KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
(Established Under Section 3 of UGC Act 1956)
Coimbatore – 641 021.

SYLLABUS

DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr. S. SAVITHIRI

SUBJECT NAME: CHEMISTRY-II SUB.CODE:18BCU403

SEMESTER: IV CLASS: II B.Sc (BIOCHEMISTRY)

18BCU403 CHEMISTRY-II 4H – 4C

Instruction Hours/week: L:4 T:0 P:0 Marks: Internal:40 External: 60 Total:100
End Semester Exam: 3 Hours

Course Objectives

1. To make the student to be conversant with the extraction of metals, coordination chemistry, preparation, properties uses and structure of naphthalene and heterocyclic compounds.
2. To make the student acquire sound knowledge of electrochemistry, biological functions of amino acids and proteins, thermodynamic laws, entropy, enthalpy change and the principles of electroplating.

Course Outcome (CO's)

1. The student understand the metallurgy of metals and the theories of coordination compounds and the industrial importance of EDTA, haemoglobin and chlorophyll.
2. Understand the concept of aromaticity and preparation of aromatic compounds including heterocyclic compounds.
3. Understand the preparation, classifications and properties of amino acids, proteins and carbohydrates.
4. Understand the concepts of first and second laws of thermodynamics.
5. Understand the fundamentals of electrochemistry.

Unit-I

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.

Unit-II

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.

Unit-III

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.

Unit-IV

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.

Unit-V

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.

SUGGESTED READINGS:

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.
3. Bahl, A., & Bahl, B.S. (2015). *A Textbook of Organic Chemistry* (21st Revised Edition). New Delhi: S.Chand & Company Pvt. Ltd.
4. Puri, B. R., Sharma, L. R. & Pathania, M. S. (2014). *Elements of Physical Chemistry* (46th Edition). Jalandhar: Vishal Publishing Company.
5. Gopalan, R., & Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

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LECTURE PLAN

DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr. S. SAVITHIRI

SUBJECT NAME: CHEMISTRY-II SUB.CODE:18BCU403

SEMESTER: IV CLASS: I B.Sc (BIOCHEMISTRY)

S.No.	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos.
		UNIT-I	
1	1	**Metals and Coordination Chemistry:** **Metals:** General methods of extraction of metals- methods of ore dressing-types of furnaces.	T1:1-3 & 7-10 R1:33-37
2	1	Reduction methods and electrical methods.	T1:4-5 R1:38-39
3	1	Types of refining-Van Arkel process-zone refining.	T1:5-7 T2:337-338 R1:39-41
4	1	**Coordination Chemistry:** Introduction- nomenclature.	T1:17-21 T2:743-744 & 752-756 R1:53-54
5	1	Werner's and Sidgewick coordination theory.	T1:21-23 T2:749-751 & 756-757 R1:47-49
6	1	Pauling's valence bond theory-chelation and its industrial importance-EDTA.	T1:23-29 T2:773-778, 747-748 & 1165-1167 R1:49-51 & 54-55
7	1	Haemoglobin and Chlorophyll-applications in qualitative and quantitative analysis.	T1:29-33 T2:1064-1066 R1:55-59

8	1	Recapitulation and discussion of important questions.	
	Total No of Hours Planned For Unit 1=08		
		UNIT-II	
1	1	**Aromatic Compounds and Heterocyclic Compounds:** **Aromatic Compounds:** Aromaticity-Huckel's (4n+2) π electron rule.	T1:34-36 T3:660-662
2	1	Aromatic electrophilic substitution in benzene-mechanism of nitration, halogenations, alkylation, acylation and sulphonation.	T1:36-39 T3:664-668 R1:146-149
3	1	Naphthalene: Isolation, preparation, properties and structure.	T1:40-48 T3:830-838 R1:150-156
4	1	**Heterocyclic compounds:** Preparation and properties of pyrrole.	T1:49-53 T3:850-854 R1:158-165
5	1	Preparation and properties of furan.	T1:53-55 T3:854-855 R1:158-165
6	1	Preparation and properties of thiophene.	T1:56-58 T3:857-858 R1:158-165
7	1	Preparation and properties of pyridine.	T1:59-62 T3:858-863 R1:165-167
8	1	Recapitulation and discussion of important questions.	
	Total No of Hours Planned For Unit II=08		
		UNIT-III	
1	1	**Amino acids, Proteins and Carbohydrates:** **Amino acids:** Introduction-classification and preparation.	T1:63-67 T3:569-573 R1:184-189
2	1	Properties of amino acids. Peptides-preparation of peptides (Bergmann method only).	T1:67-73 T3:573-576 R1:189-193
3	1	**Proteins:** Classification, properties and biological functions.	T1:74-77 T3:576-577 & 579-581

			R1:193-195
4	1	Structure of proteins. **Carbohydrates:** Introduction-classification.	T1:77-81 T3:578 & 607-611 R1:169-170
5	1	Preparation and properties of glucose.	T1:81-85 T3:611-618 R1:170-173
6	1	Preparation and properties of fructose.	T1:87-89 T3:625-628 R1:174-176
7	1	Discussion of open chain and ring structures of glucose and fructose-glucose-fructose interconversion.	T1:86 & 90-92 T3:619-625, 629-630 R1:173-174 & 176-178
8	1	Recapitulation and discussion of important questions.	
	Total No of Hours Planned For Unit III=08		
		UNIT-IV	
1	1	**Energetics:** Introduction-type of systems.	T1:93-94 T4:276-278 R1:196-197
2	1	Processes and their types-isothermal, adiabatic, reversible, irreversible and spontaneous processes.	T1:94-97 T4:279-280 R1:197-199
3	1	Statement of first law of thermodynamics-need for the second law of thermodynamics.	T1:97-98 T4:281-282 R1:199-200 & 202-203
4	1	Heat engine- Carnot cycle-efficiency and refrigerators.	T1:98-107 T4:336-339 R1:203-204 & 212
5	1	Carnot theorem- thermodynamics scale of temperature-Joule-Thomson effect.	T1:107-110 T4:337 & 295-298 R1:204-205, 209 & 200-202
6	1	Enthalpy-entropy and its significance-free energy change.	T1:110-114 T4:285-286, 339-342 & 348-350 R1:205-208
7	1	Recapitulation and discussion of important questions.	

	Total No of Hours Planned For Unit IV=07		
		UNIT-V	
1	1	**Electrochemistry:** Kohlrausch law- conductometric titrations.	T1:115-124 T4:535-536 & 545-546 R1:246-252
2	1	Hydrolysis of salts.	T1:125-132 T4:502-508 R1:270-274
3	1	Galvanic cells, E.M.F., standard electrode potentials-reference electrodes.	T1:133-135 T4:555-556 R1:253-257
4	1	Electrochemical series and its applications.	T1:135-137 T4:567-568 R1:258-259
5	1	Buffer solution-buffer solution in the biological systems.	T1:140-142 T4:498-499 R1:263-265
6	1	pH and its determination-principles of electroplating.	T1:142-152 & 153-154 T4:585-588 R1:265-266 & 261-262
7	1	Recapitulation and discussion of important questions.	
8	1	Discussion of previous ESE question papers.	
9	1	Discussion of previous ESE question papers.	
	Total No of Hours Planned for Unit V=09		
Total Planned Hours	**40**		

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

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

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

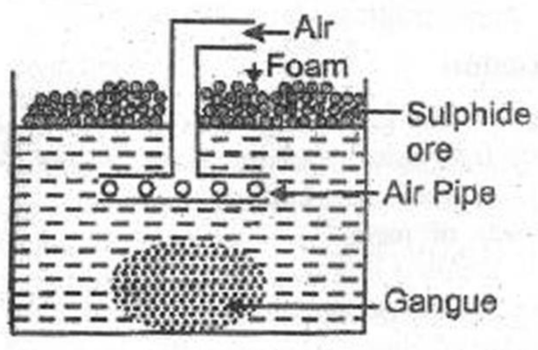
The ore, which is mined, is usually associated with rocky impurities called **gangue** or **matrix.** Ore dressing is concerned with the removal of gangue from the ore. Gangue can be separated by any one of the following ways:

(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.

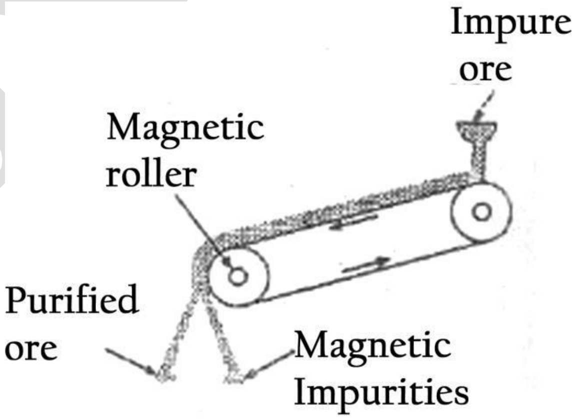
Tin stone and haematite are concentrated by this method.

(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:

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

(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

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

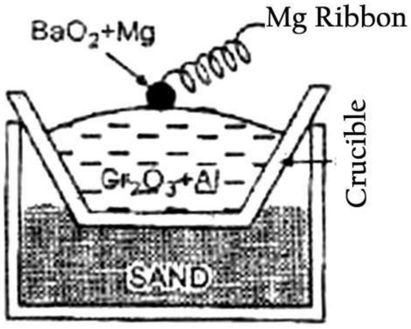
$$Na^+ + e \longrightarrow Na \quad \text{(at the cathode)}$$

$$Cl^- \longrightarrow Cl + e$$

$$2\,Cl \longrightarrow Cl_2 \quad \text{(at the anode)}$$

(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:



$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr + 408.6\ kJ$$

$$3\ Mn_3O_4 + 8Al \longrightarrow 4\ Al_2O_3 + 9\ Mn + Q\ kJ$$

$$3\ MnO_2 + 4\ Al \longrightarrow 2\ Al_2O_3 + 3\ Mn + Q\ kJ$$

(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.

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

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

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:

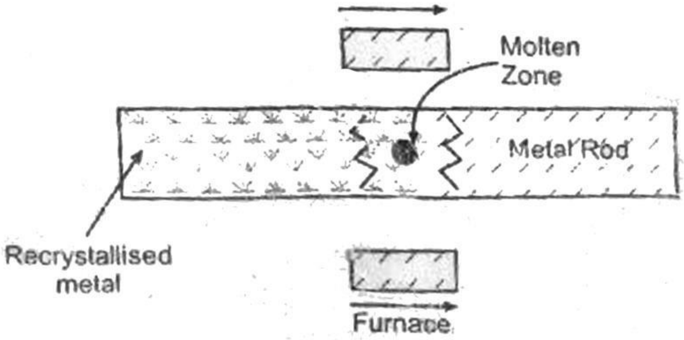
(i) **Liquation**: It is suitable where the metal is easily fusible but not the impurities. Easily fusible (like tin and lead) are heated on the sloping hearth of a reverberatory furnace. The metal melts and flow down leaving behind the infusible impurities.

(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.

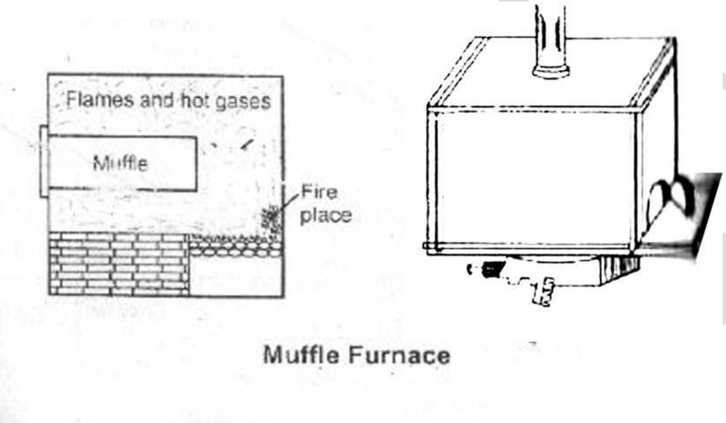
Types of Furnaces

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.



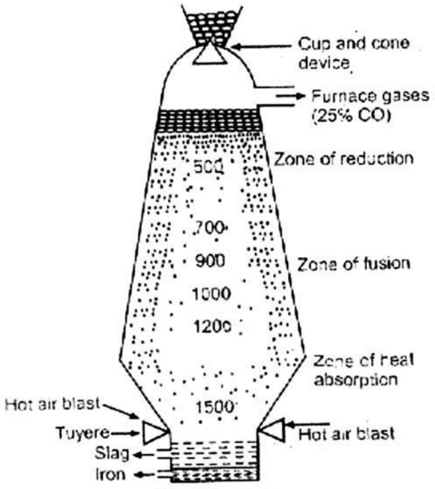
Muffle Furnace

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.

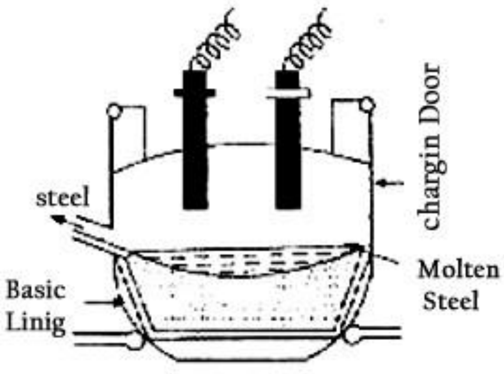
Air is heated to 820-1120 K by combustion of waste gases and blast of this hot air is blown into the furnace under pressure through 8-20 nozzles called **tuyerers.** The down coming charge meets the upward moving hot air blast. The products leave the furnace at three places-

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.

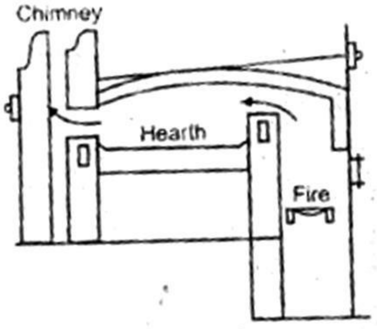


Heroult's Furnace

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	$[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_3Cl_3]$, $[Co(NO_2)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Pt(NH_3)_2Cl_4]$

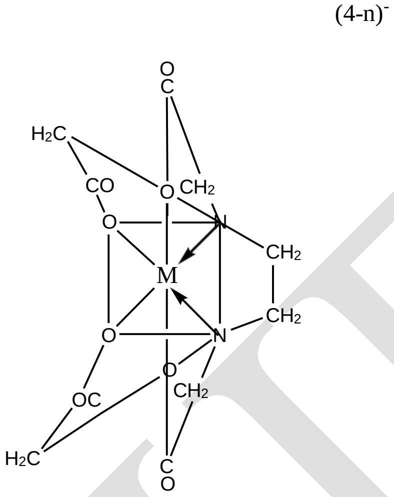
The coordination compounds differ largely from *double salts.* As the double salts tend to retain their identity even in solution, the properties of complexes are entirely different from those of the constituents.

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.

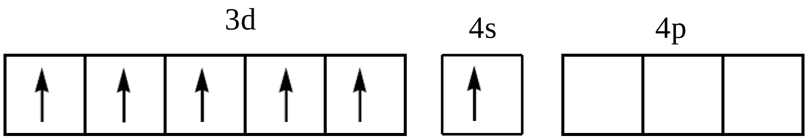
5) The complex is said to be paramagnetic if the complex contains unpaired electrons whereas a complex which does not contain any unpaired electron is diamagnetic in nature.

These points are explained in the following illustrations:

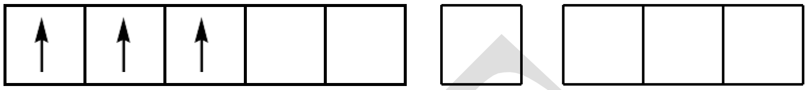
Hexa-amminechromium (III) chloride, $[Cr(NH_3)_6]Cl_3$

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) $[Ar]^{18}$

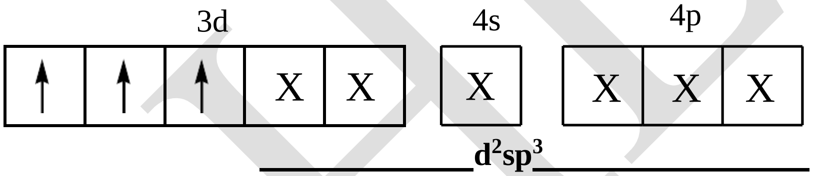


Cr(III) $[Ar]^{18}$



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.

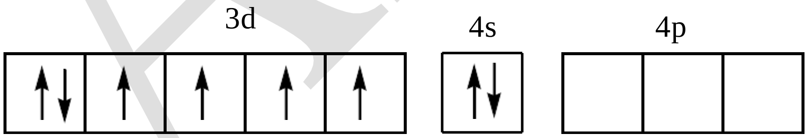
$[Cr(NH_3)_6]^{3+}$



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

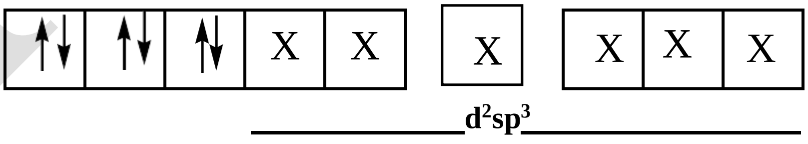
The complex anion $[Fe(CN)_6]^{4-}$ is obtained from Fe(II). The electrons present in the iron atom before the approach of six cyanide ligands are given as:

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.

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



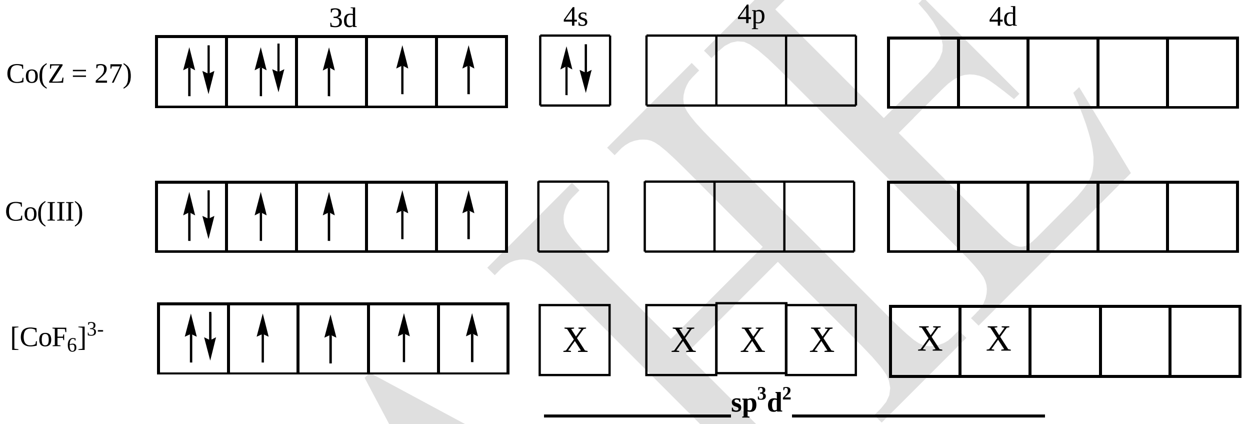
Evidently, this complex is d^2sp^3-hybridised with octahedral geometry formed from d^2sp^3-hybridisation:

$[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Pt(NH_3)_6]^{4+}$,
$[Co(NH_3)_6]^{3+}$ 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, $[CoF_6]^{3-}$

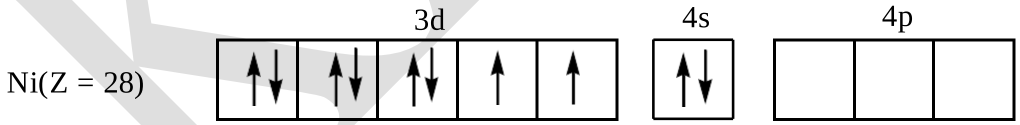
This complex is octahedral but is highly paramagnetic. The magnetic moment value at room temperature (5.0 B.M) corresponds to four unpaired electrons. To explain this, it is regarded that no electron pairing occurs in the inner 3d orbitals but outer 4d orbitals are used for hybridisation. This type of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



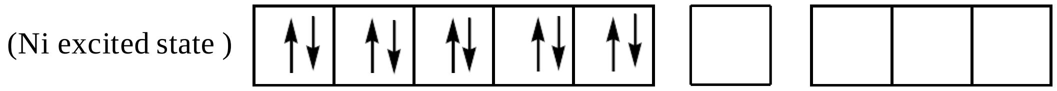
These types of complexes are known as *high spin or outer orbital complexes.* $[FeF_6]^{3-}$ belongs to this class.

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

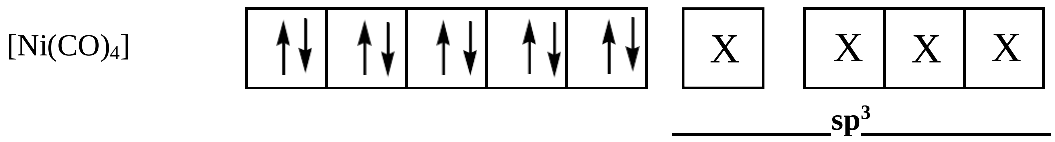
It is possible to explain the formation of tetrahedral complexes with sp^3-hybridisation in the light of VBT. The electronic configuration of nickel (Z= 28) is [Ar] $4s^2 3d^8$



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:

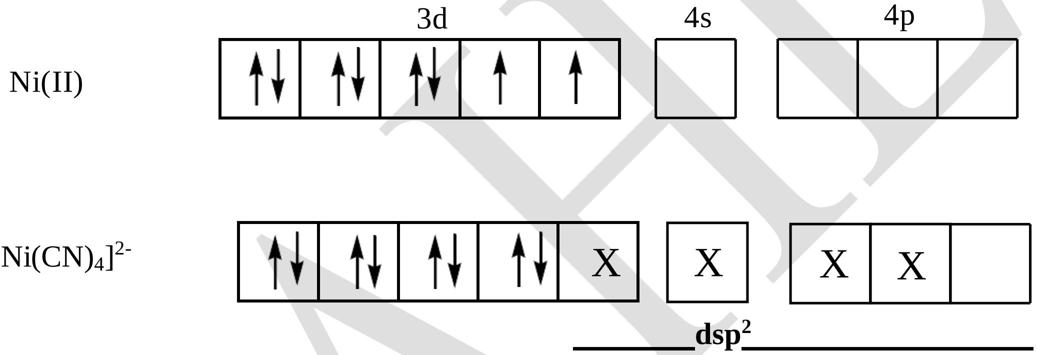


Obviously this complex is diamagnetic. The other example:

$[Zn(NH_3)_4]^{2+}$, $[ZnCl_4]^{2-}$ 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:



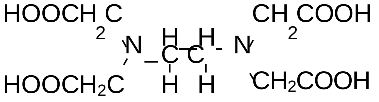
Similar situation exists for complexes of palladium (II). Platinum (II), gold (III), rhodium (I) and iridium (I).

Chelation and its industrial importance

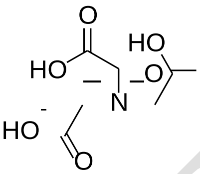
The presence of objectionable metal ions causes problems in many industries because of the adverse effects these can have on the quality of the product. These difficulties can be averted if the free metal ion concentration is considerably reduced. An effective way of achieving this is by the addition 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:

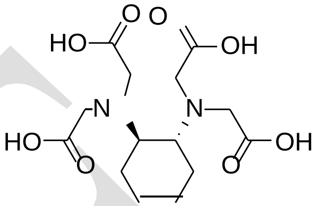
1) Ethylenediaminetetraacetic acid (Abbreviated, EDTA)
2) Nitrilotriacetic acid (abbreviated, NTA)
3) *trans*-1,2-Diaminocyclohexane N,N,N′ N′–tetraacetic acid (DCTA)



Ethylenediaminetetraacetic acid (EDTA)



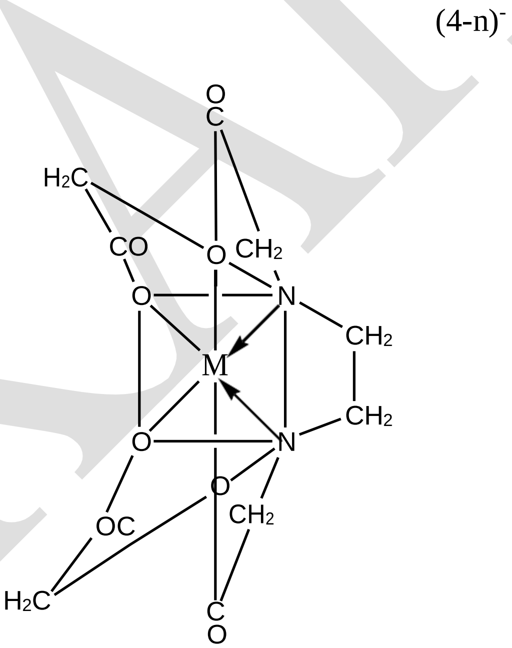
Nitrilotriacetic acid (NTA)

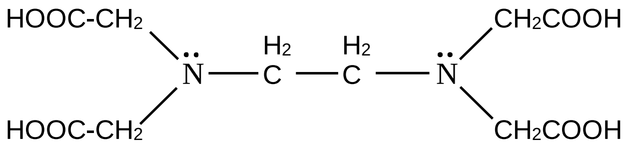


trans-1,2-Diaminocyclohexane-
N,N,N′,N′–tetraacetic acid (DCTA)

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

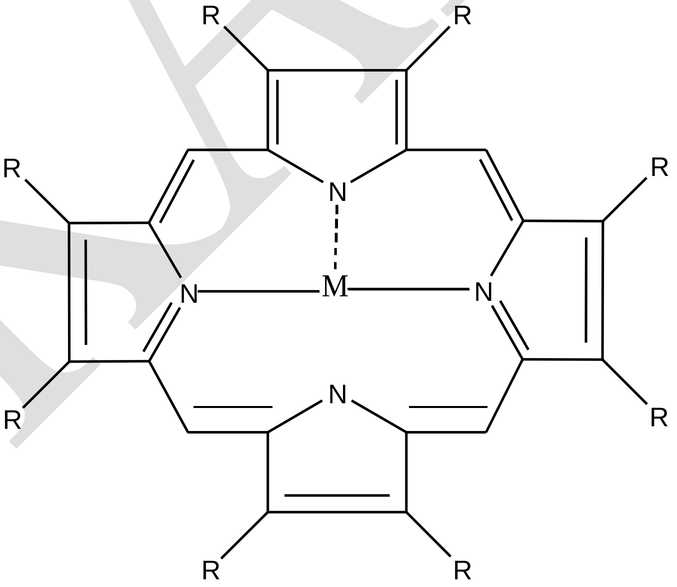
The inorganic constituents of biological system have been receving increasing attention in recent years. The importance and the presence of metallic elements in living bodies (plants and animals) have been the keen interests to the chemists. It has been observed that the majority of the essential metallic 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.

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DEPARTMENT OF CHEMISTRY

UNIT-I

METALS AND COORDINATION CHEMISTRY

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. The various compounds of metals which occur in nature and are obtained by mining are called

a) minerals b) ores c) gangue d) matrix

2. The art of winning a metal from its ore is known as

a) minerals b) ores **c) metallurgy** d) matrix

3. The ore which is mined is usually associated with rocky impurities called

a) flux b) salt c) slag **d) gangue**

4. The lime is generally used as

a) flux b) matrix c) slag d) gangue

5. The metal ion present in chlorophyll is

a) Mg(II) b) Fe(II) c) Ca(II) d) Mn(II)

6. Which one of the following is a double salt?

a) nickel tetracarbonyl b) sodium chloride

c) barium sulphate **d) ferrous ammonium sulphate**

7. What is the common denticity of EDTA?

a) 2 b) 4 **c) 6** d) 5

8. Who is regarded as the Father of co-ordination chemistry?

a) Werner b) Sidgwick c) Pauling d) Pauli

9. The EAN of nickel in $K_2[Ni(CN)_4]$ is

a) 36 **b) 34** c) 38 d) 35

10. The coordination number of central metal ion in haemoglobin is

a) 2 b) 4 **c) 6** d) 5

11. Which of the following metals occurs in the free state in nature?

a) copper b) iron **c) platinum** d) nickel

12. The naturally occurring source of the metal from which the metal can be economically extracted is called its

a) mineral b) gangue c) ore d) native ore

13. Froth floatation is suitable for concentration of

a) oxide ores b) carbonate ores c) halide ores d) sulphide ores

14. Cinnabar has the composition

a) $CuFeS_2$ b) ZnS **c) HgS** d) PbS

15. The main constituent of zinc blende is

a) $CuFeS_2$ b) CuS c) PbS **d) ZnS**

16. Which of the following is not characteristic of the metallurgical process of smelting?

a) It involves reduction b) high temperature is used c) carbon is commonly used for reduction in smelting **d) excess of air is required for smelting**

17. Which of the following metals can be obtained by the electrolytic reduction of its fused halide

a) Fe b) Hg **c) Na** d) W

18. Germanium and gallium may be purified by

a) electrolysis b) recrystallization c) distillation **d) zone refining**

19. The heating of an ore in a furnace in the absence of air to expel moisture and air is called

a) roasting b) dehydration c) poling **d) calcination**

20. A method of purifying copper ore involves

a) poling b) smelting c) magnetic separation d) electrolysis

21. Which of the following species has a square planar geometry?

a) $[Zn(NH_3)_4]^{2+}$ b) $[Fe(CN)_6]^{4-}$ c) $[Cr(C_2O_4)_3]^{3-}$ **d) $[Ni(CN)_4]^{2-}$**

22. The hexafluoroferrate(III) has a magnetic moment of 6.0 B.M; this implies that

a) It is unstable **b) it involves sp^3d^2 hybridization**

c) it involves d^2sp^3 hybridization d) it should be coloured

23. $[FeF_6]^{3-}$ is

a) an outer-orbital complex b) an inner-orbital complex

c) a spin- paired complex d) a chelate complex

24. The charge on the metal in the complex $K_3[Al(C_2O_4)_3]$ is

a) -3 b) +2 c) +4 **d) +3**

25. Which of the following ligands is not capable of forming a chelate with metals?

a) EDTA b) ethylene diamine **c) ONO^-** d) oxalate

26. Which of the following is not true of chelates?

a) they are ring compounds b) they are more stable than non-chelate complexes

c) they are sparingly soluble in water d) they do not occur in nature

27. DMG is used for the detection of

a) Zn^{2+} b) Ca^{2+} c) Fe^{2+} **d) Ni^{2+}**

28. The co-ordination number of silver in $[Ag(NH_3)_2]Cl$ is

a) 1 **b) 2** c) 3 d) 0

29. Pick out the neutral ligand?

a) chloride b) cyanide c) hydroxide **d) carbon monoxide**

30. Which one of the following is a bidentate ligand?

a) chloride b) water **c) oxalate** d) ammonia

31. Which is not the other name for EDTA?

a) versene b) complexone c) sequestrene **d) oxine**

32. Choose the binuclear complex from the following

a) $[Fe_2(CO)_9]$ b) $[Ni(CO)_4]$ c) $[Fe(CO)_5]$ d) $[Cu(NH_3)_4]SO_4$

33. The charge on the co-ordination sphere of $K[Ag(CN)_2]$ is

a) 1 **b) -1** c) 2 d) -2

34. The complex, whose IUPAC name, potassium hexacyanoferrate (II) is

a) $K[Fe(CN)_6]$ b) $K_2[Fe(CN)_6]$ c) $K_3[Fe(CN)_6]$ **d) $K_4[Fe(CN)_6]$**

35. Identify the neutral complex

a) $[Pt(NH_3)_4Cl_2]Br_2$ **b) $[Fe(CO)_5]$** c) $[Ag(NH_3)_2]Cl$ d) $K_2[Ni(CN)_4]$

36. EDTA is

a) an indicator b) a rubber c) a chelate **d) a chelating agent**

37. What is the primary valency of nickel in $[Ni(CO)_4]$?

a) 4 b) 3 c) 2 **d) 0**

38. What is the secondary valency of chromium in $[Cr(NH_3)_4Cl_2]Cl$

a) 1 b) 2 c) 4 **d) 6**

39. The structure for dsp^2 hybrdisation is

a) tetrahedron **b) square planar** c) octahedron d) trigonal bipyramidal

40. The number of unpaired electrons present in $[Cr(H_2O)_6]Cl_3$ is

a) 0 b) 2 **c) 3** d) 4

41. The types of hybridisation present in $K_2[Ni(CN)_4]$ is

a) sp^3 **b) dsp^2** c) dsp^3 d) d^2sp^3

42. Name the hybridisation present in $K_3[FeF_6]$

a) sp^3d^2 b) d^2sp^3 c) sp^3 d) dsp^2

43. Which one of the following is highly paramagnetic in nature?

a) $[Fe(CO)_5]$ b) $K_4[Fe(CN)_6]$ c) $K_3[Fe(CN)_6]$ **d) $K_3[FeF_6]$**

44. Identify the complex which is diamagnetic in nature

a) $K_4[Fe(CN)_6]$ b) $K_3[Fe(CN)_6]$ c) $K_3[FeF_6]$ d) $K_3[CoF_6]$

45. The type of indicator used in EDTA titration is,

a) neutralization indicator **b) metal ion indicator**

c) redox indicator d) precipitation indicator

46. Which is not true with EDTA?

a) relatively low price b) high water solubility

c) good chelating agent **d) denticity is four**

47. The indicator used in EDTA titration is

a) phenolphthalein b) methyl orange c) starch **d) Eriochrome Block-T**

48. The metal ion largely responsible for hardness of water are

a) Ca(II) and Mg(II) b) Ca(II) and Zn(II)

c) Ca(II) and Cu(II) d) Mg(II) and Al(III)

49. The metal ion present in haemoglobin is

a) Mg(II) **b) Fe(II)** c) Mn(II) d) Ca(II)

50. The metal ion in haemoglobin assumes

a) square planar structure b) tetrahedron structure

c) octahedron structure d) linear structure

51. The percentage of iron in haemoglobin is

a) 0.347 b) 1.23 c) 3.47 d) 2.31

52. The molecular mass of haemoglobin in around

a) 6450 **b) 64500** c) 645000 d) 6450000

53. What type of protein is haemoglobin?

a) simple protein b) fibrous protein **c) conjugated protein** d) globular protein

54. The co-ordination number of central metal ion in chlorophyll is

a) 2 **b) 4** c) 6 d) 5

55. Chlorophyll was first synthesized in the year

a) 1960 b) 1962 c) 1964 d) 1966

56. Chlorophyll is involved in

a) photosynthesis b) oxygen transport c) blood circulation d) cell growth

57. The reagent used to separate AgCl from $PbCl_2$ is

a) water **b) ammonia** c) nitric acid d) potassium chromate

58. The chelating agent used in the estimation of aluminium is

a) dimethylglyoxime **b) oxine** c) cupferon d) anthranilic acid

59. What is the colour of the precipitate formed by Ni(II) with DMG?

a) rosy red b) violet c) yellow d) black

60. Which one of the following is a redox indicator?

a) starch b) Eriochrome Block-T **c) ferroin** d) phenolphthalein

UNIT-II

SYLLABUS

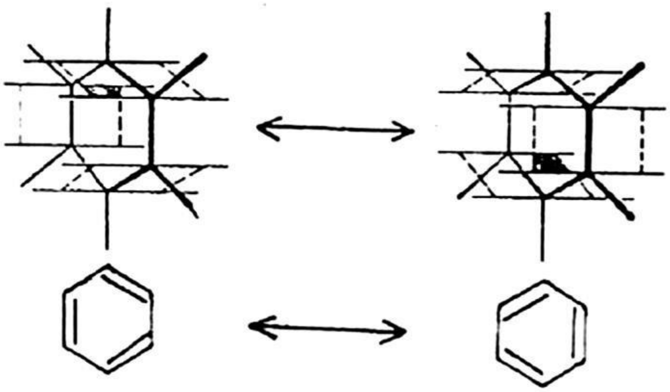
Aromatic Compounds and Heterocyclic Compounds:

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.

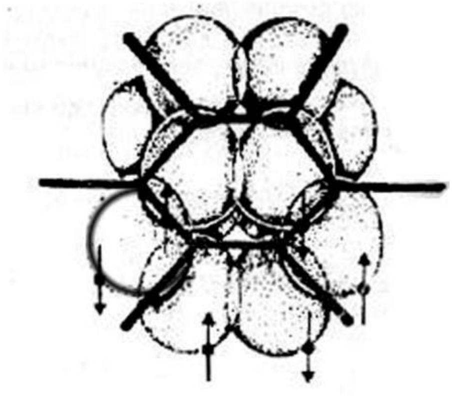
Heterocyclic Compounds: Preparation and properties of pyrrole, furan, thiophene and pyridine.

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$^-$)

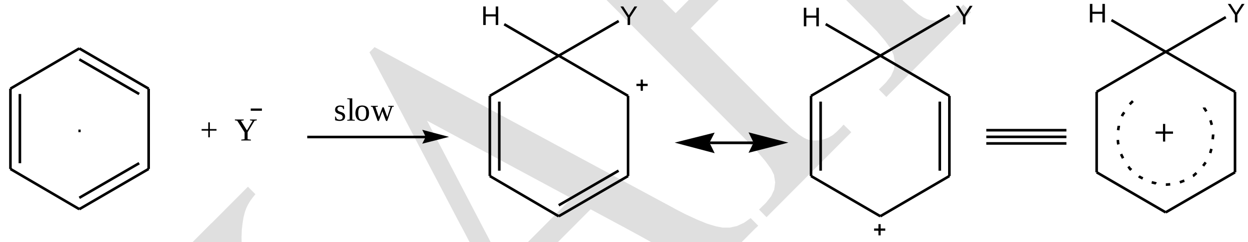
Anthracene (14π e$^-$) phenanthrene (14π e$^-$)

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.**

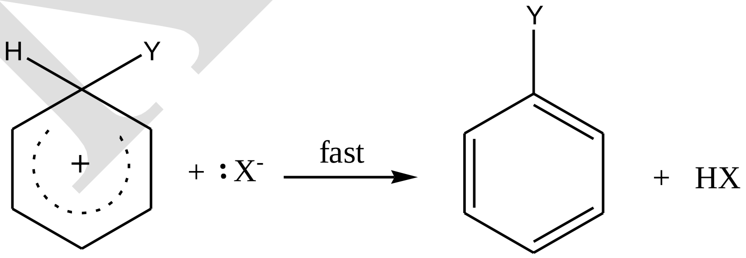
Aromatic Electrophilic Substitution Reaction

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

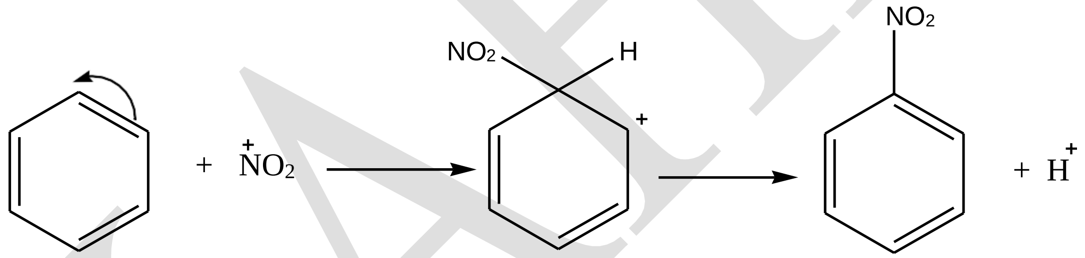
Generally nitration is carried out with a mixture of conc. nitric acid and sulphuric acid (*nitrating mixture*). When nitric acid alone is used, the reaction proceeds very slowly. There is considerable evidence that sulphuric acid helps in converting the nitric acid into *nitronium* ion, NO_2^+, which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

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

$$H_2O + H_2SO_4 \longrightarrow HSO_4^- + H_3O^+$$

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

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

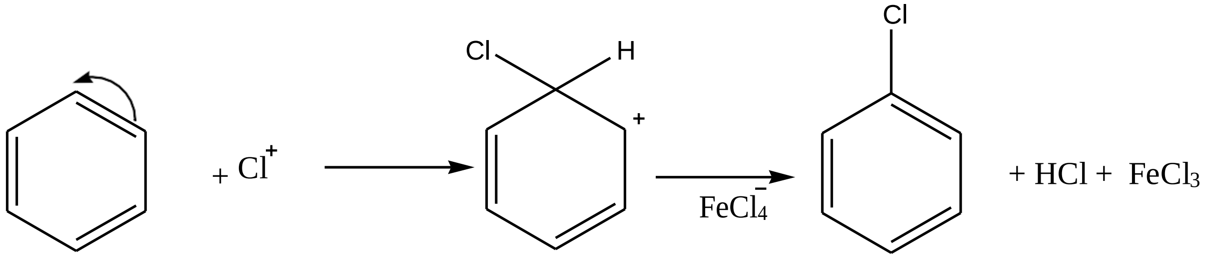


$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

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

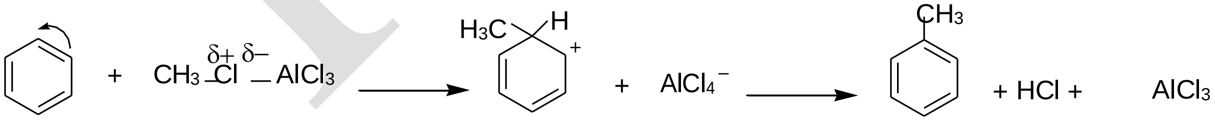
The reaction of alkyl halide or acyl halide with benzene in the presence of a Lewis acid like BF_3, $AlCl_3$ etc. is known as Friedel Crafts reaction. Hence, it can be divided in to *alkylation* and *acylation*.

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.

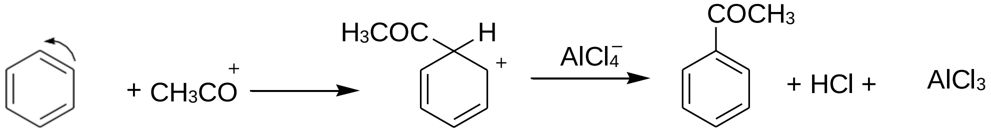
$$CH_3\text{—}Cl \xrightarrow{AlCl_3} \overset{\delta+}{CH_3} \quad \overset{\delta-}{AlCl_4} \quad (I)$$

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:

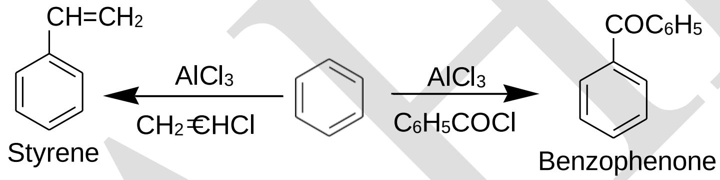
$$CH_3COCl + AlCl_3 \qquad CH_3CO^+ + AlCl_4^-$$



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:



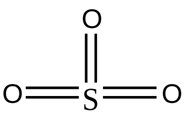
Sulphonation

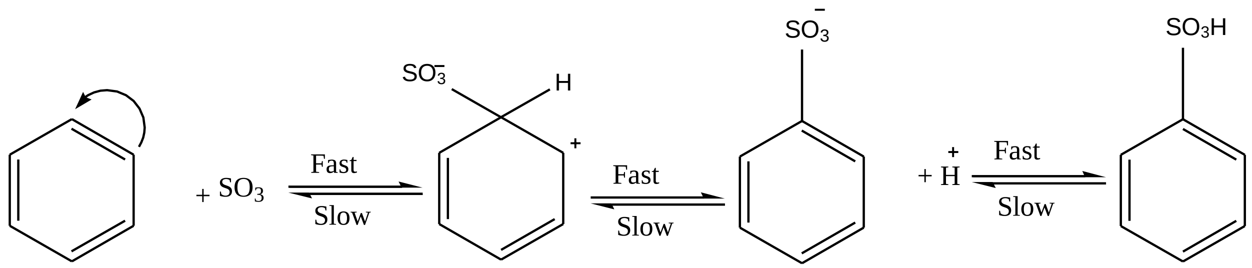
The complete details of the mechanism of this reaction are still under investigation. According to the widely accepted view, SO_3 is the electrophilic reagent and is formed in the following way**:**

$$2\,H_2SO_4 \longrightarrow SO_3 + H_3O^+ + HSO_4^-$$

fuming sulphuric acid

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.

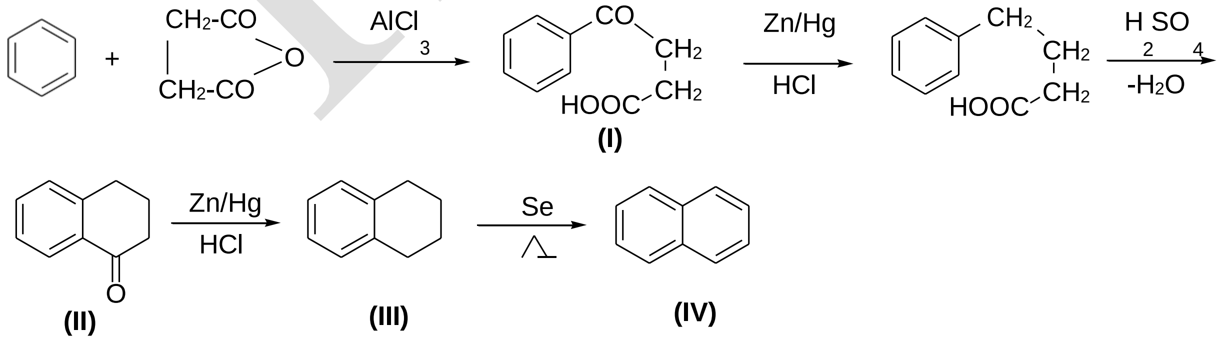
Isolation of naphthalene

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

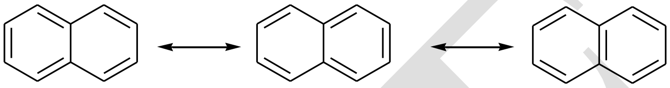
Naphthalene can be synthesized by a number of methods, the most important being the *Haworth synthesis*.

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).

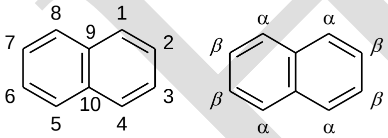


Properties of Naphthalene:

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*.

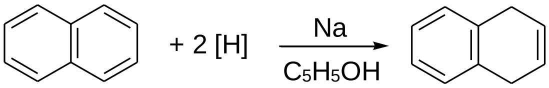
Disubstitution products are known as ortho, meta and para like benzene derivatives when two substituents are present in the same ring. 1,8 or 4,5 position is called *peri* positions. 2,6 or 3,7 position is called *amphi* positions.

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

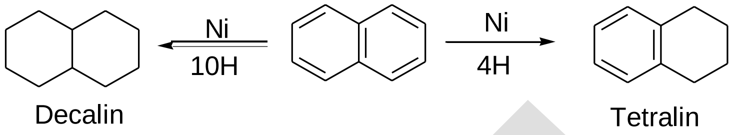
Reduction

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.

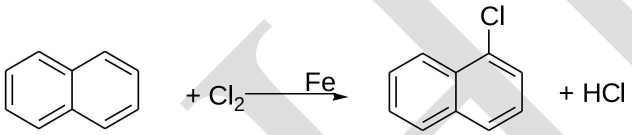


b) Catalytic reduction in presence of finely divided nickel, it gives tetrahydronaphthalene *(tetralin)*.
c) Prolonged reduction with nickel catalyst, it yields decahydronaphthalene (*decalin)*.

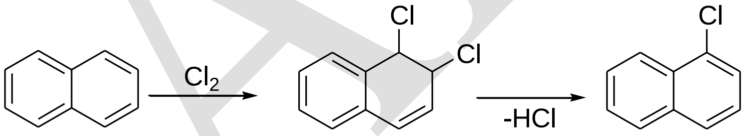


Halogenation

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

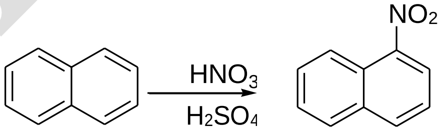


At room temperature and in the absence of a catalyst, naphthalene reacts with chlorine to give an addition compound, dichloronaphthalene. This eliminates a molecule of hydrogen chloride to form monochloro naphthalene.



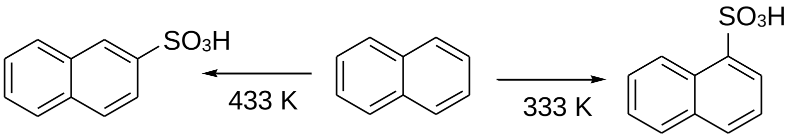
Nitration

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



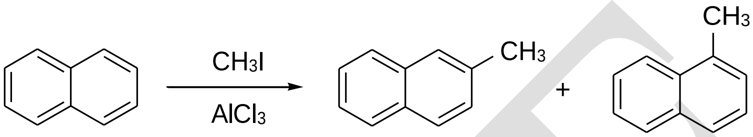
Sulphonation

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.

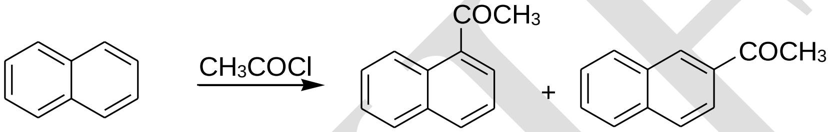


Friedel-Crafts reaction

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

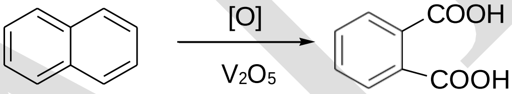


With acetyl chloride, the Friedel- Crafts reaction gives 1 and 2-acetylnaphthalene:

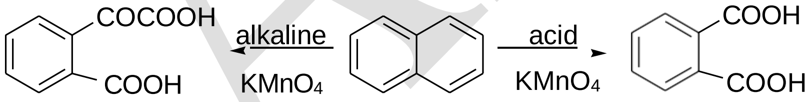


Oxidation

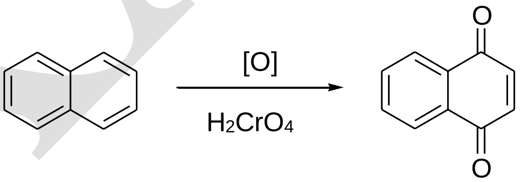
1) When naphthalene vapours mixed with air are passed over vanadium pentoxide catalyst, phthalic acid is formed.



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

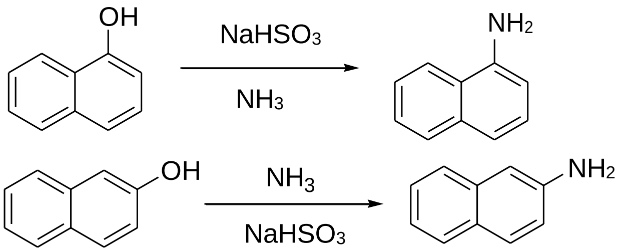


3) Naphthalene is oxidised to 1, 4-naphthaquinone with chromic acid.

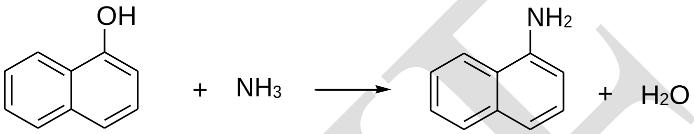


Naphthylamines

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.

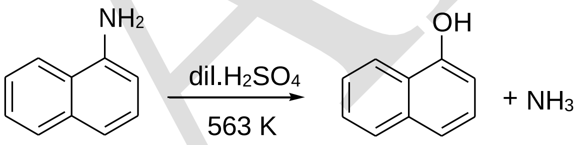


Naphthols

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

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

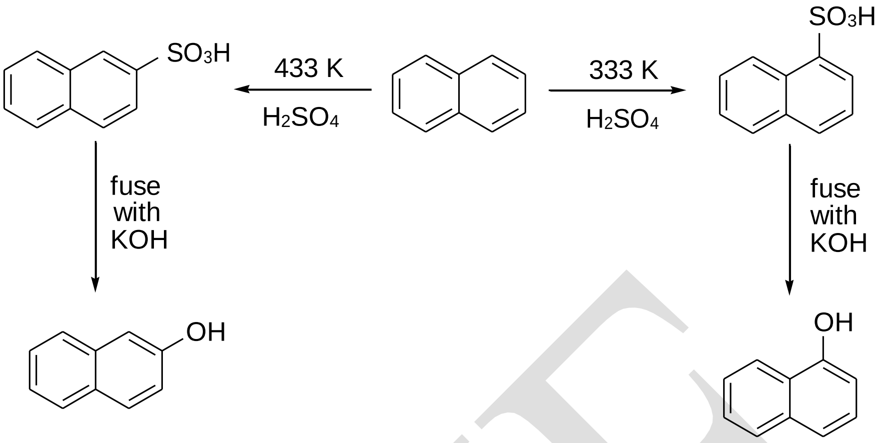
However, pure α- naphthol may be prepared by heating α- naphthaylamine with dil. H_2SO_4:



Important Conversions

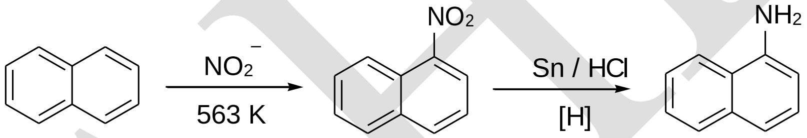
(a) Naphthalene to naphthols

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

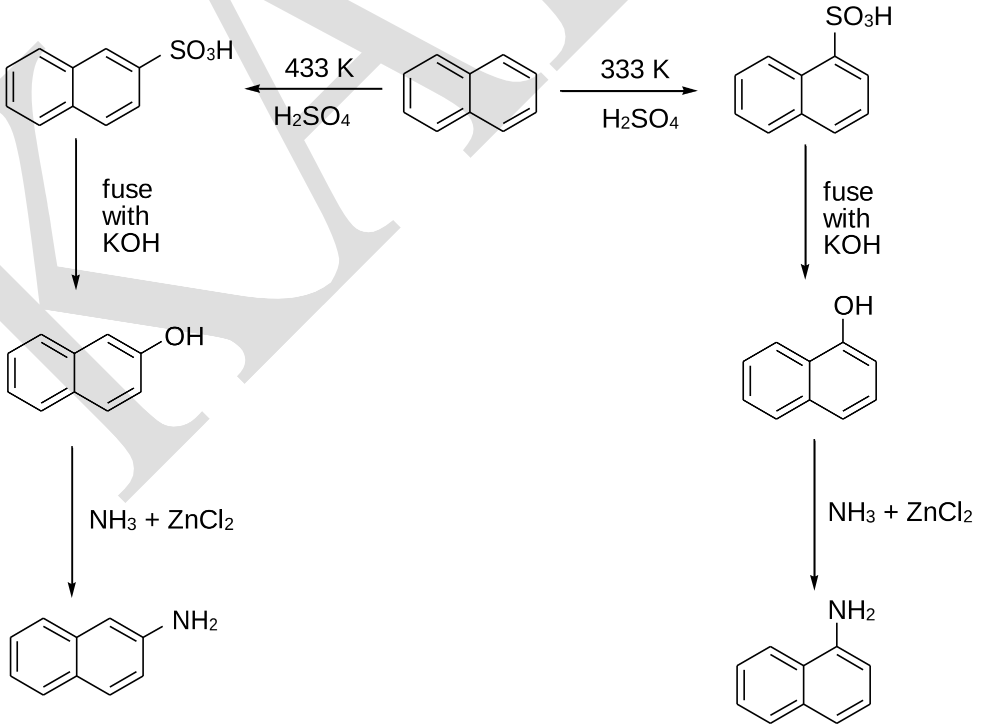


(b) Naphthalene to naphthylamines

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

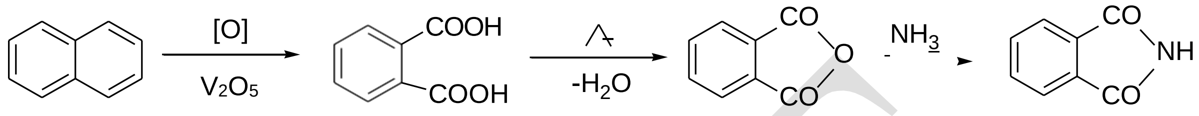


(ii) However, both *α*-and *β*-naphthylamines can be obtained from naphthalene in the following way:



(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:



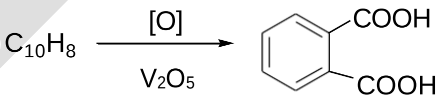
Uses

Naphthalene finds use

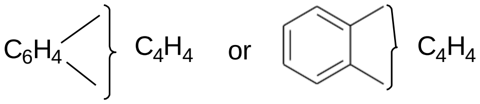
1) As an insecticide.
2) In the preparation of phthalic anhydride.
3) In the manufacture of phthalein dyes.

Structure of Naphthalene

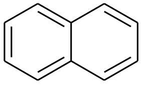
1) The molecular formula is $C_{10}H_8$.
2) Though the molecular formula suggests that it should be an unsaturated compound, it is resistant to addition reactions.
3) On the other hand, it undergoes electrophilic substitution reactions (chlorination, nitration, sulphonation) like benzene.
4) The nuclear 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:



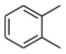
This shows the presence of at least one aromatic ring and two side chains are in ortho positions to each other. Therefore, the formula of naphthalene may be



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



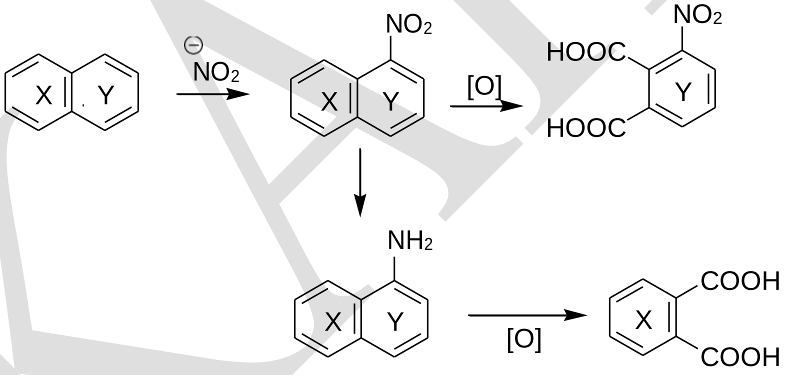
7) The presence of two benzene rings in naphthalene (Graebe, 1869) is supported from the following reactions:

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

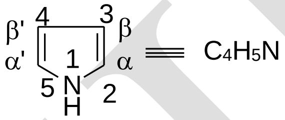
Introduction

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.

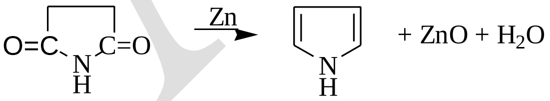
(1) Pyrrole, C_4H_5N



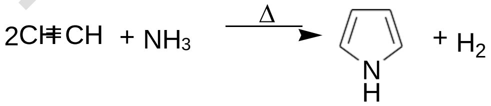
Pyrrole is an important heterocyclic compound. It is found in many natural compounds, e.g. alkaloids, chlorophyll etc. It occurs in coal tar and bone oil.

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:

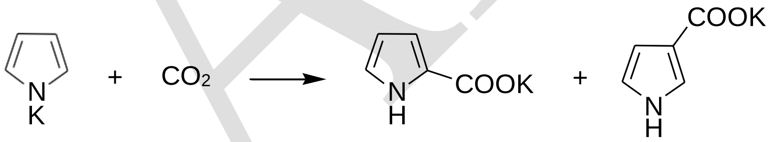
$$C_4H_4NH + HCl \longrightarrow C_4H_4NH_2^+ Cl^-$$

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).

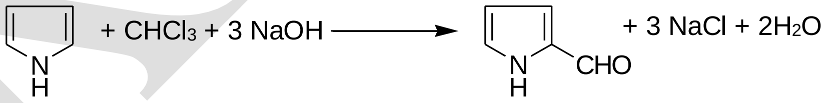
$$C_4H_4NH + KOH \longrightarrow C_4H_4N^- K^+ + H_2O$$

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

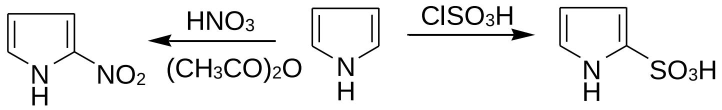
c) **Substitution reactions:** In many reactions, pyrrole resembles phenol. For example, potassio pyrrole reacts with carbon dioxide to form 2- and 3-pyrrole carboxylic acid (*Cf.* kolbe Schmidt reaction)



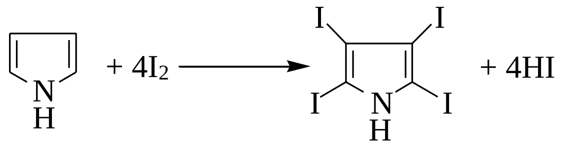
Pyrrole reacts with chloroform and sodium hydroxide to form pyrrole-2-aldehyde (*Cf.* Reimer –Tiemann reaction).



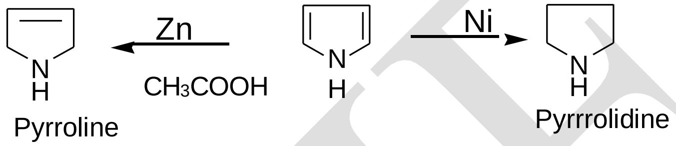
Pyrrole cannot be nitrated and sulphonated or halogenated by the methods used in the case of benzene. At 263 K, pyrrole yields 2-nitropyrrole with nitric acid in acid in acetic anhydride. With chlorosulphonic acid, pyrrole is sulphonated to form pyrrole-2-sulphonic acid.



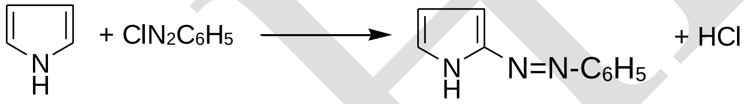
Halogenation occurs readily if the solution is alkaline. Iodine forms tetraiodopyrrole.



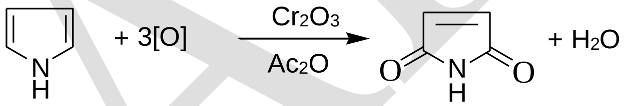
d) Reduction: With zinc dust and acetic acid, pyrrole undergoes reduction to give pyrroline (2,5-dihydropyrrole). At 473 K catalytically reducing pyrrole using nickel, pyrrolidine (tetrahydropyrrole) is formed.



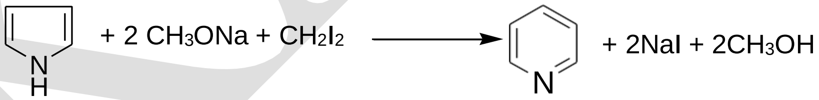
e) Coupling: Pyrrole couples with benzenediazonium chloride in a weakly acidic solution to give 2-phenyl azo pyrrole:



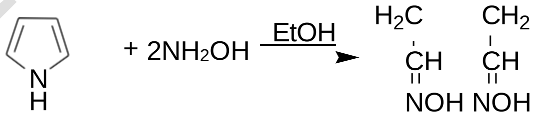
f) Oxidation : Pyrrole is oxidized by chromic acid to give maleic imide:



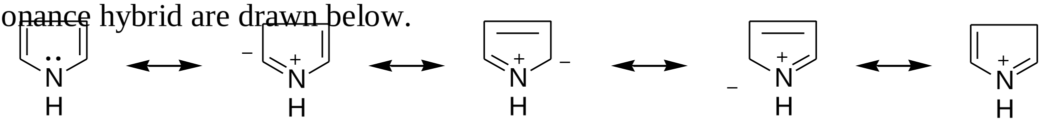
g) Ring expansion: When treated with sodium methoxide and methylene iodide, pyrrole undergoes ring expansion forming pyridine.



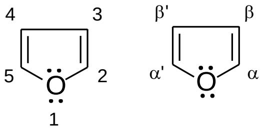
h) Ring opening reaction: When treated with ethanolic hydroxylamine, pyrrole undergoes ring opening forming succindialdoxime.



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

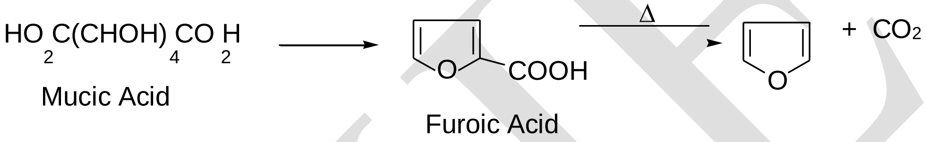


(2) Furan, C_4H_4O

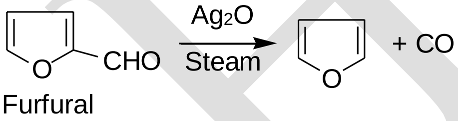


Preparation

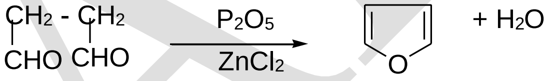
a) Furan is obtained when wood, especially pine wood, is distilled. It may be prepared by the dry distillation of mucic acid, and heating the product, furoic acid (I), at its boiling point:



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



c) By dehydration of succindialdehyde.



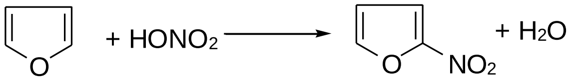
Properties

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.

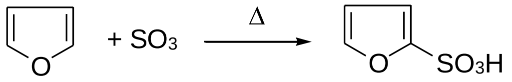
Furan, like pyrrole, is a weak base. It forms salt with mineral acids. These salts may either polymerise to produce a brown resin or undergo hydrolysis to yield succindialdehyde.

(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.

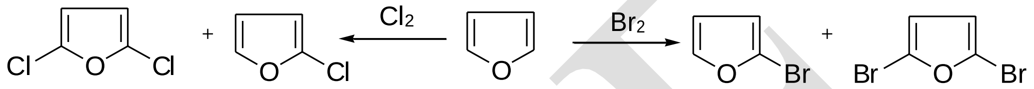
(a) Nitration: It can be nitrated with a hot solution of nitric acid and acetic anhydride to form 2-nitrofuran.



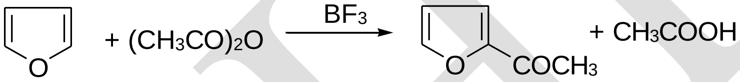
(b) Sulphonation: Furan may be sulphonated by sulphur trioxide in pyridine at 343 K to yield furan-2-sulphonic acid.



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

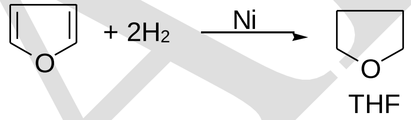


(d) Friedel-Craft's acylation: Furan can be acylated with acetic anhydride in the presence of BF_3 or $SnCl_4$ at 273 K to yield 2-acetylfuran.

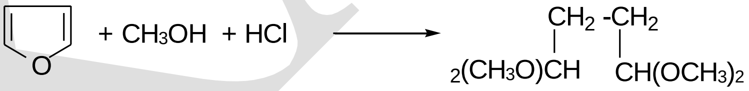


(e) Diazo coupling: Furan is not sufficiently reactive to couple with benzenediazonium chloride.

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

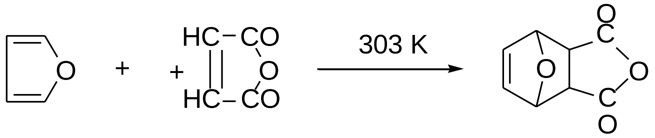


(III) **Ring opening reaction:** When treated with methanol and hydrochloric acid, furan undergoes ring opening forming the diacetal of succindialdehyde.

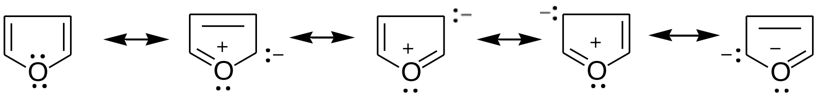


(Hydrolysis of furan with dilute hydrochloric acid also leads to ring opening)

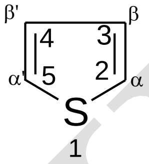
Diels-Alder Reaction: Furan is the only one of the five membered heterocyclic compounds to undergo the Diels–Alder reaction with maleic anhydride. The addition occurs across C-2 and C-5.



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.

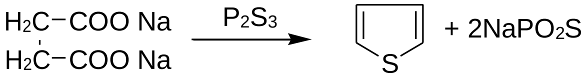
Preparation

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:

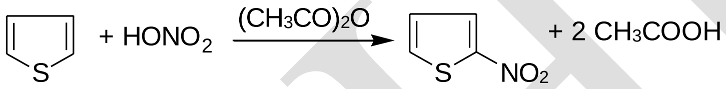
$$C_4H_{10} + 4\,S \longrightarrow \qquad + 3\,H_2S$$

Properties

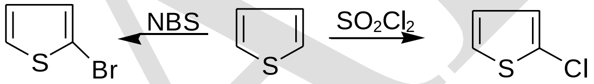
Thiophene is a colourless liquid, smelling like benzene. It is insoluble in water but soluble in organic solvents. Chemically thiophene resembles benzene rather closely. As compared with furan and pyrrole, it is comparatively more stable.

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.

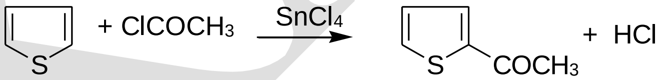
Thiophene can be nitrated by a solution of nitric acid in acetic anhydride to yield 2-nitrothiophene. Sulphonation with cold, concentrated sulphuric acid gives 2-sulphonic acid.



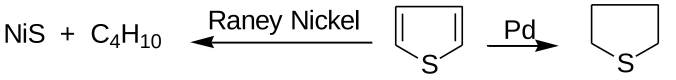
Chlorination at room temperature gives 2-chlorothiophene with SO_2Cl_2. 2-bromothiophene is obtained at room temperature when thiophene is treated with *N*-bromosuccinimide (NBS).



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.

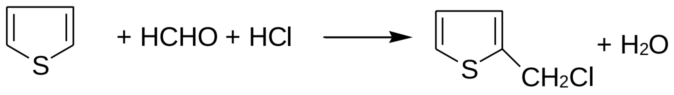


Reduction: Catalytic hydrogenation of thiophene using large amount of catalyst gives tetrahydrothiophene (**thiophan)** and using Raney nickel as catalyst thiophene is converted to n-butane, C_4H_{10}.

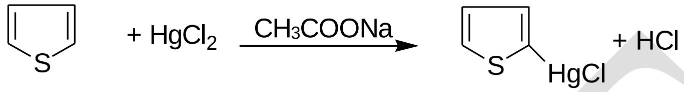


Thiophan

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



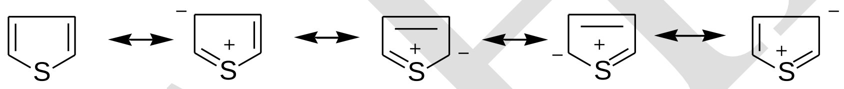
Mercuration: Thiophene undergoes mercuration with mercuric chloride in aqueous sodium acetate to produce 2-chloromercurithiophene.



Thiophene does not react with benzenediazonium chloride.

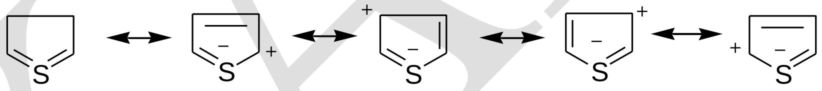
Thiophene is a resonance hybrid with resonance energy 117-130 k. J mol^{-1}. In the resonance structures written below in **group (a)** sulphur atom uses p-orbitals and in **group (b)** sulphur uses d-orbital.

(a)



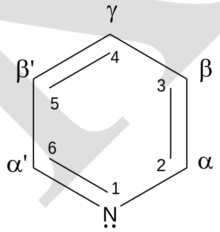
I II III IV V

(b)



VI VII VIII IX X

(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.

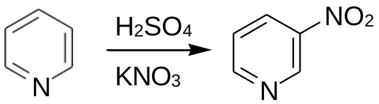
$$C_5H_5N + HCl \longrightarrow C_5H_5NH^+Cl^-$$

pyridinium chloride

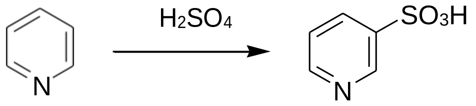
$$C_5H_5N + CH_3I \longrightarrow [C_5H_5NCH_3]^+ I^-$$

pyridine methiodide

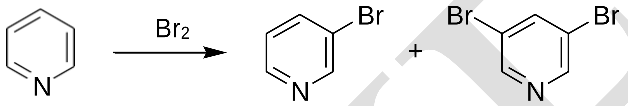
Electrophilic Sustitution: Pyridine is considerably less reactive than benzene towards electrophiles. So, it does not undergo Friedel Craft's reaction. It undergoes nitration, sulphonation and halogenations only under vigorous conditions. With conc. H_2SO_4 and KNO_3 at 573 K it gives 3-nitropyridine.



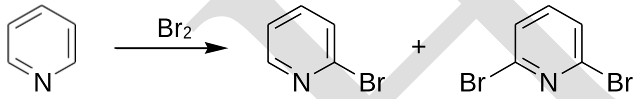
Sulphonation of pyridine is difficult. On heating with concentrated sulphuric acid at 623 K for some hours it gives pyridine-3- sulphonic acid.



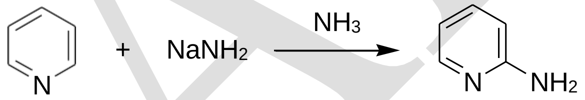
With bromine at 573 K in the presence of catalyst (pumice or charcoal) pyridine gives a mixture of 3- bromopyridine and 3, 5-dibromopyridine.



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

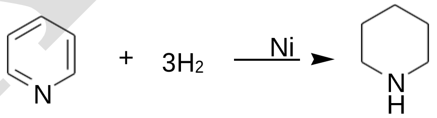


Pyridine reacts with sodamide in liquid ammonia at about 373 K to form 2-aminopyridine **(Chichibabin reaction)**. This reaction is an example of nucleophilic substitution reaction.

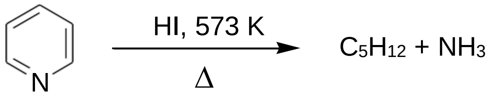


Reduction

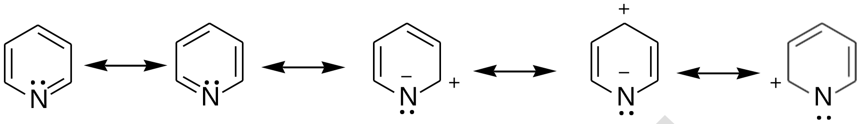
Pyridine undergoes reduction with lithium aluminum hydride or hydrogen in the presence of nickel catalyst to form piperidine.



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?

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DEPARTMENT OF CHEMISTRY

UNIT-II

AROMATIC COMPOUNDS AND HETEROCYCLIC COMPOUNDS

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. The resonance energy of benzene is

a) 126 k J mol^{-1} **b) 150 k J mol^{-1}** c) 255 k J mol^{-1} d) 351 k J mol^{-1}

2. Which is called nitrating mixture?

a) conc. HNO_3 b) aqua regia **c) conc. HNO_3 and conc. H_2SO_4** d) conc. H_2SO_4

3. What is the attacking species in nitration?

a) NO b) NO_2 c) NO^+ **d) NO_2^+**

4. The catalyst employed in Friedel-Craft s reaction is

a) $AgCl_3$ **b) $AlCl_3$** c) $FeCl_3$ d) NaCl

5. Bonding in benzene involves

a) sp^2 hybridization b) sp^3 hybridization

c) sp hybridization d) a resonance of two Kekule structure only

6. Typical substitution reaction in aromatic hydrocarbons are

a) electrophilic b) nucleophilic c) free radical d) photochemical

7. Name the reaction which is used to prepare styrene from benzene

a) halogenation **b) Friedel-Craft's reaction** c) sulphonation d) nitration

8. Naphthalene is found to be present in the_______oil fraction of coal tar

a) light **b) middle** c) heavy d) anthracene

9. Naphthalene is prepared using

a) Elbs reaction b) Friedel-Crafts reaction **c) Haworth reaction** d) Bucherer reaction

10. Naphthalene is purified using

a) crystallization **b) sublimation** c) distillation d) steam distillation

11. The reagent required to convert naphthalene into tetralin is

a) Ni b) Se c) $AlCl_3$ d) Zn/Hg + HCl

12. On oxidation of naphthalene with alkaline $KMnO_4$ forms

a) phthalic acid **b) phthalonic acid** c) phthalic anhydride d) naphthaquinone

13. Naphthalene on oxidation with chromic acid gives

a) naphthaquinone b) phthalic anhydride c) phthalic acid d) phthalonic acid

14. The number of benzene rings present in anthracene is

a) one b) two **c) three** d) four

15. A nucleophile generally has________charge

a) positive **b) negative** c) neutral d) radical

16. Nitration takes place very easily in

a) benzene **b) toluene** c) naphthalene d) anthracene

17. Furan is

a) an alcohol **b) a heterocyclic compound** c) a disaccharide d) an amino acid

18 The hydrocarbon, much useful in the synthesis of heterocyclic compounds, is

a) methane b) ethane c) ethylene **d) acetylene**

19. The heterocyclic compound, which can undergo Diels-Alder reaction, is

a) furan b) thiophene c) pyrrole d) pyridine

20. The ferrocene is an example for

a) aliphatic compound b) benzenoid compound

c) non benzenoid compound d) unsaturated compound

21. All aromatic electrophilic substitution reactions are

a) monomolecular **b) bimolecular** c) trimolecular d) tetramolecular

22. The hetero atom in thiophene is

a) O b) N c) P **d) S**

23. The position, at which the electrophilic substitution occurs in pyrrole, is

a) C-5 **b) C-2** c) C-3 d) C-4

24. Decahydronaphthalene also called as

a) β-tetralone b) tetralin c) α-tetralone **d) decalin**

25. The naphthalene is used for preparation of

a) benzoquinone b) benzoic acid **c) phthalic anhydride** d) thiophene

26. When pyrrole treated with sodium methoxide and methyene iodide gives

a) thiophene **b) pyridine** c) furan d) pyrrole

27. In pyridine the electrophilic substitution reaction takes place at

a) C-6 b) C-2 **c) C-3** d) C-4

28. Pyridine, in Chichibabin reaction gives

a) 1-aminopyridine **b) 2-aminopyridine** c) 3-aminopyridine d) 4- aminopyridine

29. What type of reaction is the Chichibabin reaction?

a) electrophili substitution b) electrophilic addition

c) nucleophilic addition **d) nucleophilic substitution**

30. Pyridine on reduction gives

a) piperidine b) pyrrole c) pyrrolidine d) aniline

31. The more basic heterocyclic compound containing nitrogen is

a) pyridine b) pyrrole c) furan d) thiophene

32. Ethyl benzene is obtained from benzene in

a) nitration b) halogenation c) sulphonation **d) Friedel-Craft's reaction**

33. In an electrophilic substitution reaction, the attacking species attacks

a) an electron-poor carbon b) a neutral carbon

c) a tertiary carbon **d) an electron rich carbon**

34. Which of the following is an electrophile?

a) H_2SO_4 b) OH^- **c) NO_2^+** d) H_3O^+

35. The halogenations of benzene requires

a) very high temperature **b) a catalyst** c) a polar solvent d) a non-polar solvent

36. In the sulphonation of benzene, the sulphonating species is

a) SO_3 b) NO_2^+ c) H_3PO_4 d) HNO_3

37. In the Friedel-Crafts alkylation of benzene, the attacking species is

a) $AlCl_3$ b) R^- **c) R^+** d) RX

38. Naphthalene is

a) an aliphatic compound b) an aromatic compound

c) an aromatic hydrocarbon d) an industrial solvent

39. Which of the following cannot be obtained by distillation of coal tar?

a) Naphthalene b) anthracene **c) ethyl alcohol** d) benzene

40. Tetrahydrofuran is a good

a) antiseptic **b) solvent** c) oxidant d) base

41. Mononitation of naphthalene gives

a) 1-nitronaphthalene b) 2-nitronaphthalene

c) 3-nitronaphthalene d) β-nitronaphthalene

42. Naphthalene on complete reduction goves

a) 1,4-dihydronaphthalene b) tetralin c) tetrahydronaphthalene **d) decalin**

43. Anhydrous $AlCl_3$ used in the Friedel-Craft reaction acts as a

a) catalyst b) solvent c) hydrogen carrier d) electrophile

44. Name the reaction which is used to prepare benzophenone from benzene

a) halogenation **b) Friedel-Crafts reaction** c) sulphonation d) nitration

45. Acetophenone is prepared from

a) halogenations reaction b) sulphonation reaction

c) Friedel-Crafts reaction d) nitration reaction

46. Naphthalene is soluble in

a) water **b) organic solvents** c) base d) acid

47. The zinc amalgam and hydrochloric acid is known as

a) Baeyer-Villiger oxidation b) Wolff-Kishner reduction

c) catalytic reduction **d) Clemmensen reduction**

48. Among pyrrole, furan and thiophene________readily undergoes Diel's Alder reaction?

a) pyridine b) thiophene c) pyrrole **d) furan**

49. The heterocyclic compound used for the denaturation of ethanol is

a) pyridine b) thiophene c) pyrrole d) furan

50. The pyridine is used as a

a) reagent **b) base, solvent and catalyst** c) catalyst d) solvent

51. ________is used as starting material in the preparation of sulphapyridine and pyridoxine.

a) pyrrole b) furan c) thiophene **d) pyridine**

52. Pyridine has resonance energy at about

a) 150 K. J mol^{-1} **b) 125 K. J mol^{-1}** c) 200 K. J mol^{-1} d) 110 K. J mol^{-1}

53. In pyridine the nucleophilic substitution reaction takes place at

a) C-5 **b) C-2** c) C-3 d) C-1

54. The dipole moment value of pyridine is

a) 1.23 D b) 2.1 D **c) 2.23 D** d) 4.23 D

55. Thiophene does not react with

a) benzene diazonium chloride b) HCHO c) NBS d) SO_2Cl_2

56. Furan is less aromatic than thiophene and pyrrole because

a) it behaves as a 1,3-diene b) it does not behaves as a 1,3-diene

c) it behaves as a 1,4-diene d) it behaves as a 1,2-diene

57. Pyrrole is a

a) weak base b) strong base c) weak acid d) strong acid

58. Pyrrole undergoes zinc and acetic acid reduction to give

a) pyrrolidine b) pyridine **c) pyrroline** d) maleic imide

59. Pyrrole couples with benzene diazonium chloride in a weak acidic solution to give

a) 2-phenyl azo pyrrole b) maleic imide c) pyridine d) tetraiodopyrrole

60. Pyrrole reacts with chloroform and sodium hydroxide to form pyrrole -2- aldehyde is an example for

a) Kolbs Schmidt reaction b) Schmidt reaction

c) Reimer-Tiemann reaction d) Diel’s Alder reaction

UNIT-

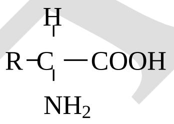
IIISYLLAB

US

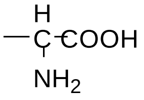
Amino acids, Proteins and Carbohydrates: Amino acids: Classification, preparation and properties. Peptides-preparation of peptides (Bergmann method only). **Proteins:** Classification, properties, biological functions and structure. **Carbohydrates:** Classification, preparation and properties of glucose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

A

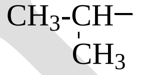
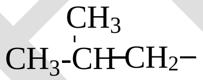
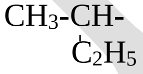
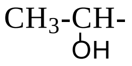
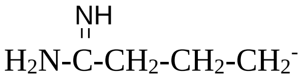
An amino acid, as the name implies, is a difunctional compound which contains both an amino and a carboxyl group. This may be regarded as a derivative of carboxylic acids in which a hydrogen atom has been replaced by an amino group. On the basis of the position of amino group with respect to the carboxyl 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,

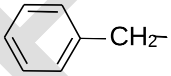
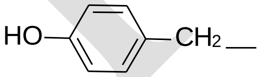
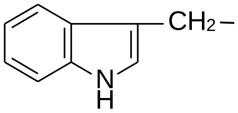
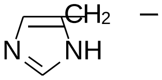


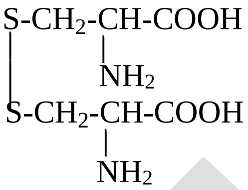
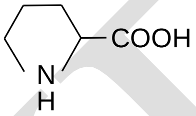
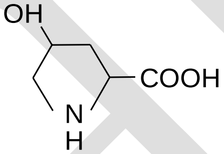
$$R-\underset{NH_2}{\overset{H}{C}}-COOH$$

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  $-\underset{NH_2}{\overset{H}{C}}-COOH$) are common toall.

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	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-$
4.	Norleucine	CH_3-CH_2-CH_2-CH_2-
5.	Leucine	 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-$
6.	Isoleucine	 $CH_3-\underset{C_2H_5}{\underset{\vert}{CH}}-$
(B) Hydroxy amino acids		
7.	Serine	HO-CH_2-
8.	Threonine	 $CH_3-\underset{OH}{\underset{\vert}{CH}}-$
(C) Basic amino acids		
9.	Lysine	H_2N-CH_2-CH_2-CH_2-CH_2-
10.	Arginine	 $H_2N-\overset{NH}{\overset{\Vert}{C}}-CH_2-CH_2-CH_2^-$

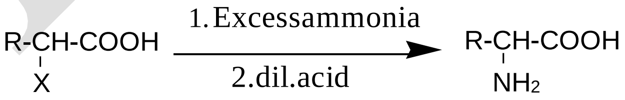
(d) Acidic amino acids		
11.	Aspartic acid	HOOC-CH_2-
12.	Glutamic acid	HOOC-CH_2-CH_2-
(E) Amide amino acids		
13.	Asparagine	H_2N-CO-CH_2-
14.	Glutamine	H_2N-CO-CH_2- CH_2-
(F) Aromatic amino acids		
15.	Phenylalanine	
16.	Tyrosine	
(g) Sulphur containing amino acids		
17.	Cysteine	HS-CH_2-
18.	Methionine	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	 $\begin{array}{l} \text{S-CH}_2\text{-}\underset{\text{NH}_2}{\text{CH}}\text{-COOH} \\ \vert \\ \text{S-CH}_2\text{-}\underset{\text{NH}_2}{\text{CH}}\text{-COOH} \end{array}$
22.	Proline	
23.	Hydroxyproline	

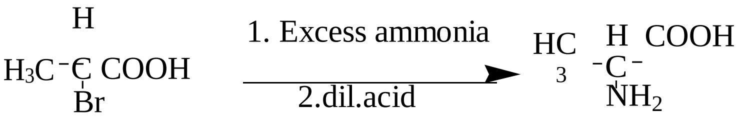
The amino acids that can be synthesized from other compounds by the tissues of the body are called *Non–essential* amino acids. The amino acids that cannot be synthesized by the body and must be supplied in the diet are called *essential* amino acids. The essential amino acids are- valine, leucine, isoleucine,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



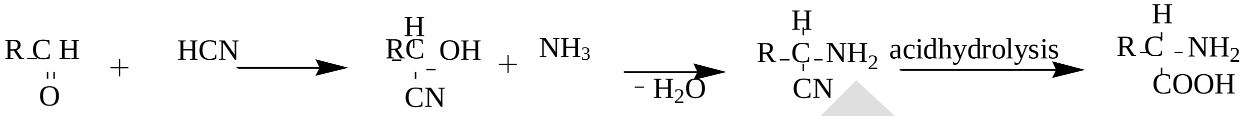
$$\text{R-}\underset{\text{X}}{\text{CH}}\text{-COOH} \xrightarrow[\text{2.dil.acid}]{\text{1.Excessammonia}} \text{R-}\underset{\text{NH}_2}{\text{CH}}\text{-COOH}$$



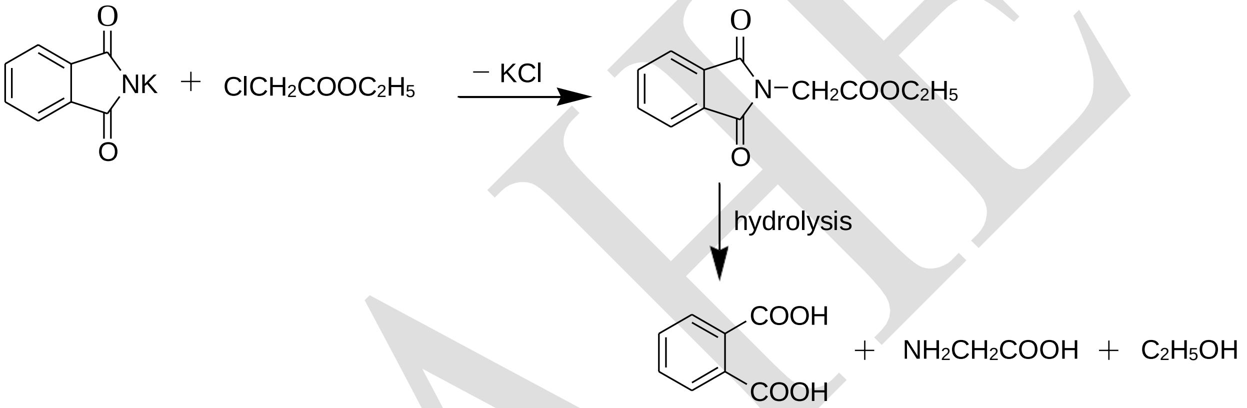
$$\text{H}_3\text{C}-\overset{\text{H}}{\underset{\text{Br}}{\text{C}}}\text{COOH} \xrightarrow[\text{2.dil.acid}]{\text{1. Excess ammonia}} \text{H}_3\text{C}-\overset{\text{H}}{\underset{\text{NH}_2}{\text{C}}}-\text{COOH}$$

α-bromopropionicacid **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 thisprocess.



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 aminoacid.



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

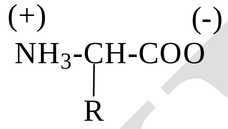
1) Some of the physical properties of amino acids differ noticeably from other organic compounds.

   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 organicsolvents.

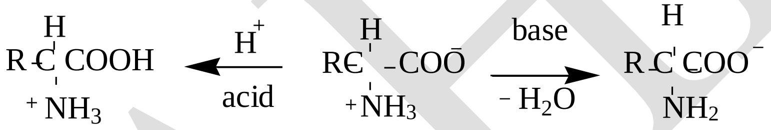
3) When measured in aqueous solutions, the dipole moment of amino acids is found to have a large value.

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 aminogroup.



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

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:



$$R\text{-}\underset{^{+}NH_3}{\overset{H}{C}}\text{-}COOH \xleftarrow[\text{acid}]{H^+} R\text{-}\underset{^{+}NH_3}{\overset{H}{C}}\text{-}CO\bar{O} \xrightarrow[-H_2O]{\text{base}} R\text{-}\underset{NH_2}{\overset{H}{C}}\text{-}COO^-$$

Zwitter ion

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, dipolarion.

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 pH10.

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

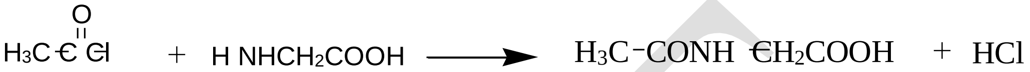
Reactions characteristic of the amino group

1) Amino acids react with strong acids to give the correspondingsalts.

$H_2N\text{-}CH_2\text{-}COOH + HCl \longrightarrow ClH_3N\text{-}CH_2\text{-}COOH$

Glycine hydrochloride

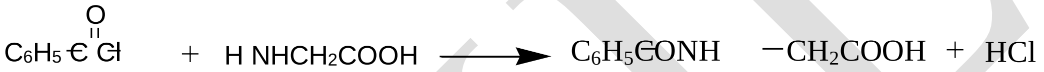
2)The amino group of amino acids can be acylated with acetyl chloride or acetic anhydride to form *N*- acylaminoacids.



$H_3C\text{-}\overset{O}{\overset{||}{C}}\text{-}Cl + H\,NHCH_2COOH \longrightarrow H_3C\text{-}CONH\text{-}CH_2COOH + HCl$

N-acetyl glycine (aceturic acid)

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



$C_6H_5\text{-}\overset{O}{\overset{||}{C}}\text{-}Cl + H\,NHCH_2COOH \longrightarrow C_6H_5\text{-}CONH\text{-}CH_2COOH + HCl$

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 haloacids.

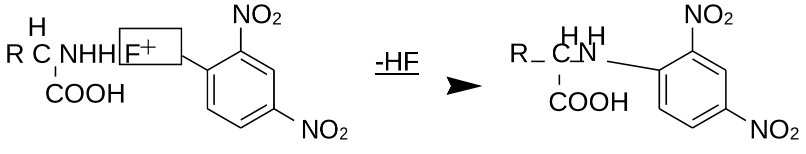
$H_2NCH_2COOH + NOCl \longrightarrow Cl\text{-}CH_2COOH + N_2 + H_2O$

Chloroacetic acid

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

$HCHO + H_2NCH_2COOH \longrightarrow H_2C{=}NCH_2COOH + H_2O$

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 formsalts.

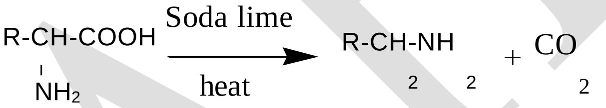
$$H_2N\text{-}CH_2\text{-}COOH + NaOH \longrightarrow H_2N\text{-}CH_2\text{-}COONa + H_2O$$

sodium amino acetate

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

$$H_2N\text{-}CH_2\text{-}COOH + C_2H_5OH \xrightarrow{HCl} \overset{-}{Cl}H_3\overset{-}{N}\text{-}CH_2\text{-}COOC_2H_5 + H_2O$$

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



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

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

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

Cupric glycinate

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

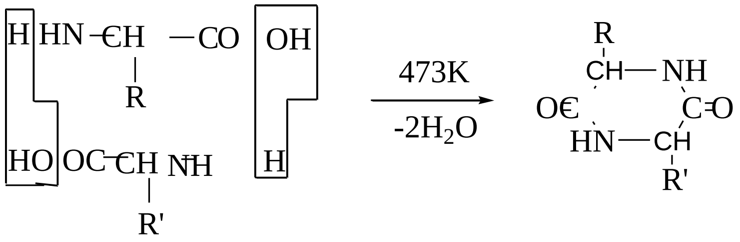
$$R\text{-}\underset{NH_2}{CH}\text{-}COOH \xrightarrow{LiAlH_4} R\text{-}\underset{NH_2}{C}H\text{-}CH_2OH$$

amino alcohol

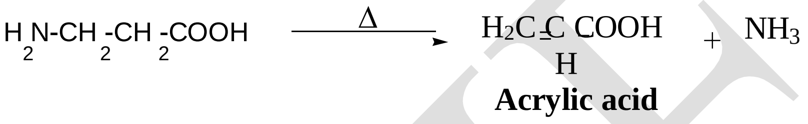
Reactions involving both the carboxyl and the amino groups

1) Action of heat on aminoacids

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

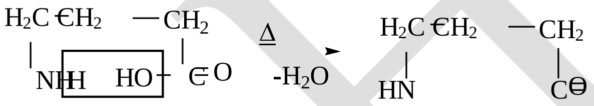


b) A β- amino acids on heating loses a molecule of ammonia to form an unsaturated acid. For example, β- amino propionic acid on heating forms acrylicacid.



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

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

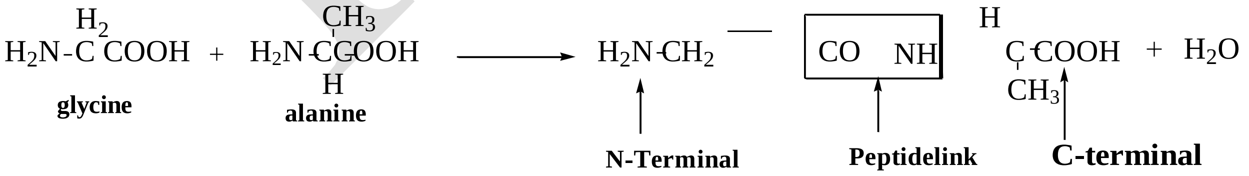


2) All α-amino acids react with ninhydrin to produce the same purplecolour.

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

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* isformed.



Thus, a *dipeptide* is formed from two amino acids. A three amino acids peptide iscalled *"tripeptide"*andsoon.Compoundsinwhichalargenumberofaminoacidsarelinkedtoeach 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.

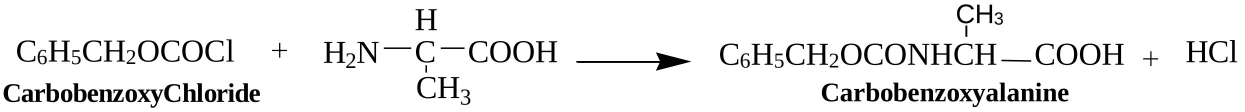
All the methods generally consist of the following three steps -

(i) Protection of amino group in the aminoacid
(ii) Formation of peptidelinkage
(iii) Removal of the protectinggroup.

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

Carbobenzoxy method (Bergmann method)

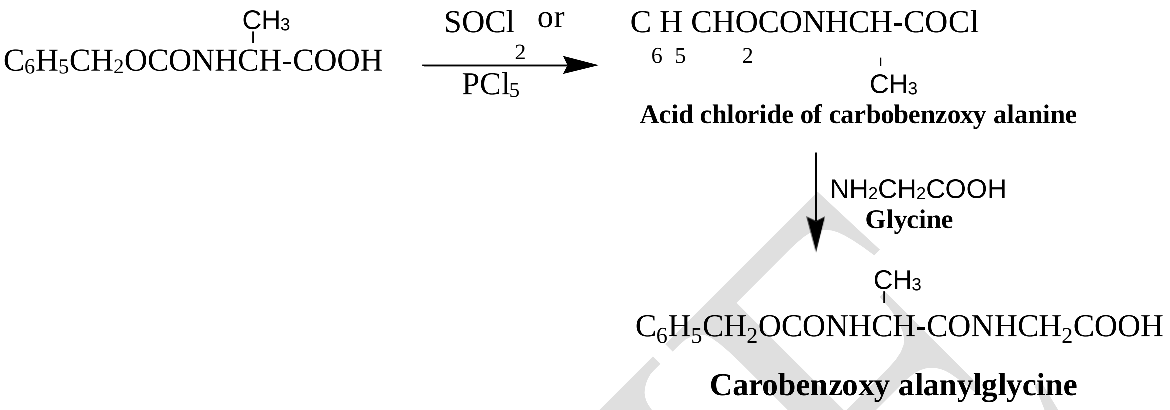
First step



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

CarbobenzoxyChloride **Alanine** **Carbobenzoxyalanine**

Second Step



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

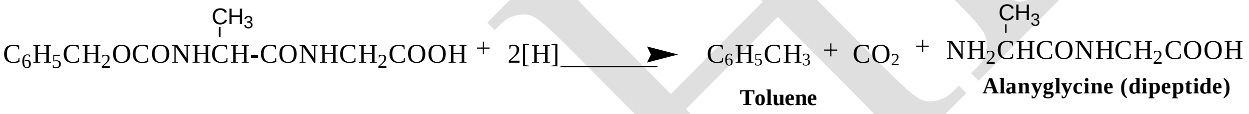
Acid chloride of carbobenzoxy alanine

$$\downarrow \; NH_2CH_2COOH \text{ (Glycine)}$$

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

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 byheat.

Example: serum albumin, egg albumin

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

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 ofwheat.

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 aminoacids.

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 commonsolvents.

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 isobtained

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 turnspink.

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 isproduced.

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 notparticipate.

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 thebody.

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

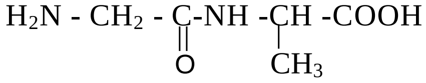
Antibodies, which are proteins, function to protect human beings against diseases

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:



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

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 possiblesequences:

Example:

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

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 sequencesas:

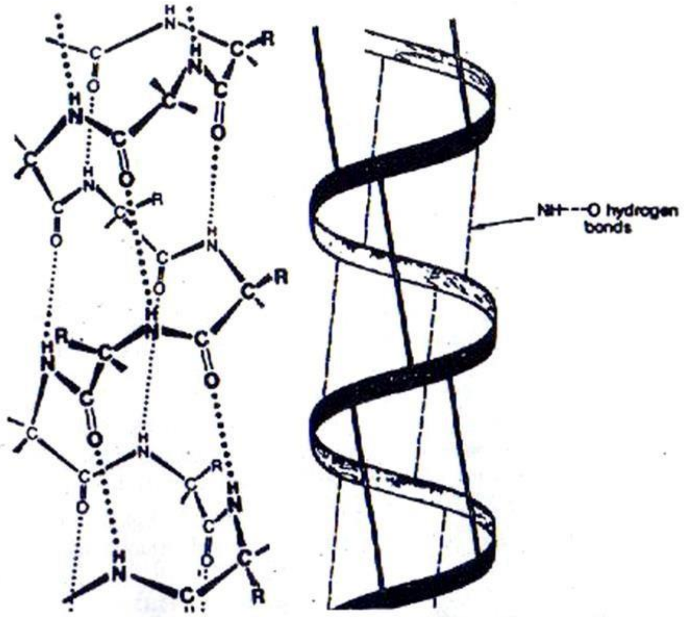
1) Ala-gly-leu 2)Ala-leu-gly 3) Gly-ala-leu

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 thefigure.

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 andpH.

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 istermed 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 inwater.

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 reducingsugar.

8) Then term *tetrose, pentose* and *hexose* are used to indicate those carbohydrates having four, five and six carbon atomsrespectively.

   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 aketohexose.

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 ofdiabetics.

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

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{dil.HCl}} n\ C_6H_{12}O_6$$

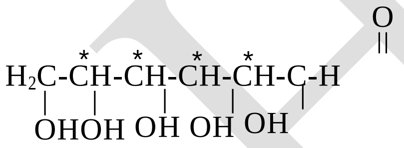
2) It is formed as an intermediate product in the fermentation of starch for the manufacture of ethylalcohol.

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, separatesout.

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

Properties

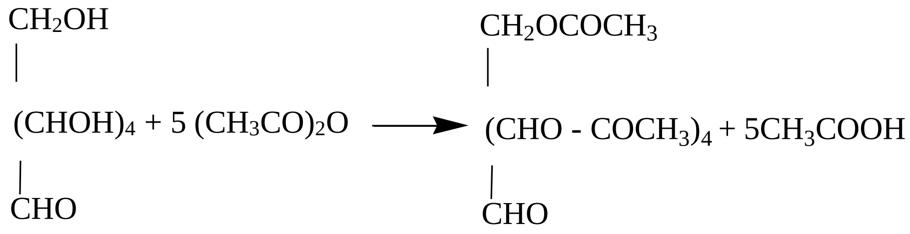
Glucose is a white crystalline solid (m.p 419 K), sweet to taste. It is readily soluble in water. Naturally occurring glucose is *dextro-rotatory* (hence, the name Dextrose) and it has four asymmetric carbon atom (marked by *).



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

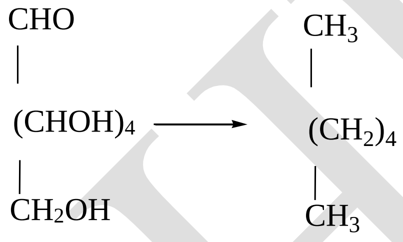
Structural formula of glucose indicates the presence of one aldehydic group, one primary alcoholic group and four secondary alcoholic groups. Chemical properties of glucose are, therefore, the properties of the above functional groups. The structural elucidation very easily follows from its reactions:

1) Quantitative analysis establishes the empirical formula asCH_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 aceticanhydride.



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

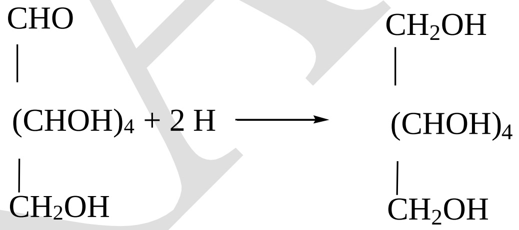
4) Reduction of glucose with concentrated hydriodic acid and red phosphorus at 373K yields 2-iodohexane. Prolonged heating produces n-hexane. This would mean that glucose is a straight chain compound of six carbonatoms.



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

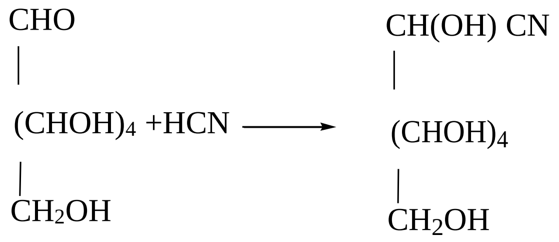
n-hexane

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, calledsorbitol.



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

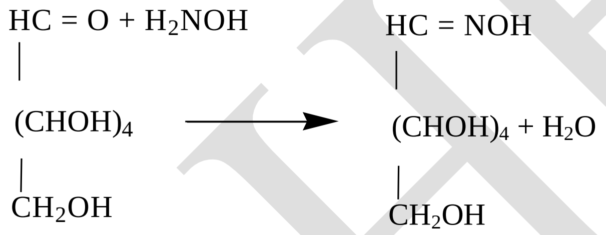
6) Glucose gives addition product with hydrogen cyanide *(but not with ammonia or sodium bisulphite).* This reaction indicates the presence of a carbonylgroup.



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

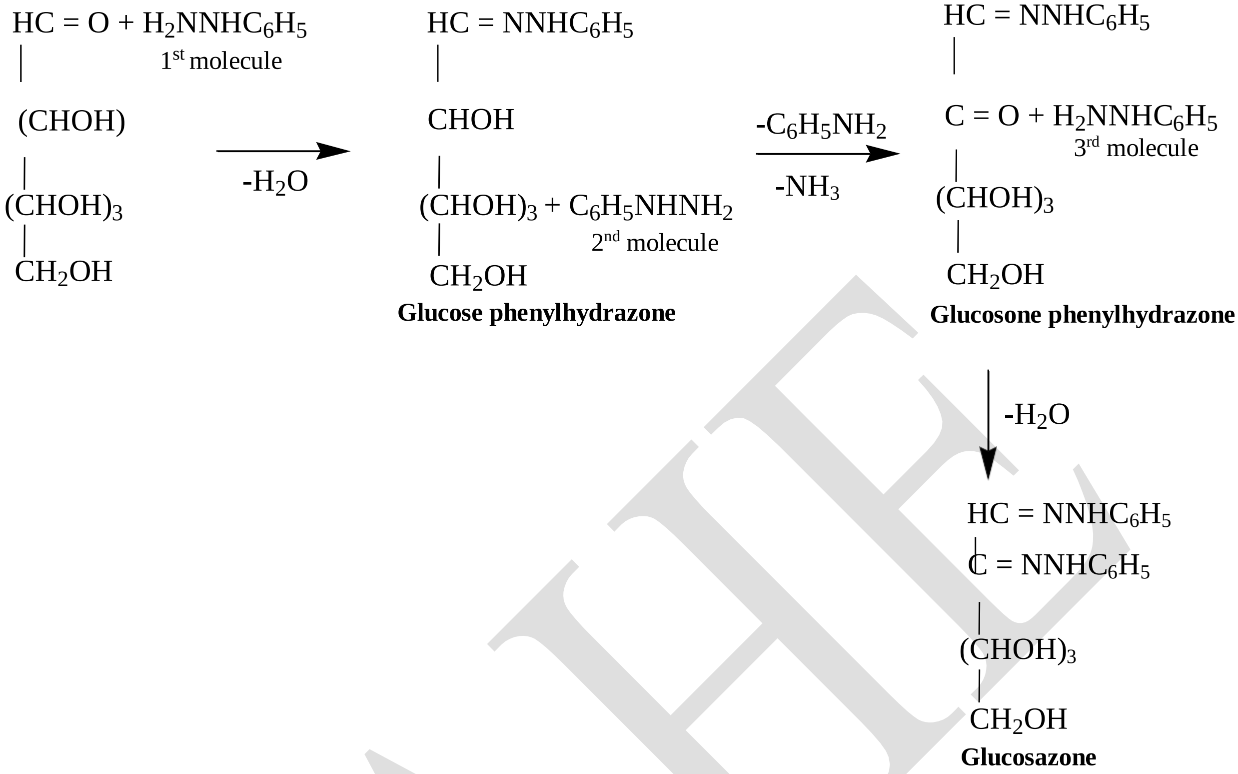
glucose cyanohydrin

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

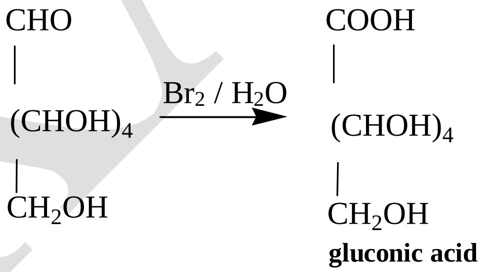


$$\begin{array}{l}\mathrm{HC = O + H_2NOH}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CH_2OH}\end{array} \longrightarrow \begin{array}{l}\mathrm{HC = NOH}\\ |\\ \mathrm{(CHOH)_4 + H_2O}\\ |\\ \mathrm{CH_2OH}\end{array}$$

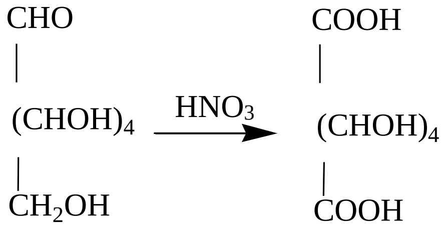
8) Glucose reacts with one molecule of phenylhydrazine in acetic acid which condenses with the aldehyde group to give *phenylhydrazone*. When warmed with excess phenylhydrazine, the secondary alcoholic group, adjacent to the aldehyde group, is next oxidised to a keto group. With this keto group, third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



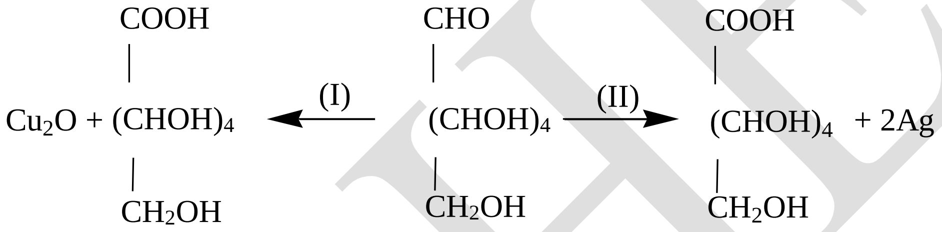
10) With strong oxidising agents like nitric acid, it is oxidised to a dicarboxylic acid, saccharic acid. Nitric acid is able to oxidise the primary alcohol group also to an acid group.



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

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 ethylalcohol.

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

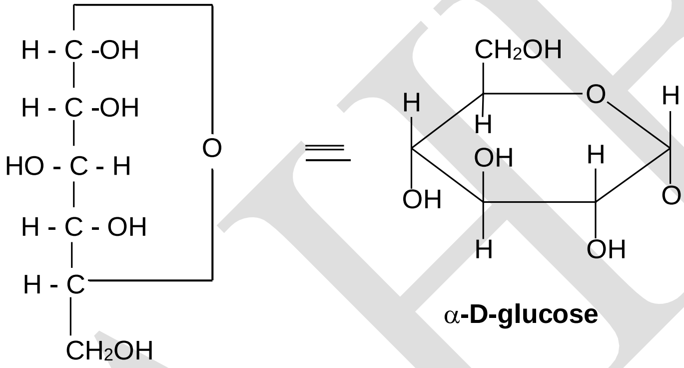
13) A dilute solution of glucose when warmed with dilute alkali solution, gives a mixture of glucose, fructose andmannose.

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

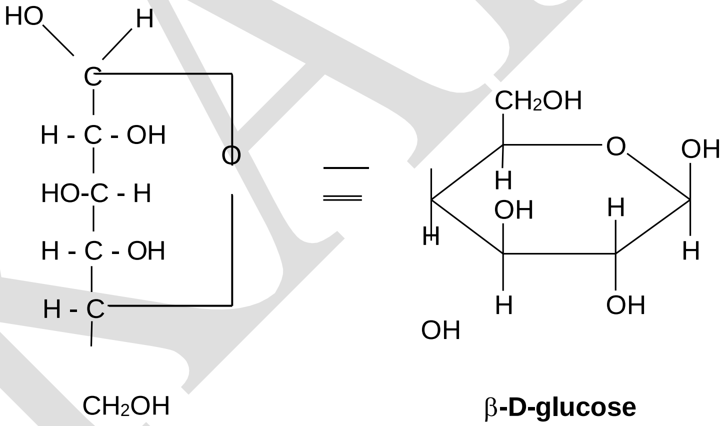
All the above reactions of glucose indicate that glucose is a polyhydric alcohol with a terminal aldehyde group and that it is a straight chain compound.

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 inconfectionery.
2) It is utilised in the manufacture of ascorbic acid (VitaminC).
3) It serves as food for invalids and as foodpreservatives.

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.

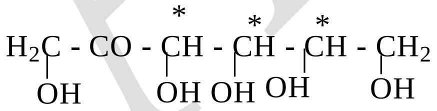
Preparation

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

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

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 offructose is$C_6H_{12}O_6$.
2) Complete reduction of fructose with HI and red phosphorus give n-hexane as the majorproducts, suggesting a straight chainformula.

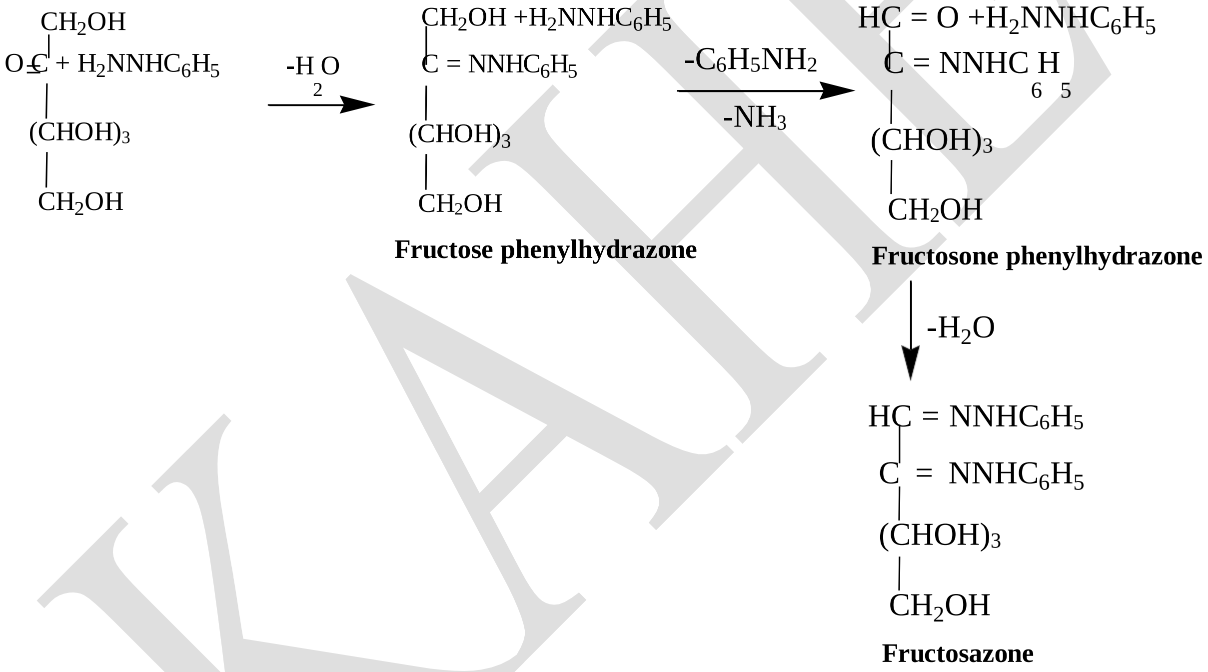
3) Fructose reacts with 5 moles of acetyl chloride or acetic anhydride to form a penta-acetate. This indicates the presence of five hydroxyl group in a fructose molecule. Since fructose is a stable compound, the five hydroxyl groups must be present on separate carbonatoms.

4) (a) Fructose reacts with hydroxylamine to form anoxime.

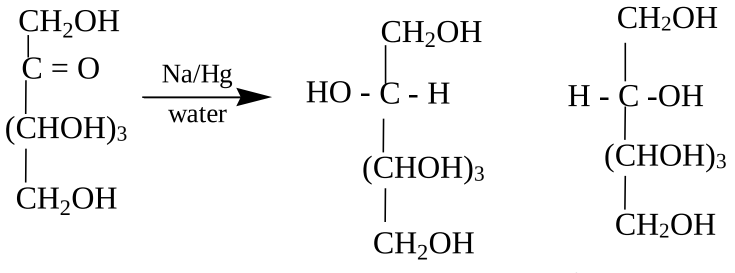
   (b) It adds with only one mole of HCN to give a cyanohydrin.

   These reactions indicate the presence of a carbonylgroup.

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

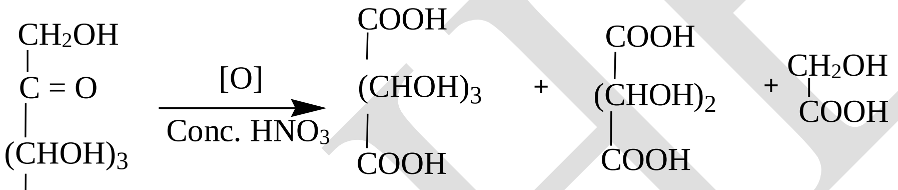


6) Reduction of fructose with sodium amalgam and water produces a mixture of two epimeric alcohols, sorbitol and mannitol because a new asymmetric carbon has been created at C_2.This indicates the presence of ketogroup.



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:

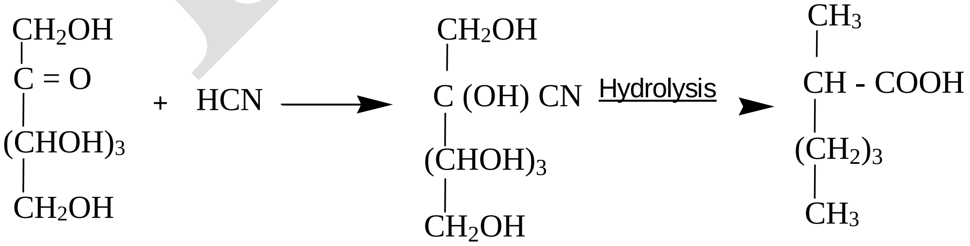


Trihydroxy glutaric acid **Tartaric acid** **Glycollic acid**

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 reducingproperties.

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 carbonatom.



2-Methylhexanoic acid

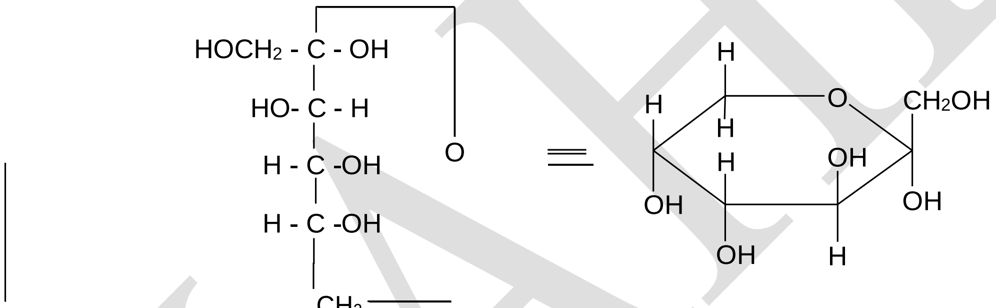
10) Fructose is fermented by yeast to ethylalcohol.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\,CO_2 + 2C_2H_5\,OH$$

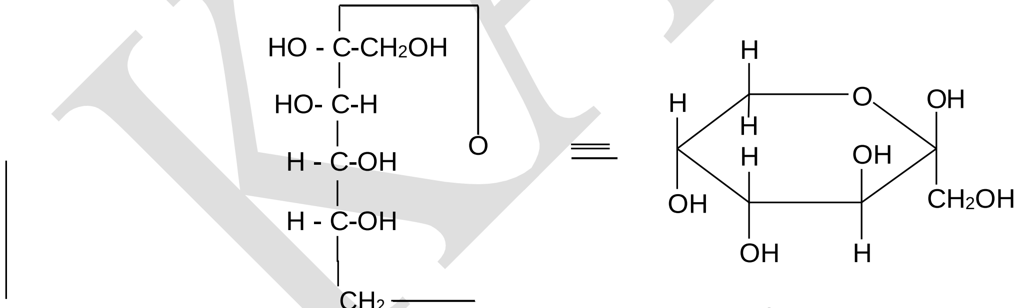
11) Fructose when warmed with dilute alkali forms a mixture of glucose, fructose and mannose like glucose.

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

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 forfructose.

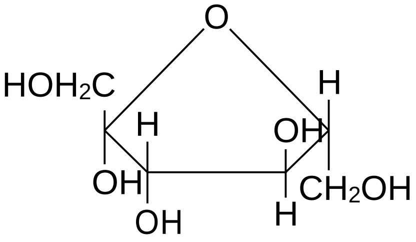


α-D-fructose



β-D-fructose

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

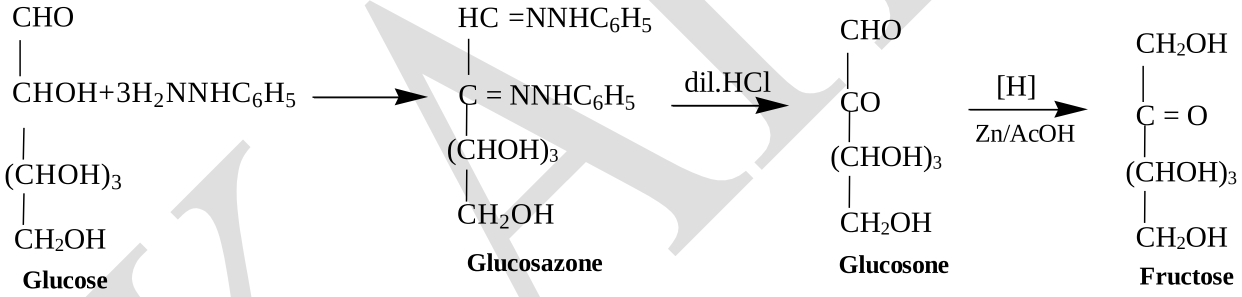


Uses

1) Fructose finds use as sweeteningagent.
2)It is used by diabetic patients in the place of canesugar.

Conversion of Glucose into Fructose

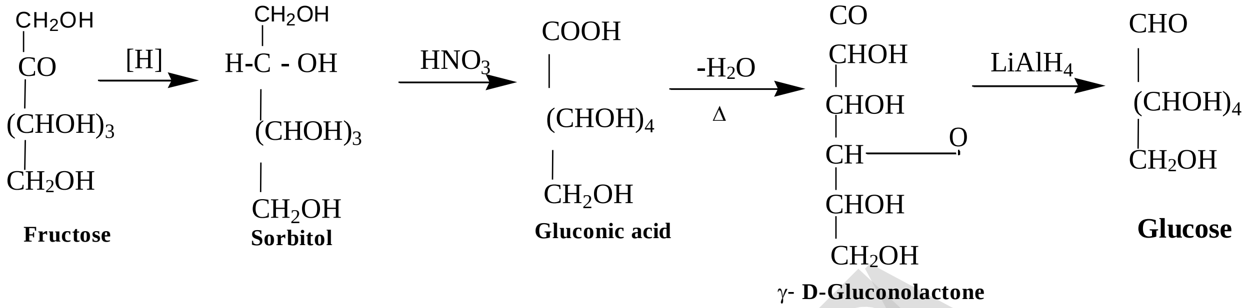
Glucose is first treated with excess phenylhydrazine in acetic acid to form glucosazone which is next hydrolysed with dil. HCl to give *glucosone.* This is then reduced with zinc and glacial acetic acid to yield fructose:



$$\begin{array}{c} CHO \\ | \\ CHOH + 3H_2NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \textbf{Glucose} \end{array} \longrightarrow \begin{array}{c} HC = NNHC_6H_5 \\ | \\ C = NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \textbf{Glucosazone} \end{array} \xrightarrow{dil.HCl} \begin{array}{c} CHO \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \textbf{Glucosone} \end{array} \xrightarrow[Zn/AcOH]{[H]} \begin{array}{c} CH_2OH \\ | \\ C = O \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \\ \textbf{Fructose} \end{array}$$

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 givebelow:



Comparative study of Glucose and Fructose

S.No.	Properties	Glucose	Fructose
1.	Nature	(i) Aldohexose (ii) Dextrorotatory	(i) Ketohexose (ii) Laevorotatory
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 PublishingHouse.

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

ReferenceBook:

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? Giveexamples.
2. What is zwitter ion and isoelectricpoint?
3. What is the action of heat on alpha-aminoacid?
4. What is meant by a peptide? Give an example with itsstructure.
5. How is glucoseprepared?
6. Write any four examples ofmonosaccharides.
7. Draw the ring structure of alpha andbeta-glucose.
8. How is fructoseprepared?
9. Define non-essential aminoacids.
10. Draw the ring structure of alpha, beta andgamma-fructose.
11. Mention the uses offructose.
12. Explain the following terms with examples: (a) disaccharide (b)polysaccharide.
13. How many chiral centres are there in glucose? How many optical isomers arepossible?
14. How is glucose established to be analdohexose?
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 ofproteins.
   (ii) Write the biological functions of proteins.
2. (i) What happens when glycine is (a) treated with HCl (b) treated withNaOH
   (c) treated with nitrous acid (d) treated withformaldehyde?
   (ii) Write in detail on the characteristics of proteins.

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

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

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

(ii) Explain Bergmann method of peptide synthesis.

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

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

6. Write in detail on the structure ofproteins.

7. Explain the preparation and properties offructose.

8. How will you effect the followingconversions?

i) Glucose to fructose ii) fructose toglucose.

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

(ii) Write the preparation of carbobenzoxy chloride.

10. Explain the preparation and properties ofglucose.

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? Giveexamples.

13. (i) Discuss any two colour reactions ofproteins.

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

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

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DEPARTMENT OF CHEMISTRY

UNIT-III

AMINO ACIDS, PROTEINS AND CARBOHYDRATES

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. Ninhydrin test is performed to identify

a) carbohydrate **b) proteins** c) vitamins d) antibiotics

2. A lactam is formed by heating the following amino acid

a) α b) β **c) γ** d) α and β

3. The number of chiral centres in glucose is

a) 4 b) 5 c) 6 d) 3

4. Glucose does not react to yield

a) a phenylhydrazone **b) a bisulphite compound**

c) a methyl glucoside d) an osazone

5. Maltose and lactose are

a) oligosaccharide **b) disaccharide** c) monosaccharide d) polysaccharide

6. The polysaccharide which on hydrolysis produced fructose only is

a) starch b) cellulose **c) inulin** d) glycogen

7. The simplest of the sugars which cannot be further hydrolysed are called

a) oligosaccharide b) disaccharide **c) monosaccharide** d) polysaccharide

8. Albumins are

a) simple proteins **b) fibrous proteins** c) glycoproteins d) chromo-proteins

9. Most of the amino acids which occur as components of proteins are

a) α-amino acids b) β-amino acids c) γ-amino acids d) carboxylic acids

10. Which among the following is not a protein?

a) albumin b) keratin c) collagen **d) penicillin**

11. Which one of the following is a disaccharide?

a) glucose b) fructose c) mannose **d) lactose**

12. Pick out a non reducing sugar from the following

a) sucrose b) fructose c) glucose d) maltose

13. Identify a ketohexose from the following

a) glucose **b) fructose** c) sucrose d) maltose

14. Glucose is, otherwise, known as

a) aldopentose b) ketopentose **c) aldohexose** d) ketohexose

15. Sorbitol is obtained from glucose using

a) HI and P **b) Na amalgam** c) Br_2 water d) conc. HNO_3

16. Glucose reacts with bromine water to form

a) gluconic acid b) saccharic acid c) sorbitol d) n-hexane

17. Which of the following dose not reduce Fehling’s solution?

a) benzaldehyde b) acetaldehyde c) glucose d) propionaldehyde

18. Glucose for fermentation requires

a) diastase b) maltase **c) zymase** d) invertase

19. _______is the sweetest of all sugars.

a) glucose b) fructose **c) sucrose** d) maltose

20. How many types of ring structures are possible for fructose?

a) 1 b) 2 **c) 3** d) 4

21. Which one of the following is laevorotatory?

a) glucose b) maltose c) sucrose **d) fructose**

22. Which is not related with inversion of cane sugar?

a) sucrose b) glucose c) fructose **d) maltose**

23. Fructose on oxidation with conc. HNO_3 gives

a) gluconic acid b) saccharic acid **c) tartaric acid** d) oxalic acid

24. Sucrose on hydrolysis gives

a) a) glucose **b) glucose and fructose** c) fructose d) mannose

25. The carbohydrate which does not show muta-rotation is

a) glucose b) fructose c) maltose **d) sucrose**

26. The sugar which is oxidized by bromine water is

a) glucose b) fructose c) sucrose d) mannose

27. Glucose gives addition product with

a) HCN b) NH_3 c) sodium bisulphite d) bromine

28. The sugar which does not form osazone is

a) glucose b) fructose **c) sucrose** d) maltose

29. Starch is

a) a salt **b) a polysaccharide** c) a sugar d) an emulsion

30. Tollen's reagent is

a) ammonium nitrate b) silver nitrate

c) ammonia silver nitrate (II) **d) ammoniacal silver nitrate (II)**

31. Glucose on fermentation yields

a) methanol **b) ethyl alcohol** c) propanol d) butanol

32. Glycine is

a) a carbohydrate **b) an amino acid** c) a sulpha drug d) an antibiotic

33. Amino acids exist in solution as

a) zwitter ion b) neutral molecule c) hydrolyzed d) associated

34. Which one of the following is a neutral amino acid?

a) serine b) lysine **c) alanine** d) tyrosine

35. The sulphur containing amino acid among the following is

a) glycine b) alanine c) phenylalanine **d) cysteine**

36. Which one of the following is an essential amino acid?

a) valine b) glycine c) alanine d) tyrosine

37. The isoelectric point of glycine is around pH

a) 6 b) 3 c) 10 d) 8

38. Which type of amino acids forms unsaturated acid on heating?

a) α **b) β** c) γ d) δ

39. Amino acid with soda lime produces

a) 1°-amine b) 1°-alcohol c) nitro compound d) peptide

40. Which is not related with amino acids?

a) zwitter ion b) isoelectric point c) denaturation **d) volatile liquid**

41. How many peptide bonds are present in a tripeptide?

a) 1 **b) 2** c) 3 d) 4

42. An example for fibrous proteins is

a) feather b) albumin c) zein d) glutalin

43. Proteins are identified using

a) chromyl chloride **b) ninhydrin** c) silver nitrate d) potassium permanganate

44. Which one of the following is not considered as protein?

a) enzyme b) hormones c) antibodies **d) ascorbic acid**

45. The origin and nature of hydrogen bonding in protein are dealt with_______structure of protein.

a) primary **b) secondary** c) tertiary d) quaternary

46. Proteins usually exist as

a) α-helix b) β-helix c) linear d) sheet

47. Which one of the following is a aromatic amino acids

a) serine b) lysine c) alanine **d) tyrosine**

48. The amino acids that can be synthesized from other compounds by the tissues of the body are called

a) amino acids **b) non-essential amino acids** c) essential amino acids d) proteins

49. Amino acids is prepared using

a) Haworth reaction b) Bucherer reaction **c) Gabriel reaction** d) Elbs reaction

50. The pH at which an amino acid does not move in a direct current electrical field is known as the

a) zwitter ion b) dipolar ion c) ampholyte **d) isoelectric point**

51. Neutral amino acids have isoelectric points from pH

a) 5.5 -6.3 b) 3- 4 c) 10-12 d) 1-2

52. Amino acids react with nitrosyl chloride to form

a) glycollic acid b) hippuric acid c) aceturic acid **d) chloro acetic acid**

53. Which one of the following is sanger's reagent?

a) fluorobenzene **b) 2,4-dinitro fluorobenzene**

c) nitrobenzene d) 2-nitrofluoro benzene

54. Amino acids react with metallic oxide in water to produce

a) simple salts b) mixed salts **c) complex salts** d) inner salts

55. α-amino acids undergo dehydration on heating to give

a) lactam b) unsaturated acids c) lactone **d) diketo piperazines**

56. All α-amino acids react with ninhydrine to produce

a) purple colour b) red colour c) orange colour d) yellow colour

57. All α-amino acids are

a) optically inactive **b) optically active** c) racemic d) dl pairs

58. Which one of the following amino acids is optically inactive?

a) glycine b) phenylalanine c) alanine d) valine

59. Peptides are condensation products of

a) acids b) amines **c) amino acids** d) keto acids

60. The protecting group, carbobenzoxy chloride is prepared from benzyl alcohol and

a) acetyl chloride b) benzoyl chloride c) cinnamoyl chloride **d) phosgene**

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.

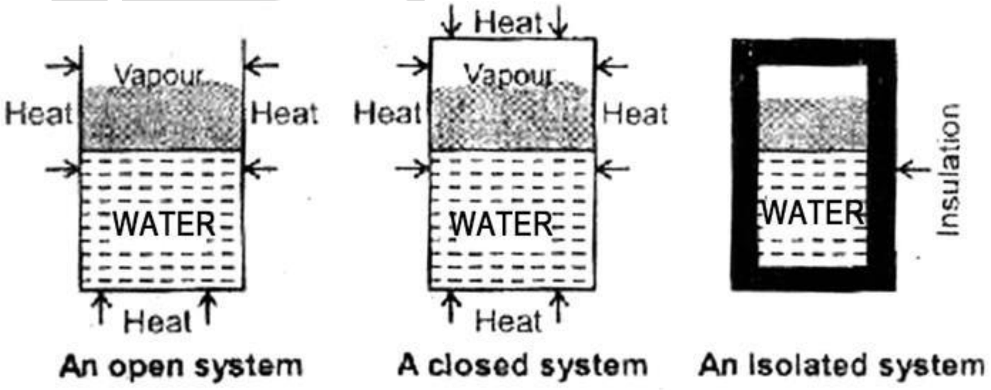
Consider a system consisting of say 100 ml water in contact with its vapour in a closed vessel. Since, the vessel is closed, no matter (liquid or vapour) can leave or enter the vessel.

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.



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.*

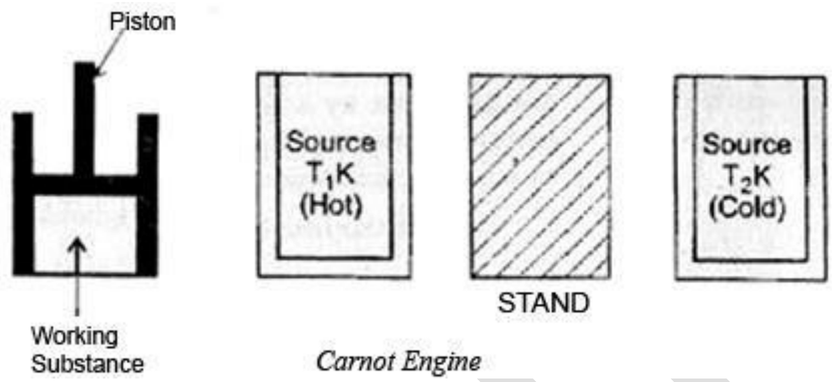
The engine consists of –

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

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

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

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

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

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

$$= 2.303\, n\, RT \log P_1/ P_2 \qquad \ldots\ldots(2)$$

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, $q = 0$.

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

$$\Delta E = - w$$

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

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,

$$W = n\, C_v(T_1 - T_2) \qquad \ldots\ldots\ldots (4)$$

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

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

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \ldots\ldots (5)$$

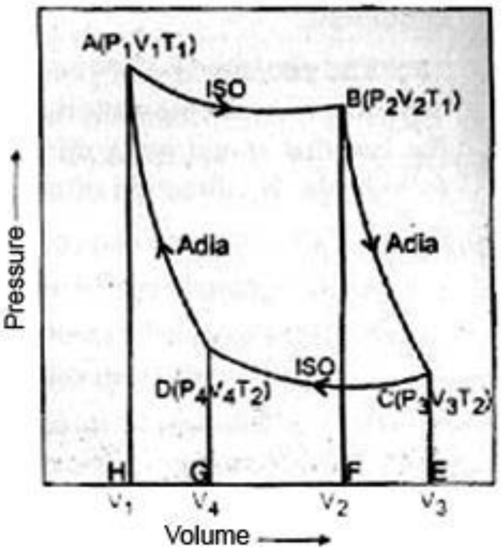
Where, $\gamma = C_p/ C_v$, in which Cp is the molar heat capacity at constant pressure.

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.

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

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

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

$$= RT_1 \ln \frac{V_2}{V_1} + RT_2 \ln \frac{V_4}{V_3}$$

….. (10)

since B and C lie on the same adiabatic,

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

…… (11)

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

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

…… (12)

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

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

$$\frac{V_2}{V_3} = \frac{V_1}{V_4} \quad \text{(or)} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

….. (13)

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

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

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

…… (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.

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

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

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

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,

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

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^{o}C. 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.

$T = 27\ ^{o}C = 300\ K$

$V_2 = 8$ lit. and $V_1 = 1$ lit.

$W = 2.303 \times 5 \times 8.314 \times 300 \log 8/1$ Joules

$W = 2.303 \times 5 \times 8.314 \times 300 \times 0.9031$ 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^{o}C. 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

$T = 25^{o}C = 298\ K$

$P_1 = 5$ atm. and $P_2 = 1$ atm.

$W = 2.303 \times 1 \times 8.314 \times 298 \log 5/1$ Joules.

$W = 2.303 \times 1 \times 8.314 \times 298 \times 0.6990$ 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, $\eta = 10\ \%$ 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

η = 500-100/500 = 400/500 = 0.8

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

η = 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

η = 400-300/400 = 100/400 = 0.25.

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

∴ Work done = quantity of heat absorbed x η

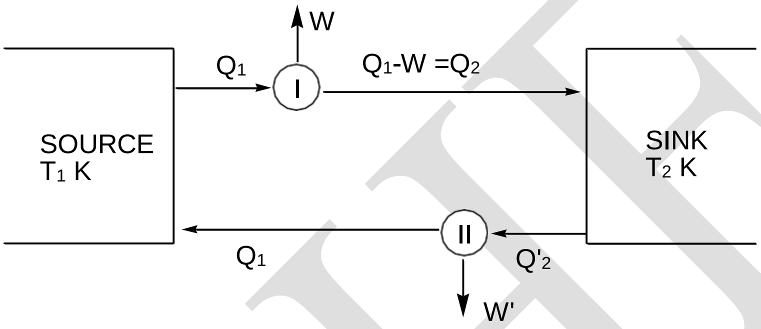
= 800 x 0.25 = **200 Joules**

(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,

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

and $T_1 > T_2$

Equation (1) can be written as

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

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,

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

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.

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

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

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

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

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

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°C and 127°C.
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?

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DEPARTMENT OF CHEMISTRY

UNIT-IV

ENERGETICS

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. How many laws are there in thermodynamics?

a) 4 **b) 3** c) 5 d) 2

2. The concept of temperature was the outcome of__________law of thermodynamics.

a) first b) second c) third **d) zeroth**

3. Which law of thermodynamics is otherwise known as law of conservation of energy?

a) zeroth **b) first** c) second d) third

4. Which of the following is a path function?

a) W b) H c) E **d) S**

5. A process, in which no heat enters or leaves the system, is called as

a) isothermal process b) isobaric process **c) adiabatic process** d) isochoric process

6. In isothermal process,

a) $\Delta T = 0$ b) ΔT is +ve c) ΔT is -ve d) $\Delta T \geq 0$

7. During an adiabatic expansion, the temperature of the system

a) decrease b) increase c) remains constant d) cannot be determined

8. Entropy of the universe tends

a) towards minimum **b) towards maximum** c) to be zero d) to be a constant

9. The work done by an ideal gas in an isothermal expansion is equal to

a) heat absorbed b) volume change c) pressure change d) zero

10. The mathematical form of first law of thermodynamics is

a) $\Delta E = q + w$ **b) $\Delta E = q - w$** c) $w = \Delta E + q$ d) $w = \Delta E - q$

11. Which of the following is a correct relationship?

a) $H = E + PV$ b) $G = H + TS$ c) $A = E + TS$ d) $C_v = C_p + R$

12. Which of the following is not a unit of entropy?

a) J K^{-1} b) eu c) cal deg^{-1} **d) J mol^{-1}**

13. For a spontaneous process,

a) $\Delta S =$ +ve b) $\Delta S = 0$ **c) $\Delta S =$ -ve** d) $\Delta S \leq 0$

14. For a reversible process,

a) $\Delta G = 0$ b) $\Delta G =$ +ve c) $\Delta G =$ -ve d) $\Delta G \neq 0$

15. The important condition for a spontaneous process is

a) $\Delta G > 0$ b) $\Delta G = 0$ **c) $\Delta G < 0$** d) $\Delta S < 0$

16. The word thermodynamics means

a) implies flow of heat b) implies flow of pressure c) volume d) density

17. Any specified portion of matter under study which is separated from the rest of the universe with a boundary is known as

a) surrounding **b) system** c) process d) matter

18. A system may consist of

a) two substances b) only one substance

c) no substance **d)one or more substances**

19. How many types frequently used in thermodynamics?

a) 1 b) 2 **c) 3** d) 4

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

a) open system b) closed system c) isolated system d) insulated system

21. The evaporation of water placed in an open beaker is an example for

a) closed system **b) open system** c) isolated system d) insulated system

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

a) open system **b) closed system** c) isolated system d) insulated system

23. A system in which exchange matter as well as energy with its surroundings is called as

a) open system b) closed system c) isolated system d) insulated system

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

a) system b) surrounding **c) process** d) state

25. A process is said to be isothermal if temperature of the system

a) changes **b) remains constant** c) do not affect d) varies

26. A process in which constant temperature is called as

a) isothermal process b) adiabatic process c) isobaric process d) isochoric process

27. The reaction is exothermic means

a) heat is evolved in the process b) heat is absorbed in the process

c) pressure is evolved in the process d) volume is evolved in the process

28. In a isothermal process the internal energy is

a) $\Delta E = 0$ b) $\Delta H = 0$ c) $\Delta E = 1$ d) $\Delta E = nC_v dT$

29. The adiabatic process heat exchanges is

a) one **b) zero** c) two d) four

30. The enthalpy of isothermal process is

a) $\Delta H =1$ b) $\Delta H \neq 0$ **c) $\Delta H = 0$** d) $\Delta H \neq 1$

31. A process which does not place infinitesimally slow is said to be an

a) isothermal process b) reversible process

c) irreversible process d)spontaneous process

32. All natural process is

a) isothermal process **b) irreversible process**

c) reversible process d) adiabatic process

33. In the reversible process the work done is

a) medium b) low c) zero **d) maximum**

34. The irreversible process takes place in

a) both direction **b) only one direction** c) multi direction d) two direction

35. Which one is the example for spontaneous process?

a) water flows down hill b) heat flows from only cold region

c) a gas expands only low pressure region d) electricity flows from only a point at a low potential

36. A piece of zinc when placed in contact with a solution of copper sulphate precipitates

a) zinc **b) copper** c) zinc sulphate d) copper sulphate

37. The spontaneous process are thermodynamically_______in nature

a) isothermal b) adiabatic c) reversible **d) irreversible**

38. The enthalpy of a system is defined by the relation

a) H = E+PV b) H = E-PV c) H = PV d) H = PV-E

39. For an endothermic reaction

a) ΔH is negative **b) ΔH is positive** c) ΔE is negative d) ΔH is zero

40. A process which proceeds of its own accord without any outside assistance is called

a) non-spontaneous process **b) spontaneous process**

c) reversible process d) irreversible process

41. Mixing of two or more gases is a _______

a) spontaneous process b) non-spontaneous process

c) reversible process d) isochoric process

42. Entropy is a measure of_______of the molecules of the system

a) concentration b) velocity c) zig-zag motion **d) randomness or disorder**

43. A machine that can do work by using heat which flows out spontaneously from a high temperature source to a low temperature sink is called

a) Carnot machine b) cyclic machine c) heat machine **d) heat engine**

44. The cycle of processes which occurs under reversible conditions is referred to as

a) cyclic process b) closed process **c) Carnot cycle** d) reversible cycle

45. The efficiency of a heat operating between 400 K and 300 K is

a) 1.0 b) 0.75 c) 0.50 **d) 0.25**

46. The free energy function (G) is defined as

a) $G = H+TS$ **b) $G = H-TS$** c) $G = TS-H$ d) $G+H = TS$

47. The work function (A) is defined as

a) $A = E-TS$ b) $A = E+TS$ c) $A = TS-E$ d) $A+E = TS$

48. Which out of the following is not a state function?

a) free energy b) work function c) entropy **d) work done**

49. A process is in the equilibrium state when

a) $\Delta G > 0$ b) $\Delta G < 0$ **c) $\Delta G = 0$** d) $\Delta G \neq 0$

50. A spontaneous reaction proceeds with a decrease in

a) entropy b) enthalpy **c) free energy** d) internal energy

51. In a process $\Delta H = 100$ KJ and $\Delta S = 100\ JK^{-1}$ at 400 K. The value of ΔG will be

a) zero b)100 KJ c) 50 KJ **d) 60 KJ**

52. When water is cooled to ice, its entropy

a) increases **b) decreases** c) remains the some d) becomes zero

53. The efficiency of Carnot's heat engine is always less then

a) zero b) two **c) one** d) three

54. The Gibb's Helmholtz equation is applicable to

a) all processes, chemical or physical

b) all processes, chemical or physical but in a closed system

c) all chemical processes in closed system

d) all physical processes in a closed system.

55. Which is the correct unit for entropy?

a) KJ mol b) JK^{-1} mol **c) JK^{-1}** d) deg^{-1}

56. The efficiency of heat engine is maximum when

a) temperature of source and sink are maximum

b) temperature of source and sink are minimum

c) temperature of source is minimum and that of sink is maximum

d) temperature of source is maximum and that of sink is minimum

57. The Joule Thomson effect is zero for an

a) real gas **b) ideal gas** c) non ideal gas d) water gas

58. The 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

a) Joule–Thomson effect b) Carnot theorem c) Carnot cycle d) efficiency

59. The_______state that working between the same temperature limits all reversible heat engine are equally efficient whatever may be working substance.

a) Carnot theorem b) Carnot cycle c) Joule Thomson effect d) heat engine

60. In isothermal process

a) $\Delta E = 0$ b) $\Delta E = 1$ c) $\Delta E \neq 0$ d) $\Delta E \neq 1$

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.

Thus, $\lambda_\alpha = \lambda_a + \lambda_c$ …..(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

$$1\text{g. equivalent of AgCl} = \frac{1000}{S}\ \text{ml}$$

∴ 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 –

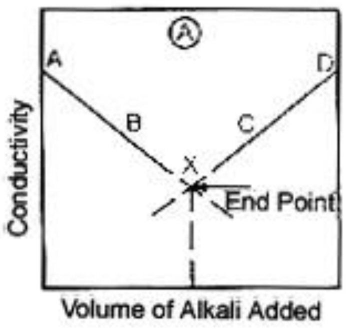
$$H^+ + Cl^- + [Na^+ + OH^-] \rightarrow Na^+ + Cl^- + H_2O \qquad \ldots\ldots (1)$$

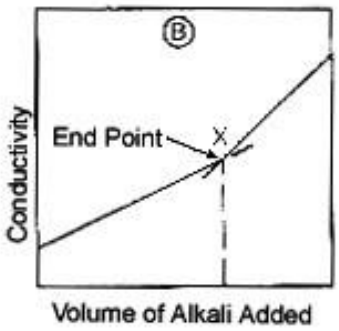
Hence, on continuous addition of sodium hydroxide, the conductance goes on decreasing till the neutralisation is complete. After the neutralisation, the further addition of alkali results in the increase in conductance against the volume of alkali added, the points will lie on a straight line, as in 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.

$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O \quad \ldots\ldots (2)$$

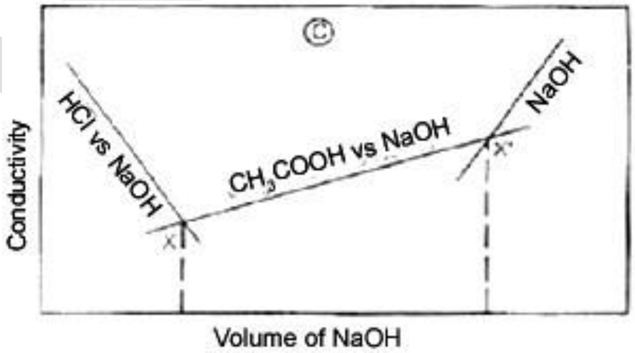




After the complete neutralisation of the acid, any further addition of alkali will show a sharp increase in conductance due to the fast moving hydroxide ion. The plot conductivity against volume of alkali added is shown in figure (B). The point of intersection (x) gives the end point.

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:

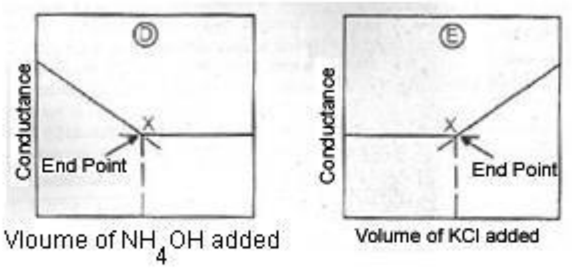
$$H^+ + Cl^- + NH_4OH \rightarrow NH_4^+ + Cl^- + H_2O \qquad \text{….. (3)}$$

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.

$$A^- + H_2O \rightleftharpoons OH^- + HA \quad \text{.......................................(1)}$$

Applying the Law of mass action to the above hydrolysis equilibrium,

$$K_h = \frac{[OH^-][HA]}{[A^-]\ [H_2O]} \quad \text{...(2)}$$

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,

$$HA \rightleftharpoons H^+ + A \quad \text{......(3)}$$

The ionisation constant of the weak acid is given by

$$K_a = \frac{[H^+]\ [A^-]}{[HA]} \quad \text{...... (4)}$$

The ionisation equilibrium of water may be written as,

$$H_2O \rightleftharpoons H^+ + OH \quad \text{...... (5)}$$

Ionic product of water, $K_w = [H^+]\ [OH^-]$ .... (6)

Dividing equation (6) by equation (4)

$$\frac{K_w}{K_a} = \frac{[H^+]\ [OH^-]\ [HA]}{[H^+]\ [A]} \quad \text{......(7)}$$

$$\frac{K_w}{K_a} = \frac{[OH^-]\,[HA\,]}{[A\ \ ]} \quad \text{...} (8)$$

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.

$$K_h = \frac{[OH^-]\,[HA\,]}{[A\ \ ]} \quad \text{......} (9)$$

Comparing equations (8) and (9)

$$K_h = \frac{K_w}{K_a} \quad \text{...} (10)$$

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

$$\underset{C(1-h)}{A^-} + H_2O \rightleftharpoons \underset{Ch}{OH^-} + \underset{Ch}{HA} \quad \text{......................} (1)$$

$$K_h = \frac{[OH^-]\,[HA\,]}{[A\ \ ]} \quad \text{........}(9)$$

$$K_h = \frac{hC \times hC}{C(1-h)} = \frac{h^2C}{(1-h)} \quad \text{.........}(11)$$

$$K_h \equiv h^2C \quad \text{........}(12)$$

Or, $h^2 = \dfrac{K_h}{C}$ .... (13)

$$h = \sqrt{\underline{Kh}\,C} \qquad \text{........(14)}$$

$$\text{Since,}\quad K_h = \frac{K_w}{K_a} \qquad \text{.......................(10)}$$

$$h = \sqrt{\frac{K_w}{K_a C}} \qquad \text{........(15)}$$

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)

$$\frac{K_w}{K_b} = \frac{[H^+]\,[OH\,]\,[BOH\,]}{[B^+]\;[OH^-\,]} \text{...} \quad (6)$$

$$\frac{K_w}{K_b} = \frac{[H^+]\;\;[BOH\,]}{[B^+]} \qquad \text{...... (7)}$$

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,

$$K_h = \frac{K_w}{K_b} \text{..} (9)$$

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

$$\underset{C(1-h)}{B^+} + H_2O \rightleftharpoons \underset{Ch}{BOH} + \underset{Ch}{H^-} \qquad \text{...... (1)}$$

$$K_h = \frac{[BOH]\,[H^+]}{[B^+]} \qquad \text{......(8)}$$

.

$$K_h = \frac{hC \times hC}{C(1-h)} = \frac{h^2C}{(1-h)} \quad .....(9)$$

$$K_h = h^2C \; .... (10)$$

or

$$h^2 = K_h/C \; ....(11)$$

$$h = \sqrt{K_h/C} \quad .....(12)$$

Since, $K_h = \frac{K_w}{K_b}$

$$h = \sqrt{\frac{K_w}{K_bC}} \quad ....(13)$$

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,

$$B^+ + A + H_2O \rightleftharpoons BOH + HA \quad ......(1)$$

$$K_h = \frac{[BOH]\,[HA]}{[B^+]\,[A\,][H_2O]} \quad ......(2)$$

The ionisation constant of the acid, HA is given by,

$$HA \rightleftharpoons H^+ + A \qquad \text{......(3)}$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \qquad \text{.. (4)}$$

The ionisation constant of the base, BOH is given by

$$[BOH] \rightleftharpoons B^+ + [OH\ ] \qquad \text{.. (5)}$$

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]} \qquad \text{.. (6)}$$

The ionic product of water, $K_w = [H^+]\,[OH^-]$.............................. (7)

Dividing the equation (7) by the product of equations (4) and (6) we have,

$$\frac{K_w}{K_a K_b} = \frac{[H^+]\,[OH^-]\,[BOH]\,[HA]}{[H^+]\,[A^-]\,[OH^-]\,[B^+]} \qquad \text{......(8)}$$

$$\frac{K_w}{K_a K_b} = \frac{[HA]\,[BOH]}{[B^+][A\ ]} \qquad \text{......(9)}$$

Omitting the concentration of water in equation (2)

$$K_h = \frac{[BOH][HA]}{[B^+][A\ ]} \qquad \text{......(10)}$$

Comparing the equation (9) with (10) we have

$$K_h = \frac{K_w}{K_a K_b} \qquad \text{....... (11)}$$

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:

$$Pt, Cl_{2(g)} \mid Cl^-$$

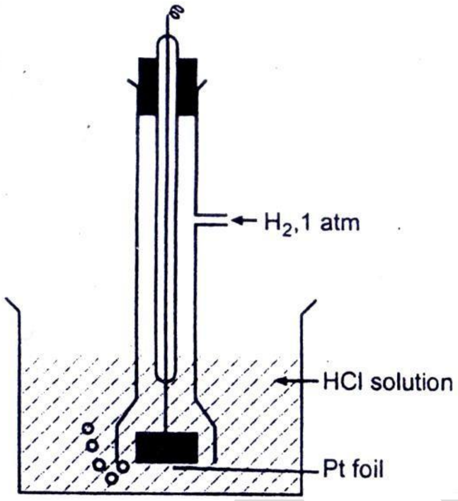
If a piece of metal is placed in a solution containing its ions, then a potential difference known as electrode potential of the metal will be set up between the metal and the solution. For example, if a rod of zinc is kept in a beaker containing zinc sulphate solution, the zinc will be negatively charged 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	$Li^+ + e^- \rightleftharpoons Li$	-3.02
2	K^+, K	$K^+ + e^- \rightleftharpoons K$	-2.92
3	Ca^{2+}, Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2.87
4	Na^+, Na	$Na^+ + e^- \rightleftharpoons Na$	-2.71
5	Mg^{2+}, Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.38
6	Al^{3+}, Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.67
7	Zn^{2+}, Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
8	Fe^{2+}, Fe	$Fe^{2+} + 2e^-$ Fe	-0.44
9	Cd^{2+}, Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	-.0.40
10	Sn^{2+}, Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0.14
11	Pb^{2+}, Pb	$Pb^{2+} + 2e^-$ Pb	-0.11
12	**$2H^+$, H_2, Pt**	**$2H^+ + 2e^- \rightleftharpoons H_2$**	**0.00**
13	Cu^{2+}, Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
14	Fe^{3+}, Fe^{2+}	$Fe^{3+} + e^-$ Fe^{2+}	+0.77
15	Ag^+, Ag	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
16	Hg_2^{2+}, 2Hg	$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$	+0.80
17	Au^+, Au	$Au^+ + e^-$ 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:

$$Fe \mid Fe^{2+} \mid \mid Cu^{2+} \mid Cu \qquad ....(1)$$

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,

$$Fe \rightleftharpoons Fe^{2+} + 2e^- \quad ; E_{298K} = 0.44 \text{ volt} ....(2)$$

Again for the reduction at the copper electrode, we get,

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad ; E_{298K} = 0.34 \text{ volt} ....(3)$$

Adding now the single electrode reactions and the single electrode potential, we find,

$$Fe \rightleftharpoons Fe^{2+} + 2e^- \quad ; E_{298K} = 0.44 \text{ volt}$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad ; E_{298K} = 0.34 \text{ volt}$$

$$Fe + Cu^{2+} \rightleftharpoons Fe^{2+} + Cu \quad ; E_{298K} = 0.78 \text{ volt} ....(4)$$

Thus, the cell reaction is:

$$Fe + Cu^{2+} \rightleftharpoons Fe^{2+} + Cu$$

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,

$$\mathrm{Cu} \mid \mathrm{Cu}^{2+} \parallel \mathrm{Fe}^{2+} \mid \mathrm{Fe} \qquad \text{........(5)}$$

The cell reaction is,

$$\mathrm{Fe} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Fe}^{2+} + \mathrm{Cu} \qquad \text{........(6)}$$

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

$$K = \frac{[H^+]\ [OH^-]}{[H_2O]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where, K the equilibrium constant. As the concentration of un-ionised water is considered to be a constant, the above equation (2) becomes

$$K = \frac{[H^+]\ [OH^-]}{k} \quad \ldots\ldots\ldots(3)$$

$$\text{or,} \quad Kk = [H^+]\,[OH^-] \quad \ldots\ldots.(4)$$

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,

$$[H^+] = [OH^-] = 1 \text{ X } 10^{-7} \text{ mole/lit} \quad \ldots\ldots.(5)$$

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.

$$pH = -\log[H^+] = \log \frac{1}{[H^+]} \ldots\ldots\ldots\ldots (6)$$

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

$$pOH = -\log [OH^-] = \log\frac{1}{[OH^-]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$\text{and} \quad pH + pOH = pKw = 14 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

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:

$$HA \rightleftharpoons H^+ + A^-$$

	HA	H^+	A^-
Initial Concentration	C	0	0
Equil. Concentration	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Application of the law of mass action to this ionic equilibrium, gives the value of dissociation constant, K_a for the acid:

$$K_a = \frac{[H+]\,[A^-]}{[HA]} \quad \text{...(9)}$$

$$= \frac{C\alpha \times C\alpha}{C\,(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \quad \text{........(10)}$$

If the acid ionises to a very small extent, α is very small and may be neglected in comparison with unity.

$$\text{Then, } K_a = C\alpha^2$$

and,

$$\alpha = \sqrt{\frac{K_a}{C}} = \frac{\lambda_c}{\lambda_\infty} \quad \text{........(11)}$$

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.

But, $[H^+] = C\alpha$□(12)

Thus, the degree of dissociation is a direct measure of hydrogen ion concentration.

$[H^+] = C\alpha$□(13)

$$= C\sqrt{\frac{K_a}{C}} = \sqrt{K_aC}$$ ....(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.

$$H^+ + e^- \rightleftharpoons 1/2\ H_2\ (1\ atm)$$ ....(1)

The voltage produced is given by Nernst equation (The derivation of this equation is beyond the scope of this book) as,

$$E_{(H^+,\ H_2)} = E_o(H^+, H_2) + 2.303\frac{RT}{F}\log[H^-]$$ ....(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,

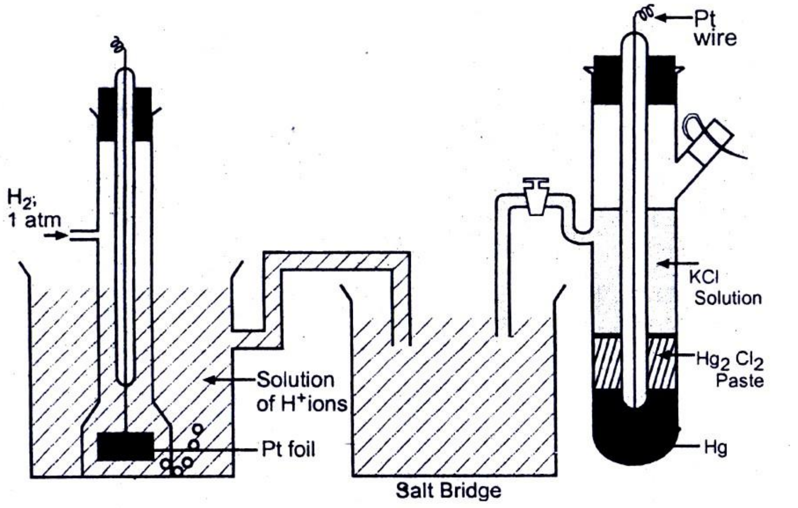
$$\frac{2.303\ RT}{F} = \frac{2.303 \times 8.134 \times 298}{96500} = 0.0591 \text{ at } 298\text{ K} \qquad ....(4)$$

Substituting the value of equation (4) in (3)

$$E_{(H^+, H_2)} = 0.0591 \log [H^+]$$

$$= -0.0591\ pH................................ (5)$$

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:

$$\text{Pt, } H_2\ (1\text{ atm}) \left| \begin{array}{l} H^+ \\ (C = \text{unknown}) \end{array} \right| \begin{array}{l} KCl \\ \text{Sat.Soln.} \end{array} \quad Hg_2Cl_2\ (\text{sat}) \Big| \ Hg \qquad .... (6)$$

$$E_{cell} = E_{calomel\ (reduction)} - E_{(H^+,\ H_2\ (reduction)} \qquad ..... (7)$$

$= 0.2422 – (-0.0591 \text{ pH})$

$= 0.2422 + 0.0591 \text{ pH}$

$\therefore \text{pH} = E_{cell} - 0.2422 / 0.0591$ ….. (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

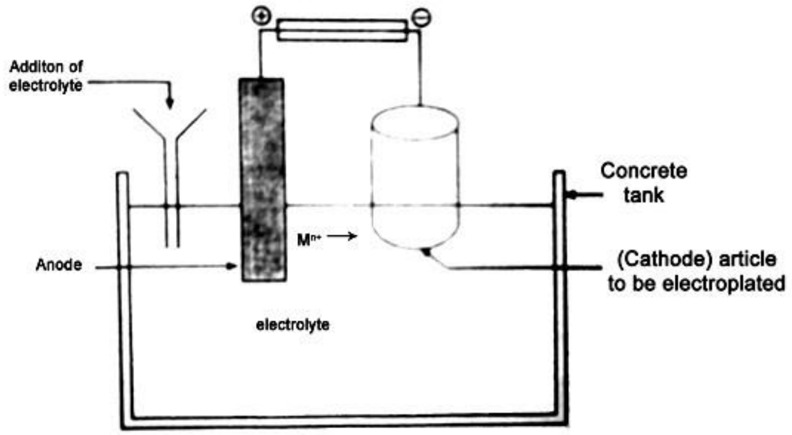
Electroplating is the art of depositing one metal over another metal with the help of electric current.

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 1.8×10^{-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?

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DEPARTMENT OF CHEMISTRY

UNIT-V

ELECTROCHEMISTRY

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. The Kohlraush's law can be used for the determination of

a) λ_∞ for weak electrolytes b) λ_∞ for strong electrolytes

c) the degree of dissociation of strong electrolytes

d) the degree of association of weak electrolytes

2. Conductometric titrations are

a) not applicable to coloured solution

b) not applicable to turbid solution

c) applicable to weak acid vs weak base titration

d) applicable to titrations where non-participating electrolytes

3. The measured emf of a cell is

a) equal to one half of the sum of electrode potentials

b) equal to the sum of electrode potentials

c) independent of temperature

d) independent of the nature of electrodes

4. The pH of an basic solution is

a) 7 **b) >7** c) < 7 d)14

5. The normal value of pH of blood plasma is

a) 3.0 b) 8.0 c) 7.0 **d) 7.4**

6. Kohlrauch law can be written as

a) $\lambda_\alpha = \lambda_c - \lambda_a$ **b) $\lambda_\alpha = \lambda_c + \lambda_a$** c) $\lambda_\alpha = \lambda_a - \lambda_c$ d) $\lambda_\alpha = \lambda_c$

7. The equivalent conductance at infinite dilution is determined by

a) Kohlrauch law b) Henderson's equation c) Ohm's law d) Faraday's law

8. The sodium acetate is an example for

a) strong electrolyte b) weak electrolyte

c) quinhydrone electrolyte d) glass electrolyte

9. Which is a weak electrolyte?

a) HCl b) CH_3COONa c) NaCl **d) CH_3COOH**

10. The unit for degree of dissociation is

a) cm b) mho c) ohm **d) mere number**

11. The unit for equivalent conductance in

a) mho cm b) ohm cm **c) mho cm^2 equ^{-1}** d) ohm cm^2 equiv

12. The degree of dissociation is also called as

a) degree of ionization b) degree of decomposition

c) degree of hydrolysis d) buffer solution

13. The carriers of electricity in metal are

a) protons **b) electrons** c) ions d) neutrons

14. Which one of the following is not an electrolyte?

a) salt solution **b) alloys** c) mixed conductors d) acids

15. In which of the following, ions are the carriers of electricity?

a) metals b) semi conductors c) mixed conductors **d) electrolytes**

16. An example for strong acid is

a) HCl b) CH_3COOH c) CH_3COONa d) NaOH

17. The conductometric titrations results are

a) random **b) accurate and precise** c) precise d) accurate

18. The conductance in an electrolyte

a) decreases on increasing the temperature **b) increases with the temperature**

c) does not depend on temperature d) depends on pressure

19. On increasing the temperature, the conductance in metals

a) decreases b) increases c) remains constant d) becomes zero

20. The type of reaction occurring at the anode during electrolysis is

a) oxidation b) reduction c) decomposition d) neutralization

21. An example for strong electrolyte is

a) $C_6H_5NH_2$ **b) HCl** c) NH_4OH d) CH_3OH

22. An example for weak electrolyte is

a) HCl b) NaOH c) NaCl **d) CH_3OH**

23. The conductometric titration curves should be

a) square b) parabola **c) straight line** d) rectangle

24. Which of the following is a weak acid?

a) HCl b) H_2SO_4 c) HNO_3 **d) CH_3COOH**

25. When a solution of given electrolyte is diluted, its specific conductance

a) increases **b) decreases** c) becomes zero d) remains constant

26. When a solution of given electrolyte is diluted, its molar conductance

a) increases b) decreases c) first increases then becomes constant d) become zero

27. The method is used most commonly to determine the pH of unknown solution.

a) colorimetric method **b) glass electrode method**

c) quinhydrone electrode method d) conductivity method

28. Kohlrausch law is useful to determine

a) specific conductance **b) equivalent conductance**

c) rate of reaction d) pH of the solution

29. pH is calculated using

a) $pH = \log 1/[H_3O^+]$ b) $pH = \log [H_3O^+]$

c) $pH = \log [OH^-]$ d) $pH= -\log[OH^-]$

30. The pH of millimolar hydrochloric acid is

a) 11 b) 14 c) 7 **d) 3**

31. The pH of 12 litre pure water is

a) 11 b) 12 **c) 7** d) 2

32. The pH of $1x\ 10^{-8}$ N HCl is

a) 7 b) 11 **c) 8** d) between 6 and 7

33. The pH of a solution is zero. Hence the solution must be

a) highly acidic b) highly basic c) neutral d) weakly basic

34. The electrode useful for determining pH is

a) gold electrode b) copper electrode **c) glass electrode** d) silver electrode

35. The pH of N/100 H_2SO_4 is

a) 1.3 **b) 2** c) 12 d) 5

36. If the pH of an acid is 5, what will be its [H^+]?

a)1x 10^{-5} b) 5 x 10^{-5} c) 1 x 10^{-7} d) 1 x 10^{-14}

37. If the K_a of an acid is 1 x 10^{-6}, what is its pK_a value?

a) 6.5 **b) 6** c) 1.6 d) 6.1

38. Which one of the following pair is a buffer solution?

a) HCl+NaCl b) NaOH+ NaCl c) NaOH+H_2SO_4 **d) CH_3COOH + CH_3COONa**

39. The mixture of NH_4Cl and NH_4OH serves as an example for

a) strong electrolyte b) weak electrolyte c) colloid **d) buffer solution**

40. The pH value of 7.4 for

a) lemon juice b) gastric juice **c) blood** d) apple juice

41. The mixture, which maintain the pH of blood, is

a) HCl+ NH_4Cl b) CH_3COOH + CH_3COONa

c) H_2CO_3+$NaHCO_3$ **d) H_2CO_3+ Na_2CO_3**

42. The pH of an acidic solution is

a) 7 b) >7 **c) < 7** d) 14

43. What is the pH of 0.01 N NaOH?

a) 2 **b) 12** c) 7 d) 14

44. The colour imparted by the universal indicator for pH 6 is

a) red b) orange **c) yellow** d) green

45. The pH of a buffer solution is calculated using

a) Ohm's law b) Faraday's laws c) Kohlrausch law **d) Henderson's equation**

46. pH + pOH =?

a) 7 **b) 14** c) 0 d) 10^{-14}

47. The dissociation constant of a weak acid is 7.2 x 10^{-10}. What is the concentration of H^+ in a 0.072 M solution of acid?

a) 0.36 x10^{-4} **b) 0.72 x 10^{-5}** c) 7.2 x 10^{-14} d) 3.6 x 10^{-7}

48. The examples for titration of a weak acid against weak base is

a) HCl+NaOH b) CH_3COOH +NaOH **c) CH_3COOH + NH_4OH** d) HCl and NH_4OH

49. Which one of the following pair is a titration of a strong acid against a strong base?

a) HCl+NaOH b) CH_3COOH +NaOH c) CH_3COOH + NH_4OH d) HCl+ NH_4OH

50. An example for precipitation titration is

a) HCl and NaOH b) CH_3COOH and NaOH

c) HCl and NH_4OH **d) $AgNO_3$ and KCl**

51. The fraction of each mole of the salt which gets hydrolyzed when dissolved in water

a) salt hydrolysis **b) degree of hydrolysis** c) hydrolysis of salt d) buffer solution

52. Ionic product of water, K_w=?

a) $[H^+]$ b) $[OH^+]$ **c)$[H^+]$ $[OH^+]$** d) $-\log [H^+]$

53. The copper metal is contact with $CuSO_4$ solution is known as

a) silver electrode **b) copper electrode**

c) hydrogen electrode d) chloride electrode

54. Pure water is

a) basic b) acidic **c) neutral** d) dipolar ion

55. The pH value of pure water is

a)12 b)11 c) 2 **d) 7**

56. The resistance to change in pH on the addition of acid or base is known as

a) buffer solution **b) buffer action** c) buffer d) base

57. Buffer solutions usually consist of a solution of_______in the presence of its salt.

a) weak acid b) weak base c) strong acid or strong base **d) weak acid or weak base**

58. The mixture of citric acid and sodium citrate serves as an example for

a) weak electrolyte b) colloid c) strong electrolyte **d) buffer solution**

59. For pure water $[H^+]$=?

a)1×10^{-14} **b) 1×10^{-7}** c) 1×10^{-5} d) 1×10^{-10}

60. Electromotive force method for the measurement of hydrogen ion concentration is not suitable for

a) unsaturated organic compounds b) saturated organic compounds

c) unsaturated acid d) saturated carboxylic acid