MODULE 1   NATURAL CYCLES AND ATMOSPHERIC CHEMISTRY

Unit 1   Concepts of Elementary Cycles
Unit 2   Characteristics of the atmosphere

UNIT 1   CONCEPTS OF ELEMENTARY CYCLES

CONTENTS

1.0   INTRODUCTION

Environmental chemistry is the study of chemical processes occurring in the environment which are impacted by humankind's activities. These impacts may be felt on a local scale, through the presence of urban air pollutants or toxic substances arising from a chemical waste site, or on a global scale, through depletion of stratospheric ozone or global warming. The focus in our courses and research activities is upon developing a fundamental understanding of the nature of these chemical processes, so that humankind's activities can be accurately evaluated.

The field of environmental chemistry is both very broad and highly interdisciplinary. Within the Department of Chemistry we have a core group of faculty whose research interests are in atmospheric and aquatic chemistry, photochemistry, and the chemistry and transport of long-lived pollutants. We interact with other chemists in the Department, with numerous other researchers at the University who have related interests, and with nearby government agencies. Indeed, the setting for the study of environmental chemistry is ideal.

Our graduate program consists of graduate courses which stress the fundamental photochemical, kinetic, analytical and transport aspects of environmental phenomena, regular seminars, and close interactions between the different research groups. We emphasize that students are able to put expertise in their own research field into a global context.
The field of environmental chemistry is rapidly expanding, and excellent employment opportunities exist in the academic, government, industrial and public policy sectors.

Cycles are sequences of events that repeat themselves in a particular pattern. In environmental chemistry, our concern basically is with **biogeochemical cycles**. Precisely, biogeochemical cycles are interconnected complex processes by which matter or elements that make up the biotic and abiotic systems are used over and over again between the living and non-living things. Some of the very important natural biogeochemical cycles include: **Carbon Cycle, Nitrogen Cycle**, **Sulphure Cycle,** and **Hydrological (Water) Cycle.**

2.0   OBJECTIVES

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

- define biogeochemical cycles
- name specific examples of biogeochemical cycles
- explain the basic transformations that go on in a named biogeochemical cycle.

3.0   HOW TO STUDY THIS UNIT
1. You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

NOTE: All answers to activities and assignment are at the end of this book. This applies to every other unit in this book.

4.0   MAIN CONTENT

4.1   Some Biogeochemical Cycles

4.2   The Carbon Cycle

The carbon cycle is the series of interconnected changes by which carbon is being continuously circulated among the natural compartments of atmosphere, biosphere, hydrosphere, geosphere and pedosphere. There are four major reservoirs involved in the carbon cycle. These are the plants, the terrestrial biosphere (fresh water systems and non-living organic material), the oceans (where we have dissolved inorganic carbon and living and non-living marine biota), and the sediments (including fossil fuels).
Living organisms are mainly composed of water and various carbon compounds hence the cycling of carbon is of prime importance to the support of life. The concentration of carbon in living matter (18percent) is about 100 times greater than its concentration in the earth (0.19percent). Carbon exists as carbon (IV) oxide (CO_2) in the atmosphere, bicarbonate ion (HCO_3^-) in water and calcium carbonate ($CaCO_3$) in carbonate rocks (limestone, chalk, coral). It is the major part of hydrocarbon molecules in petroleum and natural gas; and the main constituent of coal and dead organic matters.

In the Earth's atmosphere, carbon exists as carbon (IV) oxide in 0.03percent level by volume. This level is currently being shifted towards excess due to imbalance of anthropogenic activities (human-induced) such as excessive combustion of fossil fuels and deforestation. In 1850, atmospheric CO_2 was about 280 ppm and by 2007, it had increased to about 383 ppm.

4.2.1 Ways by which CO_2 is released into the Atmosphere

Some of the ways by which CO_2 is released into the atmosphere are:
Respiration of plants and animals: This is an exothermic reaction involving the breaking down of organic molecules, e.g. glucose, into carbon (IV) oxide and water

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

Decay of plants and animals: Fungi and bacteria breakdown the carbon compounds i.e. carbohydrates, proteins and lipids in dead plants and animals, and convert the carbon to carbon (IV) oxide in the presence of oxygen or carbon (IV) oxide and methane (CH_4) in the absence of oxygen e.g.

$$C_6H_{12}O_6 \xrightarrow{\text{Methanogens}} 3CO_{2(g)} + 3CH_{4(g)}$$
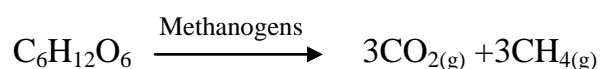
Fermentation of carbohydrates: The enzymatic decomposition of carbohydrates produces CO_2 as a by-product

$$C_6H_{12}O_{6(aq)} \xrightarrow{\text{Zymase}} 2C_2H_5OH_{(aq)} + 2CO_{2(g)}$$
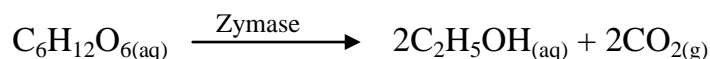
Burning of fossil and agro fuels: Combustion of fossil fuels like petroleum products, coal, natural gas and agro fuels releases CO_2 (and water vapour) into the atmosphere.

$$C_5H_{12} + 8O_2 \longrightarrow 6H_2O + 5CO_2$$
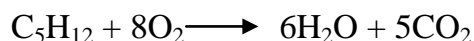
Thermal decomposition of carbonate rocks or limestone: When limestone soils are heated up or during the production of cement, CO_2 is released into the atmosphere.

$$CaCO_{3(s)} \xrightarrow{\text{heat}} CaO_{(s)} + CO_{2(g)}$$
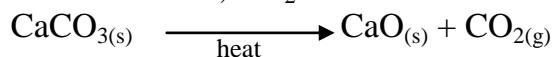
Warming of surface waters: This leads to the releasing of dissolved CO_2 back into the atmosphere.

Volcanic eruptions: During volcanic eruptions, the volcanic gases released into the atmosphere include water vapour, CO_2 and SO_2.

4.2.2 Ways by which CO_2 is removed from the Atmosphere

Photosynthesis: Primarily, photoautotrophs (plants and algae) use light energy to convert CO_2 and water to organic molecules like glucose and other carbohydrates. To a less extent, chemoautotrophs (bacteria and archaea) convert CO_2 and water to organic matter using energy derived from the oxidation of molecules of their substrates.

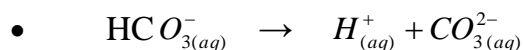$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$
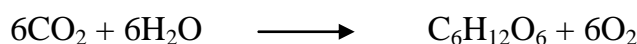
Formation of carbonic acid: Carbon (IV) oxide dissolves in rain water and droplets pass through the atmosphere. Also, at the surface of the oceans towards the poles where sea water becomes cooler, carbon dioxide dissolves in water to from carbonic acid. Carbonic acid reacts with weathered silicate rocks to produce bicarbonate ions which are used to make marine carbonates.
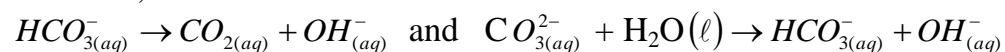
Conversion of carbon to tissues and shells: Organisms in upper ocean areas of high biological productivity convert and reduced carbon to tissues or shells.

In the oceans, the major carbon reservoir is the inorganic carbon: When CO_2 dissolves in water, a hydrated CO_2 molecule is produced which then forms an equilibrium mixture containing bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. At pH_s lower than those found in sea water, carbonic acid (H_2CO_3) will also be present. This can be summarized as:

- $CO_{2(g)} \rightarrow CO_2\,(aq)$
- $H_2O(\ell) + CO_2(aq) \rightarrow H_2CO_{3(aq)}$
- $H_2CO_{3(aq)} \rightarrow H_{(aq)}^+ + HCO_{3(aq)}^-$

- $HCO^-_{3(aq)} \rightarrow H^+_{(aq)} + CO^{2-}_{3(aq)}$

However, due to the reactions

$HCO^-_{3(aq)} \rightarrow CO_{2(aq)} + OH^-_{(aq)}$ and $CO^{2-}_{3(aq)} + H_2O(\ell) \rightarrow HCO^-_{3(aq)} + OH^-_{(aq)}$

Most ocean waters have a pH in the range 8 to 8.3 as they contain more OH^- ions than H^+ ions.

The overall reaction that takes place when CO_2 dissolves in sea water can be summarised as:

- $CO_{2(aq)} + H_2O_{(\ell)} + CO^{2-}_{3(aq)} \rightarrow 2HCO^-_3$.
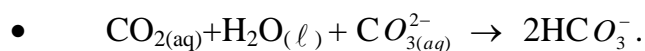
This is responsible for low concentration of CO_3^{2-} used for formation of shells. Thus as concentration of CO_2 increases in the atmosphere, more of it will dissolve in sea water to lower the concentration of

The carbon cycle shown in Fig 1 summarises all the processes so far itemised.
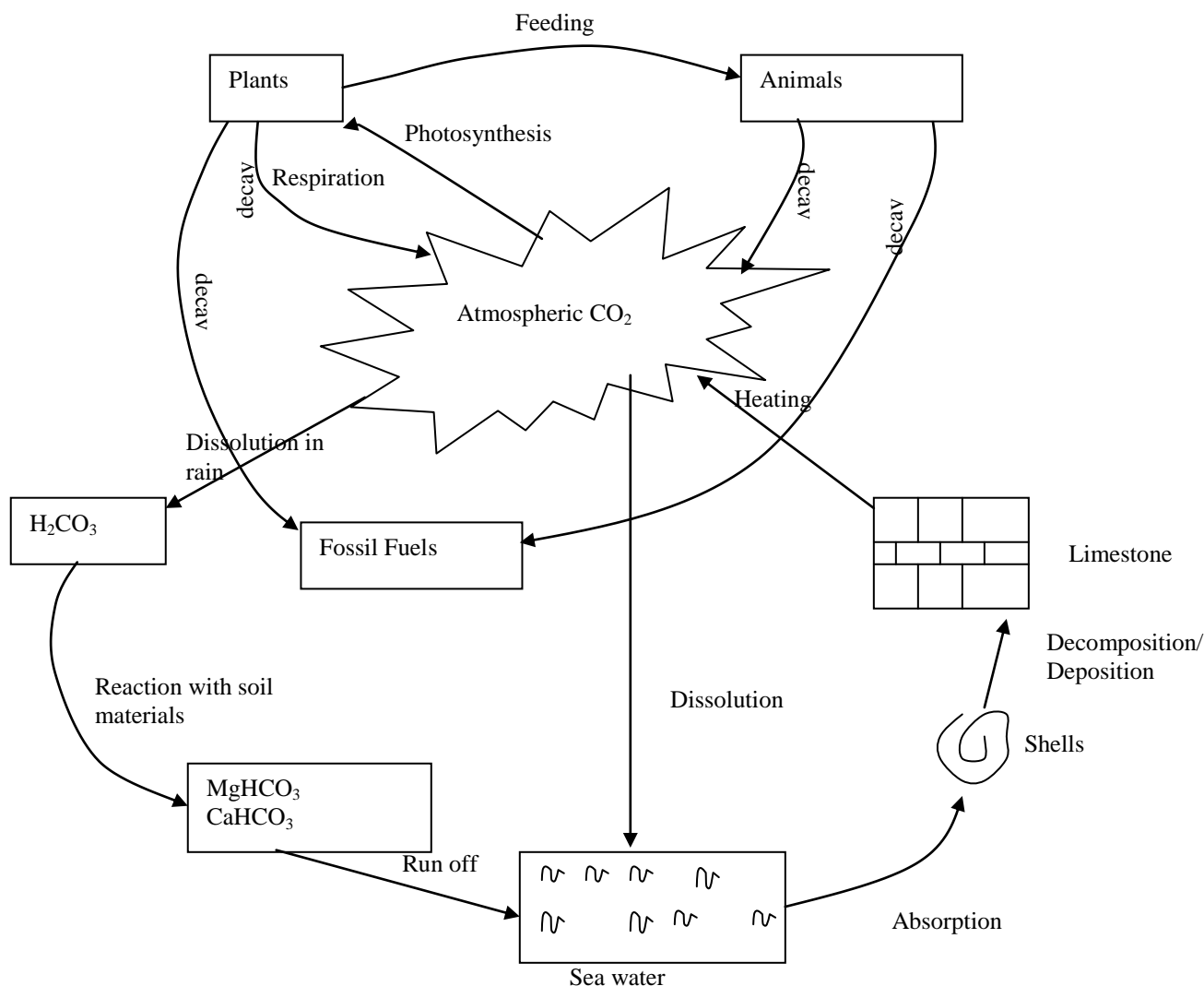

Fig. 1: The Carbon Cycle
Source: O.Y. Ababio, 2002 (modified)

4.3   The Nitrogen Cycle

The nitrogen cycle is the biogeochemical cycle that describes the gradual transformation of nitrogen and nitrogen-containing compounds in nature. It is the means by which the supply of nitrogen is distributed in nature.

The Earth's atmosphere, containing about 79percent nitrogen, constitutes the largest pool of nitrogen. Nitrogen is crucial to all life processes on earth. It is present in all amino acids, proteins and nucleic acids (RNA and DNA). Although nitrogen is abundant in the atmosphere and the majority of the air we breathe in is nitrogen (oxygen constitutes only 21percent of the air we breathe in), nitrogen is not readily available for cellular utilisation. This is because the strong triple covalent bonds between the N atoms in N_2 molecules make it relatively inert. By implication,

biochemically available nitrogen is in short supply in natural ecosystems. Hence, plant growth and biomass accumulation are limited.

In order for plants and animals to use nitrogen for their metabolic processes, N_2 gas must be converted to a chemically available form such as ammonium (NH_4^+), nitrate (NO_3^-) or organic nitrogen such as urea, (NH_2) CO. The nitrogen cycle shown in Figure 2 describes the movement of nitrogen among the atmosphere, biosphere and geosphere in different forms.

4.3.1 Basic Processes of the Nitrogen Cycle

(a)   **Nitrogen fixation**: This is the process by which the atmospheric nitrogen is converted into a form that is readily available to plants and subsequently to animals and humans. There are four ways of converting atmospheric nitrogen (N_2) into more biochemically available forms.

   (i)   **Biological fixation:** Symbiotic bacteria, e.g. *Rhizobium*, associated with the root nodules   of leguminous plants and some free-living bacteria, e.g. *Azotobacter*, are able to covert (fix) free nitrogen to organic nitrogen.

   (ii)   **Industrial fixation:** In the industrial Haber-Bosch process, atmospheric nitrogen and   hydrogen (obtained from natural gas or petroleum) are combined to form ammonia, NH_3

   $$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$
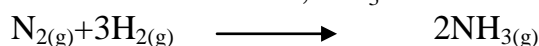
   The ammonia produced can be used to make fertilizers and explosives.

   $$2NH_{3(g)} + H_2SO_{4(aq)} \xrightarrow[\substack{450\text{-}600^oC \\ 200atm}]{\text{Iron catalyst}} (NH_4)_2\,SO_4\,(s)$$
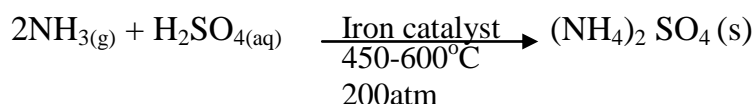
   (iii)   **Combustion of fossil fuels:** The exhaust fumes from internal combustion engines are made up of volatile matters including oxides of nitrogen.

   (iv)   **Electrical storms (lightning) and photolysis:** During electrical storms, nitrogen is oxidised to NO, which is oxidised by ozone in the atmosphere to form NO_2. NO_2 in turn is reduced back to NO by photolysis. These reactions are important aspects of atmospheric chemistry, but they are inadequate for both terrestrial and aquatic nitrogen turnover.

(b)   **Assimilation:** Plants can absorb NO_3^- or NH_4^+ ions from the soil (Nitrogen uptake) through their roots. Absorbed nitrate is first reduced to nitrite ions and then ammonium ions for subsequent incorporation into amino acids, nucleic acids and chlorophyll. In leguminous plants with root nodules, nitrogen in the form of ammonium ions can readily be assimilated. Animals and human beings are incapable of utilising nitrogen from the atmosphere or inorganic compounds hence, they depend on plants or other animals (except ruminants) that feed on plants, for their protein.

(c) **Ammonification:** At death, the proteins stored in the body of plants and animals become waste materials. Urine contains the nitrogen resulting from the metabolic breakdown of proteins in form of urea, $(NH_2)_2CO$. Urea is rapidly hydrolysed by the enzyme to ammonium carbonate, $(NH_4)_2CO_3$.

$$\begin{array}{c} NH_2 \\ \diagdown \\ \diagup \\ NH_2 \end{array} C = O + 2H_2O \xrightarrow{\text{Urease}} (NH_4)_2CO_3.$$
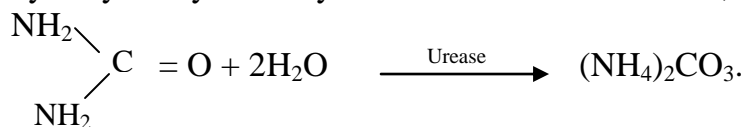
(d) **Nitrification:** The excess ammonia released by bacterial action on urea and proteins that are not used by plants is oxidised by the autotrophic nitrifying bacteria-Nitrosomonas and Nitrobacter. Under aerobic conditions, Nitrosomonas convert ammonia to nitrite while nitrite is further oxidized to nitrate by Nitrobacter.

$$2NH_3 + 3O_2 \xrightarrow[\text{Nitrosomonas}]{\text{Nitrobacter}} 2NO_2^- + 2H^+ + 2H_2O$$
$$2NO_2^- + O_2 \xrightarrow{\hspace{2cm}} 2NO_3^-$$
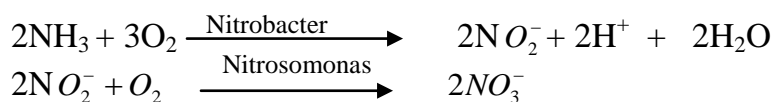
The bacteria derive energy from the oxidation processes. Some of the nitrate formed is used by plants while the excess is carried away in water percolating through the soil because the soil does not have the ability to hold nitrate for long. It is important for the nitrite ions to be converted to nitrate ions because accumlulated nitrites are toxic to plant life.

(e) **Denitrification:** Nitrate and nitrite are reduced under anaerobic conditions by pseudomonas and clostridium bacteria. Nitrate is reduced to nitrite while nitrite is reduced   to ammonia. Most of the nitrate is later reduced to nitrogen thus, completing the nitrogen cycle. This constitutes a serious loss of fertilizing matter in soil when anaerobic conditions develop. Also, some denitrifying bacteria produce N_2O from nitrate reduction. The N_2O produced enters the atmosphere and is reduced through photolysis to produce N_2 and an excited state of oxygen, which oxidizes N_2O to NO.

$$NO_3^- \rightarrow N_2 + N_2O$$
$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
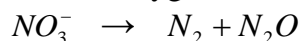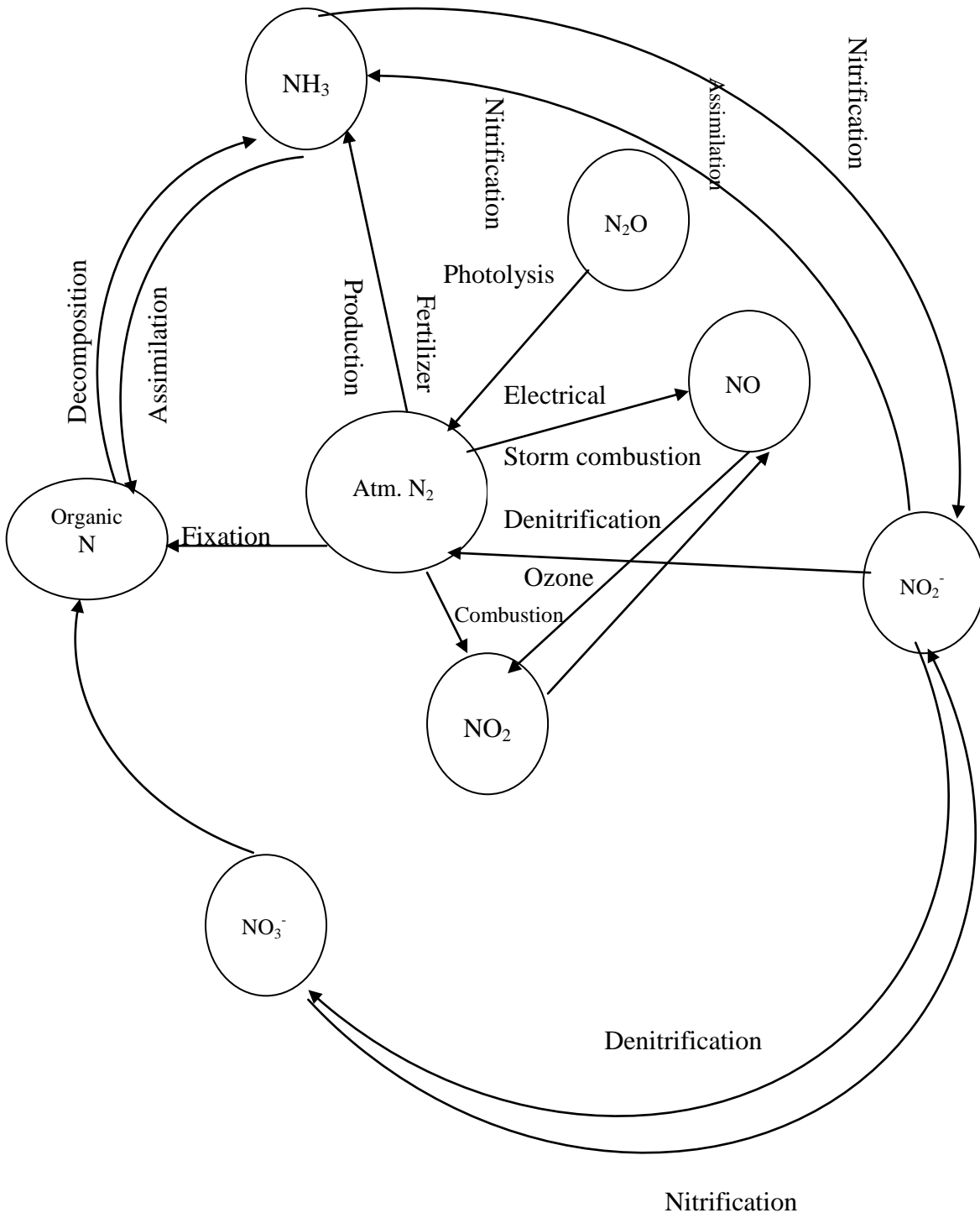
Fig. 2: The Nitrogen Cycle
Source: C.N. Sawyer et al., 2006

4.4   The Sulphur Cycle

On the earth surface sulphur exists as elemental sulphur, sulphur (iv) oxide, sulphuric acid, salts of sulphate, hydrogen sulphide, sulphur trioxide, organic sulphur compounds (such as dimethylsulphide) and amino acids (cysteine and methionine). The biogeochemical transformations of these sulphur species among the atmosphere, biosphere, hydrosphere and geosphere is called the **sulphur cycle**. Most of the sulphur on earth crust are tied up in rocks and salts or buried deep in the ocean in oceanic sediments. Sulphur enters the atmosphere through sources that are both natural (e.g. volcanic eruptions, bacterial processes, evaporation from water or decaying organisms) and human (e.g. wide-scale industrial emission of SO_2 and H_2S).

The major reservoir for sulphur is the crust, with a small, but potentially damaging proportion in the atmosphere. In the air, sulphur is usually oxidised from organic sulphur or elemental sulphur to SO_2 and SO_3 ending up as sulphate (SO_4^{2-}) in sulphate salts or sulphuric acid. The sulphate compounds dissolve in rain water and get precipitated (as rainfall) either as salts or acid rain. In the atmosphere, the oxidation of reduced forms of sulphur by dioxygen occurs without biological control; but can also occur through the actions of microorganisms in the soil, sediment and water column.

$$H_2S \rightarrow \ (S) \ \rightarrow \ SO_2 \rightarrow \ SO_3 \ \rightarrow \ SO_4{}^{2-}$$

Microorganisms in the soil or water act upon the $SO_4{}^{2-}$ in the presence of carbohydrates to finally liberate H_2S

$$S\,O_4^{2-} + H^+ + 2CH_2O \ \rightarrow \ HS^- + 2H_2O + 2CO_2 \ \rightarrow \ HS^- + H^+ \ \rightarrow \ H_2S$$
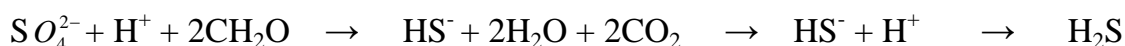
The formation of H_2S is a characteristics feature of anaerobic marine sediments. In the oceanic surface waters, dimethyl sulphide is formed much more commonly than H_2S because of the presence of the compound dimethylsulphonopropionate produced by some species of phytoplankton.

$$SO_4{}^{2-} \xrightarrow[\text{hydrosulphide}]{\text{organic}} \ H_2S + \text{organic sulphides} + [S] \xrightarrow[\text{compound}]{\text{organic}} H_2S + (CH_3)_2\, S.$$

When organic sulphur compounds are decomposed by bacteria, the initial sulphur product is usually H_2S.

$$R\text{-} SH \xrightarrow{\text{bacteria}} H_2S + RH$$
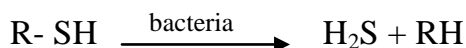
The hydrogen sulphide produced may be released as a gas to the atmosphere, where it is oxidised, or it may react with metal ions in the sediments or water columns to form insoluble sulphides.

$$H_2S + [S] \ \rightarrow \ Fe^{2+} \ \rightarrow \ FeS + FeS_2$$
$$\text{or} \quad 2Fe(OH)_3 + 3H_2S \ \rightarrow \ 2FeS + S + 6H_2O$$
$$Fe^{3+}$$

$$FeS + S \quad \rightarrow \quad FeS_2$$

Many marine phytoplankton produce compounds that breakdown to produce dimethylsulphide, $(CH_3)_2S$, a compound thought to be the major biogenically produced sulphur compound released from oceans. Dimethyl sulphide is rapidly oxidised to form SO_2 and ultimately, SO_4^{2-}. Some microorganisms in muds can generate elemental sulphur from sulphur compounds.

The black colour of many sediments is partially due to the presence of iron sulphides as well as organic matter. Oxidation of the sulphides when exposed to the surface leads to the formation of sulphuric acid:

$$2FeS_2 + 2H_2O + 7O_2 \quad \rightarrow \quad 2FeSO_4 + 2H_2SO_4.$$

This redox reaction occurs rapidly in the presence of water and dioxygen particularly when microorganisms are involved.

Fig. 3: The Sulphur Cycle
Source: C.N. Sawyer, P.L. McCarty and G.F. Parkin, 2006

4.5   The Water Cycle

Movement of water in its physical states through and around our planet is accomplished by the **water cycle**. Through evaporation, water from the ocean and soil goes as water vapour into the atmosphere and by transpiration, plants release water into the atmosphere.

In the atmosphere, as the temperature decreases, water vapour condenses into water droplets to form the clouds that precipitate as rainfall. A large proportion of this goes directly into the ocean or indirectly through run-off. Part of the water on the soil sinks down by percolation to form groundwater. The groundwater is pulled through the roots of plants and is transpired back into the atmosphere. Most of the rain and snow that fall on the continents come from plant transpiration than from ocean evaporation.

The water cycle transfers sun's heat energy to various places of the Earth; It also moves contamination or pollution round the planet. Every living thing is directly connected to the water cycle.
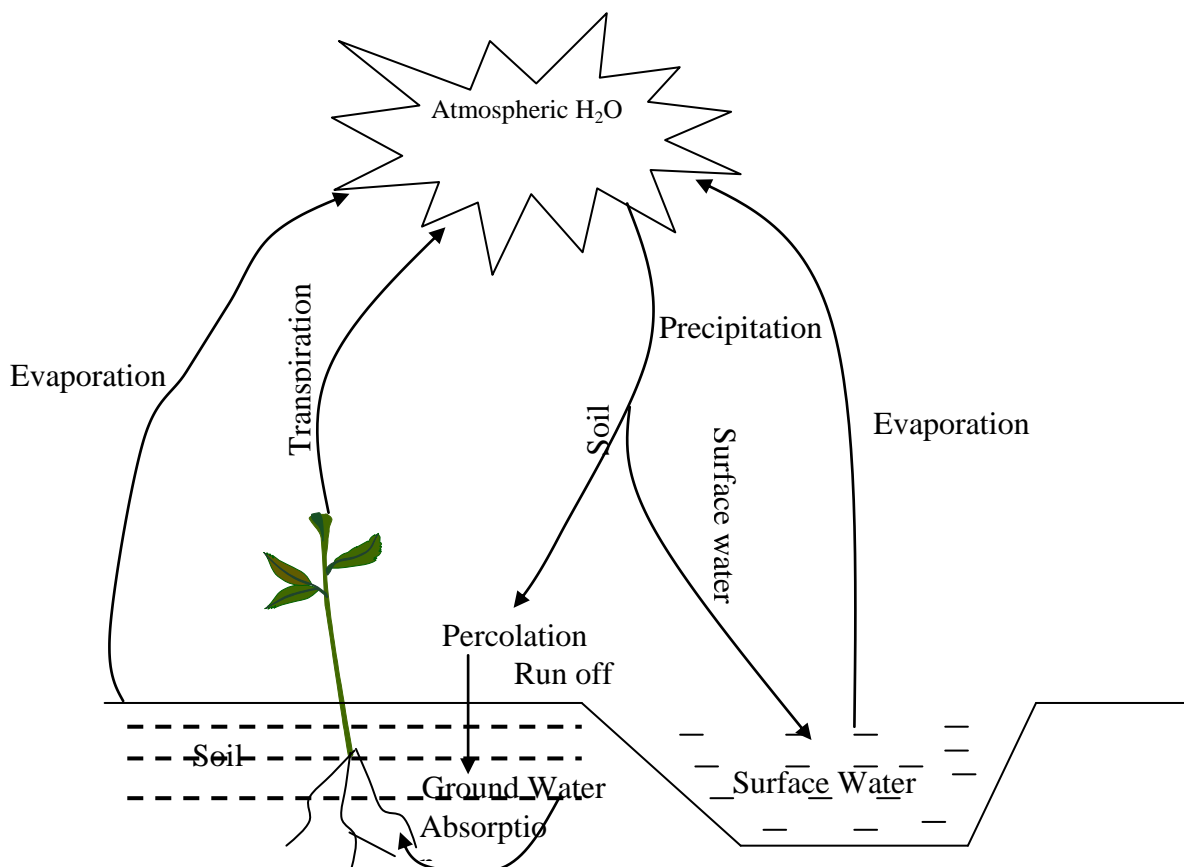

Fig. 4: The Water Cycle

5.0   ACTIVITY

1 a.   State the form(s) in which carbon exists in (i) the atmosphere, (ii) water, and (iii) rocks.
   b.   List two processes in each case that lead to the:
         (a) addition of CO_2 to atmosphere
         (b) removal of CO_2 to and from the atmosphere respectively.
   c.   Is the atmospheric level of CO_2 on a decreasing or an increasing trend currently? Explain.
   d.   Most ocean waters have a pH in the range 8 to 8.3. Briefly explain this observation using appropriate chemical equations.

2 (a)   What are the basic processes of nitrogen cycle?
   (b)   List and discuss the four ways by which atmospheric nitrogen can be converted into more biochemically available forms.
   (c)   In not more than two sentences, discuss the reason(s) why atmospheric nitrogen is not readily available for plants and animals metabolism despite its large atmospheric reservoir.
   (d)   Ground waters in most of the agricultural soils are noted for very high nitrate content.   Briefly explain this observation.

3.   Briefly explain
         (i) how elemental sulphur can be converted to a sulphite or a sulphate,
         (ii) the microbial transformation process of H_2S to SO_4^{2-} .

6.0   SUMMARY

In this unit, you have learnt that:

i.   there are various biogeochemical cycles such as the carbon cycle, the nitrogen cycle; the sulphur cycle; and the water cycle;
ii.   each biogeochemical cycle is a model that describes the complex movement of a chemical element or its species among matters usually near the Earth's surface;
iii.   there are different reservoirs for the recycled elements e.g. for nitrogen, the reservoir is the atmosphere; while for sulphur, it is the crust.
iv.   both anthropogenic and natural processes/activities add elements to or remove elements from the environmental compartments.

7.0   ASSIGNMENT

   1. (a) Explain briefly the roles of bacteria in the biogeochemical cycles of carbon, nitrogen and sulphur.
      (b) Using a simplified illustrative diagram, explain briefly either the nitrogen or carbon or sulphur cycle.

8.0   REFERENCES/FURTHER READING

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Sawyer, C. N., McCarty, P. L., & G. F. Parkin, G. F. (2006). *Chemistry for Environmental Engineering and Science,* 5th ed. New Delhi: Tata McGraw-Hill Put. Coy. Ltd.

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UNIT 2   CHARACTERISTICS OF THE ATMOSPHERE

CONTENTS

1.0   INTRODUCTION

The atmosphere is a layer of air (mixture of gases) that extends up to 700 kilometres above the Earth's surface. The atmosphere is a complex and rapidly changing part of the earth. The fluid nature of the atmosphere causes it to be the most changeable part of the Earth. The atmosphere is constantly under the influence of gravity, earth's rotation and differential heating by solar radiation. The atmosphere drives the **weather** (atmospheric variables that change rapidly-air temperature, humidity, percentage of cloudiness, type and amount of precipitation, air pressure and wind velocity) and the **climate** (the average weather condition in a region over a long period of time).

The gases in the air directly or indirectly support life on the Earth; during respiration, living things consume oxygen and release carbon dioxide; plants absorb carbon dioxide during photosynthesis and release oxygen; nitrogen is converted to useful nutrients to support plant growth and hence, that of the animals that depend on plants for survival.

2.0   OBJECTIVES

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

•   name the stratified layers of the atmosphere
•   identify the characteristics of each layer that differentiate it from the others and
•   discuss atmospheric reactions of notable environmental implications.

3.0   HOW TO STUDY THIS UNIT

1.   You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.

2.   Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.

3.   Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.

4.   Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0   MAIN CONTENT

4.1   General Composition of the Atmosphere

A greater percentage of the air in the atmosphere is made up of clear and odourless gases-nitrogen and oxygen. These two gases are called the **primary** or "**permanent**" gases. According to their relative volumes, average composition of the dry unpolluted atmosphere is given in Table 1. Varying amounts of most of these gases may be found in each of the layers of the atmosphere.

Some of the concentrations are uncertain because (i)   analytical procedures for some components have only recently reached the stage where good data can be obtained; (ii) some components such as CH_4, N_2O and CO_2 are known to be increasing in concentration at an appreciable rate; and (iii) it is questionable whether any parts of the atmosphere can be considered entirely free of pollutants or not.

The primary gases do not affect the weather unlike the trace gases. The lower atmosphere contains varying amounts of water vapour which determines its humidity. Water vapour (and to a lesser degree, CO_2) is of great importance in radiative transfer because it absorbs and emits strongly the infra-red (IR), the region of the spectrum at which earth radiates energy back to space.   Carbon dioxide plays a major role in the greenhouse effect and the attendant temperature attenuation of the earth. Various gaseous and solid impurities such as Chlorofluorocarbons (CFCs) in the atmosphere resulting from human activities contribute to the ozone layer depletion. The air also carries many kinds of dust of meteorite and terrestrial origin alongside micro-organisms, pollen and other particulate matters of anthropogenic origin.

The earth's atmosphere is a little thicker at the Equator and a little thinner at the poles because, the earth's spinning motion causes it to bulge slightly at the Equator. Because of the pull of gravity, the density of the atmosphere and the pressure exerted by air molecules are greatest near the earth's surface (approximately $1g/10^3m^3$ and 10^6 dynes/cm^2, respectively). Air pressure decreases rapidly with increasing altitude,

reaching one-half of its sea-level value at about 5,500 m (5.5 kilometres). At standard temperature and pressure (s.t.p.), 22.4 L of air weighs 28.97g.

Table 1:   Average composition of the dry unpolluted atmosphere

	Gas	Average Concentration		Approximate Residence time
		%	ppm	
1.	N_2	78.08		10^6 years
2.	O_2	20.95		5000 years
3.	Ar		9340	Not cycled
4.	CO_2		360	100 years
5.	Ne		18	Not cycled
6.	CH_4		1.8	15 years
7.	CK_r		1.1	Not cycled
8.	H_2		0.58	10 years
9.	N_2O		0.31	120 years
10.	CO		0.12	65 days
11.	Xe		0.09	Not cycled
12.	O_3		0.01- 0.1	100 days
13.	SO_2		10^{-3}- 10^{-2}	10 days
14.	NO/NO_2		10^{-6} - 10^{-2}	1 day
15.	NH_3		10^{-4}- 10^{-3}	5 days
16.	HNO_3		10^{-5}- 10^{-3}	1 day
17.	Cl_2		0.6	

Sources: J.H. Seinfeld, 1986; P. Brimblecombe, 1996; P. O' Neill, 1993.

4.2   Composition and Characteristics of the Earth's Atmospheric Layers

The Earth's atmosphere is composed of distinct layers, namely; the Troposphere, the Stratosphere, the Mesosphere, the Thermosphere and the Exosphere.

4.2.1 The Troposphere

The troposphere holds most of the air and is the place where storms occur. It extends from the Earth surface upward to a height of about 10 kilometres at the poles, 11.3 kilometres in mid-latitudes and 16.1 kilometres at the Equator. The air in the troposphere is in constant horizontal and vertical motions. Throughout the troposphere, temperature decreases with altitude at an average lapse rate of about 2^oC per 305 m reaching about -57^oC at the tropopause (the peak of the troposphere).

The troposphere may be considered in two smaller components: the part in contact with the earth surface is called the **boundary layer;** above it is the **free troposphere**. The boundary layer is normally bounded at its upper extreme by a temperature

inversion (a horizontal band in which temperature increases with height) through which little exchange of air can occur with the free troposphere above. The depth of the boundary layer is typically around 100 metres at night and 1000 metres during the day, although these figures do vary greatly. Pollutant emissions are usually emitted into the boundary layer and are constrained within it to a large extent. Free tropospheric air contains the longer-lived atmospheric components together with contributions from pollutants, which have escaped the boundary layer, and from some downward mixing stratospheric air.

The troposphere is the layer of greatest interest with respect to pollution issues because, it is the layer in which most living things exist.
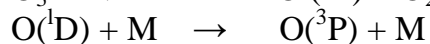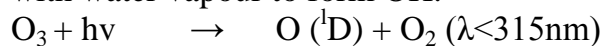

Earth surface
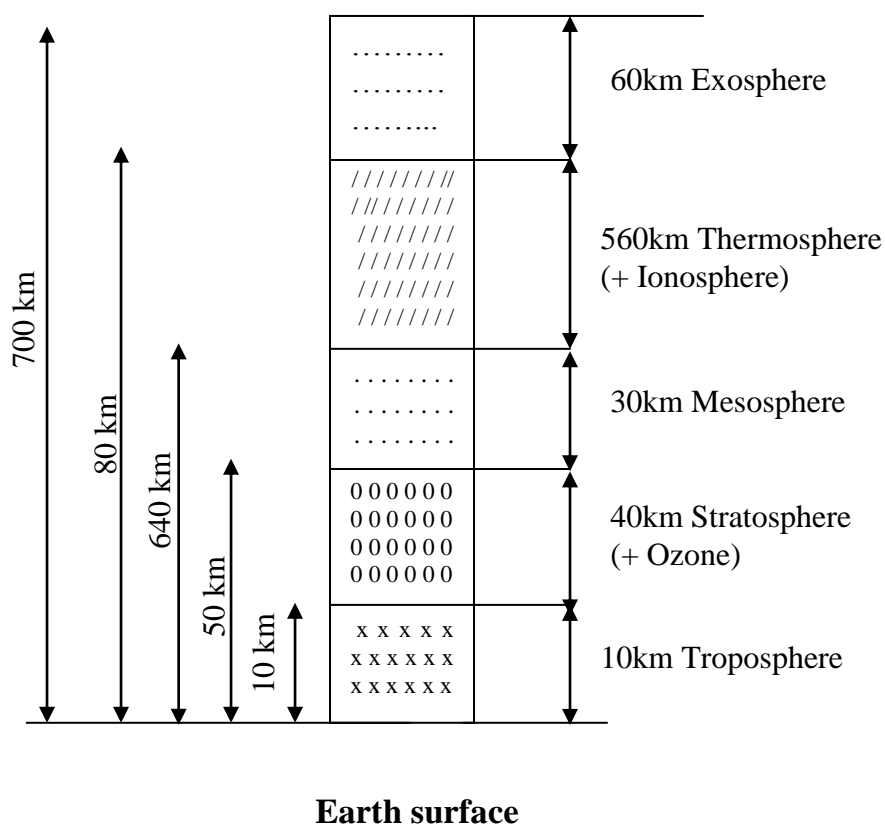
Fig. 5: The atmospheric layers

4.2.1.1   Some Important Tropospheric Chemical Transformations
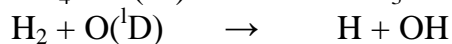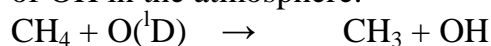
1.   **Formation of Hydroxyl Radical (OH)**
      (a)   Photolysis of ozone: When ozone undergoes photolysis in the presence of light of short wavelength (λ < 315mm) a singlet atomic oxygen O (ID) is formed. This may relax to the triplet state O (^{3}P) or may react with water vapour to form OH.
      $O_3 + hv \quad \rightarrow \quad O\,(^1D) + O_2\ (\lambda<315nm)$
      $O(^1D) + M \quad \rightarrow \quad O(^3P) + M$

or $O(^2D) + H_2O \qquad \rightarrow \qquad 2OH^-$

This is the primary source of OH in the atmosphere. (M is an inert energy absorbing molecule e.g. N_2).

(b)   Reactions of $O(^1D)$ with CH_4 and H_2. This is one of the minor sources of OH in the atmosphere.

$CH_4 + O(^1D) \quad \rightarrow \qquad CH_3 + OH$

$H_2 + O(^1D) \qquad \rightarrow \qquad H + OH$

(c)   Photolysis of HONO and H_2O_2. This produces OH directly.

$HONO + hv \qquad \rightarrow \qquad OH + NO \qquad (\lambda < 400nm)$

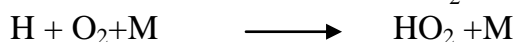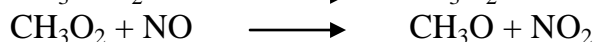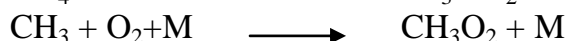$H_2O_2 + hv \qquad \rightarrow \qquad 2OH \qquad (\lambda < 360nm)$

(d)   From HO_2 radical in polluted atmospheres, HO_2 is able to give rise to OH formation.

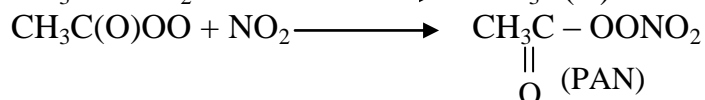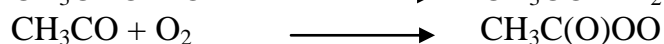$HO_2 + NO \qquad \rightarrow \qquad NO_2 + OH$
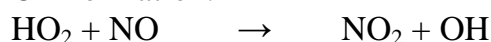
The hydroxyl radicals play a central role in the formation of ozone, peroxyacetyl nitrate (PAN), sulphuric acid and nitric acid.

2.   **Formation of ozone:** Ozone could be formed in the atmosphere (troposphere particularly) from the oxidation of CH_4 and CO in processes involving the hydroxyl radicals.

$CH_4 + OH \longrightarrow CH_3 + H_2O$

$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$

$CH_3O_2 + NO \longrightarrow CH_3O + NO_2$

$CH_3O + O_2 \longrightarrow CH_2O + HO_2$

Also, $CO + OH \longrightarrow CO_2 + H$

$H + O_2 + M \longrightarrow HO_2 + M$

Now, $HO_2 + NO \longrightarrow OH + NO_2$

$NO_2 + hv \longrightarrow NO + O(^3P) \quad (\lambda < 435nm)$

$O(^3P) + O_2 + M \longrightarrow O_3 + M$
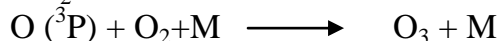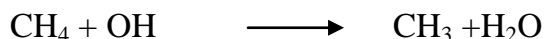
3.   **Formation of peroxyacetyl nitrate (PAN):** PAN is of interest as a characteristic product of atmospheric photochemistry, as a probable reservoir of reactive nitrogen in remote atmospheres and because of its adverse health effects on plants. Its formation is acetyl radicals, CH_3CO, formed from acetaldehyde oxidation.

$CH_3CHO + OH \longrightarrow CH_3CO + H_2O$

$CH_3CO + O_2 \longrightarrow CH_3C(O)OO$

$CH_3C(O)OO + NO_2 \longrightarrow CH_3C - OONO_2$

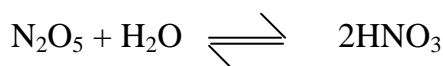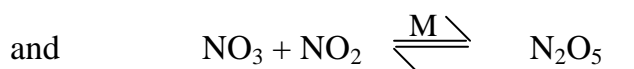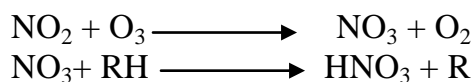$\qquad\qquad\qquad\qquad\qquad\qquad \overset{\|}{O} \;$ (PAN)

4.   **Formation of sulphuric acid:** Atmospheric oxidation of SO_2 could proceed via a range of mechanisms but formation through the hydroxyl radical reaction in the gas phase is of overwhelming importance.

$$SO_2 + OH \longrightarrow HOSO_2$$
$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$
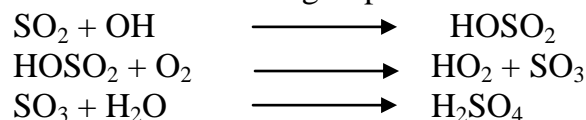
5.   **Nitric acid formation:** The main daytime route of HNO_3 formation is from the reaction:

$$NO_2 + OH \longrightarrow HNO_3$$

At night, reaction of NO_3 radical becomes important which was not operative during the day due to photolytic breakdown of NO_3. The radical is formed as follows:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
$$NO_3 + RH \longrightarrow HNO_3 + R$$

and $$NO_3 + NO_2 \overset{M}{\rightleftharpoons} N_2O_5$$

$$N_2O_5 + H_2O \rightleftharpoons 2HNO_3$$

One of the atmospheric changes that has attracted a widespread attention over the last few decades is the phenomenon of **acid rain** or **acid deposition**. Acid rain results when gaseous emissions such as sulphur oxides (SO_x) and nitrogen oxides (NO_x) interact with water vapour and sunlight and are converted to strong acidic compounds as indicated (Nos. 4 and 5) above.

4.2.2 The Stratosphere

The stratosphere is the second layer of the atmosphere as one moves upward from the earth's surface. It lies above the troposphere and below the mesosphere. The stratosphere starts at approximately 10 kilometres and extends to approximately 50 kilometres high. The altitude of the bottom of the stratosphere varies with latitude and seasons. The bottom of the stratosphere is around 16 kilometres near the equator, around 10 kilometres at mid-latitudes and around 8 kilometres near the poles. It is slightly lower in winter at mid and high-latitudes and slightly higher in the summer.
Within the stratosphere, temperature increases as altitude increases, reaching about – $3^{o}C$ at its top (the stratopause). Above the stratopause, temperature again decreases with height. In the stratosphere, air does not flow up and down, but flows parallel to the earth in a very fast moving air streams. This dynamic stability of the stratosphere is due to the warmer layers above and cooler layer below the stratosphere. The heating of the upper layer is caused by an ozone layer that absorbs solar ultra violet (UV) radiation.

The stratosphere is very dry; it contains air with little water vapour. As a result of this, few clouds are found in this layer with most clouds occurring in the lower (more humid) troposphere. However, **polar stratospheric clouds** (PSCs) nacreous clouds also called appear in the lower stratosphere near the poles in winter. They are found at altitudes of 15 to 25 kilometres and form only when temperatures at those heights dip below – 78°C. They are suspected to play some roles in the formation of "holes in the ozone layer" by catalysing certain chemical reactions that destroy ozone. Because bacterial life survives in the stratosphere, it is considered part of the biosphere.

The Stratospheric Ozone Layer Chemistry

The ozone layer is a diffused concentration of ozone (O_3) found predominantly in the stratosphere. About 90 percent of the atmospheric ozone is located within the stratosphere. Ozone actually occurs in trace amounts throughout the atmosphere with a peak concentration of about 10 ppm by volume in the lower stratosphere between about 20 to 25 kilometres altitude. The concentration of ozone in the stratosphere shows daily, annual and seasonal variations of several per cent. Therefore, it is difficult to identify and quantify changes in concentration caused by anthropogenic effects unless these are large.

The ozone layer protects life from the harmful UV rays of the sun. Whereas acid rain and photochemical oxidant pollution are somewhat localised environmental problems, modification of stratospheric ozone is a global phenomenon. The electromagnetic UV radiation from the sun that falls on the upper layers of the atmosphere is subdivided into three regions of different energy or wavelength (λ). These regions are: highest energy ($\lambda < 290$ nm), intermediate energy ($\lambda = 290 – 320$ nm) and lowest energy ($\lambda = 320 - 400$ nm).

At altitudes above 400kilometres , the majority of the oxygen is atomic because the bonds in the dioxygen molecule may be broken by UV ($\lambda < 290$ nm) to form free oxygen atoms.

$$O_2 \xrightarrow{\text{UV}} 2(O).$$

At lower altitudes, as the number of dioxygen and dinitrogen molecules increases, ozone (O_3) is formed.

$$O + O_2 + M \longrightarrow O_{3 +} M.$$
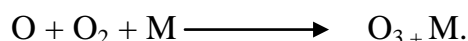
The molecular species, M, (usually N_2 or O_2) removes the excess energy produced when ozone is formed and so prevents the ozone from decomposing immediately. Ozone is destroyed by the absorption of UV and by some other naturally occurring chemical species, X, (X = NO and HO usually) in the stratosphere by a reaction sequence that regenerates these species so that they can react again.

$$O_3 \xrightarrow{\text{uv}} O + O_2$$

or $\quad\quad O_3 + X \longrightarrow O_2 + O$

$$XO + O \rightarrow O_2 + X.$$
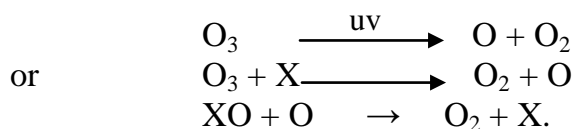
Recently, there have been significant increases in the stratospheric concentrations of Chlorine (Cl) and Bromide (Br). It has been estimated that one atom of Cl can destroy 100 000 molecules of ozone before the cycle is interrupted. The bromine cycle is not easily broken; once formed, the ozone moves towards the poles and also to lower altitudes. There is generally a higher concentration of ozone above Polar Regions because the rate of removal is slower than near the equator. The absorption of UV and infrared radiation in the stratosphere means that the temperature in the stratosphere is higher than the temperature at the top of the troposphere. This temperature inversion stabilizes air movements in the stratosphere and controls weather patterns in the stratosphere.

The stratospheric air above the Antarctic contains very little water vapour (4 – 6 ppm by volume). Consequently, nucleation and condensation to form clouds only occur at very low temperatures. When the temperature drops below – 75$^{\text{o}}$C, nitric acid trihydrate ($HNO_3.3H_2O$), NAT, particles, start to condense to form type 1 polar stratospheric clouds (Type 1 PSCs). Their formation removes nitrogen oxide species from the gas phase and traps them in the clouds as solid nitric acid. Nitrogen dioxide can break the ozone, destroying the cycle initiated by chlorine by reacting with the chlorine monoxide,
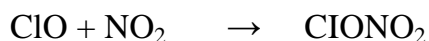
$$ClO + NO_2 \quad \rightarrow \quad ClONO_2$$

But this is prevented when the nitrogen species become locked up in the clouds. To worsen the condition, any chlorine nitrate, $ClONO_2$, that is present in the stratosphere can be destroyed by reactions that occur on the surface of the solid particles, but do not occur in the gas phase.
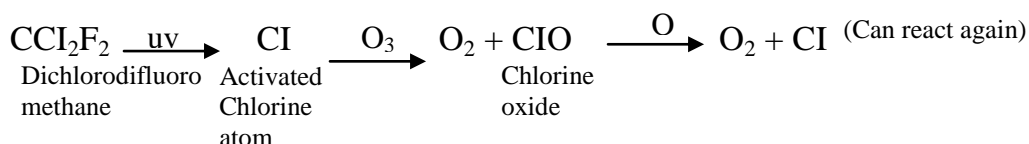
$$ClONO_2 + H_2O \quad \rightarrow \quad HOCl + HNO_3$$
$$ClONO_2 + HCl \quad \rightarrow \quad Cl_2 + HNO_3$$
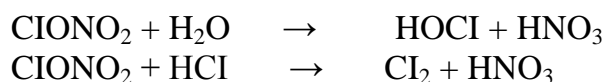
These reactions increase the quantity of the potentially reactive chlorine species Cl (from Cl_2) and HOCl and $ClNO_2$.

The increased use of chlorine compounds as refrigerants, foaming agents, solvents and in aerosol-spray cans has produced a rapid rise in the concentration of chlorine in the atmosphere. Natural levels of chlorine are about 0.6 ppb by volume. In 1992, concentrations had reached 3.5 ppb and might rise further to 4 ppb before a decline is expected.
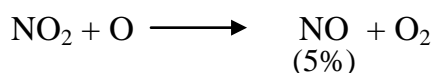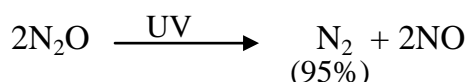
The chlorofluorocarbons (CFCs) such as CCl_3F and CCl_2F_2 were developed as inert, non-toxic compounds that could be safely used by industry and in home. Unfortunately, they are so inert that when they escape into the atmosphere they slowly pass unchanged through the troposphere and enter the stratosphere. Here, they are

subjected to photochemical decomposition under the influence of UV radiation to yield free chlorine atoms that catalyse the decomposition of ozone e.g.

$$CCI_2F_2 \xrightarrow{\text{uv}} CI \xrightarrow{\quad O_3 \quad} O_2 + CIO \xrightarrow{\quad O \quad} O_2 + CI \text{ (Can react again)}$$

Dichlorodifluoro   Activated   Chlorine
methane   Chlorine   oxide
                    atom

The CFCs have long atmospheric lifetimes (65 years for CCI_3F and 130 years for CCI_2F_2). There are enough of these compounds in the atmosphere to support the elevated stratospheric chlorine concentrations until 2100. Since anthropogenically introduced chlorine and bromine levels will remain high for so long, it is expected that there will increase in dangerous UV radiations reaching the earth's surface. Before ozone depletion began, 70 – 80 percent of the dangerous UV radiation was absorbed before reaching the earth surface. A 10 percent reduction in stratospheric ozone concentration would reduce the amount of dangerous UV being absorbed to 55 – 65 percent. This could have major effects on susceptible organisms such as plankton and land plants. Effects on humans would include increased risk of skin cancer and eye cataracts. These direct effects on human are less worrying than the interference with food production that could occur.

The increased use of fertilizers is causing an increase (0.25% per year) in the quantities of N_2O being produced by micro-organisms. Like CFCs, N_2O is very stable and passes up through the troposphere and finally enters the stratosphere. Here, (Stratosphere), is broken down under the influence of UV radiation into a mixture of about 95 percent N_2 and 5 percent NO. NO is one of the ozone destroying compounds. N_2O

$$2N_2O \xrightarrow{\quad UV \quad} N_2 + 2NO$$
$$(95\%)$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow NO + O_2$$
$$(5\%)$$

The effects of increased N_2O concentrations are relatively small and may well be balanced by increases in methane (CH_4) which is capable of increasing or preserving ozone concentrations by reacting with chlorine in the stratosphere.

4.2.3 The Mesosphere

The mesosphere is a layer of earth's atmosphere directly above the stratosphere and below the thermosphere. It extends from about 50kilometres to 85kilometres above the earth surface. The **stratosphere** and **mesosphere** together are sometimes referred to as the **middle atmosphere**. Throughout the mesosphere, temperatures decreases with height; the coldest temperatures (approx. - 90^0C) within the Earth's atmosphere are found near the top of the mesosphere i.e. within the mesopause.

Much about the mesosphere is still mysterious because, it is difficult to take instrumental measurements of the mesosphere directly. Weather balloons and other aircraft cannot fly high enough to reach the mesosphere and satellites orbit above it; it cannot also directly measure traits of this layer. Scientists use the instruments on sounding rockets to sample the mesosphere directly, but such flights are brief and infrequent.

Most meteors vaporise in the mesosphere. Some materials from meteors linger in the mesosphere such that this layer has a relatively high concentration of iron and other metal atoms. Very strange, high altitude clouds called "noctilucent clouds" or "polar mesospheric clouds" sometimes form in the mesosphere near the poles. These peculiar clouds form at a much higher altitude than other types of clouds. Odd electrical discharges similar to lightning called "sprites" and "ELVES" occasionally appear in the mesosphere dozens of kilometers above thunderclouds in the troposphere below. Within and below the mesopause, gases made of different types of atoms and molecules are thoroughly mixed together by turbulence in the atmosphere.

4.2.4 The Thermosphere

Above the mesosphere is the thermosphere. It extends for about 90 kilometres above the earth surface. It is the layer of the Earth's atmosphere which is first exposed to the sun's radiation. In the thermosphere, gas particles collide so infrequently and get sorted into strata based on the molecular mass and types of chemical elements they contain. Within this layer, UV radiation causes ionisation of the atmospheric particles, enabling radio waves to bounce off and be received beyond the horizon.

Thermospheric temperatures increase with altitude and can rise to 1500^0C and above due to absorption of highly energetic solar radiation by the small amount of residual oxygen still present. The air within the thermosphere is so thin that a small increase in energy can translate to a large temperature increase. Because of the thin air in the thermosphere, scientists cannot measure the temperature directly. They measure the density of the air by pressure drag it puts on satellites and then use the density to find the temperature.

The **ionosphere** is the very outer edge of the thermosphere. It is not a separate layer as such; it is a place where gas atoms drift into space from here. It is called ionosphere because in this part of the atmosphere where the sun's radiation is ionised, or pulled apart as it travels through the earth's magnetic fields to the north and south poles. This pulling apart is seen from the Earth as **auroras**. The colourful displays of **auroras** are called the "**Northern Lights**" or "**Aurora Borealis**" in the Northern Hemisphere, the "**Southern Lights**" or "**Aurora Australis**" in the Southern Hemisphere.

The dynamics of the lower thermosphere (below 120 kilometres) are dominated by atmospheric tide, which is driven in part, by the very significant diurnal heating. The

atmospheric tide dissipates above this level since molecular concentrations do not support the coherent motion needed for fluid flow.

4.2.5 The Exosphere

The exosphere is the highest layer of the atmosphere. Together with the ionosphere, it could be considered as part of the thermosphere extending from 500 to about 1000 kilometers (it may extend to about 10,000 kilometres above the earth's surface). This, indeed, is the upper limit of the earth's atmosphere where the atmosphere turns or merges into space.

The highly diluted gas in this layer can reach $2500^{o}C$ during the day; even though the temperature is so high, one would not feel hot in the thermosphere; because it is so near vacuum that there is not enough contact with the few atoms of gas to transfer much heat. A normal thermometer would read significantly below $0^{o}C$ due to the energy lost by radiation overtaking the energy acquired from the atmospheric gas by direct contact.

In this region of the atmosphere, hydrogen and helium are the prime components and are only present at extremely low densities. This is the zone where many satellites orbit the Earth.

5.0   ACTIVITIES

1.a.   State two reasons why the troposphere could be considered a layer of greatest interest to an environmental chemist out of all the atmospheric layers.

b.   Discuss briefly two ways by which the hydroxyl radicals can be formed in the troposphere.

c.   List and explain two roles of the hydroxyl radicals in the troposphere that could result in environmental degradation.

d.   Using chemical equations only, show the mechanism of either H_2SO_4 or HNO_3 formation in the atmosphere.

2.a.   List two naturally occurring and two anthropogenic chemical species that could lead to stratospheric ozone depletion.

b.   Briefly explain how a named chlorofluorocarbon can cause stratospheric ozone layer depletion.

6.0   SUMMARY

In this unit, you have learnt that:

i.   the earth's atmosphere consists of five more or less distinct layers: the troposphere, the stratosphere, the mesosphere, the thermosphere and the exosphere;

ii.   there are physico-chemical variations in the atmospheric layers that characterise each of the layers;
iii. the chemical reactions in the atmosphere could positively or negatively affect the atmospheric gaseous compositions; and
iv.   the ozone layer of the atmosphere shields the plankton, land plants and humans from the damaging effects of excessive dangerous UV radiation from the sun or the outer space.

7.0   ASSIGNMENT

1.   List two physico-chemical features which distinguish the stratosphere from the troposphere.
2.   What particular hazards are caused by the presence of Chlorofluorocarbons (CFCs) in the stratosphere particularly?
3.   Which of NO or N_2O do you consider of concern if it is substantially present in the atmosphere? Showing necessary chemical reactions, justify your response with a brief explanation.

8.0   REFERENCES

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Harrison, R.M. (1996). *Pollution: Causes, Effects and Control*, 3rd ed. London: The Royal Soc. of Chemistry.