Semester-II

19AEC201 ENVIRONMENTAL STUDIES 3H 3C

Instruction Hours/week:L: 3 T:0 P:0 Marks: Internal: 40 External: 60 Total:100

End Semester Exam: 3 hrs

Course Objectives

- To create the awareness about environmental problems among people.
- To develop an attitude of concern for the environment.
- To motivate public to participate in environment protection and improvement.

Course Outcomes (COs)

1. Master core concepts and methods from ecological and physical sciences and their application in environmental problem solving.
2. Master core concepts and methods from economic, political, and social analysis as they pertain to the design and evaluation of environmental policies and institutions.
3. Appreciate the ethical, cross-cultural, and historical context of environmental issues and the links between human and natural systems.
4. Understand the transnational character of environmental problems and ways of addressing them, including interactions across local to global scales.
5. Apply systems concepts and methodologies to analyze and understand interactions between social and environmental processes.
6. Reflect critically about their roles and identities as citizens, consumers and environmental actors in a complex, interconnected world.
7. Demonstrate proficiency in quantitative methods, qualitative analysis, critical thinking, and written and oral communication needed to conduct high-level work as interdisciplinary scholars and/or practitioners.

Unit I – INTRODUCTION - ENVIRONMENTAL STUDIES & ECOSYSTEMS

Environment Definition, Scope and importance; Ecosystem, Structure and functions of ecosystem. Energy flow, Food chains and food webs, Ecological succession. Classification of ecosystem. Forest ecosystem, GrasslandEcosystem, Desert ecosystem, Aquatic ecosystems (ponds, streams, lakes, rivers, oceans, estuaries).

Unit II - NATURAL RESOURCES - RENEWABLE AND NON-RENEWABLE RESOURCES

Natural resources - Renewable and Non – Renewable resources. Land resources and land use change, Land degradation, soil erosion and desertification. Forest resources -Deforestation: Causes and impacts due to mining, dam building on environment, forests, biodiversity and tribal populations. Water resources- Use and over-exploitation of surface and ground water, floods, droughts, conflicts over water.Use of alternate energy sources, growing energy needs, case studies.Role of an individual in conservation of natural resources. Equitable use of resources for sustainable lifestyles.

Unit III - BIODIVERSITY AND ITS CONSERVATION

Levels of biological diversity - genetic, species and ecosystem diversity.Ecosystem and biodiversity services: Ecological, economic, social, ethical, aesthetic and Informational value. Bio-geographical classification of India. Biodiversity patterns (global, National and local levels). Hot-spots of biodiversity. India as a mega-diversity nation. Endangered and endemic species of India. Threats to biodiversity: habitat loss, poaching of wildlife, man-wildlife conflicts.Conservation of biodiversity: in-situ and ex-situ conservation of biodiversity.

Unit IV - ENVIRONMENTAL POLLUTION

Definition, causes, effects and control measures of Air pollution, Water pollution, Soil pollution, Noise pollution.Nuclear hazards and human health risks. Solid waste management and control measures of urban and industrial wastes. Role of an individual in prevention of pollution. Case studies.

Unit V - SOCIAL ISSUES AND THE ENVIRONMENT

Concept of sustainability and sustainable development. Water conservation -Rain water harvesting, watershed management.Climate change, global warming, ozone layer depletion,acid rain andits impacts on human communities and agriculture. Environment Laws (Environment Protection Act, Air Act, Water Act, Wildlife Protection Act, Forest Conservation Act). International agreements (Montreal and Kyoto protocols).Resettlement and rehabilitation of projectaffected persons.Disaster management (floods, earthquake, cyclones and landslides).EnvironmentalMovements (Chipko, Silent valley, Bishnois of Rajasthan). Environmental ethics: Roleof Indianand other religions and cultures in environmental conservation. Environmental communication and public awareness,case studies (e.g., CNG vehicles in Delhi).Human population growth: Impacts on environment, human health and welfare.

Suggested Readings

1. Anonymous. 2004. A text book for Environmental Studies, University Grants Commission and Bharat Vidypeeth Institute of Environmental Education Research, New Delhi.
2. Anubha Kaushik., and Kaushik, C.P. 2004. Perspectives in Environmental Studies. New Age International Pvt. Ltd. Publications, New Delhi.
3. Arvind Kumar. 2004. A Textbook of Environmental Science. APH Publishing Corporation, New Delhi.

4. Daniel, B. Botkin., and Edward, A. Keller. 1995. Environmental Science John Wiley and Sons, Inc., New York.
5. Mishra, D.D. 2010. Fundamental Concepts in Environmental Studies. S.Chand & CompanyPvt. Ltd., New Delhi.
6. Odum,E.P., Odum, H.T. and Andrews, J. 1971. Fundamentals of Ecology. Philadelphia: Saunders.
7. Rajagopalan, R. 2016.Environmental Studies: From Crisis to Cure, Oxford University Press**.**
8. Sing, J.S., Sing. S.P. and Gupta, S.R. 2014. Ecology, Environmental Science and Conservation. S. Chand & Publishing Company, New Delhi.
9. Singh, M.P., Singh, B.S., and Soma, S. Dey. 2004. Conservation of Biodiversity and Natural Resources.Daya Publishing House, New Delhi.
10. Tripathy. S.N., and Sunakar Panda. (2004). Fundamentals of Environmental Studies (2nd ed.). Vrianda Publications Private Ltd, New Delhi.
11. Verma, P.S., and Agarwal V.K. 2001. Environmental Biology (Principles of Ecology).S.Chand and Company Ltd, New Delhi.
12. Uberoi, N.K. 2005. Environmental Studies. Excel Books Publications, New Delhi.

DEPARTMENT OF CHEMISTRY

LECTURE PLAN

Name of the Staff	: **Dr. K. Sundaram**
Department	: **Chemistry**
Title of the Paper	: **Environmental Studies**
Paper Code	: **19AEC201**
Class	: **I-B.Sc-Chemistry**
Year and Semester	: **2019–2022 and II-Semester**
Total Hours	: **40 Hours**

S.No	Lecture hour	Topics	Support material
UNIT-I Hours required -07			
1	1	Environment – Definition,Scope and importance of Environment	T1:1-2, 5,6
2	1	Components of environment	T1:3
3	1	Ecosystem- definition, Concept, Scope and importance of ecosystem	T1:93,94
4	1	Structure and functions of ecosystem	T1: 94,98
5	1	Energy flow and ecological succession	T1:107-115
6	1	food chains, food webs	T1:99,102
7	1	Classifications of ecosystem	T1:119
S.No	**Lecture hour**	**Topics**	**Support material**
UNIT-II Hours required -08			
1	1	Natural resources and associated problems	T1:16
2	1	Introduction: Renewable and Non-renewable Resources	T1: 16
3	1	Forest and Water resources : Use and over utilization, exploitation	T1: 17-26 T1:26-37
4	1	Mineral resources: Use and over utilization, exploitation	T1: 37-45
5	1	Food and energy resources: Use and over utilization, exploitation	T1: 47-56 T1:56-73
6	1	Land resources: Use and over utilization, exploitation	T1: 74-80
7	1	Role of an individual in conservation of natural resources	T1:82-84
8	1	Equitable uses of resources for sustainable life styles, Fire accidents and prevention	T1:85-86

S.No	Lecture hour	Topics	Support material
UNIT-III		**Hours required -08**	
1	1	Introduction, definition: genetic, species and ecosystem diversity	T1:135-137
2	1	Bio geographical classification of India	T1:137-139
3	1	Value of biodiversity: consumptive use, productive use,	T1:139-142
4	1	Value of biodiversity: social, ethical, aesthetic and option values	T1:142-144
5	1	Value of biodiversity: Biodiversity at global, national and local levels	T1:145-148
6	1	India as a mega diversity nation. Hot spots of biodiversity	T1:148-150,153
7	1	Threats to biodiversity: habitat loss poaching of wild life, Man-wildlife conflicts, Endangered and endemic species of India	T1:156-160, 161-164
8	1	Conservation of biodiversity :in-situ and ex-situ conservation of biodiversity	T1:165, 166,167
S.No	**Lecture hour**	**Topics**	**Support material**
UNIT-IV		**Hours required -07**	
1	1	Definition, causes, effects and control measures of air pollution	T1:173-182
2	1	Water and Soil pollution	T1:188-193 T1:202-204
3	1	Marine and Noise pollution	T1:200-202 T1:183-188
4	1	Thermal and Nuclear pollution	T1: 197-199 T1: 204-206
5	1	Solid waste management: Causes, effects and control measures of urban and industrial waste	T1:206,207
6	1	Role of an individual in prevention of pollution and Pollution case studies	T1: 210, 212
7	1	Disaster management: floods, earth quake, Cyclone landslides	T1:219-227
S. No	**Lecture hour**	**Topics**	**Support material**
UNIT-V		**Hours required -10**	
1	1	From unsustainable to sustainable development. Urban problems related to energy	T1: 233-238
2	1	Water conservation, rain water harvesting, water shed management	T1: 238-246
3	1	Resettlement and rehabilitation of people; its problems and concerns	T1: 246-250

4	1	Environmental ethics: Issues and possible solutions, climate change, global warming, acid rain, ozone layer depletion, nuclear accidents and holocaust	T1: 251-267
5	1	Wasteland reclamation, consumerism and waste products, Environment protection act, air act, Water act, wild life protection act	T1: 267-280, 273-276
6	1	Forest conservation act. Issues involved in enforcement of environmental legislation, Public awareness, population growth	T1: 274-276, 285-288
7	1	Variation among nations, population explosion-family welfare programme. Environment and human health. Human rights.	T1: 285-288, 295-311
8	1	Value education. HIV/AIDS, women and child welfare	T1:311-319
9	1	Role of information technology in environment and human health.	T1: 320-324
10	1	Revision and discussion of question papers ESE Question paper discussion	

TEXT BOOK:

T1: Perspectives in environmental studies, Anubha Kaushik, Cp Kaushik, IV Edition 214, New age international publishers, New Delhi-110002

UNIT-I

SYLLABUS

Metals and Coordination Chemistry:

Metals: General methods of extraction of metals-methods of ore dressing-types of furnaces-reduction methods-electrical methods-types of refining-Van Arkel process-Zone refining.

Coordination Chemistry: Nomenclature-theories of Werner, Sidgewick and Pauling-chelation and its industrial importance-EDTA-haemoglobin-chlorophyll-applications in qualitative and quantitative analysis.

Metals

Introduction

Only a few metals e.g. gold and platinum occur in nature in the native or free state. But most of the metals occur in the combined state such as their oxides, sulphides, halides and oxyanions. The various compounds of metals which occur in nature and are obtained by mining are called **minerals**. The minerals from which the metals can be conveniently, profitably and economically extracted are known as **ores**. *Thus, all ores are minerals but all minerals are not ores*. The art of winning a metal from its ore is known as **metallurgy**.

The method of extraction of metals depends on the nature of the ore employed. Therefore, it is not possible to provide a universal scheme for the extraction of all metals. However, the following three principle steps are involved in metallurgy.

First step- Concentration of the ore or ore dressing

Second step- Reduction of the concentrated ore to the metal

Third step- Refining of crude metals.

We shall study them in detail in this chapter.

I. Ore Dressing

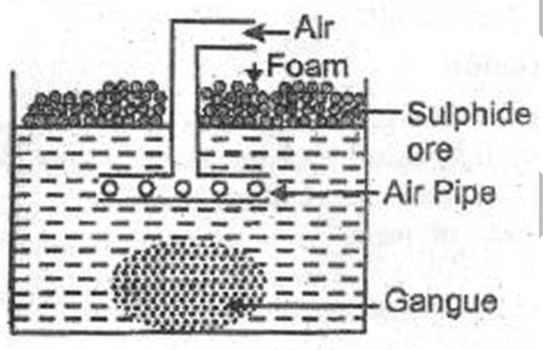
The ore, which is mined, is usually associated with rocky impurities called **gangue** or **matrix.** Ore dressing is concerned with the removal of gangue from the ore. Gangue can be separated by any one of the following ways:

(i) Hand Picking: In some cases the ore can readily be located and separated by simply picking up by hand.

(ii) Gravity separation or Concentration by washing or Hydraulic washing: The ore is first powdered and then washed with a strong stream of water. When the ore particles happen to be heavier than the gangue, the lighter earthy impurities (gangue) are washed away. The heavier ore particles settle to the bottom.

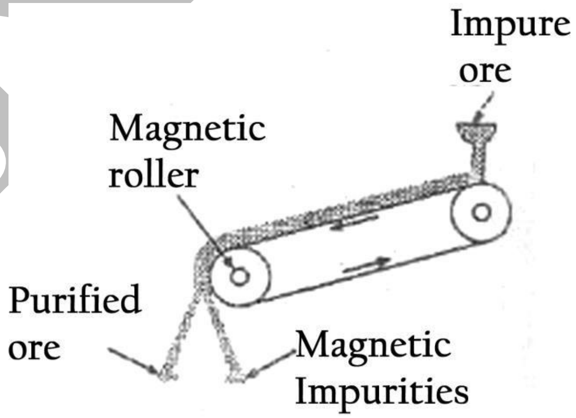
Tin stone and haematite are concentrated by this method.

(iii) Froth floatation: The sulphide ores like zinc blende, galena, copper pyrites, cinnabar are generally concentrated by this method. The powdered ore is added into water containing a foaming agent (generally, pine oil) and the whole mass is then agitated by means of compressed air.



The concentrated ore particles stick to the foam and float off with it in the form of froth. The gangue particles get wetted with water and settle down.

(iv) Electromagnetic separation: Magnetic impurities are removed by dropping the powdered ore on a travelling belt moving around two rollers one of which is an electromagnet. The magnetic impurities collect in the form of heap nearer the magnetic pulley.



For example, a mixture of wolframite, $FeWO_4$ (magnetic) and cassiterite, SnO_2 (non-magnetic) are separated by this method.

(v) Concentration by chemical methods: After employing above physical means of ore dressing, the ore is further concentrated by some chemical methods which are as follows:

(a) Calcination: It is the process of heating the ore strongly in the absence of any blast of air. The moisture and volatile impurities are removed by calcination. Carbonate ores are converted into the oxide and the mass becomes porous which can later be easily reduced to metal. Calcination is carried out in a reverberatory furnace.

$$CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2\,CuO + CO_2 + H_2O$$

(b) Roasting: The concentrated ore often contains impurities like sulphur, carbon dioxide and moisture. They are driven off by *heating the ore with excess of air* in a reverberatory furnace or blast furnace. During roasting the volatile impurities are removed and the organic impurities are burnt off. Roasting usually converts carbonate, hydroxide or sulphide ores into respective oxides.

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$

Sometimes, sulphide ores are converted into sulphate.

$$PbS + 2O_2 \longrightarrow PbSO_4$$

(c) Addition of flux: Lime, CaO, is generally used as *flux* to remove the last traces of gangue from the ore. The partially converted ore is mixed with the *flux* and heated strongly in a furnace. The very purpose of adding flux along with the ore is to convert *non fusible* material into *fusible slag*. The choice of flux depends upon the nature of the gangue.

$$\underset{\text{Flux}}{\overset{\text{Basic}}{CaO}} + \underset{\text{Gangue}}{\overset{\text{Acidic}}{SiO_2}} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

$$\underset{\text{Acidic}}{SiO_2} + \underset{\text{Basic}}{MgCO_3} \longrightarrow MgSiO_3 + CO_2$$

II. Reduction to Free Metals

There are various methods which are used to reduce the concentrated ore to the metallic stage. Some of them are discussed below:

(i) Smelting: Flux is generally used along with the reducing agent (usually carbon) and the whole process is called *smelting*. The roasted ore is mixed with coal or coke and heated in a furnace. Carbon and carbon monoxide reduce the metal oxide to the free metal:

$$Fe_2O_3 + 3C \longrightarrow 2\,Fe + 3CO$$

(ii) Reduction by heating in air: In certain cases, the ores are reduced by simple roasting. For example, cinnabar, Hg S is reduced to mercury in this way:

$$HgS + O_2 \xrightarrow{\text{Heat}} Hg + SO_2$$

(iii) Reduction by hydrogen: Hydrogen is an excellent reducing agent to convert the oxides of the metal into metals. Tungsten is produced by the reduction of its oxide with hydrogen.

$$WO_3 + 3\,H_2 \longrightarrow W + 3\,H_2O$$

This method is an expensive method when compared to carbon.

(iv) Electrolytic reduction: Very active metals like Na, K, Ca, Al etc. are produced by the electrolysis of their fused anhydrous salts. For example, sodium is produced by the electrolysis of fused sodium chloride:

On electrolysis

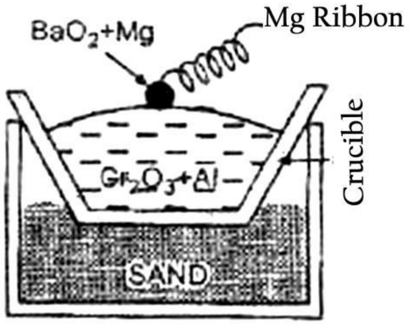
$$NaCl \longrightarrow Na^+ + Cl^-$$

$$Na^+ + e \longrightarrow Na \quad \text{(at the cathode)}$$

$$\left.\begin{array}{l} Cl^- \longrightarrow Cl + e \\ 2\,Cl \longrightarrow Cl_2 \end{array}\right\} \text{(at the anode)}$$

(v) Goldschmidt Aluminothermic process

Oxides of certain metals like Cr_2O_3, MnO_2 etc, cannot be reduced by coke. In such cases aluminium powder is used as a reducing agent. The process is known as *thermite process* and is strongly exothermic:



$$Cr_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Cr + 408.6\text{ kJ}$$

$$3\,Mn_3O_4 + 8Al \longrightarrow 4\,Al_2O_3 + 9\,Mn + Q\text{ kJ}$$

$$3\,MnO_2 + 4\,Al \longrightarrow 2\,Al_2O_3 + 3\,Mn + Q\text{ kJ}$$

(vi) Precipitation by complexation: This method is generally used in the case of noble metals like Ag and Au. The concentrated ore is dissolved in a dilute solution of sodium cyanide and then the metal is precipitated by the addition of zinc dust.

$$Ag_2S + 4\,NaCN \longrightarrow 2\,Na\,[Ag(CN)_2] + Na_2S$$

$$2\,Na\,[Ag(CN)_2] + Zn \rightleftharpoons Na_2\,[Zn(CN)_4] + 2\,Ag$$

Refining of Crude Metals

Metals produced by any one of the above methods may contain some impurities. They are refined in one or more of the following ways:

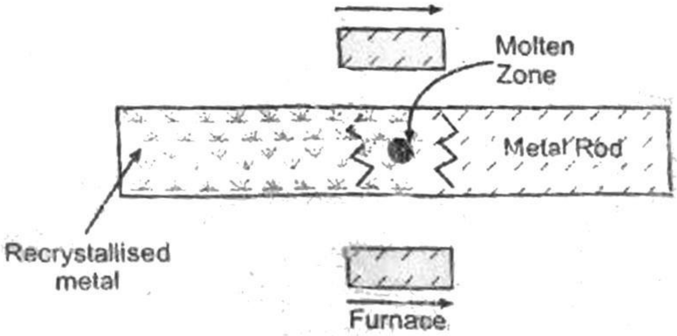
(i) Liquation: It is suitable where the metal is easily fusible but not the impurities. Easily fusible (like tin and lead) are heated on the sloping hearth of a reverberatory furnace. The metal melts and flow down leaving behind the infusible impurities.

(ii) Distillation: It is useful where the metal vapourised but not the impurities. Volatile metals (like zinc and mercury) are refined by distillation. Non volatile impurities remain behind.

(iii) Poling: It consists in stirring the molten crude metal with logs of wood. The wood gases, so produce, reduce any metallic oxides present as impurity to metal. For example, crude copper contains a little cuprous oxide as impurity which is brittle in nature. On poling the molten blister copper, the impurity is reduced to copper by wood gases.

(iv) Electrolysis: Most of the metals are refined by electrolysis. The electrolytic cell consists of crude metal as anode and the pure metal as cathode. The electrolyte consists of a solution of soluble salt of the metal. On passing electric current, pure metal deposits on the cathode. The impurities settle to the bottom or go into solution.

(v) Zone refining or Fractional crystallization: Metals like silicon, germanium and gallium are used as semi-conductors. These metals must be of very high purity and such purity is achieved by zone refining.



A circular heating coil passes slowly along a tube containing impure metals. At the heated zone the rod melts. As the heater passes on, the pure metal crystallizes while impurities pass into the adjacent molten part. The impurities are in this way swept into one end of the rod and removed.

(vi) De Boer, Van Arkel or Hot Wire Process: Metals like Ti, Zr, Si, Be, Th are refined by this process.

Impure titanium is heated with limited amount of iodine in an evacuated glass apparatus at 470 K when solid TiI_4 is formed. The vapour of TiI_4 is then allowed to enter an evacuated quartz bulb with a tungsten filament placed at its centre and electrically heated 1670 K. The vapour is decomposed to the metal in contact with filament and the metal is deposited on the filament which grows thicker. The metal is chipped off from the filament.

$$\underset{\text{Impure}}{Ti(s)} + 2\,I_2(g) \xrightarrow{470\text{ K}} TiI_4(g)$$

$$TiI_4(g) \xrightarrow{1670\text{ K}} \underset{\text{Pure}}{Ti(s)} + 2\,I_2(g)$$

The vapours of regenerated iodine react with more titanium.

This method produces titanium of very high purity. This method is very expensive and is employed for the preparation of very pure metals for special uses.

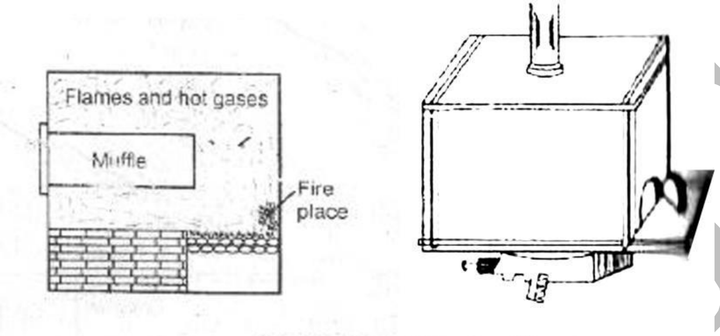
Types of Furnaces

Several types of furnaces are used in the extraction of metals from their ores. Few important furnaces have been described in the following pages.

(i) Kilns: These are large enclosed spaces with an arrangement for free access of air and are kept hot by waste gases or waste fuel from furnaces. These are used for mixing some suitable materials with ores prior they are fed into furnaces.

No chemical reaction or fusion occurs here expect little heating or drying of the ores.

(ii) Muffle furnace: A muffle is a chamber made of refractory material and is surrounded by flames and hot gases on all sides. In an electric muffle furnace, the enclosed chamber is surrounded by heating electric rods. A typical muffle furnace is shown in figure.



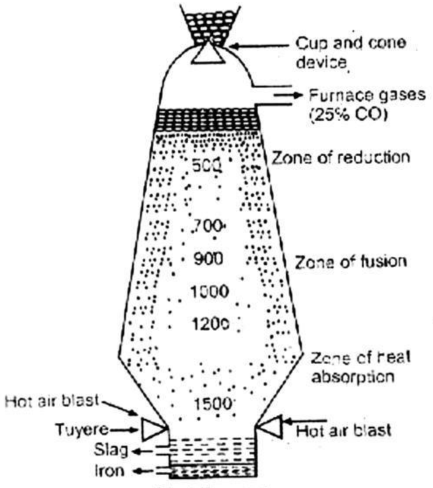
Muffle Furnace

Muffle furnace is used in metallurgy where high temperatures are required and where flames should not come in contact with the materials to be heated or the products of combustion.

These furnaces are used for **annealing** and extraction of metals like zinc.

(iii) Blast furnace: Blast furnace is used in metallurgy to heat ores directly with other materials so as to reduce ores to metallic state. The dimensions and constructional details of furnaces vary from place to place. A typical blast furnace used in the metallurgy of iron is described below.

A blast furnace is a shaft furnace of characteristic shape. It is about 30 meters high with a hearth of about 9 meters in diameter. It is made of steel plates lined inside with fire clay bricks. The hearth may be lined with carbon blocks for durability or with fire clay.



Blast Furnace

The charge is introduced through a hopper and a cup and cone arrangement at the top.

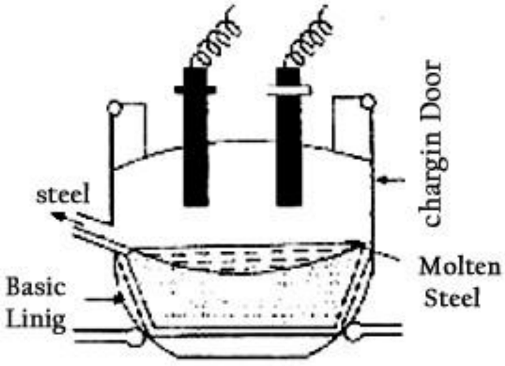
Air is heated to 820-1120 K by combustion of waste gases and blast of this hot air is blown into the furnace under pressure through 8-20 nozzles called **tuyerers.** The down coming charge meets the upward moving hot air blast. The products leave the furnace at three places-

a) Molten iron is tapped from the base of the hearth.
b) The less dense molten fusible slag floating on the molten iron is tapped through a separate out let.
c) Waste gases escape through an exit near the top.

The temperature range in the blast furnace drops from 1800 k at the tuyerers to 500 K at the top. Thus the charge descends slowly into zones of increasing temperatures.

(iv) Electric Furnaces: These are very useful where very high temperatures are required. Further, there is another important advantage with electric furnaces that the temperatures can easily be controlled by simple regulation of power supply to the furnace or the position of the electrodes etc.

These furnaces are particularly useful for electrolytic reduction. The applicability of furnace is dependent on the availability of cheap electric power. One commonly used electric furnace (Heroult's furnace) is shown in the figure.

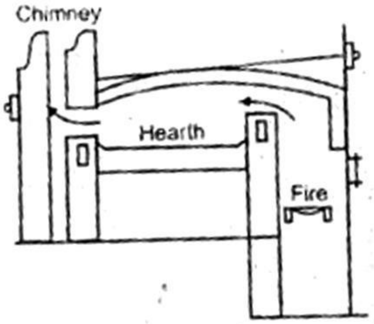


Heroult's Furnace

It consists of a steel shell lined inside with basic lining of dolomite or magnesite and provided with movable and water jacketed electrodes coming in from the roof or from the sides. On striking the electric are between the electrodes high temperature is produced to which the charge (consisting scrap steel, cast iron and iron ore) melts. The impurities present in the charge (like Si, Mn, P and S) combine with basic lining to form slag. The steel obtained is free from sulphur and gas bubbles. Very fine steel is manufactured. Since high temperatures are produced in the electric furnaces, alloy steels with high melting point can be manufactured.

(v) **Reverberatory Furnace**: These types of furnaces utilize the heat from the waste gases of furnaces, particularly blast furnace.

A flowing column of air heated by the hot fuel gases pass through the furnace. In this way, much heat is saved and the temperature of the furnace remains high throughout.



Reverberatory furnace

The average hearth is a shallow vessel of about 13 by 6 meters and about 0.75 meter deep. Over it is a roof of arched fire brick against which hot fuel gases are burnt. The hearth is lined with either a basic or an acidic lining.

Most of the open hearth furnaces are fitted with generative systems and are widely used in the manufacture of steel.

Co-ordination Chemistry

Introduction

Complex compounds, metal complexes or just complexes are compounds which contain a central metal atom or ion closely surrounded by a cluster of ions or neutral molecules called *ligands.* The ligands are electron rich species and are usually bonded to the central nuclear atom by co-ordination bonds. Hence, these complexes are often referred to as *co-ordination bonds* and are represented by a square bracket- $[Ni(CO)_4]$. In this example, nickel is the central metal atom and carbon monoxide is the ligand. The number of nearest ligands bonded to the central metal atom is known as *co-ordination number* of that metal atom. Metal complexes with coordination number 2,4,5 and 6 are shown below:

Coordination number	**Examples**
2	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
4	$[Ni(CO)_4]$, $[CuCl_4]^{3-}$, $[Pd(NH_3)_2Cl_2]$, $[Pt(NH_3)_4]^{2+}$
5	$[Fe(CO)_5]$
6	$[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_3Cl_3]$, $[Co(NO_2)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Pt(NH_3)_2Cl_4]$

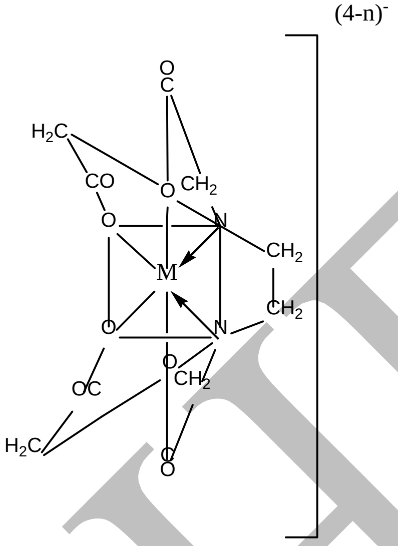
The coordination compounds differ largely from *double salts.* As the double salts tend to retain their identity even in solution, the properties of complexes are entirely different from those of the constituents.

A ligand that is capable of forming one coordinate covalent bond to the nuclear atom is called a *mono-or unidentate* ligand.

e.g.: F^-, Cl^-, CN^-, NO_2^-, H_2O, NH_3, CO and NO.

When a ligand has two groups that are capable of bonding to the central atom, it is said to be a *bi-dentate.* Common examples are-oxalate, glycinate, acetylacetonate, dimethylglyoximate, 2,2' – dipyridyl, 1, 10-phenanthroline and ethylenediamine (en).

Further, if the two bonds from a ligand appear to enclose the metal atom in a pincer like structure, the resulting complex is known as a *chelate* (G.k, *chele* = *claw*). Chelate complexes are more stable than ordinary complexes in which the ligand is monodentate. Thus, $[Cu(en)_2]^{2+}$ is more stable than $[Cu(NH_3)_4]^{2+}$. Other ligands which have upto six co-ordinating groups are known. The most common example is *Ethylene Diamine Tetra-Acetic* acid (EDTA), Versene or complexone and its complexing behavior is shown in figure (n denotes the valance of the metal).



Depending on the number of metal atoms or ions present in the complexes, they are classified as *mononuclear* (if only one metal is present) and *polynuclear* (if more than one metal is present). For example, [Ni(CO)$_4$] is a mononuclear complex whereas [Fe$_2$(CO)$_9$] is a polynuclear complex.

Nomenclature of mono-nuclear complexes

The nomenclature system given below is the one recommended by the *Inorganic Nomenclature committee* of the *International Union of Pure and Applied Chemistry*.

1) Non ionic or molecular complexes are given one word name.
2) In ionic complexes, the cation is named first, then the anion separately.
3) The ligands with negative charge end in-O, Some example are-

O^{2-}	(oxo)	Cl^-	(chloro)	NH_2^-	(amido)
OH^-	(hydroxo)	Br^-	(bromo)	NH^{2-}	(imido)
$C_2O_4^{2-}$	(oxalato)	I^-	(iodo)	$NO_2^{\ 2-}$	(nitro)
SO_4^{2-}	(sulphato)	CN^-	(cyano)	ONO^-	(nitrito)

4) Neutral ligands are named as the molecule. Example are NH_2-CH_2-CH_2-NH_2 (ethylenediamine, en) C_5H_5N (pyridine, py)
   Exceptions to this rule are-
   H_2O (*aquo*), NH_3 (*ammine*), CO (*carbonyl*), NO (*nitosyl*)
5) Positive ligands (rare) end in-ium
   NH_2-NH_3^+ (*hydrazinium*)

6) The ligands in a complex are named first and are given in the alphabetical order.
7) The number of identical ligands is given by the Greek prefixes di-, tri-, tetra-, penta-, hexa- and hepta- in the case of simple ligands.
8) The prefixes bis-, tris-, tetrakis-, pentakis-, etc. are used for complex ligands which themselves often contain the former prefixes:
   e.g–triphenylphosphine, ethylenediamine. Usually these complex ligands have polysyllabic name and their name in the complex is enclosed in parenthesis.
9) The name of the central atom is given after the ligands together with its oxidation stage designated by a Roman numeral in brackets.
10) When the complex is a cation or a neutral molecule, the name of the metal atom is unchanged, but when it is an anion, the suffix- *ate* is added.
    The above rules are illustrated in the following complexes:

Neutral Complexes

1)	$[Fe(CO)_5]$	Pentacarbonyliron(0)
2)	$[Pt(NH_3)_2Cl_2]$	Diamminedichloroplatinum(II)
3)	$[Cr(H_2O)_3Cl_3]$	Triaquotrichlorochrominum(III)
4)	$[PtNH_3(py)ClBr]$	Amminebromochloropyridine platinum(II)
5)	$[Co(NH_3)_3NO_2(CN)Cl]$	Triamminechlorocyanonitrocobalt(III)

Cationic complexes

1)	$[Pt(NH_3)_4Cl_2]\ Br_2$	Tetra-amminedichloroplatinum(IV) bromide
2)	$[Pt(NH_3)_4NO_2Cl]\ CO_3$	Tetra-amminechloronitroplatinum(IV) carbonate
3)	$[Co(en)_2H_2O\ Cl]\ SO_4$	Aquochlorobis(ethylenediamine)cobalt(III) sulphate
4)	$[Cr(H_2O)_4Cl_2]Cl$	Tetra-aquodichlorochromium(III) chloride
5)	$[Co(NH_3)_4Cl_2]Cl$	Tetra-amminedichlorocobalt(III) chloride
6)	$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
7)	$[Rh(Ph_3P)_3]Cl$	Tris(triphenylphosphine) rhodium(I) chloride
8)	$[Cu(H_2O)_4]^{2+}$	Tetra-aquocopper (II) ion.

Anionic Complexes

1)	$[Fe(CN)_6]^{3-}$	Hexacyanoferrate(III) ion
2)	$[Ni(CN)_4]^{2-}$	Tetracayanonickelate(II) ion
3)	$NH_4[Co(H_2O)_2(SCN)_4]$	Ammoniumdiaquotetrakis(thiocyanato-S) cobaltate(III)
4)	$K_3[FeF_6]$	Potassium hexafluoroferrate(III)
5)	$K[Pt(NH_3)Cl_3]$	Potassium amminetrichloro platinate(II)
6)	$K_4[Ni(CN)_4]$	Potassium tetracyanonickelate (0)
7)	$Na[Al(OH)_4]$	Sodium tetrahydroxoaluminate(III)
8)	$H[AuCl_4]$	Tetrachloroauric acid

9)	$[Ag(CN)_2]^-$	Dicyanoargentate (I) ion
10)	$Na[Co(CO)_4]$	Sodium tetracarbonylcobaltate(-I)
11)	$K_3[Fe(C_2O_4)_3]$	Potassium trioxalatoferrate(III)

Werner's Co-ordination Theory

In 1893. *Alfred Werner*, the father of co-ordination chemistry, proposed the co-ordination theory to explain the formation of co-ordination compounds. His theory has provided the basis for modern theories. Some of the more important postulates are:

1) Each metal has two kinds of valence- *primary* or ionic valence and *secondary* valence.
2) The primary valence may be satisfied only by negative ions as in simple salts.
3) The secondary valence may be satisfied by negative ions or neutral molecules.
4) Every element tends to satisfy both its primary and secondary valences.
5) Each metal has a characteristic number of secondary valences known as coordination number directed in space to give a definite geometrical arrangement. The arrangement for six secondary valences assumed to be *octahedral*. Thus, $[Co(en)_3]Cl_3$ and $[Pt(NH_3)_4Cl_2]Br_2$ are hexa-coordinated with octahedral geometry. A *tetrahedron* or a *square planar* geometry is proposed for coordination number four.
6) When a mono-negative ion is present in the coordination sphere as in $[Cr(NH_3)_5Cl]Cl_2$, it satisfies one of the primary as well as one of the secondary valences.
7) When two similar anions are in the coordination sphere, the directional property of the secondary valences gives rise to cis- and trans- isomer eg., $[Cr(NH_3)_4Cl_2]Cl$.

This theory provided not only an explanation for the isomerism that existed among the then known complexes, but also predicted the existence of optical isomers which were later isolated.

Sidgwick's Effective Atomic Number rule (EAN)

The first attempt to interpret Werner's theory was largely due to N.V. Sidgwick of the Oxford University. According to him, in most of the stable complexes, the central metal atom will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of the next highest noble gas.

For example, the total number of electrons of the central metal ion, Fe^{2+} in $[Fe(CN)_6]^{4-}$ is worked out as follows:

The atomic number of Fe = 26

Fe^{2+} (26 - 2) = 24

6 CN^- (6 x2) = 12

Effective atomic number (EAN) of Fe^{2+} in $[Fe(CN)_6]^{4-}$

= (26 - 2) + (6 x 2) = 36 (Kr)

Thus, it is found that iron in this complex acquires the krypton configuration.

The following table shows the effective atomic number of a few metals:

Atom	Atomic number "Z"	Complex	Electrons lost in ionization "e"	Electrons gained by coordination "N"	EAN= (Z-e+N)
Fe	26	$[Fe(CN)_6]^{4-}$	2	12	36 Kr
Co	27	$[Co(NH_3)_6]^{3+}$	3	12	36 Kr
Ni	28	$[Ni(CO)_4]$	0	8	36 Kr
Cu	29	$[Cu(CN)_4]^{3-}$	1	8	36 Kr
Pd	46	$[Pd(NH_3)_6]^{4+}$	4	12	54 Xe
Pt	78	$[Pt(NH_3)_6]^{4+}$	4	12	86 Rn

However, there are a number of exceptions in which the EAN may be a few units more or less than a noble gas. Few examples are given in the table.

Atom	Atomic number "Z"	Complex	Electrons lost in ionization "e"	Electrons gained by coordination "N"	EAN= (Z-e+N)
Fe	26	$[Fe(CN)_6]^{3-}$	3	12	35
Ni	28	$[Ni(en)_3]^{2+}$	2	12	38
Pd	46	$[PdCl_4]^{2-}$	2	8	52
Ag	47	$[Ag(NH_3)_2]^{+}$	1	4	50
Pt	78	$[Pt(NH_3)_4]^{2+}$	2	8	84

One class of the compounds that frequently does obey the EAN rule comprises the metal carbonyls and their derivatives. By using the rule it is even possible to predict accurately the coordination number of the simplest carbonyls and also predict whether the compounds exist as monomers.

Pauling's Valence Bond Theory (VBT)

This theory is based on the following assumptions:

1) The central metal or metal ion has a number of empty orbitals. These orbitals are used to accommodate the electrons donated by the ligands. The number of vacant orbitals is equal to the coordination number of that metal / metal ion.

2) Each ligand has atleast one lone pair of electrons in the orbital.

3) The metal orbitals and ligands orbitals can overlap to form strong bond and in this process the central metal ion can utilize different (s, p, and d) orbitals. This process is called *hybridization*. The type of hybridization is described on the basis of the hybrid orbitals. Thus, in the complex $[Zn(NH_3)_4]^{2+}$, the Zn(II) uses one s orbital and three p orbitals to form four equivalent orbitals of equal energy and this combination is labelled as *sp^3-hybridisation*. Hybridization is considered to be very important since it stabilises the complex / complex ion by releasing considerable energy. Moreover, the geometry or shape of the complex is derived only on the basis of the mode of hybridisation. The following table summarises the typical shapes of the transition metal complexes associated with different modes of hybridization.

Coordination number	**Type of hybridisation**	**Geometry**	**Example**	
4	sp^3	tetrahedral	$[Ni(CO)_4]$	$[ZnCl_4]^{2-}$
4	dsp^2	square planar	$[Ni(CN)_4]^{2-}$	$[Pt(NH_3)_4]^{2-}$
6	d^2sp3	octahedral	$[Cr(NH_3)_6]^{3+}$	$[Fe(CN)_6]^{4-}$
6	$sp^3\ d^2$	octahedral	$[FeF_6]^{3-}$	$[CoF_6]^{3-}$

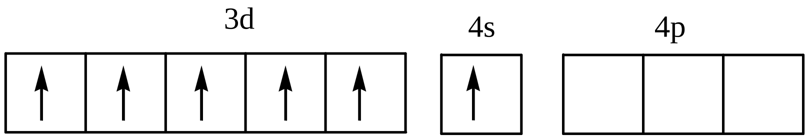
4) The non-bonding metal electrons present in the inner orbitals do not involve in the hybridisation.

5) The complex is said to be paramagnetic if the complex contains unpaired electrons whereas a complex which does not contain any unpaired electron is diamagnetic in nature.
These points are explained in the following illustrations:

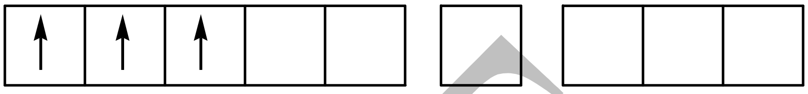
Hexa-amminechromium (III) chloride, $[Cr(NH_3)_6]Cl_3$

In this complex, it is evident that Cr(III) is the central metal ion. Since ammonia is a neutral ligand, chromium should be in the +3 oxidation state. The electronic configurations of chromium and Cr(III) are given below:

Cr(Z = 24) $[Ar]^{18}$

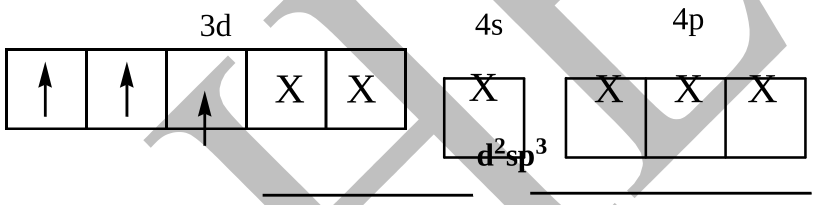


Cr(III) $[Ar]^{18}$



Evidently, Cr(III) has three electrons and these electrons occupy singly as above according to Hund’s rule. As the six ammonia molecules approach the central metal ion Cr(III), d^2sp^3–hybridization occurs. The most appropriate geometry is an octahedron and the complex is paramagnetic.

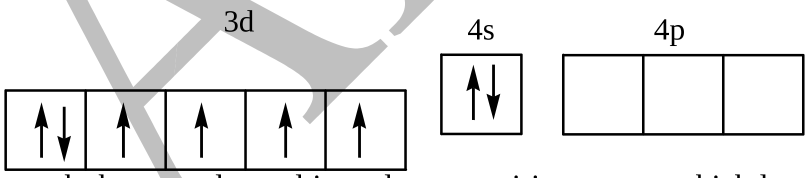
$[Cr(NH_3)_6]^{3+}$



Potassium ferrocyanide, Potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$

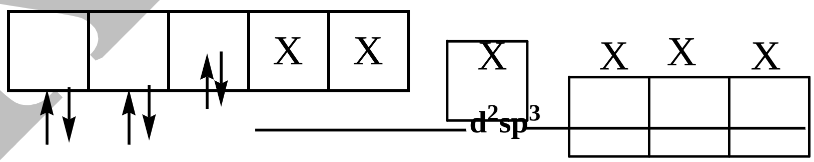
The complex anion $[Fe(CN)_6]^{4-}$ is obtained from Fe(II). The electrons present in the iron atom before the approach of six cyanide ligands are given as:

Fe(Z = 26)



When the ligands approach the central metal ion, electron pairing occurs which leaves 3d orbitals vacant. These vacant 3d orbitals along with 4s and 4p orbitals (in full) are used for hybridisation.

$[Fe(CN)_6]^{4-}$



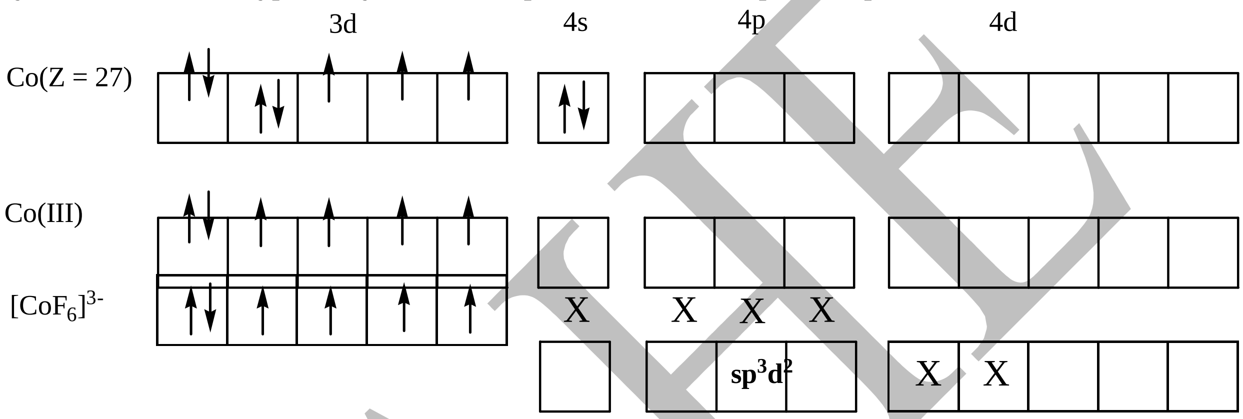
Evidently, this complex is d^2sp^3-hybridised with octahedral geometry formed from d^2sp^3-hybridisation:

$[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Pt(NH_3)_6]^{4+}$,
$[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$

These complexes are known as *inner orbital (low spin) complexes,* since the d orbital involved in the hybridization are (n-1) d orbitals.

Hexafluorocobaltate (III) ion, $[CoF_6]^{3-}$

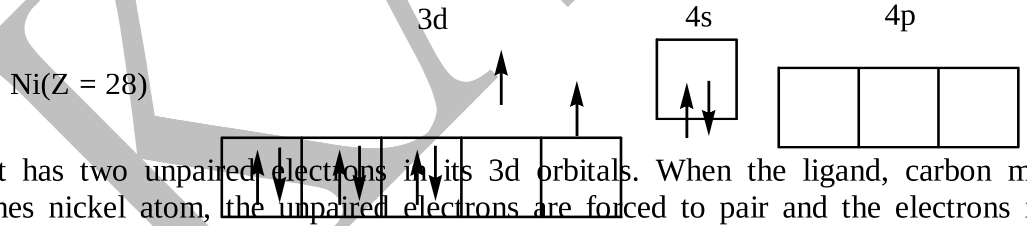
This complex is octahedral but is highly paramagnetic. The magnetic moment value at room temperature (5.0 B.M) corresponds to four unpaired electrons. To explain this, it is regarded that no electron pairing occurs in the inner 3d orbitals but outer 4d orbitals are used for hybridisation. This type of hybridization present in the complex is sp^3d^2.



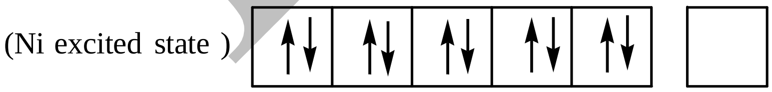
These types of complexes are known as *high spin or outer orbital complexes.* $[FeF_6]^{3-}$ belongs to this class.

Tetracarbonylnickel (0), $[Ni(CO)_4]$

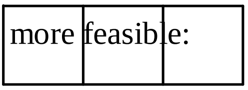
It is possible to explain the formation of tetrahedral complexes with sp^3-hybridisation in the light of VBT. The electronic configuration of nickel (Z= 28) is [Ar] $4s^2 3d^8$

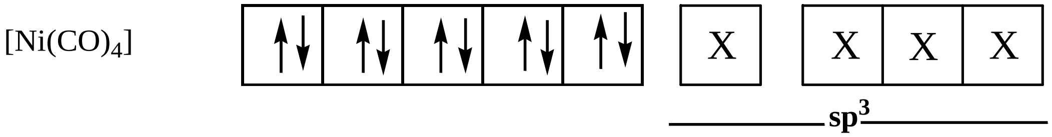


It has two unpaired electrons in its 3d orbitals. When the ligand, carbon monoxide, approaches nickel atom, the unpaired electrons are forced to pair and the electrons in the 4s orbital occupy the vacant 3d orbitals thereby leaving one 4s and three 4p orbitals vacant.



Hence, in the formation of $[Ni(CO)_4]$, sp^3- hybridization is more feasible:



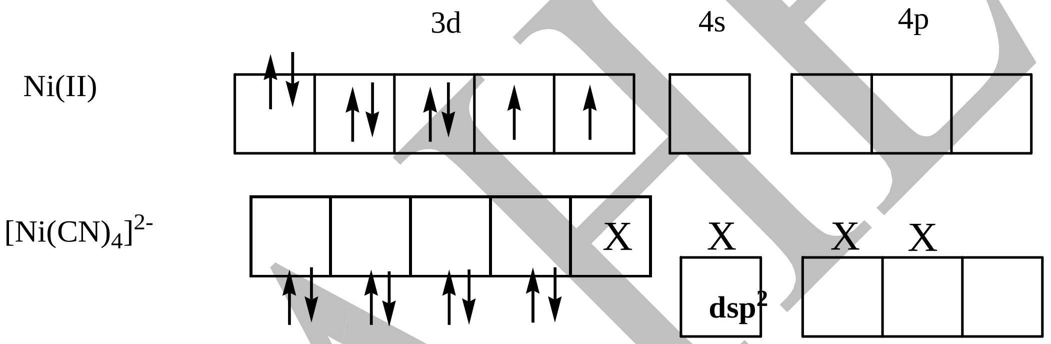


Obviously this complex is diamagnetic. The other example:

$[Zn(NH_3)_4]^{2+}$, $[ZnCl_4]^{2-}$ and $[CuCl_4]^{3-}$.

Tetracyanonickelate (II) ion $[Ni(CN)_4]^{2-}$

The metal ions having eight electrons in their d orbitals usually form square planar complexes (if their coordination number is 4), with dsp^2-hybridisation. For example, $[Ni(CN)_4]^{2-}$ is dsp^2 hybridised and is diamagnetic:



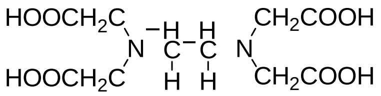
Similar situation exists for complexes of palladium (II). Platinum (II), gold (III), rhodium (I) and iridium (I).

Chelation and its industrial importance

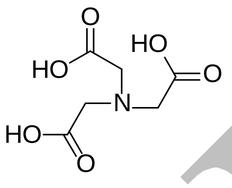
The presence of objectionable metal ions causes problems in many industries because of the adverse effects these can have on the quality of the product. These difficulties can be averted if the free metal ion concentration is considerably reduced. An effective way of achieving this is by the addition of suitable chelating agents which by complexing with the metal ion mask its characteristic reactions. The process by which a soluble complex of a metal is produced so that it is no longer precipitated by anions which form sparingly soluble salts with the free metal ion is known as *sequestration (Latin* sequestrate means to commit for safe keeping) and the reagents which bring this about are called *sequestering agents.*

Several tertiary amines that also contain carboxylic acid groups. i.e., the amino polycarboxylic acids (also known as complexones) form remarkably stable complexes with many metal ions. Their potential as sequestering agents was first recognised by *Schwarzenbach* in 1945, since that time they have been extensively investigated. The following are the names of few amino polycarboxylic acids:

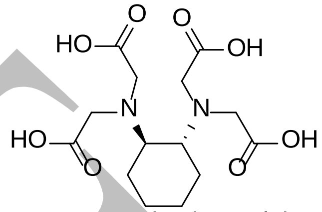
1) Ethylenediaminetetraacetic acid (Abbreviated, EDTA)
2) Nitrilotriacetic acid (abbreviated, NTA)
3) *trans*-1,2-Diaminocyclohexane N,N,N′ N′–tetraacetic acid (DCTA)



Ethylenediaminetetraacetic acid (EDTA)



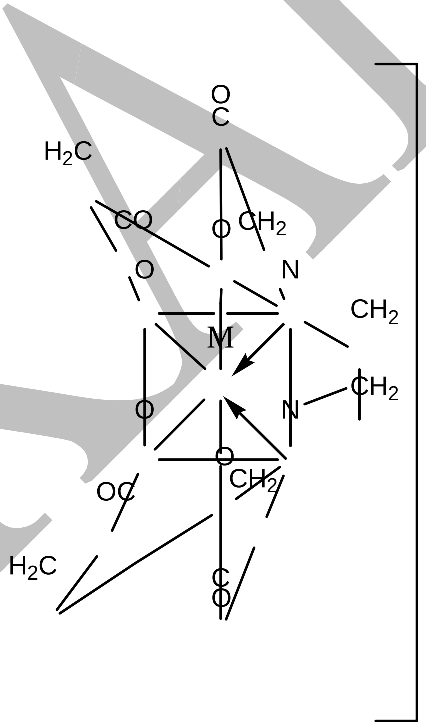
Nitrilotriacetic acid (NTA)

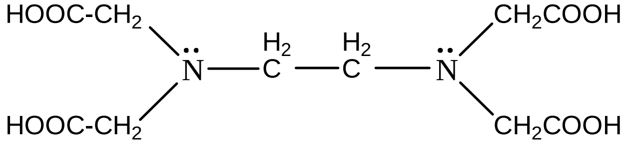


trans-1,2-Diaminocyclohexane-
N,N,N′,N′–tetraacetic acid (DCTA)

Other related substances also have been investigated but have not been widely employed in industries. We shall confine our discussion to the application of EDTA.

Ethylenediaminetetra acetic acid (known by various trivial names as Trilon B, complexone III, versene, sequestrene and Chelaton -3) has the structure.





It has four acidic hydrogens and each nitrogen atom has an unshared pair of electrons. Thus, the molecule has six potential sites for bonding with a metal ion and may be considered to be a hexadentate ligand.

There is no doubt that EDTA has the widest general industrial application because of its-

(i) Relatively low price.
(ii) High water solubility.
(iii) Strainless five membered ring formation on Chelation.
(iv) Hexadenticity, most frequently, matches with the coordination number of many metal ions.

The structure of metal-EDTA complex is given in the figure.

Some of their applications are given below:

1) One common application of EDTA is for the prevention or removal of scale in boilers.
2) Other uses of EDTA include-applications in laundry work, to eliminate harmful radio-active metals from the body, in medicine, dyeing etc.
3) Though EDTA is invariably a minor component of the detergent formulation, application of EDTA in the detergent industry include the following – liquid soap products, bar soaps, shampoos, wax removing floor cleaners and synthetic detergents.
4) *The very purpose of inventing EDTA is to shed more light on the hardness in water.*

Limestone and other calcium minerals are among the most abundant minerals in the Earth's crust. Consequently, natural water invariably contains Ca^{2+} ions and frequently bicarbonate ions. Other ions often found in natural water include Mg^{2+} and Fe^{2+}. Natural water containing objectionable concentration of Ca^{2+}, Mg^{2+} and Fe^{2+} is called "HARD".

Two types of hardness are recognised: *Non carbonate, permanent hard water-* Ca^{2+}, Mg^{2+} *or* Fe^{2+} *ions as chlorides and sulphates. Water containing these metal ions and bicarbonates is called carbonate, temporary hard water.* Hardness is usually reported in parts per million (ppm) and is calculated as calcium carbonate.

Hard water is not suitable for drinking purposes, washing purposes and industrial purposes (in boilers).

Determination of hardness of water

The hardness of water can be determined in a number of ways: *Clark's method. Hehner's method and indicator method.*

The most recent indicator method makes use of titration of the water with EDTA and an indicator which changes colour when all the calcium and magnesium have reacted. The method is rapid convenient and accurate.

The usual procedure is to add 10 ml. of a buffer solution (pH 10), three drops of the indicator (Eriochrome Black T) to a 50 ml sample of water. Titration is carried out with the standard EDTA (1 ml = 1 mg $CaCO_3$). The end point is a colour change from wine red to blue.

The total hardness = ml. of reagent used x 20.

Illustratrion

50 ml. of hard water required 6.20 ml of EDTA which is equivalent to 6.20 mg of $CaCO_3$.

$$1000 \text{ ml of water contains } = \frac{6.20 \times 1000}{50} = \mathbf{124\ mg}$$

Thus, the hardness is 124 ppm.

5) The analytical applications of EDTA are –

(i) Use as a primary standard.
(ii) The estimation of copper in steel.
(iii) The determination of the number of anions.
(iv) The extraction of beryllium free from aluminium.
(v) The prevention of metal ions forming precipitation *(masking agent).*
(vi) The estimation of (almost all) metal ions using complexometric titration.

Haemoglobin and Chlorophyll

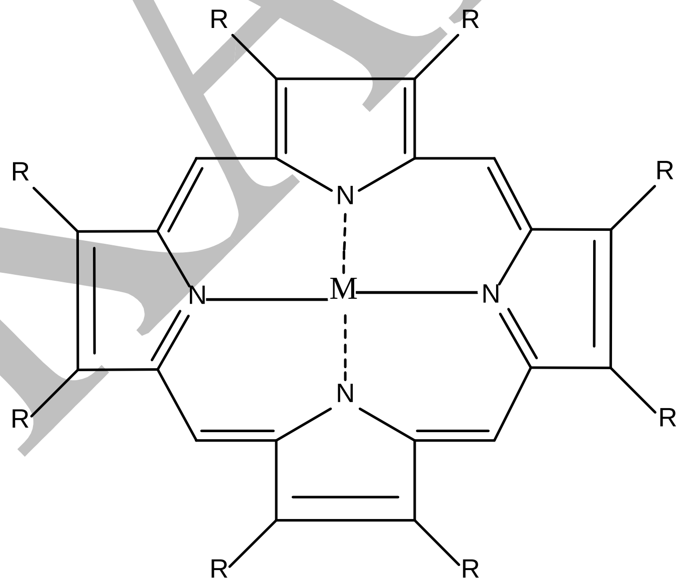
The inorganic constituents of biological system have been receving increasing attention in recent years. The importance and the presence of metallic elements in living bodies (plants and animals) have been the keen interests to the chemists. It has been observed that the majority of the essential metallic elements are transition metals whose ability to form complexes is of the most characteristic aspects of their chemistry. Many metal complexes of biological macromolecules have been isolated …. h*aemoglobin, chlorophyll, myoglobin, haemocuprin, cyanocobalamin (vitamin* B_{12}*)* and *cytochrome-C.* We shall discuss haemoglobin and chlorophyll in detail.

Haemoglobin (also called Hemoglobin)

This is the most important agent for oxygen transport in living bodies. Though its primary function is to carry oxygen, it is also involved in the transport of CO_2 and with acid-base balance of the body. Hemoglobin takes up a large volume of oxygen in the lungs and carries it to the tissues.

Hemoglobin is the red matter that makes up about 95% of the dry weight of the red blood cell. Blood of a normal male contains about 15g, hemoglobin per 100 ml. of all of which is within the red blood cell. Haemoglobin contains 0.347% iron and its molecular weight is 64,458.

Hemoglobin is a *conjugated protein* whose prosthetic group is heme. Heme is associated with globin (a protein). Heme belongs to the class of metal-porphyrins. The basic frame work of all porphyrins is built of four pyrrole rings linked together in a larger ring like structure called *porphin*. By varying the substitution of eight hydrogen atom (shown by R on pyrrole rings) with different groups, the various porphyrins found in nature are produced. *Protoporphyrin IX* is found in heme.



Each hemoglobin molecule has four heme group bound to the globin on its surface. In each heme unit of hemoglobin, Fe (II) forms a four coordinated, square planar complex using four nitrogens of the protoporphin ring. The fifth coordination position of Fe (II) is occupied by the imidazole nitrogen of histidine residue of the protein chain (globin) and the sixth position is occupied by a molecule of water (which is replaced by oxygen on oxygenation).

It has been investigated that hemoglobin can also form stable complexes with other ligands like NH_3, amines, CN^-, CO, NO and in that these ligands compete with oxygen in *oxyhemoglobin.*

Hence, oxygenation is inhibited. The toxicity and highly poisonous character of these ligands have been thus explained.

Chlorophyll

This is a green material found in plant and dose not contains chlorine or any other halogen. The name derived, in part from its colour (Greek, chloros = light green), the reminder of the name is derived from a Greek term for leaf. Although we speak of chlorophyll in the singular, there are several different compounds called chlorophyll. Among them chlorophyll-α is the most abundant. This was first synthesized by Woodward in 1960.

Chlorophyll belongs to a class of compounds with power for transmission of energy. As heme serves the purpose of oxygen transport in the animal body, so does chlorophyll a porphyrin complex of Mg (II), perform the function of capturing light energy and transmitting it to a system for utilization in chemical reaction. This helps in the *photosynthesis.*

Photosynthesis is a complex sequence of processes in which solar energy is first absorbed and ultimately glucose is formed from carbon dioxide and water in the following way:

$$6CO_2 + 6\,H_2O \xrightarrow{h\nu} \underset{\text{glucose}}{C_6H_{12}O_6} + 6\,O_2$$

The characteristic property of chlorophyll, namely the capturing and transmitting light energy to system for chemical reaction may be attributed to the nature of Mg(II) complex. Evidently, magnesium ($1s^2$, $2s^{2,}$ $2p^6$, $3s^2$) is not a transition element and can form only stable sp^3-hybridized tetrahedral complex. On the other hand, the porphyrin molecule by its rigid structure holds the four donor nitrogen atoms in the same plane and thus forces any metal ion coordinating with it to assume a square planar structure (*Cf. hemoglobin).* Hence, the planar bonds to magnesium in chlorophyll must be in strained condition. The electrons constituting these bonds can, therefore be readily excited by the absorption of light energy which may be re-emitted afterwards in the form of luminescence or transmitted to a system in a chemical reaction.

Analytical Application

I. Qualitative Analysis

a) Ag(I) is separated from Hg_2Cl_2 and $PbCl_2$ in the qualitative analysis by dissolving it as $[Ag(NH_3)_2]^+$.

b) Antimony, arsenic and tin sulphides are separated from the remaining II group sulphides since they dissolved in the presence of excess sulphide ions as the complexes, SbS_4^{3-}, AsS_4^{3-}, SnS_3^{2-}.

c) When in copper and cadmium salts solution, KCN is added in excess, both Cu and Cd form complexes-$K_3[Cu(CN)_4]$ and $K_2[Cd(CN)_4]$ respectively. These two complexes differ appreciably in their stability. When H_2S is passed in the aqueous solution of these two complexes, cadmium alone gets precipitated.

d) Nickel, magnesium and aluminium ions are easily identified by the formation of highly coloured chelates in qualitative analysis.

e) The most delicate reagent for the detection and estimation of nickel is dimethylglyoxime. This reagent reacts with nickel (II) ion in ammoniacal solution to yield a bright red, silky and bulky precipitate of the composition, $Ni(dmg)_2$.

f) Separation of zirconium and hafnium, which until recently was one of the most difficult analytical tasks, has been made simple by the use of chelates. The chelates of the two metals formed with theonyl trifluoroacetone possess different solubilities in benzene.

II. Quantitative Analysis

a) Organic reagents which give insoluble complexes are widely used for the separation and determination of metals. The neutral complexes thus obtained can be used in gravimetric analysis to estimate metal ions. The high molecular weight of such complexes reduces the significance of weighing errors. By changing the conditions such as pH, the method can be used in the presence of other metal ions. One example is the red precipitate of $Ni(dmg)_2$.

b) Oxine (8- hydroxyquinoline) reacts with a large number of metal ions forming oxinates which are crystalline precipitates. Other notable example are cupferron, acetylacetone, 1,10-phenanthroline, α-benzoin oxime, dithiozone, anthranilic acid and thiourea.

c) Many titration procedures now use EDTA in the determination of metals. These procedures usually involve competition for the metal between EDTA and a dye that can also serve as a ligand. Because EDTA tends to form chelates with most cations, it would appears at first glance to be totally lacking in specificity. In fact, however considerable control over the behavior of EDTA, as well as other chelating agents, can be achieved through pH regulation. Thus, for example, it is generally possible to determine trivalent cations without the interference from divalent species by performing the titration in a medium having a pH of about 1.

d) One of the common reduction–oxidation (redox) indicators, ferroin, is a complex. It contains the $[Fe(o\text{-}phen)_3]^{2+}$ ion, which is deep red, while the Fe(III) compound is pale blue. In a suitable oxidation-reduction titration, the removal of the colour of the ferroin is an indication that the end point has been reached. The ferroin is oxidized only after the reducing agent being titrated is completely oxidized.

Text Books:

1. Veeraiyan, V., & Vasudevan, A.N.S. (2012). *Text Book of Allied Chemistry* (II Edition). Chennai: Highmount Publishing House.

2. Puri, B.R., Sharma, L. R., & Kalia, K. C. (2017). *Principles of Inorganic Chemistry* (33rd Edition). Jalandar: Vishal Publishing Company Co.

Reference Book:

1. Gopalan, R., & Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. Differentiate minerals and ores?
2. What is meant by metallurgy and gangue?
3. What are the applications of EDTA?
4. Explain froth floatation process.
5. Define ligands.
6. Define co-ordination bonds.
7. What is the name of the ligand“en”? Draw its structure.
8. Expand EDTA. Write its structure.
9. Explain bidentate ligands with two examples.
10. Give four examples for monodentate neutral ligands.
11. Write the structure of four monodentate anionic ligands.
12. Define co-ordination number.
13. Write the formula for the following IUPAC names.
    a) Tetracarbonylnickel (0) b) Triaquotrichlorocobalt (III)
    c) Potassium tetracyanonickelate (II) d) Sodium amminetrichloroplatinate (II).
14. Define EAN rule.
15. Calculate EAN for
    a) $K_4[Fe(CN)_6]$ b) $[Pt(NH_3)_4]Cl_2$.

PART-C (Each Question Carry Six Marks)

1. Write a note on Sidgwick’s EAN concept.
2. Explain the Paulings valence bond theory with an example.
3. (i) Calculate the EAN of Fe^{2+} in $[Fe(CN)_6]^{4-}$ and Co^{3+} in $[Co(NH_3)_6]^{3+}$.

(ii) Explain zone refining.

4. Discuss the chelation and its industrial importance with reference to EDTA.

5. (i) Write in detail on Van-Arkel process.

(ii) Write the postulates of Werner’s theory.

6. Explain the structure and biological role of (i) Chlorophyll (ii) Haemoglobin.

7. (i) Write in brief on aluminothermic process.

(ii) Describe electrolytic reduction.

(iii) Explain electromagnetic separation.

8. Write in detail on the IUPAC nomenclature of complexes.

9. (i) Explain Chelation with an example.

(ii) Describe the analytical applications of metal complexes?

10. Explain i) calcination ii) roasting iii) smelting iv) electrolytic reduction.

11. Describe the types of furnace used in metallurgical industries.

12. Discuss, with examples, the various types of hybridization involved in complex compounds.

13. Explain how complex compounds are involved in qualitative analysis and quantitative analysis.

ENVIRONMENTAL STUDIES

MULTIPLE CHOICE QUESTIONS

	Questions	Opt 1	Opt 2	Opt 3	Opt 4	Answer
	Unit I					
1	The term environment literally means……………..	The surroundings	The structures	The system	The climate	The surroundings
2	The Primary consumer are also called as	herbivores	carnivores	omnivores	detritivores	herbivores
3	Valuable, practical services that help to preserve ecosystem performed by nature are called_________	ecosystem service	biological control	the green house effect	biosphere balancing	ecosystem service
4	The surrounding physical and biological factor with which organisms closely interact and remain adapted is known as __________________	nature	ecology	forest	environment	environment
5	The organic matter produced by the Photosynthetic activity of green plants is called as ____________	light energy	cellular process	energy flow	primary productivity	primary productivity
6	___________ is diffused into the ground by gravitational force	Rain water	Ocean	River water	sea	Rain water
7	Solar energy stored in material such as wood, grain, sugar, and municipal waste is called ___________	fossil fuels	biomass	geothermal energy	natural gas	biomass

8	Decomposers are otherwise called as _________	detritivores	primary consumers	organic matter	secondary consumers	detritivores
9	Light energy is transformed into chemical energy by ___________	photosynthesis	respiration	recycling	productivity	photosynthesis
10	All food chains starts with ____________ and ends with decay	environment	organisms	photosynthesis	fungi	photosynthesis
11	In grazer food chain the living plants are directly__________	destroy	consume	decay	grown	consume
12	Energy transformation through the food chain is ___________	regular	comfortable	propose	inefficient	inefficient
13	__________ is the most populated city in India	Mumbai	Calcutta	Delhi	Chennai	Mumbai
14	Any unit that includes all the organisms that interact with the physical environment is called ______________	community	population	biosphere	ecosystem	ecosystem
15	A pond, serves as a good example for a ___________ water ecosystem	fresh	brackish	marine	se	fresh
16	The type of ecosystem with the highest mean plant productivity is__________	tropical rain forest	temperate grassland	desert	tundra	tropical rain forest
17	In an aquatic ecosystem, the tropic level equivalent to cows in grasslands is___________	nekton	zooplankton	phytoplankton	benthos	zooplankton
18	Bhopal disaster occur on _____________	Dec 4, 1982	Dec 3, 1984	Dec 8, 1986	Dec 9, 1980	Dec 3, 1984

19	Which gas was liberated in Bhopal gas tragedy?	Ethyl isothiocyanate	Sodium isothiocyanate	Methyl isocyanate	Phenyl isocyanate and phosgene	Methyl isocyanate
20	Smog is a combination of___________	air and water vapour	water and smoke	smoke and fog	fire and water	smoke and fog
21	The most serious pollutant to rubber tyres is __________	CO_2	CO	O_3	NO_2	O_3
22	All species on earth together with their environments collectively comprise___________	lithosphere	hydrosphere	atmosphere	biosphere	biosphere
23	_________ is the study that deals with the interaction of organisms with their environment	Etiology	Ecology	Botany	Biology	Ecology
24	Organisms that feed upon other living organisms as a source of energy and nutrients are called as___________	producers	consumers	pests	decomposers	consumers
25	A food web is ___________	like a food chain	a set of interconnected food chains, illustrating the tropic relationships among species	the set of prey species that are consumed by animals in an ecosystem	the tropic (feeding) levels that can be observed in an ecosystem	a set of interconnected food chains, illustrating the tropic relationships among species
26	The first tropic level refers to ___________	all herbivores	all green plants	sunlight	all animals	all green plants
27	A biomass pyramid is important because it illustrates___________	how energy flows through a food we	the number of species in each tropic level	the biomass of all organisms at each tropic	the number of tropic levels in a system	the number of tropic levels in a system

				level in a system		
28	Fungi is/are __________	single-celled prokaryotes	Phototrophic eukaryotes	eukaryotes single-celled and primitive multi-celled organisms	heterotrophic eukaryotes	heterotrophic eukaryotes
29	Basidiospores are considered to be a major source of _________	airborne allergens	water borne allergens	animal feces	bioweapon	airborne allergens
30	Man and biosphere programme is affiliated with __________	UNESCO	IUCN	WWF	WIPO	UNESCO
31	_________ gases has an important role in maintaining atmospheric temperature	Nitrogen	Oxygen	Argon	Carbon dioxide	Carbon dioxide
32	Trichodermaharzianum has proved a useful microorganism for _________	reclamation of wastelands	bioremediation of contaminated soils	biological control of soil-borne plant pathogens	gene transfer in higher plants	bioremediation of contaminated soils
33	Non-Ionizing radiations with specific biological effects are__________	Gamma rays	Beta-rays	UV radiations	X-rays	UV radiations
34	Radiations are harmful as it__________	causes skin cancer	causes anemia	alters body tissues	is unstable	causes skin cancer
35	Ozone depletion in the stratosphere will cause _________	increased incidence of skin cancer	forest tires	global warming	hole	hole
36	The relationship between living and non living things is	Biodiversity	Ecosystem	Acid rain	Water	Ecosystem

	called ….					
37	Most harmful environmental pollutants are ________	natural nutrients in excess	human organic wastes	non-biodegradable chemicals	waste animal fee	non-biodegradable chemicals
38	There would be no life in the oceans without organisms called _______ and _______.	decomposers, phytoplankton	zooplankton, consumers	phytoplankton, zooplankton	zooplankton, scavengers	phytoplankton, zooplankton
39	Nuclear accidents mostly release radioactive ___________ into the atmosphere	carbon	iodine	phosphorus	sulphur	iodine
40	The predominant gas in the atmosphere is………..	Oxygen	Argon	Hydrogen	Nitrogen	Nitrogen
41	Low level ozone is referred to as ____________ ozone	troposphere	stratosphere	ionosphere	exosphere	troposphere
42	The ozone at ground level is primarily from ____________ precursors	fossil fuel	CFCs	oxygen	methane	fossil fuel
43	The most serious environmental effect posed by hazardous wastes is __________	air pollution	contamination of groundwater	increased use of land for landfills	destruction of habitat	contamination of groundwater
44	EEAT scheme was launched during _________ Five Year Plan	5th	6th	7th	8th	6th
45	The major biodiversity hotspot in Tamil Nadu is ….	western Ghats	saputhara	Kolli hills	all the above	western Ghats
46	Pottery workers are at high risk of _________ lung disease	asbestosis	asthma	silicosis	bronchitis	silicosis

47	________ water is otherwise known as potable water	Raw	Irrigation	Drinking	Surface	Irrigation
48	___________ is the totality of genes, species and ecosystems in a region	Habit	Habitat	Biodiversity	Food chain	Biodiversity
49	_____ is the primary effect of excess phosphorous in the aquatic environment	Fixation	Nitrification	Eutrophication	Radiation	Eutrophication
50	A food chain starts with a………………	consumers	scavengers	producer	decomposer	producer
51	The main source of water in India is_____________	rain water	ground water	surface water	sea water	rain water
52	_____________ are organisms consuming other living organisms	Carnivorous	Saprophages	Herbivorous	Biophages	Biophages
53	The unit of ecosystem is………	Kelvin	Biosphere	Calories	Animals	Biosphere
54	An increase in altitude is similar to an increase in latitude in that_________	it becomes more sunny	it becomes warmer	precipitation increases	it becomes colder	it becomes colder
55	In parasitism, _________	both species benefit	neither species benefits	one species benefits, but the other is weakens	one species benefits, and the other is not affected	one species benefits, but the other is weakens
56	The Solar energy is…………	Energy from the sun	Heat of the interior of earth	Energy released during Nuclear Reaction	Conversion of heat energy	Energy from the sun
57	The method of Generating electricity by using water is………	Solar Energy	Geothermal Energy	Nuclear Energy	Hydroelectrical Energy	Hydroelectrical Energy

58	___________ limits the mixing between troposphere and the other upper zones	Ozone	Stratopause	Tropopause	UV radiation	Ozone
59	Water vapor contains a huge amount of stored energy known as ______________	latent heat	solar energy	stored heat	mechanical energy	latent heat
60	The process of light energy converted to chemical energy in the green plants is called...	reduction	oxidation	photosynthesis	All the above	photosynthesis

ENVIRONMENTAL STUDIES

MULTIPLE CHOICE QUESTIONS

	Questions	Opt 1	Opt 2	Opt 3	Opt 4	Answer
	Unit II					
	_______is one of the following is the non-renewable resource	Water	Oxygen	Sunlight	Coal	Coal
	________ soil is the best for plant growth	Sandy soil	Clay	Gravel	Loamy Soil	Loamy Soil
	______________ of stratosphere provides protection to our life	Nitrogen	Hydrogen	Ozone	Argon	Ozone
	Atomic energy is obtained by using the ores of _________	copper	uranium	lithium	radium	uranium
	The death of last individual of a species is called __________	extinction	clay	vanish	climax	extinction
	Red data books provide a list of ____________	advanced plants	rare, endangered or endemic species	disease resistant animals	minerals	rare, endangered or endemic species
	The resources that can be replaced by natural ecological cycle are called……….	Natural Resources	Exhaustible Resources	Non renewable resources	Renewable Resources	Renewable Resources
	Both power and manure are provided by	thermal	nuclear	biogas	hydroelectric	biogas

	_________plants					
	The resources that are derived from bio-mass of living organisms are called __________ resources	renewable	non-renewable	environmental	natural	renewable
	___________ is the major raw material for biogas	Plant leaves	Cow dung	Mu	Grass	Cow dung
	Bio gas generation is mainly based on the principle of ___________	fermentation	degradation	purification	sedimentation	fermentation
	The movement of soil compounds is called…….	Soil Nutrition	Soil erosion	Flooding	Sedimentation	Soil erosion
	The dramatic increase in agricultural production that have been made possible by high yield “miracle crops” are called_______	biotechnical revolution	bioeconomic revolution	green house effect	green revolution	green revolution
	The nation whose government is promoting large families because of an aging population and low fertility rate is _______	United States	India	France	China	France
	Which among the following is not a renewable source of energy?	Biomass energy	Solar energy	Hydro-power	Geothermal energy	Solar energy
	Blue revolution is associated with _______	agriculture	iron and steel	irrigation	fishing	fishing
	A form of energy or matter that is essential for the functioning and sustained	resources	natural resource	environment	forest	resources

	survival of living organism within a specific population or ecosystem is called _________________					
	Water which is an universal solvent for most of the biochemical and biological process, constitutes about the total volume of ____________ billion kilometers	15	20	25	30	15
	The complete failure of monsoon rainfall with a dry climate accompanied by acute shortage of water causes _________	soil erosion	flash flood	loss of bio-diversity	drought	drought
	The study of minerals is called ______________	geology	mineralogy	mining science	metallurgy	mineralogy
	The resources that are obtained from any non-living materials are called _______resources	non-renewable	renewable	natural	environmental	non-renewable
	________________ is the degradation of land in arid, semi-arid and dry sub-humid areas	Land fertility	Desertification	Ecosystem	Vegetation	Desertification
	. …… is called poaching	Cutting of trees	growing of green plants	water storage	minerals	Cutting of trees
	_______________deserts are formed between tall	Polar	Trade win	Rain shadow	Costal	Rain shadow

	mountain ranges which prevent moisture-rich clouds from reaching areas on the ice, or protected side, of the range					
	Oil spills are a source of pollution for_____________	water	land and water	land and air	air and noise	land and water
	Air is composed of gases, water vapours and ______________	rainfall	snowfall	dust particles	light	dust particles
	_________ is a water borne disease	Small Pox	Meningitis	diarrhea	Cholera	Cholera
	Increase in global mean temperature causes _______________	greenhouse effect	forest fire	desertification	loss of fertility	greenhouse effect
	Common energy source in Indian villages is…………..	Electricity	Sun	Wood and animal dung	Coal	Wood and animal dung
	______ is the natural phenomenon, caused by an unlimited and unprecedented Rainfall	Soil erosion	Cyclone	Floods	Lightening	Floods
	________ scale is useful to record the force of win	decibel	Richter	beau fort	fujita	Richter
	The first 'Green revolution' in ___________ produced a large amount of food	1960s	1970s	1980s	1990s	1960s
	________ is a nonrenewable energy resource	Solar	Methane	Hydroelectricity	Coal	Coal
	_________ types of habitats are there in a biosphere	4	2	3	6	4

	Flora is the _______ life occurring in a particular region or time	plant	animal	human	microbial	plant
	_______ is the leading source of energy used in the United States today	coal	oil resources	natural gas	nuclear power	oil resources
	The energy used for all plant life processes is derived from _______ radiation	ultra violet	infra red	beta	solar	solar
	Of all of the energy production in the United States, _______ percentage is lost in distribution and inefficient use	10	25	40	50	40
	_________ is least likely to contain an oil trap	an anticline	fault	natural stratigraphy	syncline	syncline
	__________ rock types would most likely be the best oil reservoir	Granite	Shale	Sandstone	Salt	Sandstone
	About 75% of electricity comes from water in _________	South America	India	Australia	China	South America
	Two-thirds of the world's known oil reserves are located in ________	Siberia	gulf of Mexico and Caribbean	the middle east	Indonesia	the middle east
	Oil derived from coal, oil shales or tar sands is called ________	natural gas	biomass	syncrude	biogas	syncrude
	India ranks _______ amongst the wind-energy	first	second	third	fourth	fourth

	producing countries of the world					
	_____________ energy is derived from heated groundwater	solar	geothermal	hydroelectric	nuclear	solar
	Gobar gas is obtained from_________	manure	cow dung	crop residues	fossil	cow dung
	Water used for paper mills should not contain ____________	magnesium	sodium	iron	chlorine	iron
	Fuel cells are………………	Carbon cell	Hydrogen battery	Nuclear cell	Chromium cell	Hydrogen battery
	Photovoltaic energy is the conversion of sunlight into…………….	Chemical energy	Biogas	Electricity	Geothermal energy	Chemical energy
	Which of the following is a disadvantage of most of the renewable energy sources?	Highly polluting	High waste disposal cost	Unreliable supply	High running cost	Unreliable supply
	Steam reforming is currently the least expensive method of producing………………..	Coal	Biogas	Hydrogen	Natural gas	Hydrogen
	Which is the renewable energy source?	natural gas furnace	cows	coal burning	gas grill	cows
	Air is composed of gases, water vapours and ______________	rainfall	snowfall	dust particles	light	dust particles
	The newspaper contains one of the following toxic materials which is __________	C	P	Mg	Hg	P

	________ cycle is not a gaseous biogeochemical cycle in ecosystem	Nitrogen	Carbon	Sulphur	Phosphorus	Phosphorus
	If you are using biomass as a source of energy you might be………………	Heating with coal	Heating with natural gas	Heating with petroleum	Heating with a wood stove	Heating with a wood stove
	______that contains chemical waste and causes of damage to plants and animals	Smog	Acid Rain	Seasonal Rain	Monsoon Rain	Acid Rain
	Which of the following has nothing to do with hydropower?	Burning	Gravity	Sun	Water cycle	Burning
	Carbon dioxide is called green-house gas because it is ________	transparent to sunlight but traps heat	transparent to heat but traps sunlight	used in green-house to increase plant growth	transparent to both sunlight and heat	transparent to sunlight but traps heat
	The slow rate of decomposition of fallen logs in nature is due to their _______	poor nitrogen content	low moisture content	low cellulose content	anaerobic environment around them	low moisture content

UNIT-II

SYLLABUS

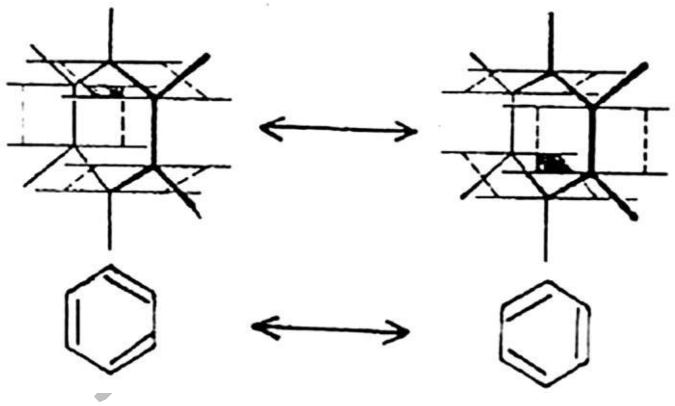
Aromatic Compounds and Heterocyclic Compounds:

Aromatic Compounds: Aromaticity-Huckel's (4n+2) rule- aromatic electrophilic substitution in benzene- mechanism of nitration, halogenation, alkylation, acylation and sulphonation. Naphthalene: Isolation, preparation, properties and structure.

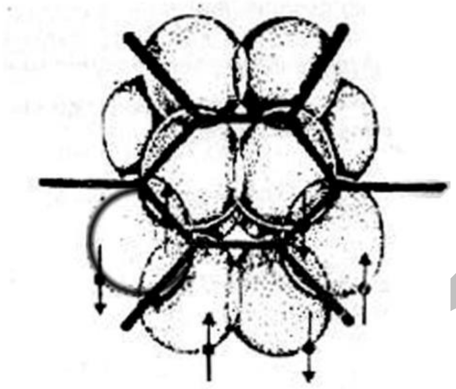
Heterocyclic Compounds: Preparation and properties of pyrrole, furan, thiophene and pyridine.

Aromatic Compounds

A study of the structure of benzene reveals that each carbon atom is sp^2 hybridised leaving the p_z electron perpendicular to the ring. The unhybridised p_z electron can overlap with its neighbour giving rise to two kekule forms as below:



This type of overlapping need not be confined to only one carbon but can take place with both the neighbours leading to the resonance structures which can be considered to have its electron cloud above and below the ring.



The relative unreactivity of benzene is due to the stability conferred by the delocalization of the π electrons over the six carbon atoms. This stability also explains why benzene shows substitution rather than addition. Because such addition reactions would lead to a product, in which delocalisation, though still possible, now involves only four carbon atoms resulting in the loss of resonance stabilisation. On the otherhand, substitution results in the retention of resonance stabilisation.

Aromaticity

Definition: An organic compound is to be aromatic, it should satisfy the following criteria-

i) The species must be planar.
ii) It must have a cyclic structure.
iii) It must contain (4n +2) delocalised π-electrons.
Where n = 0, 1, 2, ………..
iv) The species may contain unsaturated rings and undergo substitution reactions rather than addition reactions.

Benzene satisfies all these conditions and is aromatic in nature. Besides benzene, many other organic species possess aromaticity and are called **non benzenoid aromatic compounds.** There are many theories available to explain aromaticity. We shall study Huckel's rule of aromaticity.

Huckel's (4n+2) π electron rule

In order to explain aromatic nature, in 1931 the German Chemist Huckel put forward a rule.

Rule: On the basis of molecular orbital theory, Huckel stated that the presence of (4n+2) delocalised π-electrons in flat or nearly flat cyclic system is the cause of aromaticity. Here, n=0, 1, 2…

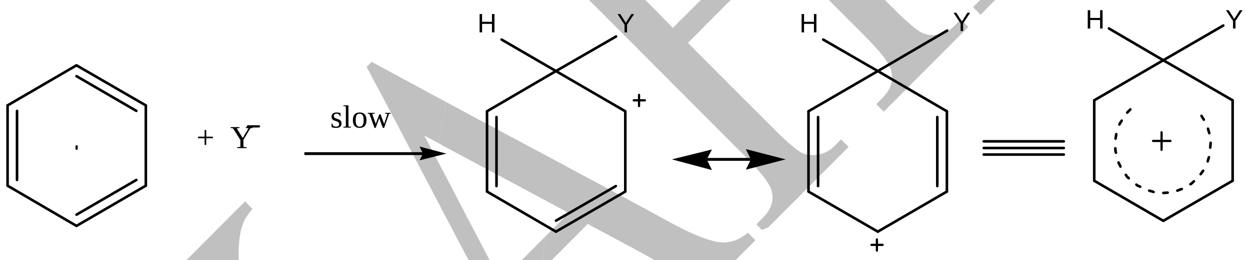
Many cyclic hydrocarbons satisfy this rule:

Benzene (6π e^-)	naphthalene (10π e^-)
Anthracene (14π e^-)	phenanthrene (14π e^-)
Chrysene (18π e^-)	naphthacene (22π e^-)

Apart from these some other compounds like ferrocene, azulene, pyridine, pyrrole and quinoline satisfy this rule and possess aromatic nature. These are called **non benzenoid aromatic compounds.**

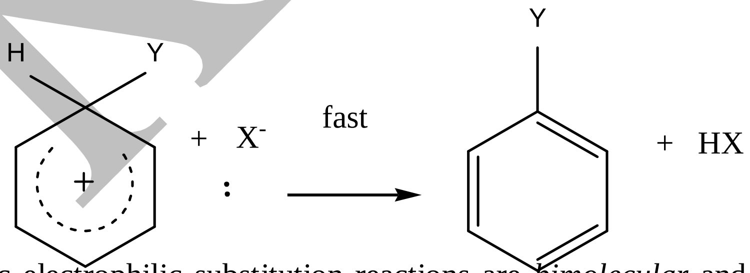
Aromatic Electrophilic Substitution Reaction

Aromatic electrophilic substitution reactions are the most widely studied reactions in organic chemistry. Analytical evidences show that the substitution reactions usually proceed in two steps. In the first step, the elctrophilic reagent attacks on the π electrons of aromatic ring to form an intermediate known as the *σ-complex* which is stabilized by resonance.



Intermediate, σ-complex

The second step involves the elimination of a proton from the intermediate by an anionic species to form substituted benzene:



All aromatic electrophilic substitution reactions are *bimolecular* and usually proceed in the presence of a catalyst. The function of the catalyst is to generate the electrophile.

We will now study some specific substitution reactions in detail.

Nitration

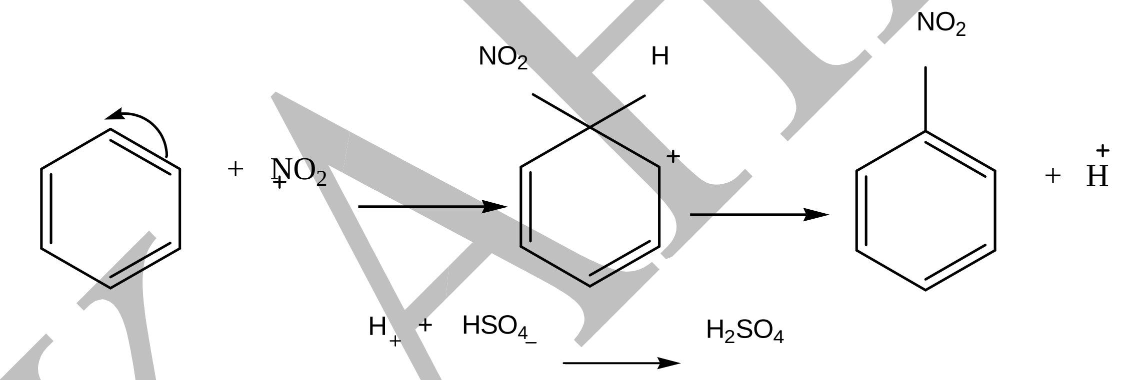
Generally nitration is carried out with a mixture of conc. nitric acid and sulphuric acid (*nitrating mixture*). When nitric acid alone is used, the reaction proceeds very slowly. There is considerable evidence that sulphuric acid helps in converting the nitric acid into *nitronium* ion, NO_2^+, which is the required electrophile.

$$HNO_3 + H_2SO_4 \longrightarrow HSO_4^- + H_2O + \overset{-}{N}O_2$$

$$H_2O + H_2SO_4 \longrightarrow HSO_4^- + H_3\overset{+}{O}$$

Adding : $HNO_3 + 2H_2SO_4 \longrightarrow 2HSO_4^- + H_3\overset{+}{O} + \overset{+}{N}O_2$

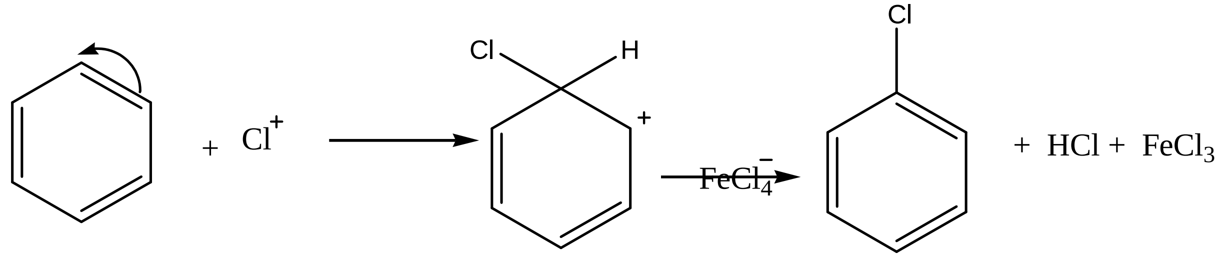
Not only sulphuric acid but also HF and BF_3 catalyse nitration by assisting the release of NO_2^+.



Halogenation

Introduction of a halogen atom into the aromatic nucleus usually takes place in the presence of a catalyst such as iron powder, $ZnCl_2$, $AlCl_3$, $AlBr_3$, $FeBr_3$, iodine, pyridine etc. The catalyst usually referred to as the *halogen carrier* is a Lewis acid. The function of the catalyst, as explained under nitration, is to provide the electrophile, X^+. L*ewis* acids increase the electrophilic character of the halogen by inducing some degree of polarisation in the halogen molecule:

$$Cl - Cl + FeCl_3 \longrightarrow \overset{+}{Cl} + Cl\text{-}FeCl_3$$



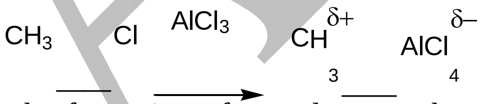
It should however be noted that no free Cl is formed in the first step of the reaction. The halogen carrier only helps to polarise the Cl-Cl bond and it is actually the positive end of the chlorine molecule acts as the electrophilic reagent.

Friedel-Crafts reaction

The reaction of alkyl halide or acyl halide with benzene in the presence of a Lewis acid like BF_3, $AlCl_3$ etc. is known as Friedel Crafts reaction. Hence, it can be divided in to *alkylation* and *acylation*.

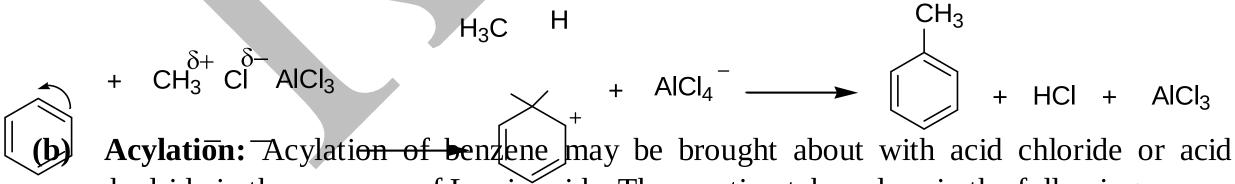
In the case of alkylation, alkyl substituted benzene like toluene, ethylbenzene etc., are formed and in the case of acylation aromatic ketones like acetophenone, benzophenone are formed.

(a) **Alkylation:** The mechanism of this reaction is similar to that of halogenation. Let us consider the reaction of methyl chloride with benzene in the presence of anhydrous $AlCl_3$. The first step as usual is the formation of the electrophile.

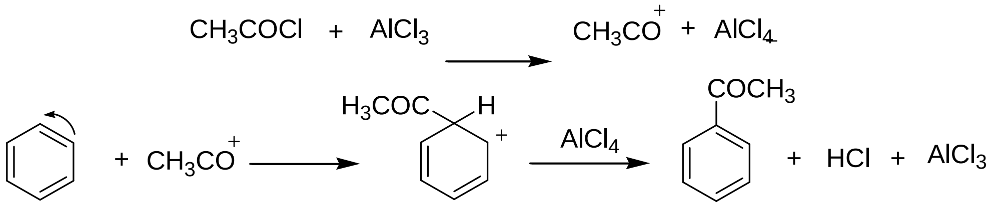


(I)

The evidence for the formation of complexes such as (I) is afforded by the fact that the labelled $AlCl_3$ is found to exchange the halogen with that of the alkyl halide. After the electrophile is formed, the reaction proceeds as follows:



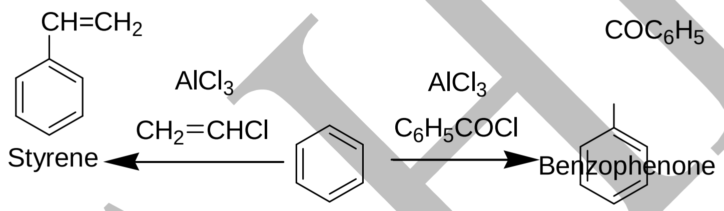
(b) **Acylation:** Acylation of benzene may be brought about with acid chloride or acid anhydride in the presence of Lewis acids. The reaction takes place in the following way:



The acylation reaction differs from the alkylation process in the following way:

1. Acylation is usually carried out in a solvent.
2. Acylation requires more catalyst than alkylation.
3. No rearranged products are formed in acylation.
4. Acylation is controlled easily so as to produce only monosubstituted product.

Other few Friedel Craft reactions are:

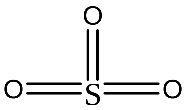


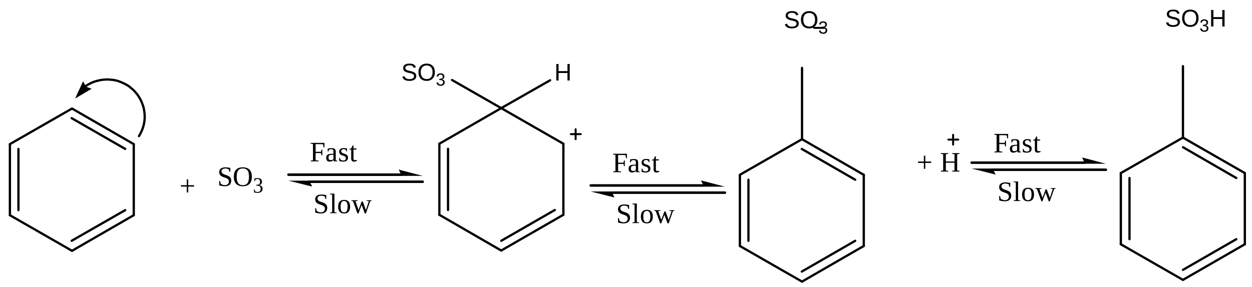
Sulphonation

The complete details of the mechanism of this reaction are still under investigation. According to the widely accepted view, SO_3 is the electrophilic reagent and is formed in the following way**:**

$$2\,H_2SO_4 \xrightarrow[\textit{fuming sulphuric acid}]{} SO_3 + H_3O^+ + HSO_4^-$$

Though SO_3 is a neutral molecule, it has powerful electrophilic (electron deficient) sulphur atom as shown by its structure:





Naphathalene, $C_{10}H_8$

Naphthalene and anthracene are called condensed nuclear hydrocarbon as two or more carbon atoms are shared in common by two or more aromatic rings.

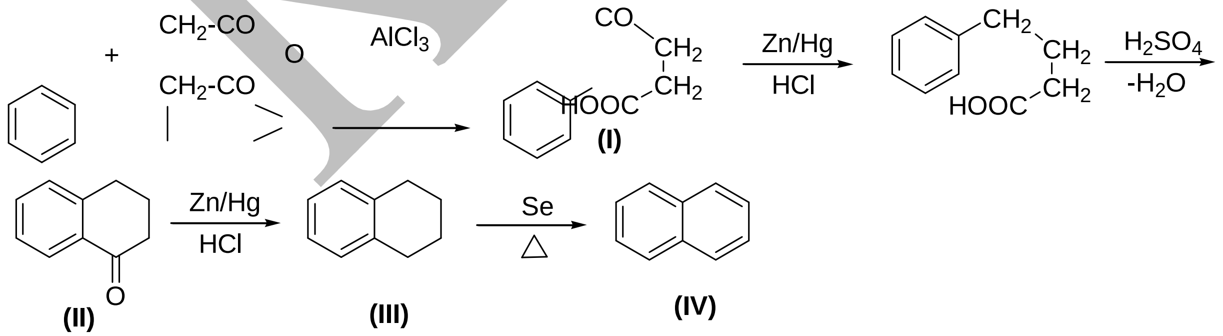
Isolation of naphthalene

It is the largest single constituent of coal tar. It occurs in the middle and heavy oil fractions of coal tar distillation. When the middle and heavy oil fractions are cooled, naphthalene crystallises out. The crude naphthalene is recovered, melted and washed with sodium hydroxide to remove phenol and then treated with conc. Sulphuric acid to remove basic impurities. Finally pure naphthalene is obtained by sublimation.

Synthesis of naphthalene

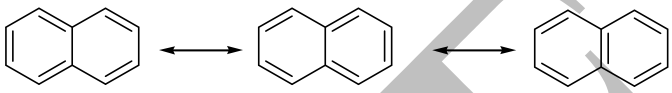
Naphthalene can be synthesized by a number of methods, the most important being the *Haworth synthesis*.

Benzene reacts with succinic anhydride in the presence of aluminium chloride to give the ketonic acid (I). This is reduced by treating with zinc amalgam and hydrochloric acid *(Clemmensen Reduction)*. The ring closer is effected by heating with conc. sulphuric acid to give a *tetralone* (II). This is subjected to Clemmensen reduction to tetrahydronaphthalene (*tetralin*, III) which on dehydrogenation with selenium gives naphthalene (IV).

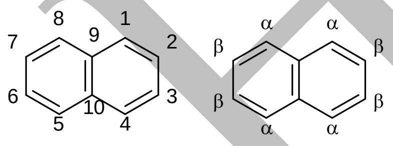


Properties of Naphthalene:

1) Naphthalene exists as white lustrous plates.
2) It is soluble in organic solvents only.
3) The melting point is 353 K.
4) It has a characteristic smell.
5) Naphthalene is considered to be a resonance hybrid, with resonance energy of 255.2 k. J/mol, of the following three contributing structures:



Naphthalene has eight replaceable hydrogen atoms in the molecule of two benzene rings, so there are two carbon atoms common to both the benzene rings. The carbon atoms of the two rings constituting the molecule of naphthalene are numbered as below and the positions of various substituents are indicated by numbers and Greek alphabets.



Naphthalene is symmetrical in structure and positions 1, 4, 5, and 8 are equivalent and positions 2,3,6 and 7 are identical. So there are two isomeric monosubstitution products. 1,4,5 and 8 positions denoted by *α*. Similarly, positions 2,3,6 and 7 are denoted by *β*.

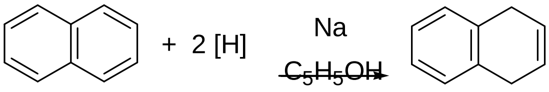
Disubstitution products are known as ortho, meta and para like benzene derivatives when two substituents are present in the same ring. 1,8 or 4,5 position is called *peri* positions. 2,6 or 3,7 position is called *amphi* positions.

Naphthalene resembles benzene in its chemical behavior. It is more reactive than benzene and readily forms substitution and addition products.

Reduction

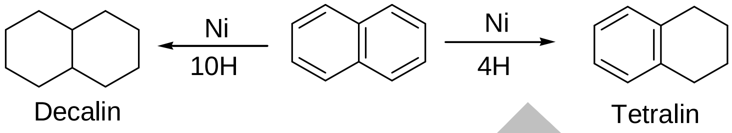
Naphthalene forms a number of reduction products depending upon the conditions of the reaction and the nature of the reducing agent.

a) When reduced with sodium and ethanol, it gives 1,4-dihydronaphthalene.



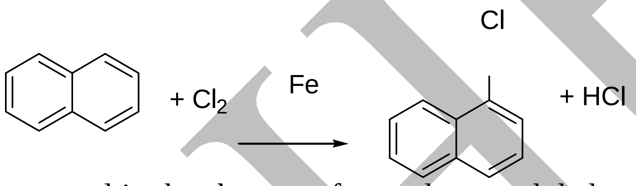
b) Catalytic reduction in presence of finely divided nickel, it gives tetrahydronaphthalene *(tetralin)*.

c) Prolonged reduction with nickel catalyst, it yields decahydronaphthalene (*decalin)*.

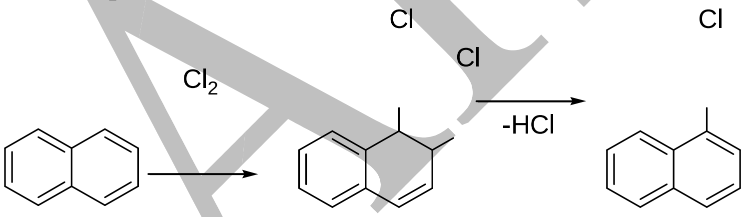


Halogenation

Naphthalene gives substitution reactions with chlorine and bromine in presence of halogen carriers like iron.

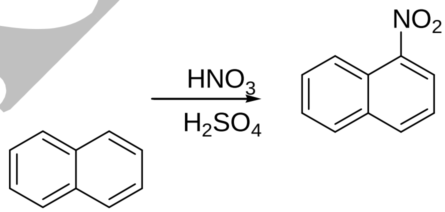


At room temperature and in the absence of a catalyst, naphthalene reacts with chlorine to give an addition compound, dichloronaphthalene. This eliminates a molecule of hydrogen chloride to form monochloro naphthalene.



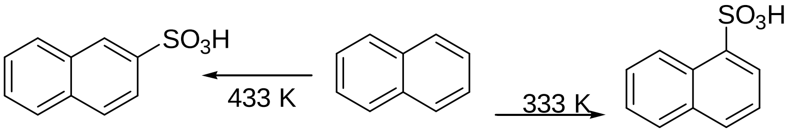
Nitration

With nitration mixture (Conc.HNO_3 and Conc.H_2SO_4) naphthalene gives 1-nitronaphthalene.



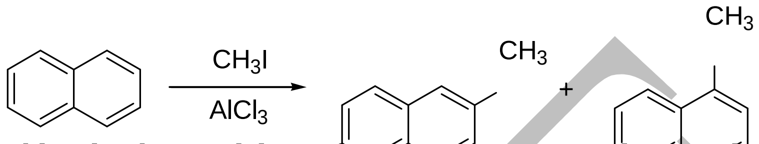
Sulphonation

With conc. H_2SO_4, naphthalene gives two different products depending upon the temperature. At 333 K, reaction with sulphuric acid gives naphthalene-α-sulphonic acid and at 433 K, the main product is naphthalene-β-sulphonic acid.

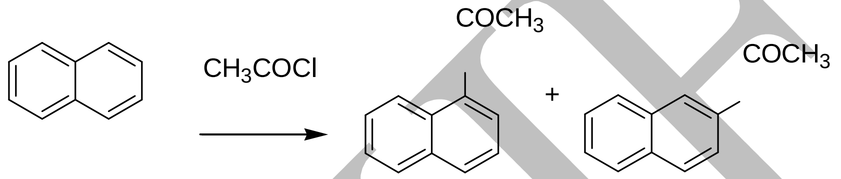


Friedel-Crafts reaction

In presence of $AlCl_3$ methyl iodide reacts with naphthalene to give a mixture of 1- and 2-methylnaphthalene.

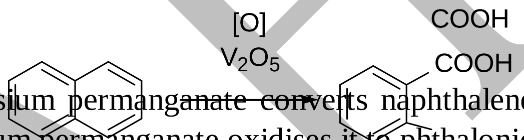


With acetyl chloride, the Friedel- Crafts reaction gives 1 and 2-acetylnaphthalene:

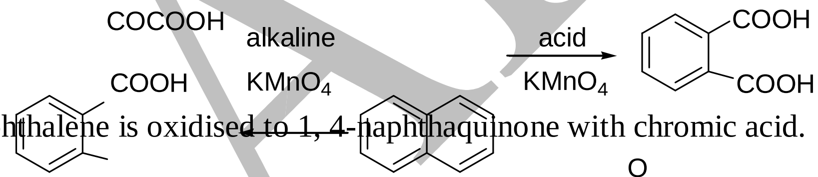


Oxidation

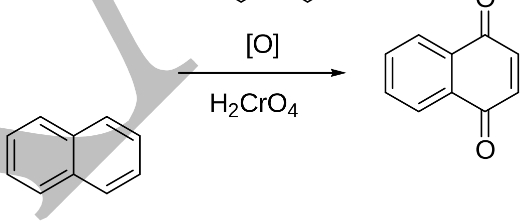
1) When naphthalene vapours mixed with air are passed over vanadium pentoxide catalyst, phthalic acid is formed.



2) Acidified potassium permanganate converts naphthalene to phthalic acid while alkaline potassium permanganate oxidises it to phthalonic acid.

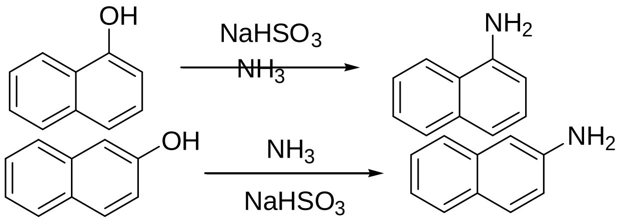


3) Naphthalene is oxidised to 1, 4-naphthaquinone with chromic acid.

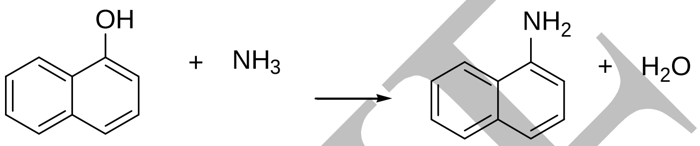


Naphthylamines

1) α-and β-naphthylamines are prepared by *Bucherer reaction*:



2) Naphthylamine may also be obtained by heating a naphthol with $ZnCl_2$ and ammonia.

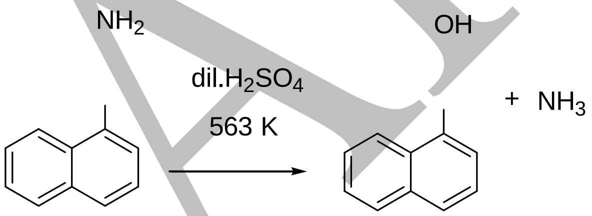


Naphthols

α-and β-naphthols are obtained by fusing the corresponding naphthalene sulphonic acid with sodium hydroxide:

$$C_{10}H_7SO_3Na + 2\,NaOH \xrightarrow{573\ K} C_{10}H_7ONa + Na_2SO_3 + H_2O$$

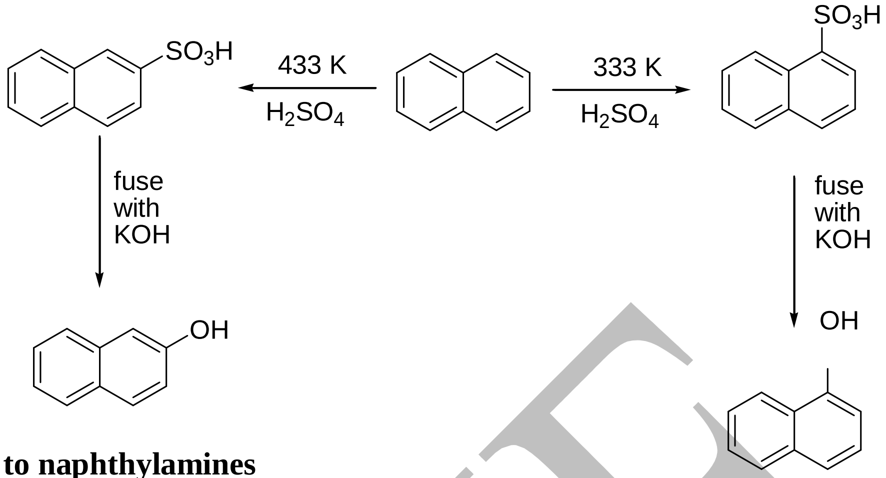
However, pure α- naphthol may be prepared by heating α- naphthaylamine with dil. H_2SO_4:



Important Conversions

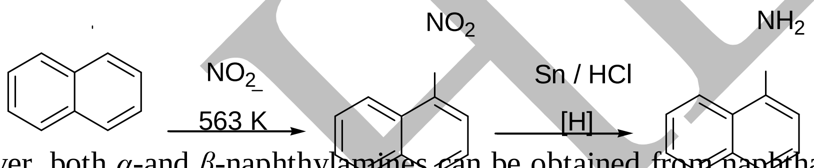
(a) Naphthalene to naphthols

Both α-and β-naphthols are obtained from naphthalene in the following way:

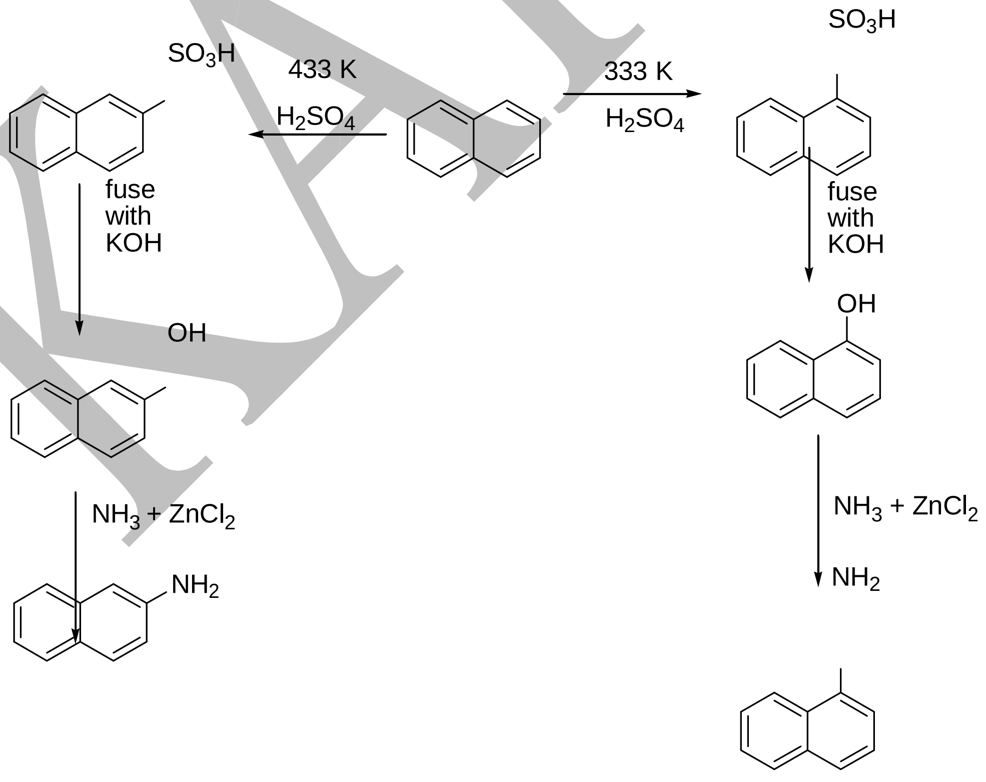


(b) Naphthalene to naphthylamines

(i) With nitration mixture naphthalene gives 1-nitronaphthalene. This on reduction with tin and hydrochloric acid forms 1-aminonaphthalene.

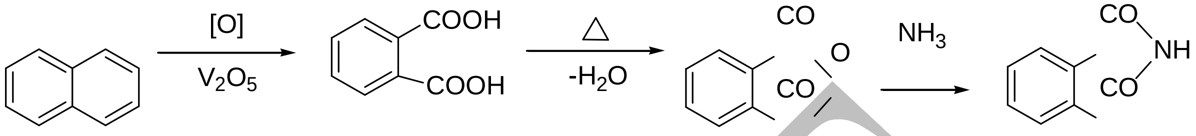


(ii) However, both α-and β-naphthylamines can be obtained from naphthalene in the following way:



(c) Naphthalene to phthalimide

When naphthalene vapours mixed with air are passed over vanadium pentoxide catalyst, phthalic acid is formed. This on further heating loses a water molecule to form phthalic anhydride. Passing ammonia over this conveniently yields phthalimide:



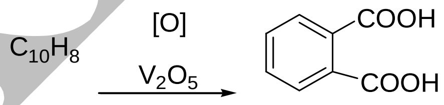
Uses

Naphthalene finds use

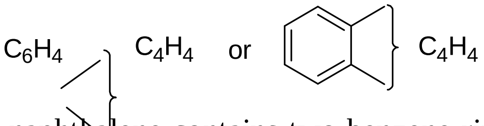
1) As an insecticide.
2) In the preparation of phthalic anhydride.
3) In the manufacture of phthalein dyes.

Structure of Naphthalene

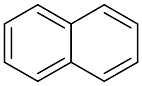
1) The molecular formula is $C_{10}H_8$.
2) Though the molecular formula suggests that it should be an unsaturated compound, it is resistant to addition reactions.
3) On the other hand, it undergoes electrophilic substitution reactions (chlorination, nitration, sulphonation) like benzene.
4) The nuclear substituted hydroxy compounds of naphthalene are phenolic in nature. The amino derivatives can be diazotized. In addition, these compounds undergo the usual coupling reactions also.
5) When naphthalene vapours mixed with air are passed over vanadium pentoxide catalyst, phthalic acid is formed:



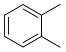
This shows the presence of at least one aromatic ring and two side chains are in ortho positions to each other. Therefore, the formula of naphthalene may be

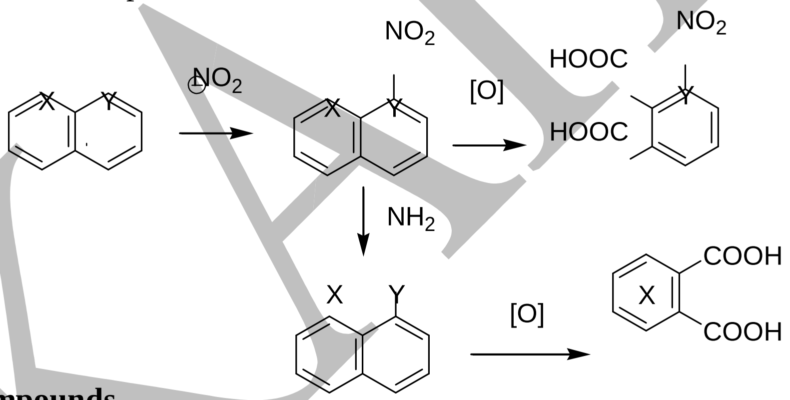


6) *Erlenmeyer* proposed that naphthalene contains two benzene rings fused to each other in the ortho positions as shown below.



7) The presence of two benzene rings in naphthalene (Graebe, 1869) is supported from the following reactions:

   a) Naphthalene on oxidation gave phthalic acid which proved the presence of  group.
   i.e., a benzene ring with two side chains in the ortho position.
   b) On nitration and subsequent oxidation, naphthalene gave nitrophthalic acid. This indicated that the nitro group was in the benzene ring and that it was the side chains which were oxidized.
   c) When nitronapthalene was reduced and the corresponding aminonaphthalene oxidised, phthalic acid was obtained.
   d) Since the amino group attached to benzene ring always renders the benzene extremely sensitive to oxidation, the benzene ring in phthalic acid obtained by the oxidation of aminonaphthalene is not the same ring as that originally containing the nitro group in nitronaphthalene. Hence atleast two benzene rings must be present in naphthalene.



Heterocyclic Compounds

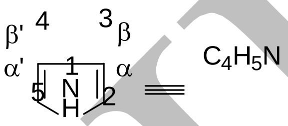
Introduction

Heterocyclic compounds are cyclic molecules having some atom other than carbon as part of a ring (**Greek**, heteros, meaning other). The most common heteroatoms are nitrogen, oxygen and sulphur. There are a number of heterocyclic rings which are easily opened and do not possess aromatic properties, e.g. ethylene oxide, γ and δ lactones etc. These are not considered to be heterocyclic compounds.

Heterocyclic compounds are particularly important because of their wide variety of physiological activities. They find use in medicine and a great deal of research is carried out to prepare new heterocyclics having therapeutic values. Upto recent years, no ring more than six atoms had been found in the nature.

In this chapter, the discussion will be centered about the compounds containing five membered rings (pyrrole, furan, thiophene) and six membered ring (pyridine). They are stable, contain conjugated double bonds and exhibit aromatic character. The numbering in these molecules begins at the heteroatom.

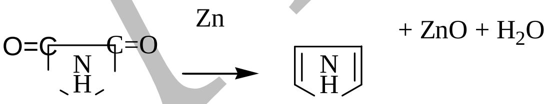
(1) Pyrrole, C_4H_5N



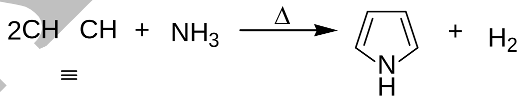
Pyrrole is an important heterocyclic compound. It is found in many natural compounds, e.g. alkaloids, chlorophyll etc. It occurs in coal tar and bone oil.

Preparation

1. **Isolation from bone oil:** Bone oil is washed with dilute alkali to remove acidic impurities and then with acid to remove basic impurities. The liquid is then fractionated. Pyrrole distills over in the fraction boiling between 373 K and 423 K. This may be purified by fusing with potassium hydroxide. Solid potassio pyrrole is formed. This on steam distillation gives pure pyrrole.
2. Pyrrole is formed when succinimide is distilled with zinc dust.



3. Pyrrole may be synthesized by passing a mixture of acetylene and ammonia through a red hot tube.



4. It is conveniently prepared by distilling a mixture of ammonium mucate and glycerol at 473 K.

$$H_4NO_2C(CHOH)_4CO_2NH_4 \xrightarrow{\text{glycerol}} C_4H_4NH + NH_3 + 2CO_2 + 4H_2O$$

Properties

It is a colourless liquid (bp.404 K), sparingly soluble in water but readily soluble in ether and alcohol. On exposure to air, it darkens rapidly and forms a resinous mass finally.

Chemically, it shows the reactions of aromatic compounds.

Some important reactions are -

a) **Basic nature :** Pyrrole is a weak, secondary amine and dissolves very slowly in cold, dilute acids:

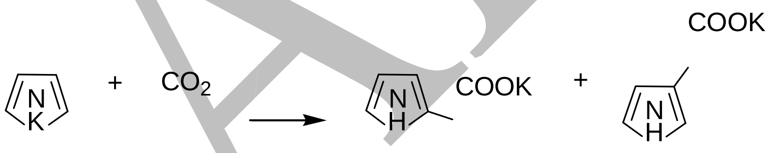
$$C_4H_4NH + HCl \longrightarrow C_4H_4NH_2^+ Cl^-$$

b) **Substitution of imino hydrogen:** The imino hydrogen of pyrrole is replaced by Grignard reagent, sodium, potassium, alkyl or acyl radicals Eg. On heating with solid potassium hydroxide, potassio pyrrole is formed (*Cf*. phenol).

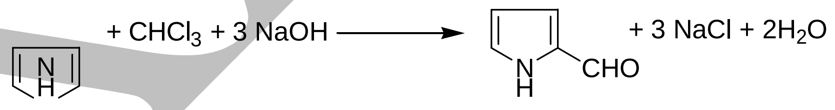
$$C_4H_4NH + KOH \longrightarrow C_4H_4N^- K^+ + H_2O$$

At 333 K pyrrole forms N-methyl pyrrole with methyl iodide. With acetyl chloride, N-acetylpyrrole is formed at 353 K.

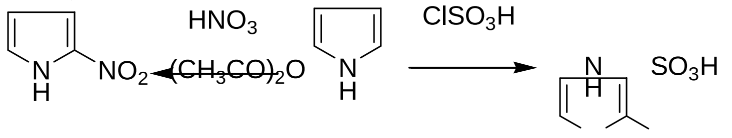
c) **Substitution reactions:** In many reactions, pyrrole resembles phenol. For example, potassio pyrrole reacts with carbon dioxide to form 2- and 3-pyrrole carboxylic acid (*Cf*. kolbe Schmidt reaction)



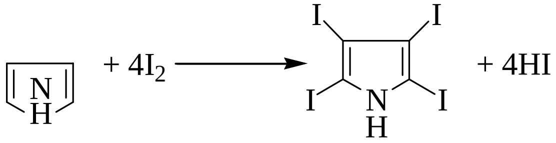
Pyrrole reacts with chloroform and sodium hydroxide to form pyrrole-2-aldehyde (*Cf*. Reimer –Tiemann reaction).



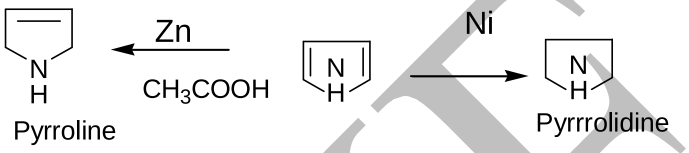
Pyrrole cannot be nitrated and sulphonated or halogenated by the methods used in the case of benzene. At 263 K, pyrrole yields 2-nitropyrrole with nitric acid in acid in acetic anhydride. With chlorosulphonic acid, pyrrole is sulphonated to form pyrrole-2-sulphonic acid.



Halogenation occurs readily if the solution is alkaline. Iodine forms tetraiodopyrrole.

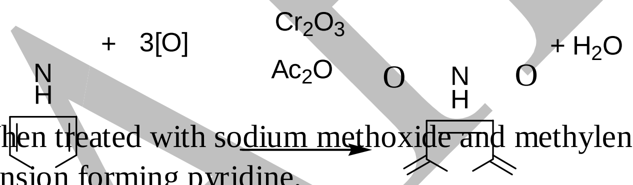


d) Reduction: With zinc dust and acetic acid, pyrrole undergoes reduction to give pyrroline (2,5-dihydropyrrole). At 473 K catalytically reducing pyrrole using nickel, pyrrolidine (tetrahydropyrrole) is formed.

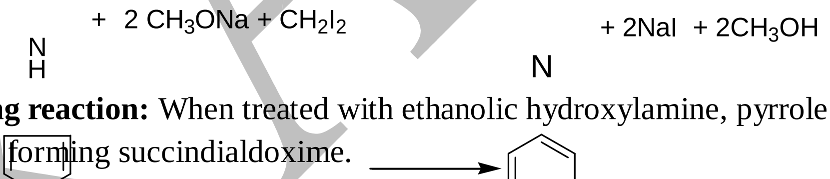


e) Coupling: Pyrrole couples with benzenediazonium chloride in a weakly acidic solution to give 2-phenyl azo pyrrole:

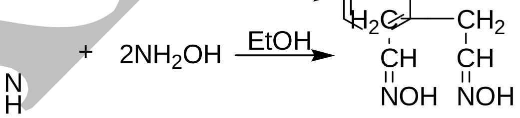
f) Oxidation : Pyrrole is oxidized by chromic acid to give maleic imide:



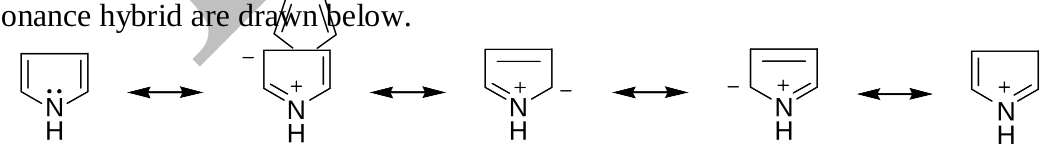
g) Ring expansion: When treated with sodium methoxide and methylene iodide, pyrrole undergoes ring expansion forming pyridine.



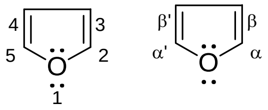
h) Ring opening reaction: When treated with ethanolic hydroxylamine, pyrrole undergoes ring opening forming succindialdoxime.



Pyrrole is a resonance hybrid with resonance energy 87.8-130 kJmol^{-1} and the possible resonance hybrid are drawn below.

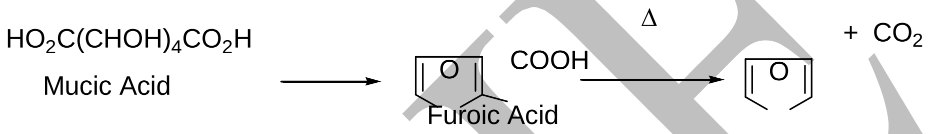


(2) Furan, C_4H_4O

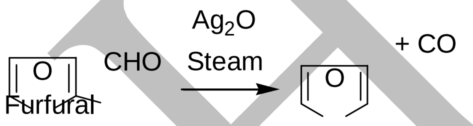


Preparation

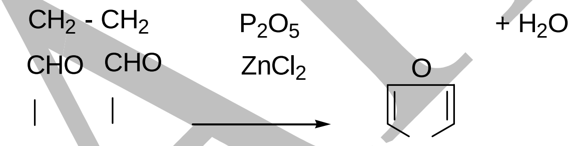
a) Furan is obtained when wood, especially pine wood, is distilled. It may be prepared by the dry distillation of mucic acid, and heating the product, furoic acid (I), at its boiling point:



b) By decabonylation of furfural in steam in the presence of silver oxide catalyst.



c) By dehydration of succindialdehyde.



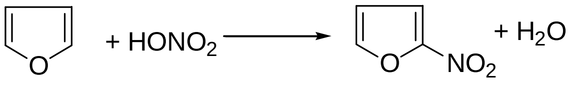
Properties

Furan is a colourless liquid (b.p.305 K), with chloroform like smell. It is only slightly soluble in water but dissolves in most organic solvents. It behaves as an aromatic compounds but in some ways it behaves as a 1,3-diene. Thus, it is less aromatic than thiophene and pyrrole.

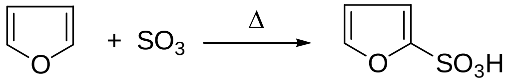
Furan, like pyrrole, is a weak base. It forms salt with mineral acids. These salts may either polymerise to produce a brown resin or undergo hydrolysis to yield succindialdehyde.

(I) **Electrophilic substitution:** Furan undergoes electrophilic substitutions mainly at C-2 and C-5. Substitution at C-3 occurs only when both these positions are already blocked.

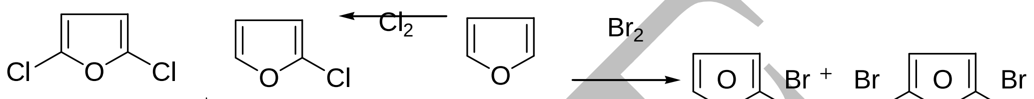
(a) Nitration: It can be nitrated with a hot solution of nitric acid and acetic anhydride to form 2-nitrofuran.



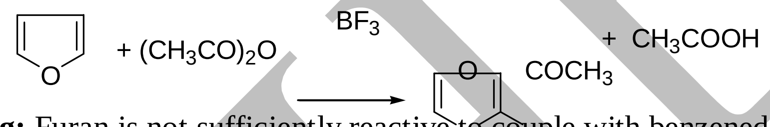
(b) Sulphonation: Furan may be sulphonated by sulphur trioxide in pyridine at 343 K to yield furan-2-sulphonic acid.



(c) Halogenation: Furan reacts vigorously with chlorine and bromine at room temperature to give polyhalogenated products, but does not react with iodine.

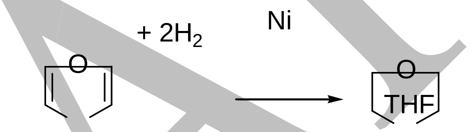


(d) Friedel-Craft's acylation: Furan can be acylated with acetic anhydride in the presence of BF_3 or $SnCl_4$ at 273 K to yield 2-acetylfuran.



(e) Diazo coupling: Furan is not sufficiently reactive to couple with benzenediazonium chloride.

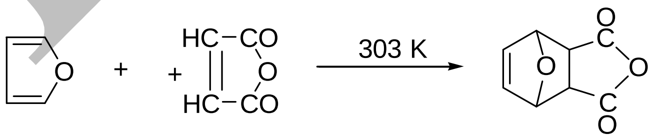
(II) Reduction : Furan is reduced catalytically to tetrahydrofuran (THF).



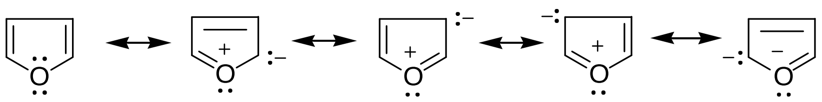
(III) Ring opening reaction: When treated with methanol and hydrochloric acid, furan undergoes ring opening forming the diacetal of succindialdehyde.

(Hydrolysis of furan with dilute hydrochloric acid also leads to ring opening)

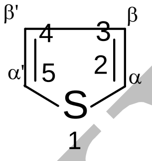
Diels-Alder Reaction: Furan is the only one of the five membered heterocyclic compounds to undergo the Diels–Alder reaction with maleic anhydride. The addition occurs across C-2 and C-5.



Furan has resonance energy of 71.0-96.0 kJ mol^{-1} and is represented as a resonance hybrid of contributing structure as below.



(3) Thiophene, C_4H_4S



From Coal Tar

Benzene, obtained from coal tar, contains thiophene. It is difficult to separate them by fractional distillation as their boiling points (357 K) are close to each other. Thiophene may be separated from benzene by shaking the mixture with cold, concentrated sulphuric acid when thiophene gives thiophene-2-sulphonic acid which is dissolved out in water. Thiophene sulphonic acid is treated with superheated steam to recover thiophene.

Another method of separation is by refluxing the mixture with aqueous mercuric acetate when thiophene is mercurated and benzene remains unaffected. Thiophene can be regenerated from the organomercury compound by treating with hydrochloric acid.

The best method of removing thiophene from benzene is by shaking with Raney nickel.

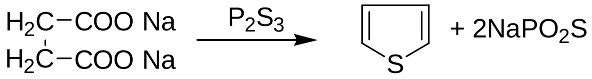
Preparation

Thiophene may be obtained –

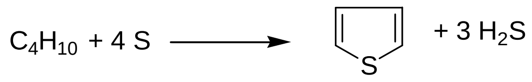
1) By passing a mixture of acetylene and hydrogen sulphide through a tube containing alumina at 673 K.

$$2\ C_2H_2 + H_2S \longrightarrow C_4H_4S + H_2$$

2) By heating sodium succinate with phosphorus trisulphide.



3) It is also obtained commercially by the reaction between n-butane and sulphur in the vapour phase:

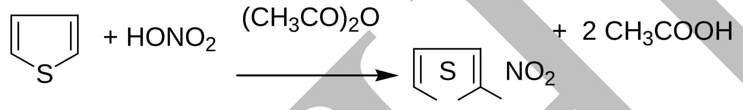


Properties

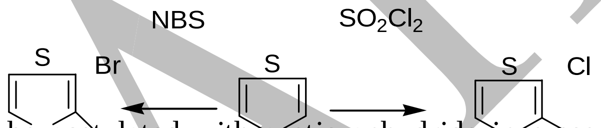
Thiophene is a colourless liquid, smelling like benzene. It is insoluble in water but soluble in organic solvents. Chemically thiophene resembles benzene rather closely. As compared with furan and pyrrole, it is comparatively more stable.

Electrophilic substitution: Thiophene undergoes electrophilic substitution reactions primarily at C-2 Substitution at C-3 occurs only when both the α and α' position are occupied.

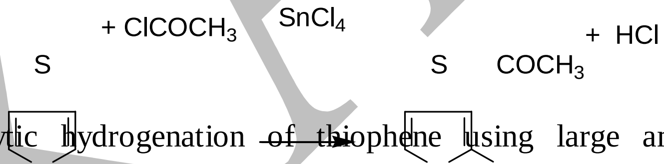
Thiophene can be nitrated by a solution of nitric acid in acetic anhydride to yield 2-nitrothiophene. Sulphonation with cold, concentrated sulphuric acid gives 2-sulphonic acid.



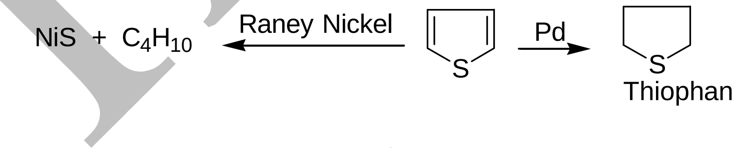
Chlorination at room temperature gives 2-chlorothiophene with SO_2Cl_2. 2-bromothiophene is obtained at room temperature when thiophene is treated with *N*-bromosuccinimide (NBS).



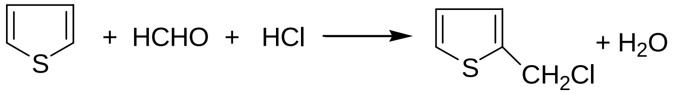
Thiophene may be acetylated with acetic anhydride in presence of phosphoric acid or with acetyl chloride in presence of stannic chloride to yield 2-acetyl thiophene.



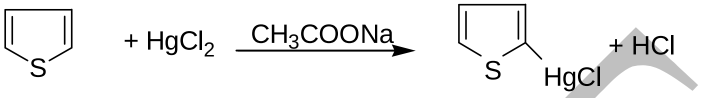
Reduction: Catalytic hydrogenation of thiophene using large amount of catalyst gives tetrahydrothiophene (**thiophan)** and using Raney nickel as catalyst thiophene is converted to n-butane, C_4H_{10}.



Chloromethylation: Thiophene reacts with formaldehyde and hydrochloric acid to give 2-chloromethyl thiophene.



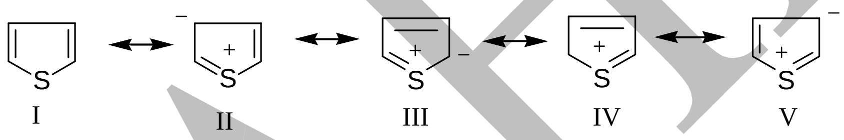
Mercuration: Thiophene undergoes mercuration with mercuric chloride in aqueous sodium acetate to produce 2-chloromercurithiophene.



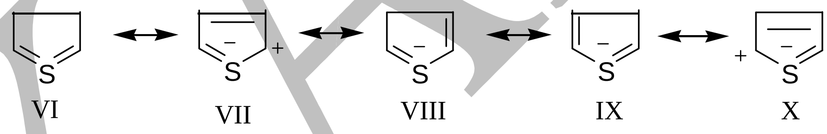
Thiophene does not react with benzenediazonium chloride.

Thiophene is a resonance hybrid with resonance energy 117-130 k. J mol^{-1}. In the resonance structures written below in **group (a)** sulphur atom uses p-orbitals and in **group (b)** sulphur uses d-orbital.

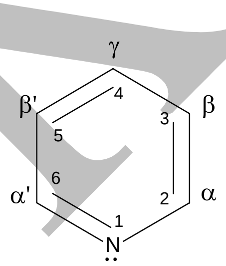
(a)



(b)



(4) Pyridine, C_5H_5N



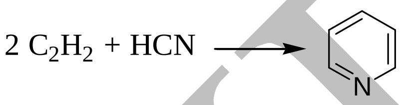
Pyridine is an important heterocyclic compound containing a six membered ring. It may be regarded as benzene in which one = CH-group has been replaced by = N-. Because of the presence of the heteroatom in the ring, three isomeric mono substituted pyridines can exist corresponding to the substituents at *α ,β or γ* (2,3 or 4) positions.

It occurs along with pyrrole in bone oil and in the light oil fraction (b.p. upto 443 K) of coal tar. It can be isolated from the latter by extracting with dilute sulphuric acid. The acid layer is separated and treated with sodium hydroxide when a dark brown liquid separates. Pyridine is obtained from this oily liquid by fractional distillation.

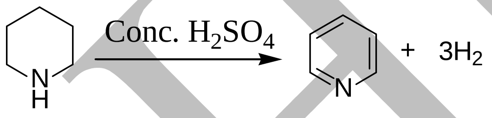
Preparation

Pyridine may be obtained-

1) By passing a mixture of acetylene and hydrogen cyanide through a red hot tube.



2) By dehydrogenation of piperidine with concentrated sulphuric acid at 573 K or with nitrobenzene at 533 K.



Properties

Pyridine is a colourless liquid (b.p 338 K) having an unpleasant odour. It is miscible with water in all proportions and is hygroscopic. Pyridine is basic in nature ($pK_b = 5.2$) and resembles benzene in many of its properties.

Pyridine is a strong tertiary amine which gives salts with inorganic acids and form quaternary salts when heated with alkyl halides.

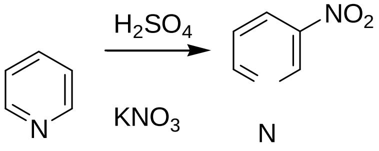
$$C_5H_5N + HCl \longrightarrow C_5H_5NH^+Cl^-$$

pyridinium chloride

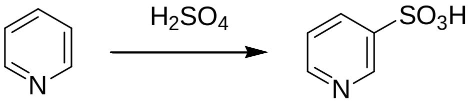
$$C_5H_5N + CH_3I \longrightarrow [C_5H_5NCH_3]^+ I^-$$

pyridine methiodide

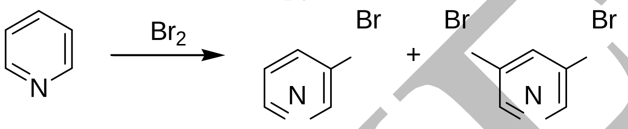
Electrophilic Sustitution: Pyridine is considerably less reactive than benzene towards electrophiles. So, it does not undergo Friedel Craft's reaction. It undergoes nitration, sulphonation and halogenations only under vigorous conditions. With conc. H_2SO_4 and KNO_3 at 573 K it gives 3-nitropyridine.



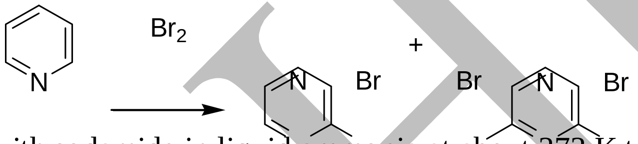
Sulphonation of pyridine is difficult. On heating with concentrated sulphuric acid at 623 K for some hours it gives pyridine-3- sulphonic acid.



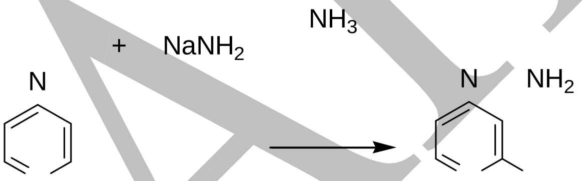
With bromine at 573 K in the presence of catalyst (pumice or charcoal) pyridine gives a mixture of 3- bromopyridine and 3, 5-dibromopyridine.



At 773 K bromination occurs at C-2 or C-2 and C-6 positions. The substitutions probably occur by a free radical mechanism.

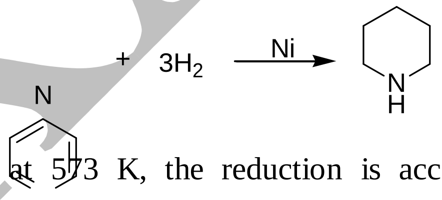


Pyridine reacts with sodamide in liquid ammonia at about 373 K to form 2-aminopyridine **(Chichibabin reaction)**. This reaction is an example of nucleophilic substitution reaction.

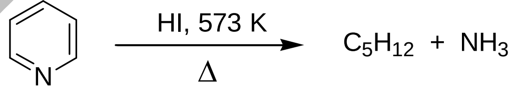


Reduction

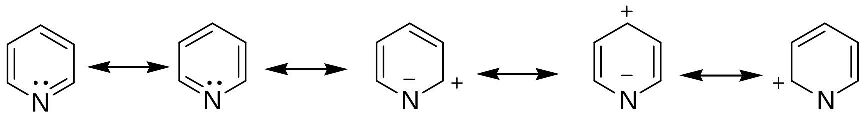
Pyridine undergoes reduction with lithium aluminum hydride or hydrogen in the presence of nickel catalyst to form piperidine.



With hydrogen iodide at 573 K, the reduction is accompanied by fission to form n-pentane and ammonia.



Pyridine has resonance energy of about 125 k. J mol^{-1}. Because pyridine has a large dipole moment of 2.23 D, it is best regarded as a resonance hybrid of the following contributing structures.



Reactivity of pyridine

A close look at the contributing structures of pyridine reveals that positions 3 and 5 will be sites for electrophilic attack. The remaining positions (2, 4 and 6) will be the sites for nucleophillic attack. Moreover, the ring is deactivated towards electrophilic reagents due to the withdrawal of electrons from the ring carbon atoms towards the nitrogen atom. Thus pyridine resembles benzene ring in nitrobenzene. Pyridine can be protonated in strongly acid medium. At that time, the positively charged nitrogen atom deactivates the ring much more than the unprotonated nitrogen atom. This is indicated by the difficulty in nitration and sulphonation in pyridine. Thus, pyridine is less reactive than benzene.

Uses

1. Due to its strong basic property and solvent properties, pyridine is used in reactions where halogen acid is to be removed as in alkylation and benzoylation.
2. It is utilized to denature ethyl alcohol.
3. It finds use as a catalyst in many reactions.
4. Pyridine is used as starting material in the preparation of sulphapyridine and pyridoxine (Vitamin B_6).

Aromaticity and Basic nature in Pyrrole and Pyridine

The prime condition for a molecule to be aromatic is that it must obey **Huckel's** (4n + 2) **rule**. According to this rule, the molecules must possess π electron cloud formed by (4n +2) electrons. Here 'n' represent may the number of ring present in the molecule. Obviously, there must be 6, 10, 14 …. electrons for delocalization if the compound is made up of 1, 2, 3…. rings respectively.

Both pyrrole and pyridine have single ring. If they were to be aromatic, then they must have six π electrons for delocalization according to Huckel's rule. Pyrrole has π electron cloud made up of six electrons. It uses the lone pair of electrons residing over nitrogen for this purpose. On the other hand, pyridine obeys Huckel's rule without using the lone pair of electrons of nitrogen atom. In other words, pyridine, as in benzene, has three alternate double bonds which satisfy the rule.

Based on the above argument, it is clear that the lone pair of electrons of nitrogen in pyrrole is not available for donation to an acid. Consequently pyrrole is weak Lewis base ($pK_b = 3.4$) and even it behaves as an acid. The lone pair of electrons on nitrogen in pyridine is available for donation. Thus, pyridine is a strong Lewis base ($pK_b = 5.2$).

Text Books:

1. Veeraiyan, V., & Vasudevan, A.N.S. (2012). *Text Book of Allied Chemistry* (II Edition). Chennai: Highmount Publishing House.

2. Bahl, A., & Bahl, B.S. (2015). *A Textbook of Organic Chemistry* (21st Revised Edition). New Delhi: S.Chand & Company Pvt. Ltd.

Reference Book:

1. Gopalan, R., & Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. Define aromaticity.
2. Write the name of four non benzenoid aromatic compounds.
3. Write the ring opening reaction of (a) pyrrole and (b) furan.
4. Write the reduction product of (a) pyrrole and (b) thiophene.
5. Write the reduction product of naphthalene.
6. How does pyridine react with (a) KNO_3 (b) Br_2?
7. Write the reaction of pyrrole with (a) KOH and (b) I_2.
8. Write any two methods of preparation of thiophene.

9. What is Chichibabin reaction?

10. Explain why pyrrole is less basic than pyridine.

11. Mention the uses of pyridine.

12. How pyrrole is able to show aromaticity?

13. Explain why pyridine is less reactive than benzene.

14. Mention the uses of naphthalene.

15. How will you convert naphthalene into phthalimide?

PART-C (Each Question Carry Six Marks)

1. What are heterocyclic compounds? Give examples. How are they named and numbered?

2. How are the following prepared from acetylene (a) pyrrole (b) pyridine (c) thiophene?

3. (i) Explain the mechanism of halogenations.

(ii) Explain the aromaticity and basic nature in pyrrole and pyridine.

4. Write notes on (i) Structure of naphthalene (ii) Nitration of benzene.

5. Give the products of the following reactions.

(i)

$$\text{Furan} + \text{Maleic anhydride} \longrightarrow ?$$

(ii)

$$\text{Pyrrole} + CH_3ONa + CH_2I_2 \longrightarrow ?$$

(iii)

$$\text{Pyridine} + NaNH_2 \xrightarrow{\text{liq } NH_3} ?$$

6. (i) How will you prepare the following from naphthalene a) naphthols b) naphthylamines.

(ii) Write any two methods of preparation of pyridine.

7. (i) How does furan react with (a) SO_3 (b) HNO_3 (c) Cl_2 (d) $(CH_3CO)_2O$.

(ii) Explain the Friedel-Crafts reaction.

8. How does thiophene react with a) $SnCl_4$ b) HNO_3 c) NBS d) SO_2Cl_2 e) CH_3COOH f) HCHO + HCl.

9. (i) Explain why benzene undergoes electrophilic substitution reactions but not addition reactions.

(ii) Define Huckel's (4n+2) π electron rule.

(iii) Explain the sulphonation of benzene.

10. (i) Write the reaction of pyrrole with a) HCl b) $ClSO_3H$ c) $C_6H_5N_2Cl$.

(ii) How does pyridine react with (a) $NaNH_2$ (b) H_2/Ni (c) HI?

11. State what happens when furan, pyrrole and thiophene are catalytically reduced.

12. Write a note on the oxidation of naphthalene.

13. Explain the preparation and properties of pyridine.

14. With equations, explain the halogenations, nitration and sulphonation of naphthalene.

15. (i) What are the differences between Friedel-Crafts alkylation and acylation reactions?

(ii) What is nitrating mixture? How is nitronium ion produced?

(iii) How will you convert pyrrole into pyridine?

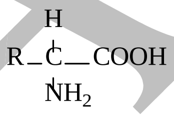
UNIT-III

SYLLABUS

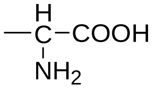
Amino acids, Proteins and Carbohydrates: Amino acids: Classification, preparation and properties. Peptides-preparation of peptides (Bergmann method only). **Proteins:** Classification, properties, biological functions and structure. **Carbohydrates:** Classification, preparation and properties of glucose and fructose- discussion of open chain and ring structures of glucose and fructose-glucose-fructose interconversion.

Amino Acids

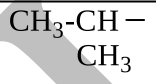
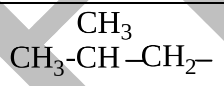
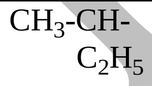
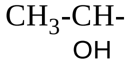
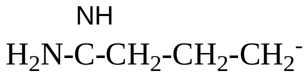
An amino acid, as the name implies, is a difunctional compound which contains both an amino and a carboxyl group. This may be regarded as a derivative of carboxylic acids in which a hydrogen atom has been replaced by an amino group. On the basis of the position of amino group with respect to the carboxyl group, these are classified as α , β and γ–amino acids. Most of the amino acids which occur as components of proteins are α-amino acids and have the general formula,

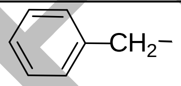
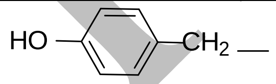
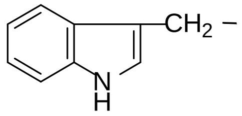
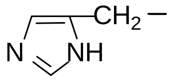


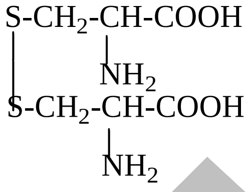
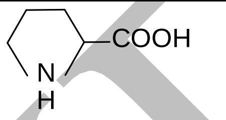
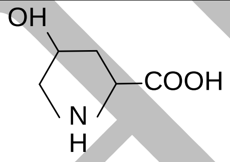
$$R-\overset{\overset{H}{|}}{\underset{\underset{NH_2}{|}}{C}}-COOH$$

The chemical classification of the amino acids is based chiefly upon the composition of the side chain or R- group. This is the feature which varies from one amino acid to another while the α- carbon, carboxyl and amino groups (i.e  $-\overset{\overset{H}{|}}{\underset{\underset{NH_2}{|}}{C}}-COOH$) are common to all.

No single means of classification can be used for all amino acids. However, the classification based on the nature of R- group is given in the table.

Amino acids		Structural formula for R-group
(A) simple or neutral amino acids		
1.	Glycine	H -
2.	Alanine	CH_3-
3.	Valine	 $CH_3\text{-}\underset{CH_3}{CH}-$
4.	Norleucine	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$
5.	Leucine	 $CH_3\text{-}\overset{CH_3}{CH}-CH_2-$
6.	Isoleucine	 $CH_3\text{-}\underset{C_2H_5}{CH}\text{-}$
(B) Hydroxy amino acids		
7.	Serine	$HO\text{-}CH_2\text{-}$
8.	Threonine	 $CH_3\text{-}\underset{OH}{CH}\text{-}$
(C) Basic amino acids		
9.	Lysine	$H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$
10.	Arginine	 $H_2N\text{-}\overset{NH}{C}\text{-}CH_2\text{-}CH_2\text{-}CH_2^-$

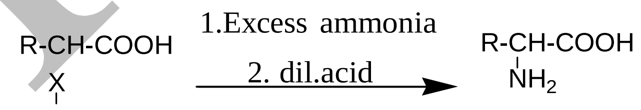
(d) Acidic amino acids		
11.	Aspartic acid	HOOC-CH_2-
12.	Glutamic acid	HOOC-CH_2-CH_2-
(E) Amide amino acids		
13.	Asparagine	H_2N-CO-CH_2-
14.	Glutamine	H_2N-CO-CH_2- CH_2-
(F) Aromatic amino acids		
15.	Phenylalanine	
16.	Tyrosine	
(g) Sulphur containing amino acids		
17.	Cysteine	HS-CH_2-
18.	Methionine	CH_3-S-CH_2-CH_2-
(H) Heterocyclic amino acids		
19.	Tryptophan	
20.	Histidine	

The amino acids which do not fit into the above classifications are given below:		
21.	Cystine	 $\begin{array}{l} S\text{-}CH_2\text{-}CH\text{-}COOH \\ \quad\quad\quad\quad NH_2 \\ S\text{-}CH_2\text{-}CH\text{-}COOH \\ \quad\quad\quad\quad NH_2 \end{array}$
22.	Proline	
23.	Hydroxyproline	

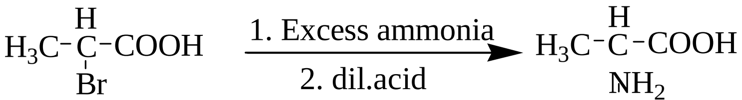
The amino acids that can be synthesized from other compounds by the tissues of the body are called *Non–essential* amino acids. The amino acids that cannot be synthesized by the body and must be supplied in the diet are called *essential* amino acids. The essential amino acids are-valine, leucine, isoleucine, phenylalanine, tryptophan, threonine, lysine, arginine, histidine and methionine.

Preparation of amino acids

A) One of the several useful syntheses of α-amino acids involves the α-halo acids in the following way.



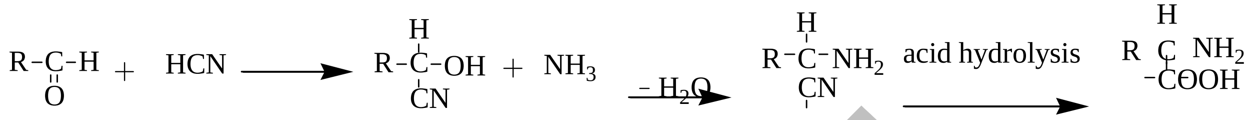
$$\underset{X}{R\text{-}CH}\text{-}COOH \xrightarrow[\text{2. dil.acid}]{\text{1.Excess ammonia}} \underset{NH_2}{R\text{-}CH}\text{-}COOH$$



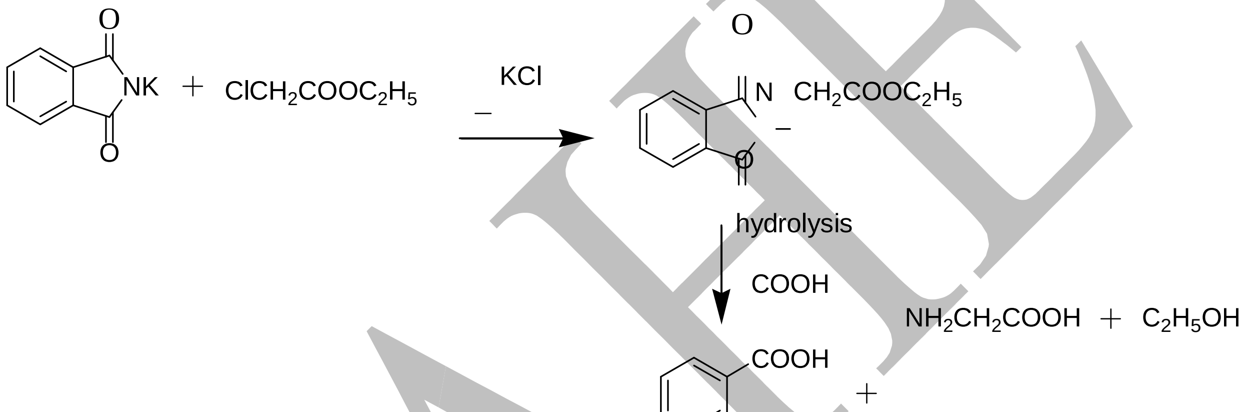
$$H_3C\text{-}\overset{H}{\underset{Br}{C}}\text{-}COOH \xrightarrow[\text{2. dil.acid}]{\text{1. Excess ammonia}} H_3C\text{-}\overset{H}{\underset{NH_2}{C}}\text{-}COOH$$

α-bromopropionic acid **α-alanine**

B) The *Strecker synthesis* of α-amino acids involves the reaction of a carbonyl compound with a mixture of ammonium chloride and sodium cyanide. These inorganic reagents react to form ammonia and hydrogen cyanide the active ingredients in this process.



C) In *Gabriel synthesis*, an ester of α-halo acid is treated with potassium phthalimide to form the corresponding substituted phthalimide which on hydrolysis yields an amino acid.



D) When hydrolyzed by strong inorganic acids or by enzymes proteins yield a mixture of α-amino acids which can be separated more conveniently into individual amino acids either by *chromatography* or by *electrophoresis*.

Properties of amino acids

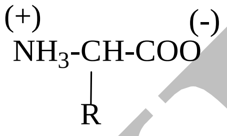
1) Some of the physical properties of amino acids differ noticeably from other organic compounds.

   For example, amino acids melt at relatively high temperatures. Decomposition usually accompanies the melting.

2) The majority of the amino acids are more soluble in water than in typical organic solvents.

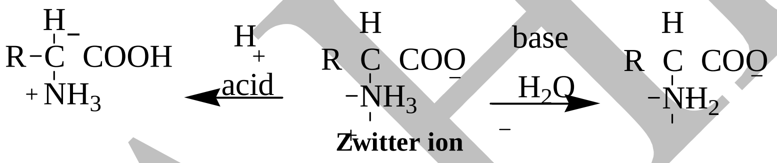
3) When measured in aqueous solutions, the dipole moment of amino acids is found to have a large value.

To account for this large value, it has been suggested that amino acids exist in solution as an *inner salt*. This is readily explained by assuming an internal neutralisation achieved by the shift of a proton from the carboxyl to the amino group.



$$\overset{(+)}{NH_3}\text{-}\underset{\overset{|}{R}}{CH}\text{-}\overset{(-)}{COO}$$

This is known, in addition to an inner salt, as a *zwitter ion*, *ampholyte* or a *dipolar ion*. Amino acids, in this form are amphoteric i.e., they react with both acids and bases:



4) Thus, in acidic solution amino acids exist as positive ions while in basic solutions they exist as negative ions. In acidic solution, an amino acid migrates towards the cathode and in basic solution it migrates towards the anode. At certain pH, the amino acid molecule would not migrate to either electrode and exists as a neutral, dipolar ion.

This pH is called the *isoelectric point* of that amino acid. Neutral amino acids have isoelectric points from pH 5.5 to 6.3. Acidic amino acids have them around pH 3 whereas basic amino acids have them around pH 10.

Though the following reactions are typical of all α-amino acids, many reactions are illustrated taking glycine as example.

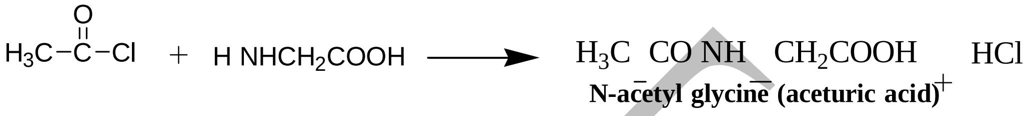
Reactions characteristic of the amino group

1) Amino acids react with strong acids to give the corresponding salts.

$$H_2N\text{-}CH_2\text{-}COOH + HCl \longrightarrow \overset{-}{Cl}\ H_3\overset{-}{N}\text{-}CH_2\text{-}COOH$$

Glycine hydrochloride

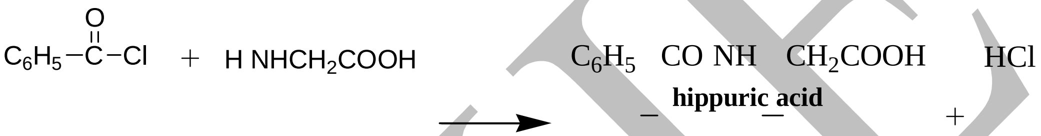
2) The amino group of amino acids can be acylated with acetyl chloride or acetic anhydride to form *N*- acylamino acids.



$$H_3C-\overset{O}{\overset{\|}{C}}-Cl + H\ NHCH_2COOH \longrightarrow H_3C\ \ CO\ NH\ \ CH_2COOH\ \ \ HCl$$

N-acetyl glycine (aceturic acid)

Similarly, with benzoyl chloride, glycine forms benzoyl glycine, *hippuric acid.*



$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + H\ NHCH_2COOH \longrightarrow C_6H_5\ \ CO\ NH\ \ CH_2COOH\ \ \ HCl$$

hippuric acid

3) Like primary aliphatic amines, amino acids react with nitrous acid to form hydroxyl acids.

$$NH_2\text{-}CH_2COOH\ \ + \ \ HONO \longrightarrow HO\text{-}CH_2\text{-}COOH\ \ N_2 + H_2O$$

Glycollic acid

4) Amino acids react with nitrosyl chloride (or bromide) to form halo acids.

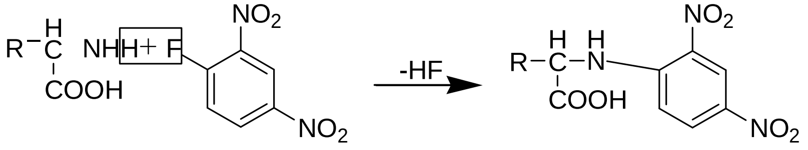
$$H_2NCH_2COOH\ \ NOCl \qquad Cl\text{-}CH_2COOH + N_2 \ \ H_2O$$

Chloroacetic acid

5) Amino acids react with formaldehyde to yield N-methyleneamino acids.

$$HCHO\ \ H_2NCH_2\ COOH \longrightarrow H_2C=NCH_2\ COOH + H_2O$$

6) Amino acids react with *Sanger's reagent* (2,4-dinitrofluorobenzene) to produce yellow coloured dinitrophenyl (DNP) amino acids (I)



(I)

Reactions characteristics of the carboxyl group

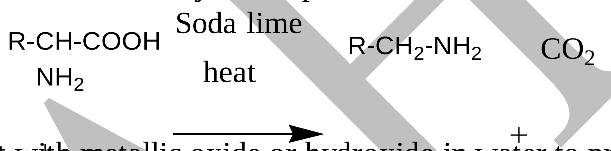
1) Amino acids react with alkalies to form salts.

$$H_2N\text{-}CH_2\text{-}COOH + NaOH \longrightarrow \underset{\textbf{sodium amino acetate}}{H_2N\text{-}CH_2\text{-}COONa} + H_2O$$

2) Amino acids may be esterified by an alcohol in the presence of an inorganic acid.

$$H_2N\text{-}CH_2\text{-}COOH + C_2H_5OH \xrightarrow{HCl} Cl^- \; H_3N^+\text{-}CH_2\text{-}COOC_2H_5 + H_2O$$

3) When heated with soda lime, they decompose into amine.



$$\underset{NH_2}{R\text{-}CH\text{-}COOH} \xrightarrow[\text{heat}]{\text{Soda lime}} R\text{-}CH_2\text{-}NH_2 + CO_2$$

4) Amino acids react with metallic oxide or hydroxide in water to produce complex salts.

$$2\,H_2N\text{-}CH_2\text{-}COOH + Cu^{2+} \xrightarrow{\Delta} \underset{\textbf{Cupric glycinate}}{Cu\,(OOC\text{-}CH_2\text{-}NH_2)_2} + 2H^+$$

5) Amino acids may be reduced to amino alcohols by lithium aluminum hydride ($LiAlH_4$).

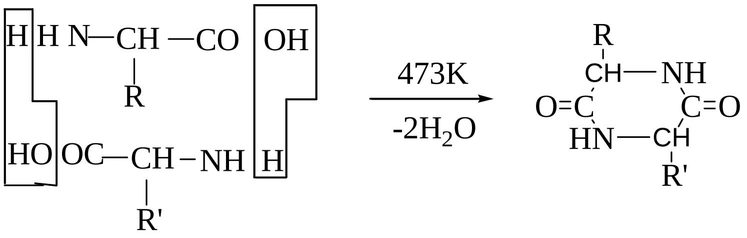
$$\underset{NH_2}{R\text{-}CH\text{-}COOH} \xrightarrow{LiAlH_4} \underset{NH_2}{R\text{-}CH\text{-}CH_2OH}$$

amino alcohol

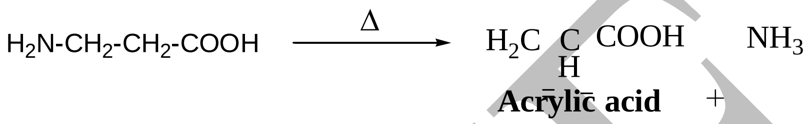
Reactions involving both the carboxyl and the amino groups

1) Action of heat on amino acids

a) α- amino acids undergo dehydration on heating to give *diketopiperazines:*



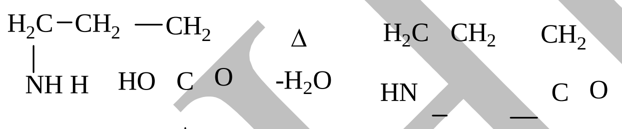
b) A β- amino acids on heating loses a molecule of ammonia to form an unsaturated acid. For example, β- amino propionic acid on heating forms acrylic acid.



$$H_2N\text{-}CH_2\text{-}CH_2\text{-}COOH \xrightarrow{\Delta} H_2C\;\underset{H}{C}\;COOH \quad + \quad NH_3$$

Acrylic acid

c) γ- amino acids on heating eliminate water and form inner amides or lactams which are cyclic:

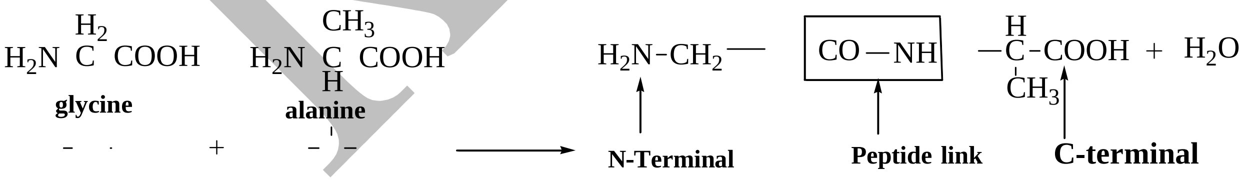


2) All α-amino acids react with ninhydrin to produce the same purple colour.

3) All α-amino acids (except glycine) are optically active.

Peptides

Peptides are condensation products of amino acids. Structurally they occupy an intermediate position between the relatively simple α-amino acids and the considerably more complex proteins. If two amino acids condense between the carboxyl group of one amino acid and the amino radical of the other, a substituted amide of a particular type, commonly referred to a *peptide* is formed.



Thus, a *dipeptide* is formed from two amino acids. A three amino acids peptide is called *"tripeptide"* and so on. Compounds in which a large number of amino acids are linked to each other through peptide bonds are known as *"polypeptides"*. Proteins are polypeptides having very high molecular weight which ranges from about 10000 to many millions.

To form the name of a peptide, give the names of the constituent amino acids in the order they appear in the molecule. The endings of all (except the amino acid with the free terminal carboxyl group) are changed from "ine" to yl". In this way, the above peptide is named as *"Glycylalanine"*.

Synthesis of polypeptide

There are many methods available to prepare peptides. Few of them are listed below:

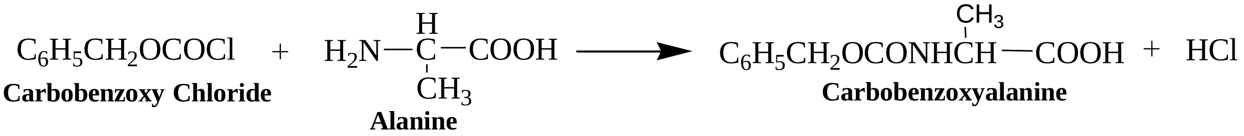
(i) Azide synthesis
(ii) Carbobenzoxy method
(iii) Chloroacid chloride synthesis
(iv) Diketopiperazine method
(v) Ester condensation
(vi) Mixed anhydride synthesis
(vii) Phthalyl synthesis
(viii) Pyrophosphite synthesis.

All the methods generally consist of the following three steps -

(i) Protection of amino group in the amino acid
(ii) Formation of peptide linkage
(iii) Removal of the protecting group.

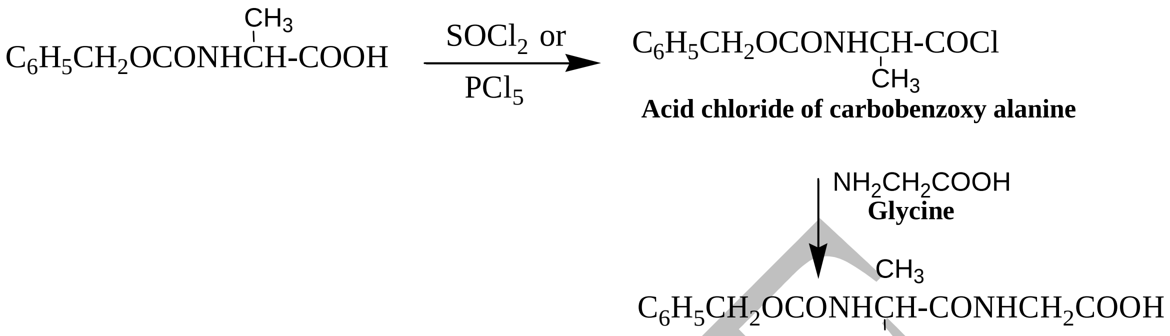
In this section, two methods to synthesis a simple dipeptide are given in detail:

Carbobenzoxy method (Bergmann method)
First step



$$C_6H_5CH_2OCOCl + H_2N-\overset{H}{\underset{CH_3}{C}}-COOH \longrightarrow C_6H_5CH_2OCONH\overset{CH_3}{C}H-COOH + HCl$$

Second Step



$$C_6H_5CH_2OCONH\overset{CH_3}{C}H\text{-}COOH \xrightarrow[PCl_5]{SOCl_2\ \text{or}} C_6H_5CH_2OCONH\underset{CH_3}{C}H\text{-}COCl$$

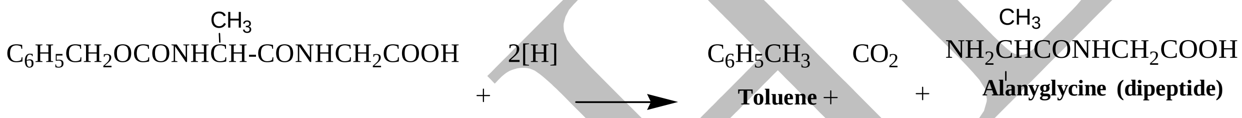
Acid chloride of carbobenzoxy alanine

$$\xrightarrow{NH_2CH_2COOH} C_6H_5CH_2OCONH\overset{CH_3}{C}H\text{-}CONHCH_2COOH$$

Glycine

Carobenzoxy alanylglycine

Third Step



$$C_6H_5CH_2OCONH\overset{CH_3}{C}H\text{-}CONHCH_2COOH + 2[H] \longrightarrow C_6H_5CH_3 + CO_2 + NH_2\overset{CH_3}{C}HCONHCH_2COOH$$

Toluene **Alanyglycine (dipeptide)**

The above sequence can be extended to the synthesis of tri, tetra and polypeptides.

The protecting group, carbobenzoxy chloride, is prepared from benzyl alcohol and phosgene as below:

$$C_6H_5CH_2OH + ClCOCl \xrightarrow{Heat} C_6H_5CH_2OCOCl + HCl$$

Diketopiperazine method

Dipeptides may be prepared by the careful hydrolysis diketopiperazines:

. **Proteins**

As pointed out earlier, proteins are polymers of amino acids. More specific structural studies have shown them to possess certain unique properties because of their giant size. The classifications of proteins are given below:

Simple Proteins

Proteins which yield only amino acids or their derivatives on hydrolysis are called simple proteins. The *further classification based on their solubility* in various solvents is given below:

a) **Albumins:** Soluble in pure water and coagulable by heat.

Example: serum albumin, egg albumin

b) **Globulins:** Insoluble in pure water, but soluble in NaCl solutions.

Example: serum albumin, (in blood), tuberin (in potato) arachin and conarchin (in peanuts)

c) **Glutelins:** Insoluble in all neutral solvents, but soluble in very dilute alkalies. The best known protein of this group is the glutelin of wheat.

d) **Prolamins:** Soluble in 70% alcohol.

Example: Gliadin (in wheat) and zein (in maize).

e) **Histones:** Soluble in water and insoluble in very dilute ammonia. On hydrolysis, they yield several amino acids among which the basic ones predominate. The important members of this group are the *thymus histones* and the globins of *haemoglobin*.

f) **Protamins:** Strongly basic proteins with low molecular weight are soluble in water, not coagulable by heat and on hydrolysis yield large amounts of basic amino acids.

Example: Salmine from *salmine sperm.*

Conjugated Proteins

Hydrolysis of conjugated proteins yield α-amino acids and a non protein material. The non-protein material is known as *prosthetic group*. On the basis of the prosthetic group present in the protein, they are classified in the following manner:

S.No.	Conjugated protein	Prosthetic group	Example
1.	Nucleoproteins	Nucleic acid	Yeast, Chromosomes
2.	Glycoproteins	Carbohydrate	Mucin, Egg white
3.	Phosphoproteins	Phosphorus	Caseinogen, Ovovitelin
4.	Haemoproteins	Haem	Haemoglobin, Myoglobin
5.	Lipoprotein	Lipids	Lipovitelins in eggs
6.	Chromoproteins	Fe, Mg, Cu	Haemoglobin, Chlorophyll, Cyanocuprin

Classification based on the shape of the molecule

1) **Globular proteins:** These proteins have relatively spherical shape. They are relatively soluble.

2) **Fibrous proteins:** Sclero proteins are chiefly fibrous proteins. These proteins resemble long ribbons or fibers in nature. These tend to be insoluble. They are found usually as components of the tougher types of tissues such as *keratins* of skin, hair and feathers. The collagens of tendons, elastins of ligaments and silk fibroin belong to this class. They are insoluble in water and other common solvents.

Characteristics of proteins

Proteins are complex nitrogenous compounds .They are very important to body growth and are of “prime importance” (Greek, *proteins means prime importance*). They have very high molecular weights. They are actually considered as polypeptides with molecular weight above 10,000. Proteins are colloidal in nature.

Proteins are amphoteric because their molecules contain both acid and basic groups. Depending on the pH of the medium they can exist as cations or anions and in an electric field they move either to the cathode or anode (*electrophoresis*). At a particular pH, which is characteristic for each protein, the positive and negative charges are balanced exactly and the protein molecule carriers no net charge. This is called the *isoelectric point* of the protein and at this point the protein molecule will not migrate in an electric field. At this pH, the protein, molecule is easily precipitated.

All proteins are optically active (*laevorotatory*)

Proteins may be coagulated i.e., precipitated irreversibly. This irreversible precipitation of protein is called *denaturation*. This can be brought about by heat, strong acids or bases or various other agents. As a result of denaturation, the proteins undergo changes physically and chemically. Solubility, molecular shape and size, biological activity of the protein may change. The optical rotation of many proteins changes as a result of denaturation. Denaturation involves changes in the secondary structure of the protein.

Proteins on hydrolysis yield amino acids. This hydrolysis may be brought about by acids, alkalies or enzymes. Enzymic hydrolysis takes very long time.

Proteins exhibit a number of colour reactions.

For example -

1) **Biuret test:** When a very dilute solution of copper sulphate is added to alkaline solution of a protein, a red or violet colour is obtained

2) **Million's test:** Mercuric nitrate in nitric acid containing traces of nitrous acid is called *Millon's reagent*. When this reagent is added to a protein solution, a white precipitate is formed and this slowly turns pink.

3) **Xanthoproteic test:** When treated with concentrated nitric acid, proteins produce a yellow colour.

4) **Ninhydrin Test:** When the protein in pyridine is treated with ninhydrin, a deep blue to violet, pink or even red colour is produced.

Biological Functions of Proteins

Proteins are intimately connected with almost all the chemical and physical activities that constitute life. In fact, there is hardly an important physiological function in which proteins do not participate.

Some proteins called *enzyme* serve as catalysts to speed up the variety of chemical transformations which living cells are able to accomplish.

Other proteins function as *hormones* whose principle activity is to control processes which occur in living things. The growth hormone produced by the pituitary gland is an example of such hormone. Likewise, haemoglobin, a protein in the blood serves as an oxygen carrier to transport oxygen from lungs to the various tissues. Still another protein, *actomyosin* participates in muscular contraction. The much familiar hormone *insulin* produced in the pancreas controls sugar metabolism in the body.

Nucleoproteins, typical conjugated proteins composed of substances called nucleic acids and simple proteins, are the main constituents of genes, the carriers of *heredity*.

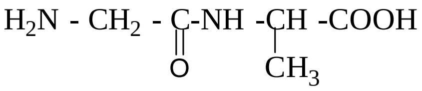
Antibodies, which are proteins, function to protect human beings against diseases

Less spectacular are the proteins such as hair and finger nails which serve as important *structural elements* of the body.

Structure of Proteins

Primary structure

The main mode of linkage of the amino acids in proteins is the peptide bond formed by the reaction of the carboxyl group of one amino acid with the amino group of another as indicated in glycylalanine (gly-ala) below:



$$H_2N-CH_2-\underset{\overset{\|}{O}}{C}-NH-\underset{\overset{|}{CH_3}}{CH}-COOH$$

The primary structure of proteins deals with the actual arrangement or sequence of various amino acids held together by peptide linkages in protein. If a peptide linkage is formed by two amino acids, there are two possible sequences:

Example:

(a) The two amino acids, glycine and alanine, give two (2! =1×2 = 2) possible sequences in the following way:

1) Glycylalanine (gly-ala) 2) Alanylglycine (ala-gly)

(b) If three amino acids (say, glycine, alanine and leucine) form peptide linkage, there are six (3! = 1×2×3 = 6) possible sequences as:

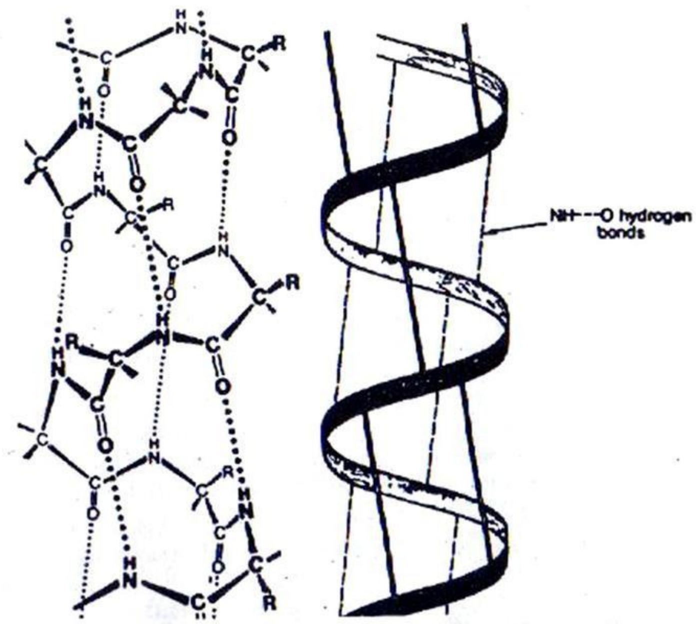
1) Ala-gly-leu 2) Ala-leu-gly 3) Gly- ala-leu

4) Gly-leu-ala 5) Leu-ala-gly 6) Leu- gly-ala

(c) Similarly, if there are “n” amino acids in a protein, they give rise to “n!” (n! = 1×2×3×4………… n) sequences.

Secondary Structure:

As discussed above, the primary structure deals with the actual arrangements of amino acids in protein. It fails to throw light on the shape configuration and conformation of the molecule.



The secondary structure of a protein deals with the shape in which the long amino acid chain exists, the way in which the proteins chain is folded and the nature of the bonds which establishes this structure.

The proteins, especially globular proteins, indicate a coiled structure in which peptide bonds are folded in a regular manner. Much of the folding is the result of linking of the carboxyl and amide groups of the peptide chain by means of hydrogen bonds. Such foldings produced or maintained by hydrogen bonding is often called the secondary structure of the proteins. Present evidences suggest that in many proteins the hydrogen bonding produces a regular coiled arrangement called *α–helix*. This secondary structure has been confirmed by X- ray studies and is shown in the figure.

Tertiary structure

The tertiary structure deals with the way which the polypeptide chains fold up into various shapes i.e., globular or ellipsoidal. This folding involves the hydrogen bonding, ionic and disulphide bonds. The tertiary structure is determined by temperature and pH.

Carbohydrates

Introduction

The term “carbohydrates’’ is used to identify a rather diverse group of materials found in nature. They are known to have important functions as constituents of both plants and animals. Carbohydrates provide a structural frame work for plants and serve as a source of energy for both plants and animals. Many industries nowadays depend on carbohydrates.

Carbohydrates, as the name implies, are composed mainly of carbon, hydrogen and oxygen, although other elements have been found in few compounds. For example *chitin*, *glucosamine* contain nitrogen. Although many of the simpler compounds have the empirical formula CH_2O as that of carbohydrates, are polyfunctional compounds. They have two kinds of functional groups- the alcoholic (hydroxyl) group and the carbonyl group. Thus, they are *polyhydroxy ketones or aldehydes.*

Classification

The behavior of carbohydrates materials towards acid hydrolysis provides the basis for an initial separation into groups.

1)The simplest of these which do not hydrolysis into smaller unit are known as “*monosaccharides’’*.
Examples: Glucose, fructose, mannose and galactose.

2) Compounds which undergo hydrolysis to liberate two or more, but fewer than eleven monosaccharide molecules are designed as *“oligosaccharides’’*

3) If the oligosaccharide, upon hydrolysis yields two monosaccharide units, then it is termed as *disaccharide* (with molecular formula, $C_{12}H_{22}O_{11}$).
Examples: Maltose and lactose.

4) If more than ten molecules of monosaccharides result during hydrolysis, the compound is referred to as a *polysaccharide.*
Examples: Starch and cellulose.

5) Generally the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet to taste. They are known as *sugars.*
6) Polysaccharides are non-sugars which are amorphous, tasteless and insoluble in water.
7) The carbohydrates may further be classified as either *reducing* or *non-reducing* sugar. All those carbohydrates which reduce *Fehling's solution* and *Tollen's reagent* are reducing sugars while others are non-reducing sugar. All monosaccharides and disaccharides (expect sucrose) are reducing sugar.
8) Then term *tetrose*, *pentose* and *hexose* are used to indicate those carbohydrates having four, five and six carbon atoms respectively.
   Example: Glucose has six carbon atoms and is a hexose.
9) If the monosaccharide posseses an aldehyde group, it is an *aldose* and that with a keto group, is a *ketose*.
10) The number of carbon atoms in conjugation with the type of carbonyl group in a sugar is indicated as *aldopentose* and *ketohexose.* The glucose, mannose and galactose are aldohexoses and fructose is a ketohexose.

Glucose

Glucose, *dextrose* (grape sugar) is the central carbohydrate of living organisms of all types, the major source of energy. It is widely distributed in nature as the monosaccharides in ripe grapes. Honey, sweet fruit and as a component of disaccharides-lactose, maltose, sucrose and cellobiose. It is the building unit from which the polysaccharides like starch, cellulose and glycogen are formed. It is also normal constituent of blood and occurs in urine of diabetics.

1) Commercially pure D(+) glucose is manufactured by heating starch with dilute hydrochloric acid under pressure:

$$(C_6H_{10}O_5)_n + n\ H_2O \xrightarrow{\text{dil.HCl}} n\ C_6H_{12}O_6$$

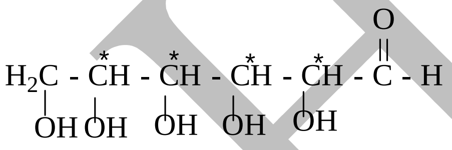
2) It is formed as an intermediate product in the fermentation of starch for the manufacture of ethyl alcohol.

3) Glucose is made by the hydrolysis of sucrose by boiling with dilute hydrochloric acid in alcoholic solution. Glucose and fructose are obtained in equal amounts. On cooling the resulting solution, glucose being less soluble than fructose, separates out.

$$\underset{\textbf{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{dil.HCl} \underset{\textbf{glucose}}{C_6H_{12}O_6} + \underset{\textbf{fructose}}{C_6H_{12}O_6}$$

Properties

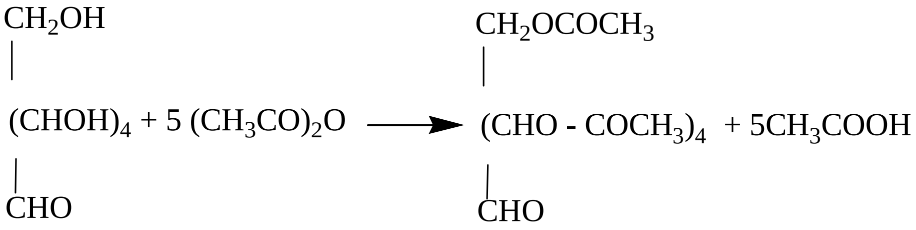
Glucose is a white crystalline solid (m.p 419 K), sweet to taste. It is readily soluble in water. Naturally occurring glucose is *dextro-rotatory* (hence, the name Dextrose) and it has four asymmetric carbon atom (marked by *).



$$\underset{OH}{\underset{|}{H_2C}} - \underset{OH}{\underset{|}{\overset{*}{C}H}} - \underset{OH}{\underset{|}{\overset{*}{C}H}} - \underset{OH}{\underset{|}{\overset{*}{C}H}} - \underset{OH}{\underset{|}{\overset{*}{C}H}} - \overset{O}{\overset{||}{C}} - H$$

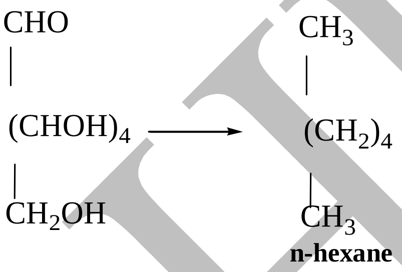
Structural formula of glucose indicates the presence of one aldehydic group, one primary alcoholic group and four secondary alcoholic groups. Chemical properties of glucose are, therefore, the properties of the above functional groups. The structural elucidation very easily follows from its reactions:

1) Quantitative analysis establishes the empirical formula as CH_2O.
2) The molecular weight of glucose determined from a study of the depression of freezing point of glucose solution, shows a value of 180. When this is compared with the empirical formula weight, the conclusion reached is that the molecular formula is $(CH_2O)_6$ or $C_6H_{12}O_6$.
3) The presence of the five alcoholic groups is indicated by its reaction with 5 moles of acetyl chloride or acetic anhydride.



$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CHO \end{array} + 5\,(CH_3CO)_2O \longrightarrow \begin{array}{c} CH_2OCOCH_3 \\ | \\ (CHO-COCH_3)_4 \\ | \\ CHO \end{array} + 5CH_3COOH$$

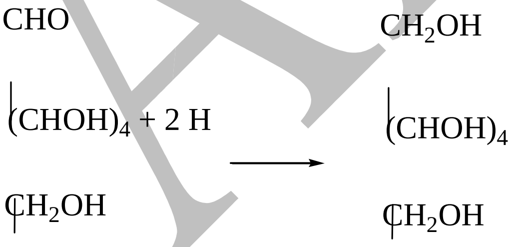
4) Reduction of glucose with concentrated hydriodic acid and red phosphorus at 373 K yields 2-iodohexane. Prolonged heating produces n-hexane. This would mean that glucose is a straight chain compound of six carbon atoms.



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ (CH_2)_4 \\ | \\ CH_3 \end{array}$$

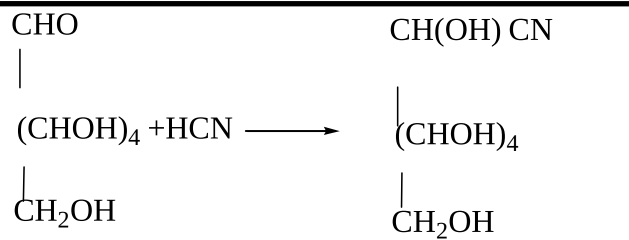
n-hexane

5) The nature of the carbonyl group is indicated by its reaction with mild reducing agent. When reduced with sodium amalgam in aqueous solution, the aldehyde group is reduced to a primary alcoholic group to yield a hexahydric alcohol, called sorbitol.



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 2\,H \longrightarrow \begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

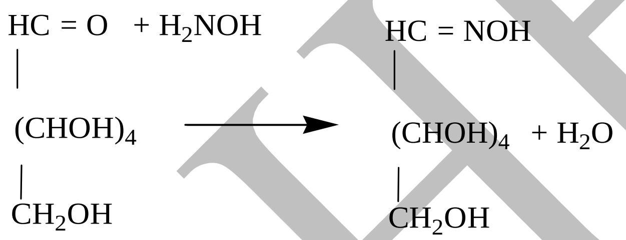
6) Glucose gives addition product with hydrogen cyanide *(but not with ammonia or sodium bisulphite)*. This reaction indicates the presence of a carbonyl group.



$$\begin{array}{l} \mathrm{CHO} \\ | \\ \mathrm{(CHOH)_4} + \mathrm{HCN} \\ | \\ \mathrm{CH_2OH} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH(OH)\,CN} \\ | \\ \mathrm{(CHOH)_4} \\ | \\ \mathrm{CH_2OH} \end{array}$$

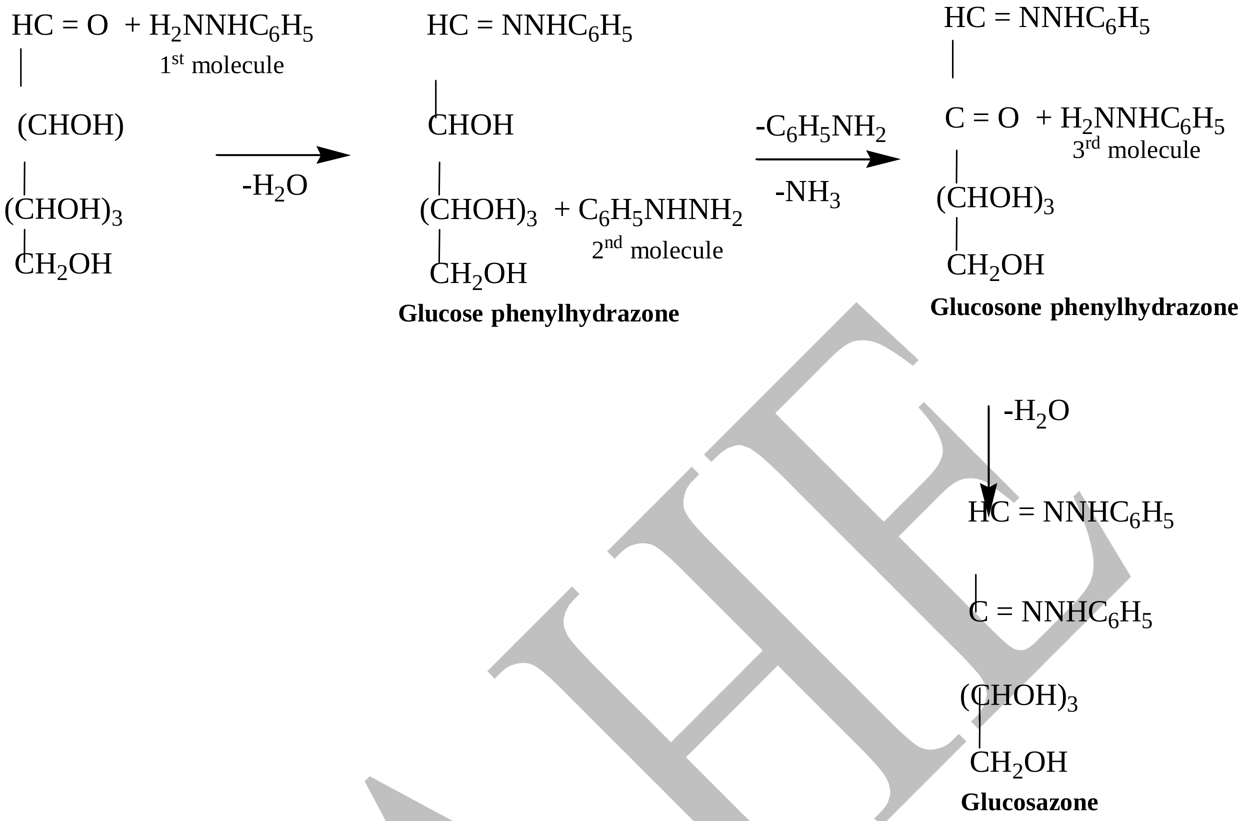
glucose cyanohydrin

7) Glucose condenses with hydroxylamine to yield the oxime with the elimination of a water molecule.

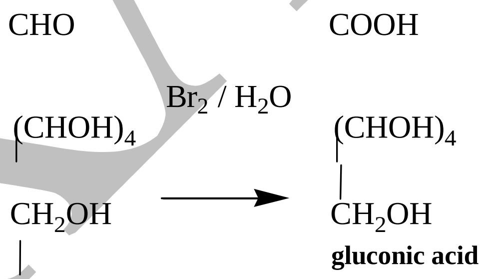


$$\begin{array}{l} \mathrm{HC = O} \;\; + \mathrm{H_2NOH} \\ | \\ \mathrm{(CHOH)_4} \\ | \\ \mathrm{CH_2OH} \end{array} \longrightarrow \begin{array}{l} \mathrm{HC = NOH} \\ | \\ \mathrm{(CHOH)_4} \;\; + \mathrm{H_2O} \\ | \\ \mathrm{CH_2OH} \end{array}$$

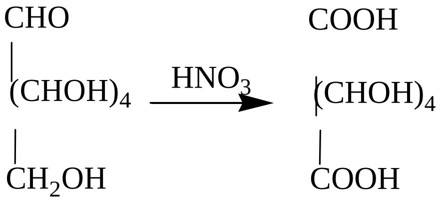
8) Glucose reacts with one molecule of phenylhydrazine in acetic acid which condenses with the aldehyde group to give *phenylhydrazone*. When warmed with excess phenylhydrazine, the secondary alcoholic group, adjacent to the aldehyde group, is next oxidised to a keto group. With this keto group, third molecule of phenylhydrazine condenses to yield *glucosazone:*



9) With mild oxidising agents like bromine water, glucose is oxidised to gluconic acid, an acid with the same number of carbon atoms. In this reaction, the aldehyde group alone gets oxidised.



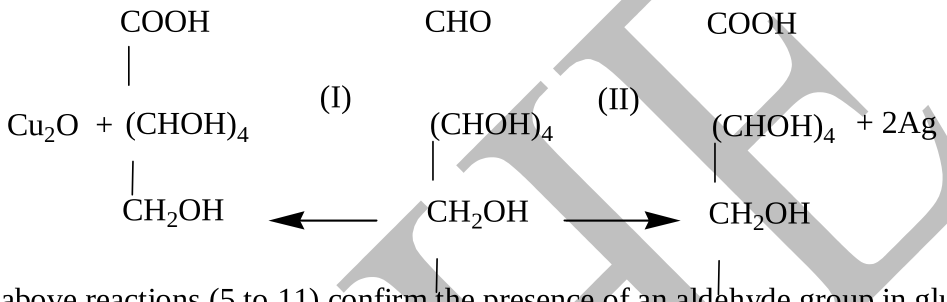
10) With strong oxidising agents like nitric acid, it is oxidised to a dicarboxylic acid, saccharic acid. Nitric acid is able to oxidise the primary alcohol group also to an acid group.



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HNO_3} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}$$

saccharic acid or glucaric acid

11) Because glucose is readily oxidised, it acts as a strong reducing agent. It reduces both Fehling's solution (I) and Tollen's reagent [ammoniacal silver nitrate, (II)]



$$Cu_2O + \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xleftarrow{(I)} \begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{(II)} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 2Ag$$

The above reactions (5 to 11) confirm the presence of an aldehyde group in glucose.

Other Reactions of Glucose

12) Glucose on fermentation yields ethyl alcohol.

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2\,CO_2 + 2C_2H_5OH$$

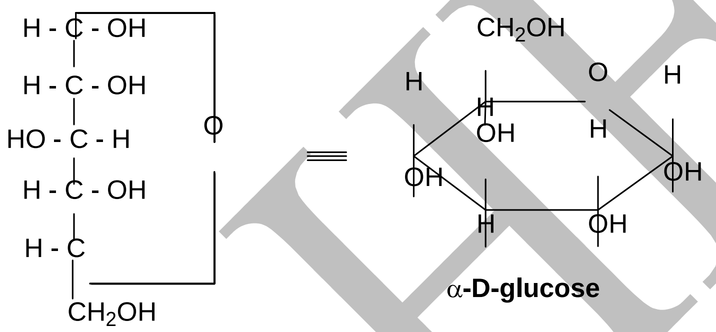
13) A dilute solution of glucose when warmed with dilute alkali solution, gives a mixture of glucose, fructose and mannose.

14) When heated with concentrated hydrochloric acid, it gives laevulic acid and hydroxymethyl furfural.

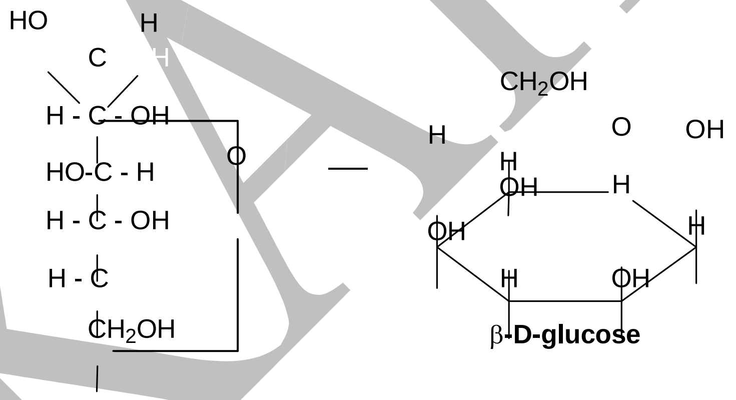
All the above reactions of glucose indicate that glucose is a polyhydric alcohol with a terminal aldehyde group and that it is a straight chain compound.

As mentioned earlier, glucose does not react with ammonia or sodium bisulphite. Further, it exists in two isomeric forms, α- and β–glucose. The evidence for these forms is *muta rotation.*

α–glucose with specific rotation +110° is obtained by crystallizing glucose from alcoholic or acetic acid solution whereas *β* – glucose with specific rotation +19.7° is obtained by crystallizing glucose from pyridine solution. An aqueous solution of glucose shows muta roration *(meaning, a change of rotation)* i.e., its specific rotation gradually falls from +110° to +52.5° in the case of *α* – glucose and increases from +19.7° to +52.5° in the case of *β* – glucose. To account for these facts satisfactorily, Tollen suggested a ring formula with no free aldehyde group. The ring structure for glucose is best representing by a hexagonal formula base on *pyran*.



α-D-glucose



β-D-glucose

Uses

1) It is used as a sweetening agent in confectionery.
2) It is utilised in the manufacture of ascorbic acid (Vitamin C).
3) It serves as food for invalids and as food preservatives.

Fructose

D (-) Fructose, (Laevulose or Fruit Sugar) $C_6H_{12}O_6$

The only important ketohexose is D (-) fructose, m.p. 368 K. In the course of its degradation in cells and tissues, glucose is converted into fructose derivatives.

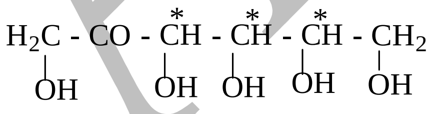
Preparation

1) Fructose is prepared in the laboratory by the hydrolysis of sucrose by boiling with dilute acids. It is formed along with glucose.
2) Fructose is obtained commercially by the hydrolysis of *inulin* with oxalic acid or dilutes sulphuric acid.

$$\underset{\textbf{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{dil.H_2SO_4} n\ C_6H_{12}O_6$$

Properties

Fructose is a white crystalline solid. It is the sweetest of all sugars. It is readily soluble in water. It is laevorotatory and therefore called *laevulose*. Structural formula of fructose indicates



$$\underset{OH}{H_2C} - CO - \underset{OH}{\overset{*}{CH}} - \underset{OH}{\overset{*}{CH}} - \underset{OH}{\overset{*}{CH}} - \underset{OH}{CH_2}$$

The presence of a keto group, two primary and three secondary (* marked, asymmetric carbons) alcoholic groups. The structure of fructose has been derived from a consideration of facts and conclusion such as the following:

1) Elemental analysis and molecular weight determination show that the molecular formula of fructose is $C_6H_{12}O_6$.
2) Complete reduction of fructose with HI and red phosphorus give n-hexane as the major products, suggesting a straight chain formula.

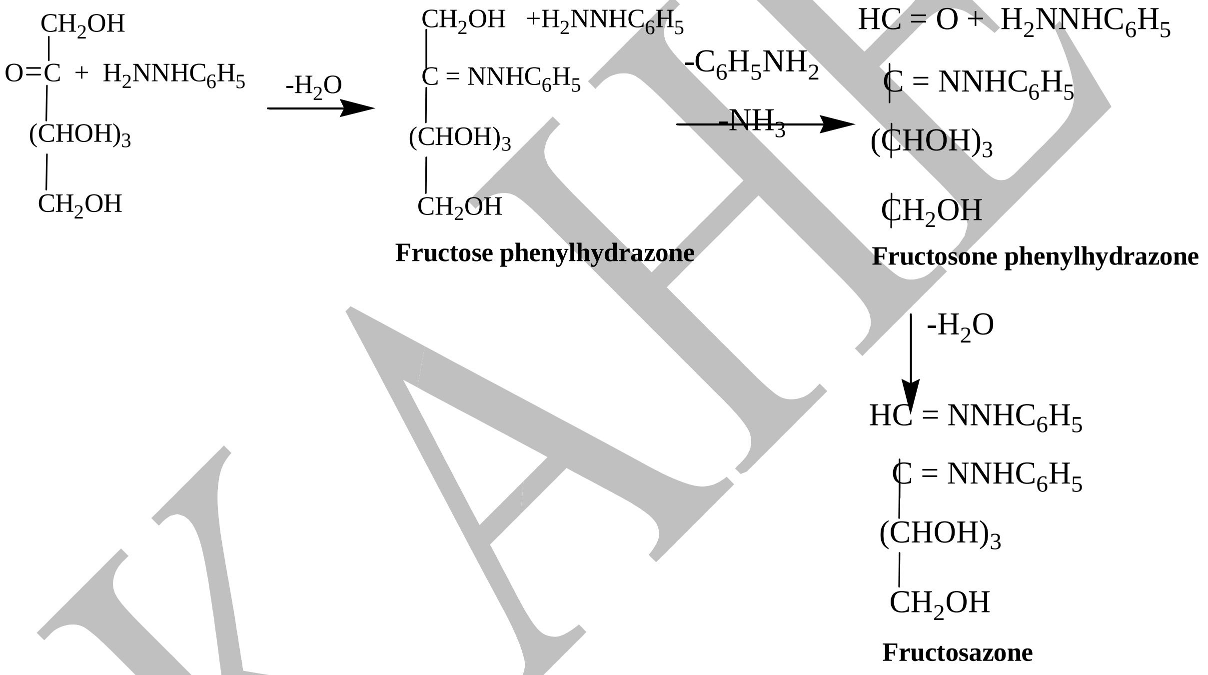
3) Fructose reacts with 5 moles of acetyl chloride or acetic anhydride to form a penta-acetate. This indicates the presence of five hydroxyl group in a fructose molecule. Since fructose is a stable compound, the five hydroxyl groups must be present on separate carbon atoms.

4) (a) Fructose reacts with hydroxylamine to form an oxime.

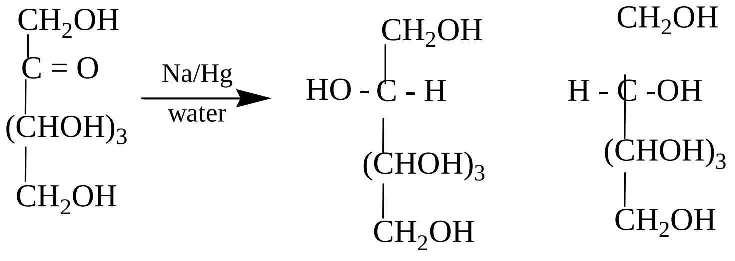
(b) It adds with only one mole of HCN to give a cyanohydrin.

These reactions indicate the presence of a carbonyl group.

5) Fructose condenses with phenylhydrazine and yields fructosazone similar to glucose. Here again the reaction proceeds in stages:

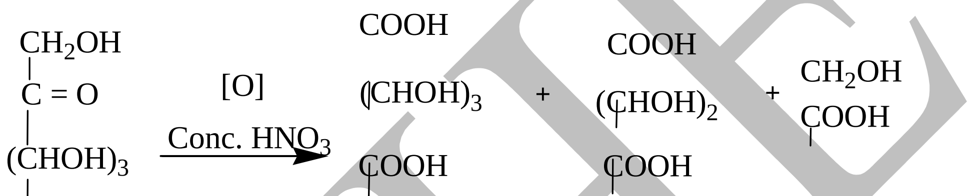


6) Reduction of fructose with sodium amalgam and water produces a mixture of two epimeric alcohols, sorbitol and mannitol because a new asymmetric carbon has been created at C_2. This indicates the presence of keto group.



Mannitol **Sorbitol**

7) Fructose is not affected by mild oxidising agents. But strong oxidising agents, like nitric acid, oxidise fructose to a mixture of trihydroxy glutaric acid, tartaric acid and glycollic acid:

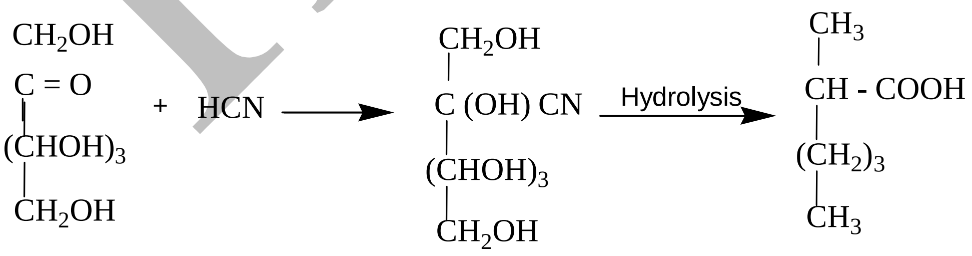


Trihydroxy glutaric acid **Tartaric acid** **Glycollic acid**

Since this oxidation occurs with the rupture of the carbon chain, the carbonyl group must be present as a keto group in fructose.

8) Fructose is a reducing sugar like glucose. Hence, it reduces both Tollen's reagent and Fehling's solution. Usually ketones do not reduce above reagents but hydroxy ketones possess reducing properties.

9) When fructose is treated with HCN it forms a cyanohydrin which upon hydrolysis and subsequent reduction gives 2-methyl-hexanoic acid. This indicates that the keto group is adjacent to one of the terminal carbon atom.



2-Methylhexanoic acid

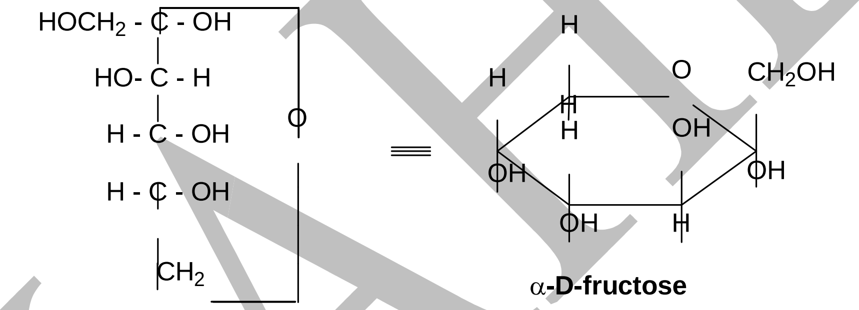
10) Fructose is fermented by yeast to ethyl alcohol.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\ CO_2 + 2C_2H_5OH$$

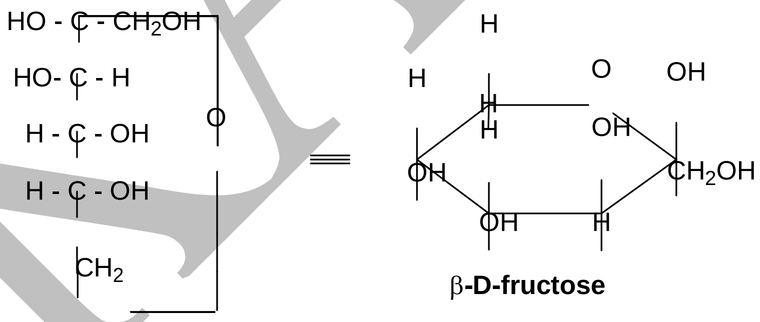
11) Fructose when warmed with dilute alkali forms a mixture of glucose, fructose and mannose like glucose.

12) When heated with conc. hydrochloric acid, fructose gives laevulic acid. They yield is better than glucose.

13) Fructose does not react with ammonia and sodium bisulphite like glucose. Moreover, it exhibits muta rotation which suggests that it exists in two isomeric forms. So, a cyclic ring formula was suggested for fructose. As in the case of glucose, the hexagonal formula based on pyran is given for fructose.

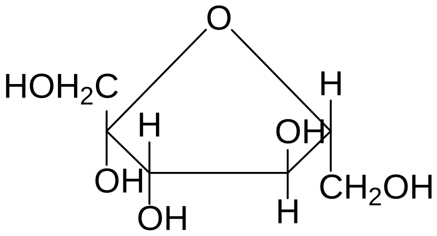


α-D-fructose



β-D-fructose

γ-fructose is also known which exists in a five membered furan ring structure:



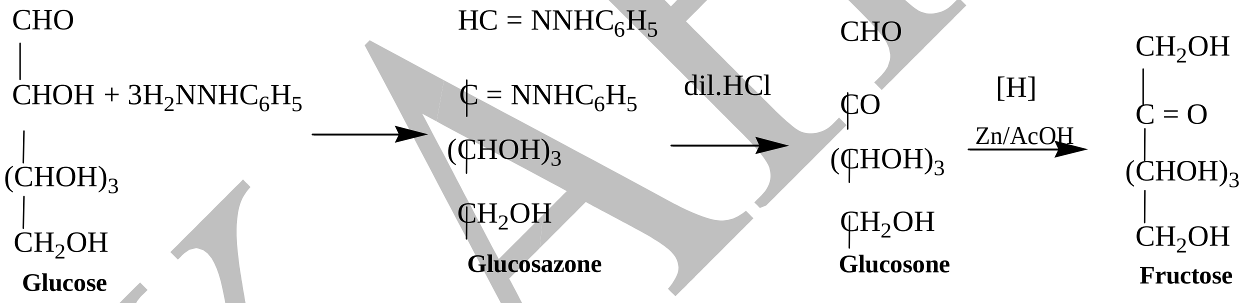
Uses

1) Fructose finds use as sweetening agent.

2)It is used by diabetic patients in the place of cane sugar.

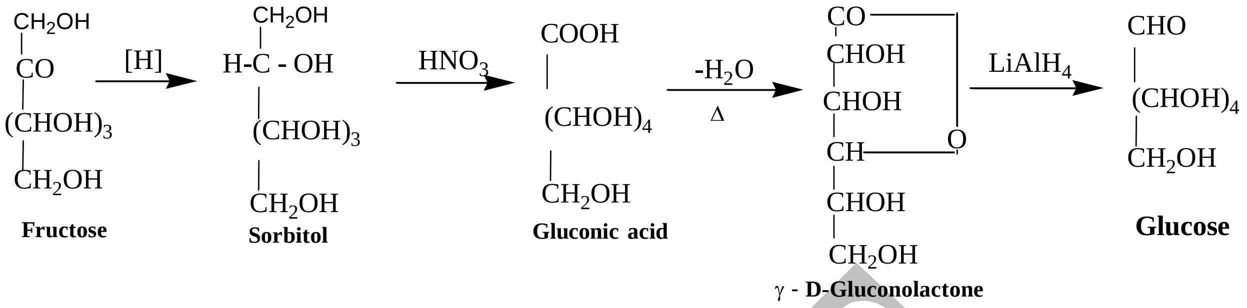
Conversion of Glucose into Fructose

Glucose is first treated with excess phenylhydrazine in acetic acid to form glucosazone which is next hydrolysed with dil. HCl to give *glucosone*. This is then reduced with zinc and glacial acetic acid to yield fructose:



Conversion of Fructose into Glucose

Fructose is first reduced with sodium amalgam to give hexitols. These are next oxidised with nitric acid to yield the corresponding mono-carboxylic acids which on treatment with dil. HCl give γ-lactones. The individual lactones are reduced with $LiAlH_4$ to obtain the corresponding aldohexoses. In this conversion, both mannose and glucose are obtained but the route for the conversion of fructose to glucose alone is give below:



Comparative study of Glucose and Fructose

S.No.	Properties	Glucose	Fructose
1.	Nature	(i) Aldohexose (ii) Dextro rotatory	(i) Ketohexose (ii) Laevo rotatory
2.	Osazone	Forms	Forms
3.	Muta rotation	Exhibits	Exhibits
4.	With HNO_3	Saccharic acid	Meso tartaric acid, glycollic acid
5.	Wit Bromine water	Gluconic acid	No reaction
6.	Fehling solution and Tollen's reagent	Reduces	Reduces
7.	With NaOH	Forms epimers	Forms epimers
8.	In Ether	Insoluble	soluble

Text Books:

1. Veeraiyan, V., & Vasudevan, A.N.S. (2012). *Text Book of Allied Chemistry* (II Edition). Chennai: Highmount Publishing House.

2. Bahl, A., & Bahl, B.S. (2015). *A Textbook of Organic Chemistry* (21st Revised Edition). New Delhi: S.Chand & Company Pvt. Ltd.

Reference Book:

1. Gopalan, R., & Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. What are essential amino acids? Give examples.
2. What is zwitter ion and isoelectric point?
3. What is the action of heat on alpha-amino acid?
4. What is meant by a peptide? Give an example with its structure.
5. How is glucose prepared?
6. Write any four examples of monosaccharides.
7. Draw the ring structure of alpha and beta-glucose.
8. How is fructose prepared?
9. Define non-essential amino acids.
10. Draw the ring structure of alpha, beta and gamma-fructose.
11. Mention the uses of fructose.
12. Explain the following terms with examples: (a) disaccharide (b) polysaccharide.
13. How many chiral centres are there in glucose? How many optical isomers are possible?
14. How is glucose established to be an aldohexose?
15. What are polypeptides? Give an example for a dipeptide and suggest a method for synthesis.

PART-C (Each Question Carry Six Marks)

1. (i) Discuss the classification of proteins.
   (ii) Write the biological functions of proteins.
2. (i) What happens when glycine is (a) treated with HCl (b) treated with NaOH
   (c) treated with nitrous acid (d) treated with formaldehyde?
   (ii) Write in detail on the characteristics of proteins.

3. (i) How are the amino acids classified? Give examples.

(ii) How will you confirm the presence of hydroxyl groups in fructose molecule?

4. (i) What happens when α–amino acid, β-amino acid and γ-amino acid are heated.

(ii) Explain Bergmann method of peptide synthesis.

5. (i) Explain (a) Strecker synthesis (b) Gabriel synthesis.

(ii) Write in detail on the classification of carbohydrates?

6. Write in detail on the structure of proteins.

7. Explain the preparation and properties of fructose.

8. How will you effect the following conversions?

i) Glucose to fructose ii) fructose to glucose.

9. (i) Explain carbobenzoxy method of peptide synthesis.

(ii) Write the preparation of carbobenzoxy chloride.

10. Explain the preparation and properties of glucose.

11. (i) How does glucose react with a) HI and P b) HCN c) NH_2OH.

(ii) What is the action of fructose with a) $C_6H_5NHNH_2$ b) Na/Hg and water c) Conc. HNO_3.

12. What are carbohydrates? How are they classified? Give examples.

13. (i) Discuss any two colour reactions of proteins.

(ii) How does an alpha amino acid reacts with a) NOCl b) CH_3COCl.

(iii) What is Sanger's reagent? Draw its structure.

ENVIRONMENTAL STUDIES

MULTIPLE CHOICE QUESTIONS

	Questions	Opt 1	Opt 2	Opt 3	Opt 4	Answer
	Unit III					
	The species rich ecosystem	Marine ecosystem	Terrestrial ecosystem	Special Ecosystem	Extra terrestrial ecosystem	Marine ecosystem
	The most fundamental level of biodiversity	Genetic diversity	Species diversity	Population	Diversity	Genetic diversity
	The lowest species diversity in the tropical areas……..	Eastern Atlantic	Eastern Pacific	Western Atlantic	Indo-Pacific Region	Eastern Atlantic
	Physically India is divided into…….	Four region	Seven region	Five region	Two region	Four region
	Some species play ecological roles that are of great importance than predicted…….	primary species	Keystone species	Climax species	Decomposers	Keystone species
	People love, live, a phenomenon called…….	Spirituality	Meditation	Peace	Biophilia	Biophilia
	Three important issues of biodiversity…………….	Commodity, Amenity, and Morality	Genus, species and population	Community, diversity and ecosystem	Flora, Fauna and Humans	Commodity, Amenity, and Morality
	Total identifies species on the earth……………	1.5 million	5-30 million	3 million	10 million	1.5 million
	Two biodiversity hotspots in India…………	Gangetic and Western Himalayas	Western Ghats and Eastern Himalayas	Peninsular and Vindhyas	J&K and Rajasthan	Western Ghats and Eastern Himalayas

	Total biodiversity hotspots in the world……………..	25	2	15	50	25
	Levels of biodiversity include all but one…………………	Genetics	Species	Population	Ecosystem	Population
	The type of diversity including all the different kinds of living things found in a certain habitat is called as…………	Species diversity	Genetic diversity	Ecosystem diversity	Population diversity	Species diversity
	A taxon with restricted geographical distribution is termed as?	Rare	Vulnerable	Extinct	Endemic	Endemic
	Conservation of biodiversity outside the natural habitat is called as……………..	Ex-situ	In-situ	Conservation	In-vivo	Ex-situ
	Which of the following does not come under the threatened categories?	Endangered	Vulnerable	Least concern	Rare	Least concern
	Biosphere reserve has following zone except one…………….	Core zone	Command zone	Buffer zone	Spherical zone	Spherical zone
	In which of the following boundaries are not circumscribed………………	Biosphere reserve	Sanctuary	National parks	Colony parks	Sanctuary
	The knowledge of which of the following factor does not help in the wildlife Management…………….	Habitat of wildlife	Behaviour of wildlife	Food habit of wildlife	Name of wildlife	Name of wildlife
	In ________ type of wildlife	Closed season	Open wildlife	Custodial	Limited entry zone	Closed season

	management the wildlife is protected from hunting mainly during breeding season and is enforced by law and if violated is punishable and termed as illegal………………….		season	management		
	The tigers are found in which of the following biosphere reserve:	Thar desert biosphere reserve	Nilgiri biosphere reserve	Namdhapa biosphere reserve	Sunderbans biosphere reserve	Sunderbans biosphere reserve
	How many biosphere reserves are present in India?	41	34	14	17	14
	Biodiversity of which organism is more in Eastern Ghats in comparison to Western Ghats?	Reptiles	Amphibian	Aves	Mammals	Amphibian
	Which one of the following is not used for *ex situ* plant conservation?	Field gene banks	Seed banks	Shifting cultivation	Botanical Gardens	Shifting cultivation
	Which one is odd for species diversity?	alpha diversity	gamma diversity	beta diversity	lamnda diversity	lamnda diversity
	Which micro organism is responsible for synthesis of antibiotics?	Bacteria	Virus	Fungus	Algae	Fungus
	Species diversity is responsible for which phenomena?	process of Evolution	speciation	For alternative types (allele) of gene	For stability and normal function of Ecosystem	For stability and normal function of Ecosystem
	How many botanical gardens are registered in	1500	80,000	800	900	800

	IABG?					
	Which of the following represent maximum number of species among global biodiversity?	Algae	Lichens	Fungi	Mosses and Ferns	Fungi
	Prolonged liberal irrigation of agricultural fields is likely to create the problem of…………………	Aridity	Metal toxicity	Salinity	Acidity	Salinity
	The greatest problem of water conservation is to reduce the amount of………………	Precipitation	Runoff water	Groundwater	Evaporation	Runoff water
	Maximum nutritional diversity is found in the group……………	Monera	Plantae	Fungi	Animalia	Monera
	Which regions are included in Biodiversity Hot-spot?	Sanctuary	National park	Garden	Only Hotspot	Sanctuary
	Which one is odd for India?	7th rank in agriculture species	origin place of 166 species of crop plants	Primary centre for domestication of ginger, turmeric, citrus, cardamom	It contains 12 mega biodiversity region	7th rank in agriculture species
	Which one is the correct pair?	Bali Tiger – Endangered species	Caspian Tiger – Extinct species	Java Tiger – Rare species	Bali Tiger -Extinct species	Caspian Tiger – Extinct species
	For which animal sunder bans is declared as a National Park?	Lion	Rhino	Tiger	Wild ass	Tiger

	Which one is odd for Amazon rain forest?	Africa	Russia	Mauritius	Java	Java
	Among the recently extinct animal, Guagga is of which country?	Mammals-472	Reptile-427	Birds-1300	piceis-3000	Mammals-472
	Which organization is active for conservation of biodiversity at world level?	WWF	WCU	a and b both	EE	a and b both
	Find odd one out :-	Project Elephant	Tiger Project	Gir Lion Project	Project Wild ass	Project Wild ass
	Which animal is remnant gene pool in the world?	Flamingo	Painted Frog	Wild ass	Spring tailed Lizard	Wild ass
	Find odd one out :	Nanda devi	Great Nicobar	Mannar	Thar	Thar
	Which is the example of ex-situ conservation?	National park	Sanctuary	Biosphere reserve	Zoo	Zoo
	Which is true for wild life conservation?	Hunting of prey	ex-situ conservation	In-situ conservation	ex-situ conservation and In-situ conservation	ex-situ conservation and In-situ conservation
	At which place animals and plants are most protected?	Botanical gardens	National Park	Zoos	Sanctuary	National Park
	Which is not applicable institute conservation?	National Park	Sanctuary	Botanical Garden	Biosphere reserve	Botanical Garden
	What is called the area which is remaining around the core zone of biosphere region?	Buffer	Transition zone	Developed zone	Peripheral zone	Buffer
	Which is the Hot spot of India?	Gangatic plain	Western Ghats	Eastern Ghats	Aravalli mountain	Western Ghats

	Which is the most appropriate method for conservation of wild life?	Vaccination	Hybridization	conservation in natural habitat	Killing of predator	conservation in natural habitat
	Where Mangroves forest found?	Dry region	Coastal region	Open area	tropical region	Coastal region
	Where are the genes of rare plants species to store?	Gene bank	Gene Library	Herbarium	Open area	Gene bank
	For which animal Project Gir is famous?	Elephant	Hangul	Tiger	Lion	Lion
	MAB means …......................	Man and biosphere programme	Mammal and biological programme	Mammal and biosphere programme	Men and biological programme	Man and biosphere programme
	Who publish Red-list ?	WWF	IUCN	MAB	IBWL	IUCN
	In India different types of mangoes species are example of …..	species diversity	Genetic diversity	Induced mutation	Breeding	Genetic diversity
	Which number is correct for Identfied popular species ?	1.1 to 1.1 million	0.5 to 1.0 million	2.5 to 3.0 million	1.7 to 1.8 million	1.7 to 1.8 million
	IUCN means …...................	International union for conservation of nature and natural resources	Indian union for conservation of nature and natural resources	International union for conservation of nature and nutrients resources	Indian Union chemical nomenclature	International union for conservation of nature and natural resources
	In India, which example has maximum varieties ?	Wheat	Rice	Mango	Tea	Mango
	In India, Western ghat is known as Hot-spot because of …..	Evergreen forest	High endemism	more height	Topical climate	High endemism

	What is important of gene diversity ?	Maintenance of species	speciation	Research of genetic code	Maintenance and research of spices	speciation
	Which is the modern concept of conservation ?	Biosphere reserve	sanctuary	National park	Protected forest	Biosphere reserve

UNIT-IV

SYLLABUS

Energetics: Type of systems-processes and their types - isothermal, adiabatic, reversible, irreversible and spontaneous processes-statement of first law of thermodynamics-need for the second law of thermodynamics-heat engine-Carnot cycle-efficiency-Carnot theorem-thermodynamics scale of temperature-Joule-Thomson effect- Enthalpy- Entropy and its significance-Free energy change.

Energetics

Energetics deals with energy changes accompanying all types of physical and chemical processes and is an important part of thermodynamics. The word "thermodynamics" *implies flow of heat*. Thermodynamics is based on three laws called the first, second and third law of thermodynamics. Before dealing the various laws, a few terms used frequently in thermodynamics are described below:

System

A system may be defined as *any specified portion of matter under study which is separated from the rest of the universe with a boundary*.

A system may consist of one or more substances.

Surroundings

The rest of the universe which might be in a position to exchange energy and matter with the system is called surroundings.

In simple cases, surroundings generally imply air or water bath in which a system under examinations is immersed.

Types of systems

The following three systems we come across frequently in thermodynamics.

i) open system ii) closed system iii) isolated system

They are explained below:

Open system

A system which can exchange matter as well as energy with its surroundings is said to be an open system.

Consider the evaporation of water placed in an open beaker. The water vapour (*matter*) will escape into the surroundings while the heat (energy) required for the vaporisation will be absorbed from the surroundings. Evidently, this is a case of an open system.

Closed system

A system which can exchange energy, but not matter with its surroundings is called a closed system.

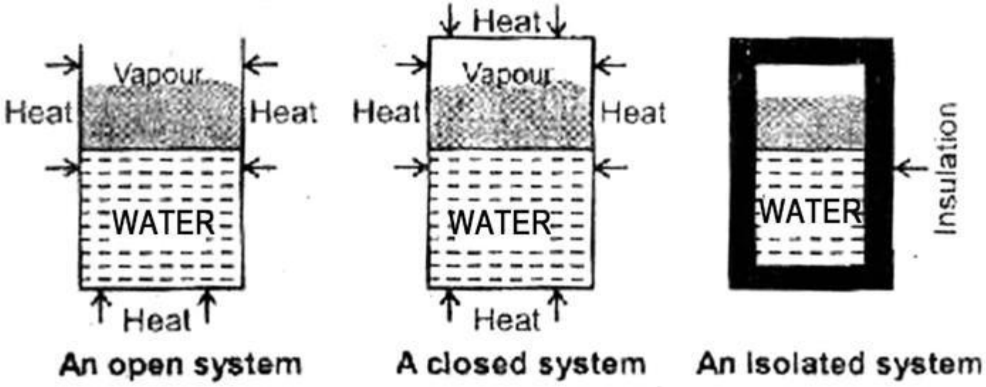
Consider a system consisting of say 100 ml water in contact with its vapour in a closed vessel. Since, the vessel is closed, no matter (liquid or vapour) can leave or enter the vessel.

Isolated system

A system which can exchange neither energy nor matter with its surroundings is called an isolated system.

In the above (closed system) example, if the vessel is also insulated, it is neither in a position to lose heat nor to gain heat from the surroundings. This is, thus, an isolated system.

The various systems are illustrated in the figure.



An open system A closed system An Isolated system

Processes and their types

The operation by which a system changes from one state to another is called a process.

Whenever a system changes from one state to another, it is accompanied by change in energy. The different types of processes are discussed.

Isothermal process

A process is said to be isothermal, if temperature of the system remains constant during each stage of the process.

Suppose a process including a chemical reaction takes place in a vessel of a closed system. As the vessel is not insulated, the system is, thus, in thermal equilibrium with the surroundings.

If the process is *exothermic* (i.e., heat is evolved in the process) then this heat is given out by the system to the surroundings. The temperature of the system, therefore, does not rise at all at any stage of the process.

If on the other hand, the reaction is *endothermic*, then the required amount of heat is absorbed instantaneously by the system from the surroundings. The temperature of the system, therefore, does not fall at all at any stage of the process.

Adiabatic process

A process is said to be adiabatic, if no heat enters or leaves the system during any step of the process.

Suppose a process, including a chemical reaction takes place in a vessel of an isolated system. In this case, no heat can leave or enter the vessel from the surroundings.

If a process, including a chemical reaction is exothermic the heat evolved remains within the system and therefore, the temperature of the system rises.

If on the other hand, a process including a chemical reaction is *endothermic,* the heat required to be absorbed is supplied by the system itself, hence, the temperature of the system falls.

The differences between isothermal process and adiabatic process are given in the table.

S.No.	Property	Isothermal Process	Adiabatic Process
1.	Temperature	remains constant	varies
2.	Heat exchange	depends on the process	zero
3.	Internal energy	$\Delta E = 0$	$\Delta E = nC_v\, dT$
4.	Work	maximum	minimum
5.	Enthalpy	$\Delta H = 0$	$\Delta H = nC_p\, dT$

Reversible process

A process carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force, is called a reversible process.

Irreversible process

A process which does not take place infinitesimally slowly is said to be an irreversible process.

All natural processes are irreversible in nature.

The different between reversible and irreversible process, are reported in the table.

S.No	Reversible Process	Irreversible Process
1.	It consists of many stages	It consists of two stages namely, initial and final

2.	It takes place slowly	It takes place with measurable rate.

3.	It takes place in both direction	It takes place in one direction only
4.	Work done is maximum	Work done is minimum
5.	The driving force is only infinitesimally greater than the opposing force.	The driving force is much greater than the opposing force.

Spontaneous process

We are familiar with the fact that many processes occur spontaneously in nature, i.e., simply leaving them to themselves.

Few examples are –

i) water flows down hill.
ii) vapours of water along with air move up.
iii) heat flows from hot region to cold region.
iv) a piece of paper can be burnt in the presence of oxygen.
v) a gas expands from a region of high pressure to a region of low pressure or in vacuum.
vi) electricity flows from a point at a high potential to a point at a lower potential.
vii) a piece of zinc, when placed in contact with a solution of copper sulphate, precipitates copper.

$$Zn_{(S)} + CuSO_{4\ (aq)} \longrightarrow ZnSO_{4\ (aq)} + Cu_{(S)}$$

We observed that the above processes occur on their own in nature and therefore, recognise them as *natural or spontaneous processes*. These processes are thermodynamically irreversible in nature.

Statement of First Law of Thermodynamics

The first law of thermodynamics is based on the cumulative experience of ages and observations. Hence, there are many ways, of stating the law. Few of them are given below:

i) Energy can neither be created nor destroyed, although it can be transformed from one form to another.

Thus, this law is known as the *law of conservation of energy*.

ii) It is impossible to construct a machine which can produce energy without the expenditure of work *(perpetual motion machine).*

iii) It is now known that the energy can be produced by the destruction of mass. The two quantities are related as:

$$E = mc^2$$

Where, E = energy produced

m = mass

c = velocity of light

iv) The mathematical statement of the first law of thermodynamics is –

$$\Delta E = q - w$$

Where, ΔE = the change in internal energy

q = quantity of heat

w = work

Need for the Second Law of Thermodynamics

The first law of thermodynamics states that when one form of energy is converted into another, the total energy is conversed. There is an element of incompleteness in the first law, as it does not indicate any other restriction on the process. However, in reality we find that many processes proceed in one natural direction and not in the reverse and it is this question that the second law is concerned. For example, metal bar having uniform temperature can spontaneously become hot at one end and cold at the other would not be a violation of the first law.

The second law establishes the direction in which energy can be transferred and the extent of a change. It predicts whether a reaction can occur spontaneously and helps us to know the equilibrium conditions.

The second law of thermodynamics is a summation of certain experiences and observations. Hence, there are many ways of stating the law that sound quite different but lead to the same goal, namely to indicate the direction of process.

a) All spontaneous processes are irreversible.
b) All spontaneous processes tend to attain equilibrium.
c) Heat cannot of itself, without the intervention of an external agency, pass from colder to a hotter body. *- R. Clausius.*
d) It impossible to obtain work by cooling a body below the lowest temperature of the system. *- Kelvin.*
e) It is impossible to construct a machine functioning in cycle which can convert heat completely into equivalent amount of work without producing changes elsewhere. *–Ostwald.*
f) It is impossible to get a continuous supply of work by cooling a body to a temperature lower than that of coldest of its surroundings. *–Thomson.*

Heat engine

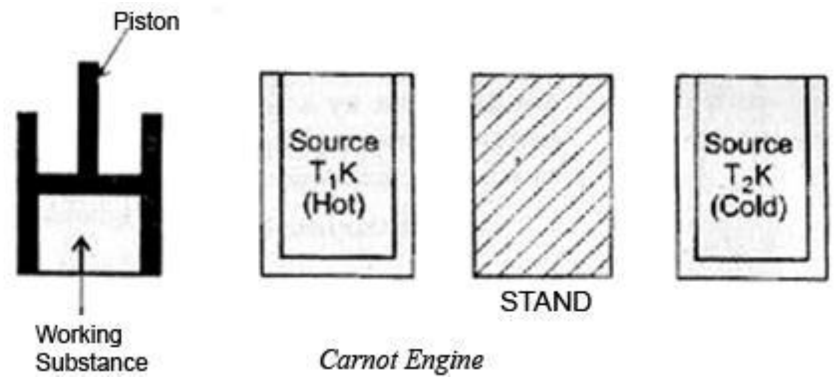
Heat engine is a device that converts heat energy into mechanical work. An ideal heat engine was proposed by Carnot and is called *Carnot's engine.*

The engine consists of –

a) Hot body or *source*, for supply of heat at higher temperature. The engine can draw heat from the source.
b) Cold body or *sink*, for the rejection of any amount of heat at lower temperature.
c) A cylinder with a perfectly conducting base and non conducting walls. A light frictionless piston moves inside the cylinder.

d) A stand with a non-conducting platform.

e) The working substance is a perfect gas. The gas is enclosed inside the cylinder. Carnot engine is shown in the figure.



Carnot Engine

Before considering the functions of a heat engine or Carnot Cycle, it is worthwhile to know about the various types of processes in thermodynamics. More often we come across two important types of processes. They are isothermal and adiabatic processes.

In an isothermal (iso = same, therm = temperature) process, the temperature remains constant throughout the process. Suppose an ideal gas adopts isothermal process, its change in internal energy ΔE is zero, since internal energy is a function of temperature.

According to the first law,

$\Delta E = q - w$

$q = w \ (\Delta E = 0)$ ….. (1)

In other words, for an ideal gas in an isothermal process the heat absorbed (q) becomes equal to work done (w) by the gas. The work of expansion of n moles of ideal gas in an isothermal process from the initial volume V_1 to the final volume V_2 at T K is given by

$$q = w = \int_{V_1}^{V_2} n\,PdV$$

$$= nRT\int_{v1}^{v2} dV/V \qquad [PV = nRT]$$

$$w = nRT \ln V_2/V_1$$

$$\text{or} \quad w = nRT \ln P_1/P_2 \qquad [P \alpha 1/V]$$

$$\text{so,}\quad w = q = 2.303\ n\ RT \log V_2/ V_1$$

$$= 2.303\ n\ RT \log P_1/ P_2 \qquad \text{……(2)}$$

Expansion or compression of a gas can also be carried out in such a way that heat is neither absorbed by it from the surroundings nor given out by it to the surroundings. In other words, the gas is thermally insulated from the surroundings. This expansion is known as adiabatic expansion. For an adiabatic process, $q = 0$.

$$\text{From the first law, } \Delta E = q - w$$

$$\Delta E = - w$$

$$\text{i.e., } - \Delta E = w \qquad \text{…… (3)}$$

Thus, the work of expansion in this case occurs at the cost of internal energy. A decrease in internal energy is accompanied by a fall in temperature.

If n moles of an ideal gas expand adiabatically from the initial volume, V_1 to the final volume, V_2, temperature will decrease from T_1 to T_2. The work of expansion is given mathematically as,

$$W = n\ C_v(T_1 - T_2) \qquad \text{……… (4)}$$

Where, C_v is the molar heat capacity at constant volume.

It is also possible to represent the adiabatic process in another way:

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \qquad \text{……….. (5)}$$

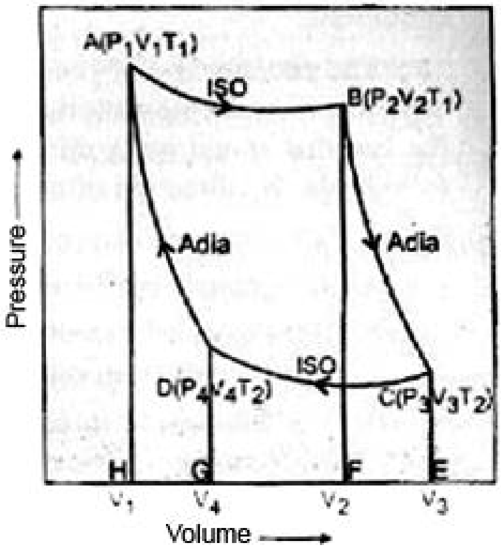
Where, $\gamma = C_p/ C_v$, in which Cp is the molar heat capacity at constant pressure.

CARNOT CYCLE

In this cycle, the working substance is one gram mole of the perfect gas. It is assumed that there are two heat reservoirs available – the source with high thermal capacity maintained at high temperature, T_1 K and the sink at lower temperature, T_2 K.

Further it is assumed that there is a perfectly heat insulating stand so that completely adiabatic process can be carried out. The Carnot cycle consist of four stages- two isothermal and two adiabatic volume changes. The cycle of operations are schematically shown on the P–V diagram (*indicator diagram*):

Initially the working substance is under the conditions represented by the point A in the indicator diagram with pressure, P_1 volume, V_1 and temperature, T_1 K, which is the temperature of the source.



Indicator Diagram

Stage.1 Isothermal expansion–AB

The cylinder is placed over the source. The working substance absorbs Q_1 k. Joules of heat from the source and expands isothermally at temperature T_1 K along the path AB till it reaches the conditions represented by the point B (P_2, V_2, T_1). In this stage, work is done by the gas and is equal to the quality of heat absorbed.

$$Q_1 = W_1 = \int_{V_1}^{V_2} PdV$$

$$= RT_1 \ln \frac{V_2}{V_1} \qquad \text{.........(6)}$$

Stage 2. Adiabatic expansion–BC

The cylinder is placed on the non-conducting platform. Now the working substance is thermally insulated from the surroundings. The gas now expands adiabatically along BC till the conditions represented by C (P_3, V_3, T_2) are reached. The gas loses heat and gets cooled to the temperature of the sink T_2K. Work is done by the gas which is given by the equation,

$$W_2 = C_v (T_1 - T_2) \qquad \text{…….(7)}$$

Stage 3. Isothermal compression-CD

The cylinder is then placed over the sink. The working substance is isothermally compressed at temperature, T_2K till it reaches the conditions given by the point D (P_4, V_4, T_2). Work is done on the gas. Q_2 k Joules of heat are rejected into the sink and is given by

$$Q_2 = W_3 = \int_{V_3}^{V_4} PdV$$

$$Q_2 = W_3 = RT_2 \ln \frac{V_4}{V_3} \qquad \text{……. (8)}$$

Stage 4. Adiabatic compression-DA

The cylinder is next placed on the non-conducting stand. The gas is adiabatically compressed along DA, till it is resorted to its initial conditions (P_1, V_1, T_1). Due to compression, the gas gets heated to T_1 K. No heat is absorbed or rejected. Work is done on the gas and it will be

$$W_4 = C_v (T_2 - T_1) \qquad \text{…..(9)}$$

As a result of these four stages, a reversible cycle is completed and the gas reaches to its original stage. The total work done (W) in a complete cycle is the algebraic sum of all these four works.

$$\therefore \; W = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \ln \frac{V_2}{V_1} + Cv\,(T_1 - T_2) + RT_2 \ln \frac{V_4}{V_3} + Cv\,(T_2 - T_1)$$

$$= RT_1 \ln \frac{V_2}{V_1} + Cv\,(T_1 - T_2) + RT_2 \ln \frac{V_4}{V_3} - Cv\,(T_1 - T_2)$$

$$= RT_1 \ln \frac{V_2}{V_1} + RT_2 \ln \frac{V_4}{V_3} \qquad \text{….. (10)}$$

since B and C lie on the same adiabatic,

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma - 1} \qquad \text{…… (11)}$$

Similarly, points A and D lie on the same adiabatic,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma - 1} \qquad \text{…… (12)}$$

From equation (11) and (12), we obtain,

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma - 1} = \left(\frac{V_1}{V_4}\right)^{\gamma - 1}$$

$$\frac{V_2}{V_3} = \frac{V_1}{V_4} \quad \text{(or)} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4} \qquad \text{….. (13)}$$

Substituting the value of $\frac{V_3}{V_4}$ from equation (13) into equation (10),

$$W = RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_2}{V_1}$$

$$= R(T_1 - T_2) \ln \frac{V_2}{V_1} \qquad \text{…… (14)}$$

EFFICIENCY

Efficiency of the heat engine is defined as *the ratio of heat converted into work to the heat drawn from the source.*

$$\text{Efficiency, } \eta = \frac{\text{quantity of heat converted into work}}{\text{quantity of heat absorbed from the source}}$$

In the above heat engine, let Q_1 k. Joules drawn from the source at temperature. T_1 K and Q_2 k joules of heat be rejected into sink at T_2 K. The quantity of heat converted into useful work will be $(Q_1 - Q_2)$ k. Joules.

$$\text{Efficiency, } \eta = \frac{(Q_1 - Q_2)}{Q_1} \quad \text{….. (15)}$$

$$= \frac{R \ln \frac{V_2}{V_1} (T_1 - T_2)}{R \ln \frac{V_2}{V_1} T_1}$$

$$= \frac{(T_1 - T_2)}{T_1} = 1 - \frac{T_2}{T_1} \quad \text{….. (16)}$$

a) It is clear from the above that, efficiency, of Carnot's heat engine is always less than one.
b) The efficiency is independent of the working substance.
c) The efficiency is one, only when $T_2 = 0$ K.
d) All reversible engines have same efficiency, provided the operation is done between the same initial and final temperatures.

Refrigerators

On the other hand, if the heat engines are working as refrigerators, the heat engines used to pump heat from a cold to a hot reservoir. The efficiency of the refrigerator is given by,

$$\eta = \frac{(T_1 - T_2)}{T_2} = \frac{T_1}{T_2} - 1 \quad \text{….. (17)}$$

Efficiency of a refrigerator increases as T_2 is lowered and may become more than one.

Worked Examples

1. Calculate the efficiency of a heat engine working between the two temperatures 27°C and 127°C.

Use, efficiency, $\eta = (T_1 - T_2)/T_1$

Given, T_1 =127°C = 400 K and T_2 = 27°C = 300 K

η = 400 - 300/400 = 100/400 = **0.25.**

2. 5 moles of an ideal gas expand isothermally and reversibly from a volume of 1 lit. to a volume of 8 lit. at 27^oC. What is the maximum work done?

The maximum work done in an isothermal reversible expansion,

W = 2.303 n RT log V_2/V_1 Joules.

Given, n = 5; R = 8.314 Joules/ deg / mole.

T = 27 ^oC = 300 K

V_2 = 8 lit. and V_1 = 1 lit.

W = 2.303 x 5 x 8.314 x 300 log 8/1 Joules

W = 2.303 x 5 x 8.314 x 300 x 0.9031 Joules

W = **25. 92 kJ.**

3. One mole of an ideal gas expands isothermally and reversibly from an initial pressure of 5 atm. to a final pressure of 1 atm. at 25^oC. Calculate the work done.

The maximum work done in an isothermal reversibly expansion,

W = 2.303 n RT log P_1/P_2 Joules.

Given n = 1, R = 8.314 Joules /deg/ mole

T = 25^oC = 298 K

P_1 = 5 atm. and P_2 = 1 atm.

W = 2.303 x 1 x 8.314 x 298 log 5/1 Joules.

W = 2.303 x 1 x 8.314 x 298 x 0.6990 Joules.

W = 3.987 kJ.

4. What percent of T_1 is in T_2 for a 10% efficiency of an heat engine? $T_1 > T_2$

The efficiency of a heat engine, $\eta = (T_1 - T_2)/T_1$

Given, η = 10 % or 0.1 and $T_1 > T_2$

$0.1 = (T_1 - T_2)/T_1$

Or $0.1\ T_1 = T_1 – T_2$

i.e., $T_2 =$ **90% T_1.**

5. What are the efficiencies of Carnot engine operating (a) as a heat engine between two reservoirs and at 500 K and 100 K and (b) as a refrigerator?

(a) Efficiency of heat engine, $\eta = (T_1 - T_2)/T_1$

Given, $T_1 = 500$ K and $T_2 = 100$ K

$\eta = 500-100/500 = 400/500 = 0.8$

(b) Efficiency of a refrigerator, $\eta = (T_1 - T_2)/T_2$

$\eta = 500-100/100 = 400/100 =$ **4.**

6. A Carnot cycle working between 400 K and 300 K takes up 800 Joules from the high temperature reservoir. Calculate the work done, the heat rejected and the efficiency.

(a) Efficiency, $\eta = (T_1 - T_2)/T_1$

Given $T_1 = 400$ K and $T_2 = 300$ K

$\eta = 400-300/400 = 100/400 = 0.25.$

(b) η = Work done/quantity of heat absorbed

∴ Work done = quantity of heat absorbed x η

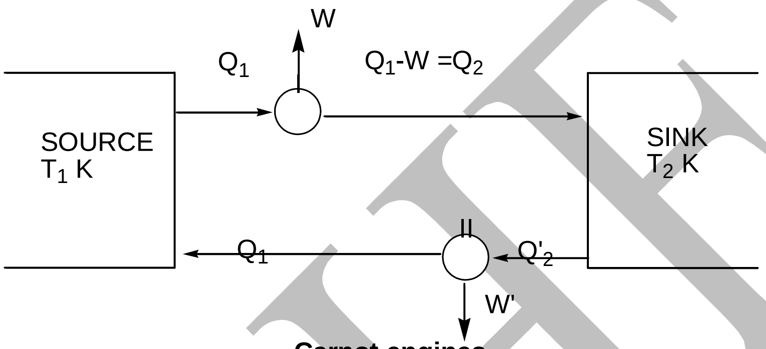
= 800 x 0.25 = **200 Joules**

(c) Quantity of heat rejected = (800 –200) = **600 Joules.**

The Carnot Theorem

In 1824, Carnot put forward a theorem known as Carnot theorem in connection with the efficiency of heat engines. The theorem states that working between the same temperature limits, all reversible heat engine are equally efficient whatever may be the working substance. In other words, we can say that the efficiency is independent of the working substance and temperature of sink and source. The theorem may be proved in the following way.

Consider two reversible engines I and II working between the same two temperatures and assume that both are having different efficiencies. Let in each cycle, engine I takes in heat Q_1 from the source at T_1, converts a part into work, W and rejects $Q_1 – W = Q_2$ to the sink at T_2. On the other hand, let engine II converts a smaller amount W' of the heat, Q_1 taken in at T_1 into work and returns a quantity, $Q_1 – W' = Q_2'$ which is greater than Q_2 to the sink at temperature T_2 as shown in figure.



Carnot engines

Now let these two engines be coupled together so that engine I operates in a direct manner i.e., takes heat from some source, performs work and gives the reminder to sink whereas, engine II functions in the reverse direction, i.e., takes heat from sink, having work done upon it and giving up heat to source. In other words, engine II functions as refrigerator. The heat and work changes in each complete cycle are as follows:

Functions	**Engine I**	**Engine II**
Heat transfer at T_1 K	Q_1	$-Q_1$
Work done	W	-W′
Heat transfer at T_2 K	$-Q_2$	Q_2'

Now, after complete cycle, we have heat transfer at

$T_2 = Q_2' – Q_2$

Work done = W – W′

Again we have, $Q_2 = Q_1 - W$ and

$$Q_2' = Q_1 - W'$$

$$(Q_2' - Q_2) = (Q_1 - W') - (Q_1 - W) = W - W'$$

or, Heat absorbed at T_2 = work done.

In this way the combined engine functioning in cycles can convert completely the whole heat into work without leaving changes elsewhere. This is contrary to the second law of thermodynamics. Hence, the two engines cannot have different efficiencies.

Thermodynamics scale of temperature

The scale of an ordinary thermometer depends upon the physical property of the substance used in thermometer. Since there is no physical property which varies continuously with temperature scale which should be independent of the properties of all substance, Kelvin in 1848 made Carnot cycle as the basis of temperature measurement.

The temperature of each heat reservoir of the thermodynamics scale is defined as proportional to the quantity of heat transferred to or from it in a reversible cycle. Disregarding the sign of the quantity for the time being, if Q_1 is the heat transferred at higher temperature and Q_2 is the heat transferred at lower temperature, then the respective temperature on the Kelvin scale T_1 and T_2 are given by,

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

When referred to Carnot heat engine, the above equation can be

written as, efficiency, $\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$

The expression defines the efficiency of the reversible engine in terms of Kelvin temperature. It is evident that the process will have efficiency as unity, when $T_2 = 0$. This temperature to which the sink were cooled so that the efficiency is one which is called the absolute zero of the thermodynamic scale. A machine is capable of converting 100% of heat into work in a reversible cyclic process only if it is operating between higher temperature and absolute zero. The size of the degree of Kelvin scale is fixed by considering the interval between the freezing and the boiling points of water into 100 equal parts on this scale. In this way the thermodynamic scale of temperature is completely defined and fixed.

Joule-Thomson Effect

The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the Joule Thomson effect.

Explanation

If a stream of a gas at high pressure is allowed to expand by passing through a porous plug into vacuum or a region of low pressure, under adiabatic conditions, it gets cooled appreciably. The cooling effect is due to decrease in the kinetic energy of the gaseous molecules, since a part of this energy is used up in overcoming van der Wall's forces of attraction existing between the molecules during expansion

Hydrogen and helium are exceptions, as they get warmed up under similar conditions.

It has been found that Joule Thomson Effect is very small when a gas approaches ideal behaviour. Hence, the Joule Thomson effect is zero for an ideal gas.

Enthalpy

Consider the following system-

$$A \longrightarrow B$$

Suppose that the change of state of the above system is brought about at constant pressure. In such a case, there will be a change in the volume. Let the volume increase from V_A to V_B at constant pressure, P.

Then, the work done (w) by the system will be,

$$w = P (V_B - V_A) \qquad \text{…..(1)}$$

From the first law,

$$\Delta E = q - w \qquad \text{…... (2)}$$

$$\Delta E = q - P (V_B - V_A) \qquad \text{…… (3)}$$

But, $\Delta E = E_B - E_A$ …… (4)

$E_B - E_A = q - P(V_B - V_A)$ …… (5)

or, $(E_B + PV_B) - (E_A + PV_A) = q$ …… (6)

The quantity, E+PV, is known as the enthalpy of a system and is denoted by H. It represents the total energy stored in a system. Thus,

$H = E+PV$ … (7)

From equation (6), $H_B - H_A = \Delta H = q$ … (8)

Since H_B and H_A are defined properties, it is evident that ΔH is also definite property depending only on the initial and final states of system. Evidently ΔH represents the increase in the enthalpy of a system when it changes from state A to state B.

From equation (5), $(E_B - E_A) + P(V_B - V_A) = q$ …. (9)

Incorporating equation (8) in equation (5),

$\Delta H = (E_B - E_A) + P(V_B - VA)$ …(10)

$\Delta H = \Delta E + P\,\Delta V$ …(11)

Where Δ V is the increase in volume undergone by the system.

Entropy

The efficiency of a heat engine is obtained using,

$$\text{Efficiency, } \eta = \frac{w}{q} = \frac{T_1 - T_2}{T_1} = \frac{q_1 - q_2}{q_1} \qquad \text{…… (1)}$$

and $T_1 > T_2$

Equation (1) can be written as

$$1 - \frac{T_2}{T_1} = 1 - \frac{q_2}{q_1} \qquad \text{… (2)}$$

Add-1 on either side of equation (2)

$$1 - \frac{T_2}{T_1} \quad -1 \quad = \quad 1 - \frac{q_2}{q_1} \quad -1 \qquad \text{….. (3)}$$

i.e., $$\frac{T_2}{T_1} = \frac{q_2}{q_1} \qquad \text{….. (4)}$$

Or, $$\frac{q_1}{T_1} = \frac{q_2}{T_2} \qquad \text{….. (5)}$$

For a reversible process equation (5) can be written as,

$$\frac{q_{\text{rev}}}{T} = \text{Constant} \qquad \text{…… (6)}$$

Where q_{rev} = Quantity of heat exchanged in a process carried out reversibly at temperature, T.

Equation (6), is an important generalization, since the quantity represents a definite quantity or state function. This function was first named as entropy by Clausius and denoted by the symbol S. The actual entropy of a system is not easily defined. It is rather more convenient to define the change in entropy, dS, for an infinitesimal stage of an appreciable reversible process which takes placed by taking; δq_{rev} joules of heat at constant temperature.

$$dS = \frac{\delta q_{\text{rev}}}{T} \qquad \text{…… (7)}$$

Where, T is the temperature in Kelvin scale. If heat enters a body, δq_{rev} is **positive** and the entropy change is **positive**.

For any appreciable changes, the change in entropy, when a system goes from the initial state A to the final state B at constant temperature, T is given by

$$\Delta S = S_B - S_A = \int_A^B \frac{\delta q_{\text{rev}}}{T} \qquad \text{……. (8)}$$

The entropy change for a finite change of state of a system at constant temperature is given by

$$\Delta S = \frac{q_{rev}}{T} \qquad \ldots\ldots (9)$$

Characteristics of Entropy

i) Like energy, entropy is also a state function and is a complete differential.
ii) ΔS is a definite quantity and depend only on the initial and final states of the system.
iii) It is quite independent of the path or manner by which the change has been brought about.
iv) Entropy can be expressed in terms of thermodynamic parameters (P, V, T).
v) Entropy of a system is an extensive property, dependent on the amount of matter in the system.

Hence, it is essential to make a mention of the quantity of the substance taken. This quantity is, usually, 1 mole.

Unit of entropy

Since, entropy change is expressed by a heat term divided by the absolute temperature, entropy is expressed in terms of calories per degree i.e., cal deg^{-1}. This is known as **entropy unit, e.u.**

In S.I. units, the entropy is expressed in terms of joules per degree Kelvin (JK^{-1})

Entropy as a measure of Randomness

All spontaneous processes are accompanied by increase of entropy. It can be shown that these spontaneous processes lead to increase in the disorder (randomness) of the system. This is evident from the following example.

It has been shown that evaporation of a liquid or melting of a solid is accompanied by increase of entropy. A solid has a definite crystal lattice, viz, ions or atoms or molecules in a solid are arranged in a definite order. The order is much less in a liquid and is least in a gas. Thus, increase of entropy implies increase in disorder. Hence, entropy is regarded as a measure of randomness

Free Energy

The sum total of the entropy change of the system and surroundings serves a criterion of spontaneity or feasibility as-

i) If the total entropy change is **positive**, the process is **feasible**.

ii) If it is **zero**, the system remains in a state of **equilibrium**.

Hence, in order to decide about the feasibility of the process, we have to know the entropy change of the system as well as that of surroundings. This is not always convenient.

Hence, we may consider entropy changes in terms of other state functions which can be determined conveniently. Two such functions are-

i) **Work function or Helmholtz free energy, A**
ii) **Gibbs free energy, G**

These are defined by equations

$A = E- TS$ ….. (1)

and $G = H – TS$ …... (2)

A and G depend on the state of the system only and for a change from one state to another state, they are given as,

$\Delta A = \Delta E- T\Delta S$ ….. (3)

and $\Delta G = \Delta H – T\Delta S$ …... (4)

Gibbs free energy, G, is a function of temperature, pressure and the number of moles of the various constituents.

i.e., $G = f (T, P, n_1, n_2, n_3 \ldots n_j)$

Where, $n_1 + n_2 + n_3 + \ldots n_j$ = Total number of moles = N

The most useful criterion to decide between reversibility and irreversibility of a process is in terms of free energy, as below –

a) If a process is thermodynamically **irreversible**
i.e., spontaneous or feasible then,
$(dG)_{T.P} < 0$ or ΔG = -ve value

b) If a process is thermodynamically **reversible** i.e., there is a state of equilibrium then,

$(dG)_{T,P} = 0$ or $\Delta G = 0$

c) If a process is thermodynamically **not feasible,** then,

$(dG)_{T,P} > 0$ or $\Delta G = +\text{ve value}$

Text Books:

1. Veeraiyan, V., & Vasudevan, A.N.S. (2012). *Text Book of Allied Chemistry* (II Edition). Chennai: Highmount Publishing House.

2. Puri, B. R., Sharma, L. R. & Pathania, M. S. (2014). *Elements of Physical Chemistry* (46th Edition). Jalandhar: Vishal Publishing Company Co.

Reference Book:

1. Gopalan, R., & Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. Define the following terms a) system b) surroundings.
2. What is meant by open and closed system?
3. Explain isolated system and process.
4. Give the Clausius and Thomson forms of the second law of thermodynamics.
5. Differentiate reversible and irreversible process.
6. Write the three examples of spontaneous process.
7. Define efficiency of a heat engine.
8. Define the term efficiency.
9. Give the units of entropy.
10. Define spontaneous process.

11. Calculate the efficiency of a heat engine working between the two temperatures 27^oC and 127^oC.
12. Explain the terms: enthalpy and free energy.
13. What are the efficiencies of Carnot engine operating (a) as an engine between two reservoirs at 500 K and 100 K and (b) as a refrigerator?
14. What are the significances of efficiency?
15. Define Joule Thomson effect.

PART-C (Each Question Carry Six Marks)

1. (i) What are the characteristics of entropy?
   (ii) 5 moles of an ideal gas expand isothermally and reversibly from a volume of 1 litre to a volume of 8 litres at 27°C. What is the maximum work done?
2. (i) State the first law of thermodynamics in different ways.
   (ii) One mole of an ideal gas expands isothermally and reversibly from an initial pressure of 5 atm. to a final pressure of 1 atm. at 25°C. Calculate the work done.
3. (i) Describe different types of systems.
   (ii) State and explain Joule Thomson effect.
4. Give the statement of second law of thermodynamics in four different ways.
5. What is a heat engine? Mention its parts.
6. Explain Carnot cycle in detail.
7. (i) Explain enthalpy with an example.
   (ii) Explain thermodynamic scale of temperature.
8. State and explain Carnot theorem.
9. (i) What are buffer solutions? Explain the importance of buffer solution in living system.
   (ii) Explain degree of hydrolysis.
10. Explain processes and their types.
11. (i) A Carnot cycle working between 400 K and 300 K takes up 800 Joules from the high temperature reservoir. Calculate the work done, the heat rejected and the efficiency.

(ii) A heat engine works between 420 K and 280 K. Find the efficiency of it is working as the refrigerator and heat engine?

(iii) What percent of T_1 is in T_2 for a 10% efficiency of a heat engine? $T_1 > T_2$.

12. (i) What are the difference between isothermal process and adiabatic process?

(ii) How is the efficiency of a refrigerator calculated?

(iii) What is meant by law of conservation energy?

13. (i) What are the applications of electrochemical series?

(ii) Describe the determination of pH of a solution using conductivity method.

14. (i) Derive the expression for the hydrolysis constant K_h for the salt of weak acid and weak base.

(ii) Define pH, pOH and pKw.

15. What would be the pH value of a) 0.0001 N HCl b) 0.005 M H_2SO_4 c) 0.005 N NaOH?

16. (i) Sketch the conductometric titration curves of the following

a) HCl Vs NaOH b) CH_3COOH Vs NaOH c) NH_4OH Vs HCl d) KCl Vs $AgNO_3$

(ii) Define salt hydrolysis.

(iii) What are the advantages of quinhydrone electrode?

ENVIRONMENTAL STUDIES

MULTIPLE CHOICE QUESTIONS

	Questions	Opt 1	Opt 2	Opt 3	Opt 4	Answer
	Unit V					
	The process of extraction, refinement, fabrication and delivery are all energy consuming and add to pollution of earth, air and water.	embodied energy	kinetic energy	potential energy	Embedded Energy	embodied energy.
	___________depends on energy mainly from fossil fuels.	rural transport	Urban transport	Metro transport	Semi urban transport	Urban transport
	As ________and __________spreads due to extensive changes in land use the once perennial rivers are becoming increasingly seasonal.	deforestation and desertification	afforestation and asertification	deforestation and afforestation	desertification and afforestation	deforestation and desertification
	Urban residential and commercial facilities are responsible for approximately _____ of greenhouse gas emissions	25%	35%	45%	65%	35%
	______________is defined as development that meets the needs of the present without	Sustainable development	Economic development	Social development	Environment development	Sustainable development

	compromising the ability of future generations to meet their own needs.					
	_______supplies water to plants near its roots through a system of tubes, thus saving water.	Drip irrigation	Well irrigation	Tube irrigation	Submersible irrigation	Drip irrigation
	The management of a single unit of land with its water drainage system is called ______	Watershed management	Rainwater harvesting	Land recreation	Drainage management	Watershed management
	______ deals with issues related to the rights of individuals that are fundamental to life and well being.	Environmental ethics	Human values	Human rights	Consumer rights	Environmental ethics
	________will be enhanced only if we can arrest and reverse the growing alienation between the people and the common property resources.	Gross Nature Product	Gross National Product	Gross Domestic product	Net Domestic product	Gross Nature Product
	________ begins by taking control over a degraded site through local participation.	pollution	energy	Watershed management	potential energy	Watershed management
	Changes in climate may affect the distribution of ________ which in turn will increase the spread of	vector species	vertebral species	fungi species	bacterial species	vector species

	disease, such as malaria and filariasis,					
	There are _____ aspects that are closely connected with ethical issues that are related to our environment.	2	3	4	5	2
	The concept of _____ is based on a thinking that the soul moves from man to animal and in reverse depending on one's actions.	karma	ahimsa	life	wilderness	karma
	_____ goddesses have been associated with specific plant species.	tree	plant	animals	trees and plants	tree
	The _______ plant is grown on the doorstep outside every home.	tulsi	money plant	green leaves	olive	tulsi
	Certain species of trees have been protected as they are valued for their _____or ________	fruit or flowers	flowers or trees	trees or fruits	trees or plants	fruit or flowers
	The ____________ is protected for its fruit around most farms even when wood becomes scarce.	banyan tree	coconut tree	mango tree	peach tree	mango tree
	The ___________is protected by tribal people as it provides edible flowers, oil from its seeds and is used to	Mohua tree	Madhuca indica	mango tree	Mohua and madhuca indica	Mohua and madhuca indica

	make a potent alcohol.					
	About ______ of the solar energy reaching the Earth is absorbed on the earth's surface which increases its temperature.	85%	75%	65%	95%	75%
	The _______ affects plant and animal life in aquatic ecosystems.	fossil fuel	oil refining	acid rain	acidic raining	acid rain
	The destruction of the ________ is seen to cause increased cases of skin cancer and cataracts.	troposphere	stratosphere	ozone layer	mesosphere	ozone layer
	After ________, the ozone layer is expected to recover slowly over a period of about 50 years.	1990	1000	2000	3000	2000
	The Montreal Protocol was signed in the year__________	1985	1986	1987	1990	1987
	Wasteland can be reclaimed for__________ by reducing the salt content which can be done by leaching and flushing.	agriculture	forestry	agro	agro forestry	agriculture
	_______implies integration of trees with agricultural crops or livestock management simultaneously.	afforestation	agro forestry	agriculture	forest	agro forestry
	Wasteland can be classified into _____forms	2	3	4	5	2

	NGO stands for ____________	non-governmental organization	non govern opportunities	not good organization	non government organization	non-governmental organization
	A Task Group set up by ______ has warned that climate change may have serious impacts on human health.	WHO	UNESCO	WTO	UNICEF	WHO
	________ was the first State in India to regulate the manufacture and use of plastics.	Tamil nadu	Andhra Pradesh	Karnataka	Himachal Pradesh	Himachal Pradesh
	____________is one of the end results of consumerism.	Materialism	consumer	consumerism	consumer	Materialism
	_____is driven by huge sum spent on advertising, designed to create both a desire to follow trends, and a personal feeling of satisfaction based on acquisition.	materials	Consumerism	materialism	consumer	Consumerism
	Reduce, Reuse, Recycle, are the____ principle, is the new concept in waste management.	3P	3Rs	4Rs	3Ps	3Rs
	___________and_________is used to make new metal products.	Metal scrap and broken glass	metal and glass	metal scrap and new glass	new glass and broken glass	Metal scrap and broken glass
	________ is used in sewage plant to make fuel.	gas	biogas	bio	biochemical	biogas

	The spirit of the proclamation adopted by the United Nations Conference on Human Environment took place in Stockholm in June ___________	1972	1872	1772	2002	1972
	The Government passed Air Act in ________ to clean up our air by controlling pollution.	1991	1981	1852	1952	1981
	VOC stands_______________	volatile organic compounds	volatile of compounds	vague of compounds	non volatile if inorganic compounds	volatile organic compounds
	(PCBs) stands for___________________	popular control board	Pollution Control Boards	population control board	all the above	Pollution Control Boards
	RTO stands for__________	road transport office	railway transport office	regional transport office	railway transport origin	regional transport office
	The Government has formulated Water Act in _________to be able to prevent pollution of water by industrial, agricultural and household wastewater that can contaminate our water sources.	1975	1974	1973	1972	1974
	The main objectives of the Water Act are to provide for ___________and abatement of	prevention	control	protect and prevention	prevention and control	prevention and control

	water pollution and the maintenance or restoration of the wholesomeness of water.					
	The Forest Conservation Act was passed in ____________	1982	1980	1981	1985	1980
	India's first Forest Policy was enunciated in ______	1951	1952	1953	1954	1952
	The Forest Conservation Act of 1980 was enacted to control ___________	afforestation	deforestation	afforestation	prevention and control	deforestation
	______are not permitted to trespass into the Reserved Forest.	cattle	kinetic energy	bus	train	cattle
	MoEF stands for___________	ministry of ecosystem and foundation	Ministry of Environment and Forests	ministry of environmental and foundation	ministry of ecosystem and forest	Ministry of Environment and Forests
	________ was recorded as the warmest year.	1988	1998	1996	1990	1998
	Project that already exist but require expansion must also apply for clearance____________	green field projects	field projects	green projects	brown field projects	brown field projects
	_________ is not intended to stop all types of development.	EIA	AMI	EMI	MMI	EIA
	March 21 is celebrated as_________	world forestry day	world health day	world heritage day	earth day	world forestry day
	April 07 is celebrated	world forestry	world health	world heritage	earth day	world health

	as__________	day	day	day		day
	…….. treatment used for the reduction of population by men	vasectomy	Tubal Ligation	both	None of the above	vasectomy
	April 22 is celebrated as___________	world forestry day	world health day	world heritage day	earth day	earth day
	June 05 is celebrated as ___________	world forestry day	world heritage day	world environment day	world population day	world environment day
	June 11 is celebrated as_____________	earth day	world health day	world environment day	world population day	world population day
	February 2 is celebrated as_____________	world wetland day	world health day	world environment day	world population day	world wetland day
	. …….. treatment used for the reduction of population by women	vasectomy	Tubal Ligation	both	None of the above	Tubal Ligation
	September 16 is celebrated as _____________	Hiroshima day	world ozone day	green consumer day	wildlife day	world ozone day
	September 28 is celebrated as__________	Hiroshima day	world ozone day	green consumer day	wildlife week	green consumer day
	October 1-7 is celebrated as____________	Hiroshima week	world ozone week	green consumer week	wildlife week	wildlife week

UNIT-V

SYLLABUS

Electrochemistry: Kohlrausch law-conductometric titrations-hydrolysis of salts-galvanic cells-E.M.F.-standard electrode potentials-reference electrodes- electrochemical series and its applications-buffer solution-buffer solution in the biological systems-pH and its determination-principles of electroplating.

Kohlrausch Law

The equivalent conductance of solution increases with dilution, until it becomes constant. This limiting value, λ_α is known as equivalent conductance at infinite dilution and are obtained by extrapolation of equivalent conductance (λ) versus concentration curves to infinite dilution (or zero concentration) for strong electrolytes. The same method cannot be used for weak electrolytes, as they fail to yield a limiting value even at very dilute conditions.

Kohlarusch investigated λ_α for different electrolytes and found an interesting relationship amongst various values.

Consider the following Table.

Equivalent conductance at infinite dilution at 298 K.

S.No.	Electrolytes	λ_α	Difference
1.	KBr	151.92	23.41
2.	NaBr	128.51	
3.	KCl	149.86	23.41
4.	NaCl	126.45	
5.	KOH	271.52	23.41
6.	NaOH	248.11	
7.	LiBr	117.09	2.06
8.	LiCl	115.03	

9.	NaBr	128.51	2.06
10.	NaCl	126.45	
11.	KBr	151.92	2.06
12.	KCl	149.86	

It is evident from the above table, that the replacement of potassium ion by sodium ion always gives the different of λ_α equal to 23.41 irrespective of the nature of anion.

Similarly, the replacement of bromide ion by chloride ion of the electrolyte always produces the same difference, i.e., 2.06. In other words, it may be said that the different in conductance of any two cations (or anions) is always constant. It is therefore obvious that when dissociation is complete every ion makes a definite contribution towards the equivalent conductance of the solution which is independent of the nature of the other ion to which it is associated.

This led Kohlrausch to state that –

The equivalent conductance at infinite dilution for different electrolytes is given by the sum of two values, one depending upon the anion and other on cation.

$$\text{Thus, } \lambda_\alpha = \lambda_a + \lambda_c \qquad \text{…..(1)}$$

Where, λ_a *and* λ_c are the contributions of the anions and cations respectively towards the equivalent conductance at infinite dilution. These contributions are known as the ionic conductance at infinite dilution.

Application of Kohlrausch Law

Calculation of λ_α for weak electrolytes

The value of equivalent conductance at infinite dilution λ_α for strong electrolytes can be obtained graphically by extrapolation. This method is not suitable for weak electrolytes as they are feebly ionised. In such cases, Kohlrausch law provides an indirect method.

To find out the equivalent conductance of acetic acid at infinite dilution, we will first determine the equivalent conductances of strong electrolytes, HCl, CH_3COONa and NaCl at infinite dilutions.

For HCl, $\lambda_\alpha HCl = \lambda_{H}^{+} + \lambda_{Cl}^{-} = x$ (say) …..(2)

For CH_3COONa, $\lambda_\alpha CH_3COONa = \lambda_{Na}^{+} + \lambda_{CH_3COO}^{-} = y$ (say) …..(3)

For NaCl, $\lambda_\alpha NaCl = \lambda_{Na}^{+} + \lambda_{Cl}^{-} = z$ (say) …..(4)

(2) + (3) – (4) gives,

$$\lambda_{H}^{+} + \lambda_{Cl} - + \lambda_{Na}^{+} + \lambda_{CH_3COO}^{-} - \lambda_{Na}^{+} - \lambda_{Cl}^{-} = x + y - z$$

or, $\lambda_{CH_3COO}^{-} + \lambda_{H}^{+} = x + y - z$

i.e, $\lambda_\alpha CH_3COOH = \lambda_{H}^{+} + \lambda_{CH_3COO}^{-} = x + y - z$

Thus, the equivalent conductance of acetic acid at infinite dilution can be calculated.

Similarly, $\lambda_\alpha NH_4OH = \lambda_\alpha NH_4Cl + \lambda_\alpha NaOH - \lambda_\alpha NaCl$ ….. (5)

It is also possible to obtain the equivalent conductance at infinite dilution of a sparingly soluble substance like silver chloride as.

$\lambda_\alpha AgCl = \lambda_\alpha AgNO_3 + \lambda_\alpha NH_4Cl - \lambda_\alpha NH_4NO_3$ …..(6)

Determination of degree of dissociation or degree of ionisation

At infinite dilution, there is complete dissociation. At certain dilution, the degree of dissociation is α. Here, α represents the fraction of molecule which are dissociated.

$$\text{Then, } \alpha = \frac{\text{Actual numer of molecules}}{\text{Total numer of molecules at infinite dilution}}$$

$$\text{or, } \alpha = \frac{\text{Actual equivalent conductance}}{\text{Equivalent conductance at infinite dilution}}$$

(∵ Equivalent conductance α No. of ions)

$$\alpha = \frac{\lambda}{\lambda_\alpha} \qquad \text{...... (10)}$$

When, λ is the equivalent conductance at particular dilution and λ_α is the equivalent conductance at infinite dilution.

While, λ can be determined experimentally, λ_α may be calculated from Kohlrausch law for weak electrolyte as,

$$\lambda_\alpha = \lambda_{anion} + \lambda_{cation}$$

Thus, the degree of dissociation can be calculated using equation (10).

Solubility of sparingly soluble salts

Substances such as AgCl, Ag_2CrO_4, $BaSO_4$, $PbCrO_4$ etc. are regarded as insoluble or sparingly soluble in water. The minute amount that is dissolved may be treated as present at infinite dilution. Hence, the determined equivalent conductance may be taken as the equivalent conductance at infinite dilution. The determination of the solubility of silver chloride at 298 K is explained here.

The salt is completely washed with conductivity water to remove soluble impurities. It is then warmed with conductivity water and cooled to 298 K. On warming, a small quantity of the salt will dissolve and rest will settle down. The conductance is determined in the usual way by placing the conductivity cell in a thermostat maintained at 298 K. The conductance of the conductivity water used in the solution is also determined and is subtracted from the conductance of AgCl solution. The product of the cell constant, (1/a) and the conductance, (1/R) gives the specific conductance (K) of the solution due to dissolved salt.

Calculation

Let the solubility of AgCl = S g.equ./lit.

∴ The volume of the solution containing

$$1g.\ \text{equivalent of AgCl} = \frac{1000}{S}\ \text{ml}$$

∴ The equivalent conductance,

$$\lambda_\alpha = K \times \frac{1000}{S}\ \text{mho cm}^2$$

Now at 298 K the equivalent conductance at infinite dilution of AgCl may be calculated by computing the ionic mobilities (conductances) for Ag^+ and Cl^- as

$$\lambda_\alpha\ AgCl = \lambda_{Ag^+} + \lambda_{Cl^-}$$

$$= 61.92 + 76.34 = 138.26\ \text{mho cm}^2$$

$$\therefore \quad \frac{1000\ K}{S} = 138.26$$

$$S = \frac{1000\ K}{138.26}\ \text{g.equ./lit.}$$

Thus, the solubility AgCl in H_2O at 298 K

$$= \frac{1000\ K}{138.26}\ \text{g.equ./lit}$$

$$= \frac{1000\ K \times 143.5}{138.26}\ \text{g./lit.}$$

Here, 143.5 is the molar mass of AgCl.

Conductometric Titrations

Many techniques are available in electrochemistry to determine the strength of a substance. A brief account of the conductometric titrations is given in this section. This method of estimation is applicable to any titration in which there is a sharp change in conductance at the end point. The principle involved in these titrations is that electrical conductance depends upon the number and mobility of the ions.

Usually to obtain accurate and precise results, it is necessary that the change of volume during titration must be as small as possible and there should not be any rise in temperature during titration.

Conductances are followed during the course of titration and values are plotted against the number of ml. of the titrant added. Conductometric curves should be straight line or nearly straight lines if few readings on each sides of the end point are considered. The end point of the titration is the point of intersection of two curves.

Titration of a strong acid against a strong base

Consider the titration of the strong acid (say, HCl) with a strong base (say, NaOH). A definite volume of the acid is pipetted out in the conductivity cell and the alkali is taken in the burette.

At the beginning of the titration, the conductance of the HCl acid solution is due to H^+ and the Cl^- ions. When the alkali is added gradually from the burette, the fast moving hydrogen ions are replaced by slow moving sodium ions in the following way –

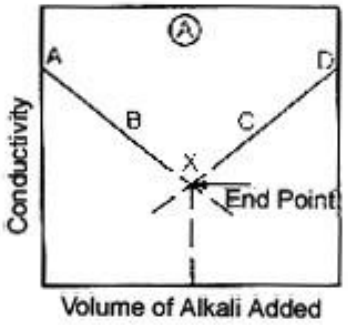
$$H^+ + Cl^- + [Na^+ + OH^-] \rightarrow Na^+ + Cl^- + H_2O \qquad \text{...... (1)}$$

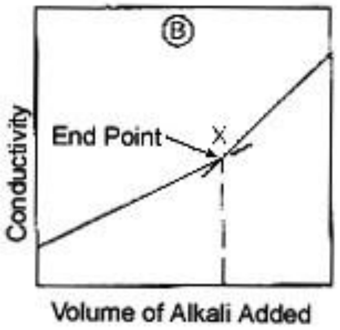
Hence, on continuous addition of sodium hydroxide, the conductance goes on decreasing till the neutralisation is complete. After the neutralisation, the further addition of alkali results in the increase in conductance against the volume of alkali added, the points will lie on a straight line, as in figure (A). The points of intersection (x) of these two lines AB and CD gives the volume of alkali required for the neutralisation.

Titration of a weak acid against a strong base

Consider the titration of a weak acid like acetic acid against a strong alkali like sodium hydroxide. At the beginning of the titration, the conductance of the solution will be very low because acetic acid is feebly ionized. When a small quantity of NaOH is added from the burette to CH_3COOH, the conductance increases due to the formation of highly ionised sodium acetate.

$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O \qquad \text{...... (2)}$$

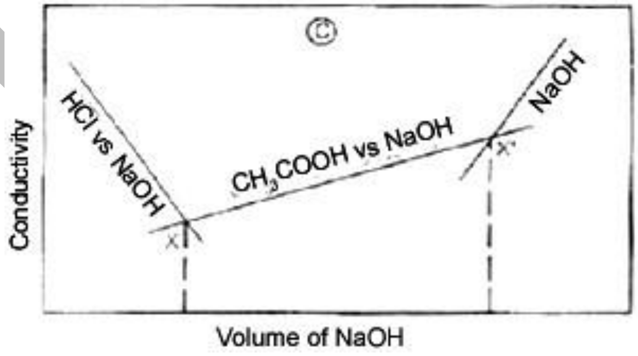




After the complete neutralisation of the acid, any further addition of alkali will show a sharp increase in conductance due to the fast moving hydroxide ion. The plot conductivity against volume of alkali added is shown in figure (B). The point of intersection (x) gives the end point.

Titration of a weak acid and a strong acid against a strong base

When a mixture of acetic acid and hydrochloride acid is titrated against sodium hydroxide, usually a combination of curves will be obtained. It will be as shown in the figure. In these types of titrations, the stronger acid (HCl) will get titrated first and the titration of the weak acid (CH_3COOH) will commence only after the complete neutralisation of the strong acid. It is very evident from the figure (C). While the first end point corresponds to the neutralisation of HCl, the second end point corresponds to the neutralisation of CH_3COOH.



Titration of a strong acid against a weak Base

In the titration of HCl and NH_4OH, the neutralisation processes may be shown as follows:

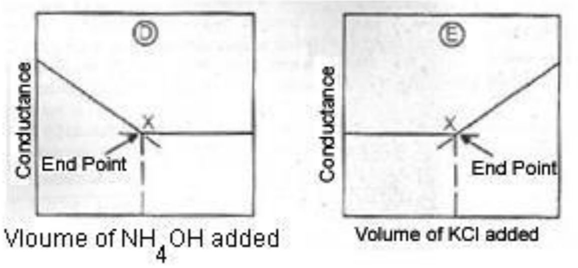
$$H^+ + Cl^- + NH_4OH \rightarrow NH_4^+ + Cl^- + H_2O \qquad \text{….. (3)}$$

When the base is added, the conductance will fall at first due to the replacement of fast moving H^+ ions by slow moving NH_4^+ ions. After the end point, further addition of NH_4OH will cause no change in conductance [Figure (D)] as the weakly ionized NH_4OH has a very small conductivity.

Conductometric precipitation titration

Many precipitation titrations are performed by conductometric methods. Consider the titration between silver nitrate and potassium chloride. The reaction involved may be represented as:

$$Ag^+ + NO_3^- + [K^+ + Cl^-] \rightarrow K^+ + NO_3^- + AgCl \qquad \text{…… (4)}$$



Potassium chloride is added to the silver nitrate solution. The conductance up to the end point will remain more or less constant because the mobility of potassium ions is nearly the same as that of the silver ions. After the end point, the conductance will begin to increase on the account of the addition of excess potassium chloride [Figure (E)].

Advantages of conductometric titrations

1. No special care is necessary near the end point, as the end point is ascertained graphically.
2. Coloured solutions, which cannot be titrated by ordinary volumetric methods with the help of indicators, can be titrated successfully.
3. The titrations of weak acids against weak base can be performed conductometrically. These are not possible in ordinary volumetric titration because they do not cause a sharp change in colour with indicators.
4. Very dilute solutions can also be titrated.

Hydrolysis of Salts

Hydrogen ion or hydroxyl ion is formed directly from the acid or base as a result of ionisation. But hydrogen ions and hydroxyl ions may be formed as a result of the reaction of an ion with water. The general type of reaction in which the cation or anion of a salt interact with the solvent water to form either hydrogen ions or hydroxyl ions, is called salt hydrolysis. Thus, the hydrolysis equilibrium represents a reverse reaction of ionisation equilibrium.

From the point of view of salt hydrolysis, salts may be divided into four categories as below-

i) Salts of strong acids and strong bases – for example, sodium chloride, potassium sulphate. These salts do not undergo hydrolysis because, the conjugate base and acid are very weak to hydrolyse water. The solution will be neutral.
ii) Salts of weak acids and strong bases – for example, ammonium acetate, potassium cyanide.
iii) Salts of strong acids and weak bases – for example, ammonium chloride, magnesium sulphate.
iv) Salts of weak acids and weak bases – for example, ammonium carbonate, ammonium acetate.

I. Hydrolysis of salt of Weak Acid and Strong Base

If the salt of weak acid and strong base represented as NaA is dissolved in water, the anion of the salt A^- will react with hydrogen ions of water to form almost unionised weak acid, HA.

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad ......(1)$$

Applying the Law of mass action to the above hydrolysis equilibrium,

$$K_h = \frac{[OH^-][HA]}{[A^-][H_2O]} \qquad ....(2)$$

Where, K_h is the hydrolysis constant of the salt.

The resulting solution will be basic, since an excess of hydroxyl ions are formed as a result of hydrolysis. This accounts for the well known fact that aqueous solutions of salts such as cyanides, acetates, borates and phosphates of alkali metals are basic.

We can calculate the extent to which hydrolysis occurs using a simple method. The ionisation equilibrium of the weak acid, HA may be written as,

$$HA \rightleftharpoons H^+ + A \qquad ......(3)$$

The ionisation constant of the weak acid is given by

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad ......(4)$$

The ionisation equilibrium of water may be written as,

$$H_2O \rightleftharpoons H^+ + OH \qquad ......(5)$$

Ionic product of water, $K_w = [H^+]\ [OH^-]$ ...... (6)

Dividing equation (6) by equation (4)

$$\frac{K_w}{K_a} = \frac{[H^+][OH^-][HA]}{[H^+][A^-]} \qquad ......(7)$$

$$\frac{K_w}{K_a} = \frac{[OH^-]\,[HA\ ]}{[A^-\ ]} \qquad \text{....... (8)}$$

We know, $K_h = \dfrac{[OH^-]\,[HA\ ]}{[A\ \ ]\,[H_2O]}$

But the concentration of water remains practically a constant and omitting it in the above equation.

$$K_h = \frac{[OH^-]\,[HA\ ]}{[A\ \ ]} \qquad \text{...... (9)}$$

Comparing equations (8) and (9)

$$K_h = \frac{K_w}{K_a} \qquad \text{......(10)}$$

Degree of hydrolysis

Definition: It may be defined as the fraction of each mole of the salt which gets hydrolysed when dissolved in water.

If h is the degree of hydrolysis and C is the concentration in mole per litre of the salt solution, then

$$\underset{C(1-h)}{A} + H_2O \rightleftharpoons \underset{Ch_-}{OH} + \underset{Ch}{HA} \qquad \text{........ (1)}$$

$$K_h = \frac{[OH\ \ ]\,[HA\ ]}{[A\ \ ]} \qquad \text{........(9)}$$

$$K_h = \frac{hC \times hC}{C(1-h)} = \frac{h^2C}{(1-h)} \qquad \text{.........(11)}$$

$$K_h \equiv h^2C \qquad \text{........(12)}$$

Or, $h^2 = \dfrac{K_h}{C}$ ....(13)

$$h = \sqrt{\frac{Kh}{C}} \qquad \text{........(14)}$$

$$\text{Since,} \quad K_h = \frac{K_w}{K_a} \qquad \text{........(10)}$$

$$h = \sqrt{\frac{K_w}{K_a C}} \qquad \text{........(15)}$$

From above discussion, it is clear that-

i) The hydrolysis constant, K_h is inversely proportional to the ionisation constant of the acid, K_a.

ii) The degree of hydrolysis (h) of the salt of a weak acid and strong base is inversely proportional to the square root of the initial concentration, C.

Again if the acid HA is weak, it is difficult to remove a proton from the acid. But the anion of the acid, A^- (i.e.) its conjugate base can easily take up a proton from water or the anion undergoes hydrolysis readily. Acetic acid is the moderately weak acid, but hydrocyanic acid is very weak acid. Hence, the cyanide ion is hydrolysed to a greater extent than acetate ion.

To summarize, the reaction of the salt of a strong base and weak acid with water, produces a basic solution.

II. Hydrolysis of the salt of a Weak Base and a Strong Acid

If the base BOH (for example, NH_4OH) is weak, its conjugate acid B^+ (i.e., NH_4^+) will be appreciably strong and hence it will tend to react with the solvent water as below :

$$B^+ + H_2O \rightleftharpoons BOH + H^+ \qquad \text{...... (1)}$$

Thus an excess of hydrogen ion is left and the resulting solution is therefore acidic. The equilibrium constant for the above hydrolysis reaction may be written as,

$$K_h = \frac{[BOH]\,[H^+]}{[B^+]\,[H_2O]} \qquad \text{...... (2)}$$

The ionisation equilibrium of the base may be written as

$$BOH \rightleftharpoons B^+ + OH^- \qquad \text{...... (3)}$$

The ionisation constant of the weak base is given by,

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]} \qquad \text{...... (4)}$$

The ionic product of water, K_w is given by

$$K_w = [H^+]\,[OH^-] \qquad \text{...... (5)}$$

Dividing equation (5) by equation (4)

$$\frac{K_w}{K_b} = \frac{[H^+]\,[OH^-]\,[BOH]}{[B^+]\,[OH^-]} \qquad \text{...... (6)}$$

$$\frac{K_w}{K_b} = \frac{[H^+]\,[BOH]}{[B^+]} \qquad \text{...... (7)}$$

The concentration of water remains practically a constant and hence omitting it in the equation (2) we have,

$$K_h = \frac{[H^+]\,[BOH]}{[B^+]} \qquad \text{...... (8)}$$

Comparing equation (7) with equation (8) we have,

$$K_h = \frac{K_w}{K_b} \qquad \text{...... (9)}$$

Degree of hydrolysis, h: If h is the degree of hydrolysis and C is the concentration in moles per litre of the salt solution, then

$$\underset{C(1-h)}{B^+} + H_2O \quad \underset{Ch}{BOH} + \underset{Ch}{H^+} \qquad \text{...... (1)}$$

$$K_h = \frac{[BOH]\,[H^+]}{[B^+]}$$

. ...(8)

$$\rightleftharpoons$$

$$K_h = \frac{hC \times hC}{\cancel{C(1-h)}} = \frac{h^2C}{(1-h)} \qquad .....(9)$$

$$K_h = h^2C \qquad ....(10)$$

or

$$h^2 = K_h/C \qquad ......(11)$$

$$h = \sqrt{K_h/C} \qquad .....(12)$$

Since,

$$K_h = \frac{K_w}{K_b}$$

$$h = \sqrt{\frac{K_w}{K_bC}} \qquad ....(13)$$

Thus the hydrolysis constant, K_h is inversely proportional to the ionisation constant of the base, K_b

The degree of hydrolysis is inversely proportional to the square root of the initial concentration, C.

The reaction of the salt of weak base and strong acid with water produces an acidic solution.

III. Hydrolysis of the salt by Weak Acid and Weak Base

In this case, since both the acid and base are weak, their conjugate pairs are strong and will appreciably interact with water. Such salts are therefore considerably hydrolysed in aqueous solution.

The hydrolysis equilibrium of the salt of a weak acid and weak base (BA) may be written as,

$$B^+ + A + H_2O \rightleftharpoons BOH + HA \qquad ......(1)$$

$$K_h = \frac{[BOH]\,[HA]}{[B^+]\,[A\ \ ][H_2O]} \qquad ......(2)$$

The ionisation constant of the acid, HA is given by,

$$HA \rightleftharpoons H^{+} + A \qquad ......(3)$$

$$K_a = \frac{[H^{+}]\,[A^{-}]}{[HA]} \qquad ......(4)$$

The ionisation constant of the base, BOH is given by

$$[BOH] \rightleftharpoons B^{+} + [OH^{-}] \qquad ......(5)$$

$$K_b = \frac{[B^{+}][OH^{-}]}{[BOH]} \qquad ......(6)$$

The ionic product of water, $K_w = [H^{+}]\,[OH^{-}]$ ......(7)

Dividing the equation (7) by the product of equations (4) and (6) we have,

$$\frac{K_w}{K_a K_b} = \frac{[H^{+}]\,[OH^{-}]\,[BOH]\,[HA]}{[H^{+}][A^{-}][OH^{-}][B^{+}]} \qquad ......(8)$$

$$\frac{K_w}{K_a K_b} = \frac{[HA]\,[BOH]}{[B^{+}][A^{-}]} \qquad ......(9)$$

Omitting the concentration of water in equation (2)

$$K_h = \frac{[BOH][HA]}{[B^{+}][A^{-}]} \qquad ......(10)$$

Comparing the equation (9) with (10) we have

$$K_h = \frac{K_w}{K_a K_b} \qquad .... (11)$$

Thus, the hydrolysis constant K_h of the salt of the weak acid & a weak base is inversely proportional to the ionisation constant of the acid & base.

If h is degree of hydrolysis and C is the concentration of the weak acid & weak base in moles per litre.

$$\underset{C(1-h)}{B^+} + \underset{C(1-h)}{A^-} + H_2O \rightleftharpoons \underset{Ch}{BOH} + \underset{Ch}{HA} \qquad \text{......} \ (12)$$

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]}$$

$$K_h = \frac{Ch \times Ch}{C(1-h)\ C(1-h)} \qquad \text{........} \ (13)$$

$$K_h = \frac{h^2}{(1-h)^2} \qquad \text{.......} \ (14)$$

$$K_h = h^2 \qquad \text{..........}(15)$$

$$\text{or,} \quad h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}} \qquad \text{........}(16)$$

Thus the degree of the hydrolysis of the salt of a weak acid & weak base is independent of the initial concentration of the salt solution.

Note: the ultimate nature of these solutions will depend upon the relative hydrolysis of the anion and cation.

i) If both anion & cation react to the same extent with water, then the solution is neutral.
ii) If the cation reacts to a larger extent with water than the anion, the solution is slightly acidic. (Eg. ammonium acetate)
iii) If the anion reacts to a larger extent with water than the cation, the solution is slightly basic. (Eg. ammonium carbonate)

Worked Example

1. Calculate the percentage of hydrolysis of 0.01 M solution of ammonium acetate. K_a for acetic acid is 1.8×10^{-5} and K_b for ammonium hydroxide is 1.8×10^{-5}.

$$h = K_w/K_a \times K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} \times 1.8 \times 10^{-5}$$

$$= \mathbf{0.00555}$$

Galvanic Cell

Standard Electrode Potential

While a chemical reaction is produced using an external resource of electricity in an electrolytic cell, a chemical reaction is made use of to produce electric current in a Galvanic of electro chemical cell. An electrochemical cell has two electrodes or two half cells. The electrode may be any system that consists of an element in contact with a solution containing its ions or an arrangement equivalent to it. For instance, copper metal in contact with $CuSO_4$ solution or Cu^{2+} ions is known as copper electrode and is represented as

$Cu | Cu^{2+}$ The interfaces, across which a potential difference exists, are shown by a single vertical line.

Chlorine gas, bubbled on the surface of an inert metal like platinum, in contact with a solution of chloride ions is known as chlorine electrode and is denoted by:

$$Pt, Cl_{2(g)} \mid Cl^-$$

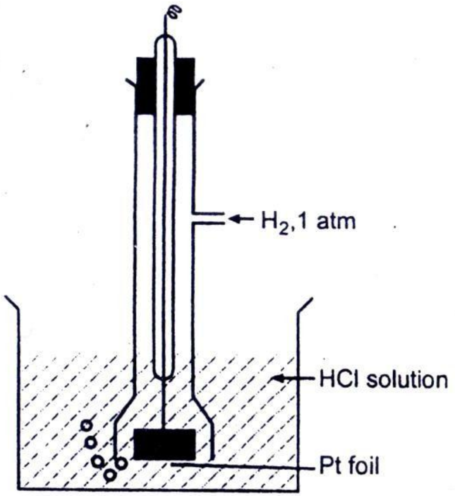
If a piece of metal is placed in a solution containing its ions, then a potential difference known as electrode potential of the metal will be set up between the metal and the solution. For example, if a rod of zinc is kept in a beaker containing zinc sulphate solution, the zinc will be negatively charged with respect to the solution and will maintain a constant potential difference provided the conditions are not altered. On the other hand, when copper is placed in contact with copper sulphate solution, the metal assumes a different charge with respect to the solution and its electrode potential is smaller. Thus, the potential generated by an electrode is known as single electrode potential. This is an equilibrium potential which arises as a result of two opposing tendencies of the metal or chlorine. They are–

1) When the metal is placed in the solution, some of its atoms tend to give up electrons to the piece of metal and go into solution as positively charged.

2) The metallic ions present already in the solution tend to take up electrons from the piece of metal and deposit themselves as neutral atom.

The potential set up when an electrode is in contact with a molar solution of its ion at 298 K is arbitrarily chosen as the standard electrode potential of the element.

It is not possible to determine the absolute value of an electrode potential directly since in doing so another electrode must necessarily be introduced to complete the circuit and it will have an electrode potential of its own. This difficult has been overcome by adopting the standard electrode potential of one particular element, hydrogen, as an arbitrary standard and giving it the value zero. The normal hydrogen electrode which is used as a standard is shown in the following figure.



It consists of a piece of platinum foil which is coated electrolytically with a form of very finely divided platinum black to give it a large surface area, suspended in a molar solution of H^+ ions. Pure hydrogen gas at one atmospheric pressure is continually bubbled into the solution to keep it saturated and to expose the foil alternatively to gas and solution. The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution. In any measurement of electrode potential, the two electrodes are electrolytically joined. A salt bridge containing a concentrated solution of potassium chloride is commonly used to provide a highly conducting path between the two. The potential difference is measured by means of a potentiometer using a standard cell like Weston Standard cell of e.m.f. 1.01830 volts at 298 K for comparison. The potential difference is known as the standard potential of the element on the hydrogen scale.

The standard (reduction) potential of the electrodes along with the electrode reactions at 298 K are reported in the table. This is known as electrochemical series or electromotive series.

The greater the negative value of the standard electrode potential given in the table, the greater is the tendency of the reduced form to lose electrons and get oxidised. Thus, lithium has the maximum negative value (-3.02 volts) and it has, therefore, the maximum negative tendency to lose electron and get oxidised to Li^+ ion. Similarly, other active metals like K, Ca, Na, Mg and Zn have strong tendency to lose electrons and get oxidised. These active metals are capable of liberating hydrogen from aqueous solutions of acids.

Calculations of cell EMF from single electrode potential

Any electrochemical reaction is the sum of the two electrode reactions, of which one is an oxidation, the other a reduction. Similarly, every cell e.m.f. may be thought of as being composed of two individual single electrode potential such that their algebraic sum is equal to the total electromotive force (e.m.f.) of the cell.

Sl.No.	Electrodes	Electrode reaction	Potential in Volt
1	Li^+ , Li	$Li^+ + e^- \leftrightharpoons Li$	-3.02
2	K^+ , K	$K^+ + e^- \leftrightharpoons K$	-2.92
3	Ca^{2+} , Ca	$Ca^{2+} + 2e^- \leftrightharpoons Ca$	-2.87
4	Na^+ , Na	$Na^+ + e^- \leftrightharpoons Na$	-2.71
5	Mg^{2+} , Mg	$Mg^{2+} + 2e^- \leftrightharpoons Mg$	-2.38
6	Al^{3+} , Al	$Al^{3+} + 3e^- \leftrightharpoons Al$	-1.67
7	Zn^{2+} , Zn	$Zn^{2+} + 2e^- \leftrightharpoons Zn$	-0.76
8	Fe^{2+} , Fe	$Fe^{2+} + 2e^- \leftrightharpoons Fe$	-0.44
9	Cd^{2+} , Cd	$Cd^{2+} +2 e^- \leftrightharpoons Cd$	-.0.40
10	Sn^{2+} , Sn	$Sn^{2+} +2 e^- \leftrightharpoons Sn$	-0.14
11	Pb^{2+} , Pb	$Pb^{2+} + 2e^- \leftrightharpoons Pb$	-0.11
12	**$2H^+$, H_2, Pt**	**$2H^+ + 2e^- \leftrightharpoons H_2$**	**0.00**
13	Cu^{2+} , Cu	$Cu^{2+} + 2e^- \leftrightharpoons Cu$	+0.34
14	Fe^{3+} , Fe^{2+}	$Fe^{3+} + e^- \leftrightharpoons Fe^{2+}$	+0.77
15	Ag^+ , Ag	$Ag^+ + e^- \leftrightharpoons Ag$	+0.80
16	Hg_2^{2+} , 2Hg	$Hg_2^{2+} + 2e^- \leftrightharpoons 2Hg$	+0.80
17	Au^+ ,Au	$Au^+ + e^- \leftrightharpoons Au$	+1.68

Electro chemical series

The sequence of elements in table 1 is known as electrochemical series or the activity series. A more complete list would be

a) Li, K, Ba, Sr, Ca, Na, Mg , Be, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, H, Cu, Ag, Hg, Au, Ce;

b) H_2O, H, SO_4^{2-} , I_2, NO_3^-, Br_2 ,O_2, $Cr_2O_7^-$, Cl_2, MnO_4^-, O_3, F_2 (all with reference to standard reduction potentials at 25°C)

Applications

(1) Of the metals listed, lithium is the strongest reducing agent; it donates its electrons most readily and cerium most reluctantly. The ease with which a metal loses electrons is directly

linked to the values of its electrode potential and hence its position in the electrochemical series. The series closely approximate to the order of reactivity of metals.

(2) Many of the reactions of metals can be summarized using either the periodic table or the activity series. The reactions of some common metals with oxygen, chlorine, water, steam and dilute acids could be predicted by writing them in the same order as they in the activity series.

(3) Lithium to sodium displaces hydrogen from water; Lithium to iron displace hydrogen from steam; Lithium to lead displace hydrogen from acids. Metals listed above hydrogen alone displace hydrogen like this.

(4) A metal can displacing from a compound any metal listed below it (Table1) but it cannot displace any metal above it. For example, when metallic zinc is added to a solution of copper sulphate, zinc displaces metallic copper. Similarly copper displaces silver from silver nitrate solution, turning the solution blue gradually due to the formation of Cu^{2+}(aq). Copper cannot displace zinc from zinc sulphate solution and silver cannot displace copper from a solution of copper nitrate.

(5) The series also applies to halogens, regarding displacement. Molecular fluorine can displace other halogens from their halides; molecular chlorine can displace bromine and iodine from the respective halides but not fluorine from displace fluorides, similarly,

Br_2 (I) +2 KI(aq) ➔ 2KBr(aq) +I_2 (s)

but, $I_{2(s)}$ +2KBr (aq) ➔ no reaction , and so on.

It should be noted that whereas the reactivity of metals increases as the electrode potentials become more negative, the reactivity of the non-metals increases as the electrode potentials become more positive. Non- metals lower down in the series are strong oxidants.

(6) Metals low in the series are very stable in their reduced form whereas those high in the series are relatively unstable. These metals oxidise readily. All metals above gold in the series occur as oxide ores. To obtain these as pure metals it is therefore necessary to reduce the oxidised forms.

(7) Corrosion is an oxidation process which occurs at the surface of a metal. The corrosion may be due to the reaction with oxygen, acids or other compounds. Gold which is at the bottom of the series does not corrode.

(8) During electrolysis metals (more electro/ positive) are increasingly difficult to discharge, but non-metallic ions discharge more easily as the electrode potentials become more negative.

Thus, the electrochemical series can be used to predict (a) the feasibility of a displacement reaction, (b) the order of discharge of ions during electrolysis and (c) in general reactivity of elements.

When the single electrode potential and reactions are available, the e.m.f. may be calculated. Suppose it is desired to know the reaction and the e.m.f. at 298 K for the cell:

$$\mathrm{Fe} \mid \mathrm{Fe^{2+}} \parallel \mathrm{Cu^{2+}} \mid \mathrm{Cu} \qquad \text{........(1)}$$

The contact between the two solutions with help of a salt bridge is indicated by a double vertical line | |.

Assume that the cell as written is correct, i.e. that the iron electrode is negative (oxidation occurs). Then, for the oxidation at the iron electrode, we have,

$$\mathrm{Fe} \rightleftharpoons \mathrm{Fe^{2+}} + 2e^- \quad ; E_{298K} = 0.44 \text{ volt} \qquad \text{.......(2)}$$

Again for the reduction at the copper electrode, we get,

$$\mathrm{Cu^{2+}} + 2e^- \rightleftharpoons \mathrm{Cu} \quad ; E_{298K} = 0.34 \text{ volt} \qquad \text{........(3)}$$

Adding now the single electrode reactions and the single electrode potential, we find,

$$\mathrm{Fe} \rightleftharpoons \mathrm{Fe^{2+}} + 2e^- \quad ; E_{298K} = 0.44 \text{ volt}$$

$$\mathrm{Cu^{2+}} + 2e^- \rightleftharpoons \mathrm{Cu} \quad ; E_{298K} = 0.34 \text{ volt}$$

$$\mathrm{Fe} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{Cu} \quad ; E_{298K} = 0.78 \text{ volt} \qquad \text{........(4)}$$

Thus, the cell reaction is:

$$\mathrm{Fe} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{Cu}$$

and the e.m.f. of this cell at 298 K = 0.78 volt.

Since the calculated e.m.f. is positive, the assumption made with respect to the electrodes is correct and the cell reaction as given is the spontaneous one.

On the other hand, had we assumed the copper electrode to be negative and iron electrode to be positive then the cell is written as,

$$Cu \,|\, Cu^{2+} \,||\, Fe^{2+} \,|\, Fe \qquad \text{........(5)}$$

The cell reaction is,

$$Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu \qquad \text{........(6)}$$

and the e.m.f. at 298 K is -0.78 volts.

Since the e.m.f. is negative the reaction written in equation (6) is not spontaneous and consequently the wrong assumption was made with electrodes.

BUFFER SOLUTION

Pure water is neutral and it has pH value of 7. If a small amount of HCl is added, the pH value becomes less than 7 and if a small amount of NaOH is added, the pH becomes greater than 7. If we take a mixture of acetic acid and sodium acetate, the pH of the mixture does not change considerably even after the addition of small amount of HCl or NaOH. Such a mixture whose pH remains constant even after the addition of small amount of acid or base is called buffer solution.

The word buffer is derived from the German word, Puffer.

The resistance to change in pH on the addition of acid or base is known as buffer action.

The magnitude of buffer action of a given buffer solution is determined by its buffer capacity.

Buffer solutions usually consist of a solution of weak acid or a weak base in the presence of its salts. Some examples are –

i) Acetic acid and sodium acetate
ii) Boric acid and borax
iii) Citric acid and sodium citrate
iv) Phthalic acid and potassium hydrogen phthalate
v) Ammonium chloride and ammonium hydroxide
vi) Borax and sodium hydroxide

vii) Sodium carbonate and sodium bicarbonate.

Buffer action: *The reactions responsible for maintaining constant pH after the addition of acid or base in buffer solutions are called buffer action*. The buffer action of acetic acid and sodium acetate mixture can be explained as follows –

Acetic acid is a weak acid and is partially ionised as below :

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Sodium acetate is a strong electrolyte and is completely ionised.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

When a small amount of acid is added to this mixture, H_3O^+ ions of the acid combines with equal number of acetate ions to form acetic acid molecules. Therefore, the net $[H_3O^+]$ and pH remains constant.

$$CH_3COO^- + H_3O^+ \longrightarrow CH_3COOH + H_2O$$

When a small amount of base is added, the OH^- ions of the base neutralises acetic acid molecules to form sodium acetate. Therefore the net $[H_3O^+]$ and pH remains constant.

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

In the case of ammonium hydroxide – ammonium chloride buffer mixture, the buffer action is as follows –

Ammonium hydroxide being a weak base is partially ionised.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Ammonium chloride is a strong electrolyte and is completely ionised.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

When a small amount of base is added to this mixture, the OH^- ions of the base combine with equal number of NH_4^+ ions to give NH_4OH.

Therefore, the $[OH^-]$, pOH and pH of the solution remains constant.

When a small amount of acid is added to the mixture, H_3O^+ ions of the acid are neutralised by NH_4OH to form NH_4^+ and water.

$$NH_4OH + H_3O^+ \longrightarrow NH_4^+ + 2H_2O$$

Therefore, the $[OH^-]$, pOH and pH of the solution remains constant.

Buffer solution in the Biological systems

Buffer and hydrogen ion concentration assume prime place in many reactions of biological. Any alteration in the pH value may lead to pathological condition. Few instances are given in this section.

1) The pH of normal human blood is 7.35 and remains constant. Carbonic acid and bicarbonate or the electrolytes in the body act as the buffer solution and control the pH of the blood. For a diabetic person, the value of pH falls to 6.8.
2) The value of pH of gastric juice lies in the pH range 1.4 to 2.0. The increase of pH causes vomiting and ulceration.
3) The activity and the efficiency of the enzymes, the biocatalysts, depend on the pH. The control of pH is very important for the digestive system because the efficiency of digestive enzyme is maximum only at a specific pH. Any deviation from the pH values hinder or even stop the action of the biocatalysts.

For example, the enzyme, pepsin is effective at pH 1.4 to 2 in the stomach.

4) Many biochemical reactions are to be carried out at constant pH in the laboratory.

pH AND ITS DETERMINATION

Water is a weak electrolyte and is known to be slightly ionised as:

$$H_2O \rightleftharpoons H^+ + OH^- \quad \ldots\ldots(1)$$

Applying law of mass action to the above equilibrium

$$K = \frac{[H^+]\ [OH^-]}{[H_2O]} \quad \ldots\ldots\ (2)$$

Where, K the equilibrium constant. As the concentration of un-ionised water is considered to be a constant, the above equation (2) becomes

$$K = \frac{[H^+]\ [OH^-]}{k} \quad \text{.........(3)}$$

$$\text{or,} \quad Kk = [H^+]\ [OH^-] \quad \text{.......(4)}$$

K_w is the ionic product of water and its numerical value at 298 K is 1×10^{-14} . In the case of pure, neutral water,

$$[H^+] = [OH^-] = 1 \text{ X } 10^{-7} \text{ mole/lit} \quad \text{.......(5)}$$

If the concentration of hydrogen ion is more than 10^{-7}, the solution is acidic. If it is less than 10^{-7}, the solution is *alkaline*.

This way of expressing hydrogen ion concentration is cumbersome. A more convenient way, without the use of negative exponent is desirable. Sorenson, a Danish biochemist in 1909, introduced a new scale called, pH scale to express the hydrogen ion concentration. According to him, pH of a solution is the negative logarithm of the hydrogen ion concentration.

$$pH = -\log[H^+] = \log \frac{1}{[H^+]} \quad \text{........(6)}$$

For pure water, $[H^+] = 1 \text{ X} 10^{-7}$ and hence, pH = 7

If the value of pH is less than 7, the solution is acidic.

If pH is greater than 7, it is *alkaline*.

As pH expresses the scale of acidity, just in the same way, pOH expresses the scale of alkalinity. It may be given as

$$pOH = -\log [OH^-] = \log \frac{1}{[OH\ \ ]} \quad \text{....... (7)}$$

$$\text{and} \quad pH + pOH = pKw = 14 \quad \text{....... (8)}$$

WORKED EXAMPLE

1. What would be the pH value of
   a) 0.0001 N HCl b) 0.005 M H_2SO_4 c) 0.005 N NaOH?
   a) Concentration of H^+ ions in 0.0001 N HCl
   = 0.0001 g. ion / lit.

$$[H^+] = 1 \times 10^{-4}$$

$$\log [H^+] = \log (1 \times 10^{-4})$$

$$\log [H^+] = -4$$

$$\therefore \quad -\log [H^+] = pH = \mathbf{4}.$$

b) Concentration of H^+ ions in 0.005 M H_2SO_4 is 2 × 0.005 g. ion / lit. Because sulphuric acid is dibasic, it undergoes the dissociation in the following way:

$$\underset{0.005\ M}{H_2SO_4} \longrightarrow \underset{2 \times 0.005 = 0.01}{2H^+ + SO_4^{2-}}$$

$$\therefore \ [H^+] = 1 \times 10^{-2}$$

$$\therefore \ pH = 2$$

c) Concentration of OH^- ions in 0.005 N NaOH,

$$[OH^-] = 5 \times 10^{-3}$$

$$\log [OH^-] = \log (5 \times 10^{-3}) = -3 + \log 5$$

$$= -3 + 0.6990 = -2.3010$$

$$-\log [OH^-] = 2.3010 = pOH$$

Therefore, $pH = 14 - pOH = 14 - 2.3010 = \mathbf{11.7}$

* * * * * * * *

A number of methods are available for the determination of pH of a solution. Some of them are –

1) Colorimetric method
2) The conductivity method
3) The electromotive force method
4) The catalytic method
5) The freezing point method
6) The pH metre method

We shall discuss few methods in detail in this section.

Colorimetric method

The pH is measured by noting the various colour changes in this method. A universal indicator (e.g., B.D.H. universal indicator) and various buffer solutions in the pH range 3 to 11 are prepared. A drop of universal indicator is added to each buffer solution and the colour change is noted. Then, few drops of universal indicator are added to the solution of unknown pH. The colour of this solution is compared with the suitable buffer solution and the pH may be determined. Comparators are employed for the matching of colour tints. Hellige comparator is generally used in water analysis.

Conductivity method

Consider the ionisation equilibrium of the weak mono basic acid HA as:

$$\begin{array}{lcccc} & HA & \rightleftharpoons & H^{+} & + & A^{-} \\ \text{Initial Concentration} & C & & 0 & & 0 \\ \text{Equil. Concentration} & C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

Application of the law of mass action to this ionic equilibrium, gives the value of dissociation constant, K_a for the acid:

$$K_a = \frac{[H+]\,[A^{-}]}{[HA]} \qquad \text{........(9)}$$

$$= \frac{C\alpha \times C\alpha}{C\,(1-\alpha)} = \frac{C\alpha^{2}}{(1-\alpha)} \qquad \text{........(10)}$$

If the acid ionises to a very small extent, α is very small and may be neglected in comparison with unity.

$$\text{Then, } K_a = C\alpha^{2}$$

$$\text{and, } \quad \alpha = \sqrt{\frac{K_a}{C}} = \frac{\lambda_c}{\lambda_\infty} \qquad \text{........(11)}$$

Where, α is the degree of dissociation, λ_c and λ_∞ are the equivalent conductance of the acid at the given concentration (λ_c) and that of at infinite dilution (λ_∞) and are determined experimentally.

$$\text{But,} \quad [H^+] = C\alpha \qquad \text{........(12)}$$

Thus, the degree of dissociation is a direct measure of hydrogen ion concentration.

$$[H^+] = C\alpha \qquad \text{........(13)}$$

$$= C\sqrt{\frac{K_a}{C}} = \sqrt{K_a C} \qquad \text{........(14)}$$

Thus, the hydrogen ion concentration in a solution of a weak acid in water at a given concentration is directly proportional to the square root of the dissociation constant of the acid.

Electromotive force method

This is a more accurate and precise method for the measurement of hydrogen ion concentration or pH determination.

When a hydrogen electrode is in contact with a solution of hydrogen ions of unknown pH, the following reaction takes place.

$$H^+ + e^- \rightleftharpoons 1/2\ H_2\ (1\ \text{atm}) \qquad \text{........(1)}$$

The voltage produced is given by Nernst equation (The derivation of this equation is beyond the scope of this book) as,

$$E_{(H^+, H_2)} = E_o (H^+, H_2) + 2.303 \frac{RT}{F} \log [H^+] \qquad \text{........(2)}$$

Where, $E_o (H^+, H_2)$ is the standard electrode potential of hydrogen electrode and its value is zero conventionally.

R is the universal gas constant,

F is the Faraday constant and

T is the temperature expressed in absolute scale.

$$\therefore E_{(H^+, H_2)} = 2.303 \frac{RT}{F} \log [H^+] \qquad ....(3)$$

Substituting, R=8.314 Joules, F= 96500 Coulombs and T = 298 K, then,

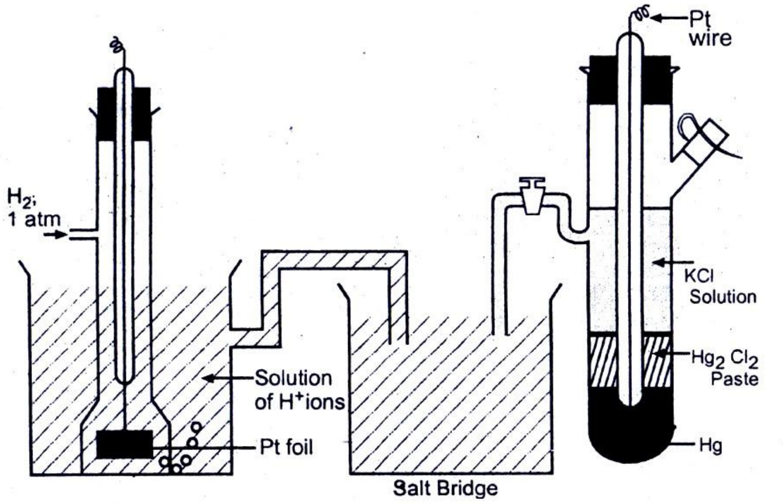
$$\frac{2.303\ RT}{F} = \frac{2.303 \times 8.134 \times 298}{96500} = 0.0591 \text{ at } 298 \text{ K} \qquad ....(4)$$

Substituting the value of equation (4) in (3)

$$E_{(H^+, H_2)} = 0.0591 \log [H^+]$$

$$= -0.0591 \text{ pH} \qquad ....(5)$$

It is evident that the potential of the hydrogen electrode depends upon the pH value of the solution with which it is in contact. Thus, the pH can be determined by combining the hydrogen electrode with a reference electrode, usually, a calomel electrode. A salt bridge of saturated or normal solution of potassium chloride is inserted in between the two electrodes to eliminate the liquid junction potential. The whole arrangement is shown in the figure.



The complete cell is represented as:

$$\text{Pt, } H_2 \text{ (1 atm)} \left| \begin{array}{l} H^+ \\ (C = \text{unknown}) \end{array} \right| \begin{array}{l} KCl \\ \text{Sat.Soln.} \end{array} \quad Hg_2Cl_2 \text{ (sat)} \left| \text{ Hg} \right. \qquad .... (6)$$

$$E_{cell} = E_{calomel\ (reduction)} - E_{(H^+,\ H_2\ (reduction)} \qquad ..... (7)$$

$= 0.2422 – (-0.0591 \text{ pH})$

$= 0.2422 + 0.0591 \text{ pH}$

$\therefore \text{pH} = E_{cell} - 0.2422 / 0.0591$ ….. (8)

By knowing the observed potential of the cell, the pH can be determined. However, the hydrogen electrode has the following defects-

1. It is not suitable for the ions having positive reduction potential e.g Cu, Ag and Au etc.
2. It cannot be employed for the solution of oxidising agents.
3. It is not suitable for unsaturated organic compounds.

From the above discussion, it is evident that some other pH indicating electrode is required. We discuss the following electrodes.

1. Glass electrode
2. Quinhydrone electrode

Glass Electrode

Glass electrode is used most commonly to determine the pH of unknown solution. It has been found by experiment that if a thin glass membrane separates two solutions, a potential is developed across the membrane. The magnitude of this potential depends on the pH of the solution.

The glass electrode consists of a thin walled glass bulb of relatively low melting and high electrical conductivity. A solution of constant pH (usually 0.1 M HCl) is taken in the bulb. A platinum wire (or Ag-AgCl electrode) is inserted to make the electrical contact. Calomel electrode is employed as reference electrode. The arrangement may be represented as.

Pt, 0.1 M HCl | glass || unknown solution | Satd. Calomel electrode

The e.m.f. of the cell is determined using a potentiometer. As we know the potential of the calomel electrode (0.2422 volt), that of the glass electrode can be easily calculated and the pH of the unknown solution is evaluated.

Advantages

The glass electrode has a number of advantages–

i) It can be used in strong oxidising solutions.
ii) It can be used in the presence of metallic ions and poisons.

iii) It is useful in the determination of pH value of coloured solution, colloidal solutions and biological fluids.
iv) It can be used in non-aqueous solutions also.
v) It can be employed in the wide pH range (0-9).
vi) A small (or even micro) quantity of the solution is sufficient for the determination of pH.

Disadvantages

i) The glass electrode does not function properly in strongly acid or strongly alkaline solution.
ii) The glass membrane of the electrode has an extremely high resistance. Hence, ordinary potentiometer cannot be used to measure the potential. Quadrant electrometers or vacuum Tube Volt Meters (VTVM) are used in such cases.

Quinhydrone electrode

Quinhydrone electrode is a kind of redox electrode. Quinhydrone is an equimolecular compound of quinone, ($C_6H_4O_2$, Q) and hydroquinone ($C_6H_6O_2$, QH_2) and when placed in solution, the following equilibrium is established.

$$C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_6O_2$$

$$\text{or,} \quad Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

A potential is established when a platinum electrode is immersed in a solution containing both Q and QH_2. The potential depends on the ratio of the concentrations of Q, QH_2 and $[H^+]$ of the system and is given by Nernst equation,

$$E = E_0 - \frac{2.303\ RT}{2F} \log \frac{[QH_2]}{[Q]\,[H^+]^2}$$

This equation can be rewritten as,

$$E = E_0 - \frac{2.303\ RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303\ RT}{F} \log [H^+]$$

As the quinhydrone is equimolecular compound of Q and QH_2 the e.m.f. is given by

$$E = E_0 + \frac{2.303\ RT}{F}\ \log\ [H^+]$$

$$= E_0 + 0.0591\ \log\ [H^+]\ \text{at}\ 298\ K$$

$$= E_0 - 0.0591\ pH$$

The value of E_0 has been found to be 0.6996 Volt.

$$\therefore E = 0.6996 - 0.0591\ pH$$

If this electrode is combined with any other reference electrode (say, saturated calomel electrode) and if the e.m.f. of the cell is determined, it is possible to calculate the pH of the solution

Satd. Calomel electrode | Unknown solution Q QH_2 Pt

$$E_{Cell} = (0.6996 - 0.0591\ pH) - 0.2422$$

$$\text{or, } 0.0591\ pH = 0.6996 - 0.2422 - E_{Cell}$$

$$pH = \frac{(0.6996 - 0.2422 - E_{cell})}{(0.0591)}$$

Advantages

i) It is easy to set.
ii) It is not bulky or space occupying.
iii) It is not easily poisoned by impurities.
iv) It can be used even when solutes are volatile.
v) It is useful in titrations.
vi) It can withstand the presence of some oxidising and reducing agents.

Disadvantages

i) Quinone forms complexes with amino acids. Hence, this electrode cannot be used in alkaline solution.
ii) As it is prone to easy oxidation by air and ionisation at pH values above 8, it cannot be used for solutions of pH more than 8.

Electroplating

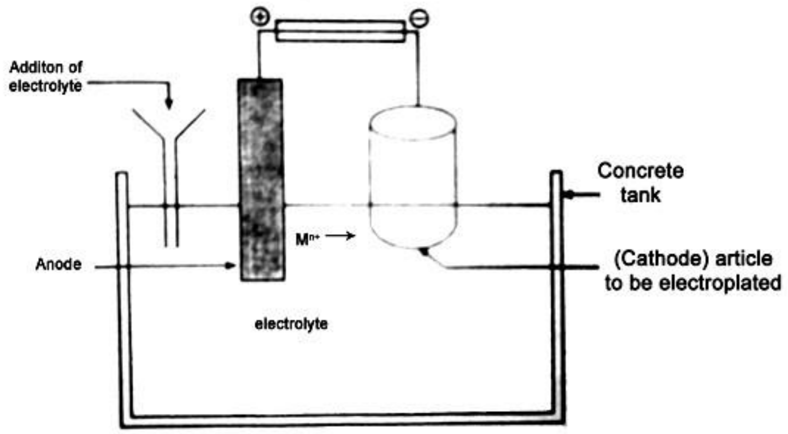
Electroplating is the art of depositing one metal over another metal with the help of electric current.

The primary reaction in electroplating is the deposition of metal from ions in solutions. The concentration of these ions in solution can be maintained in the following two ways –

i. By the addition of soluble salt of the metal.
ii. By the use of continuously dissolving anode of the metal.

The deposited metal must possess some superior properties. The iron articles are coated with tin, zinc, chromium, nickel etc. to prevent rusting and thus increases their life. Baser metals are coated with gold and silver to enhance their beauty. Since electroplating is used both for decoration and protection of the base metal from corrosion, it is important to secure a coating which is adherent, coherent, continuous and uniform.

Procedure: Electroplating is carried out in a tank which is, made of iron, concrete, soap stone, stoneware, cement, wood etc. For small scale work, it may consist of glass, enameled iron etc. It may be lined inside with a suitable material like rubber, lead or asphalt. The plates are hung in this tank from rods horizontally and its top is known as **bus-bars** which are insulated from the tank by using hard rubber.



A number of tanks are generally worked out at the same time and these may be setup in series or in parallel. The article to be electroplated is made cathode and the anode consists of the metal to be deposited or of the some insoluble substance (as in chrome plating, where lead is used as anode). Some features of electroplating are summarised in the following table.

Metal deposited	Anode	Electrolyte	Remarks
Chromium	Lead+80% Antimony	25% CrO_3 + 0.25% H_2SO_4	_
Nickel	98% Ni + NiO	30% $NiSO_4$ + 2% $NiCl_2$ + 1.25% H_3BO_3	Soft deposit as undercoat for chrome plating
Copper	Copper with lead	15-20% $CuSO_4$ +3.5% H_2SO_4 +Colloidal addition agents	Suitable for thick deposits
Zinc	Zinc or Zinc amalgam	30% $ZnSO_4$ +1.3% NaCl + 2% H_3BO_3 + 2.6% $Al_2(SO_4)_3$ + 1.3% dextrin	_
Silver	Silver	3.5% AgCN + 3.7% KCN + 3.8% K_2CO_3	CS_2 or KNO_3 used as brighteners
Gold	Gold	3.4% AuCN + 19% KCN + Na_3PO_4	Before gold plating, copper or brass plated.

Text Books:

1. Veeraiyan, V., & Vasudevan, A.N.S. (2012). *Text Book of Allied Chemistry* (II Edition). Chennai: Highmount Publishing House.

2. Puri, B. R., Sharma, L. R. & Pathania, M. S. (2014). *Elements of Physical Chemistry* (46th Edition). Jalandhar: Vishal Publishing Company Co.

Reference Book:

1. Gopalan, R., & Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. Define Kohlrausch law.
2. What are the merits of conductometric titrations?
3. Calculate the pH of M/200 KOH; $K_W = 10^{-14}$.
4. Define degree of hydrolysis.
5. How is the pH of a solution determined colorimetrically?
6. Discuss, citing two examples, the utility of conductometric titrations in analytical chemistry.
7. What are buffer solutions? Give examples.
8. Define buffer action.
9. Explain why NaCl does not undergo hydrolysis.
10. Define degree of ionisation.
11. What are the disadvantages of quinhydrone electrode?
12. Mention the disadvantages of glass electrode.
13. Bring out the any three advantages of glass electrode.
14. Write the pH value of (a) pure water (b) acidic solution (c) basic solution.
15. Define degree of dissociation.

PART-C (Each Question Carry Six Marks)

1. (i) What are the advantages of conductometric titrations?
   (ii) Describe the determination of the solubility of silver chloride using Kohlrausch law.
2. What is the principle underlying conductometric titration? Discuss the titration curves obtained in the titration of (i) a strong acid with a strong base (ii) a strong acid with a weak base.
3. (i) Describe electroplating.

(ii) How is the degree of dissociation of a weak electrolyte obtained using Kohlrausch law.

4. (i) State and explain Kolhrausch law.

(ii) Explain the application of Kolhrausch law.

5. (i) What are buffer solutions? Explain the importance of buffer solution in living system.

(ii) Explain degree of hydrolysis.

6. (i) What are the applications of electrochemical series?

(ii) Describe the determination of pH of a solution using conductivity method.

7. (i) Write notes on buffer solution in the biological systems.

(ii) Explain buffer action.

7. State Kohlrauschs law. Explain how it is useful in the calculation of equivalent conductance of a weak electrolyte.

8. (i) Derive the expression for the hydrolysis constant K_h for the salt of weak acid and weak base.

(ii) Define pH, pOH and pKw.

9. (i) Write briefly about the conductometric titration between a weak acid and a strong base.

(ii) Derive the expression for the hydrolysis constant, K_h and degree of hydrolysis, h for the salt of weak base and strong acid.

10. (i) Calculate the percentage of hydrolysis of 0.01M solution of ammonium acetate. K_a for acetic acid is $1.8\times10^{-5}$and K_b for ammonium hydroxide is 1.8×10^{-5}.

(ii) What would be the pH value of a) 0.0001 N HCl b) 0.005 M H_2SO_4 c) 0.005 N NaOH?

ENVIRONMENTAL STUDIES

MULTIPLE CHOICE QUESTIONS

	Questions	Opt 1	Opt 2	Opt 3	Opt 4	Answer
	Unit IV					
	Which of the following is not an air pollutant?	Smoke	Carbon Dioxide	Nitrogen Gas	Sulphur Dioxide	Nitrogen Gas
	Which part of plant evaporates water ?	Stomata	Fruit	Branch	Root	Stomata
	A fossil fuel is best described as_______	a flammable solid or gas	a fuel that contains carbon.	fossilized rock that will burn in a power station.	a flammable substance formed from ancient biological material.	a flammable substance formed from ancient biological material.
	An example of a non-renewable, non-fossil energy resource is_______	oil.	coal.	tidal	uranium.	tidal
	Which of the following is not a renewable energy source?	wind	solar	biomass	natural gas	biomass
	The term 'exothermic' refers to a chemical reaction ______	in which heat is absorbed.	in which heat is given out.	that proceeds very rapidly.	that requires high temperatures to begin the reaction.	that requires high temperatures to begin the reaction.
	What percentage of the coal's energy reaches the city?	approximately 30%	approximately 50%	approximately 60%	approximately 90%	approximately 90%

	How much of the energy contained in the diesel-oil fuel is not converted to electricity when burnt in the power station?	4800 kJ	3200 kJ	2400 kJ	1200 kJ	2400 kJ
	Mercury is particularly hazardous to human health because________	it bioaccumulates high up the food chain.	as a heavy metal, it can cause serious impact injury.	as a pure metal it is very soluble in water, hence easily absorbed through drinking water.	it is light and volatile, and so is widely dispersed through the environment by wind	as a heavy metal, it can cause serious impact injury.
	Which of the following is the best description of sulphur dioxide?	a gas less dense than air	a gas more dense than air	a gas insoluble in water	an acidic liquid at ordinary room temperature	an acidic liquid at ordinary room temperature
	The dosage of sulphur dioxide is best described as_________	a measure of the harm sulfur dioxide does to a person.	the amount of sulfur dioxide a person experiences in a given time.	the amount of sulfur dioxide absorbed by a person in a given time.	the amount of sulfur dioxide entering the environment in a given time	the amount of sulfur dioxide absorbed by a person in a given time.
	The toxicity of mercury is best described as_________	how mercury enters the environment.	a measure of the harm mercury does to a person.	the persistence of mercury in the environment.	how much mercury a person experiences in a given time	the persistence of mercury in the environment.
	In some regions, the combination of acid rain and smog causes damage to forests that is worse than the impact of either acid rain or	specificity.	acute toxicity.	chronic toxicity.	synergistic action.	chronic toxicity.

	smog on its own. This is an example of______					
	Which one of the following best accounts for mercury’s significant harm to the environment?	persistence	degradability	specificity	synergism	synergism
	The main purpose of the Environmental Risk Assessment is to ___	. ensure maximum local employment on the project.	. eliminate any disruption to the environment during repair.	minimize the number of people likely to object to the project	balance any environmental damage against the benefit of the repair	minimize the number of people likely to object to the project
	Which one of the following factors best indicates that the dam repair is ecologically sustainable_______	disruption to local wildlife is temporary	employment is created during the repair project	the habitat of endemic threatened populations has been disturbed	previously submerged heritage buildings can be investigated	previously submerged heritage buildings can be investigated
	After the dam is repaired, it is found that soil sediments in the flood plain of the river contain significant levels of phosphorus that were not present before the water release. A scientist suggests that this can be corrected by planting a particular type of vegetation that absorbs and bioaccumulates phosphorus from the soil. This is an example of____	recycling.	soil bioremediation.	water conservation.	waste minimization.	waste minimization.
	The dominant gas in biogas	CH4	C2 H5	CO2	NO2	CH4

	is:______					
	Maximum amount of gas found in air is ___	Oxygen	Carbon dioxide	Hydrogen	Nitrogen	Nitrogen
	which state of matter, the distance between the molecules is minimum ?	Solid	Plasma	Liquid	Gas	Plasma
	Which energy is converted into electrical energy by a solar cell ?	Nuclear Energy	Chemical Energy	Solar Energy	Magnetic Energy	Solar Energy
	Carrier of Dengue disease is___	Aedes Mosquito	Culex Mosquito	Housefly	Anopheles Mosquito	Aedes Mosquito
	Which state of India is known as 'Tiger State'?	Gujarat	West Bengal	Madhya Pradesh	Assam	Madhya Pradesh
	Which of the following has maximum speed ?	Air	Water Current	Sound	Light	Light
	Tobacco addiction is caused due to________	Cocaine	Nicotine	Caffeine	Histamine	Nicotine
	Which of the following is called artificial kidney?	dialyzer	donor kidney	tissue-matched	preserved kidney	dialyzer
	Which of the following causes AIDS ?	Bacteria	Fungus	Retro virus	TMV	Retro virus
	Global warming is caused due to ________	lack of rainfall	presence of a hole in ozone layer	human activities against nature	extinction of animals and plants	human activities against nature
	The most abundant green house gas is_____	NO_2	CO_2	O_3	SO_2	CO_2
	Which is considered as a future source of power that can meet our unlimited demand ?	Hydal power	Hydrogen	Thermal power	Solar power	Hydrogen

	What is the rate of growth of human population ?	10 million per year	90 million per year	1 million per year	80 million per year	90 million per year
	Which is a better method to dispose large amounts of water carrying relatively small amounts of chemical wastes?	land filling method	Deep-well injection	Surface impoundments	incineration	Surface impoundments
	High level radioactive waste can be managed in which of the following ways?	Open dumping	Composting	Incineration	Dumping in sealed containers	Dumping in sealed containers
	Which country has the maximum number of tube-wells in the world ?	America	Australia	China	India	India
	Which of the following is a major source of thermal pollution in water bodies?	Sewage treatment plant	Solid waste disposal sites	Thermal power plant	Biogas Treatment Plant	Thermal power plant
	Sound becomes hazardous noise pollution at decibels:	Above 80	Above 30	Above 100	Above 120	Above 80
	Disease caused by eating fish inhabiting mercury contaminated water is:	Bright's disease	Hiroshima episode	Mina-mata disease	Osteosclerosis	Mina-mata disease
	Which energy is converted into electrical energy by a solar cell ?	Chemical Energy	Nuclear Energy	Solar Energy	Magnetic Energy	Solar Energy
	Which of the following is a biodegradable waste?	Plastics	Polythene	Glass	manure	manure
	Wildlife Week is celebrated on_________	1st October to 7th October	15th October to 2 1^{s}t October	1st June to 7th June	15th June to 21st June	1st October to 7th October
	In which state of matter, the distance between the	Solid	Liquid	Gas	Plasma	Solid

	molecules is minimum ?					
	The biochemical laboratory of human body is	Stomach	Liver	Intestine	Kidney	Liver
	The nuclear accident at Chernobyl occurred in	1966	1976	1986	1996	1986
	Carbon monoxide is ________.	caused by ozone depletion	a major component of the atmosphere	extremely damaging to human blood	produced by plants during photosynthesis	extremely damaging to human blood
	Which of the following has maximum speed ?	Air	Water Current	Sound	Light	Light
	Tobacco addiction is caused due to_____	Cocaine	Caffeine	Nicotine	Histamine	Nicotine
	Ozone layer is found in ________	Thermosphere	Stratosphere	Troposphere	Mesosphere	Stratosphere
	Full form of CNG is _________	Common National Gas	Compressed Natural Gas	Common Natural Gas	Certified Natural Gas	Compressed Natural Gas
	Renewable source of energy is ________	Coal	Petroleum	Plants	Uranium	Plants
	Which pollutant causes ozone layer depletion ?	CFC	CO_2	CH_3	HNO_3	CFC
	The mosquito repellent (coils, mats and liquids) that we generally use in our homes are:____	Pesticides	Fertilizers	Sedatives	Insecticides	Insecticides
	Combustion of coal in power plant produces mainly ____ which is a major pollutant of air.	Sulphur Dioxide	Nitrogen Dioxide	Methane	Chlorofluorocarbons	Nitrogen Dioxide
	One of the problems that occur as a consequence of	movement of toxins into	increasing skin cancer in	toxins accumulating in	damage to human red blood cells	increasing skin cancer in

	CFC pollution is ________.	lakes and rivers, which poisons fish	humans	homes		humans
	A battery or cell converts ____ energy into electrical energy	Solar	Heat	Mechanical	Chemical	Chemical
	In developed countries, the two most deadly sources of indoor pollution are ________.	pesticides and cleaning agents	synthetic furniture materials and radiation from electronic equipment	radiation from electronic equipment and pesticides	radon and cigarette smoke	radon and cigarette smoke
	Which of the following plays an important role in the cause of rainfall?	Evaporation	Condensation	Both evaporation & condensation	Filtration	Both evaporation & condensation
	Bacterial and fungal spores can be included as ________.	contributors to indoor pollutants	VOCs and POPs	sources of radon in the home	problems in degrading the ozone layer	contributors to indoor pollutants
	Particulate matter dispersed as aerosols ________.	includes nitrogen oxides	may cause damage to respiratory tissues when inhaled	binds with hemoglobin, preventing hemoglobin's binding with oxygen	interacts only with surface tissues of humans, causing mild irritation	may cause damage to respiratory tissues when inhaled
	Which of the following is a consequence of acidic deposition?	It increases the likelihood of low-lying ground fogs	It results in offshore eutrophication, damaging coral reefs	It creates rainwater that can damage skin cells or cause cancers	It changes soil chemistry, leaching out important minerals	It changes soil chemistry, leaching out important minerals
	The most obvious cause of	burning trash	fires for	indoor air	burning fossil fuels	burning fossil

	industrial smog is ________.		heating food	pollution		fuels
	The acid rain form with the following pollutants ……..	CO_2 and CO	SO_2, N_2O and NO	H_2S and CO	O_2 and O_3	SO_2, N_2O and NO
	……. method is used to reduce the non-digestible solid waste	Incineration	buried	discharge in plain land	burning in open atmosphere	Incineration
	What is the used for scaling the sound?	unit	Hz	db	MHz	db
	The emission of ….. gas from refrigeration units cause ozone layer depletion	carbon monoxide	Chloro fluoro carbon	Carbon di oxide	helium	Chloro fluoro carbon
	The emitted toxic gas in Bhopal gas disaster is	Carbonyl	methyl isocyanate	Cyanide	Ethyl isocyanate	methyl isocyanate