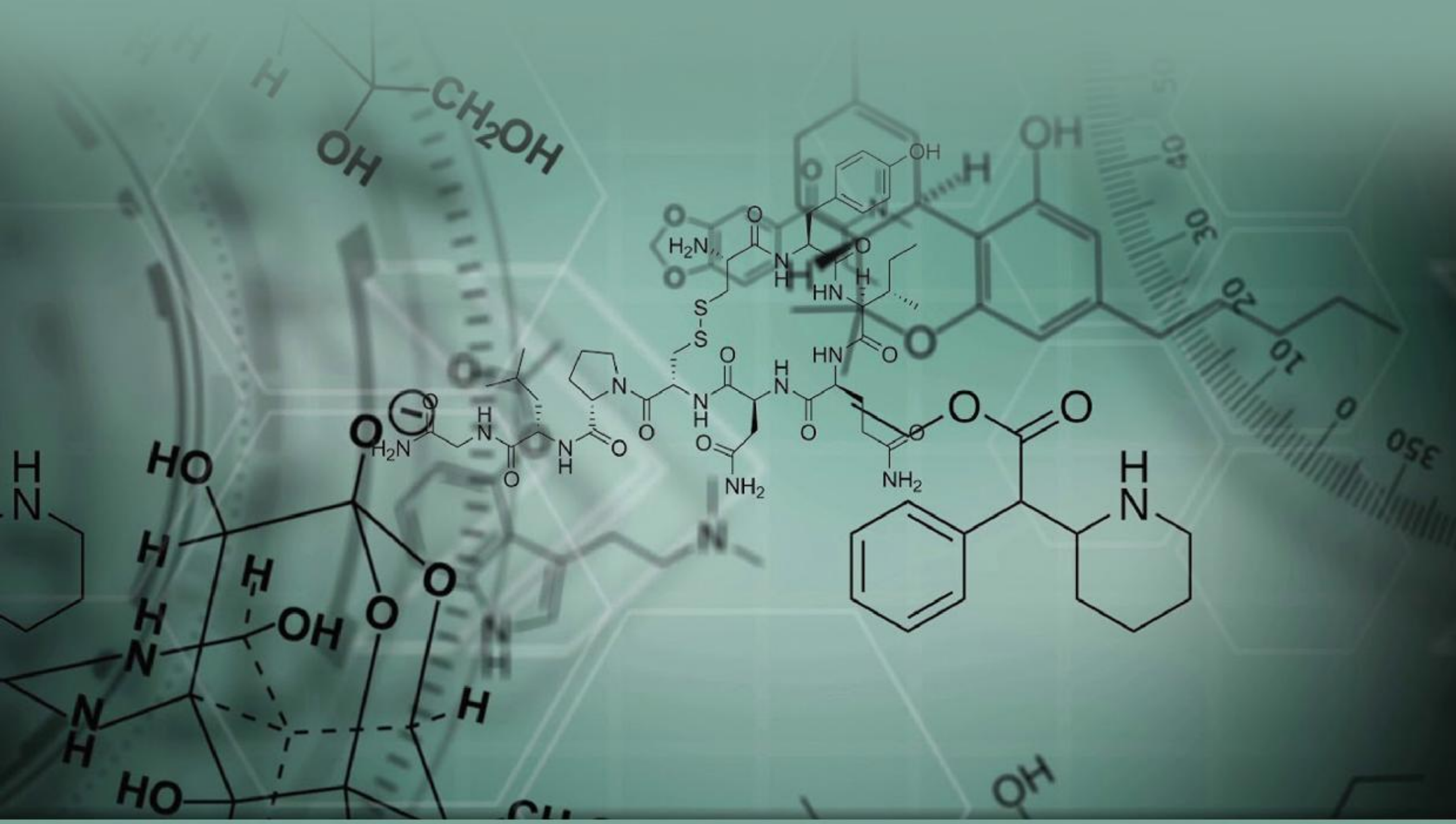
Class-12

CHEMISTRY



GENERAL EDUCATION DEPARTMENT

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SAMAGRA SIKSHA KERALA

Class 1 2 **CHEMISTRY**

SAMAGRA SIKSHA KERALA Class 12 CHEMISTRY

Unit 1: The solid state
Unit 2: Solutions
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Unit 13: Amines
Unit 14: Biomolecules
Unit 15: Polymers
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Unit. 1

SOLID STATE

Focus area

1.2 Amorphous and Crystalline solids
1.4 Crystal lattice and unit cell
1.5 Number of atoms in a unit cell
1.6 Close packed structures
1.9 Imperfection in solids
1.10 Electrical properties
1.11 Magnetic properties

Amorphous & Crystalline solids

Solids can be divided into two categories. Crystalline & Amorphous

Crystalline solid(True solids): The arrangement of constituent particles (atoms, molecules or ions) in a crystal is ordered and repetitive in three dimensions.

Amorphous solid[Pseudo solids (super cooled liquids)]: The arrangement of constituent particles(atoms, molecules or ions) in such a solid has only *short range order.*

Crystal Lattice (space lattice) and Unit cell

Crystal Lattice is the regular arrangement of constituent particle in three dimension
Unit cell is the smallest portion of a crystal lattice

Q.1 Classify the following compounds into crystalline and amorphous solid
sodium chloride, glass, quartz, rubber
Q.2 Write any two differences between crystalline solids and amorphous solids
Q.3 Differentiate between isotropy and anisotropy
Q.4 Give reason for the following
(i) Glass fixed to the windows of old buildings are found to be slightly thickened at the bottom than at the top
(ii) Some glass objects from ancient civilisations are found to be milky.
Q.5 Refractive index of a solid is found to have the same value along all direction. Comment on the nature of the solid. Explain its cleavage property.

Classification of Unit cell

(1) Primitive(simple or basic) unit cell: - Particles are present only at the corners of the unit cell

(2) Centred unit cell: - Particles are present at the corners as well as at any of the centres of the unit cell

Centred unit cells are of three types:

(i) Body-Centred Unit Cells: Such a unit cell contains one constituent particle at its body-centre besides the ones that are at its corners.

(ii) Face-Centred Unit Cells: Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) End-Centred Unit Cells: In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at the corners

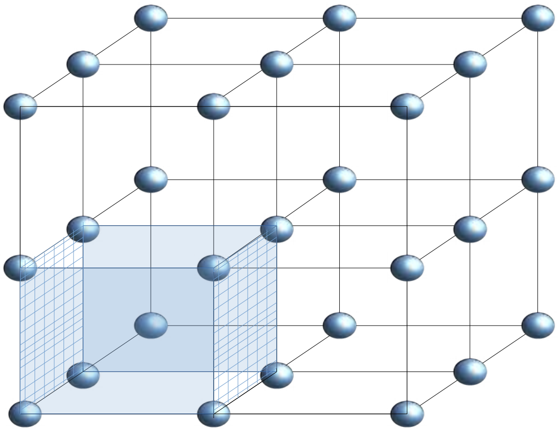
Three types of cubic unit cells

Primitive cubic unit cell has atoms only at its corner.

Body-centred cubic (bcc) unit cell has an atom at each of its corners and also one atom at its body centre.

Face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube.

Q.6 Part of a cubic crystal lattice is given below, where the shaded portion represents a unit cell. Closely observe it and answer the questions followed:



(i) If the unit cell parameters are represented by a, b, c, α, β and γ, how are their values related in this case?

(ii) If the spheres represent an element, ‘A’, calculate the number of atoms present in the shaded unit cell.

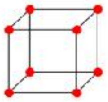
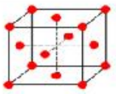
(iii) Also calculate the effective number of atoms of ‘A’ present in the portion of crystal lattice shown above

(iv) If atoms of another element ‘B’ are present at the body centres of each of the above unit cells, identify the formula of the compound so formed.

(v) If the lattice given in the picture contains only one type of particles, identify the type of three dimensional close packing developed by such an arrangement.

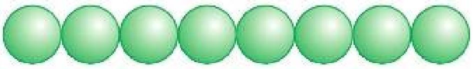
(vi) Sketch the type of cubic unit cell formed if the particles were packed in cubic close packed manner and calculate the effective number of particles in the unit cell that you have sketched.

Q.7 Complete the following table

Cubic Unit Cell		Effective number of particles (z)
Type	Figure	
1. Primitive		…………
2. body centred	……………………………	2
3. ……………………………		4

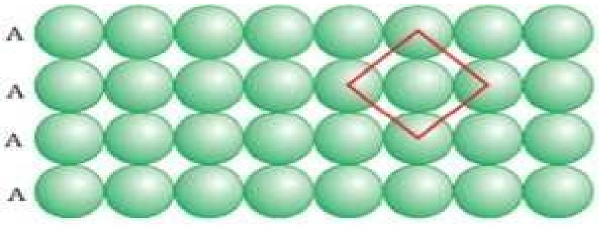
Close Packing in crystals

close packing in one dimension:



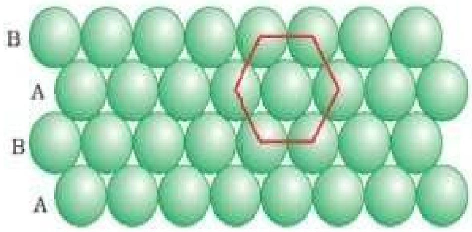
Two dimensional packing

Square close packing



Co-ordination number 4

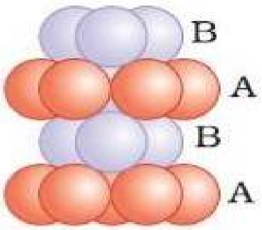
Hexagonal close packing



Co-ordination number 6

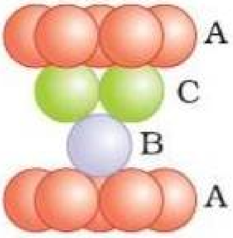
Three dimensional packing

(i) Hexagonal close packing (HCP) (ABAB…….type pattern)



Hexagonal

(ii) Cubic close packing (CCP) or Face centred cubic packing (ABCABC…….type pattern)



- In HCP and CCP co-ordination number is 12
- **The vacant sites or empty spaces in close packed structures are called voids.**

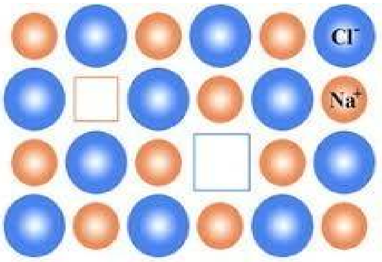
- **Tetrahedral voids-** The vacant spaces between four touching spheres having tetrahedral arrangement
- **Octahedral voids-** The void surrounded by six spheres in octahedral position

- In close packing there are one octahedral and two tetrahedral voids associated with each sphere

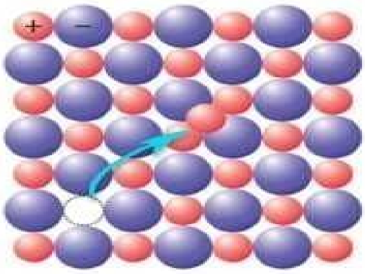
Q8. In Fe crystal, atoms are packed in ABC ABC type arrangement. Name the close packed structure.?
Q.9 Differentiate between Square close packing and Hexagonal close packing in 2 dimension.
Q.10 If N spheres are there in a close packing, what is the total number of voids present in it?
Q.11 What are voids? How will you distinguish between tetrahedral void and octahedral void?
Q.12 A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound ?

Imperfection in solids (Defects in solids)

Point defects- (i) Stoichiometric defect -The point defect that do not disturb the stoichiometry of the compound
Schottky defect:-The point defect caused by missing of equal number of ‘+’ve and ‘-’ ve ion from their normal position
Frenkel defect:- The point defect caused by dislocation of an ion from its normal site to interstitial site.



Schottky defect

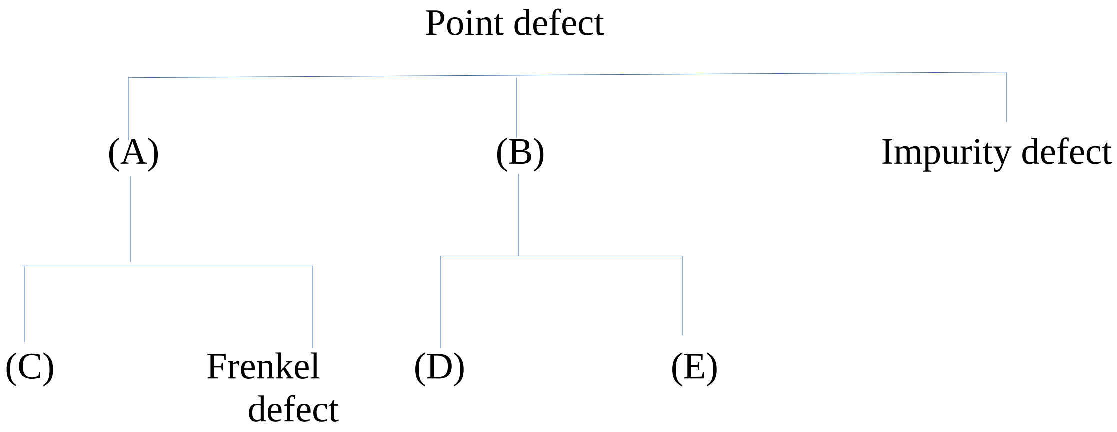


Frenkel defect

(ii) Non stoichiometric defect -The defect which disturb the stoichiometry of the compound

Metal Excess defect
(a) Anion vacancies- Negative ions may be missing from their lattice site leaving a hole. This hole occupied by an electron called **F-centre**
(b)Extra cation:- Extra cation (positive ion) is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in another interstitial site.
Impurity defects in ionic solids : Defects introduced in ionic solids by the addition of impurity ions

Q.13: complete the tree diagram for point defects in ionic solids



Q.14 What happens when LiCl is heated in presence of Li vapours.? Give reason?

Q.15.Match the following

A	**B**
Schottky defect	F-centre
Frenkel defect	$CdCl_2$ & AgCl
Metal Excess defect	NaCl
Impurity defect	AgCl
	FeO

Q.16 What is the co-ordination number of particles present in FCC crystal structure

(i) 4 (ii) 6 (iii) 8 (ii) 12

Q17 : $CaCl_2$ and NaCl are ionic compounds having cations and anions of same size, but AgBr, AgCl and ZnS having cations and anions of very large difference in ionic size. Answer the following:

(a) The type of stoichiometric defect shown by $CaCl_2$ and NaCl
(b) The type of stoichiometric defect shown by AgCl and ZnS
(c) Differentiate the properties of stoichiometric defects shown by $CaCl_2$ and ZnS
(d) From the above compounds, which compounds shows both the stoichiometric defect

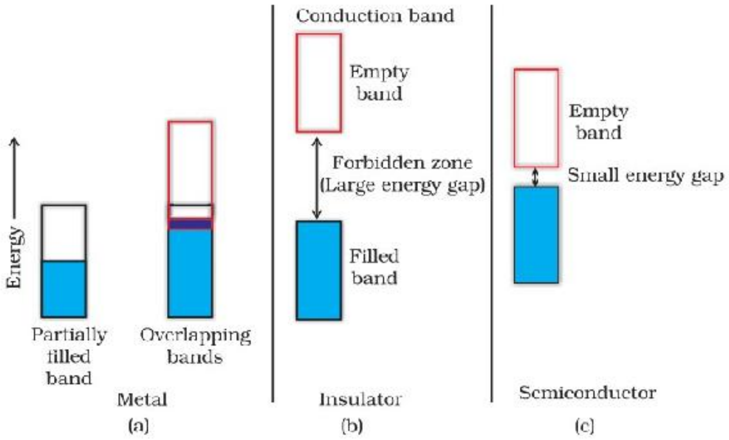
Q .18 Complete the table

Colour change in the crystal	Reason for colour change	Name of imperfection
Heating in presence of excess of K, KCl crystals become violet.		
When ZnO crystals are heated, the white coloured crystals becomes yellow.		

Electrical properties

On the basis of electrical conductivity, solids are classified into 3 types conductors, semiconductors & insulators

The conductivity of metals decreases with temperature while that of insulators and semiconductors increases with temperature.



Semiconductor: They are of two types

(a) Intrinsic semiconductor- At higher temperature certain covalent bonds are broken and released electrons are capable of conducting electricity

(b) Extrinsic semiconductor
  (i) n-type semiconductor
  (ii) p-type semiconductor

Q.19 (a) Name three types of solids classified on the basis of electrical conductivity.
(b) How will you explain such classification based on band diagram?

Q.20 Which of the following is a semiconductor material?
(a) Ga (b) As (c) Ge (d) B

Q.21 A group of 14 elements is to be converted into n-type semiconductor by Doping it with suitable impurity. To which group should this impurity belong ?
(a) 13 (b) 14 (c) 15 (d) 16

Q.22 (a) Semiconductors can be obtained by doping silicon with As or with Ga. What is the basic difference between these?

(b) What is the effect of temperature on the electrical conductivity of semiconductors?

Magnetic properties

On the basis of magnetic properties substances can be classified into five categories

Paramagnetism-The substances are weakly attracted by a magnetic field

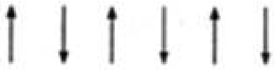
Diamagnetism-The substances which are weakly repelled by the magnetic field

Ferromagnetism-The substances are strongly attracted by a magnetic field and show permanent magnetic properties even when the magnetic field is removed

Antiferromagnetism-Here the magnetic moments are aligned in equal number in opposite direction.

Ferrimagnetism- Here the magnetic moments are aligned in parallel and antiparallel direction in unequal numbers.

Q23: Complete the table

Properties	Magnetic alignment	Nature in magnetic field	Example
Paramagnetic			
		Repelled weakly in magnetic field	H_2O, NaCl, C_6H_6
			Fe, Ni, Co. CrO_2
Ferrimagnetic		Weakly attracted by magnetic field	
			MnO

Q24.What types of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer

Q25.Each electron in an atom behaves like a tiny magnet'.Explain the two types of motions that cause magnetic moment of electrons

Q.26.Match the following

A	B
Diamagnetic substance	Fe_3O_4
Paramagnetic substance	MnO
Ferromagnetic substance	NaCl
Antiferromagnetic substance	O_2
	Fe

Answers

1. Crystalline solid – sodium chloride, Quartz
   Amorphous solids : Glass, rubber

2.

Crystalline solids	Amorphous solids
Long range order	Short range order
Sharp melting point	They do not have sharp melting point
Anisotropic	Isotropic
True solid	Pseudo solid

3. Physical properties like thermal conductivity, electrical conductivity, refractive index are different in different direction are called anisotropic and are same in all direction is called isotropic

4. (i) Glass is an amorphous solid (super cooled liquid) and it has tendency to flow
   (ii) On heating, amorphous solids become crystalline at some temperature.

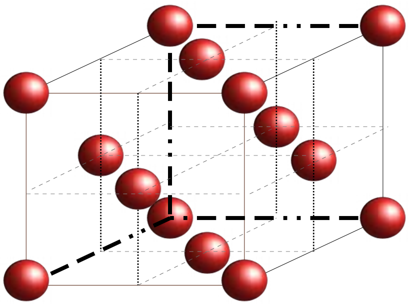
5. It is isotropic and it will be an amorphous solid. It undergoes irregular cleavage

6. (i) $a = b = c$; $\alpha = \beta = \gamma = 90^o$
   (ii) It is a simple cubic unit cell.
   Therefore, effective number of atoms per unit cell = 8 x (1/8) = 1
   (iii) The portion of lattice given here contains 8 unit cells. Therefore the effective number of particles in the given part of lattice = 8 x 1 = 8

(iv) The element, ‘A’ has simple cubic arrangement. Therefore number of atoms of ‘A’ per unit cell = 8 x (1/8) = 1
Atoms of the element ‘B’ are at the body centres of each unit cell.
Therefore effective number of atoms of ‘B’ per unit cell = 1 x 1 = 1
Therefore formula of the compound is A_1B_1 i.e., AB

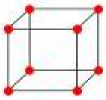
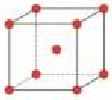
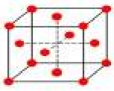
(v) AAAA..... type close packing or simple cubic lattice.

(vi) Cubic close packing refers to fcc lattice. i.e.,



Calculation of effective number of **particles:**
Corners : 8 x (1/8) = 1
Face centres: 6 x (1/2) = 3
Total number of particles per unit cell = 1 + 3 = 4

7.

Cubic Unit Cell		Effective number of particles (z)
Type	Figure	
1. Primitive		1
2. body centred		2
3. face centred		4

8. Cubic close -packed (ccp) structure

9. Square close packing: Spheres of the second row are placed just above the spheres of the first row and so on. Here spheres show vertical and horizontal alignment
Hexagonal close packing :Spheres of the second row are placed in the depression between the spheres in the first row. The spheres in the third row will be vertically aligned those in the first row and so on.

10.N spheres will form 2N tetrahedral voids and N octahedral voids

11.The vacant space in a close packed structure is called voids .
The vacant spaces between four touching sheres having tetrahedral arrangement is called tetrahedral void.

In close packing,the number of tetrahedral voids is double the number of spheres. So there are two tetrahedral voids associated with each sphere

The void surrounded by six sphere in octahedral position is called octahedral void.

In close packing, the number of octahedral voids is equal to the number of spheres. So there are one octahedral voids associated with each sphere.

12. Let the number of N atoms be x. It will form x octahedral voids and 2x tetrahedral voids.

M occupies 1/3rd of the tetrahedral voids. So number of M =1/3 (2x) =2/3x

M : N = 2/3: 1 = 2:3

Formula of the compound will be M_2N_3

13. (A) Stoichiometric defect (B) non-stoichiometric defect
(C) Schottky defect (D) metal excess defect
(E) metal deficiency defect

14. When LiCl is heated in an atmosphere of Li vapours, it becomes pink in colour

It is due to the formation of F-centre

Li atoms lose electron to form Li ions. The released electrons diffuse into the crystal and occupy anionic sites (F-centres) .These electrons impart colour to the LiCl crystal.

15.

A	**B**
Schottky defect	NaCl
Frenkel defect	AgCl
Meta Excess defect	F-centre
Impurity defect	$CdCl_2$ & AgCl

16. 12

17. (a) Schottky defect.
(b) Frenkel defect
(c)

Schottky defect	Frenkel defect
1. The defect arising due to the missing of equal number of anions and cations from the lattice site	1. The defect arising due to the misplacing of a cation from the lattice site to the interstitial site
2. It is shown by ionic solids in which the anionic and cationic sizes are almost equal.	2. This type of defect is shown by ionic solids in which cationic size is smaller than anionic size.
3. Due to this defect the density of the solid decreases.	3. Due to this defect the density of the solid remain same.

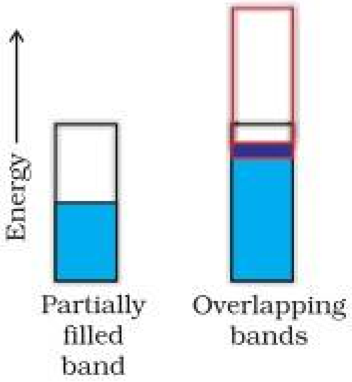
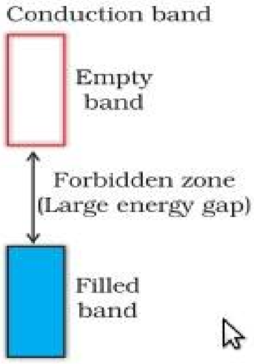
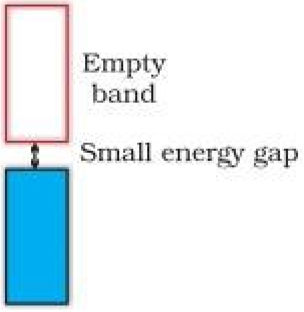
(d) AgBr.

18.

Colour change in the crystal	Reason for colour change	Name of imperfection
Heating in presence of excess of K, KCl crystals become violet.	some of the anions are missing from the lattice site of the crystal. The electrical neutrality is maintained by occupying electrons in the anionic sites. These electrons are called f-centres because they give colour	Metal excess defect due to anionic vacancies
When ZnO crystals are heated, the white coloured crystals becomes yellow.	This is because on heating, the crystal loses oxygen as follows: $ZnO \rightarrow Zn^{2+} + \frac{1}{2}O_2 + 2e^-$ The Zn ions now move to the interstitial sites and the electrons to neighbouring interstitial sites and this electrons give colour.	Metal excess defect due to extra cations at interstitial sites:

19. (a) Based on electrical conductivity, solids can be classified into three-conductors, insulators and semiconductor

(b) According to band theory of solids, the atomic orbitals of solids form molecular orbitals,which are so close in energy to form energy bands. The energy band formed by valence electrons (electron occupied highest energy band)is called valence band (VB) and the energy band formed by the orbitals just above the valence band (next higher energy band to valence band or lowest energy band unoccupied by electrons) is called conduction band (CB). The gap between VB and CB is called energy gap or forbidden zone

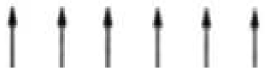
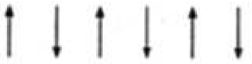
Conductors	Insulators	Semiconductor
 There is no energy gap ie, VB may be partially filled or the VB and CB may be overlapped	 Energy gap is very large	 Energy gap is very low

20. Ge
21. 15

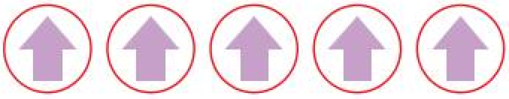
22.(a)Semiconductors obtained by doping silicon with 15th group element As is n-type and those with13th group element Ga is p-type

(b) Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band.

23.

Properties	Magnetic alignment	Nature in magnetic field	Example
Paramagnetic		Weakly attracted by magnetic field	O^2, Cu^{2+}, Fe^{3+}, Cr^{3+}
Diamagnetic		Repelled weakly in magnetic field	H_2O,NaCl, C_6H_6
Ferromagnetic		attracted very strongly in a magnetic field.	Fe,Ni,Co. CrO_2
Ferrimagnetic		Weakly attracted by magnetic field	Fe_3O_4 $MgFe_2O_4$
Antiferromagnetic		Not attracted or repelled in magnetic field	MnO

24. Ferromagnetic substances would make better permanent magnets. They are attracted very strongly by a magnetic field due to the orientation of all magnetic domain in the direction of magnetic field.



e.g.; Fe, Co, Ni, Gd, CrO_2

25. Each electron in an atom behaves like a tiny magnet due to (i) its orbital motion around the nucleus and (ii) its spin around its own axis

26.

A	B
Diamagnetic substance	NaCl
Paramagnetic substance	O_2
Ferromagnetic substance	Fe
Antiferromagnetic substance	MnO

SAMAGRA SIKSHA KERALA Class 12 CHEMISTRY

Unit. 2

SOLUTIONS

Focus Area

1. Solubility of a Gas in a Liquid
2. Vapour pressure of Liquid Solutions
3. Ideal and Non – ideal Solutions
4. Colligative properties and Molar mass determination

1. Solubility of a Gas in a Liquid

The solubility of gases increase with increase of pressure and decrease with increase of temperature.

Henry's law: $p = K_H x$

Here p is the partial pressure of the gas above the solution, K_H is the Henry's law constant of the gas and x is the mole fraction of the gas in solution

Note:

(a) Different gases have different K_H values at the same temperature.

(b) Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

(c) As temperature increases K_H of a gas increases.

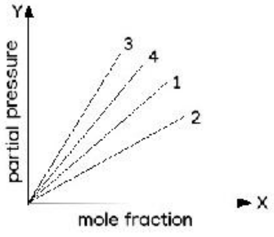
Applications of Henry's law :

(a) Soft drink bottles are sealed under high pressures of CO_2.

(b) Tanks used by scuba divers are filled with air diluted with helium.

(c) People living at high altitudes or climbers show symptoms of a condition known as anoxia.

Q1.



The variation of partial pressure(p) against mole fraction(x) of four different gases(1,2,3 and 4) in their respective solutions at the same temperature is given in the graph. Analyse the graph and answer the following:

(a) Write the general equation for a straight line.

(b) Then give a general equation for the straight lines in the graph (here y- intercept = 0) using 'p' and 'x'.

(c) Rewrite the equation by substituting the value of slope as 'K_H'.

(d) Now, identify the law corresponding to the equation that you have wrote.

(e) Give a statement of the law that you have identified above.

(f) Arrange the four gases in their increasing order of solubility.

(g) In the light of the law that you have identified, explain the following situations:

- (i) CO_2 fizz out when a soft drink bottle is opened.
- (ii) At high altitudes a climber feels physical weakness.
- (iii) If a scuba diver uses an ordinary 'tank' for breathing assistance he/she may suffer from 'bends'.

(iv) Since 'K_H' increases with temperature, what happens to aquatic life in warm water?

2. Vapour pressure of liquid solutions

(i) Raoult's Law: Partial vapour pressure of a volatile component in solution is proportional to mole fraction of that component in solution.

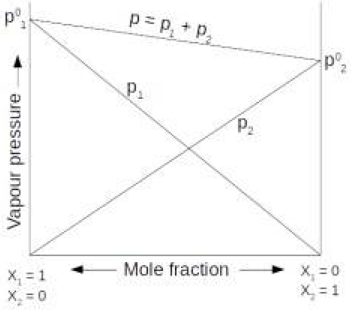
(ii) Vapour pressure of a solution containing a non volatile solute is lower than that of the pure solvent.

Q2. Raoult's law for a solution of two volatile liquids, 1 and 2 is graphically represented here(such a graph is used in physical chemistry to explain the variation of a property of two components whose mole fractions are related as $x_1 + x_2 = 1$). p_1 and p_2 are the partial pressures of 1 and 2 respectively

(a) Formulate equations for lines, p_1 and p_2 with the help of the graph.

(b) Arrive at an equation for p_{total} in terms of x_2.

(c) If component,2 is a non volatile solute($p_2 = 0$), what happens to the above equation?

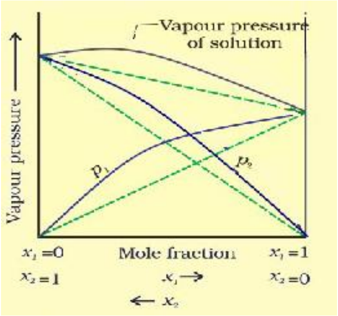


3. Ideal and Non-ideal Solutions

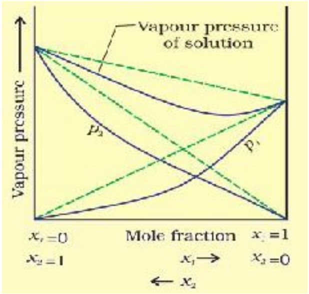
Ideal Solutions: The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. Also $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$

Non-ideal Solutions: The solutions which do not obey Raoult's law over the entire range of concentration are called non-ideal solutions. Intermolecular attractive interactions before and after mixing will be different and hence $\Delta_{mix}H \neq 0$ and $\Delta_{mix}V \neq 0$. They are of two types: Solutions exhibiting positive deviation($p_1 > p^0_1 x_1$ and $p_2 > p^0_2 x_2$) and those exhibiting negative deviation($p_1 < p^0_1 x_1$ and $p_2 < p^0_2 x_2$) from Raoult's law.

Positive deviation



Negative deviation



*Azeotropes:*azeotropes are binary mixtures having the same composition in liquid and vapour phase. There are two types of azeotropes – (i) The solutions which show a large positive deviation from Raoult's law form ***minimum boiling azeotrope*** at a specific composition and (ii) The solutions that show large negative deviation from Raoult's law form ***maximum boiling azeotrope*** at a specific composition.

Q3. Examine details given in the table and put 'tick mark' on suitable columns:

No.	Components		Intermolecular interactions	Partial vapour pressure			Value of $\Delta_{mix}H$ and $\Delta_{mix}V$			Nature of solution			Type of azeotrope, if formed
	A	B		$P_1 = p^0_1 x_1$ and $p_2 = p^0_2 x_2$	$p_1 > p^0_1 x_1$ and $p_2 > p^0_2 x_2$	$p_1 < p^0_1 x_1$ and $p_2 < p^0_2 x_2$	$\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$	$\Delta_{mix}H > 0$ and $\Delta_{mix}V > 0$	$\Delta_{mix}H < 0$ and $\Delta_{mix}V < 0$	Almost ideal	Non-ideal with positive deviation	Non-ideal with negative deviation	
a	n-Hexane	n-Heptane	A-A , B-B and A-B attractions are almost same										Not formed
b	Chloroform	Acetone	A-A and B-B attractions are stronger than A-B attraction										Maximum boiling azeotrope
c	Ethanol	Water	A-A and B-B attractions are weaker than those between A-B										Minimum boiling azeotrope
d	Phenol	Aniline	A-A and B-B attractions are stronger than those between A-B										Maximum boiling azeotrope
e	Acetone	CS_2	A-A and B-B attractions are weaker than those between A-B										Minimum boiling azeotrope
f	Benzene	Toluene	A-A , B-B and A-B attractions are almost same	√			√			√			Not formed

4. Colligative Properties and Determination of Molar mass

Colligative properties: Properties which depend on the relative number of solute particles irrespective of their nature are called colligative properties. These are:

(i) Relative lowering of vapour pressure of the solvent

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 \, , \quad \frac{p_1^0 - p_1}{p_1^0}$$ is the relative lowering of vapour pressure and x_2 is the mole fraction of the solute.

(ii) Elevation of boiling point of the solvent(ΔT_b)

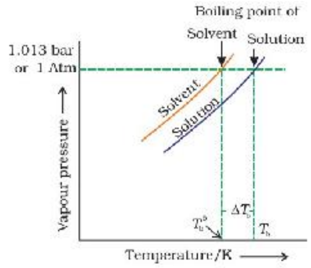
$$\Delta T_b = T_b - T_b^0 \, ;$$

(T_b = boiling point of solution, T_b^0 = boiling point of solvent)

$$\Delta T_b \propto m \, ; \text{ (m is the molality)}$$

$$\Delta T_b = K_b \, m;$$

(K_b is the molal elevation constant of the solvent)



(iii) Depression of freezing point of the solvent(ΔT_f)

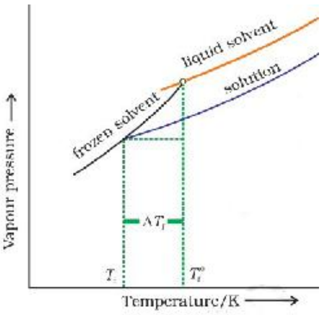
$\Delta T_f = T_f^0 - T_f$;

(T_f = freezing point of solution, T_f^0 = freezing point of solvent)

$\Delta T_f \propto m$; (m is the molality)

$\Delta T_f = K_f\, m$;

(K_f is the molal depression constant of the solvent)



(iv) Osmotic pressure of the solution(Π)

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis

$\Pi = C\,R\,T$; ('C' is the molarity of solution, 'R' is the universal gas constant and 'T', the absolute temperature)

For two solutions ***1*** and ***2*** at the same temperature,

if $\Pi_1 = \Pi_2$, ***1*** and ***2*** are said to be isotonic;

if $\Pi_1 > \Pi_2$, ***1*** is hypertonic with respect to ***2*** and ***2*** is hypotonic with respect to ***1.***

Note: ***solvent molecules always flow from a solution of lower concentration to that of higher concentration, when they are separated by a semipermeable membrane.*** Π can be measured at normal temperatures, molarity is used here and Π values are measurable for dilute solutions of macromolecules.

Q4. Some important concentration terms are explained here so that the appended questions can be solved:

Mole fraction of component ***2,***

$x_2 = \frac{n_2}{n_1 + n_2}$; (n$_1$ and n$_2$ are number of moles of ***1*** and ***2*** respectively), and $n_1 + n_2 = n_1$ for a dilute solution.

Molality of a solution of w_2 g solute(molar mass M_2) dissolved in w_1 g of solvent,

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1}$$

Molarity(C) of a solution of w_2 g solute(molar mass M_2) dissolved in V litre of solution,

$$C = n_2 / V; \quad n_2 = w_2 / M_2$$

(a) Derive expressions to calculate molar mass of a solute using different colligative property methods.

(b) Calculate the boiling point of a solution of 1.2 g of urea(molar mass = 60) dissolved in 1 kg of water(K_b = 0.52 K kg mol^{-1}), if boiling point of pure water is 100^{O}C.

(c) Think about the following situations and answer appropriately:

(i) Usually medicines for intravenous injections are made isotonic with blood cell fluid by mixing with 0.9%(w/v) NaCl solution(normal saline solution). What happens if the medicine injected is hypertonic with respect to the blood cell fluid?

(ii) Osmosis can be reversed by applying a pressure greater than osmotic pressure on the solution side, when the solvent and solution are separated by a semipermeable membrane(known as reverse osmosis). If a situation is there to purify sea water into pure water without heating it, what will be a better suggestion?

SOLUTIONS

Q1. (a) $y = mx + c$

(b) $p = mx$

(c) $p = K_H x$

(d) Henry's law

(e) "The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution"

(f) $3 < 4 < 1 < 2$

(g)

(i) When the bottle is opened the partial pressure of CO_2 over the solution is decreased so that its solubility decreases and fizz out.

(ii) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

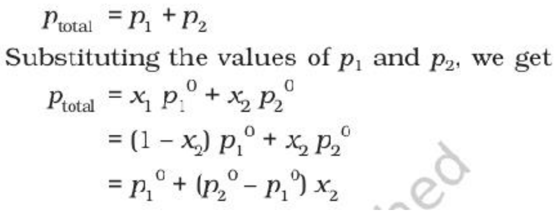
(iii) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

(iv) Since 'K_H' increases with temperature, the solubility of gas decreases. As a result the quantity of dissolved oxygen will be less in warm water than that in cold water. Therefore aquatic organisms will not be comfortable in warm water.

Q2.

(a) $p_1 = p_1^0 x_1$ *and* $p_2 = p_2^0 x_2$

(b)



$$p_{total} = p_1 + p_2$$

Substituting the values of p_1 and p_2, we get

$$p_{total} = x_1 p_1^0 + x_2 p_2^0$$
$$= (1 - x_2) p_1^0 + x_2 p_2^0$$
$$= p_1^0 + (p_2^0 - p_1^0) x_2$$

(c) $p_{total} = p_1 + p_2$

$= p_1^0 x_1$ *(since $p_2 = 0$)*

$= p_1^0 (1 - x_2)$

$= p_1^0 - p_1^0 x_2$

Rearranging the above equation,

$(p_1^0 - p_{total}) / p_1^0 = x_2$

i.e., the relative lowering of vapour pressure of a solution containing a non volatile solute is equal to the mole fraction of the solute in solution.

Q3.

No.	Components		Intermolecular interactions	Partial vapour pressure			Value of $\Delta_{mix}H$ and $\Delta_{mix}V$			Nature of solution			Type of azeotrope, if formed
	A	B		$P_1 = p^0_1 x_1$ and $p_2 = p^0_2 x_2$	$P_1 > p^0_1 x_1$ and $p_2 > p^0_2 x_2$	$p_1 < p^0_1 x_1$ and $p_2 < p^0_2 x_2$	$\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$	$\Delta_{mix}H > 0$ and $\Delta_{mix}V > 0$	$\Delta_{mix}H < 0$ and $\Delta_{mix}V < 0$	Almost ideal	Non-ideal with positive deviation	Non-ideal with negative deviation	
a	n-Hexane	n-Heptane	A-A , B-B and A-B attractions are almost same	√			√			√			Not formed
b	Chloroform	Acetone	A-A and B-B attractions are stronger than A-B attraction			√			√			√	Maximum boiling azeotrope
c	Ethanol	Water	A-A and B-B attractions are weaker than those between A-B		√			√			√		Minimum boiling azeotrope
d	Phenol	Aniline	A-A and B-B attractions are stronger than those between A-B			√			√			√	Maximum boiling azeotrope
e	Acetone	CS_2	A-A and B-B attractions are weaker than those between A-B		√			√			√		Minimum boiling azeotrope
f	Benzene	Toluene	A-A , B-B and A-B attractions are almost same	√			√			√			Not formed

Q4. (a) Refer text to derive expressions:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \qquad M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \qquad M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} \qquad M_2 = \frac{w_2 \; R \; T}{\Pi \; V}$$

(b) $\Delta T_b = K_b\,m$; (K_b is the molal elevation constant of the solvent and m is the molality of solution)

$\Delta T_b = T_b - T_b^0$; (T_b = ?, $T_b^0 = 100^{O}C = (100 + 273.15)\ K = 373.15\ K$

$K_b = 0.52\ K\ kg\ mol^{-1}$

m = n2/ mass of solvent in kg = (1.2/ 60) mol / 1 kg = 0.02 mol kg^{-1}

$\Delta T_b = 0.52\ K\ kg\ mol^{-1} \times 0.02\ mol\ kg^{-1} = 0.0104\ K$

Boiling point of solution, $T_b = T_b^0 + \Delta T_b$

= (373.15 + 0.0104) K = **373.1604 K**

(c)

(i) If the medicine is hypertonic solvent flows out of the cell and hence destroyed.

(ii) Reverse osmosis.

Unit. 3

Electrochemistry

Focus area

- **Nernst equation**
- **Variation of conductivity and molar conductivity with concentration**
- **Batteries**
- **Fuel cells**
- **Corrosion**

Pre-requisites

- Potential difference that develops between the electrode and the electrolyte is called **electrode potential.**
- When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**.
- In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution.
- The half-cell in which reduction takes place is called **cathode**
- The potential difference between the two electrodes of a galvanic cell is called the **cell potential** $\mathbf{E_{cell} = E_{right} - E_{left}}$
- Daniel cell can be represented as: $\mathbf{Zn(s) | Zn^{2+} (1M) || Cu^{2+} (1M) | Cu(s)}$
- The **electrical resistance** of any object is directly proportional to its length, l, and inversely proportional to its area $R = \rho \frac{l}{A}$ of cross section, A.
- The inverse of **resistivity(ρ)**, is called **conductivity(κ)** (specific conductance)
- The inverse of resistance, R, is called **conductance, G** $G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$
- **Molar conductivity, Λm** of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length.

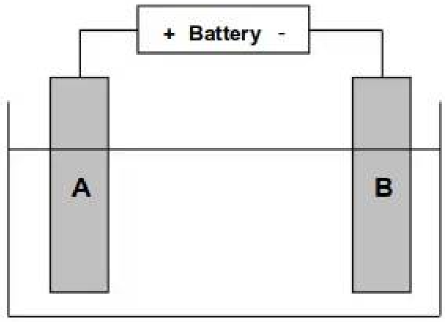
Scan the following QR codes for the above pre-requisites

1. https://www.youtube.com/watch?v=EEmBv3KAdZk
2. https://www.youtube.com/watch?v=59lKsZtr5Vg

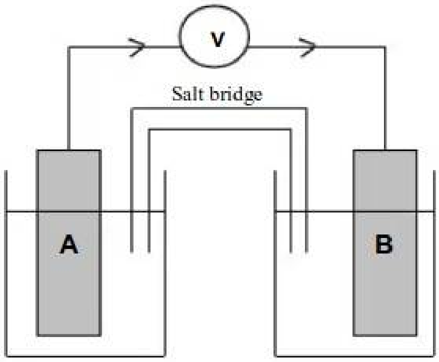
Activity 1

Consider the following two diagrams of cells:

I.



II.



(a) Which of these cells represent a galvanic cell?

(b) Assume that the following reaction is taking place in galvanic cell

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

(i) Write the reactions taking place at the anode and the cathode respectively

(ii) Write the cell representation of this cell.

(iii) Calculate the standard cell potential for the above cell (given that $E^0_{Zn^{2+}/Zn} = -0.76V$ and $E^0_{Cu^{2+}/Cu} = 0.34V$)

Activity 2

Match the following

	Column **A**		Column **B**
	property		**unit**
1	Resistance	a	Ω m
2	Conductance	b	$S\ m^2\ mol^{-1}$
3	Molar conductivity	c	$S\ m^{-1}$
4	Resistivity	d	Ω^{-1}
5	Conductivity	e	Ω

Nernst Equation

https://www.youtube.com/watch?v=JpGgs_FW-Z8

It gives the quantitative relationship of electrode potential with concentration of electrolyte and temperature

For the electrode reaction: $M^{n+}(aq) + ne^{-} \rightarrow M(s)$

The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$E^{\ominus}_{(M^{n+}/M)}$ = standard electrode potential

F = Faraday constant (96487 C mol^{-1}),
T = temperature in kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+}

Q1. Consider the following cell reaction

$$Mg(s) + 2Ag^{+}(aq) \rightarrow Mg^{2+}(aq) + Ag(s)$$

(i) Write the cell notation for the cell: ______|________||________|_______
(ii) How many moles of electrons are involved in this reaction? n =_____
(iii) Write the Nernst Equation for the cell
(iv) If a new cell is set up with the $[Ag^{+}]$ = 0.0001M and the $[Mg^{2+}]$ = 0.130M, the cell potential will be ----------(given $E^{0}_{Mg2+/Mg}$ = –2.36V and $E^{0}_{Ag+/Ag}$= 0.80V)

Variation of conductivity and molar conductivity with concentration

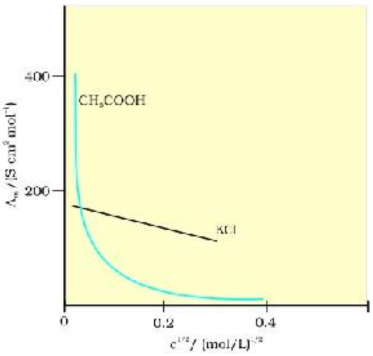
https://www.youtube.com/watch?v=0UJIxCDGXOw

- Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes.
- Molar conductivity increases with decrease in concentration. This is because the total volume, of solution containing one mole of electrolyte also increases.
- When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity**

For strong electrolytes, Λm increases slowly with dilution and can be represented by the equation

$\Lambda m = \Lambda^0 m - A\, c^{1/2}$

if we plot Λm against $c^{1/2}$, we obtain a straight line with intercept equal to Λ^0m and slope equal to '–A'.



Kohlrausch law of independent migration of ions.

The law states that ***limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.***

Thus, if $\lambda^0 Na^+$ and $\lambda^0 Cl^-$ are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\mathbf{\Lambda^0 m\ (NaCl) = \lambda^0 Na^+ + \lambda^0 Cl^-}$$

In general, if an electrolyte on dissociation gives ν+ cations and ν– anions then its limiting molar conductivity is given by: $\mathbf{\Lambda^0 m = \nu_+ \lambda^0_+ + \nu_- \lambda^0_-}$

Applications of Kohlrausch law

- to calculate **Λ^0m** for any electrolyte from the **λ^0** of individual ions.
- for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant

Q2. The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if Λ^0m for acetic acid is 390.5 S cm^2 mol^{-1}.

Batteries

(Refer:- First bell class episode17- https://www.youtube.com/watch?v=gp1n6DVhMc8 or scan the QR code

- Any battery may have one or more than one cell connected in series that we use as a source of electrical energy
- There are mainly two types of batteries.
  (i) primary batteries- The cell reaction occurs only once and cannot be reused

example: dry cell, mercury cell

(ii) secondary cell – A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again

example: lead storage battery cell, nickel cadmium cell

	Cell/ battery	**Anode and anode reaction**	**Cathode and Cathode reaction**	**Overall reaction**
1	Dry cell	Zinc $Zn(s) \rightarrow Zn^{2+} + 2e^-$	MnO_2 & C $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$	[redacted]
2	Mercury cell	zinc – mercury amalgam $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$	HgO and carbon $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$	$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$
3	Lead storage battery	Lead $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$	lead dioxide $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
4	Nickel-Cadmium cell	cadmium	$Ni(OH)_3$	$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

Q3. Analyse the following statements and write which among them are **True/False**

(a) The cell potential of Mercury cell is approximately1.35 V and remains constant during its life.

(b) A secondary cell after use can not be recharged.

(c) A nickel-cadmium cell has longer life than the lead storage cell.

(d) Mercury cell is suitable for low current devices like hearing aids.

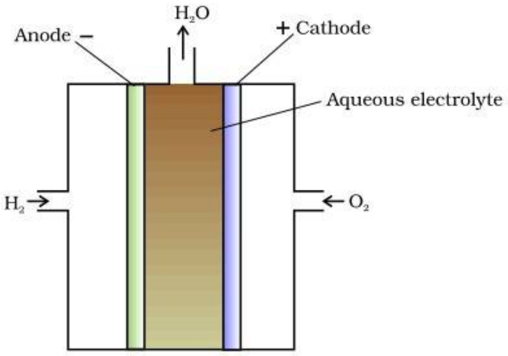
Q4. Match the following

	Column **A**		Column **B**
	Cell		**Electrolyte used**
1	Dry cell	a	ZnO and aq.KOH
2	Mercury cell	b	Aq.KOH / NaOH
3	Lead storage battery	c	A paste of NH_4Cl and $ZnCl_2$
4	Nickel-Cadmium cell	d	Dil. H_2SO_4

Fuel Cells

(Refer:- First bell class episode19 -https://youtu.be/KLzJmXvldTk)
or scan QR code

Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells.**



The electrode reactions are:

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

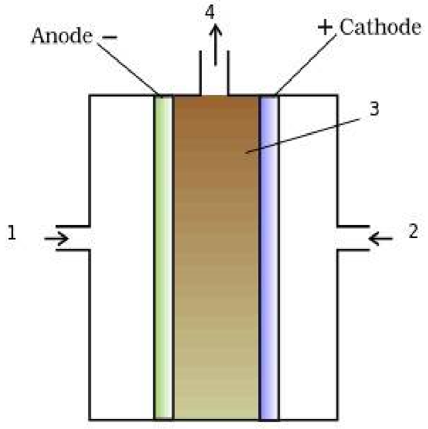
Overall reaction being:

$$\mathbf{2H_2(g) + O_2(g) \rightarrow 2H_2O(l)}$$

Advantages of fuel cell

- Highly efficient
- Pollution free working

Q5. A diagram of Hydrogen- Oxygen fuel cell is given below. Identify the components represented as 1, 2, 3 and 4



Corrosion

(Refer:- First bell class episode19 -https://youtu.be/KLzJmXvldTk)
or scan QR code

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal.

E.g., The rusting of iron, tarnishing of silver,
development of green coating on copper and bronze

Electrochemical theory of corrosion

Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Atomospheric
oxidation: $2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

Q6. Name two metals which can be used for cathodic protection of iron.

Solutions to activities and questions

Activity 1

(a) diagram II

(b) (i) Anode:- $Zn(s) \rightarrow Zn^{2+} + 2e^-$ Cathode:- $Cu^{2+} + 2e^- \rightarrow Cu(s)$

(ii) $Zn(s)|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu(s)$

(iii) $E_{cell} = E^0_R - E^0_L = 0.34V - (-0.76)V = 1.10\ V$

Activity 2

1- e, 2- d, 3- b, 4- a, 5- c

Q1.

(i) $Mg(s) \mid Ag^+(aq) \parallel Mg^{2+}(aq) \mid Ag(s)$

(ii) n =2

(iii)

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F}\ln\frac{[Mg^{2+}]}{[Ag^+]^2}$$

(iv) $E^0_{cell} = E^0_R - E^0_L = 0.80V - (-2.36)V = 3.17\ V$

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F}\ln\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 3.17\ V - \frac{0.059V}{2}\log\frac{0.130}{(0.0001)^2} = 3.17\ V - 0.21V = 2.96\ V.$$

Q2.

$$\Lambda_m = \frac{\kappa}{c} = \frac{4.95\times10^{-5}\ S\ cm^{-1}}{0.001028\ mol\ L^{-1}} \times \frac{1000\ cm^3}{L} = 48.15\ S\ cm^3\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{o}} = \frac{48.15\ S cm^2 mol^{-1}}{390.5\ S cm^2\ mol^{-1}} = 0.1233$$

$$k = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 mol\ L^{-1} \times (0.1233)^2}{1-0.1233} = 1.78 \times 10^{-5}\ mol\ L^{-1}$$

Q3. (a) True
(b) False
(c) True
(d) True

Q4. 1- c, 2- a, 3- d, 4- b

Q5. 1. H_2
2. O_2
3. Aqueous electrolyte
4. H_2O

Q6. Zn and Mg

SAMAGRA SIKSHA KERALA Class 12 CHEMISTRY

Unit 4
Chemical Kinetics

Focus Area:
4.2 Factors affecting rate of a Reaction
4.3.2 First order reaction and its half-life period
4.4 Pseudo first order reaction
4.5 Rate of reaction and Temperature

Factors affecting rate of a Reaction

The change in concentration of any one of the reactants or products per unit time is called rate of the reaction. It is affected by nature of reactants, concentration, temperature, pressure, catalyst etc. When concentration of reactants increases, rate of reaction also increases. This can be expressed by rate law. Two important terms related to a chemical reaction are order and molecularity. The sum of the powers of the concentration terms in the rate law gives the order of the reaction and the stoichiometric coefficients of balanced chemical equation gives its molecularity.

1) Name any 4 factors which affect the rate of a reaction?

2) Define rate law.

3) Define rate constant.

4) Differentiate between order and molecularity.

5) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, $r = k\,[A]^{\frac{1}{2}}\,[B]^{2}$. What is the order of the reaction?

6) The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

7) Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}\ \mathrm{L\ mol^{-1}\ s^{-1}}$

(ii) $k = 3 \times 10^{-4}\ \mathrm{s^{-1}}$

8) Differentiate between elementary and complex reactions?

9) Consider a general reaction $aA + bB \rightarrow cC + dD$.

The rate expression for the reaction is $r = k[A]^{x}\,[b]^{y}$. Establish the significance of (a+b) and (x+y) in terms of order and molecularity.

10) Complete the following:

Reaction	Order	Unit of rate constant
First order reaction	1	....
....	0	mol/L/sec
Second order reaction	....	....

11) For the reaction $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$; Rate = k $[CHCl_3]\,[Cl_2]^{1/2}$, identify the following:

a) Order of the reaction with respect to $CHCl_3$
b) Order of the reaction with respect to Cl_2
c) Overall order of the reaction
d) Molecularity of the reaction.

12) The conversion of a molecule A to B follows second order kinetics.

a) Write the rate equation for the second order reaction.

b) If the concentration of A is increased to four times, how will it affect the formation of B.

13) The following data were obtained for the reaction $X + Y \longrightarrow Z$.

Concn. of X (mol L^{-1})	Concn. of Y (mol L^{-1})	Rate (mol $L^{-1}\,s^{-1}$)
0.02	0.01	$k \times 2 \times 10^{-4}$
0.01	0.02	$k \times 2 \times 10^{-4}$
0.02	0.02	$k \times 4 \times 10^{-4}$
0.01	0.03	$k \times 3 \times 10^{-4}$

Now answer the following questions:
a) Write the rate law for this reaction.
b) What is the order of this reaction?
c) Find the rate of the reaction, if the concentration of X and Y are 3×10^{-2} and 4×10^{-3} mol L^{-1} respectively.

First order reaction and its half-life period

In first order reaction the rate of the reaction is directly proportional to concentration of the reactants. Here the order of the reaction is 1. For these reactions, the plot of log[Reactants] against time is a straight line with negative slope. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. The time taken for half of a reaction to complete is called half-life of a reaction. For a first order reaction, half-life is independent of initial concentration.

14) Write integrated rate equation for a first order reaction.

15) Write the relation between half life ($t_{½}$) and rate constant (k) of a first order reaction.

16) Calculate the time required for the completion of 90% of a first order reaction. (k = 0.2303 s^{-1})

17) Write the order of the radioactive disintegration of Uranium.

18) Plot a graph showing variation in the concentration of reactants with time for a first order reaction.

19) What is the order of a reaction, if its half life is independent of initial concentration?

20) A first order reaction is found to have a rate constant, k = 5.5 x 10^{-14} s^{-1}. Find the half-life of the reaction.

21) A first order reaction has a rate constant 1.15 x 10^{-3} s^{-1} . How long will 5 g of the reactant take to reduce 3g?

22) By deriving the equation for $t_{½}$ of first order reaction, prove that $t_{½}$ is independent initial concentration of reacting species.

Pseudo first order reaction

These are reactions which appear to follow higher order but actually follow first order kinetics. E.g. Hydrolysis of ester, inversion of cane sugar etc.

23) What is a pseudo first order reaction? Give an example.

24) Indicate the order and Molecularity of the reaction given below:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

25) For hydrolysis of methyl acetate in aqueous solution, the following results were observed.

t/s	0	30	60
CH_3COOH C/mol L^{-1}	0.60	0.30	0.15

Show that the reaction follows pseudo first order kinetics as the concentration of water remains constant.

Rate of reaction and Temperature

The rate of a reaction increases with temperature. When the temperature is increased by 10 K, the rate of the reaction and the rate constant is nearly doubled. The temperature dependence of the rate of a chemical reaction can be explained by **Arrhenius equation**. The equation is: $\boldsymbol{k = A\,e^{-E_a/RT}}$. Where k is the rate constant, A is the Arrhenius parameter, R is the universal gas constant, Ea is activation energy and T is the absolute temperature.

26) Write Arrhenius equation and explain the terms.

27) Write the equation for finding activation energy of a reaction by knowing its rate constant at two different temperatures.

28) The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction.

29) The logarithmic form of Arrhenius equation is $\ln k = \ln A - E_a/(RT)$. Plot ln k against 1/T.

30) In a reaction, the kinetic energy possessed by the maximum fraction of molecules is called ....

31) How does a catalyst increases the rate of a chemical reaction?

32) Write any 2 characteristics of a catalyst in changing the rate of a reaction.

Answers

1) Nature of reactants, concentration of reactants, temperature and pressure.

2) Rate law is a mathematical equation relating the rate of a chemical reaction and concentration of reactants.

3) R*ate constant* is defined as the rate of the reaction when the concentration of each of the reactants is unity.

4)

	Order	Molecularity
1	It is the sum of the powers of the concentration terms in the rate law expression	It is the total number of reactant species collide simultaneously in a chemical reaction
2	It is an experimental quantity	It is a theoretical quantity
3	It can be zero or fractional	It cannot be zero or fractional
4	It is applicable to both elementary and complex reactions.	It is applicable to only elementary reactions.

5) Order of the reaction = 2 + 1/2 = 2½ = 5/2

6) Since the reaction is second order, the rate law is $r = k[X]^2$

Let the initial concentration of X be a. Then the rate law for this reaction is $r = k[a]^2$

When the concentration of X is increased to three times, the final concentration becomes 3a.

Now the rate law is $r_1 = k[3a]^2 = 9.k[a]^2$ So $r_1 = 9 \times r$

i.e. the rate formation of Y is increased by 9 times.

7) i) Here the unit of k is L mol^{-1} s^{-1}. So it is a second order reaction.

ii) Here the unit of k is s^{-1}. So it is a first order reaction.

8) Elementary reactions are reactions which occur in a single step, while complex reactions occur through more than one steps.

9) (a+b) indicates molecularity and (x+y) indicates order.

10)

Reaction	Order	Unit of rate constant
First order reaction	1	s^{-1}
Zero order reaction	0	mol/L/sec (mol L^{-1} s^{-1})
Second order reaction	2	L/mol/sec (L mol^{-1} s^{-1})

11) a) 1
- b) ½
- c) 1½ or 3/2
- d) Molecularity = 2

12) a) $r = k[A]^2$

b) When the concentration of A is increased to 4 times, the rate of formation of B is increased to 16 times.

13) a) $r = k[X][Y]$

b) order = 2

c) $r = k \times 3 \times 10^{-2} \times 4 \times 10^{-3} = k \times 12 \times 10^{-5}$ mol/L/s

14) $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

where k is the rate constant, t is the time taken, $[R]_0$ is the initial concentration of reactants and [R] is its final concentration.

15) Half-life ($t_{½}$) = 0.693/k

16) For a first order reaction,

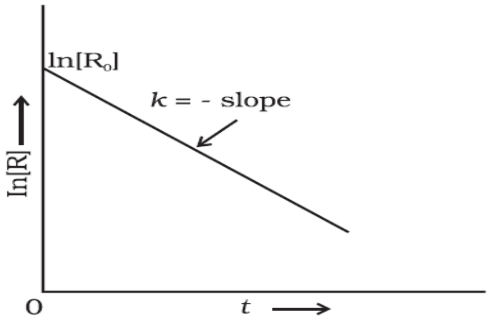
$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

For 90% completion, $[R]_0$ = 100 and [R] = 100 – 90 =10. Here k =0.2303 s^{-1}.

So $k = \frac{2.303}{0.2303} \log 100/10 = 10\ s^{-1}$

17) First order (Order = 1)

18)



19) First Order reaction

20) Here $k = 5.5 \times 10^{-14}\ s^{-1}$

We know that $t_{½} = 0.693/k = 0.693/(5.5 \times 10^{-14}) = 1.26 \times 10^{13}$ s

21) For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

Here $k = 1.15 \times 10^{-3}$ s , $[R]_0$ = 5g and [R] = 3g

So $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$= \frac{2.303}{1.15 \times 10^{-3}} \times \log \frac{5}{3}$

= 440.5 s

22) For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

When $t = t_{1/2}$, $[R] = [R]_0/2$

Substitute these values in the above equation, we get

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_0/2}$$

Or, $t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303 \times 0.3010}{k}$

Or, $t_{1/2} = \frac{0.693}{k}$

Thus for a first order reaction, half-life period is independent of initial concentration of the reacting species.

23) Reactions which appear to follow higher order but actually follow first order kinetics are called pseudo first order reactions. E.g. Hydrolysis of ester, inversion of cane sugar etc.

24) Order =1 and molecularity = 2.

25) Here the concentration of water remains constant. So, for being pseudo first order, the reaction should be first order with respect to the concentration of ester (i.e. methyl acetate). The rate constant for pseudo first order reaction is:

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad \text{where } k = k'[H_2O]$$

Here $[R]_0 = 0.6$ mol/L.

When t = 30 s, [R] = 0.3 mol/L

So, $k_1 = \frac{2.303}{30} \log \frac{0.6}{0.3} = 0.0231\ s^{-1}$

When t = 60 s, [R] = 0.15 mol/L

So, $k_2 = \frac{2.303}{60} \log \frac{0.6}{0.15} = \mathbf{0.0231\ s^{-1}}$

Since $k_1 = k_2$, it is a pseudo first order reaction.

26. The Arrhenius equation is: $k = A\, e^{-Ea/RT}$.

Where k is the rate constant, A is the Arrhenius parameter, R is the universal gas constant, Ea is activation energy and T is the absolute temperature.

27. $\log \frac{k_2}{k_1} = \frac{Ea}{2.303R} \frac{[T_2 - T_1]}{T_1.T_2}$

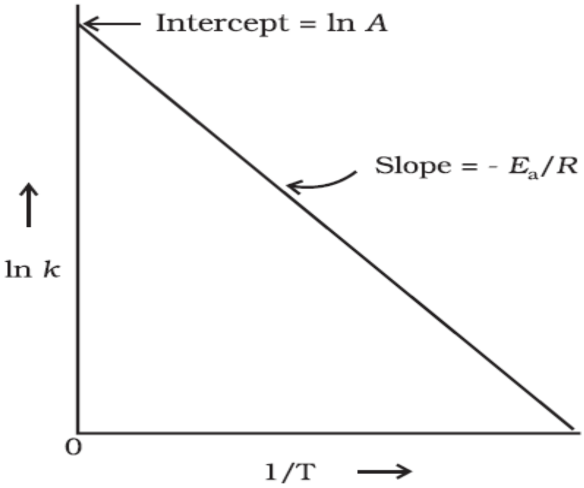
28. We know that, $\log k_2/k_1 = \frac{Ea}{2.303\ R} \frac{[T_2 - T_1]}{T_1.T_2}$

Here $T_1 = 293$ K, $k_1 = x$, $T_2 = 313$ K, $k_2 = 4x$ and $R = 8.314\ J\ K^{-1}\ mol^{-1}$

$$\log \frac{4x}{x} = \frac{Ea}{2.303 \times 8.314} \frac{[313 - 293]}{293 \times 313}$$

So, $Ea = \frac{(2.303 \times 8.314 \times 293 \times 313 \times \log 4)}{20}$ = **52854 J/mol = 52.854 kJ/mol**

29.



30. Most probable kinetic energy

31. A catalyst increases the rate of a chemical reaction by providing an alternate pathway by reducing the activation energy of the reaction.

32. The characteristics of a catalyst are:

a. A small amount of the catalyst can catalyse a large amount of reactants.

b. A catalyst does not change Gibbs energy of a reaction ($\Delta_r G$). It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

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Unit. 5
SURFACE CHEMISTRY

Focus area

5.1 Adsorption
5.2 Catalysis
5.4 Classification of colloids
5.5 Emulsions

Adsorption

Adsorption is the phenomenon of accumulation of molecular species on the surface of a solid or liquid than in the bulk

Eg. (i) Gases like O_2,H_2 ,NH_3 ,SO_2 etc are get adsorbed on the surface of charcoal

(ii)Aqueous solution of raw sugar can be de colourised by adsorbing the colouring substances by charcoal

(iii) Air becomes dry in the presence of silica gel because water gets adsorbed by silica gel.

(iv)A solution of organic dye such as methylene blue can be decolourised by adding charcoal.This is because methylene blue get adsorbed on the surface of charcoal

Types of Adsorption

Depending upon the nature of forces existing between adsorbate and adsorbent ,the adsorption can be classified into two types

(i) Physical adsorption (Physisorption)
(ii) Chemical adsorption (Chemisorption)

Physical Adsorption	Chemical Adsorption
1.The force of attraction between adsorbate molecules and adsorbent are weak vander waals forces	**1.The force of attraction between adsorbate molecules and adsorbent are strong chemical bond**
2.Enthalpy of adsorption is of the order of 20-40 KJ/mol	**2.Enthalpy of adsorption is of the order of 80-240 KJ/mol**
3.No surface compounds are formed	**3.Surface compounds are formed**
4.It is reversible	**4.It is irreversible**
5.It form multi-molecular layer	**5.It form mono-molecular layer**
6.It is not specific in nature	**10.It is highly specific in nature**

Adsorption of Gases on Solids

Effect of pressure(Adsorption isotherm)

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm

Freundlich Adsorption Isotherm

Freundlich gave the relation between the quantity of gas adsorbed by unit mass of a adsorbent and pressure at particular temperature. The relation is,

$$\boxed{x/m = KP^{1/n}}$$

Where 'x' is the mass of the gas adsorbed on mass 'm' of the adsorbent at a pressure 'P'.'K' and 'n' are constants which depend on the nature of the adsorbent and the gas at a particular temperature

Q.1 What is adsorption ? Give one example .

Q.2.Write any two differences of physisorption and chemisorption.

Q.3 (a)What is adsorption isotherm?

(b)Give the mathematical expression for Freundlich adsorption isotherm

CATALYSIS

Catalytic promoters and poisons

Certain external substances which enhance the activity of a catalyst are called catalytic promoters.

Eg:Mo is used as a promoter along with Fe catalyst in Haber process

$$N_2 + 3H_2 \xrightarrow[Mo(s)]{Fe(s)} 2NH_3(g)$$

Certain external substances which decrease the activity of a catalyst are called catalytic poisons

Eg:In the manufacture of H_2SO_4 by contact process, presence of a very minute quantity of arsenic is almost completely destroying the activity of platinum catalyst.

Types of Catalysis

(i) Homogenous catalysis

A catalytic process in which the reactant and catalyst are in the same phase is known as homogenous catalysis

Eg 1.In the Lead-chamber process SO_2 is oxidise to SO_3 in the presence of NO

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(ii) Heterogenous catalysis

A catalytic process in which the reactant and catalyst are in different phases is known as heterogenous catalysis

Eg (1) Manufacture of NH_3 from N_2& H_2 using Fe as catalyst

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_3(g)$$

Nature of solid Catalyst

The two important aspects of the solid catalyst are activity and selectivity

(i)Activity:-

The ability of a catalyst to increase the rate of reaction is called activity.

(ii) Selectivity

The ability of a catalyst to direct a particular reaction to yield a particular product is called selectivity.

ENZYMES

Enzymes are biological catalyst produced by living cells which catalyse biochemical reaction in living organism

Characteristics of Enzymes

(i)Enzyme catalyst increases the speed of reaction by many times as compared to the uncatalysed reaction

(ii) A small quantity of enzyme catalyst can increase the rate of reaction by a factor of 10^3 to 10^6

(iii)The enzyme catalyst are highly specific in nature ie,each enzyme catalyses only one type of chemical reaction

(iv)They are active at moderate temperature called optimum temperature (37^0C) and p^H around 7(5-7)

(v) The activity of enzyme is controlled by various mechanism and are inhibited by various organic and inorganic molecules

Q.4.Write any two characteristics of enzyme catalyst

Q.5.What do you mean by homogeneous catalysis? Write any one example for heterogeneous catalysis

Q6.Classify the following into homogenous and heterogenous catalysis

(i)$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_3(g)$

(ii)$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

Q7.What do you mean by activity and selectivity of catalysts?

COLLOIDS

Colloidal solutions are intermediate between true solutions and suspension. The diameter of colloidal particles is between 1nm and 1000nm(10^{-9}m to 10^{-6}m).

A colloidal solution is made up of two phase -dispersed phase and dispersion medium

Classification based on nature of interaction between dispersed phase and dispersion medium

1.Lyophilic sols (Lyophilic colloids)

Eg : Sols of gum ,gelatine, starch ,proteins and certain polymers in organic solvents

2.Lyophobic sols (Lyophobic colloids)

Eg.Sols of metals and their insoluble compounds like sulphides.

Lyophilic colloids	Lyophobic colloids
1.These are reversible in nature	1.These are irreversible in nature
2.They are quite stable and not easily precipitated by the addition of electrolyte.	2.They are less stable and readily precipitated on the addition of small amount of electrolytes,by heating or by shaking.
3.These are obtained by direct mixing	3.These sol can be prepared by only by special methods
4.They are self stabilised	4.They need stabilising agents for their preservation

Depending upon the nature of dispersed phase particles ,the colloidal solutions are classified as

1.Multimolecular colloids :- When a large number atoms or small molecules of a substance having size less than 1nm aggregate together in dispersion medium to form species having size in the colloidal range

Eg : Gold sol ,Suphur sol

2.Macromolecular colloids

When certain substances having big size molecules (macromolecules) are dispersed in a suitable solvent form a solution in which the size of the dispersed particles are in the colloidal range.Such colloids thus formed are called macromolecular colloids

Eg Starch ,cellulose,proteins ,plastics etc

3.Associated colloids

The substances which behaves as a normal electrolyte at lower concentration but exhibit colloidal properties at higher concentration due to the formation of aggregated particle called associated colloids The aggregated particle thus formed are called micelles .

The formation of micelles takes place only above a particular temperature called kraft temperature (Tk) and above particular concentration called critical micelle concentration(CMC)

Preparation of Lyophobic colloids

Electrical dispersion (Bredig's arc method)

Colloidal solution of metals such as gold,silver ,Pt etc can be prepared by this method

The metal whose sol is to be prepared is made as two electrodes immersed in dispersion medium such as water. The dispersion medium is cooled by surrounding it with a freezing mixture. An electric arc is struck between the two electrodes .The heat generated by the arc vaporise the metal which are condensed immediately to give colloidal solution

Peptization

The process of converting a freshly prepared precipitate into colloidal form by the addition of suitable electrolyte is called peptization

1.Charge on Colloidal particle

The combination of the two layers of opposite charges around the colloidal particle is called Helmholtz electrical double layer

The potential difference between the fixed layer and the diffused layer of opposite charge is called zeta potential or Electrokinetic potential

2.Brownian movement

The continuous rapid zig zag movement of colloidal particles in the dispersion medium is called Brownian movement

This phenomenon was discovered by Robert Brown

3.Tyndall Effect

The phenomenon of scattering of light by colloidal particles is known as Tyndall effect.

The bright cone of the light is called Tyndall cone

Condition for Tyndall Effect

1.Diameter of the dispersed particles should not be much smaller than the wavelength of light used

2.The refractive indices of the dispersed phase and dispersion medium should differ greatly in magnitude

Coagulation or precipitation of colloids

The process of setting of colloidal particles is called coagulation or precipitation of the sol

Hardy Shulz Rule

Different electrolytes have different coagulation value.The coagulation power of various electrolyte was studied by Hardy and Shulz. According to this rule

(i) The ions carrying the charge opposite to that of sol particles are effective in causing the coagulation of the sol

(ii)Greater the valence of the flocculating ion added,the greater is its coagulating power.

Protection of colloids

When a lyophilic sol is added to the lyophobic sol,the lyophilic particles form a layer around lyophobic particle and thus protect the lyophobic sol from precipitation by electrolyte

Q.8 (a) Which of the following is lyophobic colloid?

(i) Starch in water (ii) Gum in water (iii) Soap in water (iv) Gold sol

(b) Write any two differences between between lyophilic sols and lyophobic sols

Q.9.(a)Arrange the following electrolytes in the increasing order of coagulating power for the coagulation of As_2S_3 sol, $BaCl_2$, NaCl , $Al(OH)_3$

(b) Name and state the rule which deals with the coagulation of colloids

Q.10.(a)Which of the following is an example for macromolecular colloidal system?

(I) starch in water (ii) gold in water (iii)ferric hydroxide in water(iv) soap in water

(b)Associated colloids are also known as micelles. How are they formed ?

(c)Name the concentration above which the formation of micelle takes place

Q.11. What is the difference between multimolecular and macromolecular colloids.Give one example of each.

Q.12. What is peptization?

Q.13.(a)Which of the following is lyophilic colloids

(i)Starch in water (ii) Gold sol (iii) Ferric hydroxide sol (iv) As_2S_3 sol

(b)Explain the terms electrophoresis and coagulation

Q.14.(a)Which is Tyndall effect ?

(b)What are the conditions to be satisfied to exhibit Tyndall effect?

(c)What is a protective colloids?

Emulsions

Emulsions are colloidal solutions in which the dispersed phase as well as dispersion medium are liquids

There are two types of emulsions

(i) Oil in water type (O/W)

In this type oil is the dispersed phase and water is the dispersion medium

Eg :- Milk,Vanishing cream

(ii)Water in oil type (W/O)

In this type water is the dispersed phase and oil is the dispersion medium .

Eg:- Butter,Cream

Emulsions may be obtained by shaking both the liquids.

Emulsions of oil in water are unstable and sometimes they separate into two layers on standing.For stabilisation of an emulsion ,a third component called emulsifying agent is usually added.The emulsifying agent forms an interfacial film between suspended particles and the medium.

The emuslifying agents for O/W emulsions are proteins,gums ,natural and synthetic soaps etc and for W/O heavy metal salts of fatty acids ,lamp black, long chain alcohols etc.

Q.15.Explain the different types of emulsions and give example for each.

Q.16.How do emulsifiers stabilise emulsions ? Name two emulsifiers.

Answers

1.(a)The variation in the amount of gas adsorbed by adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm

(b) $x/m = KP^{1/n}$

2.

Physical Adsorption	Chemical Adsorption
1.It arises because of van der Waal's forces	1.It is caused by chemical bond formation
2.Enthalpy of adsorption is of the order of 20-40 KJ/mol	2.Enthalpy of adsorption is of the order of 80-240 KJ/mol
3.No surface compounds are formed	3.Surface compounds are formed
4.t is reversible	4.It is irreversible
5.It does not require activation energy	5. It require activation energy. High activation energy is sometimes needed
6.It result into multi-molecular layer on adsorbent surface under high pressure	6.It is not specific in nature

3.Adsorption is the phenomenon of accumulation of molecular species on the surface of a solid or liquid than in the bulk

Eg:- Gases like O_2,H_2,CO,Cl_2,NH_3 ,SO_2 etc are get adsorbed on the surface of charcoal

4.**Characteristics of Enzymes**

(i)Enzyme catalyst increases the speed of reaction by many times as compared to the uncatalysed reaction

(ii)Enzyme activity is highly efficient ie,one molecule of an enzyme may transform one million molecules of the reactant per minute.

(iii)The enzyme catalyst are highly specific in nature ie,each enzyme catalyses only one type of chemical reaction

(iv) The activity of enzyme is increased in the presence of certain substances ,known as co-enzyme

(v)Enzyme activity is inhibited or poisoned by the presence certain substances

5.A catalytic process in which the reactant and catalyst are in the same phase is known as homogenous catalysis

Eg (1) Manufacture of NH_3 from N_2& H_2 using Fe as catalyst

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_3(g)$$

6. Heterogenous catalysis $N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_3(g)$

Homogenous catalysis $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

7.Activity :- The ability of a catalyst to increase the rate of reaction is called activity

Selectivity:-The ability of a catalyst to direct a reaction to yield a particular product is called selectivity

8. (a) Gold sol

(b)

Lyophilic colloids	Lyophobic colliods
1.These are reversible in nature	1.These are irreversible in nature
2.They are quite stable and not easily precipitated by the addition of electrolyte.	2.They are less stable and readily precipitated on the addition of small amount of electrolytes,by heating or by shaking.
3.These are obtained by direct mixing	3.These sol can be prepared by only by special methods
4.They are self stabilised	4.They need stabilising agents for their preservation

9. (a)$NaCl < BaCl_2 < Al(OH)_3$

(b) Hardy Schulz rule

It states that the greater the valence of the flocculating ion(coagulating ion) added ,the greater is its power to cause precipitation.

10. (a) Starch in water

(b)The substance which behaves as normal electrolyte at lower concentration but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called associated colloids .The aggregated particles thus formed are called micelles

(c) Critical micelle concentration (CMC)

11. Multimolecular colloids :- When a large number atoms or small molecules of a substance having size less than 1nm aggregate together in dispersion medium to form species having size in the colloidal range

Eg : Gold sol ,Sol of sulphur

When certain substances having big size molecules (macromolecules) are dispersed in a suitable solvent form a solution in which the size of the dispersed particles are in the colloidal range.Such colloids thus formed are called macromolecular colloids

Eg Starch ,cellulose,proteins ,plastics etc

12.The process of converting a freshly prepared precipitate into colloidal form by shaking it with dispersion medium in the presence of small amount of electrolyte is called peptization

13. (a) Starch in water

(b)The process of setting of colloidal particles is called coagulation or precipitation of the sol

The movement of colloidal particle towards oppositely charged electrode under the influence of electric field is called electrophoresis

14. (a) The phenomenon of scattering of light by colloidal particles is known as Tyndall effect.

Condition for Tyndall Effect

(b) 1. Diameter of the dispersed particles should not be much smaller than the wavelength of light used

2. The refractive indices of the dispersed phase and dispersion medium should differ greatly in magnitude

(c) When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particle and thus protect the lyophobic sol from precipitation by electrolyte

15. There are two types of emulsions

(i) Oil in water type (O/W)

In this type oil is the dispersed phase and water is the dispersion medium

Eg :- Milk,Vanishing cream
(ii) Water in oil type (W/O)

In this type water is the dispersed phase and oil is the dispersion medium

e.g.; butter, milkcream

16.For stabilisation of an emulsion ,a third component called emulsifying agent is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium.

The emulsifying agents are proteins,gums ,natural and synthetic soaps ,heavy metal salts of fatty acids ,lamp black, long chain alcohols etc.

SAMAGRA SIKSHA KERALA Class 12 CHEMISTRY

Unit.6

General Principles and Isolation of Element

Focus area

6.2 Concentration of ores
6.3 Extraction of crude metal from concentrated ore
6.4.1 Ellingham diagram - extraction of Iron
6.5 Hall Heroult process (extraction of Al)
6.7 Refining

6.2 Concentration of Ores

Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as concentration, dressing or benefaction. The earthy impurities present in the ore is called Gangue. Depending on the nature of the impurities, any one of the following methods can be used to remove the gangue from the ore.

6.2.1 Hydraulic Washing

In this method the powdered ore is washed in a stream of water. The lighter gangue particles are washed away leaving behind the ore.

Qn 1: Give the principle behind the concentration of ores using hydraulic washing.

Qn 2: Give examples of ores concentrated by hydraulic washing.

6.2.2 Magnetic Separation

This method is used when either the ore or the gangue is magnetic. The powdered ore is carried on a conveyor belt which passes over a magnetic roller. The magnetic materials are collected near the magnetic roller but the non-magnetic materials are dumped away from the roller.

Qn 3: Which type of ores are concentrated by Magnetic separation?

6.2.3 Froth floatation

This method is used for the concentration of the sulphide ores. In this process, a suspension of the powdered ore is made with water, collectors (e.g. pine oil, fatty acid, xanthates etc.) and froth stabilizers (e.g. cresols, aniline etc.) are added. The mineral particles become wet by oils while the gangue particles by water. On Agitating the mixture by passing air, froth is formed which carries the mineral particles. The froth is skimmed off and dried to get the ore particles. This method can be used to separate two sulphide ores by using depressants. For e.g. in the case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

Qn 4: Give the principle behind the concentration of ores using Froth floatation method.

Qn 5: identify the role of Collectors and Depressants in the forth floatation method?

6.2.4 Leaching

This method ore is dissolved in some suitable solvent but not the impurities. The impurities left undissolved are removed by filtration and the ore is recovered by proper chemical method.

e.g. **Purification of Bauxite(Baeyer's process):**

Here the powdered ore is treated with a concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. Alumina (Al_2O_3) dissolves in NaOH to form sodium aluminate leaving behind the impurities.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. The solution is seeded with freshly prepared hydrated Al_2O_3 which induces the precipitation.

$$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3 . xH_2O(s) + 2NaHCO_3(aq)$$

The hydrated alumina is filtered, dried and heated to give back pure alumina (Al_2O_3).

Qn 6: What is the significance of leaching in the extraction of aluminium?

Qn 7: Explain the leaching of gold?

Qn 8: Mach the following:

A	B
(a) ZnS	(a) Collectors
(b) Fe_3O_4	(b) Leaching
(c) Al2O3	(c) Froth floatation
(d) NaCN	(d) Magnetic separation
(e) Xanthates	(e) depressants

Qn 8(a) Complete the table

Name of the ore	Concentration method
1. Tin stone	
2. Cu_2S	
3. Al_2O_3	
4. Fe_3O_4	
5. ZnS	

6 . 3 Extraction of Crude Metal from Concentrated Ore

The concentrated ore must be converted into more easily reducible form because metal extraction process are reduction process. So the metal extraction involves two steps

(a) conversion to oxide, and (b) reduction of the oxide to metal.

(a) conversion to oxide : involves two steps

(I) **Calcination:** In this process, ores are heated in the absence or limited supply of air.

It is used for the conversion of hydroxide and carbonate ores to oxide ore.

$$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3\ (s) + xH_2O(g)$$

$$ZnCO_3\ (s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s\ ) + 2CO_2(g)$$

(II) Roasting: In this process, ores are heated in the presence of air below the melting point of the metal. This method is used for the conversion of sulphide ores to oxide ore.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

Qn 9: Differentiate calcination and Roasting

Qn 10: Give two examples each for calcination and roasting

(b) reduction of the oxide to metal.

It involves heating the metal oxide with suitable reducing agents like C, CO or another metal. The reducing agent combines with the oxygen of the metal oxide.

$$M_xO_y + yC \rightarrow xM + y\,CO$$

6.4.1 Applications (a) Extraction of iron from its oxides

Ellingham Diagram

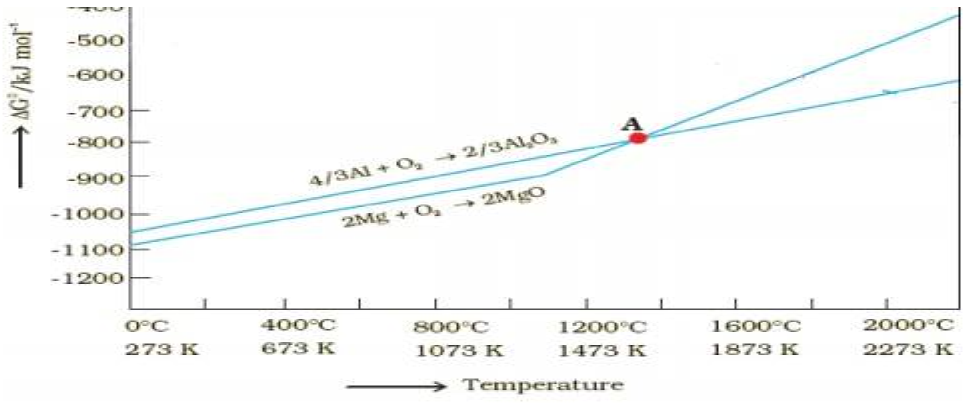
The graphical representation of Gibbs energy vs Temperature was first given by H.J.T.Ellingham and these graphs are known as Ellingham Diagram. It helps to select the reducing agent in the reduction of oxides. These diagrams help us in predicting the feasibility of thermal reduction of an ore. Here we couple two reactions – oxidation of the reducing agent and reduction of the metal oxide. If the total ΔG for the coupled reaction is negative, the overall reaction will be feasible.

Ellingham diagram normally consists of plots of ΔG^0 vs T for the formation of oxides of elements i.e., for the reaction,

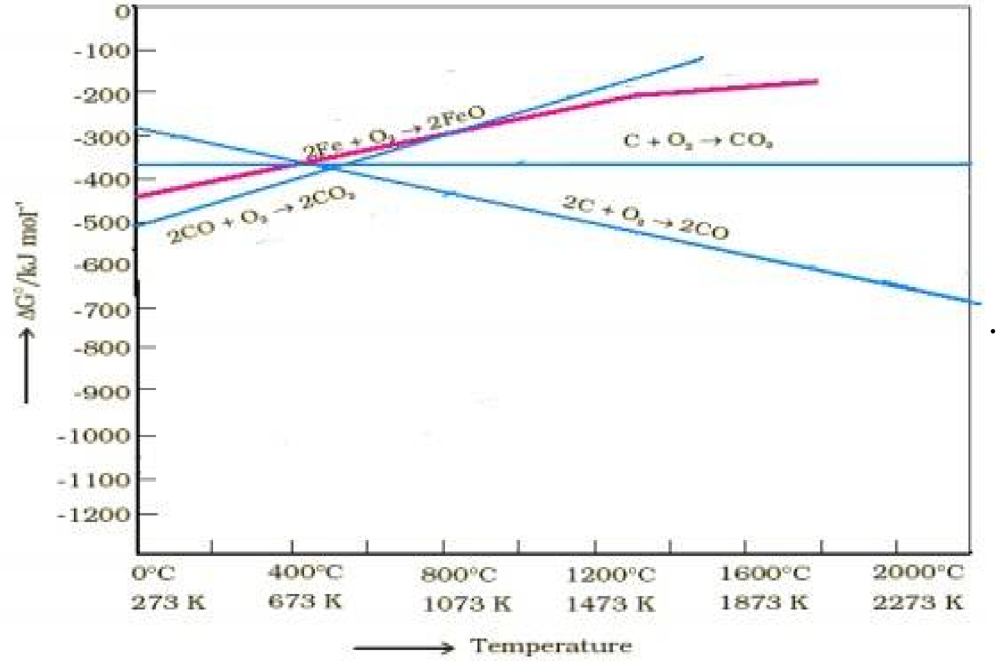
$$2xM(s) + O_2(g) \rightarrow 2M_xO(s)$$

In Ellingham diagram, there is a point (temperature) at which the ΔG values for the two reactions (oxidation & reduction) are equal. The difference in the ΔG values after that point determines whether the reduction process is feasible or not. If the difference is large negative, the reduction of the oxide of the upper line is feasible by the element represented by the lower line.

Qn 11: From the Ellinghams diagram given below, say whether Al can reduce MgO to Mg at 2273K?



Qn 12: On the basis of the Ellingham diagram given below, predict the best reducing agent among C and CO for the reduction of FeO to Fe at (i) 673K and (ii) 1073K.



Iron from Iron oxide:

a) Removal of chemical impurity: * Silica (SiO_2) is a chemical impurity which is acidic in nature present along with the ore. * A basic flux like calcium oxide (CaO) is added to remove Silica. * CaO is obtained from the Lime stone ($CaCO_3$) which decomposes to CaO and CO_2 in the furnace due to intense heat.

$CaCO_3$ (s) -------→ CaO (s) + CO_2 (g).

*The impurity SiO_2, combines with CaO to form calcium silicate ($CaSiO_3$) called Slag.

CaO (s) + SiO_2 (s) --------→ $CaSiO_3$.

b) Extraction of Iron: * The pure Haematite ore, Ferric oxide (Fe_2O_3) is reduced to iron in presence of a reducing agent Coke (carbon). * Coke (C) combines with CO_2 to form carbon monoxide which is a very good reducing agent which reduces Fe^2O^3 in to Iron (Fe).

C (Coke) + CO_2 (g) -------→ 2CO (g) ;

Fe_2O_3 (s) + 3 CO (g) -------→ 2Fe (molten) + 3 CO_2 (g)

* The slag calcium silicate ($CaSiO_3$), is lighter than molten Iron which floats over the molten iron nd also which also prevents the molten Iron to oxidise in presence of oxygen in the furnace.

* The slag and the molten Iron are collected separately as shown in the figure.

*The slag is in molten state and separates out from iron. The iron obtained from blast furnace is called pig iron. * When pig iron is melted with scrap iron and coke in presence of hot air blast, cast iron is formed. * Wrought iron or malleable iron is the purest form of commercial iron. It is prepared from cast iron by oxidizing impurities in a reverberatory furnace lined with haematite.

Qn 13: What is the role of limestone ($CaCO_3$) in the extraction of iron?

Qn 14: Which is the purest form of iron and what are its uses?

Qn 15: How is cast iron different from pig iron?

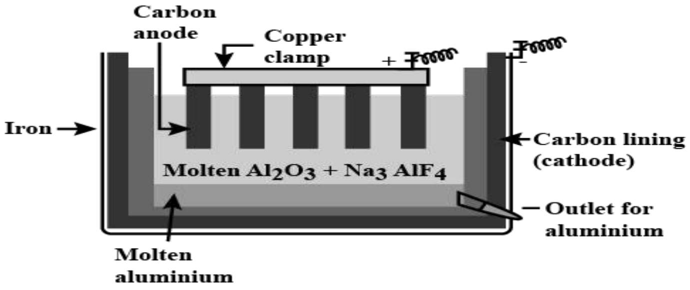
6.5.1 Hall-Heroult process

Aluminium is extracted by Hall-Heroult process. Here the purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (to lower the melting point and to increase the conductivity) and is electrolysed.

Cathode: Carbon lined steel vessel. Anode: Graphite rods.

During electrolysis Al_2O_3 is reduced to Al by carbon. $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 .



The electrolytic reactions are:

Cathode: $Al^{3+}_{(melt)} + 3e^- \rightarrow Al_{(l)}$

Anode: $C_{(s)} + O^{2-}_{(melt)} \rightarrow CO_{(g)} + 2e^-$

$C_{(s)} + 2O^{2-}$ (melt) $\rightarrow CO_{2\,(g)} + 4e^-$

Qn 16: In the extraction of aluminium graphite rods are continuously replaced. Give reason?

Qn 17: Give the equations showing the reactions involved in the extraction of Aluminium by Hall-Heroult process.

6.7 Refining :A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

a) Distillation **b) Liquation** **c) Electrolysis** **d) Zone refining**
e) Vapour phase refining **f) Chromatographic methods**

(a) Distillation: This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate. **(b) Liquation:** In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities. **(c) Electrolytic refining:** In this method, ***The impure metal is made to act as anode. *A strip of the same metal in pure form is used as cathode. *They are put in a suitable electrolytic bath containing soluble salt of the same metal *The more basic metal remains in the solution and the less basic ones go to the anode mud. .*** *The reactions are:

$$\text{Anode: } M \rightarrow M^{n+} + ne^- \qquad \text{Cathode: } M^{n+} + ne^- \rightarrow M$$

(d) Zone refining: This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. Here the metal rod is heated with a circular mobile heater from one end to the other. The process is repeated several times so that the impurities get concentrated in one end. This end is cut off. This method is very useful for the preparation of extra pure germanium, silicon,boron, gallium and indium which are used as semiconductors.

(e) Vapour phase refining : In this method, the metal is converted into its volatile compound. It is then decomposed to give pure metal.

1) Mond Process for Refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.

$$\mathbf{Ni + 4CO \text{ ---- > } Ni(CO)_4 \text{ at } 330 - 350\ K.}$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal

$$Ni(CO)_4 \longrightarrow Ni + 4CO \text{ at } 450 – 470 \text{ K.}$$

2) van Arkel Method for Refining Zirconium or Titanium: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilizes. $Zr + 2I_2 \longrightarrow ZrI_4$ **.** The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament. $ZrI_4 \longrightarrow Zr + 2I_2$

(f) Chromatographic methods:

Principle: This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

Method: The mixture is put in a liquid medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed by using suitable solvents.

Qn18: Explain van Arkel Method and its use ?

Qn19 : Give the principle underlying the process used for refining of gallium.

Qn 20 : Which type of metals can be purified by distillation ?

Qn 21: State the basis of refining a substance by chromatographic method. Under what circumstances is this method specially useful?

Qn 22: What is vapour phase refining? What are the necessary requirements for the compound to be purified by vapour phase refining?

Qn 23: Explain the refining of copper?

ANSWERS

Qn 1: This method is based on the difference in the densities of ores and gangue.

Qn 2: Oxide ores such as haematite, tin stones and native ores of Au, Ag etc.

Qn 3: This method of concentration is employed when either the ore or the impurities associated with it are magnetic in nature. e.g. in the case of iron ores.

Qn 4: This method is based on the preferential wetting of ore particles by oil and that of gangue by wate

Qn 5: Collectors increases the non-wettability of ore particles by water, e.g.,pine oils, xanthates and fatty acids. Depressants are used to prevent certain type of particles from forming the forth with air bubbles, e.g. NaCN can be used as a depressant in the separation of ZnS and PbS ores. KCN is an another depressant.

Qn 6: In this process the powdered ore is treated with a concentrated solution of NaOH at 473 – 523 K and 35 – 36bar pressure. Alumina (Al_2O_3) dissolves in NaOH to form sodium aluminate leaving behind the impurities.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. The solution is seeded with freshly prepared hydrated Al_2O_3 which induces the precipitation.

$$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq)$$

The hydrated alumina is filtered, dried and heated to give back pure alumina(Al_2O_3).

Qn 7: In the metallurgy of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement using Zn:

$$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

$$2[Au(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

Qn 8 : (a)-c , (b)-d, (c)-b, (d)- e, (d)- a

Qn 8(a):

Name of the ore	Concentration method
1. Tin stone	Hydraulic washing
2. Cu_2S	Froth floatation
3. Al_2O_3	Leaching

4. Fe_3O_4	Magnetic Separation
5. ZnS	Froth floatation

Qn 9: (I) **Calcination:** In this process, ores are heated in the absence or limited supply of air. t is used for the conversion of hydroxide and carbonate ores to oxide ore.

(II) Roasting: In this process, ores are heated in the presence of air below the melting point of the metal. This method is used for the conversion of sulphide ores to oxide ore.

Qn 10: Calcination :

$$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3\ (s) + xH_2O(g)$$
$$ZnCO_3\ (s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$
$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s\ ) + 2CO_2(g)$$

Roasting :

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

Qn 11: Calculation of ΔG value for the reduction of Mg O using Al at 2273K

$2MgO \rightarrow 2Mg + O_2$, $\Delta G = 600kJ/mol$ ---------- (1) (Reduction ΔG is +ve)
$4/3\ Al + O_2 \rightarrow 2/3\ Al_2O_3$, $\Delta G = -700kJ/mol$. -------- (2)
Coupling of above reactions, ie (1) + (2),
$2\ MgO + 4/3\ Al + O_2 \rightarrow 2Mg + O_2 + 2/3\ Al_2O_3$, $\Delta G =600 + (-700)$
$2\ MgO + 4/3\ Al \rightarrow 2Mg + 2/3\ Al_2O_3$, $\Delta G = -100kJ/\ mol.$
Al can acts as a reducing agent for reducing MgO to Mg at 2273K, because

$\Delta G < 0$ or

At 2273K, the graph of Al to Al_2O_3 lie below to the graph of Mg to MgO. So Al can easily reduce MgO to Mg.

Qn 12: (*i)* Calculation of ΔG value for the reduction of FeO using Carbon / CO at 673K

$2FeO \rightarrow 2Fe + O_2$, $\Delta G = 400 KJ/mol$ --------(1) (Reduction ΔG is +ve)
$C + O_2 \rightarrow CO_2$, $\Delta G = -380 KJ/mol$. -------- (2)
$2CO + O_2 \rightarrow 2CO_2$, $\Delta G = -420 KJ/mol$ --------- (3)
(Coupling of above reactions (1)+(2)), $\Delta G = 400 - 380 = 20 kJ/mol$
(Coupling of above reactions (1)+(3)), $\Delta G = 400 - 420 = -20 kJ/mol$

From the above, we can concluded that carbon monoxide acts as a reducing agent for reducing FeO to Fe, at 673K because $\Delta G < 0$.

(ii) Calculation of ΔG value for the reduction of FeO using Carbon / CO at 1073K
$2FeO \rightarrow 2Fe + O_2$, $\Delta G = 320 kJ/mol$ ---------- (1) (Reduction ΔG is +ve)
$C + O_2 \rightarrow CO_2$, $\Delta G = -380 kJ/mol$. -------- (2)
$2CO + O_2 \rightarrow 2CO_2$, $\Delta G = -330 kJ/mol$ --------- (3)
(Coupling of above reactions (1)+(2)), $\Delta G = 320 - 380 = -60 kJ/mol$
(Coupling of above reactions(1)+(3)), $\Delta G = 320 - 330 = -10 kJ/mol$

From the above, we can infer that carbon monoxide as well as Carbon acts as a reducing agent for reducing FeO to Fe, at 1073K because $\Delta G < 0$

Qn 13: CaO is obtained from the Lime stone ($CaCO_3$) which decomposes to CaO and CO_2 in the furnace due to intense heat. $CaCO_3 (s) \text{-------}\rightarrow CaO (s) + CO_2 (g)$. The impurity SiO_2, combines with CaO to form calcium silicate ($CaSiO_3$) called Slag.

$CaO (s) + SiO_2 (s) \text{--------}\rightarrow CaSiO_3$.

Qn 14 : The purest form of iron is wrought iron and is used in making anchors, wires, bolts etc.

Qn 15 : Pig iron has 4% carbon and can be easily cast into variety of shapes. Whereas cast iron has lower carbon content and is extremely hard and brittle.

Qn 16 : In the extraction of aluminium graphite rods act as anodes in the electrolytic cell of reduction and are the site for release of oxygen. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away.

Qn 17: The electrolytic reactions are: Cathode: $Al^{3+}_{(melt)} + 3e^- \rightarrow Al_{(l)}$

Anode: $C_{(s)} + O^{2-}_{(melt)} \rightarrow CO_{(g)} + 2e^-$;

$C_{(s)} + 2O^{2-}_{(melt)} \rightarrow CO_{2(g)} + 4e^-$

During electrolysis Al_2O_3 is reduced to Al by carbon.

$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 .

Qn 18 : This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilizes. $\mathbf{Zr + 2I_2 \dashrightarrow ZrI_4}$ **.** The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament. $\mathbf{ZrI_4 \rightarrow Zr + 2I_2}$

Qn 19 : The process used for the refining of gallium is zone refining and the principle underlying it is that the impurities are more soluble in the melt than in the solid state of the metal.

Qn 20: Distillation is used for the metals with boiling point lower then the impurities. So metals can be evaporated and separately obtained as distillate.

Qn 21: This method is based on difference in extent of adsorption of different components of a mixture on an adsorbent. The mixture is put in a liquid which is moved through the adsorbent, different components are adsorbed at different levels in the column. Later the adsorbed components are removed by using suitable solvents. Column chromatography is useful for purification of elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

Qn 22: Vapour phase refining, the metal is converted into volatile compound and collected. Then it is decomposed separately to obtain pure metal. Two necessary requirements for a compound to be purified by vapour phase refining are:-

(i) The metal should form a volatile compound with a common reagent.
(ii)The compound should be easily decomposable.

Qn 23 : Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode.

Anode: $Cu \dashrightarrow Cu^{2+} + 2e^-$; Cathode: $Cu^{2+} + 2e^- \dashrightarrow Cu$. Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum.

SAMAGRA SIKSHA KERALA Class 1 2 CHEMISTRY

Unit. 7

The p- Block Elements

Focus area

- Ammonia
- Nitric acid
- Phosphorus halides
- Sulphuric acid
- Inter halogen compounds
- Group 18 elements- Xenon halides

Prerequisites

- Properties of group 15 elements
- Properties of group 16 elements

click the link https://www.youtube.com/watch?v=0ocNAwTuXWQ

Ammonia

click the link https://www.youtube.com/watch?v=_JnxMSj7vT8

- Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.
- On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or calcium hydroxide
- On a large scale, ammonia is manufactured by Haber's process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta_f H^\ominus = -46.1 \text{ kJ mol}^{-1}$$

Q1. Fill up the blanks in the following reactions

(i) $2NH_4Cl + Ca(OH)_2 \rightarrow$ --------- + --------- + $CaCl_2$

(ii) $(NH_4)_2SO_4 + 2NaOH \rightarrow$ ------- + $2H_2O$ + ------------

Q2.Analyse the following statements and write whether **True or False**

(i) Ammonia is used to produce various nitrogenous fertilisers
(ii) Liquid ammonia is used as a refrigerant
(iii) ammonia molecule is trigonal pyramidal in structure
(iv) Ammonia gas is insoluble in water

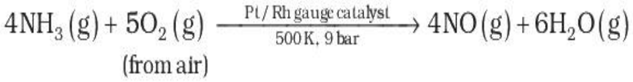
Q3. Mention the conditions required to maximise the yield of ammonia.

Q4. Why does NH_3 act as a Lewis base ?

Nitric Acid

On a large scale nitric acid is prepared mainly by Ostwald's process.

- catalytic oxidation of NH_3 by atmospheric oxygen.



$$\underset{\text{(from air)}}{4NH_3(g) + 5O_2(g)} \xrightarrow[500K,\ 9\ bar]{Pt/Rh\ gauge\ catalyst} 4NO(g) + 6H_2O(g)$$

- Nitric oxide thus formed combines with oxygen giving NO_2 .
  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
- Nitrogen dioxide so formed, dissolves in water to give HNO_3 .
  $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3\ (aq) + NO(g)$

Q5. Concentrated nitric acid is a strong oxidising agent and attacks most metals. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

(a) Fill up the blanks in the following reactions with suitable oxides of nitrogen

(i) $3Cu + 8\ HNO_3$ (dilute) $\rightarrow 3Cu(NO_3)_2 +$ .... $+ 4H_2O$

(ii) $Cu + 4HNO_3$ (conc.) $\rightarrow Cu(NO_3)_2 +$ .... $+ 2H_2O$

(iii) $4Zn + 10HNO_3$ (dilute) $\rightarrow 4\ Zn(NO_3)_2 + 5H_2O +$ ....

(iv) $Zn + 4HNO_3$(conc.) $\rightarrow Zn(NO_3)_2 + 2H_2O +$ ....

(b) Why metals like Cr, Al do not dissolve in concentrated nitric acid?

Q6. Identify **A,B and C** in the following steps of Ostwald process

$NH_3(g) + O_2(g) \rightarrow$ **A** $+ H_2O\ (g)$ (oxidation in presence of Pt)

A $+ O_2(g) \rightarrow$ **B**

B $+ H_2O(l) \rightarrow$ **C** $+ NO(g)$

Phosphorus halides

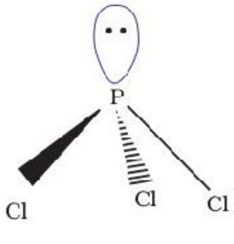
PhosphorusTrichloride

It is obtained by passing dry chlorine over heated white phosphorus.

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

It is also obtained by the action of thionyl chloride with white phosphorus.

$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$



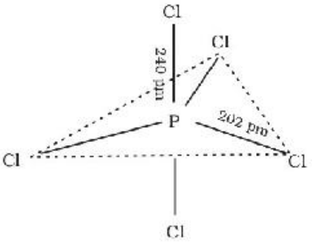
Phosphorus Pentachloride

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

It can also be prepared by the action of SO_2Cl_2 on phosphorus.

$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$



Q7. Analyse the following statements and write whether **True or False**

(i) PCl_3 has pyramidal shape in which phosphorus is sp^3 hybridised.

(ii) PCl_3 is a colourless oily liquid and hydrolyses in the presence of moisture.

(iii) PCl_5 reacts with organic compounds containing –OH group converting them to chloroderivatives.

(iv) PCl_5 has pyramidal shape in which phosphorus is sp^3 hybridised.

Q8. Give reason foe the following:

(i) PCl_3 fume in moisture

(ii) All the five bonds in PCl_5 molecule are not equivalent

Sulphuric Acid

Sulphuric acid is manufactured by the Contact Process which involves three steps:

(i) burning of sulphur or sulphide ores in air to generate SO_2 .

(ii) conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5).

(iii) absorption of SO_3 in H_2SO_4 to give Oleum ($H_2S_2O_7$).

Q9. Analyse the following statements and write whether **True or False**

(i) Concentrated sulphuric acid is a strong dehydrating agent

(ii) Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2

(iii) A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes.

(iv) Sulphuric acid has high volatility

Q10. What happens when

(i) Concentrated H_2SO_4 is added to calcium fluoride

(ii) SO_3 is passed through water?

Inter halogen compounds

- When two different halogens react with each other, inter halogen compounds are formed.
- They can be assigned general compositions as XX'_1, XX'_3, XX'_5 and XX'_7 where X is halogen of larger size and X of smaller size and X is more electropositive than X.
- The inter halogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds.

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\,K} 2ClF;$$

$$I_2 + \underset{\text{(excess)}}{3Cl_2} \rightarrow 2ICl_3$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\,K} 2ClF_3;$$

$$\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl;$$

$$Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

Q11. Match the following

	Type of Interhalogen compound		**Structure**
1	XX'_3	a	Pentagonal bipyramid
2	XX'_5	b	Bent T- shaped
3	XX'_7	c	Square pyramidal

Q12. Analyse the following statements and write whether **True or False**

(i) Interhalogen compounds are all covalent molecules and are diamagnetic in nature.

(ii) Interhalogen compounds undergo hydrolysis giving halide ion

(iii) Interhalogen compounds can be used as non aqueous solvents.

(iv) Interhalogen compounds are less reactive than halogens

Q13. Why is ICl more reactive than I_2?

Group 18 elements- Xenon halides

Xenon-fluorine compounds

Xenon forms three binary fluorides, XeF_2 , XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(xenon in excess)}}{Xe\ (g) + F_2\ (g)} \xrightarrow{673\text{ K, 1 bar}} XeF_2(s)$$

$$\underset{\text{(1:5 ratio)}}{Xe\ (g) + 2F_2\ (g)} \xrightarrow{873\text{ K, 7 bar}} XeF_4(s)$$

$$\underset{\text{(1:20 ratio)}}{Xe\ (g) + 3F_2\ (g)} \xrightarrow{573\text{ K, 60–70bar}} XeF_6(s)$$

Q14. Complete the table

Xenon halide	structure	No. of bond pairs	No. of lone pairs
XeF_2	-------(i)------------	-------(iii)--------	3
XeF_4	Square planar	------(iv)---------	----------(v)-----------
XeF_6	------(ii)-------------	6	----------(vi)-----------

SOLUTIONS TO THE p-BLOCK ELEMENTS

Q1.(i) $2NH_3$, $2H_2O$
(ii) $2NH_3$, Na_2SO_4

Q2.(i) True (ii) True (iii) True (iv) False

Q3.In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

Q4.Nitrogen atom in NH_3 has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

Q5.(a) (i) 2NO (ii) $2NO_2$ (iii) N_2O (iv) $2NO_2$
(b) because of the formation of a passive film of oxide on the surface.

Q6. **A** = NO(g) **B** = $2NO_2$(g) **C** = HNO_3 (aq)

Q7.(i) True (ii) True (iii) True (iv) False

Q8.(i) PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

(ii) PCl_5 has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

Q9.(i) True (ii) True (iii) True (iv) False

Q10.(i) CaF_2 forms hydrogen fluoride

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

(ii) It dissolves SO_3 to give H_2SO_4 .

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Q11.1-b, 2-c, 3-d
Q12.(i) True (ii) True (iii) True (iv) False
Q13.Because the bond in I-Cl is weaker than I–I bond

Q14.(i) linear (ii)distorted octahedral (iii) 2 (iv) 4(v)2 (vi)1

UNIT 8

The d-and f- Block Elements

Focus Area

8.3 Magnetic properties, formation coloured ions, formation complexes, catalytic property

8.4 Potassium permanganate and potassium dichromate

8.5.2 Atomic and ionic sizes

8.7 Some applications of d- and f-block elements

Elements from 3rd group to 12th group in the Modern Periodic table are called d-block elements. In these elements their last electron enters in the penultimate d-sub shell. They are placed in between s-block and p-block elements. They show a regular transition from the highly electropositive metals of s-block elements to the less electropositive p-block elements. So they are called transition elements.

8 . 3 General Properties of the Transition Elements (d-Block)

8.3.9 Magnetic Properties :

Transition metals show mainly two types of magnetic properties- paramagnetism and diamagnetism. Some transition metals also show ferromagnetism which is an extreme case of paramagnetism. Paramagnetism arises from the presence of unpaired electrons. For the compounds of 1 st row transition elements, it is calculated using only spin magnetic moment and it is determined by the spin only formula: $\mu_s = \sqrt{n(n+2)}$ where n is the no. of unpaired electrons and μ_s is the spin only magnetic moment in the unit of Bohr Magneton (B.M).

The magnetic moment increases with increase in no. of unpaired electrons. Thus the observed magnetic moment gives an idea about the no. of unpaired electrons present in the atom or ion.

Qn 1: In the first transition series magnetic moment increases from Sc to Cr then decreases . Give reason ?

Qn 2: Calculate the spin only magnetic moment and arrange the following ions in

the increasing order of there spin only magnetic moments?

Mn^{2+},Fe^{2+},Co^{2+},Ni^{2+}

8.3.10 Formation of Coloured

Most of the Transition metals ions or compounds are coloured. This is because of the presence of partially filled d orbitals and d-d transition is possible. In aqueous solution most of the Transition metal ions are coloured since water molecules act as the ligands. When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.

Qn 3 : Identify the colourless ion from the following pairs.

(a) Ti^{2+} and Ti^{4+} (b) Cu^{+} and Cu

8.3.11 Formation of Complex Compounds.

Transition metals form a large no. of complexes. This is due to:

1. Comparatively smaller size 2. High ionic charge

3. Presence of partially filled d orbitals 4. Ability to show variable oxidation state

Eg: $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $[Ni(CO)_4]$ etc.

Qn 4: Transition elements forms large number of complexes. Give reason?

8.3.12 Catalytic Properties.

Transition metals and their compounds act as catalysts in a large no. of chemical reactions. This is due to their large surface area and their ability to show variable oxidation state.

Qn 5: Transition metals and their compounds act as catalysts. Give reason?

8 . 4 Some Important Compounds of Transition Elements.

1. Potassium dichromate ($K_2Cr_2O_7$)

Potassium dichromate is generally prepared from chromite ore ($FeCr_2O_4$) by the following three steps.

1. Conversion of chromite ore to sodium chromate

Chromite ore is first fused with sodium carbonate in presence of air to form sodium chromate.

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

2. Acidification of sodium chromate to sodium dichromate

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodium dichromate.

$$2\ Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

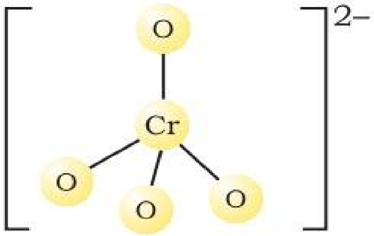
3. Conversion of sodium dichromate to potassium dichromate

The solution of sodium dichromate is treated with potassium chloride so that orange crystals of

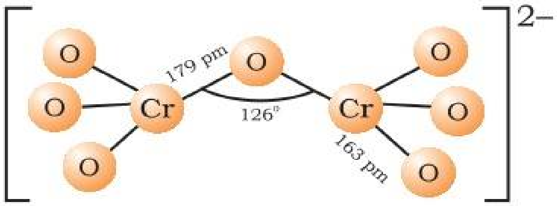
potassium dichromate crystallise out.

$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$

The structures of chromate ion, **CrO_4^{2-}** and the dichromate ion, **$Cr_2O_7^{2-}$** are shown below.



Chromate ion



Dichromate ion

oxidising Property

$K_2Cr_2O_7$ is a good oxidising agent in acidic medium. Its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Thus, acidified potassium dichromate will oxidise

1) Iodides to iodine

$$6\ I^- \rightarrow 3\ I_2 + 6$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$$

2) Iron(II) (ferrous) to iron(III) (ferric)

$$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Uses: It is used as a primary standard in volumetric analysis. It is also used as in leather industry and as an oxidant for the preparation of many azo compounds.

Qn 6: Explain the preparation of $K_2Cr_2O_7$?

Qn 7: Write the chemical equation showing the oxidising action of $K_2Cr_2O_7$?

Qn 8: Draw the structure chromate and dichromate ion?

2. Potassium permanganate ($KMnO_4$)

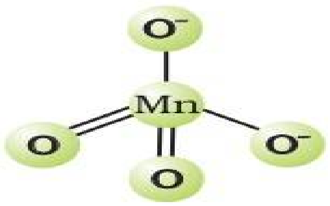
Potassium permanganate is commercially prepared from Pyrolusite (MnO_2). The preparation involves two steps. In the first step MnO_2 is fused with KOH to form potassium manganate (K_2MnO_4). Then K_2MnO_4 is electrolytically oxidised to potassium permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

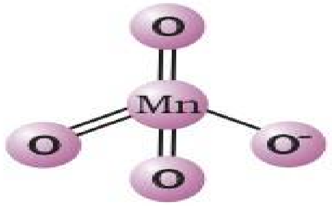
$$MnO_4^{2-} \xrightarrow[\text{In acidic medium}]{\text{electrolytic oxidation}} MnO_4^- + e^-$$

Structure of the manganate and permanganate ions are tetrahedral

The green manganate is



Tetrahedral manganate (green) ion



Tetrahedral permanganate (purple) ion

paramagnetic with one unpaired electron but the permanganate is diamagnetic.

Oxidising Property

$KMnO_4$ is a good oxidizing agent in acidic, basic and neutral media. The oxidizing action in acidic medium is due to the reaction:

$$\mathbf{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$$

Acidified permanganate solution oxidises: **1) Iron(II) to iron(III)**

$$\mathbf{5\,Fe^{2+} \rightarrow 5\,Fe^{3+} + 5e^-}$$

$$\mathbf{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$$

$$\mathbf{5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O}$$

2) Iodides to free iodine.

$$\mathbf{10\,I^- \rightarrow 5I_2 + 10e^-}$$

$$\mathbf{2 \times (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)}$$

$$\mathbf{10I^- + 2MnO_4^- + 16H^+ \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O}$$

In alkaline or neutral medium, permanganate ion is reduced to MnO_2

$$\mathbf{MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-}$$

In alkaline medium it oxidises iodide to iodate

$$\mathbf{(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-) \times 2}$$

$$\mathbf{I^- + 6\,OH^- \rightarrow IO_3^- + 3\,H_2O + 6e^-}$$

$$\mathbf{2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-}$$

Note: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Uses: It is used as an oxidising agent in acidic, basic and neutral medium. It is used as a primary standard in volumetric analysis. It is used for the bleaching of wool, cotton, silk and other textile fibres and also for the de colourisation of oils.

Qn 9: Explain the preparation of $KMnO_4$?

Qn 10: What is the difference in oxidation reaction of $KMnO_4$ in the acid medium and alkaline medium?

Qn 11: Write any two uses each of $KMnO_4$ and $K_2Cr_2O_7$

THE INNER TRANSITION ELEMENTS (f-BLOCK)

The elements in which the last electron enters in the anti-penultimate f-subshell are called f-block elements. They include lanthanides of the 6th period and actinides of the 7th period. They are also called inner transition elements. The 14 elements after lanthanum of the 6 th period are called **lanthanides or lanthanones or lanthanoids or rare earths.** They include elements from cerium (Ce) to Lutetium (Lu).

Atomic and ionic radii - Lanthanoid Contraction:

In lanthanoids, the atomic and ionic radii decrease regularly from lanthanum to lutetium. This regular decrease in the atomic and ionic radii along lanthanoid series is called lanthanoid contraction.

Reason: It is due to the poor shielding effect of f orbital electrons. In lanthanoids, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f-Subshell. Due to its diffused shape, f orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and hence the size decreases.

Consequences:

1) Due to lanthanoid contraction the 2nd and 3rd row transition series elements have similar radii.

For example, Zirconium and Hafnium have similar atomic radii.(Zr – 160pm and Hf -159pm).

2) lanthanoids have similar physical properties and they occur together in nature. So their isolation is difficult.

3) As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+},the covalent character of the hydroxides increases and hence the basic strength decreases. $La(OH)_3$ is most basic while $Lu(OH)_3$ is the least basic.

Qn 12: What is lanthanoid contraction?

Qn 13: What are the causes and the consequences of lanthanoid contraction?

8.7 Some Applications of d- and f-Block Elements

1. Iron and steels are the most important construction materials.
2. TiO is used in the pigment industry.
3. Zn, Ni, Cd and MnO_2 are used in battery cells.
4. As catalyst in different reactions.

E.g.*V_2O_5 is used as a catalyst for the oxidation of SO_2 in the manufacture of sulphuric acid.

*$TiCl_4$ with $Al(CH_3)_3$ forms the basis of the Ziegler- Nata catalysts used in the manufacture of polythene.

*Iron catalysts are used in the Habur process for the production of ammonia from N_2 /H_2 mixtures.

*Ni, Pd and Pt are used as catalyst in hydrogenation reactions. In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$.

5. Ag salts are used in the photography.

Qn 14: What is Ziegler-nata catalyst?

Qn 15: Write any two uses of d-block elements?

SAMAGRA SIKSHA KERALA Class 12 CHEMISTRY

ANSWERS

Qn 1:In first transition series, Sc to Cr no.of unpaired electrons increases ($3d^1\ 4s^2$ to $3d^5\ 4s^1$), so magnetic moment increases. But after Cr, ie from Mn to Cu($3d^5\ 4s^2$ to $3d^{10}\ 4s^1$) no. of unpaired electron decreases, there by magnetic moment decreases.

Qn 2: Mn^{2+}. $3d^5$,no.of unpaired electrons =5 , $\mu = \sqrt{5(5+2)} = 5.92$ BM

Fe^{2+}. $3d^6$, no. of unpaired electrons = 4 , $\mu = \sqrt{4(4+2)} = 4.90$ BM

Co^{2+} . $3d^7$, no. of unpaired electrons = 3 , $\mu = \sqrt{3(3+2)} = 3.87$ BM

Ni^{2+} . $3d^8$, no. of unpaired electrons = 2, $\mu = \sqrt{2(2+2)} = 2.84$ BM

$Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$

Qn 3 : (a) Ti^{2+} - [Ar] $3d^2$, Ti^{4+} - [Ar] $3d^0$ due to the presence of partially filled d orbitals Ti^{2+} is coloured, Ti^{4+} is colourless due to the absence of electrons in d-orbitals.

(b) Cu^{2+} - [Ar] $3d^9$, Cu^+ - [Ar] $3d^{10}$, due to the presence of partially filled d-orbitals, Cu^{2+} is coloured, Cu^+ is colourless due to the presence fully filled d- orbitals.

Qn 4: Transition metals form a large no. of complexes. This is due to:

1. Comparatively smaller size 2. High ionic charge
3. Presence of partially filled d orbitals
4. Ability to show variable oxidation state

Qn 5: Transition metals and their compounds act as catalysts in a large no. of chemical reactions. This is due to their large surface area and their ability to show variable oxidation state.

Qn 6 :Potassium dichromate is generally prepared from chromite ore ($FeCr_2O_4$) by the following three steps.

1. Conversion of chromite ore to sodium chromate

Chromite ore is first fused with sodium carbonate in presence of air to form sodium chromate.

$$\mathbf{4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \rightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2}$$

2. Acidification of sodium chromate to sodium dichromate

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodium dichromate.

$$\mathbf{2Na_2CrO_4 + 2\,H^+ \rightarrow Na_2Cr_2O_7 + 2\,Na + + H_2O}$$

3. Conversion of sodium dichromate to potassium dichromate

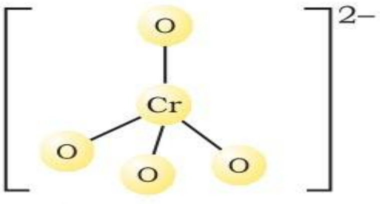
The solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out.

$$\mathbf{Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl}$$

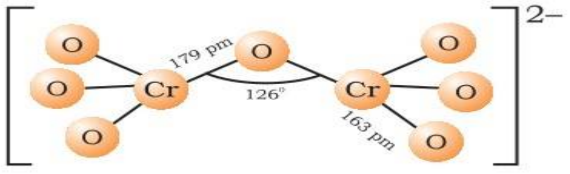
Qn 7 : oxidising action can be represented as follows:

$$\mathbf{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O}$$

Qn 8 :



Chromate ion



Dichromate ion

Qn 9 :

Potassium permanganate is commercially prepared from Pyrolusite (MnO_2). The preparation involves two steps. In the first step MnO_2 is fused with KOH to form potassium manganate (K_2MnO_4). Then K_2MnO_4 is electrolytically oxidised to potassium permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_4^{2-} \xrightarrow[\text{In acidic medium}]{\text{electrolytic oxidation}} MnO_4^{-} + e^{-}$$

Qn 10 : The oxidizing action in acidic medium is due to the reaction:

$$\mathbf{MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O}$$

In alkaline or neutral medium, permanganate ion is reduced to MnO_2

$$\mathbf{MnO_4^{-} + 2H_2O + 3e^{-} \rightarrow MnO_2 + 4OH^{-}}$$

ie, in acid medium MnO_4^- ion reduced to Mn^{2+} but in basic medium MnO_4^- ion reduced to MnO_2

Qn 11 : (1) potassium dichromate is used as a primary standard in volumetric analysis.

(2) It is also used as in leather industry and as an oxidant for the preparation of many azo compounds.

Potassium permanganate. (1) It is used as an oxidising agent in acidic, basic and neutral medium. (2) It is used as a primary standard in volumetric analysis.

Qn 12 : In lanthanides, the atomic and ionic radii decrease regularly from lanthanum to lutetium. This regular decrease in the atomic and ionic radii along lanthanide series is called lanthanide contraction.

Qn 13 : **Causes:** . In lanthanides, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f-subshell. Due to its diffused shape, f-orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and hence the size decreases.

Consequences:

1) Due to Lanthanide Contraction the 2 nd and 3 rd row transition series elements have similar radii. For example, Zirconium and Hafnium have similar atomic radii.(Zr – 160pm and Hf -159pm).

2) Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.

3) As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+},the covalent character of the hydroxides increases and hence the basic strength decreases. $La(OH)_3$ is most basic while $Lu(OH)_3$ is the least basic.

Qn 14 : $TiCl_4$ with $Al(CH_3)_3$ forms the basis of the Ziegler- Nata catalysts ,used in the manufacture of polythene.

Qn 15 : 1. Iron and steels are the most important construction materials.

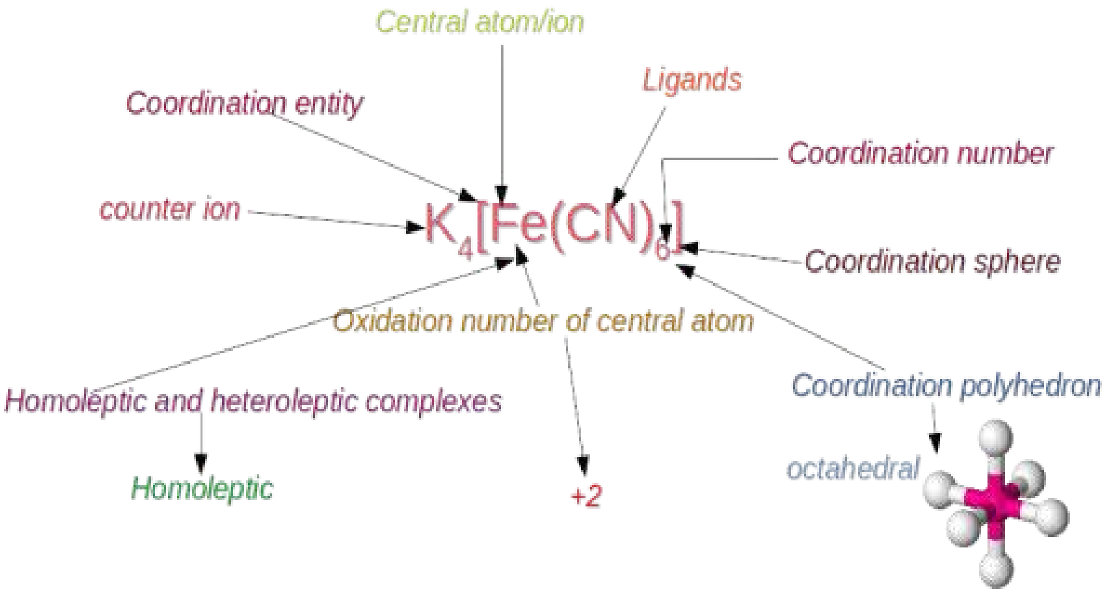
2. TiO is used in the pigment industry.
3. Zn, Ni, Cd and MnO_2 are used in battery cells.
4. As catalyst in different reactions.

Unit.9

COORDINATION COMPOUNDS

Focus Area

1. Nomenclature of Coordination Compounds
2. Isomerism in Coordination Compounds
3. Magnetic properties of Coordination Compounds
4. Importance and Applications of Coordination Compounds



1. Nomenclature of Coordination Compounds

The rules followed in assigning the IUPAC name of a coordination compound are:
(i) The cation(positive part) is named first.
(ii) The ligands are named in an alphabetical order before the name of the central atom/ion.
(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3 , carbonyl for CO and nitrosyl for NO. While writing the formula of coordination entity, these are enclosed in brackets ( ).
(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parentheses.
For example, $[NiCl_2(PPh_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II).
(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $[Co(SCN)_4]$ is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe.

(vii) The neutral complex molecule is named similar to that of the complex cation.

Q1. *The IUPAC name of two compounds are derived here. Similarly assign IUPAC names for the compounds given:*

Compound	$K_3[Fe(C_2O_4)_3]$	$[CoCl_2(en)_2]Cl$
Positive part	K^+	$[CoCl_2(en)_2]^+$
Coordination entity	$[Fe(C_2O_4)_3]^{3+}$	$[CoCl_2(en)_2]^+$
Counter ion	K^+	Cl^-
Ligands	$(C_2O_4)^{2-}$: *oxalato*	Cl^-: *chlorido*, *(en): ethane-1,2-diamine*
Central metal atom/ion	Fe^{3+}	Co^{3+}
Oxidation state of metal	+3	+3
IUPAC name	*Potassium trioxaltoferrate(III)*	*Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride*

(a) $[Pt(NH_3)_2Cl(NO_2)]$ *(b)* $[Co(NH_3)_5(CO_3)]Cl$ *(c)* $K_3[Cr(C_2O_4)_3]$ *(d)* $Hg[Co(SCN)_4]$

Q2. *Write the formulae corresponding to the IUPAC names given below:*

(a) Tetraammineaquachloridocobalt(III) chloride (b) Potassium tetrahydroxidozincate(II)

(c) Potassium trioxalatoaluminate(III) (d) Dichloridobis(ethane-1,2-diamine)cobalt(III)

(e) Tetracarbonylnickel(0)

2. Isomerism in Coordination Compounds

Isomers are two or more compounds having the same chemical formula but differ in one or more physical or chemical properties.

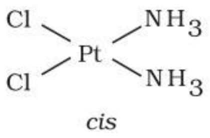
(a) Stereo isomerism : Stereo isomers have the same chemical formula and chemical bonds but they have different spatial arrangement.

(i) Geometrical isomerism: it arises due to difference in geometrical arrangement

A. cis – trans isomerism

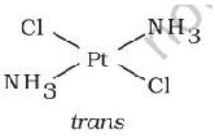
cis- isomer: Two similar groups at adjacent positions ***trans- isomer:*** Two similar groups at opposite positions

Examples:

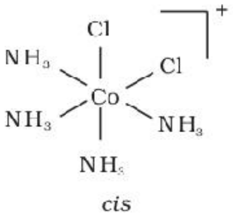


cis

and

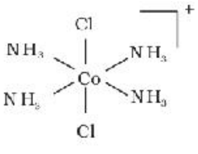


trans



cis

and



trans

Note: Tetrahedral complexes do not show cis-trans isomerism

B. facial-meridional isomerism : shown by octahedral complexes with three similar groups

facial-(fac-) isomer: 3 similar groups at the corners of an octahedral face

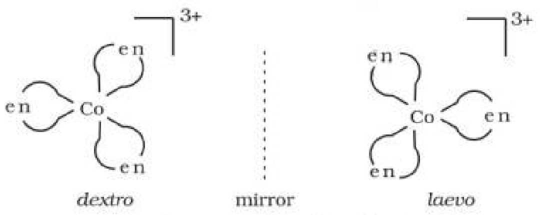
meridional-(mer-) isomer: 3 similar groups on either side of the meridian of octahedron.

Example:

fac– *mer–*

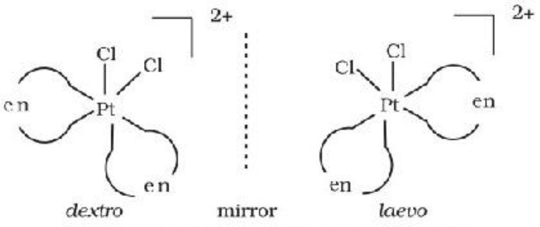
(ii) Optical isomerism: isomers show different optical activities due to chirality. i.e., isomers are non- superimposable mirror images; one isomer is dextro- (right-) rotatory while its mirror image is laevo-(left-) rotatory.

Example:



Optical isomers (d and l) of $[Co(en)_3]^{3+}$

;



Optical isomers (d and l) of cis- $[PtCl_2(en)_2]^{2+}$

Note: *Achiral: A structure and its mirror image are superimposable and hence optically innactive e.g., a tetrahedral complex with four same groups as ligands.*

(b) Structural isomerism

It arises due to the difference in structures

(i) Linkage isomerism: Linkage isomerism arises in a coordination compound containing ambidentate ligand.

Example: In the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($–NO_2$).

(ii) Coordination isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Example: $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(iii) Ionisation isomerism: It arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

Example: $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$

(iv) Solvate isomerism: Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

Example: $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

Q3. *Examine the following compounds or ions and answer the questions:*

$[Co(NH_3)_3(NO_2)_3]$, $[Pt(NH_3)_2Cl_2]$, $[Co(en)_3]^3$, $[PtCl_2(en)_2]^{2+}$, $[Ni(CO)_4]$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_3)_5(NO_2)]Cl_2$, $[Co(NH_3)_6][Cr(CN)_6]$, $[Co(NH_3)_5Br]SO_4$, $[Cr(H_2O)_6]Cl_3$

(a) Classify the above given compounds into those showing Structural isomerism, Stereo isomerism and those do not show isomerism

(b) In the group identified as structural isomers, write the type of isomerism shown by each compound.

(c) Identify the tetrahedral complex which is achiral.

(d) Which of the above compounds shows both geometrical and optical isomerism? Give the structure of the geometrical isomer which is optically active.

3. Magnetic properties of Coordination Compounds

The spin only magnetic moment, $\mu = [n(n + 2)]^{1/2}$ BM.

Q4. *The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. How many unpaired electrons will be there in the central metal ion of this complex?*

4. Importance and Applications of Coordination Compounds

No.	Area of Importance / Applications		Example / Compound Used	Explanation / Remark
	General	Specific		
1	Analytical chemistry	Qualitative and quantitative chemical analysis	Metal ions form coloured complexes with reagents like EDTA, DMG, naphthol, cupron, etc.	The familiar colour reactions given by metal ions with a number of ligands form the basis for their detection and estimation.
		Estimation of hardness of water	Hardness of water is estimated by simple titration with Na_2 EDTA.	The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.
2	Metallurgy	Extraction of silver and gold	Gold is converted to $[Au(CN)_2]^-$ and recovered from the solution by the addition of zinc	Refer Unit-6
		Purification of metals	Impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel	
3	Biological systems.	Photosynthesis	Chlorophyll is a coordination compound of Mg	The green pigment responsible for photosynthesis
		Oxygen transport in animals	Haemoglobin is a coordination compound of iron	the red pigment of blood
		Vitamins	Vitamin B_{12} is a coordination compound of cobalt	Cyanocobalamine, the anti–pernicious anaemia factor
4	Catalysts	Hydrogenation of alkenes	Rhodium complex, $[(Ph_3P)_3RhCl]$	Wilkinson catalyst
5	Electroplating	Plating with silver and gold	Use solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$	For smooth and even plating
6	Medicinal chemistry	Chelate therapy	Excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of complexes	Treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems
			EDTA is used in the treatment of lead poisoning	
		To inhibit the growth of tumers	cis–platin and related compounds	

Q5.

List five applications of coordination compounds

SOLUTIONS

Q1.

(a) $[Pt(NH_3)_2Cl(NO_2)]$: Diamminechloridonitrito-N-platinum(II)
(b) $[Co(NH_3)_5(CO_3)]Cl$: Pentaamminecarbonatocobalt(III) chloride
(c) $K_3[Cr(C_2O_4)_3]$: Potassium trioxalatochromate(III)
(d) $Hg[Co(SCN)_4]$: Mercury(I) tetrathiocyanato-S-cobaltate(III)

Q2.

(a) Tetraammineaquachloridocobalt(III) chloride : $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(b) Potassium tetrahydroxidozincate(II) : $K_2[Zn(OH)_4]$
(c) Potassium trioxalatoaluminate(III) : $K_3[Al(C_2O_4)_3]$
(d) Dichloridobis(ethane-1,2-diamine)cobalt(III) ion : $[CoCl_2(en)_2]^+$
(e) Tetracarbonylnickel(0) : $[Ni(CO)_4]$

Q3.

(a)

Structural isomers: $[Co(NH_3)_5(NO_2)]Cl_2$, $[Co(NH_3)_6][Cr(CN)_6]$, $[Co(NH_3)_5Br]SO_4$, $[Cr(H_2O)_6]Cl_3$
Stereo isomers: $[Co(NH_3)_3(NO_2)_3]$, $[Pt(NH_3)_2Cl_2]$, $[Co(en)_3]^{3+}$, $[PtCl_2(en)_2]^{2+}$
Compounds which do not show isomerism: $[Ni(CO)_4]$

(b)

$[Co(NH_3)_5(NO_2)]Cl_2$: Linkage isomerism
$[Co(NH_3)_6][Cr(CN)_6]$: Coordination isomerism
$[Co(NH_3)_5Br]SO_4$: Ionisation isomerism
$[Cr(H_2O)_6]Cl_3$: Solvate (hydrate) isomerism

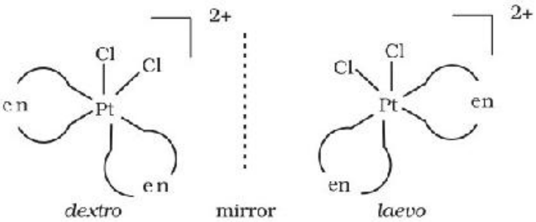
(c)

$[Ni(CO)_4]$

(d)

$[PtCl_2(en)_2]^{2+}$

cis – isomer of this compound shows optical isomerism and can be represented as



Optical isomers (d and l) of cis-$[PtCl_2(en)_2]^{2+}$

Q4.

$\mu = [n(n + 2)]^{1/2}$ BM
$= 5.9$ BM
Therefore, $[n(n + 2)]^{1/2} = 5.9$
i.e., $[n(n + 2)] = (5.9)^2 = 34.81$
OR $n = \mathbf{5}$
No. of unpaired electrons = 5

Q5.

Refer ncert vol.1text page no.262-263

SAMAGRA SIKSHA KERALA Class 12 CHEMISTRY

Unit.10
HALOALKANES and HALOARENES

Focus Area:
10.4.1 Preparation from alcohols
10.4.2 Preparation from hydrocarbons
10.6.1 Reactions of haloalkanes (Nucleophilic substitution)
10.6.2 Reactions of haloalkanes (Electrophilic substitution)
10.7.2 Trichloromethane

Preparation from Alcohols:

The -OH group present in alcohols can be replaced by halo group by reaction with PCl_3, PCl_5, $SOCl_2$, HCl or HBr in presence of anhydrous $ZnCl_2$ etc.

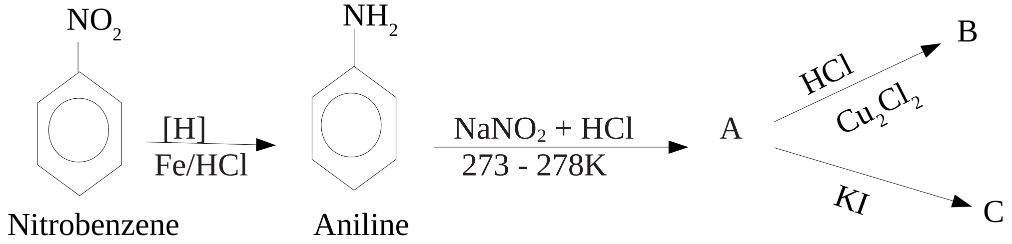
1. Write the IUPAC name of the alcohol with molecular formula C_2H_6O. What is the product obtained when it is treated with PCl_3.
2. $SOCl_2$ is the best reagent for the preparation of haloalkanes from alcohol. Comment on this statement.

Preparation from Hydrocarbons:

Haloalkanes can be prepared by the free radical halogenation of alkanes and by the addition of halogens and hydrogen halides to alkenes. Haloarenes can be prepared by the electrophilic substitution reaction and by Sandmeyer’s reaction.

3. Alkyl group is an ortho-para directing group. Identify the products formed when methyl benzene (toluene) is treated with chlorine in presence of Fe in dark. Also suggest a method for separating the products.

4.



Identify A, B and C. Give the name of the reaction which leads to the formation of B from A.

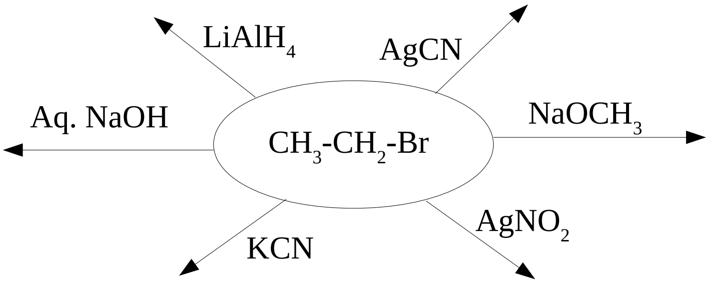
5. When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the reagent goes to the less hydrogenated carbon atom.
a) Identify the rule behind the above statement.
b) Identify the major product formed when propene is treated with HI.

Reactions of Haloalkanes – Nucleophilic substitution reactions

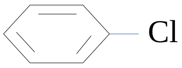
It is the replacement of a weak nucleophile by a strong nucleophile. Nucleophilic substitution reactions proceed by two mechanisms – Substitution Nucleophilic unimolecular (S_N1) and

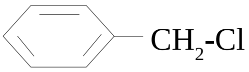
Substitution Nucleophilic bimolecular (S_N2). For tertiary (3^0) alkyl halides, the reaction proceed through S_N1 mechanism and for primary (1^0) alkyl halides, the reaction proceeds through S_N2 mechanism. Vinylic and benzylic halides also undergo nucleophilic substitution reaction by S_N1 mechanism, since the carbocations formed are resonance stabilized.

6. List out the differences between S_N1 and S_N2 reactions (mechanisms).
7. Identify the products formed in the following reactions:



8. Which of the following halides undergo S_N1 reaction faster?
(i) CH_3-CH_2-CH_2-CH_2-Cl and $(CH_3)_3C$-Cl
(ii)

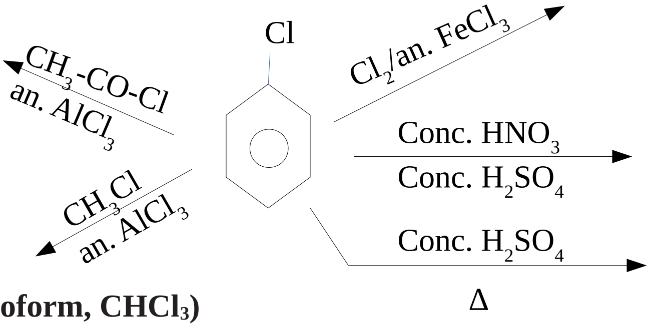




9. Molecules which are non-superimposable on their mirror images are called chiral molecules and are optically active. An equimolar mixture of (+) butan-2-ol and (-) butan-2-ol are optically inactive, eventhough they are chiral. Why? Name the process behind this.
10. What are enantiomers? Give example.

Reactions of Haloarenes – Electrophilic substitution Reactions

Here a weaker electrophile is replaced by a stronger electrophile. These are of 4 types – Halogenation, nitration, sulphonation and Friedel-Crafts reactions.
11. Identify the major products in the following reactions:



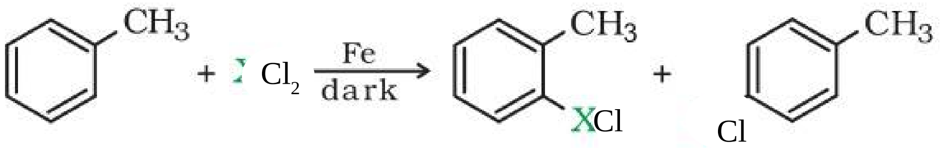
Trichlorometane (Chloroform, $CHCl_3$)

It is used as a solvent for fats, alkaloids, iodine and other substances. It is very sensitive to light and air.
12. Name the poisonous gas formed when chloroform is exposed to air.
13. Chloroform is kept in closed dark coloured bottles completely filled upto the neck. Why?

Answers

1. Ethanol (CH_3-CH_2-OH). The product obtained is ethyl chloride (Chloroethane)
2. When $SOCl_2$ is used, the biproducts formed (HCl and SO_2) are gases and so they are escaped from the reaction medium. Hence the alkyl halides formed are pure.

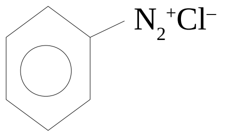
3.



o-Chlorotoluene p-Chlorotoluene

The ortho and para isomers can be easily separated due to large difference in their melting points.

4. A is Benzene diazonium chloride



B is Chlorobenzene (C_6H_5-Cl)

C is Iodobenzene (C_6H_5-I)

The conversion of benzene diazonium chloride to chlorobenzene is known as Sandmeyer's reaction.

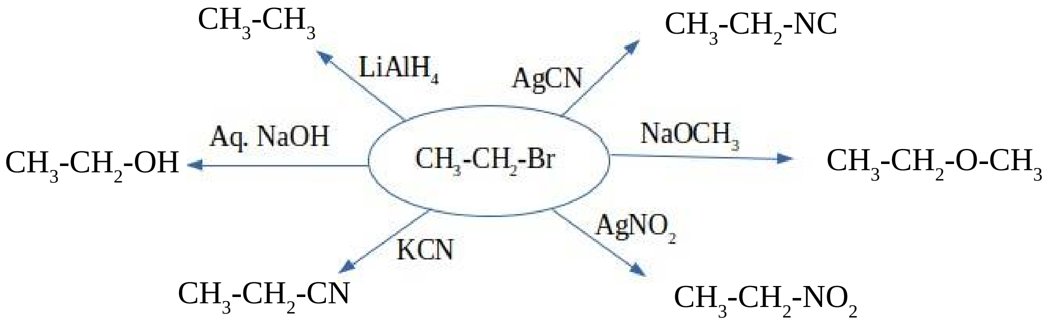
5. a) Markownikoff's Rule

   b) 2-iodopropane (CH_3-CHI-CH_3)

6. Differences between S_N1 and S_N2 reactions

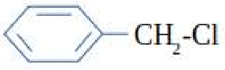
S_N1 Reaction	S_N2 Reaction
Proceeds through two steps	Proceeds through a single step
An intermediate carbocation is formed	No intermediates are formed
Order of the reaction is 1	Order of the reaction is 2
The order of reactivity of alkyl halide is $3^0 > 2^0 > 1^0$.	The order of reactivity of alkyl halide is $1^0 > 2^0 > 3^0$.

7.



8. (i) $(CH_3)_3C$-Cl (Since tertiary alkyl halides are more reactive to S_N1 reaction).

   (ii)

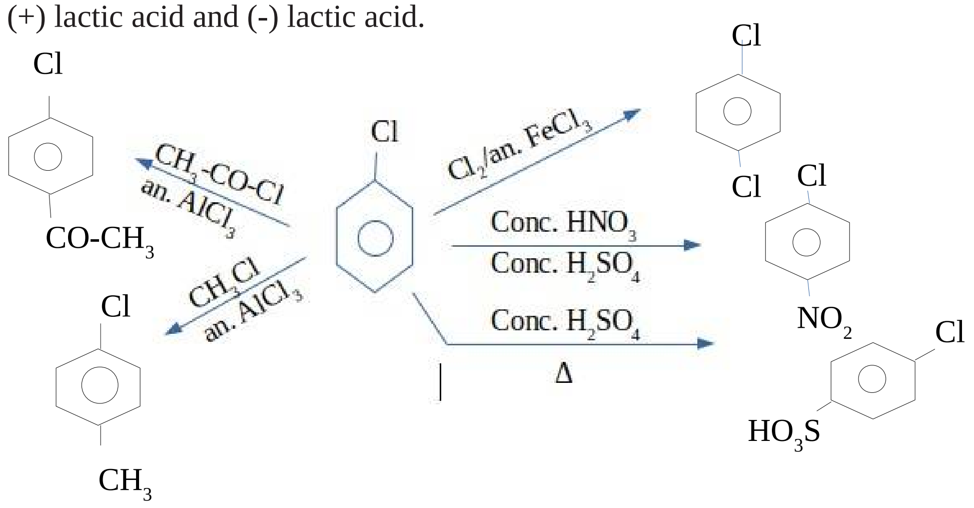


(Since the benzyl carbocation formed is resonance stabilized)

9. This is because the optical rotation of (+) butan-2-ol is cancelled by that of (-) butan-2-ol. The process is known as recemisation.

10. Stereoisomers which are related to each other as non-superimposable mirror images are called enantiomers. E.g. (+) lactic acid and (-) lactic acid.

11.



12. Phosgene (Carbonyl chloride, $COCl_2$)

13. Chloroform is slowly oxidised by air in presence of light to form an extremely poisonous gas known as carbonyl chloride ($COCl_2$). So it is kept in dark coloured bottles.

Unit.11

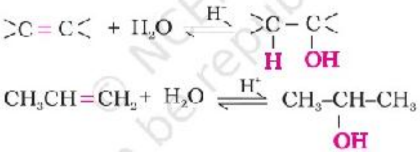
ALCOHOLS, PHENOLS AND ETHERS

Focus Area

1. Preparation of Alcohols (from alkenes, carbonyl compounds and Grignard reagent)
2. Preparation of phenol (from haloarenes and diazonium salts)
3. Chemical Reactions (Lucas Test, Dehydration, Nitration of Phenol and Reimer – Teimann Reaction
4. Commercially important alcohols – Ethanol
5. Preparation of Ethers – Williamson Synthesis
6. Chemical Reactions – Friedel Craft's Reaction

1. Preperation of Alcohols (from alkenes, carbonyl compounds and Grignard reagent)

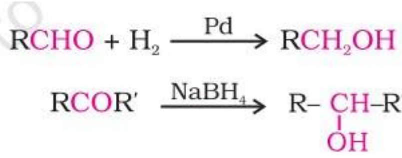
A. From alkenes by *acid catalysed hydration(i*n case of unsymmetrical alkenes, the addition follows Markovnikov's rule)



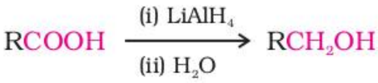
B. From carbonyl compounds

(i) By reduction of aldehydes and ketones by addition of hydrogen in the presence of finely divided platinum, palladium or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$).

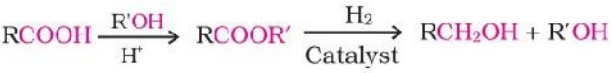
Note:Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



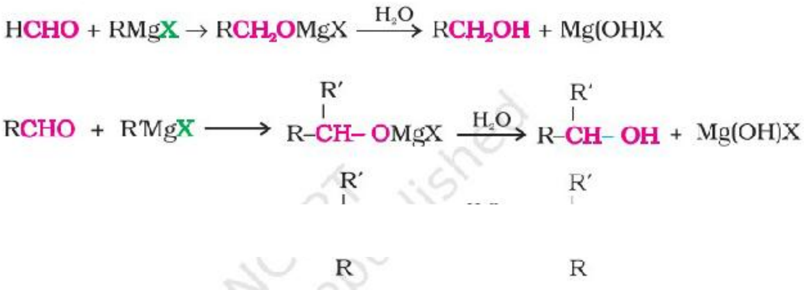
(ii) By reduction of carboxylic acids and esters by lithium aluminium hydride.



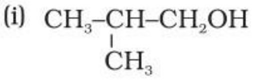
Note: Commercially, acids are reduced to alcohols by converting them to the esters followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

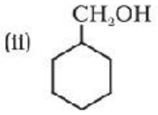


C. From Grignard reagents

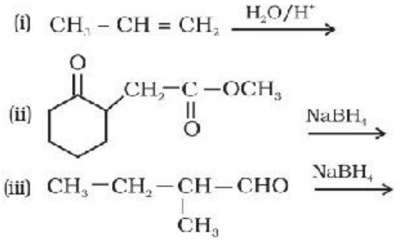


Q1. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?


(i) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$



Q2. Write structures of the products of the following reactions:



2. Preperation of phenol (from haloarenes and diazonium salts)

A. From haloarenes

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced

B. From diazonium salts

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($NaNO_2$ + HCl) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.

Q3. How can we prepare phenol from the following compounds?

(i) Chlorobenzene (ii) Aniline

3. Chemical Reactions (Lucas Test, Dehydration, Nitration of Phenol and Reimer – Teimann Reaction

A. Lucas test (Reaction with hydrogen halides): Alcohols react with hydrogen halides to form alkyl halides.

$$ROH + HX \rightarrow R–X + H_2O$$

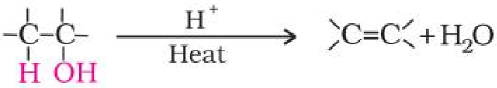
The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution.

Tertiary alcohols produce turbidity immediately as they form the halides easily.

Secondary alcohols produce turbidity within five minutes.

Primary alcohols do not produce turbidity at room temperature.

B. Dehydration: Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H_2SO_4 or H_3PO_4, or catalysts such as anhydrous zinc chloride or alumina.

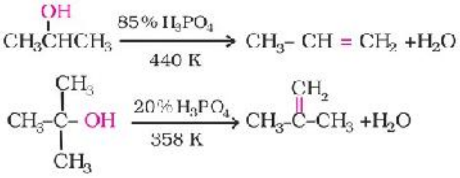


$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[\text{Heat}]{H^+} \rangle C{=}C\langle + H_2O$$

Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Secondary and tertiary alcohols are dehydrated under milder conditions. For example,



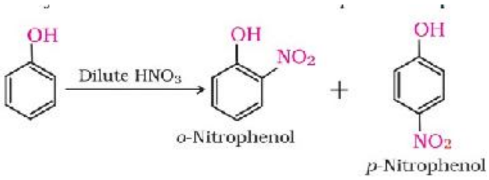
$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\overset{||}{C}}-CH_3 + H_2O$$

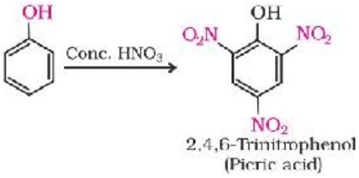
Thus, the relative ease of dehydration of alcohols follows the following order:

Tertiary > Secondary > Primary

C. Nitration of phenol: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenols.

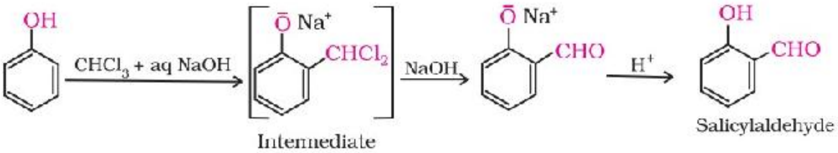


With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol.



D. Reimer-Tiemann reaction

On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction.



Q4. Explain Lucas Test.

Q5. Which alcohol does give 2-methylpropene on dehydration?

Q6. How are the following compounds prepared from phenol?

(i) Salicylaldehyde (ii) Picric acid (iii) p-nitrophenol

4. Commercially important alcohols – Ethanol

Ethanol:

Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

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

Note: The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

Q7. Write a note on the commercial preparation of ethanol.

5. Preperation of Ethers – Williamson Synthesis

Williamson synthesis:

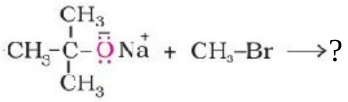
An alkyl halide is allowed to react with sodium alkoxide.

R–O–R’ + Na X

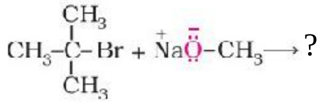
$R\text{–} X + R'\text{–}O^- Na^+$

Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves SN_2 attack of an alkoxide ion on primary alkyl halide.

Q8. Predict the product in each of the following cases:

(i)


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\ddot{\underset{..}{O}}\overset{+}{Na} + CH_3\text{–}Br \longrightarrow ?$$

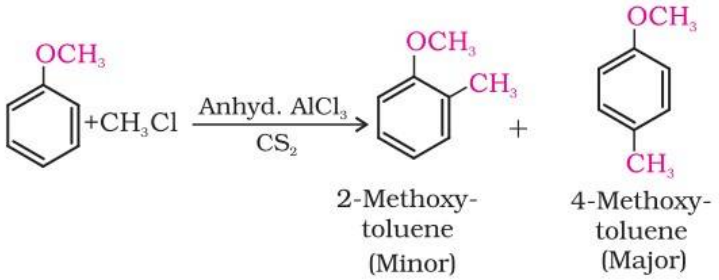
(ii)


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + \overset{+}{Na}\ddot{\underset{..}{O}}-CH_3 \longrightarrow ?$$

6. Chemical Reactions – Friedel Craft’s Reaction

Friedel-Crafts reaction: Anisole undergoes Friedel-Crafts reaction, i.e., the alkyl and acyl groups are introduced at ortho and para positions by reaction with alkyl halide and acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.

Example:



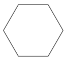
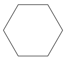
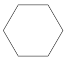
Q9. How will you convert methoxy benzene to:

(i) 4-methoxytoluene and (ii) 4-methoxyacetophenone

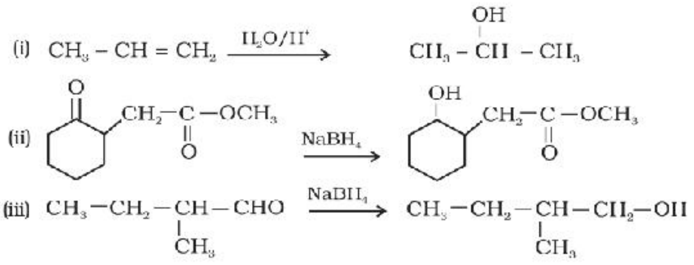
SOLUTIONS

Q1.

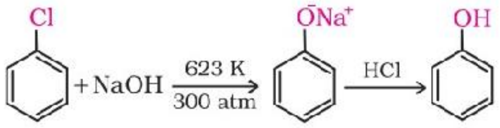
(i) HCHO + $(CH_3)_2CHMgBr$ ⟶ $(CH_3)_2CH\text{-}CH_2\text{-}OMgBr$ ⟶ ***$(CH_3)_2CH\text{-}CH_2\text{-}OH$*** + Mg(OH)Br

(ii) HCHO + -MgBr ⟶ $\text{-}CH_2\text{-}OMgBr$ ⟶ $\text{-}CH_2\text{-}OH$ + Mg(OH)Br

Q2.



Q3.
(i) From Chlorobenzene



(ii) From Aniline

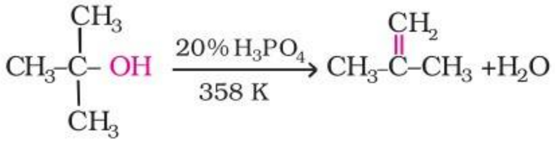
Q4.
Lucas test : Alcohols react with hydrogen halides to form alkyl halides.

$$ROH + HX \rightarrow R\text{–}X + H_2O$$

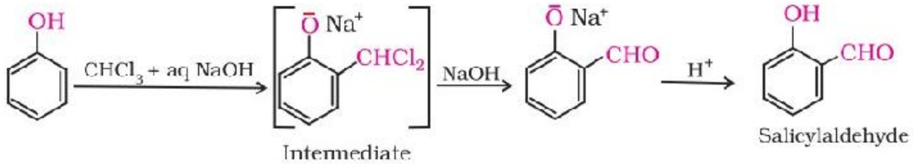
The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution.
Tertiary alcohols produce turbidity immediately as they form the halides easily.

Secondary alcohols produce turbidity within five minutes.
Primary alcohols do not produce turbidity at room temperature.

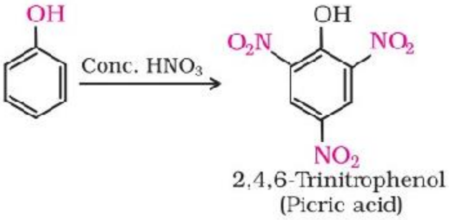
Q5. 2-methylpropan-2-ol. The reaction is as shown below:



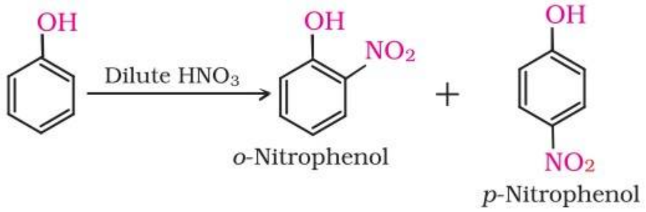
Q6.
(i) Salicylaldehyde from phenol



(ii) Picric acid from phenol

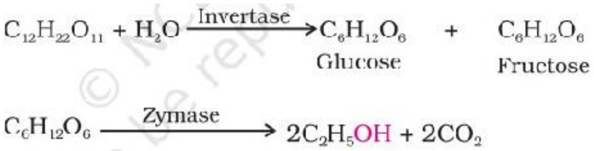


(iii) p-nitrophenol from phenol



The ortho and para isomers can be separated by steam distillation.

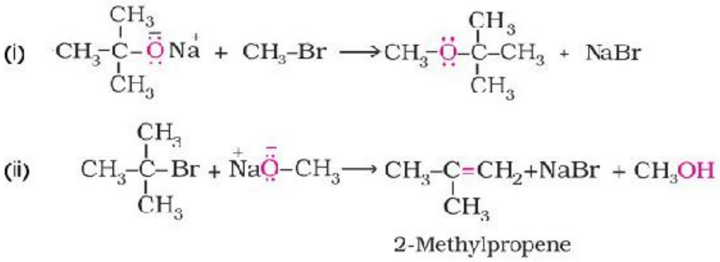
Q7. Commercial preparation of ethanol:
Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.



$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

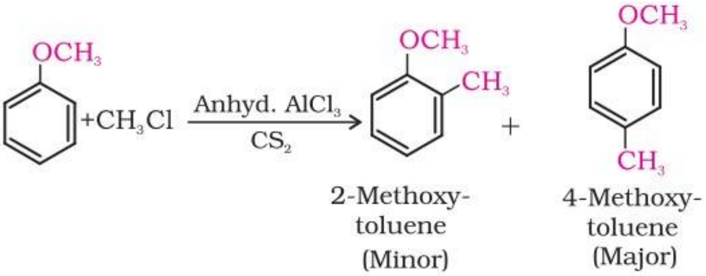
$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Q8. Predict the product in each of the following cases:

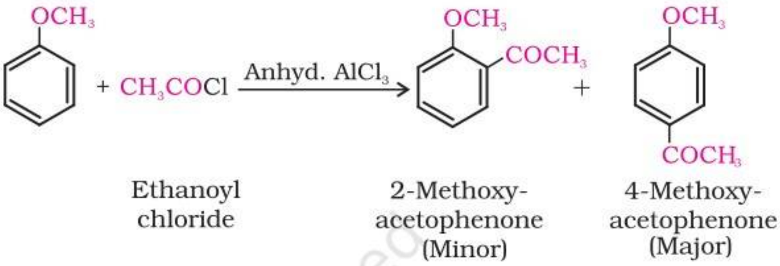


Q9. How will you convert methoxy benzene to:

(i) Conversion methoxybenzene to 4-methoxytoluene



(ii) Conversion methoxybenzene to 4-methoxyacetophenone



Unit. 12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

FOCUS AREA

Preparation of aldehydes and ketones

(By oxidation of alcohols, by dehydrogenation of alcohols, Rosenmund reduction, Etard reaction, Gatterman – Koch reaction, Friedel Craft's reaction)

Chemical reactions

(Reduction, Oxidation, Aldol condensation, Cannizzaro reaction)

Preparation of Carboxylic acid

(from aldehydes and ketones, from alkyl benzene).

Chemical reactions

(acidity, reaction with ammonia, Kolbe electrolysis, Hell – Volhard Zelinsky reaction, Ring substitution).

Preparation of aldehydes and ketones:-

By oxidation of alcohols: Primary alcohol on oxidation gives aldehydes and secondary alcohol on oxidation gives ketones.

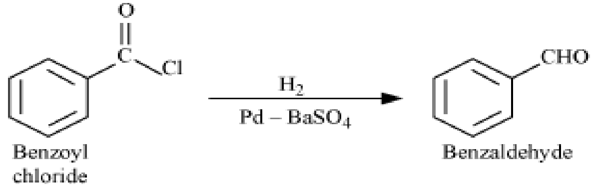
$$R\text{-}CH_2\text{-}OH \xrightarrow{[O]} R\text{-}CHO, \quad R\text{-}CHOH\text{-}R \xrightarrow{[O]} R\text{-}CO\text{-}R$$

$$CH_3 - CH = CH - CH_2 - OH \xrightarrow{PCC} CH_3 - CH = CH - CH\,O$$

By dehydrogenation of alcohols: Primary alcohol on dehydrogenation gives aldehydes and secondary on dehydrogenation gives ketones with heated Cu at 573 K

$$R\text{-}CH_2\text{-}OH \xrightarrow{Cu/573K} R\text{-}CHO\ (\text{Aldehyde}), \quad R\text{-}CHOH\text{-}R \xrightarrow{Cu/573K} R\text{-}CO\text{-}R(\text{Ketone})$$

Rosenmund reduction: Partial reduction of acyl chloride (acid chloride) to aldehyde in presence of palladium on barium sulphate is called Rosenmund reduction.



Q. 1. (a) Write the product obtained when benzoyl chloride is reduced with H_2 in presence of Pd and $BaSO_4$

(b) Write the name of the above reaction.

Q. 2. Convert the following:

(a) Benzoyl chloride to benzaldehyde.
(b) Ethanol to ethanal.
(c) But – 2 – enol to But – 2 – enal

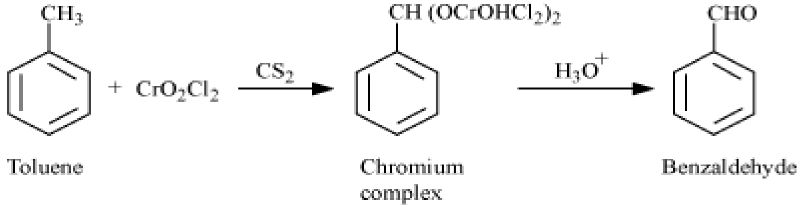
Q. 3. Identify the products of the following reactions:

(a) $CH_3CH_2CH_2OH \xrightarrow{H^+ /K_2Cr_2O_7}$

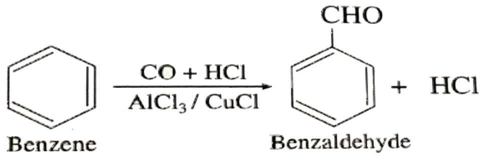
(b) $CH_3 - CH = CH - CH_2\,OH \xrightarrow{PCC}$

Q. 4. Explain the reactions – Rosenmund reduction.

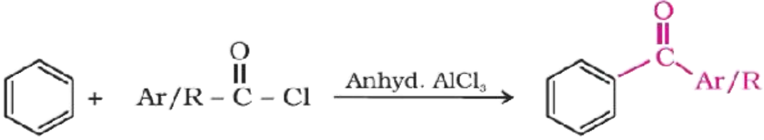
Etard reaction: Conversion of toluene to benzaldehyde with chromyl chloride in carbon disulphide followed by hydrolysis is called Etard reaction.



Gatterman – Koch reaction: Conversion of benzene to benzaldehyde with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride or cuprous chloride is called Gatterman – Koch reaction



Friedel Craft's reaction: Introduction of acyl group to a benzene or substituted benzene in presence of anhydrous aluminium chloride is known as Friedel-Crafts acylation reaction.



Q. 5. Explain the following reactions.

(a) Etard reaction
(b) Gatterman – Koch reaction
(c) Friedel Craft's reaction

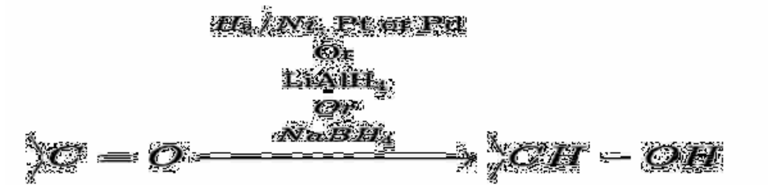
Q. 6. Convert the following:

(a) Toluene to benzaldehyde
(b) Benzene to benzaldehyde

Chemical reactions of aldehydes and ketones

Reduction:

Reduction to alcohols – Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) or H_2 in presence of Ni



Reduction to hydrocarbons:-

Clemmensen reduction:- The reduction of aldehydes or ketones to the corresponding hydrocarbons on treatment with zinc amalgam and concentrated hydrochloric acid is called Clemmensen reduction

Wolff-Kishner reduction:- The reduction of aldehydes or ketones to the corresponding hydrocarbons on treatment with hydrazine followed by heating with potassium hydroxide in ethylene glycol is called

Wolff -Kishner reduction.

Q. 7. Explain the following reactions.

(a) Clemmensen reduction

(b) Wolff – Kishner reduction.

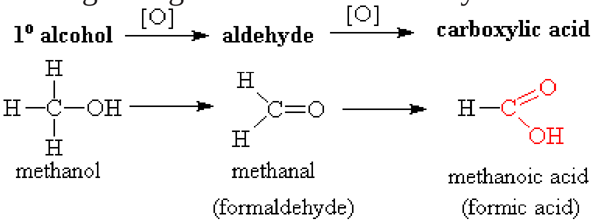
Q. 8. Convert the following:

(a) Ethanal to ethane

(b) Propanone to propane

Oxidation:-

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollen's reagent and Fehling's reagent also oxidise aldehydes. Ketones are generally oxidised under vigorous conditions.



The mild oxidising agents given below are used to distinguish aldehydes from ketones:

(i) Tollens' test: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollen's reagent), a bright silver mirror is produced due to the formation of silver metal.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$$

(Silver mirror)

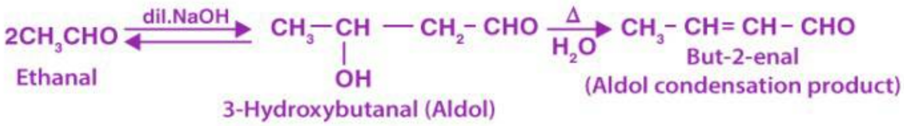
(i) Fehling's test: On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.

$$RCHO + 2Cu^{2+} + 5OH^- \rightarrow RCOO^- + Cu_2O + 3H_2O$$

(Red – brown ppt)

Q. 9. Give a chemical test to distinguish between Propanal and propanone.

Aldol condensation:- Aldehyde or ketones with α – hydrogen when treated with dil. alkali (NaOH) undergo self condensation to form the corresponding β – hydroxy aldehyde or β – hydroxy ketone and is called Aldol condensation.



Eg. Ethanal on Aldol condensation gives β – hydroxy butanal and on heating gives but – 2 – enal.

Q. 10. The reaction in which the carbon – carbon bond formation occur with

(a) Clemmenson's reduction (b) Aldol condensation

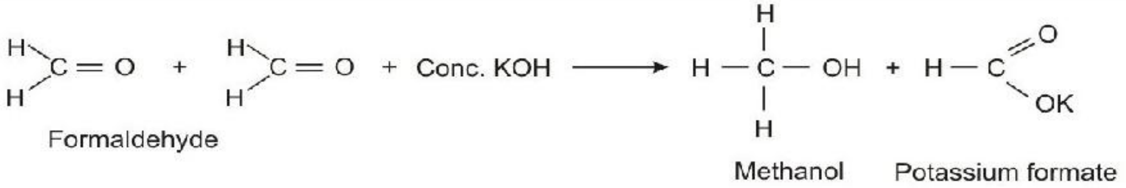
(c) HVZ reaction (d) Wolff Kishner reduction

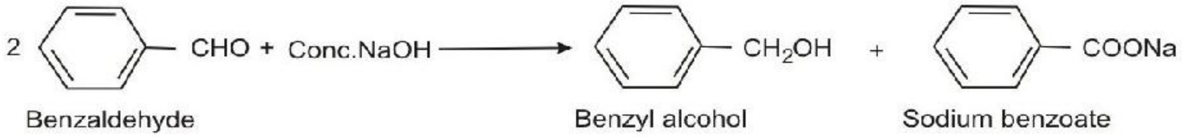
Q. 11. An aldehyde 'A' is treated with dilute NaOH to form a compound 'B' called 3 – hydroxy butanal.

(a) Identify A
(b) Write the name of the above reaction.
(c) Write the product formed when B is heated.

Cannizzaro reaction:- Aldehyde without α – hydrogen undergo self oxidation and reduction in presence of conc. alkali (NaOH/KOH) to form acid salt and alcohol and is called Cannizzaro reaction.

Eg. Methanal (Formaldehyde) and benzaldehyde undergo Cannizzaro reaction





Q. 12. Explain Cannizzaro reaction with a suitable example.

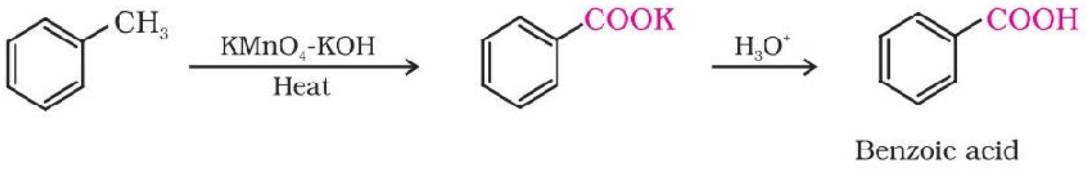
Preparation of Carboxylic acid:-

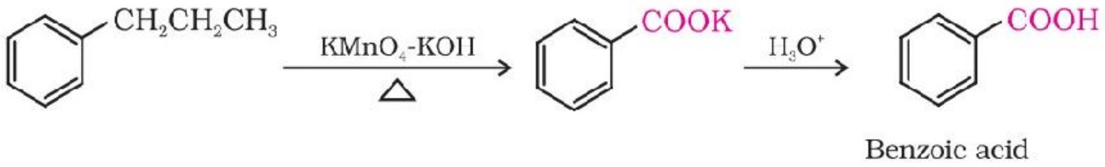
From aldehydes – Aldehyde on oxidation with mild oxidising agents gives carboxylic acid.

$$RCHO \xrightarrow{[O]} RCOOH$$

From alkyl benzene –

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate.





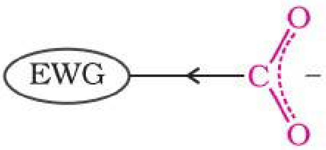
Q. 13. Convert the following:
(a) Toluene to benzoic acid
(b) Propyl benzene to benzoic acid.

Chemical reactions of carboxylic acid:-

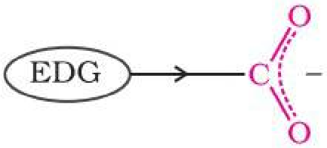
Acidity:- Carboxylic acids are stronger acids than alcohols and phenols. Because conjugate base of carboxylic acid, carboxylate anion is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom.

Q. 14. Carboxylic acid is more acidic than phenol and alcohol.

Effect of substituents on the acidity of carboxylic acids:- Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid. Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid. As the acidity increases pk_a value decreases.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

Q. 15. (a) Explain the effect of substituents on the acidity of carboxylic acid.

(b) Arrange the following carboxylic acids in the increasing order of acidity:

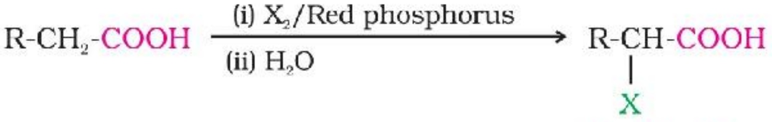
CH_3COOH, F – CH_2COOH, HCOOH, Cl– CH_2COOH

Q. 16. Chloro acetic acid is more acidic than acetic acid. Why?

Reaction with ammonia:- Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides.

Kolbe electrolysis:- Alkali metal salts of carboxylic acids undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as Kolbe electrolysis.

Hell – Volhard Zelinsky reaction:- Carboxylic acids with α-hydrogen when treated with chlorine or bromine in the presence of red phosphorus to give α- halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} \underset{\substack{| \\ X}}{R\text{-}CH\text{-}COOH}$$

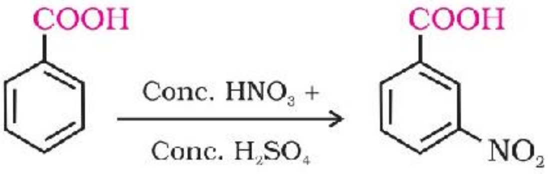
X = Cl, Br

α – Halocarboxylic acid

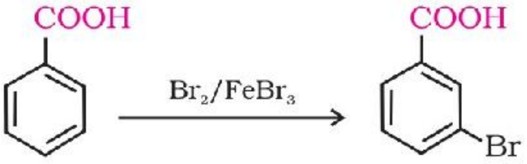
Q. 17. Identify the carboxylic acid which cannot give HVZ reaction.

(a) CH_3COOH (b) CH_3CH_2COOH (c) $CH_3CH(CH_3)CH_2COOH$ (d) HCOOH

Ring substitution:- Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. But they do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.



m-Nitrobenzoic acid



m-Bromobenzoic acid

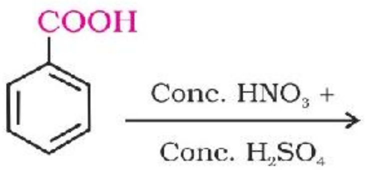
Q. 18. Give reason:

(a) Benzoic acids undergo electrophilic substitution reactions only at meta position of the ring.

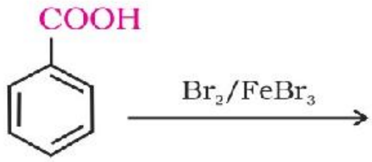
(b) Benzoic acids do not undergo Friedel-Crafts reaction.

Q. 19. Complete the following.

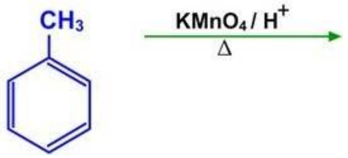
(i)



(ii)

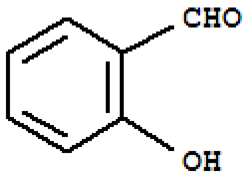


(iii)



Q. 20. The aldehyde used to preserve biological specimens is _______

Q. 21. Write the IUPAC name of the following compound:



Q. 22. Write the structure of 2, 4 – dimethyl pentan – 3 – one.

Q. 23. Give the products of the following.

(a) Acetic acid is treated with chlorine in the presence of red phosphorus

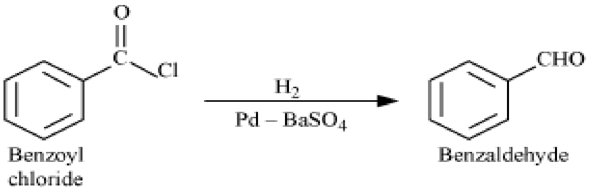
(b) Reduction of butanal with Zinc – amalgam and concentrated HCl

(c) Reduction of propanone with hydrogen in presence of nickel.

ANSWERS

1. (a) Benzaldehyde, C_6H_5–CHO
   (b) Rosenmund reduction

2. (a)



(b) CH_3-CH_2-OH $\xrightarrow{Cu/573K}$ CH_3-CHO (Ethanal)

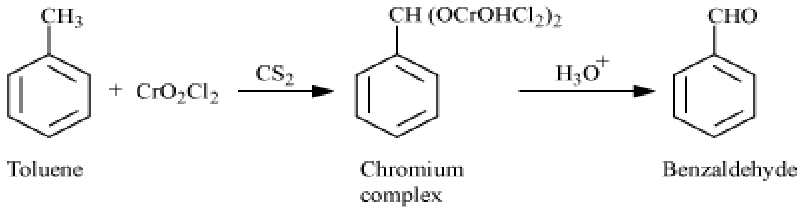
(c) CH_3 – CH = CH – CH_2 – OH $\xrightarrow{PCC}$ CH_3 – CH = CH – CH O

3. (a) CH_3–CH_2–CH_2OH $\xrightarrow{H+¿K2Cr2O7}$ CH_3–CH_2–COOH
   (b) CH_3 – CH = CH – CH_2OH $\xrightarrow{PCC}$ CH_3 – CH = CH – CHO

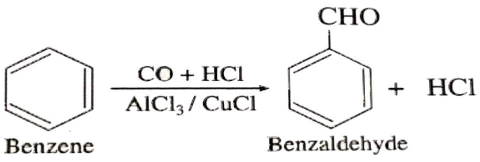
4. (a) Partial reduction of acyl chloride (acid chloride) to aldehyde in presence of palladium on barium sulphate is called Rosenmund reduction.

5. (a) Conversion of toluene to benzaldehyde with chromyl chloride in carbon disulphide followed by hydrolysis is called Etard reaction.
   (b) Conversion of benzene to benzaldehyde with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride or cuprous chloride is called Gatterman – Koch reaction.
   (c) Introduction of acyl group to a benzene or substituted benzene in presence of anhydrous aluminium chloride is known as Friedel-Crafts acylation reaction.

6. (a)



(b)



7. (a) The reduction of aldehydes or ketones to the corresponding hydrocarbons on treatment with zinc - amalgam and concentrated hydrochloric acid is called Clemmensen reduction.
   (b) The reduction of aldehydes or ketones to the corresponding hydrocarbons on treatment with hydrazine followed by heating with potassium hydroxide in ethylene glycol is called Wolff – Kishner reduction.

8. (a) $CH_3 - CHO \xrightarrow{Zn-Hg/Conc.HCl} CH_3 - CH_3$

(b) $CH_3 - CO - CH_3 \xrightarrow{Zn-Hg/Conc.HCl} CH_3 - CH_2 - CH_3$

9. Tollen's test. Propanal gives silver mirror with Tollen's reagent, while propanone does not.

10. (b) Aldol condensation

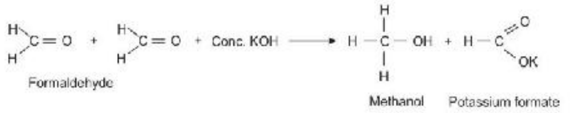
11. (a) A = CH_3–CHO

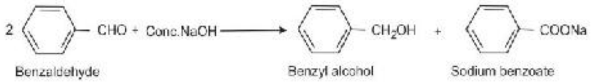
(b) Aldolcondensation

(c) $CH_3 - CH = CH - CHO$, But – 2 – enal

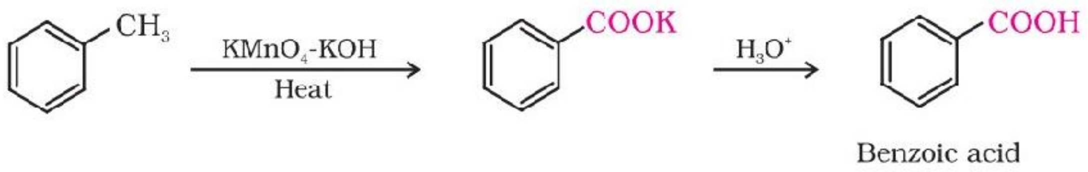
12. Aldehyde without α – hydrogen undergo self oxidation and reduction in presence of conc. alkali (NaOH/KOH) to form acid salt and alcohol and is called Cannizzaro reaction.

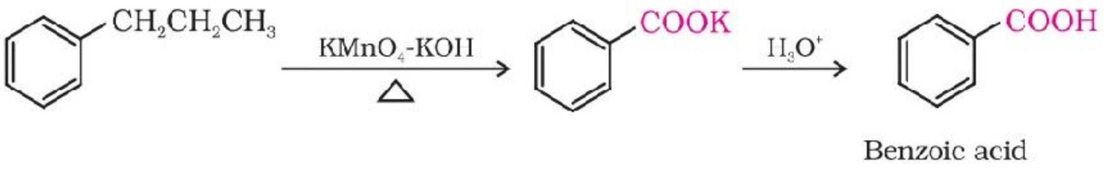
Eg. Methanal (Formaldehyde) and benzaldehyde undergo Cannizzaro reaction





13. (a) and (b)





14. Because the conjugate base of carboxylic acid, carboxylate anion is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom.

15. (a) Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid. Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid. As the acidity increases pk_a value decreases

(b) $CH_3COOH < HCOOH < Cl - CH_2COOH < F - CH_2COOH$

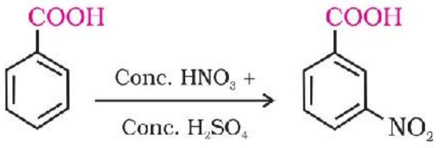
16. Chlorine is an electron withdrawing group (EWG), which stabilises the carboxylate anion and hence strengthens the acid.

17. (d) HCOOH

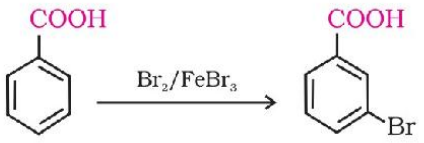
18. (a) In benzoic acid, the carboxyl group acts as a deactivating and hence meta-directing.

(b) In benzoic acid, the carboxyl group is deactivating and the catalyst aluminium chloride, lewis acid gets bonded to the carboxyl group.

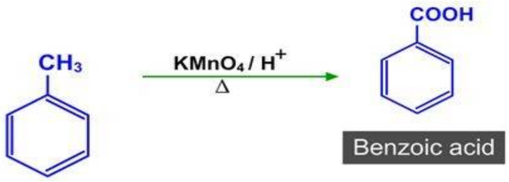
19. (i), (ii) and (iii)



m-Nitrobenzoic acid



m-Bromobenzoic acid



20. Formalin
21. 2 – Hydroxybenzaldehyde.
22. $CH_3–CH(CH_3) – CO– CH(CH_3) – CH_3$

23. (a) Chloroacetic acid, $CH_2(Cl)–COOH$
    (b) Butane, $CH_3–CH_2–CH_2–CH_3$
    (c) $CH_3–CH(OH)–CH_3$, Isopropyl alcohol (2 – Hydroxy propane)

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Unit.13

Amines

Focus area

- Preparation of Amines
- Chemical Reactions
- Chemical Reactions of diazonium salts

Prerequisites

Scan QR code and watch plus two class 65 on victers channel

or

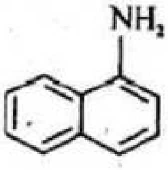
click https://www.youtube.com/watch?v=G792ZZ1ViDg

- Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons.
- Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.
- Nomenclature of amines

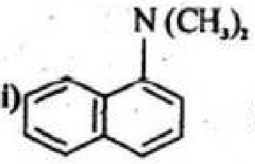
Q.1

Classify the following as primary (1°), secondary (2°) and tertiary (3°) amines

(i)



(ii)



(iii) $(C_2H_5)_2\,CHNH_2$ (iv) $(C_2H_5)_2NH$

Q.2

Amines are derivatives of ________(i)________ in which the nitrogen forms ____(ii)__ bonds and contains __(iii)__ lone pair(s) of electrons

Q.3

Match the following

1	CH_3NH_2	a	Ethanamine
2	$C_2H_5NH_2$	b	Benzamine
3	$(C_2H_5)_2NH$	c	N-Ethylethanamine
4	$C_6H_5NH_2$	d	N,N-Dimethylmethanamine
5	$(CH_3)_3N$	e	Methanamine

Preparation of Amines

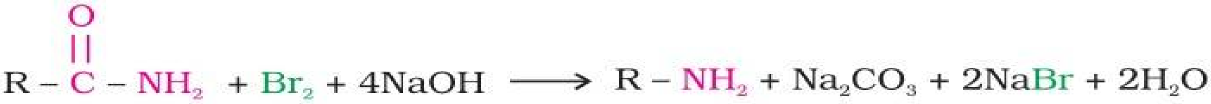
1. Reduction of nitriles: Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines. Used for preparation of amines containing one carbon atom more than the starting amine.

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

2. Reduction of amides: The amides on reduction with lithium aluminium hydride yield amines.

$$R-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiA1H_4} R-CH_2-NH_2$$

3. Hoffmann bromamide degradation reaction: This method is used for the conversion of an amide to a primary amine with one carbon atom less than that present in the amide. In this method, an amide is treated with Bromine and ethanolic solution of NaOH to give an amine



$$R-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Q.4

Complete the table

compound	reagent	product
RCN	H_2/Ni	-----------(i)---------------
R-CO-NH_2	$LiAlH_4$ and H_2O	---------- (ii)----------------

---------(iii)-------------	Br_2 and NaOH	$R-NH_2$

Q.5

Write chemical equations for the following conversions:
(i) CH_3-CH_2-Cl into $CH_3-CH_2-CH_2-NH_2$
(ii) $C_6H_5-CH_2-Cl$ into $C_6H_5-CH_2-CH_2-NH_2$

Q.6 Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.
(ii) the amine produced by the Hoffmann degradation of benzamide.

Chemical Reactions

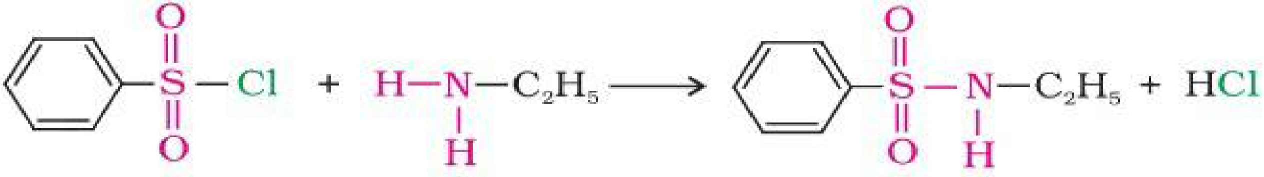
1. Carbylamine reaction : Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

2.Reaction with arylsulphonyl chloride [Hinsberg Test]: This test is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

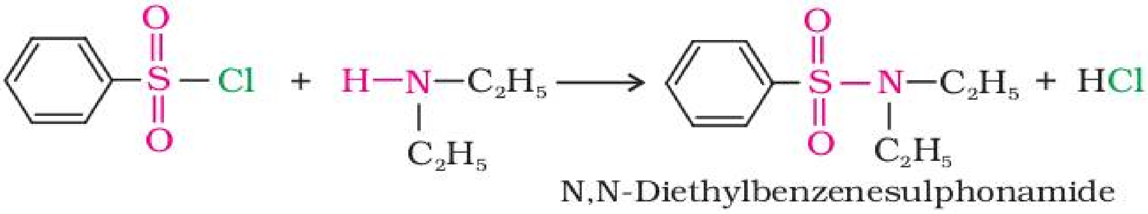
Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is known as Hinsberg's reagent.

(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide. It is strongly acidic and soluble in alkali



N-Ethylbenzenesulphonamide
(soluble in alkali)

(b) In the reaction with secondary amine, N,N-diethyl- benzenesulphonamide is formed. It is not acidic and hence insoluble in alkali.

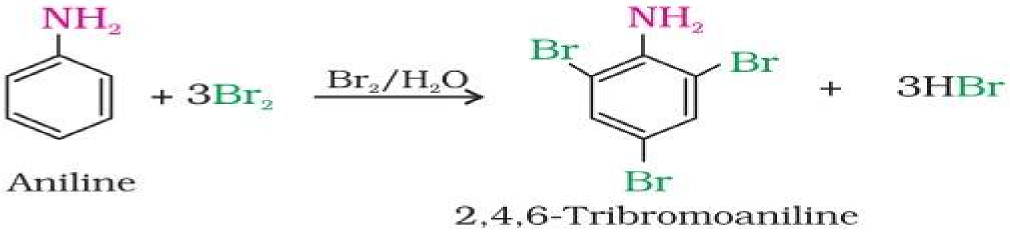


(c) Tertiary amines do not react with benzenesulphonyl chloride.

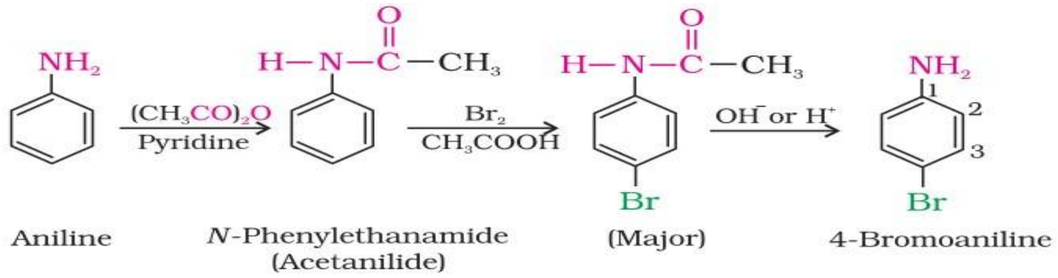
Q7. Describe a method for the identification of primary, secondary and tertiary amines.
Also write chemical equations of the reactions involved.

3. Electrophilic substitution : Ortho- and para-positions to the $–NH_2$ group become centres of high electron density. Thus $–NH_2$ group is ortho and para directing and a powerful activating group

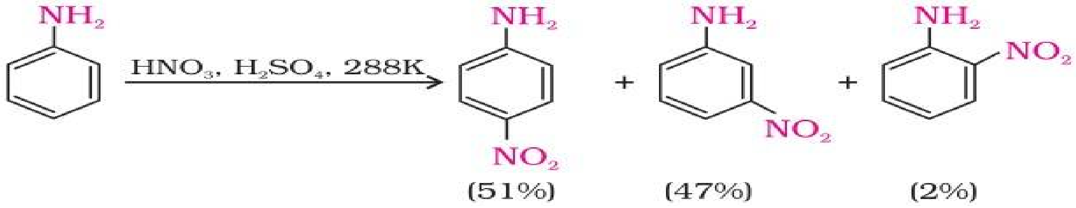
(a) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



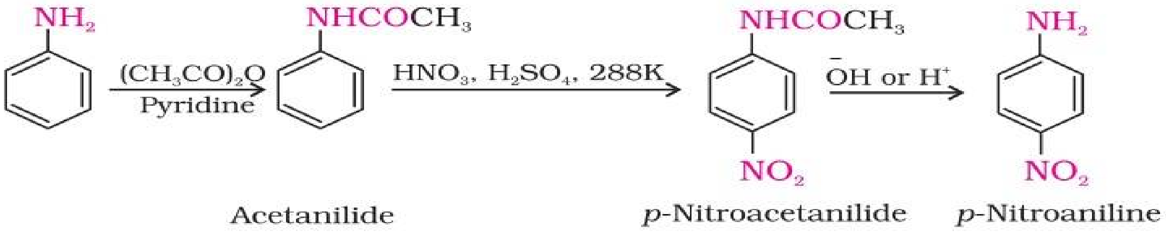
To prepare o-bromoaniline and p-bromoaniline, first reduce the activating power of $–NH_2$ group by protecting it through acetylation with acetyl chloride or acetic anhydride. Then the resulting acetanilide is brominated by Br_2 in acetic acid followed by hydrolysis, we get p-bromoaniline (4- bromoaniline) as the major product.



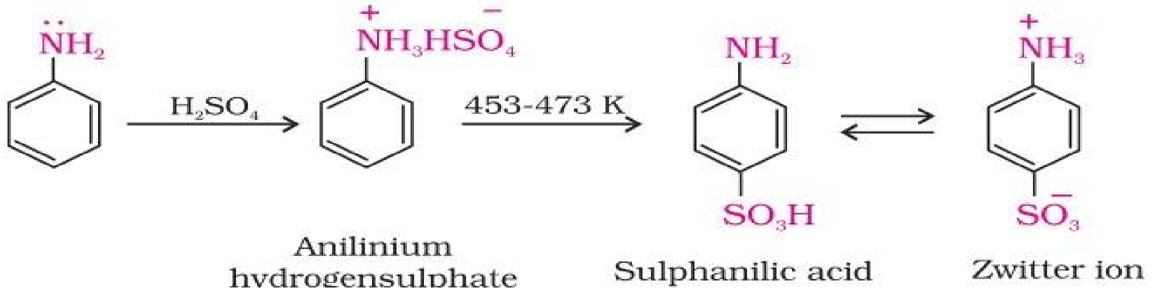
(b) Nitration: Direct nitration of aniline with conc. HNO_3 and conc. H_2SO_4 gives a mixture of ortho, meta and para nitroanilines and some tarry (tar-like) products.



In strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. So a large amount of meta-isomer is formed. For the preparation of p-nitroaniline, the $–NH_2$ group is first deactivated by acetylation. The acetanilide thus formed is nitrated followed by hydrolysed.



(c) Sulphonation: Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.

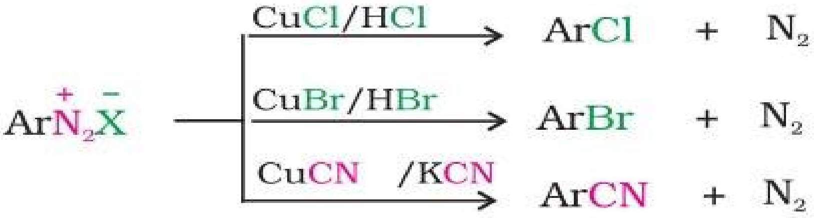


Aniline does not undergo Friedel-Crafts reaction (alkylation and acylation) since it form salt with anhydrous aluminium chloride, which is used as catalyst in the reaction.

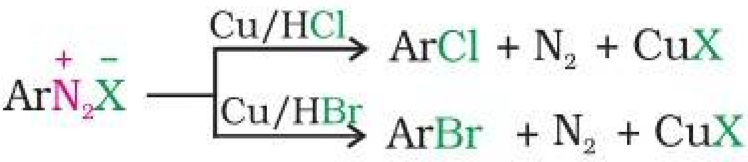
1

3.9 **Chemical Reactions of diazonium salts:**

1. Replacement by halide or cyanide ion: The Cl , Br and CN nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called **Sandmeyer reaction.**

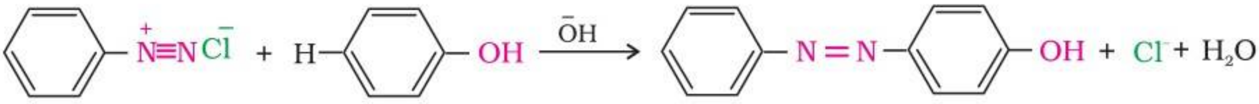


If cuprous halide is replaced by copper powder, the reaction is called **Gattemann's reaction**.

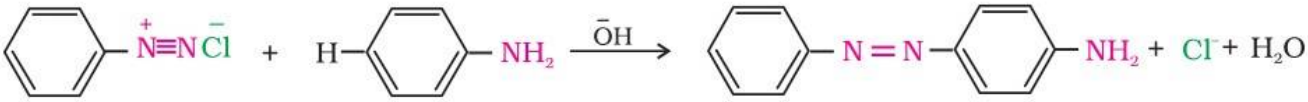


Reactions involving retention of diazo group coupling reactions:

When benzene diazonium chloride is treated with phenol or aniline, the para position of is coupled with the diazonium salt to form p-hydroxyazobenzene or p-aminoazobenzene. This type of reaction is known as coupling reaction.



p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene
(yellow dye)

Q8.Write short notes on the following:
(i) Carbylamine reaction
(ii) Diazotisation
(iii) Hofmann's bromamide reaction

(iv) Coupling reaction
(v) Sandmeyer reaction.

Q9. Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

Q10.An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write IUPAC names of compounds A, B and C.

SOLUTIONS TO AMINES

Q1.(i) 1° (ii) 3° (iii) 1° (iv) 2°

Q2.(I) ammonia, (ii) 3 (iii) 1

Q3.1- e, 2- a, 3- c, 4- b, 5- d

Q4.(i) RCH_2NH_2 (ii) RCH_2NH_2 (iii) $R\text{-}CO\text{-}NH_2$

Q5.

(i) $\underset{\text{Chloroethane}}{CH_3–CH_2–Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\text{Propanenitrile}}{CH_3–CH_2–C\equiv N} \xrightarrow{\text{reduction}} \underset{\text{Propan-1-amine}}{CH_3–CH_2–CH_2–NH_2}$

(ii) $\underset{\substack{\text{Chlorophenylmethane}\\ \text{(Benzyl chloride)}}}{C_6H_5–CH_2–Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\substack{\text{Phenylethanenitrile}\\ \text{(Benzyl cyanide)}}}{C_6H_5–CH_2–C\equiv N} \xrightarrow{H_2/Ni} \underset{\text{2-Phenylethanamine}}{C_6H_5–CH_2–CH_2–NH_2}$

Q6. (i) $CH_3CH_2CH_2CONH_2$ butanamide
(ii) $C_6H_5NH_2$ aniline or benzenamine

Q7. refer Hinsberg Test

Q8. refer notes given above

Q9. (i) A= CH_3CH_2CN B= $CH_3CH_2CONH_2$ C= $CH_3CH_2NH_2$
(ii) A=C_6H_5CN B= C_6H_5COOH C=$C_6H_5CONH_2$
(iii) A= CH_3CH_2CN B= $CH_3CH_2NH_2$ C=CH_3CH_2COOH
(iv) A=$C_6H_5NH_2$ B=$C_6H_5N_2Cl$ C=C_6H_5OH

Q10. A= BENZOIC ACID B= BENZAMIDE C=ANILINE

Unit.14

Biomolecules

Focus Area

14.1.1 Classification of carbohydrates
14.1.2 Monosaccharides (Preparation of glucose from sucrose)
14.1.3 Disaccharides (glycosidie linkage, invert sugar)
14.1.4 Sarch, glycogen
14.2.4 Denaturation of protein
14.5.1 Chemical composition of nucleic acids

The molecules present in living system like carbohydrates, proteins, nucleic acids, lipids, vitamins etc. which are essential for the growth and maintenance of our body are called Biomolecules.

Carbohydrates

These are the hydrates of carbon and most of them have a general formula $\mathbf{C_x(H_2O)_y}$. They can be defined as polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Some of the carbohydrates are crystalline, water soluble and sweet in taste. They are called sugars. Carbohydrates which are not crystalline, water insoluble and have no sweet taste are called non-sugars. Carbohydrates are also called ‘Saccharides’.

14.1.1 Classification of Carbohydrates.

(A) Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups.

1) Monosaccharides: These are carbohydrates which cannot be hydrolysed into simpler units of polyhydroxy aldehydes or ketones.

E.g. glucose, fructose, ribose, galactose etc.

2) Oligo saccharides: These are carbohydrates which give two to ten monosaccharide units on hydrolysis. They are further classified as disaccharides, tri saccharides, tetra saccharides etc.

E.g. Sucrose,maltose, lactose.

Sucrose on hydrolysis gives one molecule each of glucose and fructose, maltose gives two molecules of glucose while lactose gives one molecule each of glucose and galactose.

3) Polysaccharides: These are carbohydrates which give a large number of monosaccharide units on hydrolysis. E.g. starch, cellulose, glycogen etc.

Qn 1: What are monosaccharides?

Qn 2: Identify monosaccharides, oligo sacchrides, and polysaccharide from the following carbohydrates and give reason?

(a) galactose (b) maltose (c) cellulose

(B) Based on their reducing character:

Based on this, carbohydrates are of two types – reducing sugar and non-reducing sugar.

Carbohydrates which contain free aldehydic or ketonic groups (which reduce Fehling'ssolution and Tollens' reagent) are called **reducing sugars**, while those which do not contain free aldehydic or ketonic group are called **non-reducing sugars**. All monosaccharides are reducing sugars. Disaccharides like maltose and lactose are reducing while sucrose is non-reducing.

Qn 3: Disaccharides like maltose and lactose are reducing while sucrose is non-reducing. Give reason?

(C) Based on the functional group and no. of carbon atoms: A monosaccharide containing an aldehyde group is known as **aldose**, while a monosaccharide containing a ketonic group is known as **ketose**. Monosaccharides containing 3 carbon atoms are called **triose,** 4 carbon atoms are called **tetrose** etc.

14.1.2 Monosaccharides.

Preparation of glucose : From sucrose (Cane sugar): If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

$$\mathbf{C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6}$$

Qn 4: Write a short note on the preparation of glucose?

14.1.7 Disaccharides. disaccharides on hydrolysis with dilute acids or enzymes yield two molecules of either the same or different monosaccharides.

Glycosidic Linkage

During the formation of a disaccharide or polysaccharide, the monosaccharide units are joined together through C-O-C linkage. Such a linkage is called glycosidic linkage.

Invert Sugar

Cane sugar (sucrose) on hydrolysis gives an equimolar mixture of D(+)glucose and D(-)fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{D(+)Glucose } (+52.5^{o})}{C_6H_{12}O_6} + \underset{\text{D(-)Fructose } (-92.4^{o})}{C_6H_{12}O_6}$$

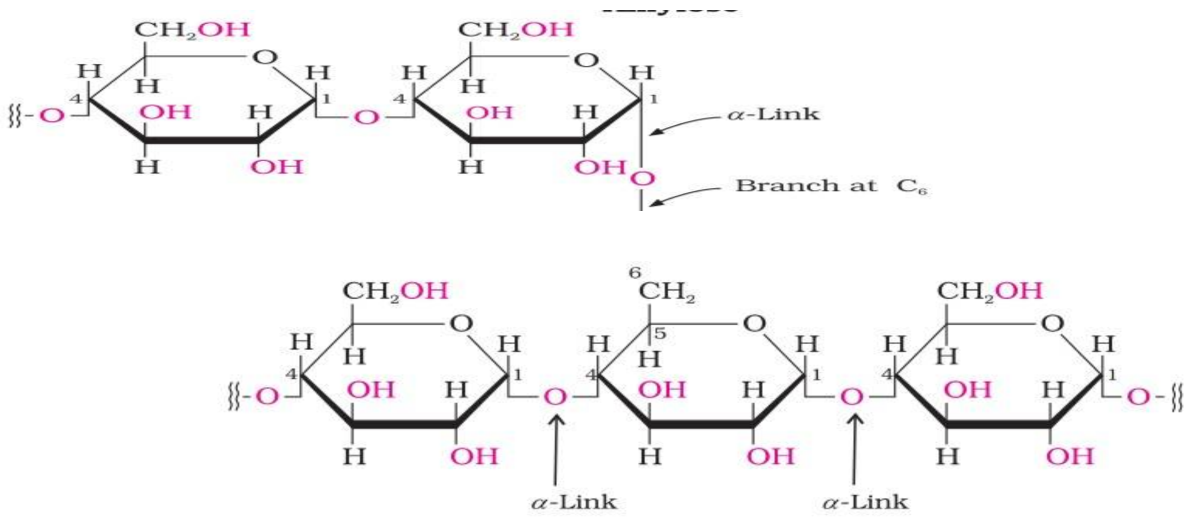
Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar.

Qn 5: What do you understand by the term glycosidic linkage?

Qn 6: Cane sugar (sucrose) on hydrolysis gives an equimolar mixture of D(+)glucose and D(-)fructose, it is known as invert sugar. Give reason ?

14.1.8 Polysaccharides

(i) Starch: Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of **α-glucose** and consists of two components— **Amylose and Amylopectin.** Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 **α-D-(+)-glucose** units held by **C1– C4 glycosidic linkage.** Amylopectin is insoluble in water and constitutes about 80- 85% of starch. It is a branched chain polymer of α-D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas
branching occurs by C1–C6 glycosidic linkage.



(ii) Glycogen: The carbohydrates are stored in animal body as glycogen. It is also known as animal starch because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

Qn 7: Write a short note on the glycosidic linkage present in the Starch?
Qn 8 : What is glycogen? How is it different from starch?

14.2.4 Denaturation of Proteins

They occur in every part of the body and form the fundamental basis of structure and functions of life. They are also required for growth and maintenance of body. The word protein is derived from Greek word, "proteios" which means primary or of prime importance. All proteins are polymers of α-amino acids.

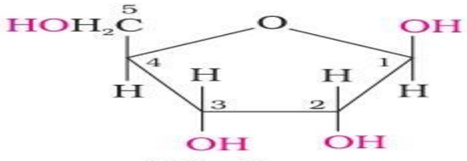
When a protein is subjected to physical change (like change in temperature) or chemical change (like change in pH), it loses the biological activities. This process is called denaturation of protein. During denaturation, primary structure of protein does not change, but secondary and tertiary structures are destroyed.

E.g. coagulation egg white on boiling, curding of milk etc.

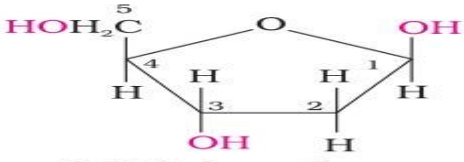
Qn 8 : What is the effect of denaturation on the structure of proteins?

14.5.1 Chemical Composition of Nucleic Acids

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is **β-D-2-deoxyribose** where as in RNA molecule, it is **β-D-ribose.**



β–D–ribose



β–D–2–deoxyribose

They are long chain polymers of nucleotides and are responsible for transmission of heredity. These are of two types – deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

Nucleic acid contains a pentose sugar, phosphoric acid unit and a nitrogen base. In DNA, the pentose sugar is β–D-2-deoxy ribose, while in RNA, it is β–D-ribose.

DNA contains 4 bases – Adenine (A), Guanine (G), Cytosine (C) and Thymine (T). [A, G, C &T].

RNA contains the bases Adenine (A), Guanine (G), Cytosine (C) and Uracil (U). [A, G, C & U]

The pentose sugar combines with the base to form nucleoside, which combines with the phosphoric acid group to form nucleotide. The nucleotide units combine to form nucleic acid.

Qn 9: Write the important structural differences between DNA and RNA.

DNA	RNA
1.	1.
2.	2.
3.	3.

ANSWERS

Qn1 : These are carbohydrates which cannot be hydrolysed into simpler units of polyhydroxy aldehydes or ketones. E.g. glucose, fructose.

Qn 2 : (a) Galactose ($C_6H_{12}O_6$)- Only one saccharide unit, so it is a monosaccharide.
(b) maltose ($(C_6H_{12}O_5)_2$)- on hydrolysis maltose gives two molecules of glucose, so it is a disaccharide .
(c) cellulose($(C_6H_{12}O_5)_n$)– On hydrolysis cellulose give a large number of monosaccharide units, so it is a polysaccharide.

Qn 3 : Carbohydrates which contain free aldehydic or ketonic groups (which reduce Fehling's solution and Tollens' reagent) are called **reducing sugars**, while those which do not contain free aldehydic or ketonic group are called **non-reducing sugars**. All monosaccharides are reducing sugars. Disaccharides like maltose and lactose are reducing while sucrose is non-reducing.

Qn 4 : From sucrose (Cane sugar): If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

$$\mathbf{C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6}$$

Qn 5 : During the formation of a disaccharide or polysaccharide, the monosaccharide units are joined together through C-O-C linkage. Such a linkage is called glycosidic linkage.

Qn 6 : Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose D(+)Glucose (+52.5°) D(-)Fructose (-92.4°)

Qn 7 : It is a polymer of **α-glucose** and consists of two components— **Amylose and Amylopectin.**

Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 **α-D-(+)-glucose** units held by **C1– C4 glycosidic linkage.** Amylopectin is insoluble in water and constitutes about 80- 85% of starch.

It is a branched chain polymer of α-D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.

Qn 8 : During denaturation, primary structure of protein does not change, but secondary and tertiary structures are destroyed.

Qn 9 :

DNA	RNA
1.DNA is double stranded	1.RNA is single stranded
2. The pentose sugar is deoxy ribose	2. The pentose sugar is ribose
3. DNA contains 4 bases – Adenine (A), Guanine (G), Cytosine (C) and Thymine (T). [A, G, C &T],	3. RNA contains the bases Adenine (A), Guanine (G), Cytosine (C) and Uracil (U). [A, G, C & U]

Unit. 15

POLYMERS

FOCUS AREA

15.1 **Classification of polymers** .

Addition and condensation polymers

(Teflon, Nylon – 6,6, Nylon – 6, PVC, Polystyrene, Polyethene)

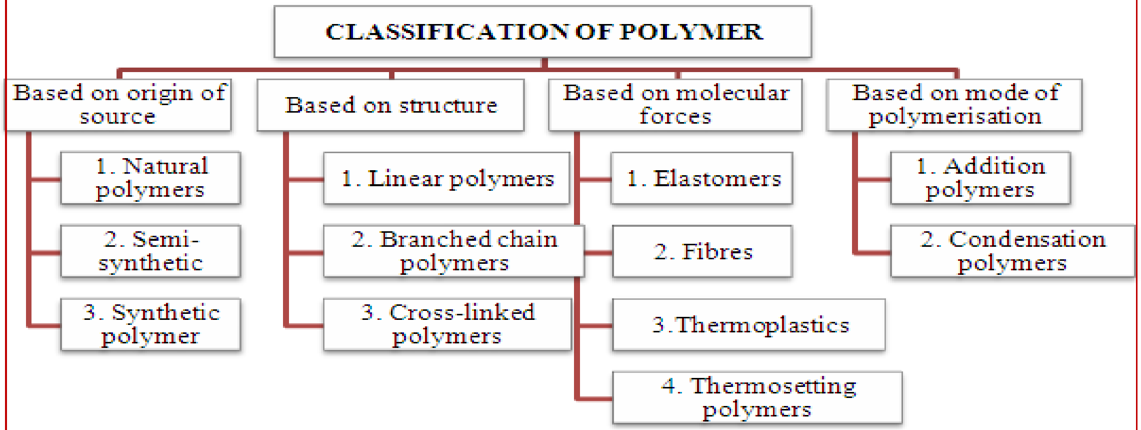
15.2.4 **Rubber** (Natural rubber, Vulcanisation)

15.4 **Biodegradable polymers**

Polymerisation:- The process of formation of polymers from their monomers.

Q. 1. What is polymerisation?

Classification of polymers



Classification based on source

1. **Natural polymers:** These polymers are found in plants and animals**.**

Eg: Proteins, cellulose, starch, resins and rubber.

2.**Semi-synthetic polymers.**

Eg: Cellulose acetate (rayon) and cellulose nitrate.

3. **Synthetic polymers:** Man-made polymers extensively used in daily life

Eg: Plastic (Polythene), Synthetic fibres (Nylon 6,6), Synthetic rubbers (Buna - S)

Classification based on mode of polymerisation

Addition polymers:- Polymers formed by the repeated addition of monomer molecules possessing double or triple bonds.

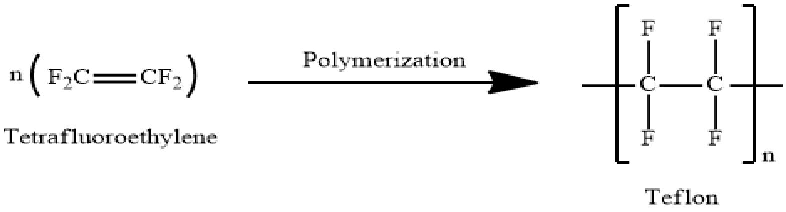
Eg: Teflon, Polyethene, Polystyrene, Buna-N, etc.

Two types –

Homopolymers	Copolymers
Addition polymers formed by the polymerisation of a single monomeric species.	Addition polymers formed by the polymerisation of two different monomeric species.
Eg: Polythene, Polystyrene etc.	Eg: Buna-S, Buna-N, etc.

Teflon is an addition homopolymer of tetrafluoroethene (tetrafluoroethylene).

Uses: (1) Used for non – stick surface coated utensils. (2) used in making oil seals.



Q. 2. (a) What is Teflon?
(b) Mention any two uses of it.

Q. 3. Name the polymer used for making non – stick surface coated utensils.

Polyethene: an addition homopolymer of ethene.

(i) Low density polythene: It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator. Used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

(ii) High density polythene: It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

Polystyrene is an addition homopolymer of styrene.

Uses: (1) Used as electrical insulator, wrapping material.
(2) Manufacture of toys, radio and TV cabinets etc.

Q. 4. Addition polymerisation is used for the production of important polymers.
(a) Give one example for the addition polymer.
(b) What are the two types of addition polymers? Explain with an example.

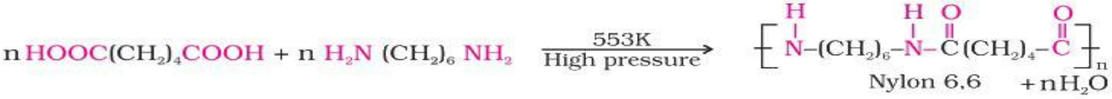
2. **Condensation polymers:-** Polymers formed by the repeated condensation reaction between two different bi-functional or poly functional monomeric units.

Eg: Terylene (Dacron), nylon 6, 6, nylon 6, etc.

Terylene is formed by the condensation polymerisation of terephthalic acid with ethylene glycol.

Uses: (1) Manufacture of fabrics
(2) Manufacture of tyre cords, seat belts etc.

Nylon 6, 6 is formed by the condensation polymerisation of hexamethylene diamine with adipic acid.

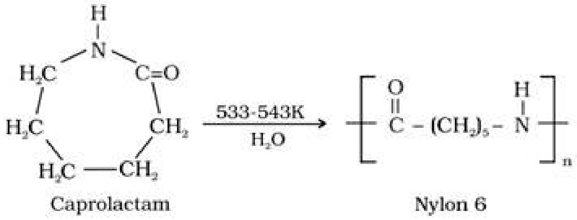


$$n\,HOOC(CH_2)_4COOH + n\,H_2N\,(CH_2)_6\,NH_2 \xrightarrow[\text{High pressure}]{553K} \left[\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n + nH_2O$$

Nylon 6,6

(1) Used in textile industry
(2) Used in making sheets, bristles for brushes etc.

Nylon 6 is formed by the condensation polymerisation of caprolactam.



Uses: (1) Manufacture of tyre cords

(2) Manufacture of fabrics, ropes etc.

Q. 5. What is the monomeric repeating unit of nylon – 6.

Q. 6. Name the polymer used for the manufacture of tyre cords.

Q. 7. How are polymers classified on the basis of polymerisation reaction?

Rubber: Rubber is a natural polymer and possesses elastic properties.

Natural rubber:- It is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as *c*is-1,4-polyisoprene.

The *cis*-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

In rubber molecules, all the double bonds have cis configuration so the chains are not able to come close enough for effective attraction. Hence rubber does not exist as straight chain but has a coiled structure.

Presence of double bond makes rubber reactive. It also has a large capacity to absorb water.

Vulcanisation of rubber:- Heating of natural rubber with sulphur and an appropriate additive to improve its physical properties is called vulcanisation. During vulcanisation sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.

Q. 8. Name the monomer of natural rubber.

Q. 9. Natural rubber obtained from rubber latex is soft and sticky.

(a) Suggest a method to improve the stiffness of rubber.

(b) Explain the above method.

Biodegradable polymers

Polymers that can be broken into small segments by enzyme catalysed reaction.

1. Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV):-

It biodegradable copolymer of 3-hydroxybutanoic acid and 3 - hydroxypentanoic acid.

PHBV undergoes bacterial degradation in the environment.

Uses: (1) Used in specialty packaging

(2) Used in orthopaedic devices and in controlled release of drugs.

2. Nylon 2 – nylon 6:-

It biodegradable copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid [$H_2N–(CH_2)_5–COOH$]

Uses: (1) Used as thread in bristles for toothbrushes.

(2) Making strings of musical instruments.

Q. 10. What are biodegradable polymers? Write an example.

Q. 11. Match the following :

(i) Polytetrafluoroethene	(a) Terylene
(ii) Cis -1,4 - polyisoprene	(b) Teflon
(iii) Ethylene glycol - Terephthalic acid	(c) Natural rubber

ANSWERS

1. The process of formation of polymers from their monomers.
2. (a) An addition homopolymer of tetrafluoroethene (tetrafluoroethylene) is called teflon.
   (b) (1) Used for non – stick surface coated utensils. (2) used in making oil seals.
3. Teflon
4. (a) Polyethene.
   (b)

Homopolymers	**Copolymers**
Addition polymers formed by the polymerisation of a single monomeric species.	Addition polymers formed by the polymerisation of two different monomeric species.
Eg: Polythene, Polystyrene etc.	Eg: Buna-S, Buna-N, etc.

5. Caprolactam
6. Nylon – 6
7.

Addition polymers	**Condensation polymers**
Polymers formed by the repeated addition of monomer molecules possessing double or triple bonds.	Polymers formed by the repeated condensation reaction between two different bi-functional or poly functional monomeric units.
Eg: Teflon, Polyethene, Polystyrene, Buna-N, etc.	Eg: Terylene (Dacron), nylon 6, 6, nylon 6, etc.

8. Isoprene (2-methyl-1, 3-butadiene).

9. (a) Vulcanisation
   (b) Heating of natural rubber with sulphur and an appropriate additive to improve its physical properties is called vulcanistion. During vulcanisation sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.
10. Polymers that can be broken into small segments by enzyme catalysed reaction.
    Eg: Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV)
11.

(i) Polytetrafluoroethene	(b) Teflon
(ii) cis -1,4 - polyisoprene	(c) Natural rubber
(iii) Ethylene glycol - Terephthalic acid	(a) Terylene

Unit. 16

CHEMISTRY IN EVERYDAY LIFE

FOCUS AREA

16.3.1 Antacid
16.3.3 Neurologically active drug
16.3.4 Anti microbials (antiseptics, disinfectants)

Antacid

Drug used to the pH of stomach. Over production of acid in the stomach causes irritation and pain.

Eg. Ranitidine, Sodium hydrogen carbonate or a mixture of aluminium and magnesium hydroxide. Metal hydroxides are better alternatives because of being insoluble; these do not increase the pH above neutrality.

Q. 1. What is antacid? Give examples.

Neurologically active drug

Used for the treatment of stress and mental diseases.

Eg. Tranquilizers and analgesics are neurologically active drugs.

Tranquilizers: are drugs used for the treatment of stress and mental diseases. They form an essential component of sleeping pills.

Eg. Valium and serotonin.

Chlordiazepoxide and meprobamate are suitable for relieving tension.

Equanil is used in controlling depression and hypertension.

Derivatives of barbituric acid are important class of tranquilizers.

Q. 2. What are tranquilizers? Give examples.

Analgesics: Drug acting to relieve pain. Eg. Aspirin

Two types:

(i) Non-narcotic (non-addictive) analgesics: Eg. Aspirin and paracetamol.
(ii) Narcotic (addictive) analgesics: Eg. Morphine, heroin, codeine.

Q. 3. What are analgesics? How are they classified? Give examples.

Anti microbials

Antiseptics and Disinfectants:

Drug used to kill or prevent the growth of microorganisms.

Antiseptics	Disinfectants
Chemicals which kill or prevent the growth of microorganisms and can be applied to tissues	Chemicals which kill or prevent the growth of microorganisms and cannot be applied to tissues
Applicable to wounds, cuts etc.	Applicable to floors, drainage system etc.
Eg. 0.2 % solution of phenol, dettol, Furacine	Eg. 1 % solution of phenol, sulphur dioxide

Some antiseptic in use:

Dettol: A mixture of chloroxylenol and terpineol.

Bithionol: Compound added to soaps to impart antiseptic properties.

Tincture of iodine: An alcohol – water mixture containing 2 – 3 % iodine.

Phenol is used both as antiseptic and disinfectant.

Q.4. What is the difference between antiseptics and disinfectants?

Q.5. What is dettol? What is its use?

Q. 6. What is tincture of iodine? What is its use?

Q. 7. Give the name of a substance which can act both as antiseptics as well as disinfectant.

(Phenol. 0.2 % solution of phenol is a antiseptics while 1 % solution of phenol is a disinfectant)

Q. 8. Match the following:

Column I	Column II
(i) Antacid	(a) 1% phenol
(ii) Antibiotic	(b) 0.2 % phenol
(iii) Antiseptics	(c) Aspirin
(iv) Disinfectant	(d) Tetracycline
	(e) Ranitidine

ANSWERS

1. Drugs used to neutralize gastric acids are called antacid.

   Eg. Ranitidine, Sodium hydrogen carbonate etc.

2. Drug drugs used for the treatment of stress and mental diseases are called tranquilizers.

   Eg. Valium and serotonin etc.

3. Drugs acting to relieve pain are called analgesics.

   Eg. Aspirin

   Two types:

   (i) Non-narcotic (non-addictive) analgesics: Eg. Aspirin and paracetamol, etc.

   (ii) Narcotic (addictive) analgesics: Eg. Morphine, heroin, codeine, etc.

4.

Antiseptics	**Disinfectants**
Chemicals which kill or prevent the growth of microorganisms and can be applied to tissues	Chemicals which kill or prevent the growth of microorganisms and cannot be applied to tissues
Applicable to wounds, cuts etc.	Applicable to floors, drainage system etc.
Eg. 0.2 % solution of phenol, dettol, Furacine	Eg. 1 % solution of phenol, sulphur dioxide

5. A mixture of chloroxylenol and terpineol is called dettol. It is used as an antiseptic.
6. An alcohol – water mixture containing 2 – 3 % iodine is called tincture of iodine. It is used as an antiseptic
7. Phenol
8. (i) - (e), (ii) - (d), (iii) - (b), (iv) - (a)

GENERAL EDUCATION DEPARTMENT

[redacted]