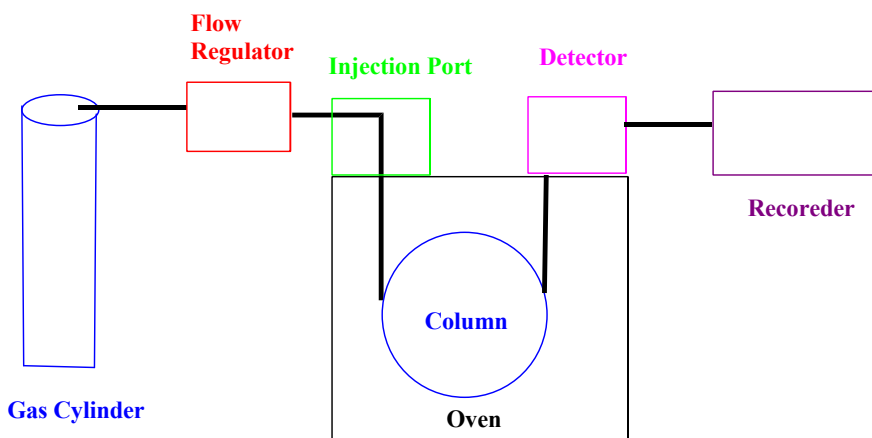


Figure 14.1: Different components of Gas-Liquid Chromatography

1. Injection Port: In injection port, the sample is injected with the help of micro-syringe through a silicon rubber septum and this rubber septum reseals itself after the injection of sample into the column. The injection port is kept into an oven so that if the sample is in liquid state then it can be converted into the vapour phase first and then it is carried into the column with the help of an inert gas *i.e.* carrier gas.

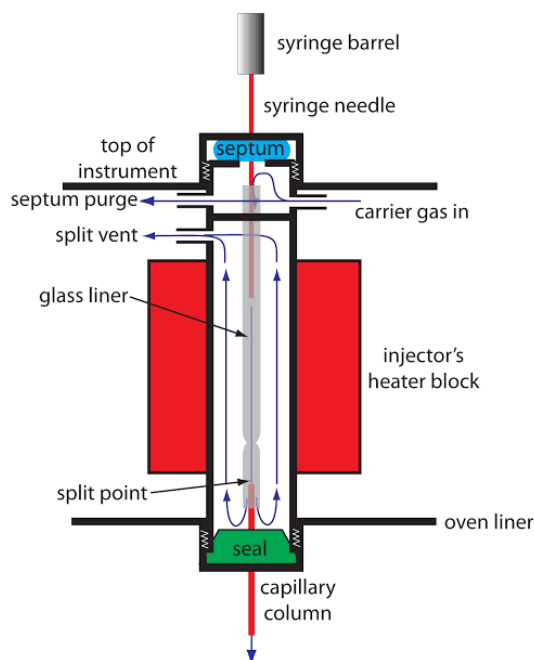


Figure 14.2: Injection port of Gas Liquid Chromatography

In a packed column, 0.1 to 10 μL sample is injected whereas in capillary column, only a small volume of sample is injected. If the sample is in solid state then the sample is placed into a glass ampule and the sample is crushed after placing it in the gas stream.

Injection Temperature: The injection temperature should be high so that the sample can be easily vaporized into the column but it should not be too high, otherwise it will degrade the rubber septum.

2. Columns: Two types of columns are used in GLC:

- **Packed Columns:** Packed columns are of various shapes such as coiled tubes, U- shaped tubes and W- shaped tubes but the commonly used packed columns are coiled tube. These are 1 to 10 cm long and 0.2 to 0.6 cm wide. Columns are made up of Teflon, glass and stainless steel. For inertness, glass column is preferred but for longer columns stainless steel is preferred so that they can be straightened for packing. GLC column is coated with non- volatile liquid.
- **Capillary Columns:** Capillary columns are 25 to 100 mm long and 0.25 to 0.50 mm wide and these are made up of silica and glass. Capillary columns are most commonly used instead of packed columns. Capillary columns are also known as open- tubular columns.

Column temperature: Column temperature is less than injection temperature. It is about 50 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$. If the temperature of column is too high, then the sample is converted firstly into gaseous phase and elution takes place which will lower the quality of resolution. The temperature of column should not be too low because at low temperature, resolution will increase but sensitivity will decrease due to the slow elution of sample and peaks will separated by larger gaps.

3. Detectors: They produce an electrical signal proportional to solute concentration or mass flow rate. GLC detectors are of various types:

- **Thermal conductivity detectors (TCD):** TCD contains a heated filament with an applied current. It is also known as cathetometer. Thermal conductivity detectors are most commonly used detectors for a wide range of solutes. The sensitivity of these detectors is fair. It is about 5 to 20 ng. In TCD the carrier gas containing solute is passed through the cell due to which the change in the filament current occurs. Then the current change is compared with the current in reference cell and the difference is measured and the signal is generated. In TCD, Hydrogen and Helium used as a carrier gas because they have very high thermal conductivity as compared to the other gases. TCD is used for the analysis of permanent gas such as CO₂.
- **Flame Ionization Detectors (FID):** These detectors are used for all organic substances. FID is good for the detection of all hydrocarbons but some oxygenated products respond poorly. The sensitivity of these detectors is very good in the range of about 10 to 100 pg. FID is based on the principle of ionization. Mostly organic compounds after passing through the flame produce ions which are attracted towards oppositely charged electrodes and are measured. The number of ions collected is proportional to the number of carbon atoms in the sample. Signal is generated when the number of ions hitting the electrodes is measured. In FID He and N₂ gases are used as carrier gas.
- **Electron Capture Detector (ECD):** These detectors are used for all those substances that have affinity to capture the electrons, they do not give any signal for aliphatic and naphthenic hydrocarbons. The sensitivity of ECD for halogen containing substances is excellent. The sensitivity is about 0.05 to 1 pg. In ECD the carrier gas is passed which results in the production of electrons and then which produces current between the electrodes. The signal is generated by measuring the amount of lost current. Here carrier gases used are nitrogen and argon.

Detector Temperature: Detector temperature should be high to prevent the condensation of sample components.

4. Recorder: Recorder is a device that records the data from the detector and draws that onto the chart paper.

Operational Procedure:

- The sample is injected into the gas stream first and then it enters into the column.
- The components of the mixture are then passed in a stream of gas through the column.
- Then distribution of compound takes place between the phases in different extents and elute out at different time and therefore, having different retention time.

- The compound which dissolves in the stationary solvent is having more retention time than others and hence, elute out slowly.
- The volatile compounds having lower boiling point emerges out rapidly.
- The compounds that are emerging out from the column are detected with the help of detector.
- Then the recorder plots the signals detected by the detector as a chromatogram.
- Then the peaks will be observed for each component of mixture on a chromatogram.

14.2.3 Applications:

- GLC is used for qualitative and quantitative analysis of organic compounds.
- GLC technique is used in many fields such as in agriculture industry, food industry, pharmaceutical, environmental field, forensic field, biotechnology field, cosmetic industry and chemical industry.
- GLC is useful for the estimation of pesticide and insecticide residues in food and other consumables.
- It is useful in the detection of pollutants in water and other food stuffs.
- In this technique very minute amount of substance can also be measured.
- As the volatile samples are needed for this technique so the samples of human breath, blood, saliva and other secretions which contains large amount of volatile organic substances can be easily analyzed by this this technique.
- This technique is also useful for the analysis of effects of environment.
- GLC is also useful for determining the components of air in air samples.
- GC/MS is used in identifying the amount of chemicals in drugs in pharmaceuticals industries.
- This technique is also useful to measure the amount of chemicals needed for their products in cosmetic industries.
- It is highly sensitive technique.
- In this technique the analysis is highly accurate and precise.

ADVANTAGE OF GLC OVER GC CHROMATOGRAPHY

- In GLC the process of separating the compounds in a mixture is carried out between a gas mobile phase and a liquid stationary phase whereas in column chromatography mobile phase is liquid and stationary phase is solid.
- In GLC temperature of gas phase can be controlled but in column chromatography there is no way of controlling any temperature of mobile phase.

SAQ 1

What are different mobile and stationary phase used in Gas Liquid Chromatography.

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SAQ 2

What is different component used in Gas Liquid chromatography?

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14.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

HPLC is a powerful technique used for separation and analysis of components of mixtures. It yields high performance and high speed compared to traditional columns because of forcibly pumped mobile phase creating pressure due to which it is also referred as high- pressure liquid chromatography.

In twentieth century, liquid chromatography was discovered for separating coloured compounds. In 1906 Mikhail S. Tswett a (Russian botanist) used this technique to purify mixtures of plant pigments into the pure constituents, on the basis of their interaction to the stationary phase.

Tswett filled an open glass column with particles such as chalk powder (calcium carbonate) and alumina, using petroleum ether. The sample (solvent extract of homogenized plant leaves) to be separated was then poured in the column and allowed to pass through the particle bed.

14.3.1 PRINCIPLE OF HPLC

The principle of separation is adsorption. Separation of components takes place due to difference in affinity of compounds towards stationary phase. Compounds with stronger attachment to the particles (stationary phase) moved slower, while the compounds with strong attachment to the solvent (mobile phase), moved faster. This is because the compounds in the sample get distributed differently between the mobile phase and the stationary phase.

HPLC is a type of column chromatography that draws a sample mixture in the solvent (mobile phase) through a column with chromatographic packing material (stationary phase) at high pressure. The sample is being carried by a moving gas (stream of helium or nitrogen).

HPLC has the ability to separate and identify the compounds, present in the sample which are in very trace amounts (as low as parts per million) and can be dissolved in the liquid. It is applicable for both volatile and non-volatile compounds. It is used in qualitative as well as quantitative analysis, due to its high resolution. Sample retention time will vary depending on the interaction of sample with stationary phase, the solvent used and the molecule being analysed. As the sample passes through the column it interacts between two phases at different rate due to different polarities of the analytes. Because of this versatility, this technique is being used in many industries such as pharmaceutical, environmental, forensics and chemicals.

14.3.2 INSTRUMENTATION

- Pump to force mobile phase through a system; suitable pressure gauges *i.e.*, flow meters control such pressure (fig 3).
- Sample injection port or valves to inject sample in the system of the mobile phase as head of separation column.
- Separation column in which sample components are separated into separate peaks before elution and finally.
- The detectors and read out device, including computer accessories. First, we would consider mobile phase, stationary support and stationary phase, kind of the columns and finally various kinds of detectors employed in analysis.

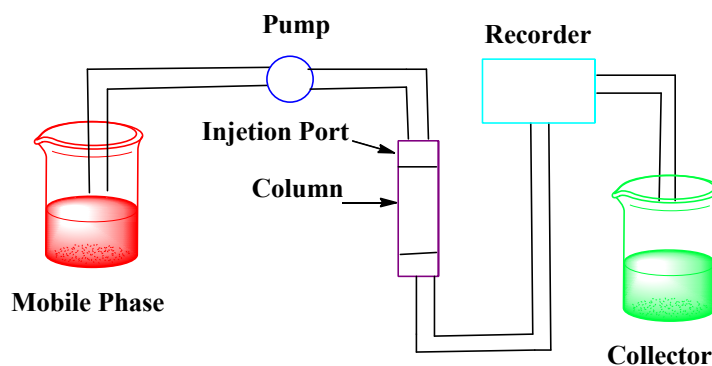


Figure 14.3: Different components of HPLC

FUNCTIONING OF HPLC:

- The liquid sample is injected in small volume into a tube packed with small particles (3μ to 5μ in diameter) called stationary phase.
- This is where the individual components of the sample are moved down to the column with a liquid (mobile phase) forced through the column by high pressure delivery by a pump.

- The components of the mixture are separated by the column packing, due to various chemical or physical interactions between their molecules and the packing particles.
- The separated components are detected at the exit of the column by a flow-through device (detector) that measures their amount. The response obtained from the detector is called a liquid chromatogram.
- In terms of principle, LC and HPLC work the same way except the speed, efficiency, sensitivity and ease of operation of HPLC is much more superior.

Chromatogram: It is a graphical presentation of detector response which is used as a measure of the concentration of the analytes in the effluent versus effluent volume or time.

Baseline: Baseline is a portion of chromatogram recording which is attained when mobile phase arises from the column.

Column heater is used to maintain consistent temperature in the column in order to get accurate results.

14.3.3 TYPES OF CHROMATOGRAPHY

I BASED ON THE MODE OF SEPARATION

1. Normal Phase HPLC

In this method analytes are separated on the basis of polarity. Normal Phase HPLC uses polar stationary phase (hydrophilic) and a non-polar mobile phase (hydrophobic). Therefore, stationary phase is mostly silica and mobile phase may be hexane, chloroform, methylene chloride, diethyl ether or mixtures of these. Polar sample interacts better with the polar surface of column and persists for longer time than less polar material, as they elute out fast. Alumina, a porous particulate form of aluminum oxide is used as a stationary phase. It has a highly active basic surface and is more hygroscopic than silica. Its activity is measured according to Brockmann scale for water content.

2. Reverse phase HPLC

The stationary phase is non-polar (hydrophobic) in nature, while the mobile phase is a polar liquid (hydrophilic), such as mixtures of water and methanol or acetonitrile. Reverse phase HPLC functions on the principle of hydrophobic interactions hence the non-polar material in the sample will retain for longer in the column than the polar.

Non polar-non polar bonds and polar-polar bonds have more affinity than nonpolar-polar bonds. Reverse phase chromatography is more commonly used for drugs, as they are usually hydrophilic.

Table 1: Difference between Normal Phase and Reverse Phase HPLC

	Normal phase	Reversed phase
Stationary phase	Polar (silica gel)	Non-polar (C18)
Mobile phase	Non-polar (organic solvent)	Polar (aqueous/organic)
Sample movement	Non-polar fastest	Polar fastest
Separation based on	Different polarities (functionality)	Different hydrocarbon Content

II BASED ON PRINCIPLE OF SEPARATION

1. Adsorption Chromatography

In this chromatography the molecules of solute bond directly to the surface of the stationary phase. The efficiency of separation depends on:

- Solubility of molecule in mobile phase.
- Binding strength to the stationary phase.

Greater the binding strength slower will be the movement of the molecules. The matrix of stationary phase can be made of alumina or silica. Silica (SiO_2) is acidic in nature whereas alumina can be acidic, basic or neutral. To increase the resolution/separation, the surface should be of uniform in size and the surface area should be increased.

2. Affinity Chromatography

This is most selective chromatographic technique is based on the specific reversible interaction between the one kind of solute molecule need to be purified and the affinity ligand immobilized to a solid support.

Example: the molecule that is immobilized on a stationary phase could be an antibody to some specific protein. When solute containing mixture of proteins is passed through this immobilized molecule, only a specific protein reacts with this antibody, thereby binding it to the stationary phase. By changing the ionic strength or pH, this protein can be later extracted.

3. Ion- Exchange HPLC

Ion exchange chromatography allows the separation of ions and polar molecules based on the charge they carry. Here like charges repel each other and unlike attracts. This technique is used for ionic or ionisable samples like- proteins, small nucleotides and amino acids. The stationary phase is based on the nature and strength of the acidic and basic functions and the ions types they attract and retain. The positively charged ions are separated by cation exchange method on a negative surface. The negatively charged ions are separated by the anion exchange method on a positive surface. Strong ion exchangers (bear functional groups like (quaternary amines or sulfonic acids) are always ionised, and separate weak ions. Weak ion exchangers (secondary amine or carboxylic acid functional group) may

get neutralized at certain pH and lose their ability to retain ions by charge, but when charged they separate strong ions.

Retention is based on the attraction between solute ions and charged species. The stronger the charge on the sample, the stronger will be the attachment to the ionic surface and thus, the longer it will take to elute out. The mobile phase acts like an aqueous buffer, where both, ionic strength and pH control the elution time. Resin (stationary solid phase) is used to attach anions or cations covalently onto it. Oppositely charged solute ions in the mobile phase are attached to the resin by electrostatic forces of attraction.

4. Ion-pair chromatography

In this chromatographic technique, ions in the solution can be neutralized or paired and then separated as an ion-pair on a reverse-phase column. Ion-pairing agents are nothing but the ionic compounds comprising of hydrocarbon chain which imparts hydrophobicity to retain the ion pair on a reversed-phase column.

5. Gel permeation chromatography

The interaction between the stationary phase and solute does not take place. The materials used to fill the column have precisely controlled pore sizes. The gaseous or liquid phase passes through a porous gel separating the molecules based on their size. The pore size is normally small and excludes the larger solute molecules, but allows smaller molecules to enter the gel, due to which they flow through a larger volume. This results in larger molecules passing through the column at a faster rate compared to the smaller ones. Larger molecules get washed first from the column, as smaller molecules penetrate inside the pores of the packing material and get separated later.

6. Chiral chromatography

This technique helps in separation of stereoisomers. In enantiomers, there are no physical or chemical differences apart from being three-dimensional mirror images. To enable this technique, either mobile phase or stationary phase should themselves be chiral to provide different affinities between the analytes.

BASED ON ELUTION TECHNIQUE

1. Isocratic elution

In this separation technique, the mobile phase composition remains constant throughout the procedure.

2. Gradient elution

It is the process of separation in which the mobile phase composition is changed. In this technique, the retention of the later eluting components is decreased, so that they elute faster.

BASED ON TYPE OF ANALYSIS

1. Qualitative analysis

It is the analysis of the substance in order to know the nature of its chemical constituents. We can separate the individual components but cannot find the quantity.

2. Quantitative analysis

It is used to determine the amount and proportion of the chemical constituents. Quantity of the impurity and individual components can be found out.

14.3.4 APPLICATIONS OF HPLC TECHNIQUES

Pharmaceutical Application

- Tablet dissolution study of pharmaceutical dosages form.
- Pharmaceutical quality control.

Environmental Application

- Detection of phenolic compounds in drinking water.
- Bio-monitoring of pollutants.

Applications in Forensics

- Quantification of drugs in biological samples.
- Identification of steroids in blood, urine etc.
- Forensic analysis of textile dyes.
- Identification of cocaine and other abusive drugs in blood and urine

Food and Flavour

- Determination of quality of water and soft drinks
- Sugar analysis in fruit juices.
- Analysis of polycyclic compounds in vegetables.
- Preservative analysis

Applications in Clinical Tests

- Urine analysis, antibiotics analysis in blood.
- Analysis of bilirubin, biliverdin in hepatic disorders.
- Recognition of endogenous neuropeptides in extracellular fluid of brain, etc.

Why HPLC is preferred over other chromatography techniques?

- HPLC works under pressure of around 50-350 bar, unlike liquid chromatography which relies on the force of gravity to pass through the mobile phase. Due to this small sample amount can be separated.
- Column dimensions are 2.1-4.6 mm diameter and 30-250 mm length, and are made with smaller adsorbent particles (2 μ m-50 μ m), this gives it a superior resolving power (ability to distinguish compounds).
- HPLC is intensely fast and efficient. It uses a pump, preferably than gravity, to force a liquid solvent through a solid adsorbent material, with different chemical components separating out as they move at different speeds.
- Highly sensitive because whole process of completion takes only 10-30 minutes only.
- Accurate because whole system is automated.

DISADVANTAGE OF HPLC

- It is costly and complex because it requires large quantities of expensive solvents
- Lack of ideal universal detector.
- Less separation efficiency than capillary gas chromatography.
- Relatively difficult for novices.

ULTRA PERFORMANCE LIQUID CHROMATOGRAPHY

It is an advanced type of HPLC, which has better instrumentation and column technology which leads to increase in resolution, speed and sensitivity in liquid chromatography. Columns are made with much smaller particles (1.7 micron) and instrumentation with specialized capabilities designed to deliver mobile phase at 15,000 psi (1,000 bar) which gives new level of performance.

SAQ 3

What is reverse and normal phase HPLC?

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SAQ 4

What are the different components of HPLC?

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14.4 SUPER CRITICAL FLUID CHROMATOGRAPHY

Supercritical fluid chromatography was first proposed in 1958 by Jim Lovelock. He suggested that polar components could be separated by using inorganic gases, above their critical points as a chromatographic mobile phase, where mobile phase was considered to be inert carrier.

Ernst Klesper was first to actually separate thermally labile porphyrins using a fluid above its critical point. He used di-chlorodifluoromethane and mono-chlorodifluoromethane as mobile phase.

After Klesper's paper, scientists aimed to find the perfect mobile phase by examining purine, nucleotides, steroids, sugar, amino acids, and many more substances using gases such as He, N₂, CO₂ and NH₃.

Currently SFCs involve a silica (or silica + modifier) packed column with CO₂ (or CO₂ + modifier) mobile phase.

Supercritical fluid chromatography

This technique uses highly compressed gases above its critical temperature and pressure as mobile phase instead of an organic solvent. Its principle is similar to those of high -performance liquid chromatography (HPLC), but Supercritical fluid chromatography (SFC) typically uses carbon dioxide as mobile phase.

Supercritical fluid is any substance which exists above its critical point of pressure and temperature, where distinct liquid and gas phases do not exist.

Critical point is the point at which two phases of a substance become indistinguishable from one another. It is the end point defined by critical pressure and critical temperature.

The fluid can solubilize the material of interest with manipulation of pressure and temperature. The sample is placed in an extraction vessel and to dissolve the sample it is pressurized with CO₂. Sample is transferred to a fraction collector and CO₂

loses its solvating power after depressurizing it causing the precipitate of desired material. Condensed CO₂ can be recycled.

Why CO₂ is used?

Supercritical fluid chromatography uses CO₂ modified with the organic solvents and sometimes a highly polar additive. CO₂ is preferred because:

- Easily available
- Has an accessible critical point
- Relatively safe
- Inexpensive
- Miscible with wide range of highly polar modifiers
- Non-toxic in nature
- Non-flammable during reaction
- Dissolving power and selectivity can be controlled by selection of suitable pressure/temperature combination.

Modifiers or co-solvents

SFC applications are performed on comparatively polar stationary phases having CO₂ modified with an organic solvent and sometimes even other highly polar components, called additives such as acids and bases.

Methanol is widely used modifier and most polar modifiers which is completely miscible with CO₂.

Advantage of methanol as modifier

- It is widely available and inexpensive.
- It has low UV cut-off.
- It has relatively low toxicity.
- It is completely miscible with CO₂.

Physical properties of supercritical fluid

Density

Density of supercritical fluid lies between that of a gas and liquid, but it is closer to that of a liquid. Density increases with increase in pressure at constant temperature. However, as the temperature increases with constant pressure, density of supercritical fluid decreases. It is a better carrier than gases due to its higher density.

Viscosity

Viscosity of supercritical fluids is almost same as a gas and one-tenth of that of a liquid. They are less resistant than liquids towards component flowing through.

Diffusivity

Supercritical fluid has a diffusivity of 100x that of a liquid and 1/1000 to 1/10000 x less than a gas. Liquid has less diffusivity than supercritical fluid. Diffusivity is directly proportional to temperature and inversely to pressure. Higher the diffusivity, faster will be the chances of carrier for analytical applications.

ADVANTAGE OF SFC OVER NORMAL HPLC

- HPLC is comparatively expensive than SFC as it requires high purity solvent as mobile phase and further its purification but no such thing is required for CO₂.
- Due to high diffusivity of the supercritical fluid it has much greater resolving power and shorter column lengths can be used as more interactions can occur in shorter span. Supercritical fluids have low viscosities which allows high flow rate with low pressure and faster analysis (5 to 10 X faster).
- It produces less toxic and flammable waste.

ADVANTAGE OF SFC OVER GC

- It allows fast analysis of thermally labile compounds.
- It has wide range of detectors as compared to GC.
- Supercritical fluids have greater solvating power so SFC has larger molecular ranges which involve non-volatile molecules, polar to be analyzed.
- Compounds with high molecular weight can be analyzed.

Instrumentation

Supercritical fluid chromatography (SFC) instrument consist of a mobile phase container which usually is a pressurized gas cylinder, mobile phase, a modifier, a pump, an injector, an oven, a column in a thermostatic compartment, a microprocessor, and detector (fig 4).

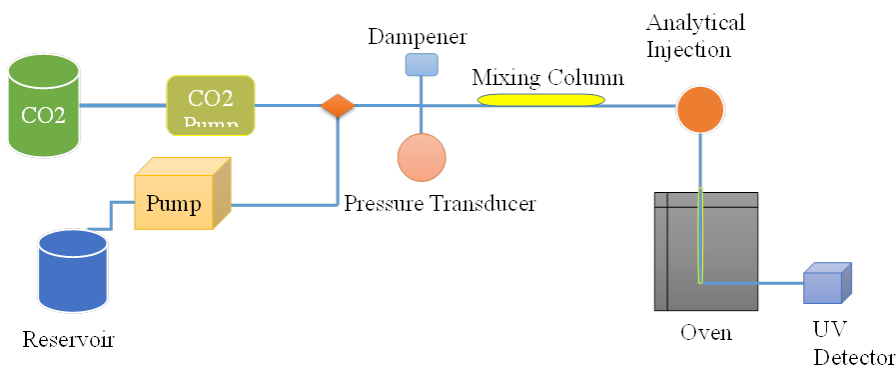


Figure 14.4: Different components of SFC

Stationary phase

Open tubular columns and packed columns are two most common columns used in SFC. It has internal coating of cross-linked siloxanes material as a stationary phase. Length of columns ranges from 10 to 20 m.

Mobile phase

The most common supercritical fluid which is used in SFC is carbon dioxide because of critical temperature and pressures are easy to approach. Other than carbon dioxide, ethane, n-butane, ammonia, NO₂, THF can be used.

Modifier

A second fluid which is called modifier fluid such as (alcohol, chloroform, cyclic ethers *etc.*) improves the solvating ability of supercritical. It increases the column efficiency for highly retained nonpolar solute.

Columns

There are two types of analytical columns used in SFC *i.e.* packed and capillary. Packed columns are those which contain small deactivated substances that adheres to the stationary phase. Capillary columns are the open tubular columns having small internal diameter and are made of fused silica.

Pumps, Injectors and Ovens

A pump is needed for the stable transfer of liquid CO₂. Incoming CO₂ and pumps head should be kept cold to maintain CO₂ in a liquid state. Syringe pumps are used for packed columns. Supercritical fluid is injected by switching of the content of a sample loop into the carrier fluid at the entrance of a column using auto sampler. For precise temperature control of the mobile phase to achieve stable extraction thermo stated column ovens are used.

Microprocessor

It is used for control pumping pressure, oven temperature and detector performance.

Detectors

Flame ionization detector normally present in GC can be used in SFC. It can also be coupled with mass spectrometry, an UV-visible spectrometer or an IR spectrometer.

DISADVANTAGE OF SFC

- There is limited choice of mobile phases and unwanted reactions with mobile phase.
- SFC is applicable only for highly polar compounds and proteins.
- Maintaining pressure is difficult.
- High-pressure vessels are expensive and bulky.

- High capital investment is required for equipment.
- It is not suitable for water-soluble analytes.
- Cleaning of instrument is time consuming.

APPLICATION OF SFC

- It is used in quality control of chiral drugs.
- Polynuclear aromatic hydrocarbons in automobile exhaust, polyole-finic antioxidants polyethoxylated alkylphenols are analyzed successfully using SFC.
- It is used for separation of thermally labile pesticides without resorting to sample derivatization.
- It has beneficial application in forensic science as it used for identification and analyses of explosive containing nitrate ester, nitramines, and drugs of abuse like amphetamines, cocaine, and other related compounds.
- Organo-metals of thermally labile category, metal chelates, heavy metals, can be separated using SFC.
- It is used for separation of the oligomers in a sample of the nonionic surface TritonX100.
- Separation of components widely varying in their boiling points.
- It is used for extraction of fat from food products.
- It is used for photo-resist cleaning.
- It is used for fractionation and purification of polymers e.g. removal of unchanged monomers from polymers.

Table 2: Critical pressure and critical temperature of selected substances, and their notable properties

(https://www.waters.com/waters/en_IN/PreparativeSFC/nav.htm?cid=134932612&locale=en_IN)

Substance	Critical temp. (°C)	Critical pressure (bar)	Notable Properties
Carbon dioxide	31	74	Physical state easily changed
Water	374	221	Extreme conditions needed
Methanol	240	80	Extreme temperature needed
Ammonia	132	111	Highly corrosive
Freon	96	49	Environmentally unfriendly
Nitrous Oxide	37	73	Oxidizing agent
n-Butane	152	38	Highly flammable

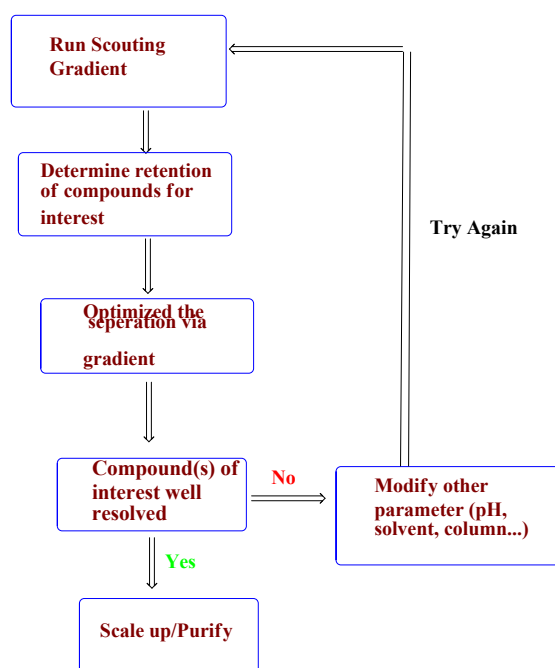


Figure 14.5: Working principle of SFC

SAQ 5

What do you mean by critical temperature and critical pressure of particular solvent?

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SAQ 6

What is modifier or co-solvent?

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14.5 APPLICATION OF CHROMATOGRAPHIC TECHNIQUE IN ENVIRONMENTAL MONITORING

There are many applications of chromatography that help to monitor the environment. It helps to keep our food safe and air and water clean.

- HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) helps to determine the presence of Fluazinam in soil. Fluazinam is pesticide widely used against the fungal disease in potato cultivation. A specific HPLC method using a diode array detector (DAD) helps to measure the presence of Fluazinam in soil.
- Gas chromatography helps in measuring the ubiquitous pollutants in the environment.
- HPLC technique is used for analysis air and water pollutants and for monitoring pesticide level in environment. HPLC is used by federal and state regulatory agencies to survey food and drug products.
- Gas chromatography is used for the determination of the volatile organic compound (VOCs) in air. Volatile organic compound are a cause of concern for human health due to their increased presence in the indoor environment. They are responsible for a phenomenon called as a sick building syndrome (SBS). Air monitoring method is used for assessing the indoor pollution.
- There are numerous gases found in the industrial process and are harmful for plants and human being such as sulphur dioxide, hydrogen sulphide. Gas chromatography is used for the detection of these types of gases present in the air.
- Gas chromatography is most widely used for the determination of trace organic compounds present in environment.
- Both natural and synthetic food colours are added to foods to improve their acceptability and to make them more popular. Paper chromatography has been primarily used for analysis of food colours in ice creams, sweets, drinks and beverages, to ensure that only edible colours are added and no non-permitted colouring agents are added to the foods.
- Certain organic compounds such as carbohydrates and amino acids are identified or detected from a complex mixture of organic compounds with the help of paper chromatography. It is used to separate anions and amino acids.
- Thin layer chromatography is used for the determination of the various plant extract. With TLC we also investigated the flavour components of the juices of citrus fruits.
- Column chromatography is used for identification and determination of non-volatile or strongly polar compounds in air and in surface, waste, and drinking waters.

- Size exclusion chromatography is used for the removal of DOC (dissolved organic carbon) from the drinking water.
- In size exclusion chromatography a gel Filtration-Based Method is used for the Purification of Infectious Rotavirus Particles for Environmental Research Applications.
- Soil and water measurement contamination of soil and water can come from many areas, including acid rain, pesticides industrial waste and raw sewage. These all are detected by GC-MS technique.
- Gum Arabic is a polysaccharide widely used in food industry as a viscosity modifier or gelling agent. The physical properties and processability of these water-soluble polymers are related to their molecular weight distribution, which can be determined by gel permeation chromatography.
- GC has been used for differentiation of petroleum-type pollutant and to study the fate of petroleum-type pollutants in underground and surface waters.
- GC-MS technique is used to study of the bioremediation potential of microorganisms for crude oil biodegradation.
- In different samples of water (ground water, surface water and drinking water), the content of non-polar organic compounds, which are detectable by high performance thin layer chromatography (HPTLC).
- Column chromatography helps in determination and separation of cardiac glycosides in digitalis leaf.
- Column chromatography is best method to separate active component from plant materials.
- Volatile samples, human breathe, blood, saliva and other secretions containing large amounts of organic volatiles can be easily analyzed using GC. The knowledge of the amount of compound in a given sample gives a huge lead in studying the effects on human health and on the environment as well.
- Air samples can be analyzed using GC. Mostly, GC coupled with FID is used by air quality control units in order to determine the components of a given air sample. Though other detectors are also useful, FID appears to be the most appropriate due to its sensitivity and resolution and also for its ability to detect very small molecules as well.

SAQ 7

What are the different applications of Gas chromatography to monitoring the environment?

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14.6 LET US SUM UP

Chromatographic techniques are used for the quantitative and qualitative analysis in various pharmaceuticals, food and dyes industries. Column chromatography has various disadvantages including manual setup, time consuming and accuracy. To overcome the problems, various advanced techniques have been developed like gas liquid chromatography, HPLC Super critical liquid chromatography and their application which are being employed not only in industries but also for monitoring the environment. GLC is an advanced technique compared to conventional chromatography. The separation of compounds present in a mixture is carried out between a 'gas' mobile phase and a 'liquid' stationary phase in GLC. However, in column chromatography, mobile phase is liquid and stationary phase is solid. In GLC temperature of gas phase can be controlled, but in column chromatography there is no way of controlling any temperature of mobile phase. Like this HPLC is more advanced than GLC in the manner that HPLC works under pressure of around (50-350 bar), unlike liquid chromatography which relies on the force of gravity to pass through the mobile phase. Due to this small sample amount can be separated. Column dimensions are 2.1-4.6 mm diameter and 30-250 mm length, and are made with smaller adsorbent particles (2 μ m-50 μ m), this gives it a superior resolving power (ability to distinguish compounds). HPLC is comparatively expensive than SFC as it requires high purity solvent as mobile phase and further its purification but no such thing is required for CO₂. Due to high diffusivity of the supercritical fluid it has much greater resolving power and shorter column lengths can be used as more interactions can occur in shorter span. Supercritical fluids have low viscosities which allows high flow rate with low pressure and faster analysis (5 to 10 X faster). Nowadays many applications of chromatographic techniques are being used to monitor the environmental conditions. It helps to keep our food safe and air/ water clean.

14.7 GLOSSARY

Capillary columns: GC columns, e.g. WCOT, PLOT, having a bore of 0.1-0.7 mm with a 0.1-5 μ m film of stationary phase coated onto the inner wall of a pure silica glass column 10-50m long, high column efficiency, Neff, and excellent resolution are achieved. Capacity of the stationary phase is very low so a sample injection splitter is used to introduce approximately 0.01 fill of sample onto the column

Capillary column gas chromatography: Gas chromatography using columns 10-100 m long with an internal diameter of 0.1-0.7 mm, usually with the stationary phase bonded to the internal wall (WCOT). Capillary columns have high efficiencies (Neff) and give rapid analysis times. chromatography, IUPAC (1993) "Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary while the other moves in a definite direction.

Gas chromatography GC: GC employs a gaseous mobile phase, e.g. nitrogen or helium, and usually a liquid stationary phase, e.g. non-polar Apiezon (alkane grease), OV101 (polymethyl siloxane) or polar PEG 20M (polyethylene glycol).

Separation is affected by competition between attraction of the components for the stationary phase and volatility at the column temperature being used, that is, retention forces versus partial vapour pressure in the mobile phase.

High performance liquid chromatography HPLC : It employs a liquid mobile phase and solid or bonded liquid stationary phase. High resolution and column efficiency is achieved by using 3-10 μ m microporous or micropellicular column packing materials. In reverse phase chromatography an aqueous buffer containing varying amounts of a miscible organic solvent is used as the polar mobile phase, e.g. 1 % acetic acid/methanol, 1 % ammonium acetate/methanol and ODS as a non-polar stationary phase.

Injection port: It is a facility for introducing the sample mixture into the mobile phase. In GC the injector is maintained at least 50°C above the maximum column temperature to be used and the sample is introduced via a rubber septum using a micro litre syringe; for HPLC see multiport injection valves

Supercritical fluid chromatography, SFC: A super critical fluid is produced when a gas, e.g. carbon dioxide is maintained above its critical pressure (73 atm) and temperature (31 °C). The super critical fluid is used as the mobile phase with GC like capillary columns or HPLC reverse phase columns and a flame ionisation or flame photometric detector.

14.8 TERMINAL QUESTIONS

1. What are the advanced chromatography techniques used by pharmaceutical industries and researchers?
2. What is the working principle of Gas Liquid Chromatography?
3. What is the advantage of GLC over column chromatography?
4. What is the advantage of HPLC over GLC?
5. What is the advantage of UPLC over HPLC?
6. What are the different applications of advanced chromatography techniques?

ANSWERS

Self-Assessment Questions

1. Correctly fixing up, requires some mechanical expertise and physical modification, time consuming. It requires constant care monitoring while performing the experiment.
2. Stationary phase is a non- volatile liquid layer coated on a solid surface and mobile phase is carrier gas and which is inert in nature *i.e.* unreactive gas such as N₂, He and Ar.
3. Inject port, column, detector and recorder.

- 4.
- | | Normal phase | Reversed phase |
|----------------------------|--------------------------------------|-------------------------------|
| Stationary phase | Polar (silica gel) | Non-polar (C18) |
| Mobile phase | Non-polar (organic solvent) | Polar (aqueous/organic) |
| Sample movement | Non-polar fastest | Polar fastest |
| Separation based on | Different polarities (functionality) | Different hydrocarbon Content |
5. Different component of HPLC
- The solvent reservoir or multiple reservoirs
 - A high pressure pumps
 - A column
 - Injector system
 - Detector
6. The critical temperature of a substance is the temperature at and above which vapor of the substance cannot be liquefied, no matter how much pressure is applied. The critical pressure of a substance is the pressure required to liquefy a gas at its critical temperature. Some examples are shown below.
7. SFC applications are performed on relatively polar stationary phases with CO₂ modified with an organic solvent and sometimes other highly polar components, such as acids and bases, called additives. Methanol is widely used modifier and most polar modifiers which is completely miscible with CO₂.
8. Soil and water measurement contamination of soil and water can come from many areas, including acid rain, pesticides industrial waste and raw sewage. These all are detected by GC-MS technique.

TERMINAL QUESTIONS

1. These are gas chromatography, gas liquid chromatography, HPLC, super critical fluid chromatography.
2. The GLC is based on the partition of stationary phase and mobile phase. Stationary phase is liquid and it is selected on the basis of polarity by the rule of “like dissolves like” so the selected liquid solution is polar liquid which is able to interact with the solute particles. The sample mixture after passing through the stationary phase and mobile phase will separate on the basis of partition coefficient. Partition coefficient (K_g) = Conc. of solute in liquid / Conc. of solute in gas
3. Advantage of GLC over column chromatography:
 - In GLC the process of separating the compounds in a mixture is carried out between a gas mobile phase and a liquid stationary phase whereas in column chromatography mobile phase is liquid and stationary phase is solid.

- In GLC temperature of gas phase can be controlled but in column chromatography there is no way of controlling any temperature of mobile phase.

4. HPLC is preferred over other chromatography in following ways

- HPLC works under pressure of around (50-350 bar), unlike liquid chromatography which relies on the force of gravity to pass through the mobile phase. Due to this small sample amount can be separated.
- Column dimensions are 2.1-4.6 mm diameter and 30-250 mm length, and are made with smaller adsorbent particles (2 μ m-50 μ m), this gives it a superior resolving power (ability to distinguish compounds).
- This technique is fast
- Highly sensitive
- Accurate
- Automated

5. HPLC is comparatively expensive than SFC as it requires high purity solvent as mobile phase and further its purification but no such thing is required for CO₂.

Due to high diffusivity of the supercritical fluid it has much greater resolving power and shorter column lengths can be used as more interactions can occur in shorter span. Supercritical fluids have low viscosities which allows high flow rate with low pressure and faster analysis (5 to 10 X faster).

- It produces less toxic and flammable waste.
- Advantage of SFC over GC
- It allows fast analysis of thermally labile compounds.

6. Applications of chromatography techniques

- HPLC helps to determine the presence of Fluazinam in soil. Fluazinam is widely used pesticide used against the fungal disease in potato cultivation. A specific HPLC method using a diode array detector (DAD) which helps to measure the presence of Fluazinam in soil.
- Gas chromatography helps in measuring the ubiquitous pollutants in the environment.
- HPLC technique is used for analysis air and water pollutants and for monitoring pesticide level in environment. Federal and state regulatory agencies use HPLC to survey food and drug products.
- Gas chromatography is used for the determination of the volatile organic compound (VOCs) in air. Volatile organic compound are a cause of concern for human health due to their increased presence in the indoor environment. They are responsible for a phenomenon called as a sick

building syndrome (SBS). Air monitoring is being used to assess indoor pollution.

- There are numerous gases found in the industrial process and are harmful for plants and human being such as sulphur dioxide, hydrogen sulphide. Gas chromatography is used for the detection of these types of gases present in the air.
- Gas chromatography is most widely used for the determination of trace organic compounds present in environment.
- Both natural and synthetic food colours are added to foods to improve their acceptability and to make them more popular. Paper chromatography has been primarily used for analysis of food colours in ice creams, sweets, drinks and beverages. To ensure that no non-permitted colouring agents are added to the foods, only edible colours are permitted for use.
- Certain organic compounds such as carbohydrates and amino acids are identified or detected from a complex mixture of organic compounds with the help of paper chromatography. It is useful in the separation of anions and amino acids.

UNIT 15 : RADIOCHEMICAL TECHNIQUES

Structure

- 15.1 Introduction
 - 15.1.1 Learning Outcomes
- 15.2 Basics of Radiochemical techniques
 - 15.2.1 Isotopes, Radioactive Decay, Units to Measure Radio Activity, Hal Life,
- 15.3 Carbon dating
- 15.4 Radioactive Labeling
- 15.5 Tracer Technique
- 15.6 Isotope Dilution
- 15.7 Measurement of Radiation
 - 15.7.1 Geiger Muller Counter
 - 15.7.2 Scintillation Counter
 - 15.7.3 Gamma Counter
 - 15.7.4 Neutron Activation Analysis
- 15.8 Application of Radiochemical Techniques in Environmental Monitoring
- 15.9 Summary
- 15.10 Glossary
- 15.11 Terminal Questions
- 15.12 Answers
- 15.13 References and Further Readings

15.1 INTRODUCTION

Radiochemical techniques are mainly used to detect substances in minute quantities in many circumstances the concentration of analytes would be in the range of 10^{-6} moles (micromoles) or 10^{-9} (Nano mole). The limitation of chemical methods is to detect the concentrations above 10^{-7} mole. Owing to this limitation of chemical methods unable to detect the analytes at lower concentrations as mentioned above. To overcome this situation researchers came up with an alternative, that's how radio chemical tracer techniques came into existence. The inception of isotopes, radioactivity and its associated techniques pave the way to assess and analyze the substances in quantities of Pico mole (10^{-12}) mole or even femto mole (10^{-15}). This ability of radioisotopes enabled the researchers to develop and design various experimental approaches that can address the needs of various problems in the field of biology, medicine and more such allied fields. The molecules or compounds that are labeled with radioisotopes are called tracers because these tracers enable the scientists to track or follow the changes that are taking place in the labeled compound when compared to non-radiolabeled compounds. Hence this technique referred as tracer technique. Radioisotopes allowed the science fraternity to understand and provided clues that many macromolecules like proteins, lipids, carbohydrates and nucleic acids are synthesized and composed of some basic elements. Radioisotopes

are widely used to understand the metabolic pathways which further paved the ways to establish the field of metabolomics.

In this unit you will be studying about radioactive decay, carbon dating and various principles and applications of tracer techniques and their applications with special emphasis to environment. Few YouTube links and references to online content have been provided for the benefit of learners (Any material adapted from web-based resources in this unit is being used for educational purpose only and not for commercial purpose).

15.1.1 Learning Outcomes:

After studying this unit you shall be able to:

- define the terms like isotope, radioactive decay and half-life;
- conceptualize the importance of carbon dating;
- explain the principles behind instruments measuring radioactivity;
- sketch the instruments used for measuring radioactivity; and
- describe the importance of radio isotopes in day to day life.

15.2 BASICS OF RADIOCHEMICAL TECHNIQUES

Before going to discuss the detailed principles of radiochemical techniques let us discuss some of the frequently used terms in this unit.

15.2.1 Isotopes:

Literal meaning of Iso is ‘similar’. Isotopes possess different atomic weights with same atomic number of the same element. The chemical properties of these isotopes are identical. In other words these “isotopes own same number of protons and differ in the number of neutrons”. Substances having natural isotopes need to be purified and this is done in an atomic reactor or nuclear reactor. Unstable isotopes are known as radioisotopes. To obtain stability they undergo radioactive decay. This phenomenon is commonly observed in elements of higher atomic numbers. Some of the commonly used radio isotopes are listed in the table 15.1

Examples: $^{12}_6\text{C}$ $^{14}_6\text{C}$ $^{16}_8\text{C}$ $^{18}_8\text{C}$

Table 15.1 Isotopes used in the field of Biological studies

Isotope	Stable/ Radioactive	Emission	Half life	Maximum energy (MeV)*
^2H	Stable			
^3H	Radioactive	β	12.3 yrs	0.018
^{13}C	Stable			
^{14}C	Radioactive	β	5730 yrs	0.155
^{15}N	Stable			
^{18}O	Stable			
^{24}Na	Radioactive	β & γ	15 hrs	1.39

^{31}P	Stable			
^{32}P	Radioactive	β	14.3 days	1.71
^{35}S	Radioactive	β	87 days	0.167
^{45}Ca	Radioactive	β	163 days	0.254
^{59}Fe	Radioactive	β & γ	45 days	0.46, 0.27
^{131}I	Radioactive	β & γ	8 days	0.335, 0.608

(MeV)*=milli electron volts

15.2.2 Radioactive decay (λ)

An unstable isotope to obtain stability undergoes ionization through emitting ionizing radiation. These ionizing radiations are in the form of alpha (α), beta (β), and gamma (γ) rays. This phenomenon is the natural ability of any radio isotope and hence this is known as radioactive decay. For biological assays both β and γ rays are frequently used. Refer table 15.2 for the important properties of these radiations.

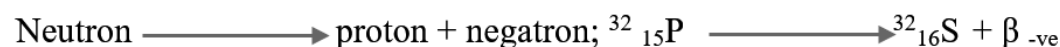
Table 15.2 Properties of different types of radiations

Alpha rays	Beta rays	Gamma, X-rays, & Bremsstrahlung
Heavy Charged Particle	Light Charged Particle	Electromagnetic radiation(em)
More Toxic than other forms of radiation	Toxicity same as em radiation per unit of energy	Toxicity same as β radiation per unit of energy
Not penetrating	Penetration varies with source	Highly penetrating

Let us discuss in brief about different types of emissions:

Negatron emission

In this type of emission or decay a neutron is converted to proton by releasing a negatively charged beta particle which is known as negatron (β -ve). By virtue of this reaction there is a loss in neutron and gain in a proton number. However, the mass number of the atom remains constant as unchanged.



Decay by positron

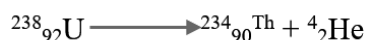
This reaction takes place by emitting a positive beta (β +ve) particle that is “positron” from a proton and forming neutron. Positrons being highly unstable interact with electrons and destroy. Due to this two gamma rays generated.



Alpha particle emission

Isotopes having high atomic number usually undergo α particle emission. Helium nucleus is the best example to explain α -particle emission. This emission leads to

reduction in atomic number by two values and mass number by 4. α -emitters are rarely used in biological studies.



Gama Particle mission

In this type of emission electromagnetic radiation is produced which is less intense than X-rays. In practical γ -rays released after β -and α -emission. Gamma decay is observed when there is excess energy in the nucleus of an atom. γ - emission does not induce any change in atomic or mass number.

Let us explore some of the commonly used units of radioactivity;

15.2.3 Units to Measure Radio Activity

Half-life ($t_{1/2}$)



Half-life is the time required for half of the nuclei in a radioactive sample to decay. Hence it is represented as $0.5/\lambda$.

Becquerel (Bq)

The system international units use Becquerel (Bq) as the unit of radioactivity.

1bq is equal to 1 disintegration per second (1 d.p.s).

Previously Curie was used as the unit of radioactivity.

Curie (Ci)

This is the unit to measure the radio activity.

Curie equivalent to the amount of radioactivity to that of 1 gram of radium present in a given radioisotope. 2.22×10^{12} disintegrations per minute (dpm).

Details of units used to express radioactivity are provided in table 15.3.

Table 15.3 Units used to express radio activity.

Unit	Definition	Relationship to other units
Millicurie(mc)	One thousandth of a curie	$mc=10^{-3}$ $mc=10^3 \mu c$
Curie(c)	A quantity of radionuclide disintegrating at a rate of 3.7×10^{10} atoms/sec	$c=10^3 mc$ $c=10^6 \mu c$
Microcurie(μc)	One millionth of a curie 3.7×10^4 disintegrations/sec	$\mu c=10^{-6} \cdot c$ $\mu c=10^{-3} \cdot c$

Counts/min(cpm)	Number of β particles detected/ min by a detective device	$\text{cpm} = \frac{\text{dpm}}{\text{efficiency of counting device}}$
Radiation absorbed dose(rad)	Energy imparted to a unit mass of matter by ionizing radiation(100ergs/g)	$0.87\text{rad}=\text{r}$
Roentgen(r)	An exposure dose of X/ γ radiation so that 1.61×10^{12} ion pairs are produced/gram of air	$\text{r}/0.87=\text{rad}$
Disintegration/min(dpm)	Number of atoms disintegrating/min	$2.2 \times 10^6 \text{dpm}=1 \mu\text{c}$

Self-Assessment Question 1

Fill in the blanks with correct answers

- _____ radiation is highly penetrating.
- _____ radiation has got light charged particle.
- Negatron is a _____.
- Radioactive decay represented by _____.
- Radioisotope with maximum half-life _____.



Up to now we have studied about types of radiation, radioactive decay and units of radioactivity. Let us move on to carbon dating.

15.3 CARBON DATING

Radiocarbon dating discovered by Willard Libby in 1946, he was professor of Chemistry at University of Chicago. For his discovery he has been honored with Nobel Prize in the year 1960. This method mainly based on measuring the levels of radio carbon-14 (^{14}C) in a substance or material. Radiation counting devices are used to perform carbon dating studies. Elemental carbon exists as both non-radioactive and radioactive isotope forms.

W. Libby (<https://images.app.goo.gl/JNti17Cw6NkEfY6V7>)

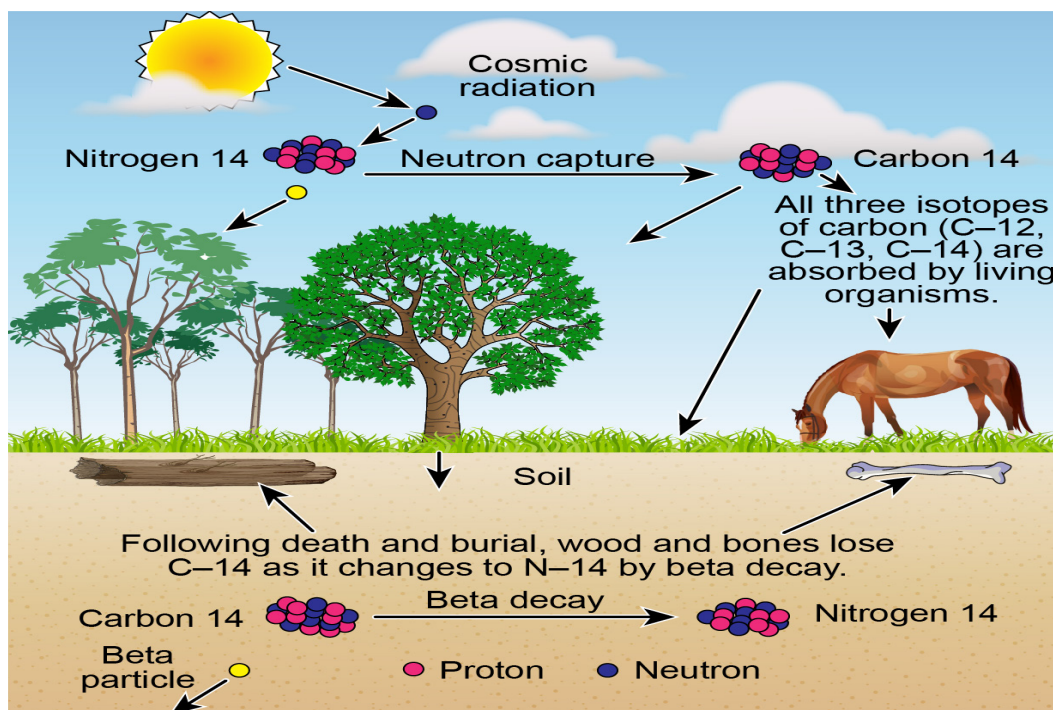
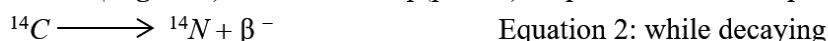
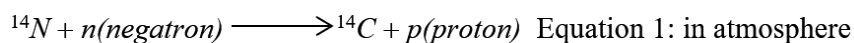


Fig. 15.1 : Carbon dating mechanism

It is interesting to know that certain plants and animals can synthesize labeled compounds through their metabolic processes when provided ^{14}C -labeled nutrients. For example: *Canna indica* can produce labeled glucose and pigeons can produce uric acid (end product of proteins metabolism).

Let us understand the concept of carbon dating by assuming a simple fact that living organisms including humans take radiocarbon that is ^{14}C when they are alive and it gets accumulate in some parts of the body. In atmosphere this radiocarbon is produced from ^{14}N and ^{14}N through its interaction with cosmic particles. Later this radiocarbon accumulates into air and oceans. From there ^{14}C radiocarbon enters into plants (Fig. 15.1). The living organisms that are consuming atmospheric carbon for their survival would be taking radiocarbon, ^{14}C . This is how the radiocarbon is entering into a living system. The moment the organism dies it won't be consuming any radiocarbon but starts releasing radiocarbon (refer equation 1 and 2). In simple words once after death radiocarbon start decaying and there won't be any addition of new radiocarbon.



Scientifically it is proved that, the ratio of $^{14}\text{C} / ^{12}\text{C}$ is equal to the atmospheric ratio. Whereas this ratio is altered (less compared with atmosphere) in the case of dead and deteriorating animals or plants. Hence by measuring the available quantities of both ^{12}C and ^{14}C it is possible to calculate the age of the material. While studying the decaying materials it is noted that the levels of ^{14}C diminish and the levels of newly formed ^{14}N increases.

For the decay of half of the radiocarbon it takes almost 5730 years. This time taken to reduce radiocarbon to half of its original quantity is referred as half Life. Hence to estimate the age of any fossil material especially the studies of anthropology,

archaeology or zoology scientists use to measure the amount of radiocarbon in that fossil and the quantity gives the age of the particular material.

Learners are advised to watch the given YouTube link (<https://youtu.be/8wYvKeSK1IY>) and also to read the research article entitled “¹⁴C Activity and Global Carbon Cycle Changes over the Past 50,000 Years”, published by Huguen et al., 2004 available at <https://europepmc.org/article/med/14716006>.

Factors affecting availability of radiocarbon:

- Environmental pollution is the major factor affecting carbon dating. For example uncontrolled emission of carbon intermediates into the atmosphere will affect the ratio of stable and radio carbons.
- Unexpected changes in the marine environment like Tsunami will also influence the carbon cycle.
- Any abnormality in cosmic radiation will also affect the formation of radio carbon.

15.4 RADIOACTIVE LABELING

The prerequisite to use radioisotopes in biological system is to incorporate them into the compound being investigated. For instance if a researcher is interested to study the DNA need to incorporate phosphorus-32 (P32) into to the DNA double helix. Such incorporation of isotope into a compound is known as labeling. P32 is the label and DNA is labeled molecule. Here it is interesting to know that there are two procedures to prepare labeled compounds. They are like organic synthesis and bio synthesis.

Organic synthesis

In this method the ability of an organic chemist to synthesise desired label compound is explored widely. By using the existing skills of organic synthesis it is possible to introduce label in a specific position of the molecule.



Bio synthesis

This method is used to synthesise complex labeled compounds, which cannot be synthesized using organic synthesis methods. Biosynthesis is useful to produce compounds that have significance in in pharmacology like nicotine, morphine and many more. Biosynthesis method extensively used to produce carbohydrates like glucose, fructose and other important plant sugars ¹⁴C labeled carbon dioxide. However after biosynthesis these compounds need to be isolated using analytical techniques like centrifugation, chromatography and crystallography. Researchers also developed hemoglobin labeled with radioactive iron, thyroid hormones with radioactive Iodine 131, Adenosine tri phosphate labeled with P32 and Cholesterol labeled with radioactive acetic acid. Similarly plant pigments and other important secondary metabolites have been synthesized. Limitation of bio synthesis is the purity of the desired compound and unwanted contamination of the material.

15.5 TRACER TECHNIQUE:

The discovery of tracer method for radioactive tracing took place in the early 20th century at that time the term “isotope” is yet to be defined. George Hevesy in 1911 discovered the process of radioactive tracing. At the time of this discovery he was working with Rutherford’s where radium was prepared from uranium ore by means of co- precipitation using lead chloride. Those days all radioactive isotopes considered to be new radioactive elements and respectively named after their corresponding current element in an alphabetical order based on series of decay. For example, radium (Ra) A to F is used to represent as RaA, RaB and so on. Where, George was interested to separate RaD from lead chloride. For this work he received Nobel Prize in the year 1943.

Since then the use of isotopes as tracers in the study of chemical processes and understanding metabolisms started. Apart from radioisotopes, stable isotopes can also be used as tracers. Measuring stable isotopes is an expensive deal when compared to radioisotopes. In radioisotopes the energy of nuclear radiation is independent of physical and chemical properties like temperature and pressure.

15.5.1 How it works:

Technically a tracer is an indicator that will help the researcher or the investigator to track and follow the target. In daily life we use the word ‘tracing’ when we are in search for the missing things. Coming to the radioisotopes tracers, means that *“an isotope which is being used to investigate the presence or identify a target molecule inside a living system or in an environment or in any experimental setup”*. For better understanding we can compare these tracers with chemical indicators that are used in 10 + 2 chemistry laboratory titration experiments to detect the end point of a titration. These tracers do not influence the reaction process or affect the system which is being studied under optimal experimental conditions. However, if there is any influence by these isotopes that can be taken care while analysing the results and in majority of the cases these influences are negligible. Tracers mimics the properties of elements being investigated for example, ^{14}C radioisotope is used extensively to study the element carbon and its associated metabolic pathways. By using such similar radioisotopes to tag or bind with target elements is known as labeling. Taking the advantage of labeled elements, one can establish the complete metabolism and pathways of certain molecules is known as tracer studies.

The following points need to be considered while selecting a tracer

1. Both the duration of the investigation and the Half-life should be compatible.
2. Avoid using isotopes with too short or too long half-life. As isotopes will limit the duration of the investigation as well as cause harm to the surrounding environment and the animal being investigated.
3. Also do not use an isotope with weak radiation. It is significant to note that isotopes with high beta and Gamma radiation energy are widely used.
4. Always use sufficiently pure radio isotopes as tracers.

15.5.2 Tracer Applications:

1. Carbon-11 is used to identify the location of biomolecules in different locations of the body and organ scanning
2. Carbon-14 is used to assess the participation of reactants and products of a metabolic reaction
3. Americium-241 is used in industry especially for smoke detection, and as quality control isotopes to monitor the process and check the dimensions of products being produced.
4. Tracer technique is also used in the industry to check the thickness of the products by using different radiations.
5. In the field of molecular biology sulphur labeled isotopes are used to analyse proteins and phosphorus isotopes are used to analyse DNA and RNA samples.
6. Tracer techniques also used to check the permeability of biological membranes by using hydrogen isotopes.
7. Isotopes like Technetium-201 and Thallium are extensively used in the field of diagnosis and imaging of organs. Carbon isotopes are used to perform radio immuno assay (RIA) and enzyme-linked immunosorbent assay (ELISA) the two popular diagnostic techniques.
8. Radioisotope Californium-252 is used in moisture monitoring equipment's.
9. In the field of oil exploration Cesium-137 is widely used
10. Sodium-24 radioisotopes are used in locating leakages inside the gas pipes, refrigeration coils and leaks in oil wells.

15.6 ISOTOPE DILUTION

Till now we have studied about tracer techniques. Now in this section we will explore a small but important topic in the field of radiochemical techniques.

This method is used in quantifying the unknown concentration of a radioactive element in a sample by means of mass spectra photometer. This method is useful to quantify the naturally occurring isotopes without radioactivity. If the quantity of naturally occurring isotope is too low then it is difficult to quantify the amount isotope present in the sample. In such situations we will be adding similar isotope externally to the sample and will be comparing the amount of radioactivity before and after the addition of external isotope to the sample. The difference between these two radio activities will tell us the amount of the naturally occurring isotopes present in the sample. Hence this method can be called isotopic enrichment method where isotopically enriched form of analyte is going to be produced.

For example:

If we are going to add radium to the 'X' isotope present in a sample, then radium is considered as tracer and the 'X' is considered as labeled or tagged.

The method of adding external isotope to the existing sample is known as ‘doping’ or ‘spiking’. The process is known as isotope dilution. We hear the word doping or spiking when a fitness test conducted on the sports personnel before and after the game. However, the sports regulatory authorities measure the levels of undesirable steroids or chemical compounds consumed by the sports personnel to enhance their performance.

15.7 MEASURING RADIOACTIVITY

Theoretically it is assumed that any ideal instrument that can measure radioactivity would detect all types of radiation or radioisotope decay. But practically there is no such instrument, but use separate detector for each type of radiation. In the following sections we will be discussing about different types of instruments that are used for measuring radio activity. Figure 15.2 shows the schematic flow of measuring radioactivity.

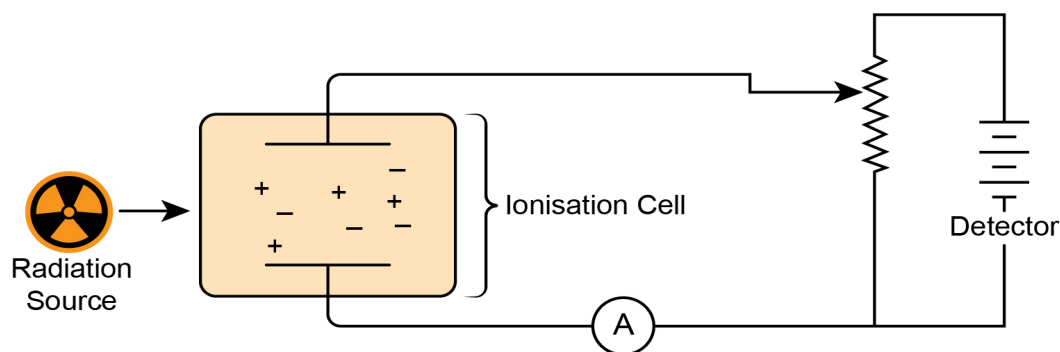


Figure 15.2. Shows flow of radiation and its measurement.

15.7.1 Geiger Müller (GM) counter

GM counter is one of the simplest devices to measure the nuclear radiation like α , β , and γ rays. Sometimes this GM counter can also be used to measure neutrons through alternative methods. However GM counter is widely considered for the measurement of β -particle by using gas ionization method.

Apparatus

The major components of this GM counter include hollow metallic cylinder and inside the cylinder there is an inert gas like argon, helium or neon along with small amount of quenching agent. Quenching agents like butane, propane, ethanol, bromine and chlorine are used. The sides of the cylinder are connected to a negative electrode that is cathode through the center of the cylinder and there is a metallic anode which is made of tungsten (Fig. 15.3.). Both cathode and anode are connected through load resistance that is helpful to measure the drop in electric potential. This resistance is connected to a pulse counter which will count it and display a tiny pulse or current. Detection of radiation or nuclear particle in this instrument occurs through pulse counter.

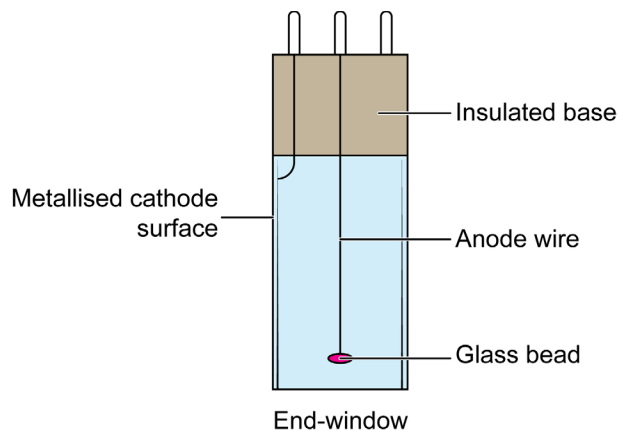


Figure 15.3. Geiger Müller Tube

Principle

Gas amplification or Avalanche effect is the force behind this apparatus. The electrons produced through ionization will further ionize (primary ionization) the gaseous molecules leading to the generation of two more electrons these newly formed electrons further ionizes (secondary ionization) two more electrons each (Fig 15.4). Such reaction occurs continuously before it reaches the anode and causes a chain reaction (tertiary, quaternary and more) which is referred as *avalanche effect*. These electrons reach anode and travels through the circuit and create a potential drop which is measured by amplifier and pulse counter. These electrons after completing single circuit reach back to the cathode. There they combine with the positive ions to create neutral molecules and bring back to the initial state inside the chamber. This entire process of ionization and avalanche effect creates 1 count in the GM counter.

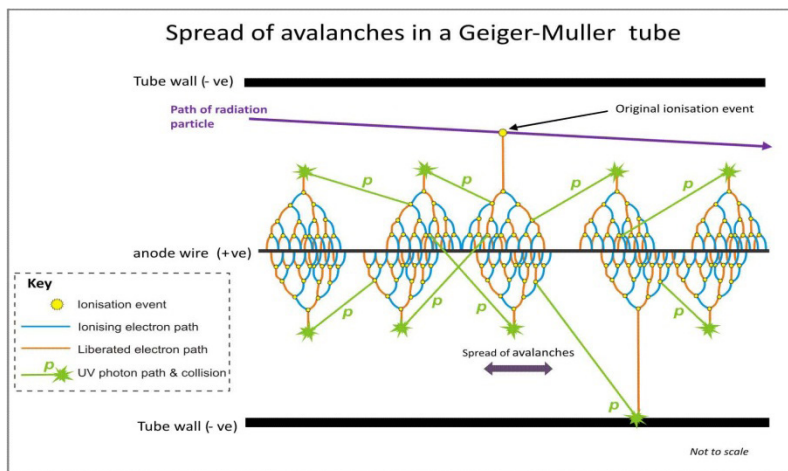


Figure 15.4. Avalanche Effect (By Dougsim - Own work, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=22417438>)

Working mechanism

When an external energy particle enters into this metallic chamber it creates ionization of the gas particles. In this ionization the energy present in the external particle is transferred to the gaseous molecule. This energy enables gas molecule to liberate two different ions one is negatively charged electron (e^-) and a positive ion (+). These two ions are going to experience a high electric field that is created due

to the presence of cathode and anode along with a 1000-3000 volt capacity battery. Due to their charges these two ions move towards oppositely charged anode and cathode. That is electron moves towards central anode and the positive ion moves towards the walls of the gaseous tank.

Radiation  gas molecule  electrons

After every count GM counter undergoes a phase known as “dead phase”. That means during this phase GM counter cannot measure the new radiation entering into the gas tank. If we assume, technically during dead time the entire avalanche process is takes place inside the tank. Here it is important to note that the current pulse received by the electrode is proportional to the energy of the nuclear particle entering the gas tank.

Role of quenching agent

The major role of quenching agents is to reduce the unwanted radiation or fluorescence intensity. In this subsection we will explore the detailed process of quenching with suitable examples.

To achieve the best detection of radioactivity we need to measure the signal produced by the nuclear particle. In other words we need to measure or catch hold of the ions produced only by the gas present inside the GM counter. While discussing the working mechanism, we have observed that positive ions move towards cathode sometimes these positive ions attracts the electrons from the nearby gas atoms to become neutral atoms. Due to such recombination processes there is a possibility of short wavelength UV radiation and X-rays. Both of these can ionize the gas atoms and produce ions that can cause unwanted ionization. To minimize such self-generating ionization during recombination quenching agents play a key role. Example butane is a potential quenching agent when helium is used as a major inert gas in the GM counter, as butane has the lower ionization potential when compared to helium. The positive ions produced by helium will acquire an electron from the quenching gas butane to produce a neutral helium atom and positively charged butane ion. These butane ions move towards the gas tank that is cathode to pair with electrons that have completed one complete circuit and reached the gas tank. In this way butane becomes neutral again.

Advantages and Limitations of GM counter:

- In GM counter maximum gas amplification is achieved
- Voltage fluctuation has little effect on GM counter
- GM counters are one of the reliable, sensitive and low cost stable counting devices that operate on gas ionization.
- Due to high time of 200 to 400 microseconds GM counters are not efficient to measure continuous radiation. In other words it is not suitable to measure huge number of radiation particles at a time.
- The second limitation is it cannot distinguish between the energy levels of two different nuclear particles.

So far, we have discussed about GM counter that works based on gas ion amplification. However, all the particles that are generated inside the GM counter do not reach the electrode, due to the limitations in its geometry and design. This problem could be solved by using liquid scintillation counting. The loss of particles has been minimized and the chances of reaching the electrode have been enhanced. The best part of scintillation counting is, the sample to be studied is dissolved in a solvent containing fluorescent substance (Table 15.4).

15.7.2 Scintillation counter:

Scintillation is the “ability to emit the light after exposure to the external radiation or nuclear particle”. Scintillation is the property of the material (refer table 15.4) present inside the apparatus and is known as scintillator. In this scintillation process electrons move from high energy state to low energy states during this process they release light energy in the form of photons. These light photons upon reacting with the photo cathode will generate single primary photo electron which is indirectly representing by the nuclear radiation that is entering into the scintillation counter.

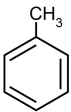

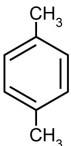
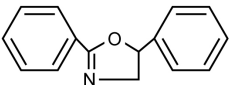
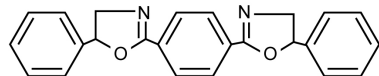
Solvents and Fluors commonly used in liquid scintillation counting	
Solvents	
Toluene	
1, 4-Dioxane	
p-Xylene	
Fluors	
PPO	
POPOP	

Table. 15.4. Solvents used as scintillation counting. Owing to the usage of solvent as scintillating material this is also known as liquid scintillation.

Apparatus

This scintillation detector consists of two major parts one is chamber containing scintillation material and the other one is photomultiplier tube. Scintillating material is placed on top of photomultiplier tube (PMT). There is a photo cathode that is helpful in absorbing the light photons generated by the scintillation material (Fig. 15.5). As the name indicates PMT is useful for the multiplication of photoelectrons that are generated by the photo cathode.

Principle

Nuclear radiation produced by nuclear material when interacts with scintillating material produces light photons these photons further interacts with photocathode producing primary photo electrons and this is also known as photoelectric effect.

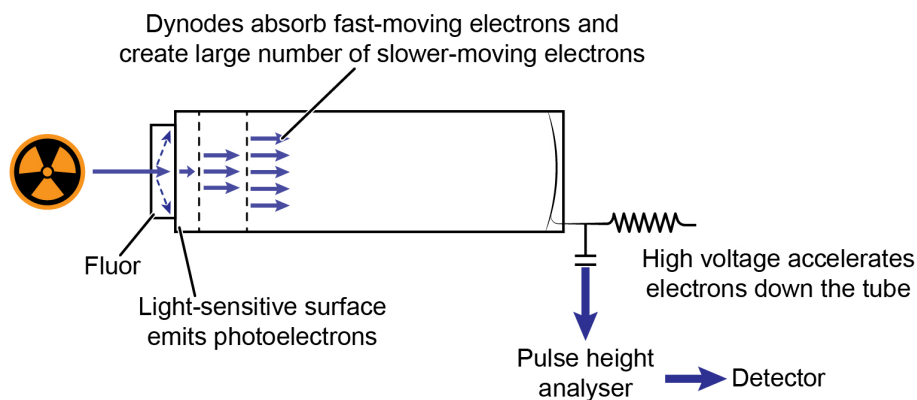


Fig. 15.5. Scintillation counter

Mechanism

When light photons hit the photocathode, it is going to produce primary photoelectrons and these primary photoelectrons are going to interact with dynodes that are arranged in a systemic manner inside the PMT tube. It is important to know that these dynodes are nothing but electrodes and these electrodes ranging from 100 to 600 volts. The primary electrons after hitting the first dynode with approximately 100 volts will produce double the number of secondary photoelectrons which now directed towards the another electrode that is dynode with higher capacity of 200 volts. This accelerated moment of photoelectrons from lower to higher dynodes is due to the potential difference between each dynode. You can assume that at the end of this process there will be a cumulative number of photoelectrons that have been multiplied at every interaction with dynode having higher voltages. At the end these electrons reach the anode that is located at the bottom of the PMT. This is connected to an electronic counter which can measure the current pulse generated by these electrons.

Applications

- Scintillation detectors are efficient in providing the energy of the incident radiation and the nuclear particle.
- This counter also gives the information about the intensity of the incident radiation.

15.7.3 Gamma counter:

Up to now you have studied about GM and scintillation counters. Now you shall be studying Gamma counter.

Measuring of gamma rays can be performed by using external scintillation detectors. They mainly used to study the proteins and antibodies in the field of biology. Thallium-activated sodium iodide crystal $[\text{NaI}(\text{TI})]$ well is used to place the sample. Gamma (γ) rays being high energy radiation can easily come out of the glass or plastic container used to keep the sample (Fig 15.6). Later γ -rays will interact with the thallium crystal and produce electrons. These electrons by interacting with the $[\text{NaI}(\text{TI})]$ crystal produce fluorescence which is detected by

the PMT connected to the thallium crystal. PMT tube acts similar to that of the scintillation counting. Iodine-126 (^{126}I) and ^{131}I are commonly used isotopes in γ -ray detection. γ -radiation has got low radiation power but has high penetration power.

Learners are advised to watch the video available at the given YouTube link to know how to operate gamma spectroscopy and capture gamma spectrum. (<https://www.youtube.com/watch?v=htuKwRqTcgQ>).

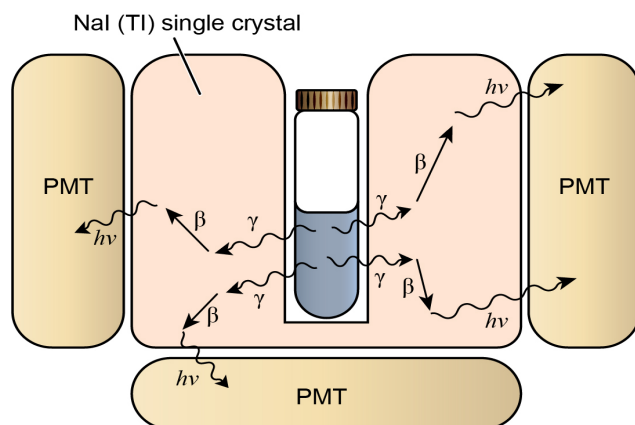


Figure 15.6. Gamma ray detection

Self-Assessment Question 2 Choose the correct option

1. In the atmosphere radiocarbon is produced from ^{14}N (True / False).
2. Carbon dating is based on measuring the levels of ^{14}N (True / False).
3. Millicurie is greater than micro curie (True / False).
4. Isotope with poor radiation acts as potential tracer (True / False).
5. Sulphur based isotopes are used to detect proteins (True / False).
6. Avalanche effect is observed in scintillation counter (True / False).
7. Butane is not a potential quenching agent (True / False).
8. Toulene cannot be used in gamma ray detection (True / False).

15.7.4 NEUTRON ACTIVATION ANALYSIS (NAA):

NAA was discovered in the year 1936 by two scientists named as George Charles and Hilde Levi. NAA is used to measure the elements based on their characteristic radiation formed when they interact with neutron. In this method both qualitative and quantitative determination of elements is possible. The very basic principle working behind this technique is, bombarding trace elements with a high flux of neutrons followed by measuring the rate of decay or emitting radiation (Fig 15.7). Upon bombarding with neutrons these elements form radioactive isotopes and emit specific radiation. This emitting radiation can be measured by using a suitable radio activity determining instrument or counter as discussed above. We all know that each element has its own half-life through which one can measure the speed of decay. By comparing the formed radiation spectrum with known radioactive isotope spectrum

it is easy to identify the element present. For easy understanding we can compare these spectrums with that of chemical signatures which are unique and specific to individual elements just like our fingerprints that are used for developing biometric security systems. The advantage of this method is, there is no loss or less damage to the sample being investigated this is found most significant while analysing antique or historic samples like paintings and other artworks being examined.

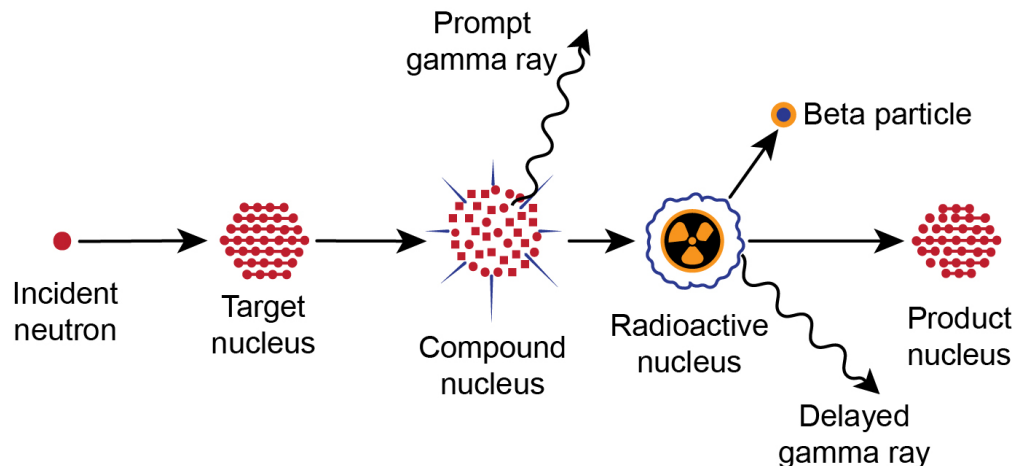


Figure 15.7. Principle of Neutron activation analysis

Applications of NAA:

Similar to the applications of tracer techniques NAA has also got a wide range of applications in the field of environmental monitoring, agriculture, instrumentation, medicine, biotechnology and forensic science etc.

1. Archaeology: NAA is used to characterize archaeological specimens like chert, obsidian, pottery and limestone to relate the artifacts to sources establishing their chemical signatures.
2. Environmental studies: extensively used to study the migration of chemical fertilizers, air pollutants and pesticides in the ecosystem. It is also used to study the contamination caused by mining of radioisotopes.
3. Quality control: used to monitor the contamination of freshwater and the bioaccumulation of heavy metals like selenium, arsenic and lead in food chain through release of industrial effluents to into agriculture fields.
4. Pharmacology studies: NAA is used to monitor the advantages and disadvantages of metal ions used in the preparation of medicine. According to the study conducted by Harvard medical School it is found that supplementation of 200 micrograms per day selenium help to treat colon cancer along with other vital organs like lungs and prostate.
5. Forensic investigation: it is used to investigate the presence of trace elements in the forensic samples like hair and nail.

15.8 APPLICATIONS OF RADIOISOTOPES IN ENVIRONMENTAL MONITORING:

The use of isotopes in environmental studies falls into the following categories like to study the climate change of oceans and seas, isotope hydrology of groundwater, seawater interactions, radio ecology bio monitors and the changes in atmosphere along with radio matrix and some of the quality assurance fields. Let us discuss some of these areas.

Climate change

The information about the past environmental conditions is obtained by analysing stable isotopes and other trace elements present in corals. Paleoceanic study will provide the status and information of un altered chemical and physical conditions that were existing inside the sea and seawater. In addition to this delta 18 O levels were monitored to know the coral bleaching in coastal East Africa. By monitoring the ratio of carbon 14 to carbon 12 of corals the time history of forests can be reconstructed. A research study conducted by Fink in Australia using the long-lived Cosmo genic radio isotopes such as ^{10}Be , ^{14}C , ^{26}Al and ^{36}Cl provided the information about chronological frameworks and rates of climate processes.

Oceans and Seas: According the research conducted by Schlosser *et al.*, Tritium (^3H) is a widely used tracer for understanding the changes in the hydrosphere, including the oceans, continental surface waters and groundwater. This study explains that the “distributions of tritium in the Southern Ocean and discuss the circulation. A study conducted on surface waters of the Atlantic Ocean by The IAEA-MEL’s Radiometric Laboratory in Monaco, in collaboration with several marine institutes, during 1994 – 2003 a research project on Worldwide Marine Radioactivity Studies (WOMARS) found that “the presence of anthropogenic ^3H , ^{90}Sr , ^{137}Cs and $^{239,240}\text{Pu}$ in the Atlantic Ocean, and in surface waters for the periods of 1991-1995 and 1996-2000, and average concentrations for 2000 are discussed. According to this study “The highest radionuclide concentrations have been observed in the Irish Sea due to discharges from the Sellafield reprocessing facility, and in the Baltic Sea due to the Chernobyl accident”.

Isotope Hydrology

A research work conducted by Porntepkasemsan and K. Srisuksawad suggested that “use of water containing elevated levels of ^{226}Ra in any of irrigation system can result in the contamination of the vegetation, either directly or through uptake from soil contaminated through the irrigation process”.

According to research conducted by E. Fisher *et al.*, using $\delta^{18}\text{O}$ of calcite precipitating on Geochemical and isotopic studies show that lake hydrology is dominated by the local meteoric groundwater system.

Radioisotope Ecology:

^{129}I is widely used by P. Kershaw *et al.*, to estimate transport rates in the Coastal current and in an elegant submarine-based study in the Arctic Ocean which showed

an increase in the inflow of Atlantic Water. Also presence of ^{137}Cs and plutonium isotopes could be because of sea water contamination.

(learners are advised to refer the given web link for further details and to get more information on this topic, please visit <https://www-pub.iaea.org/MTCD/Meetings/PDFplus/2004/cn118forma.pdf>).

15.9 SUMMARY

In this unit we have studied about the basics of radiochemical techniques like isotopes radioactive decay and various units used to measure the radioactivity. Apart from that we have discussed about the terminology that is frequently used while studying radioisotopes and the techniques associated with it. The concept of carbon dating is widely used by anthropologist and paleontologist to estimate the age of dead or decaying material obtained from fossils.

By using radioactive labeling we can monitor the flow and transformation of molecules or elements in a living system or in an ecosystem. At the mid of this unit we have discussed about techniques that are popularly used to measure the radiation. At the end of this unit we have mainly focused on the principles and brief working mechanisms along with their applications with special reference to environment.

15.10 GLOSSARY

Anion: A negatively charged ion that is produced and attracted towards the anode (+ve electrode) during electrolysis

Cation: A positively charged ion that is produced and attracted towards the cathode (-ve electrode) during electrolysis

Ionisation: The process of acquiring charge by atoms either by losing or gaining electrons

Isotope: (*iso* = similar or equal; *topos* = place/position) : Diverse forms of an element with different atomic weight and identical chemical properties. (also have the same number of protons but different numbers of neutrons)

Photon (*photo* = light): Fundamental particle of light.

Radiation: energy released in the form of waves or particles from an unstable atom.

Radioactivity: spontaneous emission of radiation from the nucleus of an unstable atom.

Tracer: A molecule or atom used to label a target molecule and can be tracked.

15.11 TERMINAL QUESTIONS

1. Define the radioactive decay. Give suitable examples for alpha and beta emissions.
2. Give a detailed note on Carbon dating.
3. What is tracer? Explain the significance of tracer techniques?
4. Explain the instrument and procedure used to measure the beta radiation?
5. Give a note on scintillation process and working mechanism of scintillation counter.
6. What is Neutron activation analysis? Give any five applications?

15.12 ANSWERS

SAQ 1.

1. γ ; 2. β 3. β -ve 4. Δ ; 5. ^{14}C .

SAQ 2.

1. T; 2. F; 3. T; 4. F; 5. T; 6. F; 7. F; 8. T

Terminal questions

1. The ability of a radioactive isotope to emit radiation by an element to attain stability is known as radioactive decay. Refer section 15.2.2.
2. Carbon is a process used to measure the age of a fossil material. This is mainly done by measuring the levels of radioactive carbon. Refer section 15.3.
3. A molecule or atom used to label a target molecule and can be tracked. Refer section 15.5 for complete details.
4. Geiger Müller counter is used to measure beta particles. Refer section 15.7.1 to more details.
5. Refer section 15.7.2 for complete details on scintillation counters.
6. NAA is a method for both qualitative and quantitative determination of elements. The very basic principle working behind this technique is, bombarding trace elements with a high flux of neutrons followed by measuring the rate of decay or emitting radiation (Refer Fig 15.6 and section 15.7.4 for complete details).

15.13 FURTHER READINGS

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**Analytical
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