CHEMISTRY WORK BOOK
CLASS - XII

State Council of Educational Research and Training
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CHEMISTRY WORK BOOK

Class - XII

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রতন লাল নাথ
মন্ত্রী
শিক্ষা দপ্তর
ত্রিপুরা সরকার

বার্তা

শিক্ষার প্রকৃত বিকাশের জন্য, শিক্ষাকে যুগোপযোগী করে তোলার জন্য প্রয়োজন শিক্ষাসংক্রান্ত নিরন্তর গবেষণা। প্রয়োজন শিক্ষা সংশ্লিষ্ট সকলকে সময়ের সঙ্গে সঙ্গে প্রশিক্ষিত করা এবং প্রয়োজনীয় শিখন সামগ্রী, পাঠ্যক্রম ও পাঠ্যপুস্তকের বিকাশ সাধন করা। এস সি ই আর টি ত্রিপুরা রাজ্যের শিক্ষার বিকাশে এসব কাজ সুনামের সঙ্গে করে আসছে। শিক্ষার্থীর মানসিক, বৌদ্ধিক ও সামাজিক বিকাশের জন্য এস সি ই আর টি পাঠ্যক্রমকে আরো বিজ্ঞানসম্মত, নান্দনিক এবং কার্যকর করবার কাজ করে চলেছে। করা হচ্ছে সুনির্দিষ্ট পরিকল্পনার অধীনে।

এই পরিকল্পনার আওতায় পাঠ্যক্রম ও পাঠ্যপুস্তকের পাশাপাশি শিশুদের শিখন সক্ষমতা বৃদ্ধির জন্য তৈরি করা হয়েছে ওয়ার্ক বুক বা অনুশীলন পুস্তক। প্রসঙ্গত উল্লেখ্য, ছাত্র-ছাত্রীদের সমস্যার সমাধানকে সহজতর করার লক্ষ্যে এবং তাদের শিখনকে আরো সহজ ও সাবলীল করার জন্য রাজ্য সরকার একটি উদ্যোগ গ্রহণ করেছে, যার নাম ‘প্রয়াস’। এই প্রকল্পের অধীনে এস সি ই আর টি এবং জেলা শিক্ষা আধিকারিকরা বিশিষ্ট শিক্ষকদের সহায়তা গ্রহণের মাধ্যমে প্রথম থেকে দ্বাদশ শ্রেণির ছাত্র-ছাত্রীদের জন্য ওয়ার্ক বুকগুলো সুচারুভাবে তৈরি করেছেন। ষষ্ঠ থেকে অষ্টম শ্রেণি পর্যন্ত বিজ্ঞান, গণিত, ইংরেজি, বাংলা ও সমাজবিদ্যার ওয়ার্ক বুক তৈরি হয়েছে। নবম দশম শ্রেণির জন্য হয়েছে গণিত, বিজ্ঞান, সমাজবিদ্যা, ইংরেজি ও বাংলা। একাদশ দ্বাদশ শ্রেণির ছাত্র-ছাত্রীদের জন্য ইংরেজি, বাংলা, হিসাবশাস্ত্র, পদার্থবিদ্যা, রসায়নবিদ্যা, অর্থনীতি এবং গণিত ইত্যাদি বিষয়ের জন্য তৈরি হয়েছে ওয়ার্ক বুক। এইসব ওয়ার্ক বুকের সাহায্যে ছাত্র-ছাত্রীরা জ্ঞানমূলক বিভিন্ন কার্য সম্পাদন করতে পারবে এবং তাদের চিন্তা প্রক্রিয়ার যে স্বাভাবিক ছন্দ রয়েছে, তাকে ব্যবহার করে বিভিন্ন সমস্যার সমাধান করতে পারবে। বাংলা ও ইংরেজি উভয় ভাষায় লিখিত এইসব অনুশীলন পুস্তক ছাত্র-ছাত্রীদের মধ্যে বিনামূল্যে বিতরণ করা হবে।

এই উদ্যোগে সকল শিক্ষার্থী অতিশয় উপকৃত হবে। আমার বিশ্বাস, আমাদের সকলের সক্রিয় এবং নিরলস অংশগ্রহণের মাধ্যমে ত্রিপুরার শিক্ষাজগতে একটি নতুন দিগন্তের উন্মেষ ঘটবে। ব্যক্তিগত ভাবে আমি চাই যথাযথ জ্ঞানের সঙ্গে সঙ্গে শিক্ষার্থীর সামগ্রিক বিকাশ ঘটুক এবং তার আলো রাজ্যের প্রতিটি কোণে ছড়িয়ে পড়ুক।

(রতন লাল নাথ)

CONTRIBUTORS & PROOF CHECKING :

Sri Saibal Roy, Teacher.
Sri Gautam Roy Barman, Teacher.
Sri Biswajit Chowdhury, Teacher.
Smt. Sila Gan Chaudhuri, Teacher.

Content

Chapter - 1

The Solid State

Chapter at a glance :

1) The solid state, the particles are closely packed and are held together by strong intermolecular attractive force.

2) Solids are with –

   a) Definite shape and volume.

   b) High density and low compressibility.

   c) With less vapour pressure.

3) Types of solids depending on three demension arrangement :-

Crystalline solids	Amorphous solids
(i) Solids with ordered arrangement of particles in three dimension.	(i) Solids with irregular arrangement of particles without any shape.
(ii) They are true solids.	(ii) They are pseudo solids or super cooled liquids.
(iii) They have long range order.	(iii) They have short range order only.
(iv) They are anisotropic in nature.	(iv) They are isotropic in nature.
(v) They melt at a sharp and characteristic temperature.	(v) They gradually soften over a range of temperature.

4) Types of Solids depending on bonding :-

Types of solid	Particles	Bonding/Attractive forces	Example
Ionic	Ions	Coulombic or electrostatic	NaCl, MgO, KCl
Covalent	Atoms	Covalent bonding	SiC, SiO_2
Metallic	Positive ions in a Sea of delocalised electrons	Metallic bonding	Ag, Cu
Molecular	Molecules	1.Dispersion	Ar
		2.Dipole - Dipole interaction	HCl
		3. H - bonding	H_2O(ice)

5) Space lattice or crystal lattice :

A regular three dimensional arrangement of particles in space is called space lattice or crystal lattice.

There are only 14 possible three dimensional lattices. These are called Bravais lattices.

6) Unit cell :

Unit cell is the smallest unit of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterised by :

(a) its dimensions along the three edges ('a', 'b' and 'c'). These edges may or may not be mutually perpendicular.

(b) angels between the edges (α, β, γ). Thus, a unit cell is characterised by six parameters (a, b, c, α, β, γ).

7) Crystal system :

On the basis of geometrical consideration, there are seven primitive unit cells –

Crystal system	Edge lengths	Axial angels	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	KCl
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Hgs
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	SnO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$CaCO_3$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	$PbCrO_2$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma \neq 120°$	ZnO
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$

8) Cubic crystal system :

For cubic crystal system, there are three types of Bravais lattices (simple cubic, body centred cubic and face centred cubic)

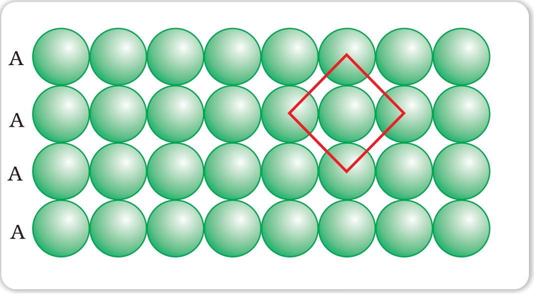
Type of cell	Number of atoms at corner	Number of atoms at faces	Number of atoms in centre of cube	Total atoms
Primitive cubic (Sc)	$\frac{1}{8} \times 8 = 1$	–	–	1
Body centred cubic (Bcc)	$\frac{1}{8} \times 8 = 1$	–	1	2
Face centred cubic (Fcc)	$\frac{1}{8} \times 8 = 1$	$\frac{1}{2} \times 6 = 3$	–	4

9) Close packing of particles in two dimensions :-

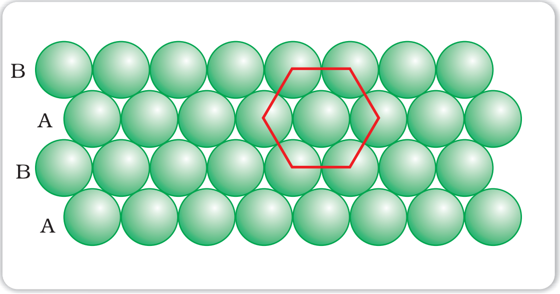
This type of close packing can be generated by stacking the rows of close packed spheres. This can be done in two different ways –

(a) Square close packing (SCP)

(b) Hexagonal close packing (HCP)



(a)



(b)

10) Close packing of particles in three dimensions :-

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other.

(i) Three dimensional close packing from two dimensional square close packed layers – This type of lattice has AAA .... type pattern. Its unit cell is the primitive cubic unit cell or simple cubic unit cell.

(ii) Three dimensional close packing from two dimensional hexagonal close packed layres – This type of lattice has AB AB AB ...... type pattern whose unit cell is hcp and ABC ABC ABC ..... type pattern whose unit cell is CCP or fcc.

11) Voids : In close packed arrangement, some space or holes are created amongst the sphere (atom). Two types of voids are present in the crystal.

(a) **Octahedral void** - Radius of octahedral void (Ro) = 0.414 R

(b) **Tetrahedral void** - Radius of tetrahedral void (Rt) = 0.225 R

12. (i) **Number of octahedral voids per unit cell** = Z

(ii) Number of tetrahedral voids per unit cell = 2Z

(Where Z = No. of atoms per unit cell)

(iii) Number of voids of Fcc (CCP) = 3Z = 3 × 4 = 12

Octahedral void (Z) = 4

Tetrahedral void = 2Z = 2 × 4 = 8

(iv) In Fcc, Octahedral voids are located at the centre of edges (3) and one at the body centre of unit cell.

(v) In Fcc, all tetrahedral voids are within the unit cell, two on each body diagonal, each tetrahedral void is at a distance of $\frac{\sqrt{3a}}{4}$ from the corner (a = edge length).

13) Relation between edge length (a), radius (r) and nearest neighbour distance(d) :

(i) Simple cubic structure (SC) :-

$a = 2r = d$

(ii) Body centred cubic (Bcc) structure :

$a = \frac{4r}{\sqrt{3}}$, $d = 2r = \frac{\sqrt{3}}{2} \times a$

(iii) Face centred cubic (Fcc) structure :

$a = 2\sqrt{2}\, r$

$d = 2r = \frac{a}{\sqrt{2}}$

14) Packing efficiency for cubic crystal system :

$$\text{Packing Efficiency (P.E)} = \frac{z \times \text{volume of sphere}}{\text{volume of the unit cell}} \times 100\%$$

Volume of unit cell = a^3 (where, a = edge length)

volume of sphere = $\frac{4}{3}\pi r^3$

(i) P.E of simple cubic (SC) structure = 52.4% (P.E=Packing Efficiency)

voids of simple cubic (SC) structure = 47.6%

(ii) P.E of BCC structure = 68%

voids of BCC structure = 32%

(iii) P.E of FCC (CCP) and hcp structure = 74%

Voids of Fcc (CCP) and hcp structure = 26%

15) CCP and hcp are highly efficient and 74% space of the crystal is occupied by atoms and only 26% space remain voids. In either of them (ccp and hcp), each sphere is in contact with twelve spheres. Thus, the Co-ordination number = 12.

16) **Density of Crystal :**

$$\text{Density } (\rho) = \frac{Mass\ of\ unit\ cell}{Volume\ of\ unit\ cell}$$

$$\Rightarrow \qquad \rho = \frac{Z \times M}{a^3 \times N_A}$$

Where, Z = number of atoms per unit cell

M = Molar Mass

N_A = Avogadro's number

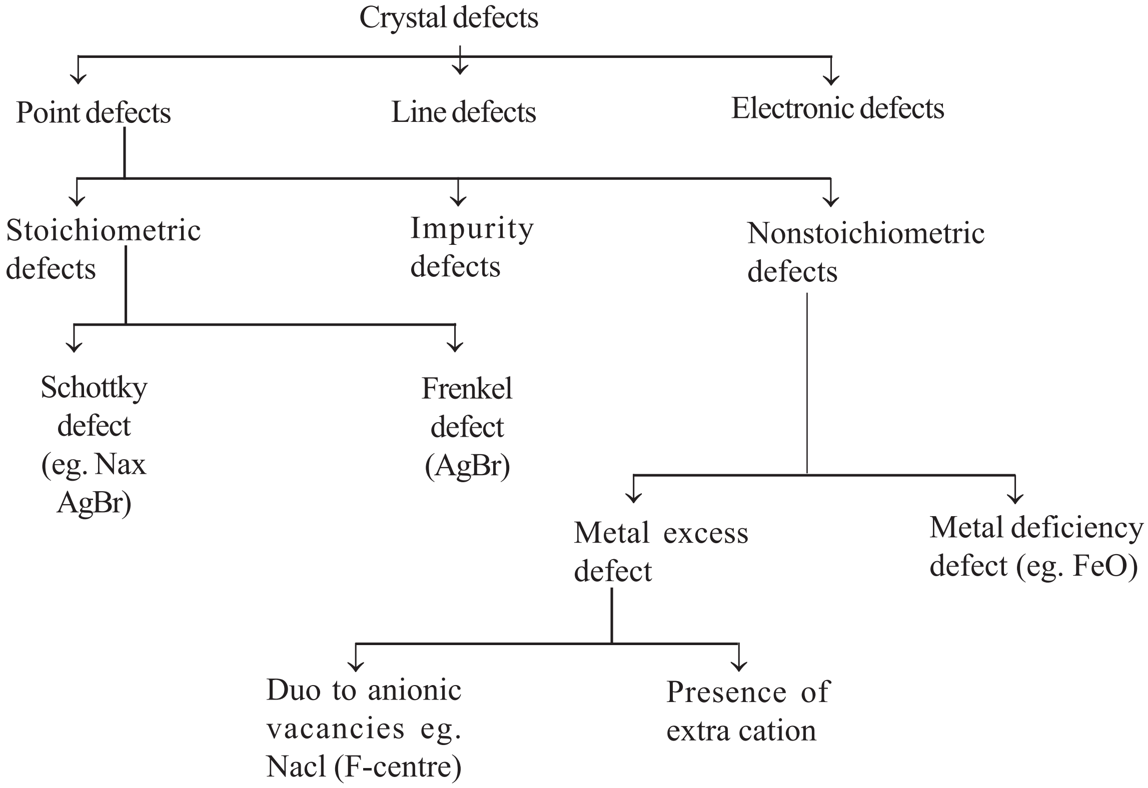
a = Edge length (in cm)

17) **Radius ratio** $\left(\frac{r_+}{r_-}\right) = \frac{Radius\ of\ Cation}{Radius\ of\ Anion}$

$\frac{r_+}{r_-}$	Geometry	Co-ordination number	Example
0.155 – 0.225	Triangular planer	3	B_2O_3
0.255 – 0.414	Tetrahedral	4	ZnS
0.414 – 0.732	Octahedral	6	NaCl
0.732 – 1	Cubic	8	CsCl

18) Imperfection in solids :

Deviation from ideal arrangement of particles is known as imperfection (defects).



19) Electrical properties of solids :

Solids exhibit an amazing range of electrical conductivities. On the basis of conductivity, solids are classified as conductors, semi conductors, and insulators.

Conductors : Conductivities ranging between ($10^4 \rightarrow 10^7$) $ohm^{-1}\ m^{-1}$

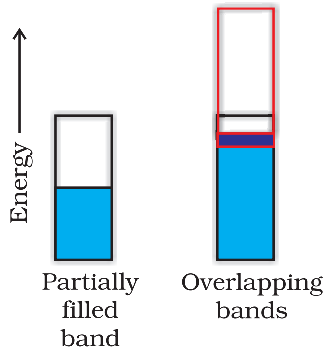
Insulators : Conductivities ranging between ($10^{-20} \rightarrow 10^{-10}$) $ohm^{-1}\ m^{-1}$

Semiconductors : Conductivities ranging between ($10^{-6} \rightarrow 10^4$) $ohm^{-1}\ m^{-1}$

20) Mechanism of electrical conductor :

The atomic orbitals of atoms form molecular orbitals which together forms a band. Outermost filled energy band is valence band and next empty band in which electrons can move is called conductor band.

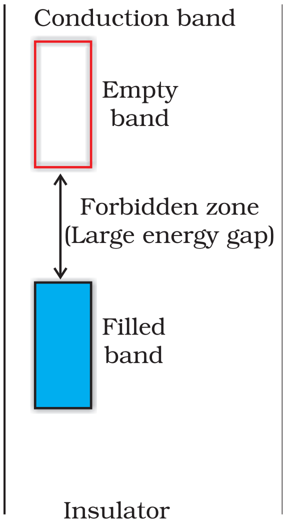
(i) In case of conductors (metal), valence band and conductor band overlaps that allow the electrons to flow through the material with minimal applied voltage.



Metal

(a)

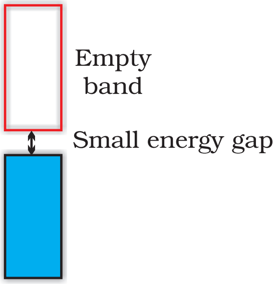
(ii) In case of insulators, the band gap between the valence band and the conduction band is so large that electrons can not jump from valence band to the conduction band.



Insulator

(b)

(iii) In case of semi conductors, the band gap between the valence band and the conduction band is small. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.



Semiconductor

(c)

21) Extrinsic semi conductor are of two types :

(a) n – type semi conductors :

Silicon + group 15 element

(b) p – type semi conductors :

Silicon + group 13 element

22) Magnetic properties of solids :

(Solids show magnetic properties due to magnetic moment (orbital and spin) of electron.)

(a) Paramagnetic -: They are weakly attracted by the magnetic fields. They contain atleast one unpaired electron in the orbital. $\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}$

(b) Diamagnetic -: They are weakly repelled by the magnetic fields. All the electrons in the orbitals are paired and are completely filled. $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

(c) Ferromagnetic -: They are strongly attracted by the magnetic field. They can be magnetised permanently. $\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}$

(d) Anti – ferromagnetic -: Their net magnetic moments is zero. Their dipole moments are arranged in compensatory way. $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

(e) Ferrimagnetic -: They possess small magnetic moments. They have unequal number of parallel and anti–parallel arrangements of magnetic moments. $\boxed{\uparrow}\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}\boxed{\downarrow}$

A. MCQ type questions :

Choose the correct answer : (Marks -1)

1. The number of atoms present in each unit cell of a fcc crystal is –

(a) 6 (b) 8 (c) 4 (d) 2

2. In a face - centred cubic unit cell, edge length is –

(a) $\frac{4}{\sqrt{3}}r$ (b) $\frac{4}{\sqrt{2}}r$ (c) 2r (d) $\frac{\sqrt{3}}{2}r$

3. Which of the following is correct for sodium chloride unit cell ?

(a) $r_+ + r_- = a$ (b) $r_+ + r_- = a/2$ (c) $r_+ + r_- = 2a$ (d) $r_+ + r_- = \sqrt{2}a$

4. Due to Frenkel defect, the density of ionic solids –

(a) decreases (b) increases (c) does not change (d) None of these

5. Schottky defect in crystals is observed when –

(a) equal number of cations and anions are missing from the lattice.

(b) unequal number of cations and anions are missing from the lattice.

(c) anion leaves its normal site and occupies an interstitial site.

(d) density of the crystal is increased.

6. Which of the following crystals does not exhibit Frenkel defect ?

(a) AgCl (b) AgBr (c) KBr (d) ZnS

7. In a face centred cubic cell, the contribution of an atom at a face of the unit cell is –

(a) $\frac{1}{2}$ (b) 1 (c) 2 (d) 3

8. Percentage of free space in a body centred cubic unit cell is –

(a) 34% (b) 28% (c) 30% (d) 32%

9. With which one of the following elements silicon should be doped to give p-type semiconductor?

(a) Selenium (b) Boron (c) Germanium (d) Arsenic

10. The appearance of colour in solid alkali metal halides is generally due to –

(a) Schottky defect (b) Frenkel defect

(c) Interstitial position (d) F - centres

11. The number of octahedral voids per atom present in a cubic close packed structure is –

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

12. In calcium fluoride (CaF_2), the Co-ordination numbers for Ca^{2+} ion and F^- ion are –

(a) 4 and 2 (b) 6 and 6 (c) 8 and 4 (d) 4 and 8

13. The correct order of packing efficiency in different types of unit cell is –

(a) fcc > bcc > simple cubic (b) fcc > bcc > simple cubic

(c) fcc > bcc > simple cubic (d) bcc > fcc > simple cubic

14. What is the co-ordination number in a square close packed structure in two dimensions ?

(a) 2 (b) 3 (c) 4 (d) 6

15. Which crystal system has $a \neq b \neq c, \alpha = \beta = \gamma = 90°$

(a) Cubic (b) Orthorhombic (c) Hexagonal (d) Triclinic

16. The packing fraction for a body centred cube is –

(a) 0.54 (b) 0.68 (c) 0.74 (d) 0.42

17. The white ZnO turns yellow on heating because of –

(a) Schottky defect (b) Frenkel defect

(c) Metal deficiency defect (d) Metal excess defect

18. Which of the following compound exhibits both Schottky and Frenkel defects ?

(a) NaCl (b) AgCl (c) AgI (d) AgBr

19. The Co-ordination numbers of Na^+ ion and Cl^- ion in NaCl crystal are –

(a) 6, 8 (b) 6, 6 (c) 8, 6 (d) 4, 6

20. Iodine molecules are held in the crystals by –

(a) London forces (b) Coulombic forces

(c) Covalent bonds (d) dipole - dipole interactions

21. Which of the following is not the characteristic of ionic solids ?

(a) Very low value of electrical conductivity in the molten state.

(b) Brittle nature

(c) Very strong forces of attraction

(d) Anisotropic nature

22. The edge length of the unit cells in terms of the radius of spheres constituting fcc, bcc and simple cubic unit cell are respectively –

(a) $2\sqrt{2}\,r, \frac{4r}{\sqrt{3}}, 2r$ (b) $\frac{4\pi}{\sqrt{3}}, 2\sqrt{2}\,\pi, 2\pi$

(c) $2\pi, 2\sqrt{2}\pi, \frac{4\pi}{\sqrt{3}}$ (d) $2\pi, \frac{4\pi}{\sqrt{3}}, 2\sqrt{2}\,\pi$

23. The number of carbon atoms in a unit cell of diamond is –

(a) 1 (b) 4 (c) 8 (d) 10

24. Density of a crystal is given by the formula – a

(a) $\frac{ZM}{a^3 N_A}$ (b) $\frac{a^3 M}{Z N_A}$ (c) $\frac{N_A M}{Z a^3}$ (d) $\frac{a^3 N_A}{ZM}$

25. The relation between atomic radius and edge length of a body centred cubic unit cell –

(a) $r = a/2$ (b) $r = \frac{\sqrt{3}}{4} a$ (c) $r = \frac{3a}{4}$ (d) $r = \sqrt{a/2}$

26. An ionic compound has a unit cell consisting of A+ ions at the corners of a cube and B^- ions on the centres of the faces of the cube. The formula of the compound would be –

(a) AB (b) A_2B (c) AB_3 (d) A_3B

27. In a compound, atoms of the element 'Y' form CCP lattice and those of the element 'X' occupy 2/3rd of tetrahedral voids. The formula of the compound will be –

(a) X_3Y_4 (b) X_4Y_3 (c) X_2Y_3 (d) X_2Y

28. Silicon doped with arsenic is –

(a) n - type semi conductor (b) p - type semi conductor

(c) a metallic conductor (d) an insulator

29. Which of the following lattices has the highest packing efficiency ?

(a) simple cubic lattice (b) body centred cubic lattice

(c) hexagonal close packed lattice (d) All are having same packing efficiency.

30. How many chloride ions are surrounding sodium ion in sodium chloride crystal ?

(a) 4 (b) 8 (c) 6 (d) 12

(B) Assertion - Reason type questions : (Each question carries 1 mark)

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given.

Choose the correct answer out of the following choices –

(a) Both assertion (A) and reason (R) are correct and reason (R) is the correct explanation of assertion (A).

(b) Both assertion (A) and reason (R) are correct, but the reason is not the correct explanation of assertion.

(c) Assertion (A) is a correct statement, but the reason is a wrong statement.

(d) Assertion (A) is wrong but reason (R) is correct.

(1) Assertion (A) : Schottky defect is generally shown by the compounds with high co-ordination number.

Reason (R) : In Schottky defect, equal number of anions and cations are missing from the lattice sites.

(2) Assertion (A) : The total number of atoms present in a face centred cubic unit cell is four.

Reason (R) : Face centred cubic unit cell has atoms only at its corners.

(3) Assertion (A) : The packing efficiency is maximum for the fcc structure.

Reason (R) : The co-ordination number is 12 in fcc structure.

(4) Assertion (A) : Due to Schottky defect, the density of crystalline solid decreases.

Reason (R) : In Schottky defect, no cations or anions leave the lattice.

(5) Assertion (A) : Among the seven crystal systems, triclinic is the most unsymmetrical in nature.

Reason (R) : For triclinic system, $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$

(6) Assertion (A) : KCl shows Schottky defect.

Reason (R) : Both K^+ and Cl^- ions have almost same size.

(7) Assertion (A) : F - centres import colour to the crystals.

Reason (R) : Due to Frenkel defect F-centres are formed.

(8) Assertion (A) : Ferromagnetic solids are attracted very strongly by magnetic fields.

Reason (R) : They are used to make permanent magnet.

(9) Assertion (A) : For face centred cubic lattice, packing efficiency is 74%.

Reason (R) : Number of atoms present in a fcc unit cell is two.

(10) Assertion (A) : Due to frenkel defect, the density of the crystalline solid remains same.

Reason (R) : In frenkel defect, no cations or anions leave the lattice.

(C) Very short answer type questions : (Each question carries 1 mark)

1. What is unit cell ?
2. How many atoms are present in the unit cell of a Fcc lattice ?
3. Which point defect decreases the density of crystals ?
4. What is F – centre ?
5. What is the number of atoms per unit cell of the body centred cube ?
6. What is the packing efficiency of a fcc structure ?

7. What is the co-ordination number of atoms in a cubic close packed structure ?
8. Give one example of a compound which shows both Schottky and Frenkel defect.
9. For which crystal system, $a = b = c, \alpha = \beta = \gamma \neq 90°$
10. Give one example of an ionic solid.
11. A cubic solid is made up of two atoms A and B. Atoms A are present at the corners and atoms B are at the face centres. What is the formula of the compound ?
12. What is the co-ordination number of Na^+ and Cl^- ion in NaCl crystal ?
13. What is packing efficiency ?
14. What is the relationship between the radius of the atom (r) and edge length (a) of the unit cell or a fcc structure ?
15. Arrange the following in order of increasing packing efficiency : simple cubic unit cell, body centred cubic unit cell, face centred cubic unit cell.
16. What type of defect can arise when solid is heated ?
17. A group 14 element is to be converted into n- type semi conductor by doping it with a suitable impurity. To which group should the impurity element belong ?
18. What type of substances would make better permanent magnets ; ferromagnetic or ferrimagnetic?
19. Give and example of amorphous solid.
20. How many lattice points are there in one unit cell of a face centred cubic lattice.
21. What are n-type semi conductor ?
22. What is the co-ordination number of octahedral void ?
23. What type of semi - conductor is produced when silicon is doped with arsenic ?
24. What is the co-ordination no of Ca^{2+} and F^- ions in CaF_2 crystal ?
25. Which non - stoichiometric point defect forms F-centres ?
26. Which point defect in crystals does not alter the density of the solid ?
27. What type of interactions hold together the molecules in a polar molecular solid ?
28. What type of stoichiometric defect is shown by NaCl ?
29. What is the co-ordination number for a value of radius ratio between 0.414 – 0.732 ?
30. Which type of defect increases the density of the crystal ?
31. How many kinds of space lattices are possible in a crystal ?
32. What is meant by ‘doping’ in a semi conductor ?
33. What type of stoichiometric defect is shown by AgCl ?

(D) Short answer type questions : (Each question carries 2 mark)

1. Define crystalline solids. Give one example.

2. What are Ferromagnetic substances ? Give example.

3. Write two points of differences between Schottky and Frenkel defect .

4. Gold (atomic radius = 0.144 nm) crystallises in a face centred unit cell. What is the length of the side of the unit cell ?

5. Why does white zinc oxide (ZnO) become yellow upon heating?

6. The compound CuCl (Formula mass = 99 $g.mol^{-1}$) has F.C.C structure like ZnS. Its density is 3.4 $g.cm^{-3}$. What is the length of the edge of unit cell ? ($N_A = 6.02 \times 10^{23}\ mol^{-1}$).

7. Define the following :

   (i) Schottky defect (ii) Frenkel defect (iii) F – centre.

8. An element with density 11.2 $g.cm^{-3}$ forms f.c.c lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of the element. (Given : $N_A=6.022 \times 10^{23}\ mol^{-1}$).

9. How will you distinguish between the following terms :

   (i) Tetrahedral and Octahedral voids.

   (ii) Crystal lattice and unit cell.

10. Why does LiCl acquire pink colour when heated in Li vapours ?

11. A solid with cubic crystal is made of two elements ‘P’ and ‘Q’. Atoms of Q are at the corners of the cube and ‘P’ at body centre. What is the formula of the compound ?

12. What are n-type and P-type semi conductors ?

13. What are intrinsic semi conductors ? Give examples ?

14. What are extrinsic semi conductors ? Give examples ?

15. What is packing efficiency ? Calculate the packing efficiency in body-centred cubic crystals.

16. Explain how vacancies are introduced in a solid NaCl crystal when divalent cations are added to it.

17. Define the term “ point defects” ? Mention the main difference between stoichiometric and non-stoichiometric point defects.

18. Explain the following terms :

    (i) Ferrimagnetism

    (ii) Antiferromagnetism

    (iii) 13 – 15 compounds

19. Tungsten crystallises in a body centred cubic unit cell. If the edge of the unit cell is 316.5 Pm, calculate the radius of the tungsten atom.

20. If NaCl is doped with 10^{-3} mole percent of $SrCl_2$, what is the concentration of cation vacancy ?

21. Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fraction of nickel exist as Ni^{2+} and Ni^{3+}?

22. Differentiate between anisotropy and isotropy by giving examples.

23. Explain how you can determine the atomic mass of an unknown metal if you know its mass density and the dimensions of unit cell of its crystal .

24. Account for the following :

    (i) Schottky defects lower the density of related solids.

    (ii) Conductivity of silicon increases on doping it with phosphorous.

25. A compound forms hcp structure. What is the total number of voids in 0.5 mol of it ? How many of these are tetrahedal voids ?

26. How will you distinguish between the following pairs of terms :

    (i) Tetrahedral and octahedral voids.

    (ii) Crystal lattice and unit cell.

27. Calculate the number of unit cells in 8.1 g of aluminium if it crystallises in a fcc structure.

28. Give reasons :

    (i) In stoichiometric defects, Nacl exhibits Schottky defect and not Frenkel defect.

    (ii) Silicon on doping with phosphorous form n-type semi conductor.

    (iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances.

29. Exlain how many portions of an atom is located at (a) corner (b) body centre (c) face centred and (d) edge centred of a cubic unit cell.

30. In an fcc arrangement of 'A' and 'B' atoms. 'A' atoms are present at the corners of the unit cell and 'B' atoms are present at the face centres. If one atom of 'A' is missing from its position at the corner, what is the formula of the compound ?

31. A compound made up of elements 'A and 'B' crystallises in a cubic close - packed structure. Atoms 'A' are present on the corners as well as face centres, whereas atoms 'B' are present on the edge-centres as well as body centres. What is the formula of the compound ?

32. Define the term 'point defects'. Mention the main differences between stoichiometric and non-stoichiometric point defects.

33. Write the relationship between atomic radius (r) and edge length (a) of the cubic unit cell for – (i) simple cubic unit cell (ii) bcc unit cell (iii) fcc unit cell.

E. Long answer type questions : (Each question carries 5 marks)

1. (i) In corundum, oxide ions are arrranged in hcp array and the aluminium ions occupy two third of octahedral voids. What is the formula of corundum ?

   (ii) A compound AB crystallises in bcc lattice with unit cell edge length of 380 Pm. Calculate (a) the distance between the oppositely charged ion in the lattice. (b) Radius of A^{+1} if radius of B^{-1} is 175 Pm.

(2) Give reasons :

   (i) Molecular solids are generally soft and easily compressible.

   (ii) The energy required to vapourise one mole of copper is smaller than that of energy required to vapourise one mole of diamond.

   (iii) All metals have metallic bonds but some metals are soft and having low melting points and some are hard and having highmelting points.

   (iv) Covalent crystals like diamond and silicon carbide are quite hard and difficult to break .

   (v) Ionic solids, inspite of being made up of ions, do not conduct electricity.

3. Explain the term "ionic radius ratio" and its significance in case of ionic crystals. Calculate the ratio for the alkali metal bromides on the basis of the data given below and predict the form of the crystal structure in each case.

ion	ionic radius (in Pm)
Li^+	74
Na^+	102
K^+	138
Rb^+	148
Cs^+	170
Br^-	195

4. (i) In a crystalline solid, anions Y^{-1} are arranged in CCP arrangement. Cations X^{+} are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, write the formula of the solid.

   (ii) An element crystallises in fcc lattice having edge length 400 Pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure.

5. (i) In terms of band theory, what is the difference –

      (a) between a conductor and an insulator.

      (b) between a conductor and a semi conductor.

   (ii) Classify each of the following as being either P-type or n-type semi conductor.

      (a) Ge doped with In

      (b) B doped with Si

6. How the crystalline solids are classified on the basis of the nature of bonding ? Give suitable examples and nature of the forces present in different types of solids.

7. Calculate the packing efficiency and percentage of voids in the following types of unit cells :

   (i) Simple cubic unit cell

   (ii) Body centred cubic unit cell

   (iii) Face centred cubic unit cell

Answer

Answer key (MCQ):

1. c 2.b 3.b 4. c 5. a 6. d 7. a 8. d 9. b 10. d 11. d 12. c
13. a 14. c 15. b 16.b 17. b 18. d 19. b 20. c 21. a 22. a 23. b 24. a
25. b 26. c 27. b 28. a 29. c 30. c

B. Answer key (Assertion - Reason type):

1. b 2. c 3. d 4. c 5. d 6. d 7. c 8. b 9. c 10. d

Chapter - 2

Solution

Chapter at a glance :

- A homogeneous mixture of two or more pure non-reacting substances whose composition can be varied within certain limits is called a true solution. A solution with two constituents is called a binary solution (eg.- a solution of NaCl in water). Of the two components the smaller proportion or amount is called solute & the one present in excess is called solvent. For example - in aqueous solution of sugar, water is the solvent & sugar is the solute.
- Depending upon the nature of the components acting as solvent, solution may be classified as solid solutions, liquid solutions, gaseous solutions etc.

Table : Types of Solutions

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

- A solution containing water as slovent is known as aqueous solution. eg. sugar solution in water.
- A solution containing solvent other than water is known as non-aqueous solution. eg. iodine solution in alcohol.

Concentration of solutions :

- The amount of the solute present in a given quantity of the solution or the solvent implies the concentration of the solution.
- There are several ways by which the concentration of the solution can be described quantitatively.

(i) **Mass percentage (W/W) :** The mass of solute (g) present in 100g of a solution is defined as its mass percentage.

$$\text{Mass \% of a component} = \frac{mass\ of\ the\ component\ in\ the\ solution}{total\ mass\ of\ the\ solution} \times 100$$

For example, if a solution is described as 10% NaCl in water by mass, it means that 10g of NaCl is dissolved in 90g of water to form 100g solution.

(ii) **Volume percentage (V/V)** is described as,

$$\text{volume percent of a component} = \frac{volume\ of\ the\ component \times 100}{total\ mass\ of\ solution}$$

For example - 10% ethanol solution in water means that 10 mL of ethanol is dissolved in 90 mL of water to form a solution of 100 mL.

- Both mass percent & volume percent are simple ratios and have no units.

(iii) **Mass by volume percentage (W/V)** - It is the mass of solute dissolved in 100 mL of the solution.

(iv) Parts per million : When solute is present in trace quantities its concentration is expressed in parts per million (ppm)

$$ppm = \frac{mass\ of\ solute\,(g) \times 10^6}{mass\ of\ solution\,(g)}$$

or

$$ppm = \frac{volume\ of\ solute}{volume\ of\ solution} \times 10^6$$

$$ppm = \frac{mass\ of\ solute\,(g)}{volume\ of\ solution\,(mL)} \times 10^6$$

The degree of hardness of water is normally expressed as ppm. Similarly, the concentration of the poisonous gases in air is also expressed as ppm.

(v) Mole fraction :

It is the ratio of number of moles of a particular component to the total number of moles of all the components. For a binary solution made up of components A & B, mole fraction of

$$A(X_A) = \frac{n_A}{n_A + n_B} \text{ and mole fraction of } B(X_B) = \frac{n_B}{n_A + n_B}$$

Where n_A and n_B are the number of moles of component A & B respectively.

(vi) Molarity :

Molarity (M) is defined as the number of moles of solute per litre of solution.

$$Molarity(M) = \frac{number\ of\ moles\ of\ solute}{volume\ of\ solution\ (in\ litre)}$$

$$(M) = \frac{n_B}{V(mL)} = \frac{W_B \times 1000}{M_B \times V(in\ mL)}$$

Where n_B is the number of moles of solute, W_B is weight of solute, v is the volume of solution, M_B is the molar mass of solute.

Unit is mol L^{-1} or Molar (M)

Molarity of a solution depends on temperature. So, when molarity is used for expressing the concentration of solution, temperature must be mentioned.

(vii) Molality :

Molality is defined as the number of solute per kg of the solvent.

$$\text{Molality (m)} = \frac{number\ of\ moles\ of\ solute}{mass\ of\ solvent\ (in\ kg)}$$

$$m = \frac{n_B}{W}$$

$$= \frac{W_B}{M_B \times W_A}$$

Where n is the number of moles of solute, W_B is weight of solute, W_A is wight of solvent, M_B is the molar mass of solute. Its unit is mol Kg^{-1} or molal (m).

- Molality and mole fraction do not change with change in temperature. So molality is considered better for expressing the concentration of solution as compared to molarity.

- Relationship between Molarity & Molality :

$$\text{Molality (m)} = \frac{1000M}{M \times M_B - 1000d}$$

Where m is the molality, M is the molarity, d is the density of solution, M_B is the molar mass of solute.

- Normality is the number of gram equivalents of solute dissolved per litre of the solution.

$$Normality\,(N) = \frac{number\ of\ gram\ equivalent\ of\ solute}{volume\ of\ solution\,(in\ litre)}$$

$$N = \frac{W_B \times 1000}{E_B \times V}$$

W_B is the mass of the solute, E_B is the equivalent weight of solute, V of solution is mL.
It is expressed in g. equiv L^{-1} unit.

- **Strength of a solution (S) :**

The mass of solute (in g) dissolved in 1L solution is known as its strength in g L^{-1} .

S = Molarity of solution × Molar mass of solute

S = Normality of solution × Equivalent mass of solute.

- **Relationship between Molarity and Normality :**

Molarity × molar mass of solute = Normality × equivalent mass of solute

$$Normality = \frac{Molarity \times molar\ mass\ of\ solute}{equivalent\ mass\ of\ solute}$$

$$\frac{Molarity \quad molar\ \ mass\ of\ solute}{molar\ mass\ of\ solute\ /\ valency\ factor}$$

Normality = Molarity × Valency factor

$$N \quad = \quad M \quad \times \quad n$$

(i) for an acid, n = its basicity (ii) for a base, n = its acidity (iii) for a salt, n = no. of total charge of cations or anions present in one molecule.

- **Concept of dilution :**

The term dilution means addition of solvent in a solution, where the

a. amount of solute (W_B)

b. molar of solute (M × V)

c. number of gram equivalent of solute (N × V)

remains unchanged even after dilution.

- Molarity on mixing solutions :

$$M_1V_1 + M_2V_2 = M_3 (V_1 + V_2)$$

- Normality on mixing solutions :

$$N_1V_1 + N_2V_2 = N_3 (V_1 + V_2)$$

- **Solubility :**

  The maximum amount of solute that can be dissolved in a specified amount of solvent at constant temperature is called its solubility. Solubility is affected by nature of solute, solvent as well as by temperature and pressure.

- **Solubility of solid in a liquid :**

  Polar solutes are soluble in polar solvent and non-polar solvent are solute in non-polar solvent due to similar inter molecular forces,or we may say like dissolves like.

- When solid solutes are dissolved in a solvent then following equilibrium exists.

$$\text{solute} + \text{solvent} \underset{\text{crystallisation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{solution}$$

- Solubility of solids in liquid solvent is effected by temperature. If dissolution is exothermic (ΔH sol. <O) then solubitity decreases with increase in temperature and endothermic (ΔH sol. >O) then solubility increases with increase in temperature.

- Solubility of solids is not affected by pressure significantly, since solids are highly incompressible.

- **Solubility of Gases in Liquid :**

  Solubility of gases is highly effected by pressure and temperature. Increase in pressure increases solubility and increase in temperature decreases solubility. Dissolution of gas in liquid is exothermic in nature. During dissolution of gas pressure of gas, decrease. Some gases (like O_2,N_2, Ne) are less soluble in water and some gases (like NH_3, HCl) are highly soluble in water.

- **HENRY's LAW :**

  The law states that at a constant temperature. The solubility of a gas in liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

  Or,

  Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

  Or,

  The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution (This is the most common statement).

$$p = K_H \times \;,\; K_H = \text{Henry's constant.}$$

  Henry's constant is not a universal constant. It depends on nature of gas and temperature.K_H increases with increase in temperature, so the different gases have different K_H values at the same temperature.

Table : Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	K_H /kbar	Gas	Temperature/K	K_H/kbar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	$1.83\ 10^{-5}$
N_2	303	88.84	Methane	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611
O_2	303	46.82			

This suggests that K_H is a function of the nature of the gas. Henry's law finds several applications in industry and explains some biological phenomena.

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- To avoid bends, as well as the toxic effects of high concentrations of N_2 gas in blood, the tanks used by scuba divers are filled with air diluted with helium 11.7% , 56.2% N_2 and 32.1% O_2.
- 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 & tissues of people living at high altitudes and mountaineers. This may lead to anoxia.
- **Limitations of Henry's law :**

  a. The gas should not undergo any chemical change.

  b. The gas should not undergo association or dissociation in the solution.

  c. The pressure of gas is not too high and temperature is not too low.

- **VAPOUR PRESSURE of a LIQUID :**

  At a constant temperature, the pressure exerted by the vapours of a liquid on its surface when they (liquid and its vapours) are in equilibrium, is known as vapour pressure.

- Factors affecting vapour pressure are

  a. Nature of liquid.

  b. Temperature - vapour pressure of a liquid increases with increase in temperature.

- **RAOULT'S LAW :**

  a. **For a solution of volatile liquids,** the partial vapour prssure (P_1) of any component at constant temperature is equal to vapour pressure of pure component ($P_1°$) multiplied by mole fraction of that component (x_1).

$$p_1 = p_1^\circ\, x_1$$

similarly, $$p_2 = p_2^\circ\, x_2$$

According to Dalton's law of partial pressures, the total pressure (P total)

Over the solution phase in the container will be sum of the partial pressures of the components of the solution and is given as –

$$\begin{aligned} \text{p total} &= p_1 + p_2 \\ &= P_1^\circ\, x_1 + P_2^\circ\, x_2 \\ &= P_1^\circ\,(1 - x_2) + P_2^\circ\, x_2 \\ &= P_1^\circ + (P_2^\circ - P_1^\circ)\, x_2 \end{aligned}$$

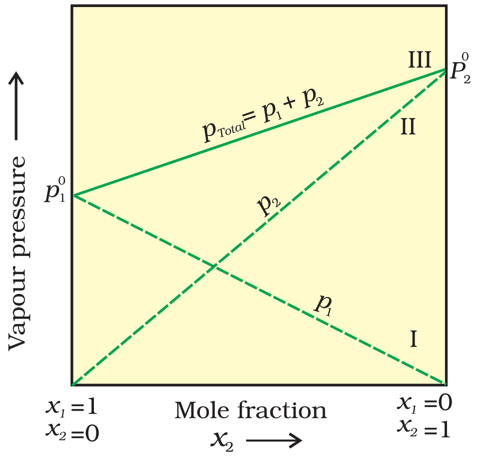


Fig. *: The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2, respectively). The total vapour pressure is given by line marked III in the figure.*

- **Raoult's law as a special case of Henry's law :**

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given solution is given by $p_1 = p_1^\circ\, x_1$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and its solubility is given by Henry's law, which states that $p = K_H . x$. If we compare the above equations of Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction. So Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_1°.

- **Raoult's law for non-volatile solute :**

For a solution containing non-volatile solute present in a volatile solvent (eg- aqueous solution of sugar, salt, urea etc.) Raoult's law may be stated as the vapour pressure of solution (p_1)

containing a non-volatile solute at a given temperature is equal to the product of the vapour pressure of the pure solvent ($p_1°$) and its mole fraction (x_1). $p_1 = p_1° x_1$

- **Ideal solutions :**

  The solutions which obey the Raoult's law over the entire range of concentration and temperature are known as ideal solution.

- **Characteristics of an ideal solution :**

  (i) Enthalpy change of mixing the pure components to form the solution is zero, ΔH solutions = 0 (heat is neither absorbed nor evolved).

  (ii) Volume change of mixing should be zero. ΔV mixing = 0

  (iii) There should be no chemical reactionn between the components A and B.

  (iv) The inter molecular attractive forces between A – A = B – B = A – B.

  (v) Observed vapour pressure of solution = calculated vapour pressure of it.

  (vi) $p_1 = p_1° x_1$ $\quad$ $p_2 = p_2° x_2$

  A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Some examples of ideal solutions are –

  a. n - hexane and n - heptane

  b. benzene and toluene

  c. ethyl bromide and ethyl chloride

  d. chlorobenzene and bromobenzene etc.

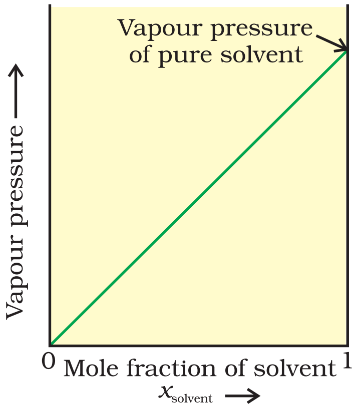


***Fig.** If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.*

- **Non-ideal solution :**

  When a solution does not obey Raoult's law over the entire range of concentration, then it is called non-ideal solution. For non - ideal solution ,

  (i) A - A interaction ≠ B - B interaction ≠ A - B interaction

  (ii) ΔH solution ≠ o $\quad$ Δ V mixing ≠ o

  (iii) $p_1 \neq p_1° x_1$ $\quad$ $p_2 \neq p_2° x_2$

For example – Ethanol and water solution, chloroform and acetone solution.

- **Non-ideal solutions having positive deviation from Raoult's law :**

  In this type of deviation A - B interactions are weaker than A - A or B - B interactions and leads to the increase in vapour pressure of the resultant solution than expected.

  For example – Solution of ethanol and water, benzene & acetone, ethanol and acetone etc.

  All these solutions form minimum boiling azeotrope.

  In these solutions

  (a) $p_1 > p_1^\circ x_1$ $\qquad$ $p_2 > p_2^\circ x_2$

  and also $p_{total} > p_1^\circ x_1 + p_2^\circ x_2$

  (b) ΔH mix > o (endothermic dissolution)

  (c) ΔV mix > o (volume increases after dissolution)

- **Non - ideal solutions having negative deviation from Raoult's law :**

  In this type of deviation, the inter molecular attractive forces between A - A and B - B are weaker than those between A - B and leads to decrease in vapour pressure. For example - solution of water and Nitric acid ; chloroform and acetone ; chloroform and benzene etc.

- All these solutions form maximum boiling azeotrope.

  In this solutions –

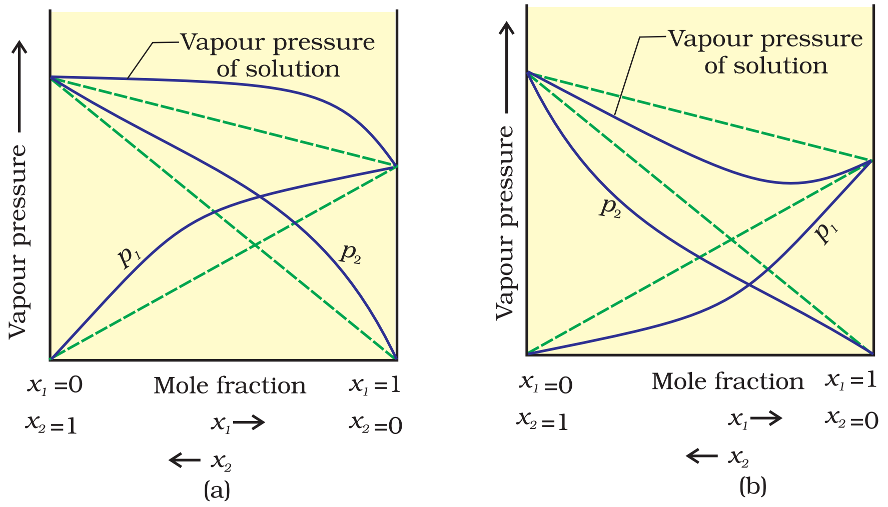
  (a) $p_1 < p_1^\circ x_1$ $\qquad$ $p_2 < p_2^\circ x_2$

  and also $P_{total} < p_1^\circ x_1 + p_2^\circ x_2$

  (b) ΔH mix < o (exothermic dissolution)

  (c) ΔV mix < o (volume decreases during dissolution)

Fig.
The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.



(a) (b)

- The type of liquid mixture which boils at the same temperature and pressure without undergoing any change in composition is known as constant boiling mixture or azeotropic mixure or azeotrope.
- **COLLIGATIVE PROPERTIES :**

  The physical properties of dilute solutions which depends upon the relative number of solute particles and does not depend upon the nature of solute particles are called colligative properties. These properties are applicable only for dilute solutions.

  The following are colligative properties.

  (a) Relative lowering in vapour pressure of solvent.
  (b) Elevation of boiling point (ΔT_b)
  (c) Depression of freezing point (ΔT_f)
  (d) Osmotic pressure of the solution

◆ **Relative lowering in vapour pressure :** For the dilute soultion of a non voletile solid solute, it is the ratio of lowering of vapour pressure and vapour pressure of pure solvent ($p_1°$) which is equal to the mole fraction of solute (x_2).

Relative lowering of vapour pressure = $\dfrac{p_1° - p_1}{p_1°}$

$$\frac{p_1° - p_1}{p_1°} = x_2 = \frac{n_2}{n_1 + n_2}$$

Where, p_1 = vapour pressure of solution, $p_1°$ = vapour pressure of pure solvent,

n_2 = no. of moles of solute

n_1 = no. of moles of solvent.

For dilute solution, $n_2 << n_1$

$$\frac{p_1° - p_1}{p_1°} = \frac{n_2}{n_1} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

Where, W_1 = mass of solvent, M_1 = molar mass of solvent W_2 = mass of solute, M_2 = Molar mass of solute.

- Relative lowering of vapour pressure is temperature independent.
- **Elavation of Boiling point :**

  The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure.

  When a non-volatile solute is dissolved in a pure solvent, its vapour pressure decreases than that of the solvent and boiling point increases. The difference in boiling point of pure solvent ($T_b°$) and that of solution (T_b) is called elevation of boiling point (ΔT_b) .

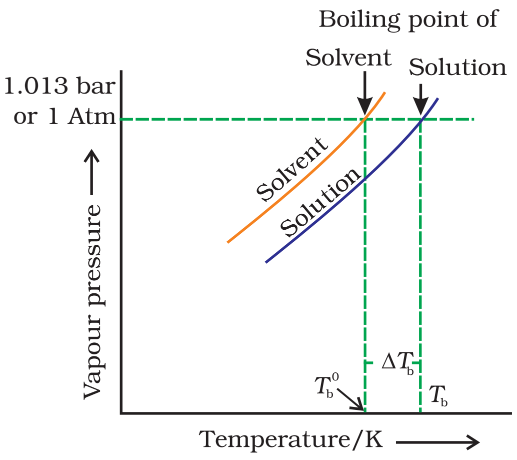


Fig. *: The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.*

- **Raoult's law of elevation of boiling point :**

  For the dilute solution of a non-volatile solid solute, the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration (m) of the solution.

$$(\Delta T_b) \propto m$$

or $$(\Delta T_b) = K_b . m$$

where, K_b is a constant known as molal elevation constant or ebullioscopic constant.

- Its unit is K kg mol^{-1}
- The value of K_b depends only on the nature of solvent but not on the nature of solute.
- It is used for determination of molar mass of a solute.

If W_2 g of a solute of molar mass M_2 is dissolved in W_1 g of solvent, then the molality of the solution (m) is –

$$m = \frac{W_2 / M_2}{W_1 / 1000} = \frac{W_2 \times 1000}{M_2 \times W_1}$$

Now, $$\Delta T_b = Kb \times m$$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

or $$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

- **Depression of freezing point :**

  The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other. At this temperature liquid and solid states of a substance have the same vapour pressure.
- When a non-volatile solute is dissolved in a pure solvent the vapour pressure of the solvent is lowered.
- According to Raoult's law of depression of freezing point, when a non-volatile solid is dissolved in a pure solvent its vapour pressure decreases which is directly proportional to its molal concentration (m).

$$\Delta T_f \propto m$$
$$\Delta T_f = K_f \times m$$

where, ΔT_f = depression of freezing point.

K_f = molal depression constant or cryoscopic constant.

- Its unit is degree kg mol^{-1}

  or k kg mol^{-1}
- K_f only depends on the nature of solvent.
- If W_2 g of a solute of molar mass M_2 is dissoved in W_1 g of solvent and it caused a depression of freezing point ΔT_f, then

$$\Delta T_f = k_f \times m$$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

or, $$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

If the values of K_f, W_2, W_1, ΔT_f are known to us, molar mass of the solute M_2 can be determined.

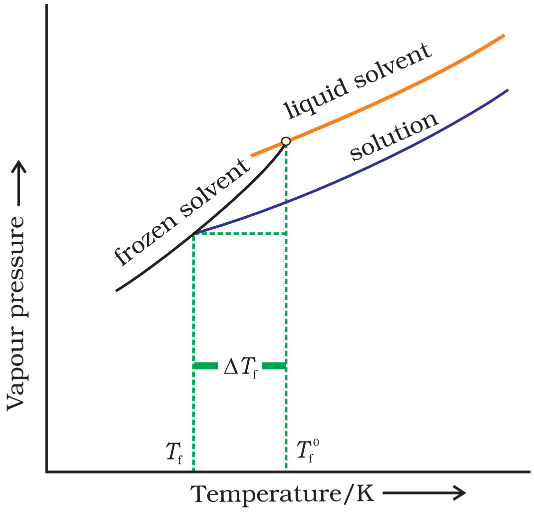


Fig. : Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution.

◆ Antifreeze solution is an additive which lowers the freezing point of a water based liquid that is a fluid, such as methanol or ethylene glycol, added to vehicle engine coolant to protect the system from freezing even in sub-zero temperature.

◆ **Osmosis :**

The spontaneous net flow of solvent molecules through semipermeable membrane from solvent to a solution or from a dilute solution to a concentrated solution is called Osmosis.

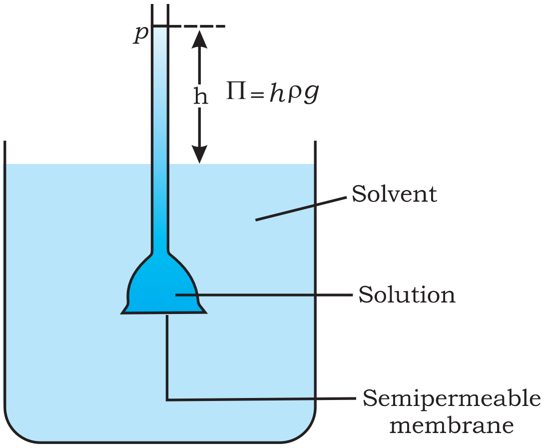


Fig. Level of solution rises in the thistle funnel due to osmosis of solvent.

- **Osmotic pressure :**

  The extra pressure that is applied to just stop the flow of solvent to solution across a semipermeable membrane is called osmotic pressure of the solution.

  For dilute solutions,osmotic pressure (π) is proportional to the molar concentration (C) of the solution at a given temperature (T). So, $\pi = CRT$ (R is the gas constant)

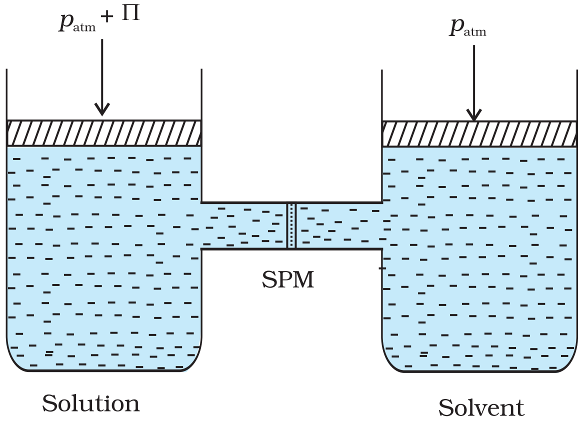


Fig. : *The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.*

  or $\pi = \frac{n_2}{V} RT$

  Here V is the volume of a solution (in litres) .

  Containing n_2 moles of solute. If W_2 grams of solute of molar mass M_2 is present in solution, then n_2 =

  $n_2 = \frac{W_2}{M_2}$, so we can write $\pi V = \frac{W_2}{M_2}$ RT

$$\text{or,} \quad M_2 = \frac{W_2 RT}{\pi V}$$

  If the values of W_2 T, π ,V are known, we can get the value of M_2 .

- Measurment of osmotic pressure provides another method of determining molar masses of solutes like proteins, polymers and other macromolecules.
- As compared to other colligative properties value of $\boldsymbol{\pi}$ is large enough even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly used for biomolecules (as they are generally not stable at higher temperature) & polymers have poor solubility.
- At constant temperature, osmotic pressure of a dilute solution depend upon the number of solute particles, but not on the nature of solute.
- **Isotonic solution :** Two solutions having same osmotic pressure at a given temperature are called Isotonic solutions. Such solutions have same molar concentration.
- **Hypotonic solutions :** A solution is called hypotonic, if its concentration is lower than that of the solution separating it by a semipermeable membrane. A hypotonic solution has less osmotic pressure.
- **Hypertonic solution :** A solution is called hypertonic, if its concentration is higher than that of the solution separating it by a semipermeable membrane. A hypertonic solution has higher osmotic pressure.

- **Reverse osmosis :** The direction of osmosis can be reversed, if a pressure larger than the osmotic pressure is applied to the solution side. The pure solvent flows out of the solution through the semipermeable membrane. This phenomenon is called reverse osmosis.

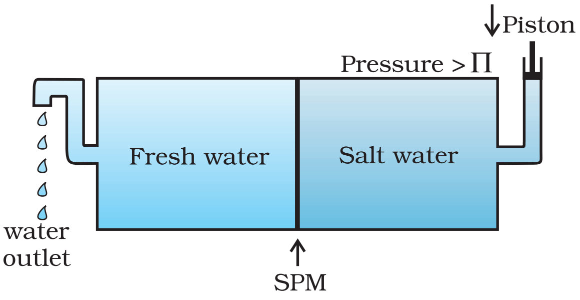


Fig. : Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

◆ **Abnormal molecular mass :**

If the molecular mass calculated with the help of colligative property is found to be different from the theoretical molecular mass, it is called abnormal molecular mass.

If the solute particles exist in dissociated or associated form in solution, the calculated molecular mass using colligative property is found to be abnormal.

(i) When there is dissociation of solute into ions, the experimentally determined molar mass is always lower than the true value.

(ii) When there is association of solute molecules into dimer or polymer the experimentally determined molar mass is always greater than the true value.

◆ **Vant Hoff factor :**

The ratio of the observed (experimental) value of a colligative property to the normal (calculated) value of the same property is called as vant Hoff factor (i)

$$i = \frac{observed(\exp erimental)\ colligative\ property}{theoretical\ (calculated)\ colligative\ property}$$

$$= \frac{Normal\ molar\ mass}{Abnormal\ molar\ mass}$$

$$i = \frac{Total\ number\ of\ moles\ of\ particles\ after\ association\ /\ dissociation}{Number\ of\ moles\ of\ particles\ before\ association\ /\ dissociation}$$

◆ In case of association, value of i is less than unity while for dissociation it is greater than unity. For example, the value of i for aqueous Kcl solution is almost 2, Kcl (aq) → K^+(aq) + Cl (aq) while the value for ethanoic acid in benzene is nearly 0.5 . 2. CH_3COOH $\qquad$ $(CH_3COOH)_2$. If i = 1, it indicates the solute neither dissociates nor associates.

◆ Inclusion of vant Hoff factor modified the equations for colligative properties as follows :

Relative lowering of vapour pressure of solvent, $\frac{p_1{}^\circ - p_1}{p_1{}^\circ} = i\,\frac{n_2}{n_1}$

Elevation of boiling point, $\Delta T_b = i\,K_b\,m$

Depression of freezing point $\Delta T_f = i\,.\,K_f\,.\,m$

Osmotic pressure of solution, $\pi = i.\ n_2.\ \frac{RT}{V}$

A. Select the correct answer : (1 mark each)

1. The mixure which shows positive deviation from Raoult's law is

a) Benzene + Toluene b) Acetone + Chloroform

c) Chlorothane + Bromoethane d) Ethanol + Acetone

2. Isotonic solutions have same

a) Vapour pressure b) Freezing temperature

c) Osmotic pressure d) Boiling temperature

3. The mixture that forms maximum boiling azeotrope is

a) Heptane + Octane b) Water + Nitric acid

c) Ethanol + Water d) Acetone + Carbon di sulphide

4. Which of the following is dependent on temperature ?

a) Molality (b) Molarity

c) Mole fraction d) weight percentage

5. The vant's Holf factor (i) for a dilute aqueous solution of the strong electrolyte $Ba(OH)_2$ is –

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

6. If equimolar solutions of $CaCl_2$ & $AlCl_3$ in water have boiling point t_1 & t_2 respectively, then

(a) $t_1 > t_2$ (b) $t_1 + t_2 < 0$ (c) $t_1 = t_2$ (d) $t_1 < t_2$

7. The freezing point depression constant (k_f) of benzene is 5.123 k kg mol –1. The freezing point depression for the solution of molality 0.078 m containing a non-electrolyte solute in benzene is –

(a) 0.80k (b) 0.40k (c) 0.60k (d) 0.20k

8. The osmotic pressure of solution increases if –

(a) Temperature is decreased (b) Concentration is decreased

(c) number of solute particle is increased (d) Volume is increased

9. Which of the following liquid pairs will show negative deviation from Raoult's law ?

a) Water – ethanol b) Water – hydrochloric acid

c) Water – nitric acid d) Acetone – chloroform

10. The value of Henry's constant –

a) increases with increase in temperature

b) remains constant at all temperature

c) decreases with increase in temperature

d) with increase in temperature it first increases & then it decreases.

11. People living in high altitude have low oxygen concentration in blood & cell fluids due to –

a) low temperature | b) high atmospheric pressure
c) low partial pressure of oxygen in air | d) both a and b

a) low temperature

b) high atmospheric pressure

c) low partial pressure of oxygen in air

d) both a and b

12. As a result of osmosis, the volume of the concentrated solution till the solutions becomes equally concentrated on both sides of SPM –

a) gradually decreases

b) gradually increases

c) suddenly increases

d) none

13. Which can pass through semipermeable membrane ?

a) molecules of solvent

b) simple ion

c) molecules of solute

d) complex ion

14. Which solution will exert highest osmotic pressure ?

a) 1M glucose solution

b) 1M urea solution

c) 1M alum solution

d) 1M NaCl solution

15. The average osmotic pressure of human blood is 7.8 bar at 37°c. What is the concentration of an aqueous NaCl solution that could be used in the blood stream.

a) 0.16 mol L^{-1}

b) 0.32 mol L^{-1}

c) 0.60 mol L^{-1}

d) 0.45 mol L^{-1}

16. Of the following 0.10 m aqueous solution, which one will exhibit the largest freezing point depression ?

(a) KCl

(b) $C_6H_{12}O_6$

(c) $Al_2(SO_4)_3$

(d) K_2SO_4

17. Which of the following compounds can be used as antifreeze in automobile radiators more efficiently at very low temperature ?

a) Nitrophenol

b) Ethanol

c) Methanol

d) Glycol

18. Camphor is often used in molecular mass determination because –

a) it has a very high cryoscopic constant

b) it is volatile

c) it is solvent for organic substances

d) it is readily available

19. A molal solution is one that contains one mole of a solute in

a) 1000g of the solvent

b) one litre of the solution

c) one litre of the solvent

d) 22.4 litres of the solution

20. If a thin slilce of raw mango or sugar beet is placed in concentrated NaCl solution, then

a) it will lose water from its cells

b) it will absorb water from solution

c) it will neither absorb nor lose water

d) it will dissolve in solution

B. Assertion - Reason type questions : (1 marks each)

The following questions given below consist of Assertion (A) & Reason (R). Use the key to select the correct answer.

a) Both A & R are correct and R is correct explanation for A.

b) Both A & R are correct but R is not the correct explanation for A.

c) A is correct but R is incorrect.

d) Both A & R are incorrect.

1. Assertion : Molarity of a solution changes with temperature.
   Reason : Molarity is a colligative property.
2. Assertion : In an ideal solution, ΔH mixing is zero.
   Reason : A - B interactions are same as A - A and B - B interactions.
3. Assertion : The molecular mass of acetic acid was determined by depression in freezing point method in benzene and was found to be different.
   Reason : Water is polar and benzene is non-polar.
4. Assertion : Ethyl alcohol and water form maximum boiling azeotrope.
   Reason : Attractive force in solution tend to increase.
5. Assertion : Greater the molal depression constant of the solvent used, less is the freezing point of the solution.
   Reason : Depression in freezing point depends upon the nature of the solvent.
6. Assertion : Azeotropic mixtures are formed only by non-ideal solutions and they may have boiling points either greater than both the components or less than both the components.
   Reason : The composition of the vapour phase is same as that of the liquid phase of an azeotropic mixture.
7. Assertion : When methanol is added to water, boiling point of the solution increases.
   Reason : When a volatile solute is added to a volatile solvent elevation in boiling point is observed.
8. Assertion : Isotonic solutions do not show any osmosis when placed side by side.
   Reason : Isotonic solutions have same solute concentrations.
9. Assertion : When NaCl is added to water a depression in freezing point is observed.
   Reason : The lowering of vapour pressure of a solution causes depression in the freezing point.
10. Assertion : Molecular mass of benzoic acid, when determined by colligative properties is found high.
    Reason : Dimerization of benzoic acid takes place.

C. Very short answer type questions : (1 mark each)

1. Define ideal solution.
2. What are azeotropes ?
3. Define mole fraction.
4. What are isotonic solutions ?
5. What is meant by the term Reverse Osmosis ?
6. What are colligative properties ?
7. On addition of 1mol of glucose to 1 litre of water the boiling point of water increases – Why ?
8. What do you mean by abnormal molar mass ?
9. In non-ideal solution, what type of deviation shows the formation of minimum boiling azeotropes?
10. The bottle of liquid ammonia is generally cooled before opening the seal – Why ?
11. Name the most commonly used semipermeable membrane in the laboratory.
12. Why does not molality of the solution change with temperature ?
13. How is Henry's law constant related to the solubility of a gas in a solvent ?
14. What should be the maximum concentration of the solute in case a solution is to be ideal ?
15. Are equimolar solutions of NaCl and $C_6H_{12}O_6$ isotonic ?
16. When dried fruits & vegetables are placed in water, they slowly swell up and look fresh. Why ? What is the effect of temperature on this process ?
17. Why does water boil at lower temperature in simla than in Delhi ?
18. Name a solid solution.
19. Aerated water bottles are kept in refrigerator or under water during summer, Why ?
20. If sea-fishes are shifted to river water, they can not survive, why ?

D. Short answer type questions : (2 marks each)

1. Define - Molality & molarity.
2. What do you mean by –
   (i) Abnormal molar mass
   (ii) Vant Hoff factor

3. What is osmotic pressure ? How is osmotic pressure related to the concentration of a solute in a solution ?
4. Explain why on addition of 1 mol glucose to 1 litre water the boiling point of water increases.
5. What role does the molecular interaction play in a solution of alcohol & water ?
6. Why do gases always tend to be less soluble in liquids as the temperature is raised ?
7. How can you explain Raoult's law as a special case of Henry's law ?
8. Why are aquatic species more comfortable in cold water in comparison to warm water ?
9. Will the elevation in boiling point be same if 0.1 mol of sodium chloride & 0.1 mol of sugar is dissolved in 1L of water ? explain.
10. What is meant by elevation in boiling parts ? Is it a colligative property ? Why ?
11. Calculate the molarity of a solution having 5g of NaOH dissolved in 450 mL of the solution.
12. The density of 85% sulphide acid is 1.7 g cm^{-3} . What is the volume of the solution which contains 17g of H_2SO_4 ?
13. A sample of drinking water was found to be contimanated with $CHCl_3$, supposed to be carcinogen. The level of contamination was 15 ppm (by mass).
    i) Express this in percent by mass.
    ii) Determine the molarity of chloroform in the water sample.
14. How many mL of 0.1 M HCl are required to react completely with 1g mixture jof Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two ?
15. Calculte the osmotic pressure of a solution obtained by mixing 100 ml 3.4% urea (M = 60) solution and 100 ml 1.6% sucrose (M= 342) solution at 20°C.
16. What is the osmotic pressure of 5% glucose solution at 33.3°C ?
17. 0.684g of sugar dissolved in 100g of water depresses the freezing pointt of water by 0.037°C. Determine the cryoscopic constant (Kf) of water (molar mass of sugar = 342)
18. When two liuquids A & B are mixed, the resulting solution is found to be cooler. What does it indicate?
19. What happens when RBC come in contact of 0.1% Nacl solution ?
20. What is plasmolysis ? Write one application of it.

E. Answer in Short : (3 marks each)

1. What is the expected deviation from ideal solution behaviour when acetone and chloroform are mixed to form a solution ?

2. (a) What is osmotic pressure ?

   (b) Osmotic pressure is generally prefered for determining the molecular masses of proteins. Explain?

3. A 10% solution (by mass) of sucrose in water has a freezing point of 269.15K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15K . (molar mass of sucrose = 342 g mol^{-1} , molar mass of glucose = 180 g mol^{-1})

4. At 100°C the vapour pressure of a solution of 6.5g of a solute in 100g water is 732 mm. If $K_b = 0.52$, calculate the boiling point of the solution.

5. Calculate the mole fraction of benzene solution in ccl_4 containing 30% by mass.

6. Calculate (i) molality (ii) molarity (iii) mole fraction of KI is the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}.

7. A 1.0 g of substance of molecular formula AB_2 when dissolved in 25g of benzene reduced the freezing point by 1.6 K while 1.0g of substance AB_3 on mixing with the same amount jof benzene depressed the freezing point by 1.25 K. Determine the atomic mass of A and B. (K_f for benzene = 5.1 K Kg mol^{-1})

Solution / Answer key

A. Select the correct option (MCQ) :

1. d 2. c 3. b 4. b 5.d 6. d 7. b 8. c 9. a 10.a 11. c 12. b
13. a 14. c 15. a 16. c 17. d 18. a 19. a 20.a

B. Assertion & Reasoning :

1. c 2. a 3.a 4.d 5. a 6. b 7. d 8. c 9. a 10. a

Chapter - 3

Electrochemistry

Chapter at a glance :

The study of production of electricity from energy released during spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations is known as electro chemistry. The subject is of importance both for theoretical and practical consideration. Electro chemistry is therefore, a very vast subject. In this unit we will study only some of its important elementary aspects.

Electrochemical transformation :

The transformations which take place under the influence of electric energy is known as electro chemical transformation. Electro chemical transformations may be studied in two parts –

(i) **Electromotive chemistry :** The branch of electro chemistry in which the study of transformation of chemical energy to electrical energy. during spontaneous chemical reactions is known as electromotive chemistry and the instrument of operator used to study this change is known as electrochemical cell. example - Daniell cell, dry cell, battery, fuel cell.

(ii) **Electrolysis :** The branch of electro chemistry in which transformation of electrical energy to chemical energy is studied is known as electrolysis and the operator used to bring this transformation is known as electrolytic cell or voltameter. Solvey kelner cell, Down’s cell etc used to produce NaOH and Na. Electrical energy is passed through these cell to carry out non-spontaneous chemical reaction.

- * In galvanic cell anode is negatively charged and cathode is positively charged. In electrolytic cell anode is positively charged and cathode is negatively charged.
- * In galvanic cell generally salt bridge is used. In electrolytic cell salt bridge is not required.

Electrochemical cell or Galvanic cell :

The electrochemical cell in which chemical energy are transformed into electrical energy with the help of redox reaction is known as electrochemical or Galvanic cell.

Daniel cell :

Daniel cell is such type of cell where the overall redox reaction can be expressed as –

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

This reaction is a combination of two half-reaction which take place in different part of the cell.

(i) $Cu^{2+} + 2e^{-} \rightarrow Cu\ (s)$ reduction half reaction which takes place in copper electrode partially dipped in 1M $CuSO_4$ solution in another beaker. It acts as cathode.

(ii) $Zn\ (s) \rightarrow Zn^{2+} + 2e^{-}$ oxidation half reaction which takes place in zinc electrode partially dipped in 1 M $ZnSO_4$ solution in another beaker. It acts as anode.

The two solutions in different beakers are connected through salt bridge.

Salt bridge :

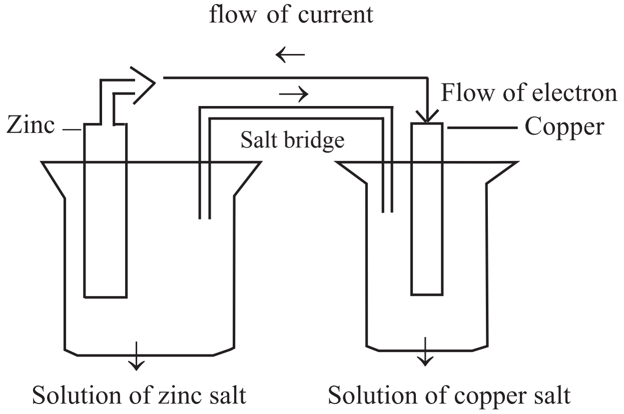
Salt bridge is prepared by taking a concentrated solution of an electrolyte where the velocity of cation and anion are same (like KCl, KNO_3, NH_4NO_3 etc.) and mixing this electrolyte with small amount of Agar-Agar. This mixture is heated and then cooled in a U shaped glass tube.

Uses of Salt bridge :

(i) Salt bridge helps in maintaining electrical neutrality between two electrolytic solution placed in different pot.

(ii) Due to salt bridge electrolytic solution of one half cell cannot mix with electrolytic solution of another half cell.

Composition of Daniell cell is shown in the following picture.



Structure of Daniell cell

Electrode potential :

A potential difference develops between the electrode and the electrolyte which is called electrode potential. It represent the tendency of accepting of electron or releasing electron of the electrode. Now a days standard reduction potential is accepted as standard electrode potential.

Oxidation electrode potential :

The half cell where oxidation occurs is known as anode and in-respect of solution its potential is negetive.

Reduction electrode potential :

The half cell where reduction occurs is known as cathode and in respect of solution its potential is positive.

There exists a potential difference between the two electrode and as soon as the switched on the electrons flow from negative electrode to positive electrode and as per accepted IUPAC convention current flow is opposite to that of electron flow.

Cell potential :

The potential difference between the two electrodes of a galvanic cell is called the cell potential i.e the difference between the electrode potentials of cathde and anode i.e reduction potential difference is the cell potential. It is also called the cell electromotive force (emf) of the cell. It is now accepted convention that we keep the anode on the left and the cathode on the right, pulting a vertical line between metal and electrolyte solution and puting a double vertical line between the two electrolytes connected by salt bridge we represent a galvanic cell.

Example – In case of Daniell cell the following redox reactions takes place in two different part-

(i) $Cu^{2+} + 2e^- \rightarrow Cu\,(S)$ [Reduction half cell reaction - Cathode]

(ii) $Zn\,(S) \rightarrow Zn^{2+} + 2e^-$ [Oxidation half of cell reaction - Anode]

The overall reaction is –

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

$$E_{cell} = E_{right} - E_{left}$$

We can represent the cell as follows –

$$Zn / ZnSO_4 // Cu / CuSO_4 \quad \text{or}$$

$$Zn / Zn^{2+}\,(aq) // Cu^{2+}\,(aq) / Cu$$

Oxidation half cell (anode) // Reduction half cell (Cathode)

Standard electrode potential and standard hydrogen electrode :

Since the potential of individual half cell cannot be measured a half cell named as standard hydrogen electrode [$Pt(s)/H_2(g)/H^+(aq)$] whose potential as taken as zero at all temparature as convention and with respect to it the potential of another half cell is measured at 298K. This potential is known as standard electrode potential. If oxidation takes place at the other electrode after adding it with hydrogen electrode then the value of standard electrode potential will be negative and it reduction takes place at the electrode after connecting it with hydrogen electrode then the value of standard electrode potential will be positive.

Electrochemical series :

Taking standard electrode potential (E°) of hydrogen electrode as zero and with respect to it when we arrange standard electrode potential (standard reduction potential) of other half cells according to their values we get a series known as electro chemical series or electro potential series.

Some applications of electrochemical series :

(i) Those metals which have standard electrode potential as negetive i.e they are placed above hydrogen in electro chemical series only they can reduce H^+ ion to H_2 gas in dilute acid solution.

(ii) The metals placed in upper level of electro chemical series have higher tendency to release electrons, have low reduction potential i.e higher tendency to get oxidesed. on the other hand metals in lower level of electro chemical series have lower tendency to release electron, have higher value of reduction potential i.e lower tendency to get oxidised. That is why any metal in higher level of electro chemical series dispalces metal placed at comparitively lower level of electro chemical series from their respective salt solutions.

(iii) From reduction potential of electrode (half cell) the spontaneity of oxidation - reduction reaction taking place at the half cell can be predicted.

(iv) Depending on relative position of electrode and from the standard reduction potential of electrode the standard emf of can be calculated.

(v) From the position in electro chemical series one can assume activity of metals and their position in nature.

Nernst equation of electrode potential :

The potential of a electrode depends on the concentration of electrolytic solution. The relation between electrode potential and concentration of electrolytic solution was established by scientist Nernst generally known as Nernst equation.

A general electrode reaction can be represented as –

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

For this reaction Nernst equation can be written as –

$$E\, M^{n+}/_{M} = E°M^{n+}/_{M} - \frac{2.303RT}{nF}\log\frac{1}{\left[M^{n+}\right]}$$

Where,

$E\, M^{n+}/_{M}$ = Electrode potential

$E°M^{n+}/_{M}$ = Standard electrode potential

F = Faraday constant = 96500C

R = Universal gas constant = 8. 314 $JK^{-1}mo^{-1}$

T = Temparature (kelvin scale)

n = number of electron taking part in redox reactions.

$[M^{n+}]$ = concentration of the species M^{n+}

Electromotive force (EMF) :

In open circuit condition difference between the electrode potential of two electrodes in Galvanic cell is know as electro motive force (EMF) of the cell. It is represented as E_{cell}. In respect of reduction potential.

$E_{cell} = E_{cathode} - E_{Anode}$

In standard state

$E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{Anode}$

For Daniell cell the cell potential can be represented as

$E_{cell} = E_{(Cu2+/Cu)} - E_{(zn2+/zn)}$

$$= E^\circ_{(Cu2+/Cu)} - \frac{RT}{2F}\ln\frac{1}{\left[Cu^{2+}(aq)\right]} - E^\circ(zn^{2+}/zn) + \frac{RT}{2F}\ln\frac{1}{\left[Zn^{2+}(aq)\right]}$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{2F}\ln\frac{\left[zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

Similarly for a general electro chemical reaction

$aA + bB \xrightarrow{ne^-} cC + dD$ the Nernst equation can be written as –

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[C]^C[D]^d}{[A]^a[B]^b}$$

Equilibrium constant from Nernst equation :

At equilibrium there is no change of concentration of Cu^{2+} or Zn^{2+} ion in Daniell cell and at that moment voltameter shows zero readings. At that moment we can write Nernst equation as –

$$E_{cell} = o = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{\left[zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

If $\frac{\left[zn^{2+}\right]}{\left[Cu^{2+}\right]}$ = Kc and T = 293K then we can express the above equation as -

$$E^\circ_{cell} = \frac{2.303RT}{2F}\log\frac{\left[zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$E^\circ_{cell} = \frac{0.059}{2}\ \log Kc$$

We can calculate equation constant Kc from the equation.

$$E^\circ_{cell} = \frac{0.059}{n}\log Kc$$

Relation between Electrochemical cell and Gibbs free energy of reaction :

The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. If $\Delta_r G$ is the Gibbs energy of the reaction then we can write,

$\Delta_r G = - nF\ E\ (cell)$ | E = Electromotive force of the cell.

| nF = amount of charge passed.

Ionic conductance :

The inverse of resistance R, is called conductance (G). The conductivity of electrolytic (ionic) solutions depends on –

(i) The nature of the electrolyte added.

(ii) Size of the ions produced and their solvation.

(iii) The nature of solvent and its viscosity.

(iv) Concentration of the electrolyte.

(v) Temparature

Unit of conductance :

Unit of conductance in C.G.S unit is ohm^{-1} or Ω^{-1} or mho. The SI unit of conductance is siemens(S).

Specific Conductance :

If the resistance of a electrolytic solution confined between two electrodes having cross section area A and separated by a distance of l, is, R then R can be written as –

$$R = r\frac{l}{A}$$

or

$$R = \rho \frac{l}{A}$$

$$R = \frac{l}{K \wedge} \qquad \left| K = \frac{1}{\rho} \right. = \text{specific conductance}$$

$$K = \frac{l}{RA}$$

Unit of specific conductance = $\text{Ohm}^{-1}\ \text{Cm}^{-1}$

= mho Cm^{-1}

Cell constant :

Specific conductance (K) = $\frac{1}{R} \times \frac{l}{A}$

The ratio $\frac{l}{A}$ is known as cell constant and is represented as G*.

Molar conductance :

The conductance of an electrolytic solution can be measured if cell constant and resistance of the solution of cell is known , by the following equation

$$K = \frac{cell\,cons\tan t\,(G^*)}{R}$$

If one mole electrolyte is dissolved in a volume of electrolytic solution kept between two electrodes such that the distance between to two electrode is 1cm then the conductance of solution is known as molar conductance. It is represented as $\wedge_m$.

$$\wedge_m = \frac{Kc}{C}$$

$$\text{or } \wedge_m = \frac{K \quad 1000}{M}$$

CGS unit of molar conductance ($\wedge_m$) is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. Molar conductance ($\wedge_m$) in SI unit is = $\text{Scm}^2\text{mol}^{-1}$

Relation of conductance and molar conductance with concentration :

Conductance and Molar conductance both changes with concentration of electrolyte.

(i) conductance always decreases with decrease in concentration of electrolyte for both strong electrolytes and weak electrolytes.

(ii) with the decrease in concentration of solution molar conductance increases because it has been found that decrease in K on dilution of a solution is more than compensated by increase in its volume.

when concentration approaches zero, the molar conductivity is known as limiting molar conductivity ($\wedge_m^\circ$). The variation of $\wedge_m$ with concentration is different for strong and weak electrolytes.

(i) Strong electrolytes :

For strong electrolytes $\wedge_m$ increases slowly with dilution.

(ii) Weak electrolytes :

For weak electrolytes like acetic acid the degree of dissociation increases with dilution and as a result number of ions in total volume also increases. In this case $\wedge_m$ increases steeply on dilution especially near lower concentrations. At infinite dilution (concentration $C \Rightarrow o$) $\alpha = 1$, i.e, electrolyte dissociates completely.

At a such low concentration the conductivity of the solution is so low that it cannot be measured accurately. In this case $\wedge_m^\circ$ is measured with the help of Kohlrausch law.

Kohlrausch law :

At infinite dilution molar conductivity of an electrolyte can be represented as the sum of the individual contribution of the anions and cations of the electrolyte.

$\Lambda^\circ_m = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$ Λ°_m = molar conductivity at infinite dillution of the solution .

ν_+ and ν_- is no of cations and anions respectively.

λ°_+ and λ°_- are the limiting molar ionic conductivities of cation and anion repectively.

* If at any concentration c, $\propto$ is the degree of dissociation, then we can represent $\propto$ as a ratio of molar conductivity $\wedge_m$ and molar conductivity at infinite dilution $\wedge_m^\circ$.

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$$

$$= \frac{\text{molar conductivity of the solution}}{\text{molar conductivity at infinite dilution}}$$

Equivalent Conductance :

If one gm equivalent of an electrolyte is dissolved in litre of solution placed between two electrode of specific size separated by 1 cm distance then the conductance of the solution is known as equivalent conductance represented by $\wedge_e$, $\wedge_e = \dfrac{K \;\; 1000}{C}$

Relation between molar conductance and specific conductance :

$$\wedge_m = K \times \frac{1000}{M}$$

M = molarity of electrolytic solution.

$\wedge_m$ = molar conductance

K = specific conductance

Relation between specific conductance and cell constant :

$$K = \frac{1}{R} \times \frac{l}{A}$$

where, R = resistance

$\frac{l}{A}$ = cell constant

K = specific conductance.

Relation between equivalent conductance and specific conductance:

$$\wedge_e = K \times \frac{1000}{N}$$

Where, $\wedge_e$ = equivalent conductance

K = specific conductance

N = normality of electrolytic solution.

Relation between molar conductance and equivalent conductance :

$$\wedge_e = \frac{\wedge_m}{z}$$

Where, $\wedge_e$ = equivalent conductance

$\wedge_m$ = molar conductance

z = total valency of cation or anion present per unit of formula weight.

Faraday's laws of Electrolysis :

First law :

The amount of substance deposited or consumed at electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte (solution or melt)

If Q coulumb of electricity is passed through an electrolytic solution and amount of substance deposited or consumed at electrode is W then according to first law of Faraday

$$W \propto Q$$

$$W = z \times Q$$

$$W = z \times I \times t$$

Where, z = electrochemical equivalence

Q = I × t = current flow × time

Second law :

The amounts of different substances liberated at different electrode by passing same amount of electricity through electrolytic solution in molten or dissolved state is proportional to their chemical equivalent weight (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

If same amount of current is passed through two different electrolytic solution (AX and BX) and W_1 and W_2 gm of substance is liberated at two electrodes then according to Faraday's second law we can write

$$W_1 \propto E_1 \ , \ W_2 \propto E_2$$

$\therefore \dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$ /Where E_1 and E_2 are Electrochemical equivalent of AX and BX.

Combination of Faraday's first law and second law :

According to Faraday's first law

$W \propto Q$ /when E is constant

According to Faraday's second law

$W \propto E$ / when Q is constant

$$\therefore W = \frac{Q \times E}{F} = \frac{EIT}{96500}$$

Where, W = amount of substance evolved

Q = amount of electricity passed

E = chemical equivalence

F = Faraday's constant

I = Current flow

t = time

Relation between Faraday (F), Avogadros Number (N), and charge of electron (e).

we know 1 gm equivalent ion carry 1 Faraday of electricity

$\therefore$ charge of 1 gm equivalent of ions having valency n = nF

$\therefore$ charge of one ion having valency $n = \dfrac{nF}{N}$

If charge of one electron is e, charge of one electron having valey n = ne

$$\therefore ne = \frac{nF}{N}$$

$$\therefore e = \frac{F}{N}$$

Where, e = charge of electron

F = Faraday's constant

N = Avogadro's number

Battery :

Battery is a Galvanic cell or combination or two of more Galvanic cell which act as a source of Direct current (DC).

It may be divided in two catagories –

(i) Primary battery or cell

(ii) Secondary battery or cell

Primary battery :

In this type of battery the reactants taking part in chemical reaction inside the cell gradually vanishes. At last stage battery cannot produce electricity and it is removed. example - Dry cell, laclance cell. This type of battery is used in radio and watches. In this type of cell zinc cup acts as anode and cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon.

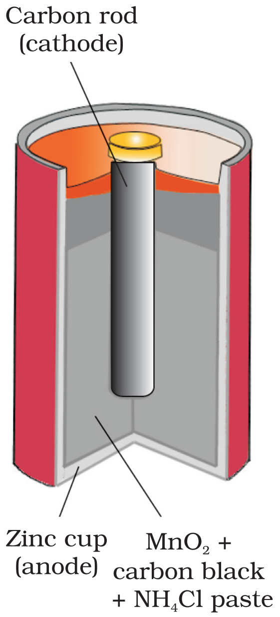


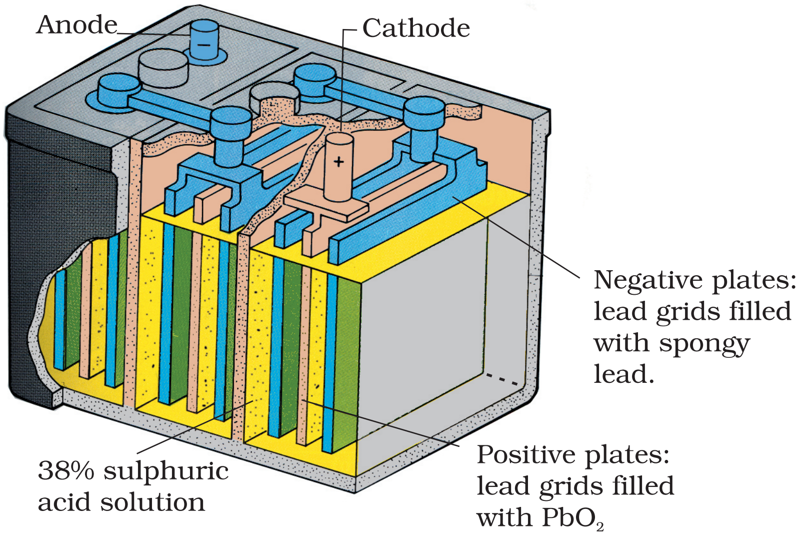
Fig. :A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.

Secondary Battery :

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. It is commonly used in automobiles and invertors. Example lead storage battery. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrotype.

The overall cell reaction consisting of cathode and anode reaction is –

$$Pb\ (s) + PbO_2\ (s) + 2\ H_2SO_4\ (aq) \rightarrow 2PbSO_4(s) + 2H_2O\ (l)$$



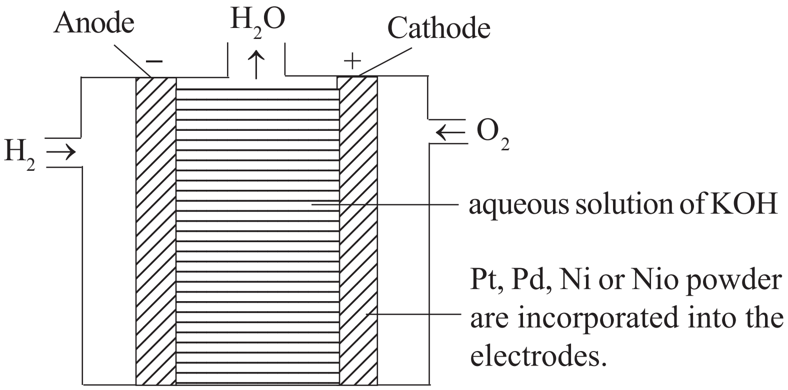
Another important secondary cell is the micked cadium cell. The overall reaction can be represented as –

$$Cd\ (s) + 2Ni(OH)_3\ (s) \rightarrow CO\ (s) + 2Ni(OH)_2(s) + H_2O\ (l)$$

Fuel cell :

These are specially designed Galvanic cell in which the energy obtained from combustion of fuels like hydrogen, methane, methanol etc are converted directly into electrical energy. In this type of cell reactants can be fed continuously to the electrons and products are removed continuously from the electrolyte compartment.

One of the most successful fuel cells using H_2 and O_2 are used for providing electrical power. It is also used in space shuttle.



Fuel cell

Cathode reaction : $O_2\,(g) + 2H_2O(l) + 4l^{-} \rightarrow 4OH^{-}\,(aq)$

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

Overall reaction :

$$2H_2(g) + O_2\,(g) \rightarrow 2H_2O(l)$$

Fuel cell acts with 70% efficiency compared with thermal plants whose efficiency is about 40% . Fuel cells are pollution free.

Corrosion :

Corrosion basically is an electrochemical phenomenon where metal is oxidised in presence of water and air in open environment and form metal oxide. The rusting of iron, farnishing of silver, development of green coating on copper and bronze are some of examples of corrosion.

The anode and cathode reaction related with rusting of iron may be expressed as –

Anode reaction : $2Fe\,(s) \rightarrow 2Fe^{2+} + 4e^{-}$

Cathode reaction : $O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)$

The overall reaction can be represented as –

$$2Fe(s) + O_2(g) + 4H^{+}(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

The ferrus ions are further oxidised by atmospheric oxygen to ferric ions. It come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 . XH_2O$) .

Corrosion of metal can be prevented by covering the surface of metal with paint or chemical substance (like bisphenol).

Another important method is to cover the surface of metal by other metals (Sn, Zn etc.) that are inert or react to save the object. Now a days electrochemical method is used with metal electrode like Mg, Zn which corrodes itself to save the object from corrosion.

Hydrogen economy :

The policy to use hydrogen as a source of renewable and non polluting source of energy is known as hydrogen economy. Both the production of hydrogen by electrolysis of water and hydrogen combustion in a fuel cell and both the related technologies are based on electro chemical principles.

A. Select the correct answer (MCQ) : (1 mark each)

1. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is –

(a) LiCl > NaCl > KCl
(b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl
(d) LiCl > KCl > NaCl

2. The number of faradays required to reduce one mole of Cu^{2+} to metalic copper is –

(a) One
(b) Two
(c) Three
(d) Four

3. The unit of equivalent conductance is :

(a) $ohm^{-1}\ cm^{2}\ eqniv^{-1}$
(b) $ohm^{-1}\ cm^{2}\ gm^{-1}$
(c) $ohm\ cm^{2}\ qgniv^{-1}$
(d) $ohm^{-1}\ mol^{-1}$

4. In normal hydrogen electrode, the concentration of H^{+} ion is –

(a) 0.1 (M)
(b) 0.2 (M)
(c) 1M
(d) 2M

5. The main function of salt bridge is –

(a) to allow ions to go from one half-cell to another.
(b) to provide link between two half cells.
(c) to keep the emf of the cell positive.
(d) to maintain electrical neutrality of the solution in two half cells.

6. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called –

(a) Cell potential
(b) cell emf
(c) potential difference
(d) cell voltage

7. Best way to prevent rusting of iron by –

(a) making iron cathode greasy
(b) putting in saline water
(c) both of these
(d) none of these

8. $\wedge^{\circ}_{m}(NH_4OH)$ is equal to -

(a) $\wedge^{\circ}_{m}\ (NH_4OH) + \wedge^{\circ}_{m}(NH_4Cl) - \wedge^{\circ}\ (HCl)$
(b) $\wedge^{\circ}_{m}\ (NH_4Cl) + \wedge^{\circ}_{m}\ (NaOH) - \wedge^{\circ}\ (NaCl)$
(c) $\wedge^{\circ}_{m}\ (NH_4Cl) + \wedge^{\circ}_{m}\ (NaCl) - \wedge^{\circ}\ (NaOH)$
(d) $\wedge^{\circ}\ (NH_4OH) - \wedge^{\circ}_{m}\ (NaOH) + \wedge^{\circ}\ (NaOH)$

9. The quantity of charge required to obtain one mole of alumunium from Al_2O_3 is –

(a) 1F (b) 6F (c) 3F (d) 2F

10. The SI unit of molar conductivity is ;

(a) Sm^2mol^{-1} (b) $Sm^{-1}mol^{-1}$ (c) $Sm^{-2}mol$ (d) Sm^3mol^{-1}

11. Which of the following statement is correct ?

(a) Equivalent conductance decreases with dilution.

(b) Specific conductance increases with dilution.

(c) Specific conductance decreases with dilution.

(d) Equivalent conductance increases with increasing concentration.

12. In an electro chemical cell, the electrons flow –

(a) from cathode to anode (b) from anode to cathode

(c) from anode to solution (d) from solution to cathode

13. Passage of 1 Faraday of electricity through a solution of $CuSO_4$ deposits :

(a) 1 mole of Cu (b) 1 8 atom Cu
(c) 1 mole cule of Cu (d) 1g equivalent Cu.

14. In SI system the relation between equivalent conductance ($\wedge_e$) , specific conductance (K) and equivalent concentration (C) is :

(a) $\wedge_e = \frac{K}{C}$ (b) $\wedge_e = \frac{K \times 1000}{C}$

(c) $\wedge_e = \frac{K \times 10^{-3}}{C}$ (d) $\wedge_e = \frac{K \times 10^{-6}}{C}$

15. The cell constant (K) for an electrical conductivity cell having two electrodes of area A placed at a distance of *l* is expressed by :

(a) $K = l/A$ (b) $K = l^2/A$ (c) $K = A/l$ (d) $K = \frac{1}{Al}$

16. The SI unit of conductivity (specific conductance) is :

(a) Sm (b) Sm^{-1} (c) $S^{-1}m^{-1}$ (d) None

17. Faraday's laws of electrolysis are related to the :

(a) atomic number of the cation (b) atomic number of anion

(c) equivalent weight of the electrolyte (d) speed of the cation

18. Select the one that is a secondary cell :

    (a) Mercey (b) Fuel cell (c) Dry cell (d) Ni-Cd cell

19. When a lead storage battery is discharged –

    (a) lead is formed (b) lead sulphate is consumed

    (c) Sulphuric acid is consumed (d) SO_2 is evolved

20. Specific conductivity of a solution –

    (a) increases with dilution (b) decreases with dilution

    (c) remains unchanged with dilution (d) depends on mass of electrolyte

21. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to –

    (a) increase in ionic mobility of ions

    (b) 100% ionisation of electrolyte at normal dilution

    (c) increase in both ie; number of ions and ionic mobility of ions

    (d) increase in number of ions

22. The standard electrode potential is measured by –

    (a) Electrometer (b) Voltmeter (c) Pyrometer (d) Galvanometer

B. Assertion - Reason type questions : (1 marks each)

In each of the following questions, two statements are given, one is assertion (A) and the other is reason (R). Examine the statements carefully and mark the correct answer according to the instructions give below :

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).

(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).

(c) If (A) is correct , R is wrong .

(d) If (R) is correct , A is wrong.

1. Assertion : In an electricity cell, the anode is positive and cathode is -ve terminal.

   Reason : In the electrolytic cell, electrons are supplied by external source.

2. Assertion : Zinc liberates H_2 gas from dilute HCl .

   Reason : Hydrogen is below zinc in electro chemical series.

3. Assertion : Current stops flowing when $E_{cell} = 0$

Reason : Equillibrium of cell reaction is attained.

4. Assertion : Copper sulphate solution can be stored in zinc vessel.
Reason : Zinc is less reactive than copper.

5. Assertion : Molar conductance of an electrolyte increases with dilution.
Reason : Ions move faster in dilute solutions due to decrease in interionic attractions.

6. Assertion : Galvanised iron does not rust.
Reason : Zinc has more negative electrode potential than iron.

7. Assertion : Cu is less reactive than hydrogen .
Reason : $E^{(0)}_{Cu^{2+}/Cu}$ is negative.

8. Assertion : For measuring resistance of an ionic solution an AC source is used.
Reason : Concentration of ionic solution will change if DC source is used.

9. Assertion : $\wedge_m$ for weak electrolytes shows a sharp increase when the electrolytic solution is dilluted.
Reason : For weak electrolytes degree of dissociation increases with dilution of solution.

10. Assertion : Fluoride ion (F^-) is not oxidised by MnO_2 while Cl^- ion is readily oxidised.
Reason : Fluorine has highest reduction potential among all halogens.

C. Very short answer type questions : (1 mark each)

1. What is the SI unit of molar conductance ?
2. What do you mean by one Faraday?
3. Amount of charge in culumb carried by avodadro number of electrons is ______?
4. State the main purpose of using salt bridge.
5. State one difference between Galvanic cell and electrolytic cell.
6. The reduction potential of two metal A and B are given below –

$$E^o_{A+/A} = -0.60V\ ,\ E^o_{B+/B} = -0.90V$$

among this two which one will reduce the ion of another.

7. If cell reaction attains equilibrium what will be the potential difference of the cell?
8. What is the chemical formula of rust ?
9. The molar conductance of NH_4OH at infinite dilution is 271.1 $Scm^2\ mol^{-1}$. What will be the molar conductance of 1.3% 0.1(M) solution?

10. What is the relation between specific conductance and molar conductance?

11. If 2F current are passed through $CuSO_4$ solution the amount of Cu deposited in gm is ?

12. Which one among the following will have more conductance?

    0.1M HCl and 0.1M CH_3CO_2H

13. Which cell is used in space ship as electro chemical cell ?

14. What is the role of CO_2 gas in rusting ?

15. Why $ZnCl_2$ is added in dry cell?

16. Can we store $CuSO_4$ solution in iron vessel ?

17. Zn liberates H_2 gas from dilute HCl but Cu metal does not, why?

18. What is electrochemical series?

19. State Kohlraush law?

20. What do you mean by reduction potential ?

21. Write the structure of the cell from the following cell reaction –

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

22. Write Nernst equation.

23. Write the relation between electrochemical cell and Gibbs free energy of reaction.

24. What is the unit of resistance ?

25. Write the relation between cell constant, conductivity and resistance?

26. How molar conductivity at infinite dilution is expressed?

27. Write the cell from the following cell reaction –

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

28. Write the overall reaction of Ni-Cd cell.

29. Write the name of two fuels beside H_2, which can be used in fuel cell.

30. Define fuel cell.

D. Short answer type questions : (2 marks each)

1. Arrange the following metals in accordance with power of displacing another metal from the solution of their salt –

   Al, Cu, Fe, Mg and Zn

2. Arrange the following in increasing order of reducing power from the given electrode potential value.

   $K^+/K = -2.93v$, $Ag^+/Ag = 0.80v$

   $Hg^{2+}/Hg = 0.79v$, $Mg\ 2^+/Mg = -2.37v$

   $Cr^{+3}/Cr = -0.74v$

3. Define molar conductance for a electrolytic solution.

4. What do you mean by cell constant.

5. What is fuel cell ? give example.

6. State faraday's first law of electrolysis.

7. What amount of charge is required to reduce 1 mole Al^{3+} to Al.

8. Calculate the amount of charge of 1 mole of electrons.

9. Explain the conductance of a solution decreases with dilution.

10. What do you mean by standard electrode potential ?

11. What do you mean by standard hydrogen electrode? Give an example of its use.

12. Wheather copper sulphute solution can be stored in zinc vessel? explain.

13. Write the structure of the cell related with the following reaction –

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

14. Calculate Gibbs free energy for the following reaction –

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

15. Write the mathematical expression of Faraday's second law of electrolysis and explain the symbol used.

16. Conductance of ionic solution depends on which factors?

17. What is the unit of molar conductance? Mention its relation with specific conductance.

18. State Kolhrush law of free movement of ions.

19. What is the difference between primary battery and secondary battery?

20. If 2.40A current is passed through $AgNO_3$ solution for 20 min, calculate the amount of Ag deposited in gm unit.
21. Can we store 1M $AgNO_3$ in allumunium vessel?
22. Write down the relation between E^o and $\Delta G^{(-)}$. What is the unit of molar conductance?
23. What is the difference between primary cell and secondary cell?
24. Calculate the amount of electricity required to produce 0.400g Cu from $CuSO_4$ solution in 30 minutes.

E. Answer the following questions : (Marks - 3)

1. Draw the structure of Daniell cell and show its parts.
2. What is salt bridge? Write about its constituents and use.
3. Write Nernst equation of electrode potential. If the standard electrode potential of Daniell cell is 1.IV then calculate standard Gibbs free energy for the following reaction –

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

4. Write the structure of Galvanic cell for the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. Write about the reactions taking place in each electrode.
5. At 298K temparature the conductance of 0.20M KCl solution is 0.0248 Scm^{-1}. Calculate molar conductance of the solution.
6. Calculate the amount of charge/current required to oxidise 1mol H_2O to O_2.
7. Calculate the amount of charge required in faraday to get 20.0g Ca from molten $CaCl_2$.
8. A cell having 0.00M KCl solution shows 1500Ω resistance at 298K temparature. It conductance of 0.001M KCl solution at 298K is 0.146×10^{-3} Scm^{-1} then calculate the cell constant.
9. Calculate emf of decimolar Daniell cell at 25°C temparature. Given $E^\circ_{Zn^{2+}/Zn} = -0.76v$ and $E^\circ_{Cu^{2+}/Zn} = +0.34v$.
10. At infinite dilution molar conductance of HCl, NaCl and CH_3COONa are 426.2, 126.5, 91.0 ohm^{-1} cm^2 mol^{-1} recpectively. Based on these values calculate molar conductance of CH_3COOH at infinite dilution.
11. Establish the relation, $e = \frac{F}{N}$ (symbols bear their usual meaning)
12. What do you mean by emf and standard emf of Galvanic cell? Write down the relation between standard emf and Gibbs free energy related with cell reaction.
13. Write down Nernst equation for the cell reaction of Daniel cell. If concentration of Zn^{2+} ion is increased what will be its effect on E_{cell}.

14. $2\ Cr\ (s) + 3Fe^{2+}\ (0.1M) \rightarrow 2Cr^{3+}\ (-0.01m) + 3Fe\ (s)$

    From the above reaction calculate emf at 298K. Given : $E^\circ_{Cr^{3+}/Cr} = -0.74v$

    $E^\circ_{Fe2+/Fe} = -0.44v$

15. Calculate the equilibrium constant for the following reaction –

    $$Fe(s) + Cd^{2+}\ (aq) \rightleftharpoons Fe^{2+}(aq) + Cd\ (s)$$

    given $E^o_{Cd^{2+}/Cd} = -0.40v$ and $E^o_{Fe^{2+}/Fe} = -0.44v$

16. Calculate the maximum work from the following electro chemical cell –

    given $E^o_{Zn^{2+}/Zn} = -0.76v$ and $E^o_{Cu^{2+}/Cu} = +0.34v$

17. At 25° C equivalent conductance of NH_4Cl, NaOH and NaCl at infinite dilution is 130, 217.6 and 108.9 $ohm^{-1}\ cm^2\ gequiv^{-1}$ recepctively. Calculate $\wedge^\circ$ of NH_4OH at this temparature.

18. When 0.6 ampere current is passed for 40 min through $CuSO_4$ solution 0.2964 gm Cu is deposited. What will be electro chemical equivalence of copper.

19. If 200 milli ampere current is passed through moltenr NaCl for 1min. Calculate the amount of mole of Cr formed.

20. Explain the reason for rusting of iron.

21. If $\wedge^\circ m\ (NaCl) - \wedge^\circ m\ NaNO_3 = 3.70hm^{-1}\ cm^2\ mol^{-1}$ then calculate $\wedge^\circ LiCl - \wedge^\circ LiNO_3$

22. Explain the probability of the following reaction –

    $$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

    Given the standard electrode potential of

    Zn^{2+}/Zn and Cu^{2+}/Cu are –0.76v and +0.34v respectively.

23. Calculate the time required to deposit 1.27 g Cu at cathode by passing 2A current through $CuSO_4$ Solution.

    ($Cu = 63.5\ gmo1^{-1}$, $1F = 96500\ Cmol^{-1}$)

24. $Zn\ (s)\ |\ Zn^{2+}\ (0.0004M)\ ||\ Cd^{2+}\ (0.2M)\ |\ Cd\ (s)$

    Calculate emf and ΔG for the above reaction.

    Given $E^\circ_{(Zn^{2+}/Zn)} = -0.763v$, $E^\circ_{(Cd^{2+}/Cd)} = -0.403v$

25. The electrical resistance of a column of $0.05\ mol^{-1}$ NaOH solution of diameter 1cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

F. Long answer type question : (Marks - 5)

1. Write the Nernst equation and calculate emf of the following cells at 298K

   (i) Mg(s) | Mg^{2+} (0.0001M) || Cu^{2+} (0.001M) | Cu(s)

   (ii) Pt (s) | Br^- (0.010M) | Br_2 (*l*) || H^+ (0.030M) | H_2(g) (1bar) | Pt(s)

2. How much electricity in term of coulomb for the oxidation of

   (i) 1 mol of H_2O to O_2 ?

   (ii) 1 mol of FeO to Fe_2O_3?

3. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity if $\wedge°m$ for acetic acid is 390.5 Scm^2 mol^{-1}. What is its dissociation constant?

4. Three electrolytie cells A,B,C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are connected in series. A steady current of 1.5 amperes was passed through then until 1.45g of silver deposited at the cathode of cell . How long did the current flow? What mass of copper and zinc we deposited?

5. (i) How conductance is measured?

   (ii) Rusting is a electro chemical phenomenon – explain.

6. Explain with reason –

   (i) If Mg is placed in contact with iron pipe corrosion of iron does not take place .

   (ii) Conductivity of a solution decrease with dilution.

7. Two electrolytic cell are in connected in series in which one contain $AgNO_3$ solution and another containing dilute H_2SO_4 solution. 2.5 ampere of current produce 1.078 gm Ag

   (i) What amount of current is used?

   (ii) What is the mass of oxigen produced?

   (iii) What is the duration of time of electricity?

Answer of MCQ :

1. b	2. d	3. a	4. c	5. d	6. b	7. a	8. b
9. c	10. a	11. c	12. b	13. d	14. b	15. a	16. b
17. c	18. d	19. c	20. b	21. a	22. b		

Chapter - 4

Chemical Kinetics

Chapter at a glance :

1) **Rate of Reaction :** Rate of a chemical reaction can be defined as the decrease in the concentration of reactants or increase in the concentration of products per unit time.

Consider the Chemical reaction

$A+B \longrightarrow C + D$

Rate of chemical reaction

$$= -\frac{\Delta}{\Delta t}[A] = -\frac{\Delta}{\Delta t}[B] = \frac{\Delta[c]}{\Delta t} = \frac{\Delta[D]}{\Delta t}$$

Significant of –Ve Sign : Rate of reaction is a positive quantity. With respect to time concentration of the reactant decreases & it become –Ve. So to make it positive –Ve sign is used

$$\text{i.e} - \left\{-\frac{\Delta[A]}{\Delta t}\right\}$$

2) **Average rate of reaction :** It can be defined, rate of disappearance of reactant or rate of appearance of product of a long time of interval.

$$\text{i.e, Average rate of reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time interval}}$$

3) **Instantaneous rate of reaction :**

During the reaction, rate of change of concentration i,e rate of disappearance of reactant or rate of appearance of product at any moment i,e time of interval is very very small.

$$\lim_{\Delta t \to O} \frac{-\Delta[A]}{\Delta t} = \lim_{\Delta t \to O} \frac{-\Delta[B]}{\Delta t} = \lim_{\Delta t \to O} \frac{\Delta[C]}{\Delta t} = \lim_{\Delta t \to O} \frac{\Delta[D]}{\Delta t}$$

i.e $-\frac{d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$

i,e Instantaneous rate of reaction $-\frac{d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$

4) **Unit of rate of reaction :**

mol L^{-1} S^{-1} or mol L^{-1} min^{-1} or atm S^{-1} or atm min^{-1}

5) **Factors influence the rate of chemical reaction :**

- Concentration of reactant : Rate of chemical reaction increases with increasing the concentration of reactant because No. of collision increases.
- Nature of reactants & Products :

$2\ NO + O_2 \longrightarrow 2\ NO_2$ ——— (I)

$2\ CO + O_2 \longrightarrow 2\ CO_2$ ——— (II)

Rate of reaction of 1st one is more. Because bond order of NO. is 2.5 while bond order of CO is 3.

- Temperature : Rate of reaction increases with increasing temperature, almost all chemical reactions i,e exothermic and endothermic. Rate of reaction for most of the chemical reaction is become double for every 10°C rise - in temperature.
- Surface area of solid reactants : Rate of reaction increases with increasing the surface area of the solid reactants.
- Presence of catalyst : Generally rate of reaction increases in presence of catalyst because catalyst reduce the activation energy of the reacting molecules.
- Sunlight :

$H_2 + Cl_2 \xrightarrow{\text{Dark}}$ No reaction

$H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2\ HCl$

6) **Law of mass action :**

At a given temperature the rate of a chemical reaction is directly proportional to the product of the molar concerntration of the reactants.

For example, $A + B \longrightarrow C$

Rate of reaction = K [A] [B]

K is the proportionality constant. This is known as rate constant. Rate of reaction can be measured with the help of rate constant.

If value of K is more, reaction is faster.

7) **Rate Law expression :**

or

Rate Law or Rate equation :

Rate Law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

It should be remembered that rate Law of any reaction can't be predicted by looking at the balanced chemical equation i,e theoratically but it must be determined experimentally.

For example,

$$aA + bB + cC \longrightarrow - \text{Pdts}$$

Rate of reaction = $K [A]^p [B]^q [C]^r$

This rate Law is experimentally determined i,e p, q & r values are experimentally determined. Hence value of p, q & r may or may be equal to the stoichiometric - coefficients (a, b & c) of the reactants.

8) **Order of a reaction :** Sum of powers of the concentration of the reactants in the rate Law expression is called the order of a chemical reaction.

The order of chemical reaction for the reaction.

$$aA + bB + cC \longrightarrow \text{Pdts}$$

Rate = $K [A]^p [B]^q [C]^r$

Therefore overall rate of reaction (n)

$$= p + q + r$$

If n = 1, then it is 1st order reaction

n = 2, then it is 2nd order reaction.

(i) with respect to 'A' order of reaction is 'p'

(ii) with respect to 'B' order of reaction is 'q'

(iii) with respect to 'C' order of reaction is 'r'

order of reaction may be zero, whole number, even or fractional.

9) Some examples of 1st order, 2nd order, zero oder & fractional order of reaction :

i) $N_2O_5\,(g), \longrightarrow 2NO_2\,(g) + \frac{1}{2}O_2$

Rate of reaction = $K\,[N_2O_5]$

ii) $SO_2Cl_2 \longrightarrow SO_2\,(g) + Cl_2\,(g)$

Rate of reaction = $K\,[SO_2Cl_2]$

iii) Radio active change.

All the above examples are of first order reaction.

iv) $2NO_2\,(g) \longrightarrow 2NO\,(g) + O_2\,(g)$

Rate of reaction = $K\,[NO_2]^2$

v) $NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)$

Rate of reaction = $K\,[NO_2]\,[O_3]$

All the above reactions are of 2nd order reaction.

vi) $2NH_3\,(g) + O_3\,(g) \xrightarrow{pt} N_2\,(g) + 3H_2\,(g)$

Rate of reaction $= K\,[NH_3]^O$

$= K$

It is zero order reaction

10) **Unit of rate constant :**

Unit of rate constant is determined with the help of overall order of reaction with respect to time.

i,e unit of $K = (\text{mol L}–1)^{1–n}\ S^{-1}$

Here *n* is the order of reaction

So for 1st order reaction,

$K = S^{-1}$

For 2nd order

$K = (\text{mol L}^{-1})^{1-2}\ S^{-1}$

$= (\text{mol L}^{-1})^{-1}\ S^{-1}$

$= (\text{mol L}^{-1})^{-1}\ S^{-1}$

$= \text{L mol}^{-1}\ S^{-1}$

For 3rd order

$K = (\text{mol L}^{-1})^{1-3}\ \text{S}^{-1}$

$= (\text{mol L}^{-1})^{-2}\ \text{S}^{-1}$

$= \text{L}^{2}\ \text{mol}^{-2}\ \text{S}^{-1}$

For zero order

$K = \text{mol L}^{-1}\ \text{S}^{-1}$

11) **Elementary reaction :**

A chemical reaction which occurs in a single step but no intermediate is formed is called elementary reaction.

Such as $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

12) **Complex reaction :**

Chemical reactions which involve more then one step is called complex reaction. The slowest step is the rate determining step.

Such as $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Above reaction takes place in the following way.

Step–1 $NO_2 + NO_2 \longrightarrow NO + NO_3$(slow step)

Step–2 $NO_3 + CO \rightarrow CO_2 + NO_2$ (Fast step)

$$\overline{NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)}$$

Rate : $= K[NO_2]^2$

13) **Molecularity :**

Molecularity is the Number of molecules, atoms, free radicals or ions which are required for a simple chemical reaction.

Molecularity of a chemical reaction is always a whole number. It is never be fractional, zero as negative. It is theoretical concept.

For example,

i) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

Molecularity is one

ii) $2HI(g) \longrightarrow H_2(g) + I_2(g)$

Molecularity is two

iii) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Molecularity is three

Example of tri molecular reaction is very less. Example of tetra molecular reaction or more than tetra molecular is almost nil.

14) **Integrated rate expression :**

The Integrated rate equations for different order reactions can be derived in the following way

a) Zero order reaction

Let us consider a zero order reaction

$A \longrightarrow$ product

Let us consider initial concentration of reactant is $[A]_o$ and after time 't'. Concentration of reactant become [A].

Rate of reaction $\Rightarrow -\dfrac{d[A]}{dt} = K[A]^0$

$$\Rightarrow -\frac{d[A]}{dt} = K$$

$$\Rightarrow -d\ [A] = K\ dt$$

Integrating both sides, we get,

$$-\int d\,[A] = k\int dt + I\ ;$$

$\Rightarrow \quad -[A] = kt + I$ .... (1) where I = Integration constant

When t=0, $[A] = [A]_0$

From equation (1), $= -[A]_0 = I$

Putting the value of 'I' $= -[A]_0$ in equation (1), we get,

$$-[A] = kt - [A]_0$$

$$\Rightarrow \quad [A]_o - [A] = kt$$

$$\Rightarrow K = \frac{[A]_0 - [A]}{t}$$

b) First Order Reaction

Let us consider a first order reaction.

$A \longrightarrow$ Product.

Let the initial concentration of the reactant is $[A]_0$ and concentration of reactant becomes $[A]$ after time 't'

Rate of reaction $\Rightarrow -\dfrac{d[A]}{dt} = K[A]$

$$\Rightarrow \; -\frac{d[A]}{[A]} = K\,dt$$

Integrating both sides, we get,

$$\int -\frac{d[A]}{[A]} = K\int dt \;;$$

$\Rightarrow$ $-\ln[A] = kt + I$ .... (1) where I = Integration constant

When $t=0$, $[A] = [A]_0$

From equation (1), We get,

$$-\ln[A]_0 = I$$

Putting the value of 'I' in equation (1), we get,

$$-\ln[A] = kt - \ln[A]_0$$

$$\Rightarrow \quad \ln[A]_0 - \ln[A] = kt$$

$$\Rightarrow \quad \ln\frac{[A]_0}{[A]} = kt$$

$$\Rightarrow \quad K = \frac{1}{t}\ \ln\frac{[A]_0}{[A]}$$

$$\Rightarrow \quad K = \frac{2\cdot 303}{t}\ \log\frac{[A]_0}{[A]}$$

15) **Half-life ($t_{1/2}$) of a reaction :** (Equation of half life of different reactions)

It is defined as the time in which the concentration of a reactant is reduced to one-half of its initial concentration

For a zero order reaction, $K = \dfrac{[A]_0 - [A]}{t}$

When t is $t_{1/2}$, then $[A] = \dfrac{[A]_0}{2}$

$$\therefore\ \mathrm{K} = \frac{[\mathrm{Ao}]_0 - \dfrac{[\mathrm{A}]_0}{2}}{t_{1/2}}$$

$$\Rightarrow t_{1/2} = \frac{[\mathrm{A}]_0}{2\mathrm{K}}$$

For a first order reaction, K = log $\frac{2\cdot 303}{t}\log\frac{[\mathrm{A}]_0}{[\mathrm{A}]}$

When t is $t_{1/2}$, then $[A]$ become $\frac{[A]_0}{2}$

$$\mathrm{K} = \frac{2\cdot 303}{t_{1/2}}\log\frac{[\mathrm{A}]_0}{\frac{[\mathrm{A}]_0}{2}}$$

$$t_{1/2} = \frac{2\cdot 303}{K}\ \log 2$$

$$t_{1/2} = \frac{0\cdot 693}{k}$$

16) **Pseudo-first order reactions**

When a second order reaction involving two different reactants is carried out in presence of a large excess of one reactant, rate of the reaction becomes dependent only on the concentration of other reactant and the reaction is found to be first order with respect to this reactant. Such reaction are called Pseudo first order reactions.

Example : Hydrolysis of Sucrose in acidic medium.

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

Sucrese glucose fouctose

17) **Temperature Co-efficient of a reaction**

The ratio of rate constants of a reaction of two different temperatures which differ by 10°c is termed as temperature Co-efficient of a reaction. With increasing the temperature by 10°c, rate of reaction is almost to be double.

$$\text{Temperature Coefficient} = \frac{\text{Rate constant at (T+10) C}}{\text{Rate constant at 10 C}}$$

18) **Arrhenius equation**

The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation.

$$K = A.e^{-\frac{E_a}{RT}}$$

Taking the logarithm in both side, the equation becomes

$$2.303 \log K = 2.303 \log A - \frac{E_a}{2.303\ RT}$$

This equation is simillar with the equation of straight line, y = mx + c,

$$\text{Where slope} = -\frac{E_a}{2.303\ RT}$$

Where, A = frequency factor

E_a = activation energy (in J/mol)

R = universal gas constant

T = temperature.

19) **Activation energy**

The minimum amount of energy in excess of average energy, which the reacting species must possess to become active and suitable to undergo a reaction, is known as activation energy of the reaction.

Determination of activation energy from rate constant

Activation energy = Threshold energy

– Average kinetic energy of the reacting molecules.

E_a= E (Threshold) – E (reactants)

If the value of activation energy is less rate of reaction will be more.

In case of exothermic reaction.

Activation energy of forward reaction

< Activation energy of back-ward reaction

In case of endothermic reaction

Activation energy of backward reaction

< Activation energy of forward reaction

$\Delta H = E_a\text{(Forward)} - E_a\text{(Backward)}$

$$\log\frac{K_2}{K_1}=\frac{E_a}{2\cdot 303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

From the values of K_1 and K_2 at temperatures T_1 and T_2, E_a can be calculated.

Threshold energy :

The minimum energy that all colliding molecules must possess in order to make the collisions effective & successful, is called threshhold eneargy

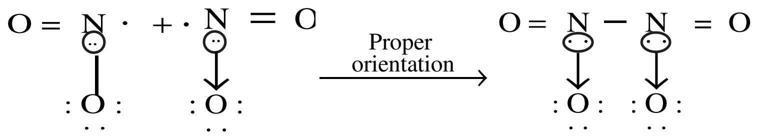
20) **Collision Theory**

For reactions to occur i.e. for effective collisions, the reacting molecules will have to cross two barriers.

i) **Energy barrier :** To bring effective collisions, the reactant molecules must acquire a minimum amount of energy state. This minimum energy is called threshold energy.

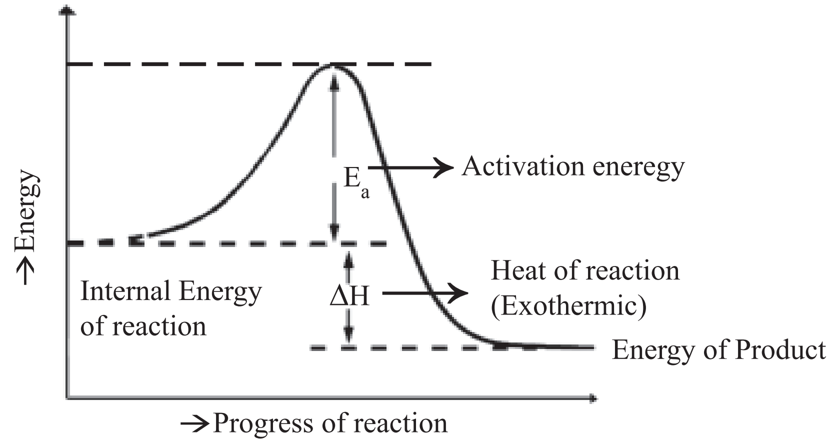
ii) **Orientation barrier :** Molecules associated with threshold energy must have the proper orientations towards one another during their collisions for a reaction to occur.

For Example :

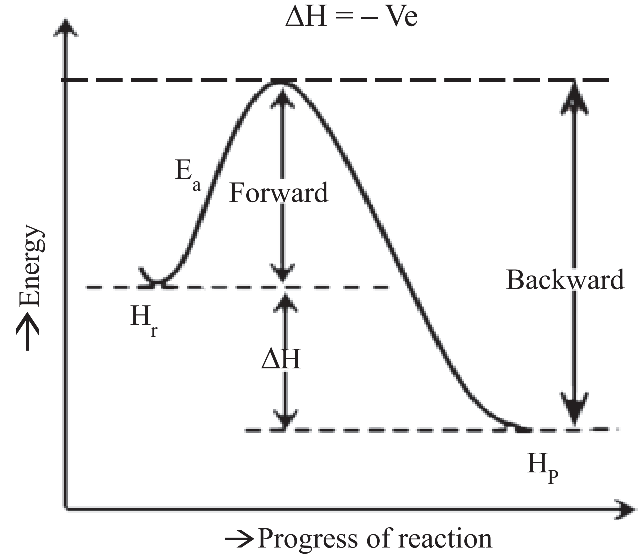


$$O=\underset{\underset{:\ddot{O}:}{|}}{N}\cdot + \cdot\underset{\underset{:\ddot{O}:}{\downarrow}}{N}=O \xrightarrow{\text{Proper orientation}} O=\underset{\underset{:\ddot{O}:}{\downarrow}}{N}-\underset{\underset{:\ddot{O}:}{\downarrow}}{N}=O$$

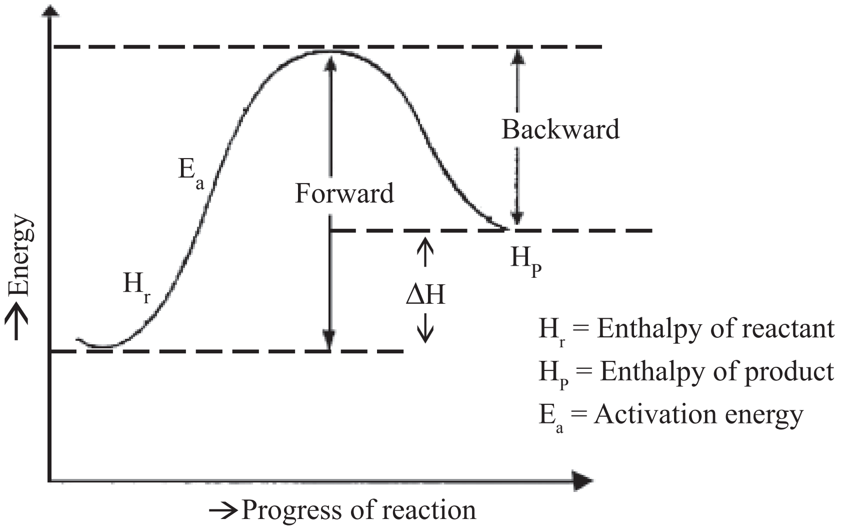
Graph of Energy vs progress of Reaction



Exothermic reaction
ΔH = – Ve

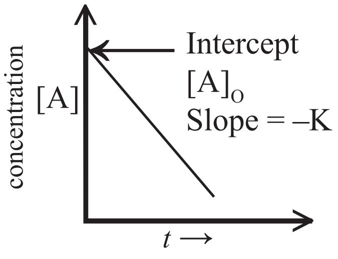


Endothermic reaction
ΔH = + ve

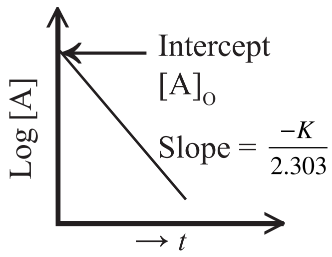


Different graphs

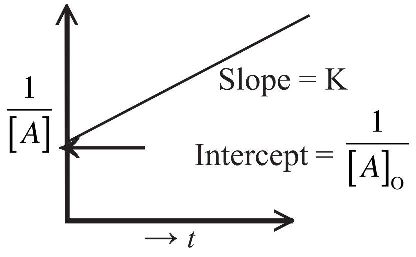
1. Graphs of correcentration vs time of different order reaction.



Zero order reaction

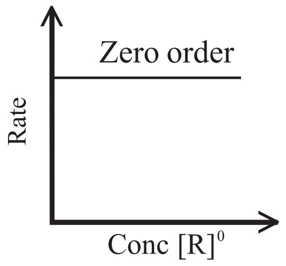


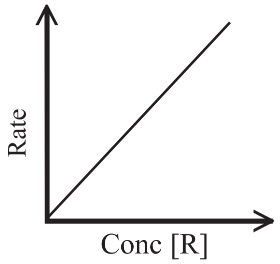
First order reaction



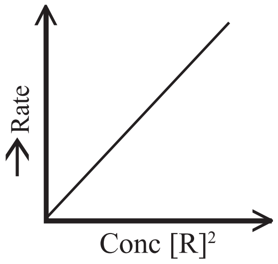
Second order reaction

2. Graphs of Rate vs concentration.



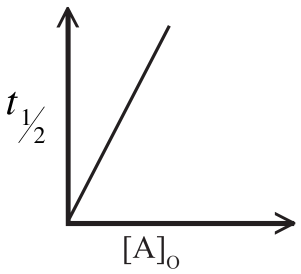


First order

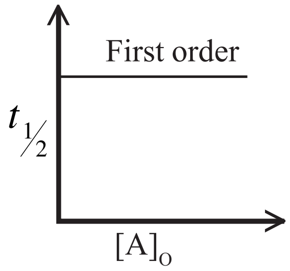


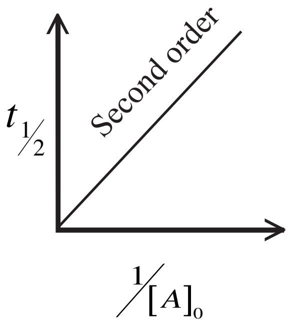
Second order

Graphs of half life $\left(t_{1/2}\right)$ & initial concentration $[A]_0$



Zero order





A. Select the correct answer (MCQ) : (1 mark each)

1. Rate law for the reaction A+ 3B ⟶ C as found to be, rate = K [A] [B]

   Concentration of reactant 'B' is doubled. Keeping the concentration of 'A' constant, the value of rate constant will be

   a) Same b) doubled c) quadrupled d) halved

2. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, if $\frac{d}{dt}[NH_3] = 2\times10^{-4}$ mol L^{-1} S^{-1}, the value of $-\frac{d}{dt}[H_2]$ would be

   a) 3×10^{-4} mol L^{-1} S^{-1}

   b) 4×10^{-4} mol L^{-1} S^{-1}

   c) 6×10^{-4} mol L^{-1} S^{-1}

   d) 1×10^{-4} mol L^{-1} S^{-1}

3. On increasing the pressure three times, the rate of reaction of $2H_2S + O_2 \rightarrow$ product, would increase

   a) 3 times b) 9 times c) 12 times d) 27 times .

4. Which of these does not influence the rate of reaction?

   a) Nature of the reactants

   b) Concentration of the reactants

   c) Temperature of the reaction

   d) Molecularity of the reaction

5. The unit of rate constant depends upon

   a) rate of reaction

   b) order of reaction

   c) molecularity of reaction

   d) All of the above.

6. The value of rate constant for a first order reaction is $2.303 \times 10^{-2}\ S^{-1}$, . What will be the time required to reduce the concentration to $\frac{1}{10}$ th of its initial concentration?

   a) 100 s b) 10 s c) 2.303 s d) 23.03 s

7. The value of rate constant of a reaction is 2.303×10^{-2} L $mol^{-1}\ S^{-1}$. What is the order of the reaction.

   a) zero b) first c) second d) fractional

8. The unit of rate constant for first order reaction is–

   a) mol $L^{-1}\ S^{-1}$ b) S^{-1} c) L $mol^{-1}\ S^{-1}$ d) $L^2\ mol^{-2}\ S^{-1}$

9. The first order integrated rate equation is–

   a) $K = {}^{x}\!/_{t}$

   b) $K = -\dfrac{2\cdot 303}{t} \log \dfrac{a}{a-x}$

   c) $K = \dfrac{1}{t} \ln \dfrac{a}{a-x}$

   d) $K = \dfrac{1}{t} \dfrac{x}{a(a-x)}$

10. When plotted a graph of concentration versus time for zero order reaction, then the value of slope is–

    a) $-\frac{k}{2 \cdot 303}$ b) –2.303 k c) – k d) $\frac{-Ea}{2 \cdot 303R}$

11. For which order half-life period is independent of initial concentration?

    a) zero b) first c) second d) third

12. For a given reaction $t_{1/2} = \frac{1}{k_a}$, the order of the reaction

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

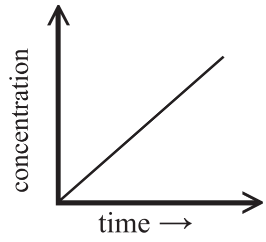
13. According to Arhenius equation, the slope of log k versus $\frac{1}{T}$ plot is

    a) $-\frac{Ea}{2 \cdot 303R}$ b) $-\frac{Ea}{2 \cdot 303}$ c) $-Ea/2 \cdot 303RT$ d) $Ea/2 \cdot 303RT$

14. The activation energy of a reaction at a given temperature is found to be 2.303 RT J mol^{-1}. The ratio of rate constant to the Arhenius factor is –

    a) 0.01 b) 0.1 c) 0.02 d) 0.001

15. The graph of concentration of reactant versus time is given below. What is the order of the reaction?



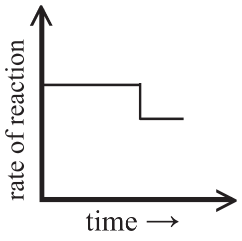
    a) 1 b) 2 c) 3 d) 0

16. For a gaseous reaction, the units of rate of reaction are–

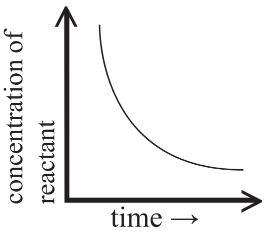
    a) L atm S^{-1} b) atm S^{-1} c) atm mol^{-1} S^{-1} d) mol S^{-1}

17. Which of the following graph is true for zero order reaction?

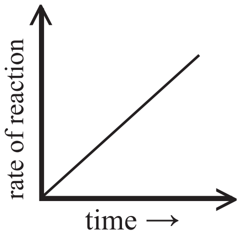
i)



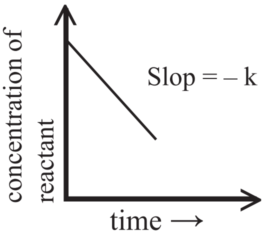
ii)



iii)



iv)



a) i & ii) b) i & iv c) i, ii & iv d) iii & iv

18. Which of the following expression is correct for the rate of reaction given below ?

$$5Br^-(aq)+BrO_3^-(aq)+6H^+(aq)\rightarrow 3Br_2(aq)+3H_2O(l)$$

a) $-\frac{\Delta}{\Delta t}\left[Br^-\right]=5\frac{\Delta\left[H^+\right]}{\Delta t}$

b) $\frac{\Delta\left[Br^-\right]}{\Delta t}=\frac{6}{5}\frac{\Delta\left[H^+\right]}{\Delta t}$

c) $\frac{\Delta\left[Br^-\right]}{\Delta t}=\frac{5}{6}\frac{\Delta\left[H^+\right]}{\Delta t}$

d) $\frac{\Delta\left[Br^-\right]}{\Delta t}=6\frac{\Delta\left[H^+\right]}{\Delta t}$

19. For which type of reaction order and moleoularity have the same value?

a) first order reaction

b) bimolecular reaction

c) trimolecular reaction

d) elementary reaction

20. The conversion of molecules x to y follows second order kinetics. If concentration of x is increased to three times, the rate of formation of y will be–

a) increase by three times.

b) decrease by three times.

c) increase by nine times.

d) decrease by nine times.

21. For a reaction A+B → product; the rate law is given by $r = K[A]^{1/2}[B]^2$. What is the order of the reaction? [NCERT]

    a) $\frac{2}{3}$ b) $\frac{5}{2}$ c) $\frac{1}{2}$ d) $\frac{3}{2}$

22. The unit and value of rate constant and that of rate of reaction are same for–

    a) zero order b) first order c) second order d) third order

23. A first order reaction is 50% completed in 1.26×10^{14} S. How much time would it take for 100% completion?

    a) 1.26×10^{15} S b) 2.52×10^{14} S c) 2.52×10^{14} S d) infinite

24. For the decomposition of azoisoprapane to hexane and nitrogen at 543 K, the following data are obtained calculate the rate constant.

t (s)	**p (mm of Hg)**
0	35.0
360	54.0
720	63.0

    a) 2.21×10^{-3} S^{-1} b) 3.48×10^{-3} S^{-1}

    c) 1.26×10^{-3} S^{-1} d) 8.46×10^{-3} S^{-1}

25. Consider the Arhenius equation given below and mark the correction option.

$$K = Ae^{-E_a/RT}$$

    a) Rate constant increases exponentially with increasing activation energy and decreasing temperature.

    b) Rate constant decreases exponentially with increasing activation energy and decreasing temperature.

    c) Rate constant increases exponentially with decreasing activation energy and decreasing temperature.

    d) Rate constant increases exponentially with decreasing activation energy and increasing temperature.

26. For the decomposition of N_2O_5 at a particular temperature according to equations

$$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$$

$$N_2O_5 \rightarrow 2\,NO_2 + 1/2\,O_2$$

The activation enertgies are E_1 and E_2 respectively then

a) $E_1 > E_2$ b) $E_1 < E_2$ c) $E_1 = 2E_2$ d) $E_1 = E_2$

27. The decomposition of A into product has values of K as 4.5×10^3 S^{-1} at 10°C and energy of activation 60 KJ mol^{-1}. At what temperature would K be 1.5×10^4 S^{-1}?

    a) 273.15 K b) 24.19°c c) 280.39 K d) 45.29°c

28. The decompoistion of hydrocarbon follows the equation $K = (4.5\ 10^{11}\ S^{-1})\ e^{-28000}$ K/T. Calculate the activation enerty E_a.

    a) 232.79 KJ mol^{-1} b) 425.25 KJ mol^{-1} c) 300 KJ mol^{-1} d) 885.2 KJ mol^{-1}

29 Which of the following statements is incorrect about the collision theory of chemical reaction?

a) It considers reacting molecules or atoms to be hard spheres and ignores their structure features.

b) Number of effective collisions determines the rate of reaction.

c) Collision of atoms or molecules possessing sufficient threshold energy results into product formation.

d) Moleculs should collide with sufficient threshold energy and proper orientation for the collision to be effective.

30. Radioactive decay is a–

a) First order reaction

b) Zero order reaction

c) Second order reaction

d) Third order reaction

31. In any unimolecular reaction–

a) only one reacting species is involved in the rate determining step.

b) the molecularity of the reaction is one and the order is zero.

c) both molecularity and order of reaction are one.

d) All of the above are true.

32. The rate of a chemical reaction doubles for every 10°C rise in temperature. If the temperature is raised by 50°C, the rate of reaction increases by about.

    a) 10 times b) 24 times c) 32 times d) 64 times

B. Assertion - Reason type questions : (1 marks each)

Directions (Q nos. 33 to 37) each of these questions contains two statements. Statement I (Assertion) and statement-II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below :

a) Assertion is true, Reason is true, Reason is a correct explanation for Assertion.

b) Assertion is true, Reason is true, Reason is not a correct explanation for Assertion.

c) Assertion is true, Reason is false.

d) Assertion is false, Reason is true.

33. Assertion : Order and molecularity are same

Reason : Order is determined experimentally and malecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

34. Assertion : Rate constants determined from Arrhenius equation one fairly accurate for simple as well as complex molcules.

Reason : Reactant melecules undergo chemical change irrespective of their orientation during collision.

35. Assertion : In the reaction $I_2 + 2\,S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2\,I^-$, the two $S_2O_3^{2-}$ ions are used are every I_2.

Reason : The rate of disappearance of I_2 is one half the rate of disappearance of $S_2O_3^{2-}$.

36. Assertion : The numerical value of specific rate constant is independent of the concentration of any species present in the reaction mixture.

Reason : When a reaction is carried out in aqueous solution and some alcohol is added to the reaction mixture, the rate of reaction will not change.

37. Assertion : Lower the activation energy, faster is the reaction.

Reason : If the activation energy of reaction is zero, temperature will have no effect on rate constant.

C. Very short answer type questions : (1 mark each)

38. The dissocation of N_2O_5 follows the following mechanism :

$$N_2O_5 \rightarrow NO_2 + NO_3 \text{ (slow)}$$

$$NO_3 + N_2O_5 \rightarrow 3\,NO_2 + O_2 \text{ (fast)}$$

What is the molecularity of the reaction in the rate determining step?

39. The unit of rate constant of the a reaction is $dm^{\frac{3}{2}}\ mol^{-1/2}S^{-1}$. What is the overall order of the reaction.

40. For the first order reaction A $\longrightarrow$ 2B, rate expressed by any one of the following rate equation.

$$\text{i)}\ -\frac{d[A]}{dt} = K_1\ [A] \quad \text{ii)}\ \frac{d[B]}{dt} = K_2\ [B]$$

Find the relation between K_1 & K_2.

41. What is the unit of a chemical reaction?
42. What is the unit of reaction rate?
43. What is rate constant of a reaction?
44. Define order of a chemical reaction?
45. Give an example of zero order equation.
46. Give an example of fractional order reaction.
47. What is molecularity?
48. Define half life period.
49. Define activation energy.
50. What is temperature co-efficient of a reaction?
51. Write the Arrhenius equation.
52. Mention any two factors that affect the rate constant of a reaction.
53. What is average reaction rate?
54. What is instantaneous reaction rate?
55. What is the relation between thereshold energy and activation energy.

D. Short answer type questions : (2 marks each)

1. What is pseudo first order reaction? Give example.
2. Write differences between order and molecularity of a reaction.
3. State law of mass action.
4. Define elementary and complex reaction. Give example.
5. Will the molecularity of a zero order reaction be zero? Explain.
6. Write two point of differences between reaction rate and rate constant.

7. Why molecularity of reaction cannot be more than 3?

8. What is the effect of catalyst on the rate of a reaction?

9. Write the collision theory of reaction rate.

10. In the reaction $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ rate of formation of NO was 6.4×10^{-4} mol L^{-1} S^{-1}. Determine the rate at which NH_3 gets consumed and steam is formed.

E. Answer the following questions : (Marks - 3)

1. How do the following factors affect the rate constant of a reaction?

   a)) Concentration of the reactant

   b) Temperature

   c) Catalyst

2. Derive an expression for integrated rate equation of zero order reaction. Show that half-life of a zero order reaction is proportional to initial concentration of reactant.

3. Derive an expression for integrated rate equation of first order reaction. Show that half-life of a first order reaction does not depend on the initial concentration of the reactant.

4. A first order reaction takes 60 minutes for 75% completion. Determine its half-life.

5. Show that for any first order reaction, the time required for the completion of 99.9% of the reaction is 10 times the half life of the reaction.

6. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtain.

t/s	0	10	20
$[CH_3COOCH_3]$ / mol L^{-1}	0.10	0.05	0.025

   (i) Show that it follows Pseude first order reaction, as the concentration of water remains constant

   (ii) Calculate the average rate of reaction between the time interval 10 to 20 S

(Given: $\log 2 = 0.301$)

7. Calculate the activation energy of a reaction if the rate of the reaction is doubled while the temperature of the reaction system is incereased from 27°C to 37°C .

8. Benzenediazonium chloride dissociates as :

$$C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$$

At O°C, if the concentration of diazonium salt is doubled, rate of evalution of N_2 is also doubled. Find the order of the reaction.

F. Answer the following questions : (Marks - 5)

1. a) What is the unit of rate constant of 1st order reaction?

   b) What is molecularity of a chemical reaction?

   c) A first order reactionis 50% complete in 1.26×10^{14}S. How much time would it take for 100% completion

Answer Key

A. Select the correct answer (MCQ) : (1 mark each)

1. (b) 2. (a) 3. (d) 4. (d) 5. (b) 6. (a) 7. (c) 8. (b) 9. (c) 10. (c) 11. (b)

12. (d) 13. (a) 14. (b) 15. (d) 16. (b) 17. (b) 18. (c) 19. (d) 20. (c) 21. (b)

22. (a) 23. (d) 24. (a) 25. (d) 26. (d) 27. (b) 28. (a) 29. (c) 30. (a) 31. (a)

32. (c) 33. (d) 34. (c) 35. (c) 36. (b) 37. (a) 38. (1) 39. $^{3}\!/_{2}$ 40. $K_2 = 2K_1$

41. See Key point 42. See Key point 43. See Key point

44. See Key point 45. $2HI(g) \xrightarrow[\text{High pressure}]{\text{Au}} H_2(g) + I_2(g)$

46. $CH_3CHO(g) \xrightarrow{450°c} CH_4(g) + CO(g)$

47. See Key point

48. See Key point

49. See Key point

50. See Key point

51. See Key point

52. See Key point

53. See Key point

54. See Key point

55. Threshold energy = Average energy + Activation energy.

Chapter - 5

Surface Chemistry

Chapter at a glance :

- Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating bulk phases by a hyphen or slash. For exmple, the interface between a solid and a gas may be represented as solid/gas or solid-gas.
- Many important phenomena, like corrosion, electrode processes, hetrogenous catalysis, dissolution and crystallisation occur at interfaces.
- The surface chemistry finds many applications in industry, analytical work and daily life situations.

  Adsorption : The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption.

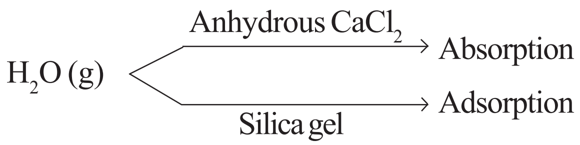
  Adsorbent : The solid substance on the surface of which adsorption takes place is called adsorbent.

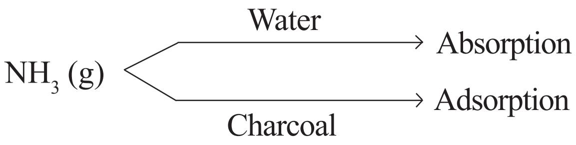
  eg - Activated charroal, Silica gel, Platinum, Paladium, Nickel, Gelatin, Starch, Al_2O_3 etc.
- **Adsorbate :** The molecular species, gases or liquids which accumulates or concentrates at the surface is termed as adsorbate.
- The air becomes dry in presence of silica gel because the water molecules, gel adsorbed on the surface of the gel. Here silica gel is the adsorbent & moisture is (or water molecules are) adsorbate.
- Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances (adsorbate) are adsorbed by the charcoal (adsorbent).
- **Desorption :** The process of removing an adsorbed substance from the surface of the adsorbent by heating or by reducing pressure is called desorption.
- **Absorption :** The process in which a substance is uniformly distributed throughout the body of a solid or liquid is called absorption.
- **Sorption :** It is the process in which both adsorption & absorption take place simutaneously.
- When a chalk stick is dipped in ink, the surface retains the colouring pigments due to adsorption, while

the solvent goes into the chalk stick due to absorption. In this process both adsorption and absorption takes place simutaneously, so it is sorption.

- Some time we find the same substance get absorbed or adsorbed on different surfaces.

For example –





- **Mechanism of Adsorption :**

Adsorption is due to the fact that the surface particles of the adsorbent are in different environment than the particles inside the bulk. In the adsorbent all the forces acting between the particles are mutually balanced but on the surface, particles are not surrounded by atoms or molecules on all sides & so they possess unbalanced or residual attractive forces, these forces are responsible for attracting the absorbate particles on the surface. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given pressure and temperature.

- (i) Adsorption is an exothermic process, so, $\Delta H = -$ Ve
- (ii) During adsorption, freedom of movement of gases decrease, so, $\Delta S = -$ Ve
- (iii) Adsorption is a spontaneous process, so, $\Delta G = -$ Ve, but ΔS total > O
- Difference between Adsorption and absorption –

Adsorption	**Absorption**
1. It is a surface phenomenon.	1. It occurs throughout the body of the material.
2. It involves higher concentration of the gas or liquid at the surface of a substance.	2. It involves uniform distribution of the molecular species throughout the bulk.
3. It is rapid in the beginning and slows down near the equilibrium.	3. It occurs at a uniform rate.
4. It is a fast process.	4. It is a slow process.

- **Enthalpy of Adsorpation :** The enthalpy change for the adsorption of one mole of an adsorption on the surface of adsorbent is called enthalpy of adsorption.
- **Types of adsorption :** Depending upon the nature of forces between molecules of adsorbate and adsorbent , adsorption is of two types.
- **Physisorption (or physical adsorption) :** If the adsorbate is held by weak vander waal's forces on the surface of the adsorbent, the adsorption is called physisorption.
- **Chemisorpation (or chemical adsorption) :** the adsorption in which the forces holding the adsorbate on the surface of adsorbent are as strong as in chemical bonds, the adsorption is called chemisorpation.

Comparison of Physisorption and Chemisorption

Physisorption	Chemisorption
1. It arises because of van der Waals' forces.	**1.** It is caused by chemical bond formation.
2. It is not specific in nature.	**2.** It is highly specific in nature.
3. It is reversible in nature.	**3.** It is irreversible.
4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	**4.** It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ mol^{-1})in this case.	**5.** Enthalpy of adsorption is high (80-240 kJ mol^{-1}) in this case.
6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	**6.** High temperature is favourable for adsorption. It increases with the increase of temperature.
7. No appreciable activation energy is needed.	**7.** High activation energy is sometimes needed.
8. It depends on the surface area. It increases with an increase of surface area.	**8.** It also depends on the surface area. It too increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure.	**9.** It results into unimolecular layer.

- **Factors affecting rate of adsorption of gases on solid surface :**

  (i) **Nature of adsorbent :** Adsorption is directly proportional to surface area of adsorbent. More is the surface area of the solid adsorbent, more will be the rate of adsorption.

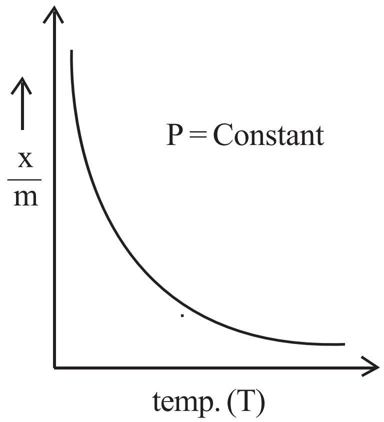
  (ii) **Nature of adsorbate :** Adsorption is directly proportional to critical temperature of gas. Higher the critical temperature of a gas, greater the ease of liquefaction, i.e. greater the vander wall's forces of attraction and so greater is the rate of adsorption.

(iii) Effect of temperature :

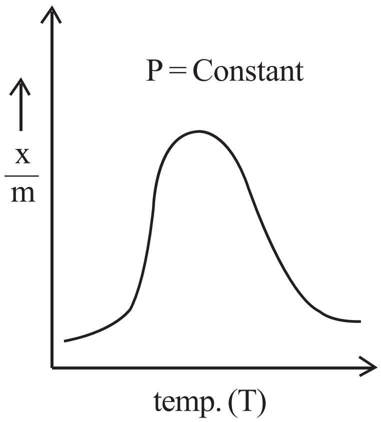
Adsorbate + adsorbent $\rightleftharpoons$ Adsorption, $\Delta H = -\text{Ve}$,

Generally adsorption decrease with increase in temperature, as adsorption is exothermic process. Physisorption shows regular decrease with temperature. But chemisorption first increase then decrease with temperature, because it is specific, requires activation energy & in this process supplied heat may be used as its energy of activation.

- **Adsorption isobar :** A plot of extent of adsorption $\frac{x}{m}$ [x = mass (in g) of adsorbent, m = amount of absorbate (in g or mL)] versus temperature at constant pressure is called adsorption isobar.



For Physisorption



For Chemisorption

- **(iv) Effect of pressure :**

  At constant temperature, if pressure is increased, the rate of adsorption increases linearly.
- **Adsorption isotherm :** If temperature is kept constant, the curves plotted between the amount of the gas adsorbed $(\frac{x}{m})$ on the surface of the adsorbent and the corresponding pressure (p) are known as Adsorption isotherm.
- **Freundlich Adsorption isotherm :** It gives a relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure (p) at constant temparature.

$$\frac{x}{m} = K \,.\, p^{1/n} \quad (n > 1)$$

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

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \left(\textit{in general } \frac{1}{n} \textit{ is } 0.1 \textit{ to } 0.5 \right)$$

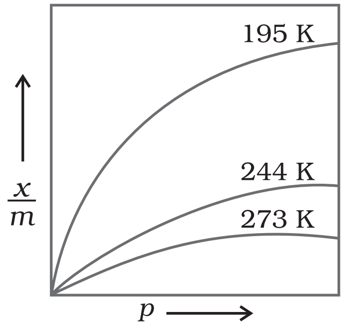


Fig. *Adsorption isotherm*

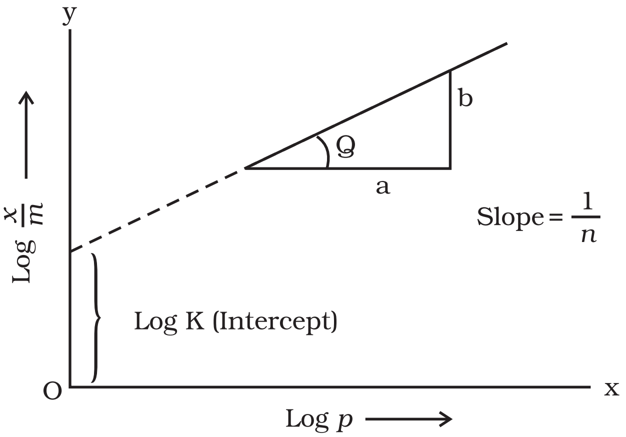


Fig. *Freundlich Isotherm*

The logarithmic form of equation holds good over a limited range of pressure

- When $\frac{1}{n} = 0$, $\frac{x}{m}$ = constant, the adsorption is independent of pressure.
- When $\frac{1}{n} = 1$, $\frac{x}{m} = K.p$ i.e, $\frac{x}{m} \propto p$, the adsorption varies directly with pressure.
- Freundlich equation can explain the adsorption from solutions (liquid + solid), in which concentration of the solution is considered in place of pressure of gas. For example - solution of a dye and charcoal when shaken together, the solution becomes colourless.

  $\frac{x}{m} = KC^{\frac{1}{n}}$ (C is the concentration of liquid at equilibrium state of adsorption and n > 1)

  taking log on both sides $\log \frac{x}{m} = \log K + \frac{1}{n} \log c$
- Freundlich adsorption isotherm fails at high pressure of gas and in multi moleculars layers.
- Some applications of Adsorption :
  - (i) In removing colouring matter from solution.
  - (ii) In gas masks.
  - (iii) In chromatography.
  - (iv) In dyeing of cloth.
  - (v) In adsorption analysis.
  - (vi) In separating noble gases.
  - (vii) In Ion – exchange resins.
  - (viii) In dehumidifiers.
  - (ix) In curing diseases.
  - (x) In Froth Floatation.

- **Catalysis :** The substances which increases the rate of a reaction but themselves remain chemically and quantitatively unchanged after the reaction are called catalysts and the phenomenon is called catalysis.

$$2\ KClO_3 \xrightarrow[473-633\,K]{MnO_2} 2\ KCl + 3O_2$$

In this reaction MnO_2 is the catalyst.

- **Promoters :** The substances which increases the activity of catalysts are called promoters.

$$N_2\ (g) + 3H_2\ (g) \underset{Mo(s)}{\overset{Fe(s)}{\rightleftharpoons}} 2\ NH_3(g)$$

In Haber's process Fe is the catalyst and Mo is promoter.

- **Inhibitors :** The substances which decrease the rate of any chemical reaction are called catalytic inhibitors.

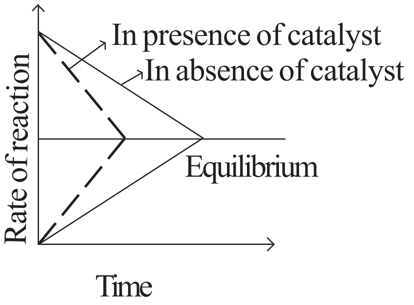
$$Na_2SO_3 + \frac{1}{2}\ O_2 \xrightarrow{C_2H_5OH} Na_2SO_4$$

In this reaction C_2H_5OH is the inhibitor.

- **Poison :** The substances which decrease the activity of catalysts are called catalstic poison. For example –Fe is used as catalyst in production of NH_3 by Haber process. Presence of H_2S gas decreases the reaction rate. So H_2S acts as catalyst poison.
- **Autocatalysts :** When one of the products of the reaction begins to act as a catalyst, it is called auto catalyst. Initially the reaction rate is slow, but as soon as the products come into existance, the reaction rate increases. The process is called autocatalysis.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + \underset{\text{auto catalyst.}}{C_2H_5OH}$$

- **Characteristics of Catalysts :**
  - (i) Catalysts are genrally specific in nature.
  - (ii) A catalyst does not initiate a reaction and does not change the nature of products.
  - (iii) Only a very small amount of catalyst is sufficient to catalyse a reaction.
  - (iv) A catalyst remains unchanged in mass & chemical composition but can change their physical state.
  - (v) Catalysts can change rate constant of a reaction, but does not change free energy of reaction.
  - (vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to decrease the time to achive the equilibrium state.



Types of catalysis :

- **Homogeneous catalysis :** When the reactants, products and the catalyst are in the same phase (i.e, liquid or gas) the process is said to be homogenous catalysis.

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

  $CH_3COOCH_3\ (l) + H_2O\ (l) \xrightarrow{HCL(l)} CH_3COOH\ (aq) + CH_3OH\ (aq)$

- **Heterogeneous catalysis :** The catalytic process in which the reactants and the catalyst are in different phases is called heterogeneous catalysis.

  eg. $2\ SO_2\ (g) + O_2\ (g) \xrightarrow{Pt(s)} 2\ SO_3\ (g)$

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

- **Adsorption theory of Heterogeneous catalysis :** The modern adsorption theory is the combination of intermediate formation theory and old adsorption theory. It considers, there are free valencies on the surface of solid catalyst and mechanism involves the following steps.

  (i) Diffusion of reactants to the surface of catalyst.

  (ii) Adsorption of reactant molecules on the surface of catalyst by forming loose bonds.

  (iii) Occurance of chemical reaction on the catalyst surface through formation of an intermediate.

  (iv) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.

  (v) Diffusion of reaction products away from the catalyst's surface.

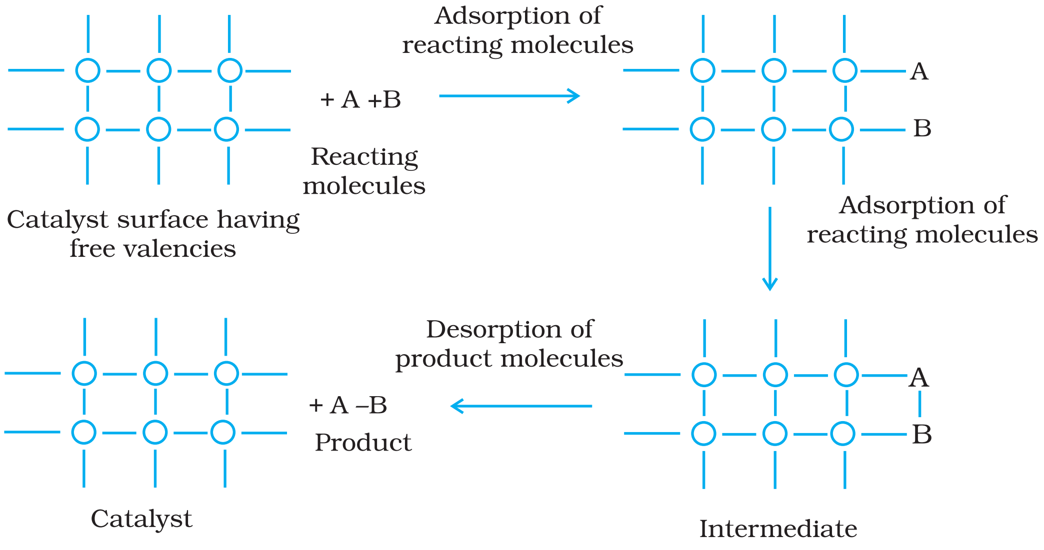
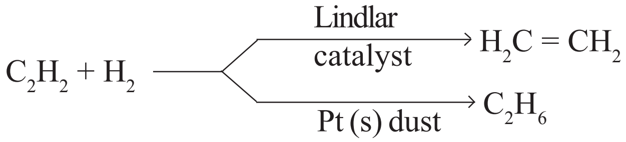


Fig. Adsorption of reacting molecules, formation of intermediate and desorption of products

- **Important features of solid catalysts :**
    - **(i) Activity :** It is the ability of the catalyst to increase the rate of a reaction.
    - **(ii) Selectivity :** It is the ability of a catalyst to direct a reaction to yeild a particular product selectively, when under same reaction conditions many products are possible.



$$C_2H_2 + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar}} H_2C = CH_2$$

$$C_2H_2 + H_2 \xrightarrow[\text{Pt (s) dust}]{} C_2H_6$$

- **Shape - Selective catalysis by zeolites :** The catalytic reaction that depends upon the pore strcture of the catalyst and the size of the reactant and product molecules is called shape–selective catalysis. The pore size is generally in range 260 – 740 pm. Zeolites are shape selective catalyst having honey comb structures. zeolite catalyst, ZSM – 5 is used in petroleum industry to convert aleohols into gasoline by dehydration.

- **Enzyme catalysis :** Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are protein molecules of high molecular mass and form colloidal solutions in water. Enzymes catalyse biochemical reactions.

  Some importat enzyme catalysed reactions are given in the table below :

Some Enzymatic Reactions

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins → Amino acids

- **Characteristics of enzyme catalysis :**
    - **(i) Highly specific nature :** One catalyst cannot catalyse more than one reaction.
    - **(ii) Most highly efficient :** One molecule of an enzyme may transform one million molecules of the reactant per minute.
    - (iii) Each enzyme has a temperature in which a maximum rate of reaction is achieved, which is called **optimum temperature** of it. Enzymes are highly active under optimum temperature (298 k to 310k).
    - (iv) The enzymatic activity is increased in the presence of certain substances, known as **co-enzymes.**

(v) Some metal ions such as Na^+, Mn^{2+}, CO^{2+}, Cu^{2+} etc act as activators which increase the activity of specific enzymes are called **activators.**

(vi) Influence of inhibitors or poisons : The inhibitors interact with the active functional groups on the enzymes surface and often reduce or completely destroy the catalytic activity of enzyemes. The use of many drugs is related to their action as enzyme inhibitors in human body.

◆ **Mechanism of enzyme catalysis :** The enzyme catalysed reactions may be considered to proceed in two steps .

(i) Binding of enzyme (E) to substrate (s) to form an activated complex (Es*)

$$E + S \rightarrow ES^*$$

(ii) Decomposition of the activated complex to form product (p).

$$Es^* \rightarrow E + P$$

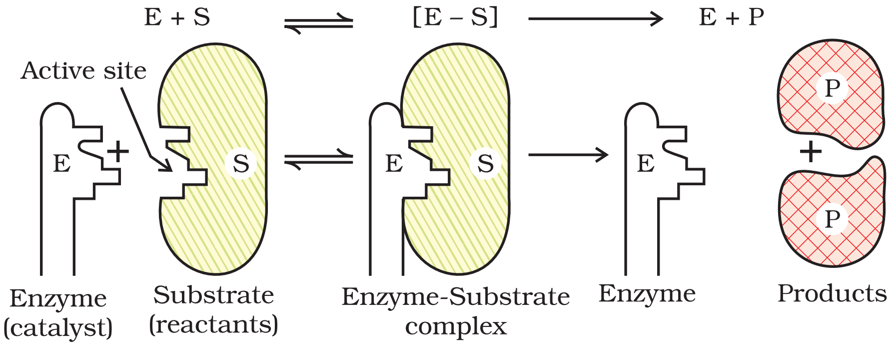


Fig. : Mechanism of enzyme catalysed reaction

◆ **Co–enzymes :** Certain substances, which can increase the activity of enzymes are known as co-enzymes.

Some Industrial Catalytic Processes

Process	Catalyst
1. Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723-773K temperature. Now-a-days, a mixture of iron oxide, potassium oxide and alumina is used.
2. Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$	Platinised asbestos; temperature 573K.
3. Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \rightarrow \underset{\text{oleum}}{H_2S_2O_7(l)}$ $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673-723K.

- **Colloids :** A colloid is a heterogeneous system in which one phase is dispersed as very fine particles in another substance called dispersion medium. The size of colloidal particles is in the range 1 to 1000 nm (10^{-9} to 10^{-6} m).

  eg. Smoke, Milk, Fog, Cloud, Hair-cream etc.

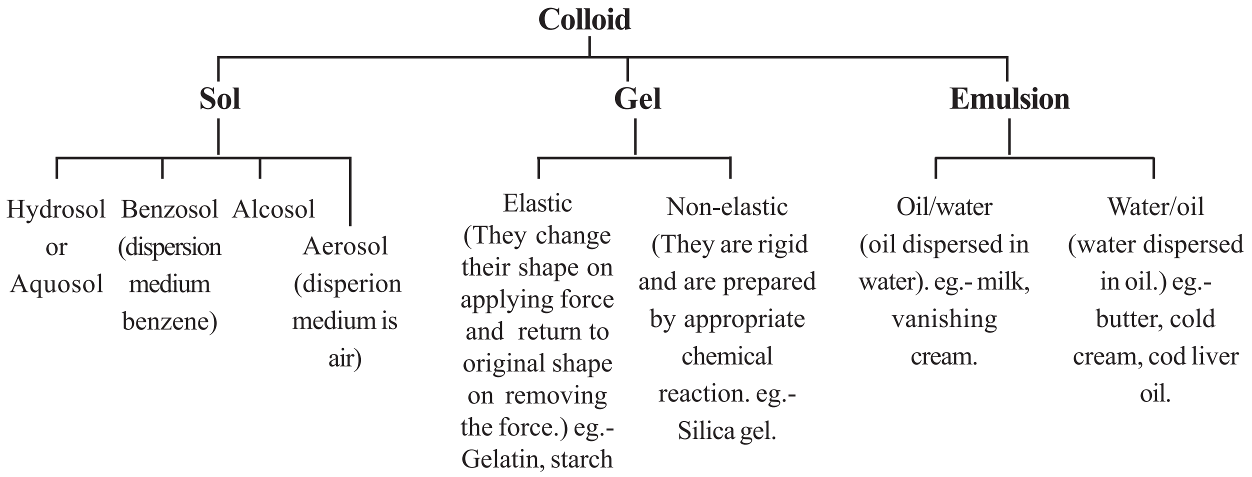
- **Classification of colloids :** Colloids are classified on the basis of the following criteria.
  - (i) Physical state of dispersed phase and dispersion medium.
  - (ii) Nature of interaction between dispersed phase and dispersion medium.
  - (iii) Type of particles of the dispersed phase.

(i) Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible.

Types of Colloidal Systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, butter
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam, rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

- Out of the various types of colloids, the most common are sols (solids in liquids), gels (liquids in solids) and emulsions (liquids in liquids).
- If the dispersion medium is water, the sol is called aquasol or hydrosol.
- If the dispersion medium is alcohol, it is called alcosol.



(ii) Classification of colloids based on nature of interaction between dispersed phase and dispersion medium

- **Lyophilic colloids :** The word 'lyophilic' means liquid–loving. Those substances which when mixed with a suitable solvent as the dispersion medium diretly forum the colloid are called lyophilic substances and the colloid thus formed are called lyophilic colloids these are quite stable.
- If the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. So these sols are also called reversible sols.

  eg. gum, gelatine, starch, rubber etc.
- **Lyophobic collids :** The word 'Lyphobic' means liquid hating. The substances like some metals and metal sulphides when mixed with dispersion medium do not form colloidal sol easily, but can be prepared only by special methods and the colloid formed by them are called lyophobic colloids.
- These sols are unstable, dispersed phase is readily precipitated (or coagulated) on addition of small amounts of electrolytes, by heating or by shaking. These sols are also called irreversible sols. Lyophobic sols need stabilising agents for their preservation. Lyophobic sols show more tyndall effect.

(iii) Classification based on type of particles of the dispersed phase :

Multimolecular colloids	**Macromolecular colloids**	**Associated colloids (Micelles)**
Formed by aggregation of a large number of atoms or smaller molecules (having a diameter of less than 1 nm) of substances.	Formed by aggregation of big sized molecules. These are polymers with high molecular mass, in which the size of the macromolecule may be in the colloidal range (1 to 1000 nm). eg - (i) Naturally occuring – Starch, Cellulose, Proteins, Enzyme. (ii) Man made – Polythene, Nylon.	These are the substances which behave as normal strong electrolytes at low concentration but get associated at higher concentration and behave as colloid. These associated particles are also called micelles. eg. - Soap & Detergent.

- Critical micelle concentration (CMC) is the concentration above which associated colloids and micelles are formed. For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1}.
- Kraft temperature (T_k) is the temperature above which micelles are formed.
- Soap is sodium or potassium salt of a higher fatty acid and may be represented a $RCOO^- Na^+$.

  eg.– Sodium stearate $CH_3(CH_2)_{16}COO^- Na^+$.

Preparation of colloids :

(i) Chemical methods : Colloidal dispersions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction, hydrolysis. These molecules then aggregate leading to formation of sols.

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposotion}} As_2S_3 + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S\ (sol) + 2H_2O$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe\ (OH)_3\ (sol) + 3\ HCl$$

$$2\ AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Re duction}} 2\ Au\ (sol) + 3HCOOH + 6HCl$$

(ii) Electrical disintegration (Bredig's Arc method) : This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum etc which involves dispersion as well as condensation.

(iii) Peptization : The dispersion of a freshly precipitated material into a colloid by the action of a suitable electrolyte (peptizing agent) is termed as peptization. eg - Freshly precipitated Ferric hydroxide on treatment with a little of ferric chloride solution at once forms a dark reddish brown sol. Here $FeCl_3$ acts as peptizing agent.

Purification of colloidal solutions :

◆ The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution.

◆ Purification of colloidal solutions can be done by the following processes –

(a) Dialysis : It is the process of removing a dissolved substance from a colloid by diffusion through a suitable membrane (like parchment paper, cellophane membrane or animal bladder). The aparatus used for dialysis is called dialyser.

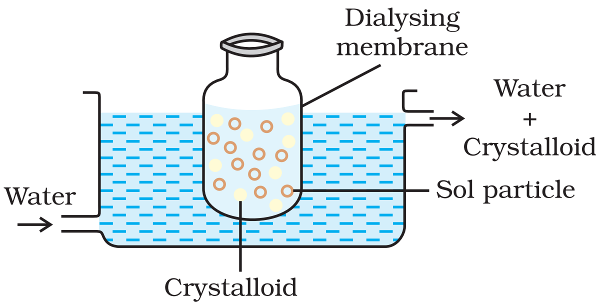


Fig. : Dialysis

(b) Electrodialysis : The process of dialysis is very slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is an electrolyte. The process is then named as electrodialysis.

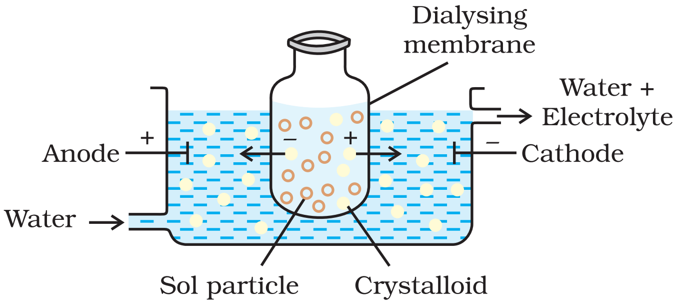


Fig. : Electro-dialysis

(c) Ultrafiltration : The process of separating the colloidal particles from the solvent and the soluble solutes present in the colloid by specially prepared filters, which are permeable to all particles except the colloid particles. For ultrafiltration, the pores of the filter paper are reduced in size by impregnating with collodian solution. Collodian is a 4% solution of nitro-cellulose in mixture of alcohol and ether.

- **Hardy - Schulze rules :**

  (i) Oppositely charged ions are effective for coagulation.

  (ii) The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation.

  eg.- $Al^{3+} > Ba^{2+} > Na^{+}$

  for negatively charged colloids.

  $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

  for positively charged colloids.

- The potential difference between the fixed layer and diffused layer of opposite charges surrounding the colloids is called **zeta potential**.

- **Electrophoresis :** The movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution is called electrophoresis. Movement of the particles towards cathode is called cataphoresis and towards anode is called anaphoresis.

- **Gold number :** It is the minimum weight (in mg) of a protective colloid required to prevent the coagulation of 10 mL of a standard hydro gold sol when 1mL of 10% NaCl solution is added to it.

A. Select the correct answer (MCQ) : (1 mark each)

1. Which of the following is used to adsorb water ?

(a) Silica gel (b) anlydrous $Bacl_2$

(c) hair gel (d) Charcoal

2. 'Sorpation' means –

(a) adsorption (b) absorption

(c) desorption (d) both adsorption and absorption.

3. Zeolites are –

(a) water softener (b) catalyst

(c) both a and b (d) none of the these

4. The nature of colloidal solution obtained when excess $FeCl_3$ is added to $Fe(OH)_3$ precipitate is –

(a) (–) vely charged (b) (+) vely charged

(c) no change (d) none of the above

5. Which of the following process is used in the purification of colloidal solution ?

(a) dialysis (b) coagulation

(c) peptization (d) electrophoresis

6. Which property of the colloids is not dependent on the charge on colloidal particles ?

(a) coagulation (b) electrophoresis

(c) tyndall effect (d) electrodialysis

7. Colloidal solutions show in water –

(a) paramagnetism (b) scattering of light (tyndal effect)

(c) refraction (d) none of the above

8. In freundlich adsorption isotherm, the value of $\frac{1}{n}$ is –

(a) 1 in case of physisorption (ii) 1 in case of chemisorption

(iii) between 0 and 1 in all cases (iv) between 2 and 3 in all cases

9. Fog is a colloidal system of –

(a) gas in liquid (b) liquid in gas

(c) gas in gas (d) gas in solid

10. Butter is an example of –

(a) water in oil emulsion | (b) liquid - liquid colloidal system
(c) oil in water emulsion | (d) solid - solid colloidal system

11. In Haber's process for production of NH_3 –

(a) Fe acts as catalyst | (b) Mo acts as a catalyst
(c) Fe is autocatalyst | (d) none of the above

12. Which one of the following statements is incorrect about enzyme catalysis ?

(a) Enzyme action is specific

(b) Enzymes are mostly proteinous in nature

(c) Enzymes are least reactive at optimum temperature

(d) Enzymes are denatured by ultraviolet rays and at high temperature

13. Lyophobic colloids are –

(a) reversible | (b) irreversible
(c) water loving | (d) solvent loving

14. 'Greater the valency, the higher is the coagulating power of ion'. This rule was introduced by –

(a) Hardy - schulze | (b) Graham
(c) Kossel and Lewis | (d) Faraday

15. The capacity of an ion to coagulate a colloidal solution depends on –

(a) its shape | (b) the amount of its charge
(c) The sign of the charge | (d) both (b) & (c)

16. Gold number is a measure of –

(a) the amount of gold present in the colloidal solution

(b) the amount of gold required to coagulate the colloid

(c) the amount of gold required to protect the colloid

(d) none of the above

17. The extent of adsorption of a gas on a solid depends on –

(a) nature of the gas | (b) pressure of gas
(c) temperature of the system | (d) all of the above

18. Which forms multi molecular layers during adsorption –

    (a) physical adsorption (b) vander waals adsorption

    (c) Freundlich adsorption (d) all of these

19. Which acts as a promoter for nickel in the hydrogenation of oils ?

    (a) Cu (b) Mo (c) Fe (d) Pt

20. Which is not correct for catalyst –

    (a) Catalyst can initiate a reaction.

    (b) It does not alter the position of equilibrium in a reversible rection.

    (c) A catalyst remains unchanged in quality and composition at the end of reaction.

    (d) Catalysts are sometimes very specific in respect of a reaction.

B. Assertion - Reason type questions : (1 marks each)

These questions consist of two statements each as Assertion & Reason. While answering these questions you are required to choose any one of the following four responses.

(a) If both Assertion and Reason are true & reason is correct explanation of the Assertion.

(b) If both Assertion and Reason are true but reason is not correct explanation of the Assertion.

(c) If Assertion is true but Reason is false.

(d) If both Assertion and Reason are false.

1. Assertion : Catalyst is more effective in powdered form.

   Reason : Number of free valencies increase.

2. Assertion : Zeolite is shape selective catalyst.

   Reason : Size of the pores of the catalyst are such that they can trap only selective molecules.

3. Assertion : Lyophilic sol is more stable than lyophobic sol.

   Reason : Lyophilic sol have greater solvation energy then lyophobic sol.

4. Assertion : Langmuir adsorption is a single layer phenomenon.

   Reason : It is due to vander waal's forces.

5. Assertion : Filtration of colloidal particles is not possible by fitter paper.

   Reason : Size of colloidal particle is less than pores of fitter paper.

6. Assertion : Associated colloids are formed by aggregation of large number of ions in concen trated soap solution.

   Reason : Because associated colloids have more than one colloidal particles.

7. Assertion : Micelles are formed by surfactant molecules above the critical micelle concentration (CMC)

Reason : The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

8. Assertion : In case of chemisorption , $\frac{x}{m}$ first increase then decrease with temperature.

Reason : The initial increase is due to the fact that heat supplied acts as activation energy. The decrease afterwards is due to the exothermic nature of adsorption at equilibrium.

9. Assertion : The micelle formed by sodium stearate in water has $-COO^-$ groups at the surface.

Reason : Surface tension of water is reduced by the addition of stearate.

10. Assertion : Aqueous gold colloidal solution is red in colour.

Reason : The colour arises due to scattering of light by colloidal gold particles.

11. Assertion : Reaction of SO_2 and H_2S in the presence of Fe_2O_3 catalyst gives elemental suphur.

Reason : In the above reaction SO_2 is a reductant.

12. Assertion : Physical adsorption of molecule on the surface requires activation energy.

Reason : Because the bonds of adsorbed molecules are broken.

13. Assertion : A gas mixed with another gas forms a colloidal solution.

Reason : Mixture of gases always form homogenous system.

14. Assertion : Hydrated Fe_2O_3 can be easily coagulated by sodium phosphate in comparison to KCl.

Reason : Phosphate ions have a higher negative charge than chloride ions. So they are more effective for coagulation.

15. Assertion : During the preparation of ice-cream, gelatin is added in it.

Reason : Ice-creams are emulsions that get stabilized by gelatin as it act as an emulsifying agent.

C. Very short answer questions (one mark each) :

1. What is adsorption ?
2. Out of physisorption and chemisorption which has higher enthalpy of adsorption ?
3. Write one similarity between physisorption and chemisorption.
4. What is the effect of temperature on chemisorption ?
5. What is the role of desorption in the process of catalysis ?
6. What do you mean by Gold number ?

7. What is zeta potential ?
8. What is peptization ?
9. What is electrophoresis ?
10. How is sol different from an emulsion ?
11. To which colloidal system does milk belong ?
12. Why is tyndall effect shown by colloidal solutions ?
13. What are associated colloids ?
14. What is the dispersed phase & dispersion medium in milk ?
15. Why is a finely divided substances more effective as an adsorbent ?

D. Short Answer Type Questions : (Mark- 2)

1. State Hardy sehulze rule. When of the following is most effective electrolyte is the coagulation of $Fe(OH)_3$ Sol among NaCl, $BaSO_4$, Na_3PO_4
2. What do you mean by activity and selectivity of catalysts?
3. A colloid is formed by adding $FeCl_3$ in excess of hot water. What will happen if excess NaOH is added to this colloid ?
4. Physisorption is multilayered while chemisorptions is minilayered- Why.
5. How can you explain the stability of colloidal sols?
6. Define Kraft temperature, Critical micelle concentration.
7. What is the difference between multimolecular and macromolecular colloids?
8. How do emulsifiers stabilise emulsion?
9. What is meant by shape selective catalysis, of reactions?
10. How can a colloidal solution and true solution of same colour be distinguished from each other?
11. Give one example each of 'oil in water' and 'water in oil' emulsion.
12. Why is adsorption always exothermic?
13. Give one example each of lyophilise sol and lyophobic sol.
14. A data is formed at the meting point of sea water and river water why? Explain.
15. Sun looks red at the time of setting. How can you explain it?

E. Answer The Following Questions : (Mark- 3)

1. Explain the following :

   i) Fe $(OH)_3$ sol coagulates on additions of K_2SO_4 solution to it

   ii) Passing electric current through a colloidal solution remover the particles from it.

   iii) Rate of physisorption decreases with rise of temperature. (1×3= 3)

2. i) Write the expression for freundlich's equation to describe the behavious of adsorption from solution.

   ii) What causes change on sol particles? (1+2= 3)

3. Give reason for the following -

   i) Rough surface of catalyst is more effective than smooth surface.

   ii) Ne gets easily adsorbed over charcoal than He.

   iii) Smoke is passed Through charged plates before allowing it to come out of the chimneys in factories.

   (1×3= 3)

4. Explain Why?

   i) Alum is applied on a cut to stop bleeding

   ii) Sky appears blue in colour.

   iii) Chemisorptions increases with increase in temperature. (1×3= 3)

5. What do you mean by adsorption isopteran. State Freundlich adsorption isotheral. (1+2= 3)

6. How can you explain?

   i) Artificial rain is caused by spraying salt over clouds.

   ii) Same Substance can act both as colloids and crystalloids.

   iii) if is necessary to remove CO when ammonia is obtained by Haber's Process? (1×3= 3)

Answer Key

A. Select the correct answer (MCQ) : (1 mark each)

1. (a)
2. (d)
3. (c)
4. (b)
5. (a)
6. (c)
7. (b)
8. (c)
9. (b)
10. (d)
11. (a)
12. (c)
13. (b)
14. (a)
15. (d)
16. (d)
17. (d)
18. (d)
19. (a)
20. (a)

B. Assertion - Reason type questions : (1 marks each)

1. (a)
2. (a)
3. (a)
4. (c)
5. (a)
6. (b)
7. (b)
8. (a)
9. (a)
10. (a)
11. (C)
12. (d)
13. (d)
14. (a)
15. (a)

Chapter - 6

General principles and processes of Isolation of elements

Chapter at a glance :

The entire scientific and technological process used for isolation of the metal from its ores in feasible and commercially viable way is known as metallurgy. Some metals are placed below hydrogen in electrochemical series and their standard reduction potential is positive. These are chemically less reactive. Gold, platinum etc occurs in free state in nature. The reactivity of Cu, Hg, Ag are more compared to Au and Pt and occur as compound. On the other hand, the metal, placed above hydrogen in electrochemical series. The standard reduction potential of such metals are negative. That is why their tendency to lose electron and get oxidised is very high. They are very ractive. Their oxides are very stable. They do not occur in free state in nature, like Li, K, Na, Cu, Mg, Al, Zn, Fe etc.

Metals may remain in free state or as a compound mixed with many impurities. They are called minerals. Many minerals may contain metal but the minerals from which extraction of metal is chemically feasible and commercially viable is known as ores. For examples, out of clay (Al_2O_3, $2SiO_2$, $2H_2O$) and bauxite (Al_2O_3 , $2H_2O$), bauxite is considered as ores of aluminium because extraction of aluminium from bauxite is commercially and chemically more viable than clay. Similarly Iron pyrites is not an ore of Iron but haematite is. That is why all ores are minerals but all minerals are not ores.

The unwanted materials mixed with ores like sand, soil, other compounds are known as gangue.

Extraction of metal from ores and refining involves the following steps :–

Concentration of Ores :

Removal of the unwanted materials (eg sand, clays, etc) from the ore is known as concentration. It involves several steps and selection of these steps depend upon the differences in physical properties of the compound of the metal present and that of the gangue. The steps are as follows –

1. Hydraulic washing and gravity separation :

This is a type of gravity based separation in which an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.

2. Magnetic separation :

If either the ore or the gangue (one of the two) is capable of being attracted by a magnetic field, then such separation are carried out. The ground ore is carried on conveyer belt which passes over a magnetic roller. The magnetic substances remain in belt.

Table : Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2 (OH)_4 Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

Froth Floatation Method :

This method has been in use for removing gangue from sulphide ores like PbS, $CuFeS_2$, ZnS etc. In this process, a suspension of the powdered ore is made with water. To it collectors (Pine oils, fatty acids, xanthates etc) and froth stabilisers (like cresols, aniline) are added. The mineral particles become wet by the oils while the gangue particles by water. A rotating paddle agitates the mixure and draws air in it. As a result froth is formed which carries the mineral particles. Due to light wight of froth it carries the ores with it and skimmed off. Sometimes it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using depressants. For example in case of an ore containing Zns and PbS, NaCN is used as depressant. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

Leaching :

The process is used when the ore is soluble in some suitable solvent. like in the principal ore of aluminium, bauxite, usually contains SiO_2, iron oxides and TiO_2 as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473 - 523k and 35 - 36 bar pressure. This way Al_2O_3 is leached out as sodium aluminate. Impurities, SiO_2 dissolves forming sodium silicate. Other imparities left behind.

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

The aluminate in solution is neutralized by passing CO_2 gas.

$$2Na[Al\ (OH)_4]\ (aq) + CO_2\ (g) \rightarrow Al_2O_3.\ x\ H_2O\ (s) + 2NaHCO_3\ (aq)$$

In this way dissolving the ores in a suitable solvent and removing many impurities present in ore is known as leaching or degestion. To accelerate the precipitation of ML_2O_3 small amount of freshly prepared hydrated Al_2O_3 is added in solution. this is known as seeding.

$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3 . x H_2O(s) + 2NaHCO_3(aq)$

The sodium silicite remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3.

Extraction of crude metal from concentrated ore :

Metallic oxides are easier to reduce and through reduction most of the metal are extracted from their oxide. Thus isolation of metals from concentrated ore involves two major steps –

a. Conversion to oxide, and

b. Reduction of the oxide to metal.

Conversion of ore to metal oxide are carried out by two process –

1. **Calcination :**

Calcinlation is done by heating the concentrated ore below its melting point. (in absence of air or controlled supply of air). As a result volatile matter in ores escapes leaving behind the metal oxide. For For example –

$$Fe_2O_3 . XH_2O\ (s) \xrightarrow{\Delta} Fe_2O_3\ (s) + XH_2O\ (g)$$

$$Zn\,CO_3\ (s) \xrightarrow{\Delta} ZnO\ (s) + CO_2\ (g)$$

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

Roasting : In roasting the ore is heated in a regular supply of air in a furnace at a temparature below the melting point of the metal. Due to roasting water vapour, Sulphur, Arsenic and phosphorus present in ore separates out as volatile oxides. Sulphide ores at higher temparature are oxidised to metal oxide. For example –

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

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

$$2Cu_2S + 3O_2 \longrightarrow 2\,Cu_2O + 2SO_2$$

Calcination and Roasting are carried out at reverberatory furnace. If the ore cantains iron, it is mixed with silica before heating as a result iron oxide forms slag as ferrous silicate.

$$FeO + SiO_2 \longrightarrow FeSiO_3\ (slag)$$

Reduction of oxide to metal :

For active metal like alkaline metal (Na, K etc) or alkaline earth metal (like, Cu, Mg etc.) or aluminium electroreduction process is used for extraction of metal. For less reactive metal like - Zinc, Iron, Copper, Tin, etc carbon reduction process is used for extraction. Because these metals have lower tendency for oxygen compared to carbon. Coke powder is used as reducing agent in this process, Carbon monoxide formed due to incomplete combustion of carbon also acts as reducing agent. The whole process takes place in blast furnace. This is also known as smelting.

Extraction of iron from haematite ore by carbon reduction process may be represented by following reactions –

$$Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$$

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$$

$$FeO + CO \xrightarrow{\Delta} Fe + CO_2$$

Flux and slag :

At the time of reduction of calcinated or roasted ore, some chemical compound are mixed and heated depending on the nature of gangue present in ore. As a result the gangues are converted to other compounds and separated in molten state. The newly formed molten compounds are known as slag. The acidic (like SiO_2, $Na_2B_4O_7$, $10H_2O$) or basic (like $CaCO_3$, $MgCO_3$, Fe_2O_3 etc) compound mixed are known as flux.

Flux + gangue = slag

Example : In ores of Iron SiO_2 remain present as gangue. So basic flux (Cao) is added . SiO_2 (gangue) + Cao (flux) = $CuSiO_3$ (slag).

In copper ore , Feo remain present as gangue. So acidic flux (SiO_2) is added.

$FeO + SiO_2 = FeSiO_3$ (slag)

gangue + flux

Thermodynamic Principles of Metallurgy :

From the concepts of thermodynamics, i.e, from the Gibbs equation of energy change $\Delta G° = \Delta H° - T \Delta S°$, we can predict about the spontaneityor feasibility of reduction of metal oxide by a reducing agent. We know for a spontaneous process the necessary condition is $\Delta G < O$, i.e, ΔG should be negative. ΔG can be negative when –

1. ΔS becomes positive when temparature (T) increases, then $T\Delta S$ increases so that $\Delta H < T\Delta S$ and from the above equation ΔG becomes negative.

2. If oxidation and reduction of two reactions are put together in a overall reaction and ΔG becomes negative then resultant reaction will be feasible. These reactions are known as coupling reaction.

   Scientist U.J.T Ellingham used a graph to show the change of Gibbs free energy which help to explain the influence of temparature on the stability of metal oxide or compounds such diagrams help us in predicting the feasibility of thermal reduction of an ore.

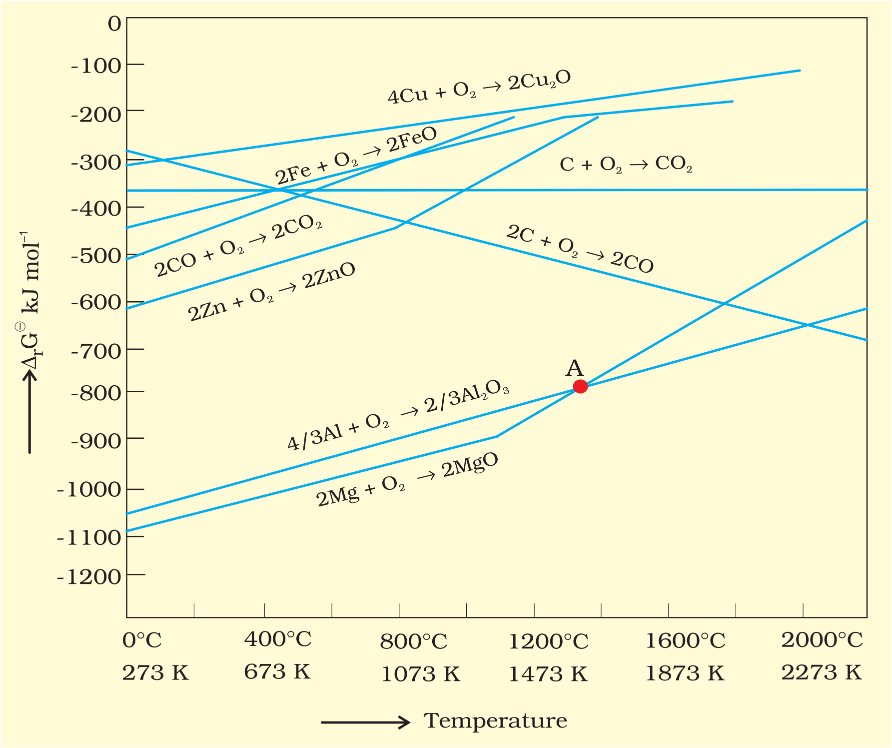


Fig. : Gibbs energy ($\Delta_r G^\ominus$) vs T plots (schematic) for the formation of some oxides per mole of oxygen consumed (Ellingham diagram)

Features of Ellingham Diagram :

(1) $2xM(s) + O_2(g) \longrightarrow 2M_xO$ for this type of reactions like –

$[2\ Zn + O_2 \longrightarrow 2\ ZnO\ ,\ 4Cu + O_2 \longrightarrow 2\ Cu_2O$

$2Fe + O_2 \longrightarrow 2FeO\ ,\ 2CO + O_2 \longrightarrow 2CO_2]$

Gas is used to prepare oxides as a result in this process molecular randomness decreases. As a result ΔS becomes negative and consequently from $\Delta G = \Delta H - T\Delta S$, $T\Delta S$ becomes positive and when temparature is raised the change of $\Delta_f G°$ also occurs in higher direction and $\Delta_f G°$ vs T plot shows positive slope.

(2) Except solid → liquid or liquid → Gaseous type of change, energy plot is a straight line having a positive slope.

(3) On increasing temperature the plot reaches a point where it bisects $\Delta_f G° = O$ line. Below this temparature $\Delta_f G°$ is negative and M_xO is stable. Above this point $\Delta_f G°$ of oxide is positive as a result M_xO decomposes spontaneously.

Electrochemical principles of Metallurgy :

In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be expressed by the following equation.

$\Delta G° = -nFE°$ | n = number of electrons taking part in reduction process.

E° = elctrode potential of redox couple formed in the system.

Since more reactive metals have large negative values of the electrode potential, their reduction is difficult. If the difference of two E° (values corresponds to a positive E° value) and consequently negative ΔG° then the less reactive metal will come out of the solution and more reactive metal will go to the solution.

example - $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

Extraction of iron from its oxides :

In the Blast furnace, reduction of iron oxides takes place in different temparature ranges. After concentration through calcination / roasting (to remove water, to decompose carbonates and to oxidise sulphides) the oxide ore of iron are mixed with limestone and coke and fed into Blast furnace –

(1) At 500 - 800k (lower temparature range in the blast furnace)

The following reactions take place

$$3\,Fe_2O_3 + CO \rightarrow 2\,Fe_3O_4 + CO_2$$

$$Fe_3O_4 + 4CO \rightarrow 3\,Fe + 4CO_2$$

$$Fe_2O_3 + CO \rightarrow 2\,FeO + CO_2$$

At 900 - 1500k (Higher temparature range in the blast furnace)

$$C + CO_2 \rightarrow 2\,CO$$

$$FeO + CO \rightarrow Fe + CO_2$$

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$FeO + C \rightarrow Fe + CO$$

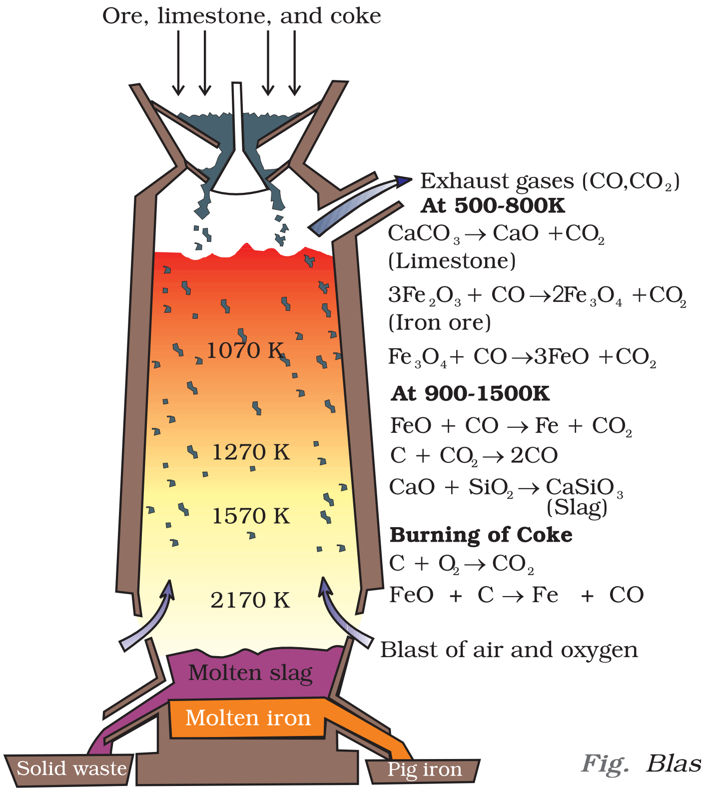


Fig. Blast furnace

Extraction of copper (Cu) :

Copper pyrites

↓ 1. Crushed

2. Concentration by froth floation process.

Concentrated copper pyrites

↓ Roasting

$2\ CuFeS_2 + O_2 \rightarrow Cu_2S + 2\ FeS + SO_2$

↓ Smelting

roasted ore + Sand + Coke

↓

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow$

$FeO + SiO_2 \rightarrow FeSiO_3$ (slag)

↓ Copper Matte

Bassemer converter

↓ [Sand + hot air]

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

Auto reduction $2\ Cu_2O + Cu_2S \rightarrow 6\ Cu + SO_2\uparrow$

↓

Blister copper

↓ 1. Poling

2. Electrolytic refining

↓

Pure copper

Extraction of Aluminium from alumina (Al_2O_3) :

Pure alumina (Al_2O_3) is bad conductor of electricity and its melting point (2323k) is also high. That is why cryolyte (Na_3AlF_6) and Fluospar (CaF_2) are added with alumina to reduce its melting point (1173k) and convert it to a good conductor of electricity. Electrolysis of molten mixure gives aluminium at cathode and $CO + CO_2$ at anode.

Steel vessel with lining of carbon acts as cathode and graphite anode is used.

The overall reaction is –

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

The electrode reactions are

$$\text{Cathode : } Al^{3+}(\text{molten}) + 3e^{-} \rightarrow Al\,(l)$$

$$\text{Anode : } C\,(s) + O^{2-}\,(\text{molten}) \rightarrow CO\,(g) + 2e^{-}$$

$$C\,(s) + 2O^{2-}\,(\text{molten}) \rightarrow CO_2(g) + 4e^{-}$$

Oxidation - Reduction :

Extraction of some non metal (like chlorine) and some metal (like gold and silver) is basically oxidation process.

Extraction of chlorine from brine may be represented by following reaction –

$$2Cl^{(-)}(aq) + 2H_2O(l) \rightarrow 2OH^{-}(aq) + H_2(g) + Cl_2(g)$$

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. For example –

Distillation :

This process is used to refine volatile metal like zinc, mercury, cadmium.

Liquation :

Tin and Lead is refined in this process.

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. Soluble salt of a metal is used as electrolyte. Due to electrolysis metal cation get reduced and get deposited at cathode and same amount of metal from anode get oxidised and dissolves in solution as cation. In this process anode slowly get consumed and volume of cathode increases. The more basic metal remains in the solution and the less basic ones go to the anode mud and get deposited below anode.

Copper, Zinc, Tin, Lead, Silver, Nickel, Chromium, aluminium like metals are refined through this process.

Zone refining :

This method is based on the principle that the impurities are more soluble in the molten state than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal and heated. The molten zone moves along with the heater which is moved forward. As a result the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and impurities get concentrated at one end. This end is cut off. This method is very useful for production of semiconductor and other metals of very high purity, eg. Germanium, Silicon, Boron, Gallium and Indium.

Vapour phase refining :

In this method the metal is converted into its volatile compound by using easily available reactants and then decomposed to give pure metal. example – Ni, Ti, Zr are refined by this process.

Mond process for refining Nickel :

In this process,nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.

$$Ni + 4CO \xrightarrow{330-350k} Ni(CO)_4$$

In later stage the carbonyl is subjected to higher temparature so that it is decomposed to give pure metal.

$$Ni\ (CO)_4 \xrightarrow{450-470k} Ni + 4CO$$

Van Arkel method for refining Zirconium or Titanium :

In this process impure metals like Zr and Ti is heated in an evacuated vessel with iodine. The metal iodide formed is covalent and volatile.

$$Zr + 2I_2 \rightarrow ZrI_4$$

In the later stage metal iodine is decomposed on a tungsten filament, electrically heated to about 1800k to get pure metal.

$$ZrI_4 \xrightarrow[\tan gsten]{1800k} Zr + 2I_2$$

A. Select the correct answer (MCQ) : (1 mark each)

1. Which metal is used in galvanisation –

a) Pb b) Cr c) Zn d) Cu

2. $Ti\ (s) + 2I_2\ (s) \xrightarrow{523k} TiI_4(g) \xrightarrow{1700k} Ti\ (s) + 2I_2\ (g)$

The above equation is related with –

a) Cupellation b) Poling c) Van Arkel d) Zone refining

3. Galvanisation is carried out on Iron with zinc coating but the reverse process is not possible. because–

a) Zinc is lighter then Iron.

b) Melting point of zinc is lower than Iron.

c) The electrode potential of zinc is less negative campared to Iron.

d) The electrode potential of zinc is more negative then Iron.

4. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with –

a) FeS b) CO c) Cu_2S d) SO_2

5. The metal purified by poling process is –

a) Sodium b) blister copper c) Zinc d) Silver

6. Removing the impurities of sulphur by heating the are in presence of air is known as –

a) Calcination b) Roasting c) Smelting d) Concentrating

7. Which of the following ores are concentrated by froth floatation process –

a) Haematite b) Galena c) Copper pyrites d) Magnetite

8. For which of the following Ellingham diagram can be drawn –

a) Sulphide b) Oxide c) Halide d) For all

9. Van Arkel process of refining is used for –

a) Zr b) Si c) Ge d) Na

10. Which of the following is not included in refining of metal –

a) Distillation b) Thermit process c) Smelting d) Mond process

11. For which oxide carbon reduction process is not possible ?

a) ZnO b) Al_2O_3 c) CuO d) Fe_2O_3

12. The reducing agent in self reduction process –

a) S b) S^{-2} c) O^{2-} d) SO_2

13. The impurity present in bouxite is –

a) CuO b) ZnO c) Fe_3O_4 d) SiO_2

14. Which one of the following is an ore of Iron ?

a) Pyrolusite b) Magnetite c) Melachite d) Cassiterite

15. Which gas is used to separate Nickel from cobalt in Mond process ?

a) CO b) CO_2 c) NH_3 d) O_2

16. For which metal zone refining process is used ?

a) Al b) Ge c) Cu d) Ag

17. The role of ethylxanthate in froth floatation process is –

a) To make the ore heavy b) To make the ore lighter

c) To attract ore towards water d) To separate ore from water

18. In which of the processes metal is obtained in molten state –

a) Froth floatation process
b) Calcination
c) Roasting
d) Smelting

19. Froth floatation is related with –

a) adsorption
b) absorption
c) Cuagulation
d) Precipitation

20. The process through which ore is heated below its melting point in presence of air, is –

a) Roasting
b) Calcination
c) Reduction
d) Distillation

21. By complete roasting of ZnS, the substance we get is –

a) only Zinc
b) only zinc oxide
c) Zinc oxide and suphur
d) Zinc oxide and sulphur dioxide

22. The element present in Anode mud in electro refining of copper is –

a) Iron
b) Silver
c) Aluminium
d) Tin

23. Which one is produced in Bessemer converter ?

a) Steel
b) wrought Iron
c) Cast Iron
d) Pig Iron

24. The chemical composition of magnesite is –

a) $MgCO_3$, $CaCO_3$
b) MgCl . KCl . $6H_2O$
c) $MgSO_4$. H_2O
d) $MgCO_3$

25. German silver Alloy contains –

a) Cu, Zn and Ni
b) Cu and Zn
c) Cu and Sn
d) Cu, Sn and Zn

B. Assertion - Reason type questions : (1 marks each)

a) Both assertion and reason are true and reason is the correct explanation of assertion.
b) Both assertion and reason are true but reason is not the correct explanation of assertion.
c) Assertion is true but reason is false.
d) Assertion is false but reason is true.

1. Assertion : Bauxite (Al_2o_3, $2H_2O$) is an ore of Aluminium.
   Reason : High quality alluminium can be extracted from bauxite easily and at a low cost.

2. Assertion : Copper and silver exist freely in nature.
   Reason : Polarising power of copper and silver is high. They polarize sulphide ion with relatively bigger size and form stable sulphide compound.

3. Assertion : Metals like sodium and potassium are highly reactive and cannot be found in free state in nature.

   Reason : Sodium and potassium are highly electro positive, they easily lose electron and form stable oxide.

4. Assertion : Froth floatation process is used mainly for concentration of sulphide ore.

   Reason : The tendency of sulphide ore to get wet by oils is less compared to gangue.

5. Assertion : CuO can be reduced by carbon but CaO cannot be reduced by carbon.

   Reason : Electropositive nature of Ca is more than copper.

6. Assertion : Zn is extracted by roasting of ZnS.

   Reason : Roasting of ZnS give ZnO which is highly stable compound.

7. Assertion : In case of Iron extraction basic flux is used but in extraction of copper acidic flux is used.

   Reason : SiO_2 remains with ores of iron as gangue and in case of copper ore FeO remains as gangue.

8. Assertion : $2C(s) + O_2(g) \rightarrow 2CO(g)$, ΔS° for the reaction is negative.

   Reason : $\Delta_f G^\circ$ vs T plot for the reaction has negative slope.

9. Assertion : Extraction of aluminium by electro reduction of Al_2O_3 is very tough.

   Reason : Pure alumina has a melting point at 2050°c. So electrolysis of alumina at this temparature leads to vapourisation of most of aluminium.

10. Assertion : Aluminium can be extracted by carbon reduction of pure alumina (Al_2O_3).

    Reason : Aluminium is a highly electro positive metal and it has high attraction towards oxygen.

C. Very short answer type question : (Marks - 1)

1. What is seeding ?
2. Write the chemical formula of Duralumin.
3. Among haematite and iron pyrites which one is the ore of Iron ?
4. What is gangue ?
5. Write chemical formula of bauxite.
6. For which type of ores froth - floatation method is used ?
7. What is leaching ?
8. Define smelting ?
9. Name two metals which are extracted using carbon reduction process.
10. What is thermite mixture ?

11. Name two metals extracted by self reduction process.
12. Complete the following reaction –

$$Cu_2S + Cu_2O \xrightarrow{\Delta} ?$$

13. Name some metals extracted by electro reduction process.
14. Give example of acidic flux and basic flux.
15. What is steel ?
16. What is spigel ?
17. What is matte ?
18. What is spelter ?
19. Which is the most abundant metal on the surface of earth ?
20. What is the role of cryolite in extraction of pure aluminium from bauxite ?
21. Mention the process used to extract Na and K.
22. What is 'Fool's gold' ?
23. Name the most popular process for preparation of steel .
24. Which is the purest form of iron ?
25. Which one is more suitable for reduction of ZnO, C or CO ?
26. What is horn silver ?
27. Write the molecular formula of cryolite.
28. Name the most abudant element present in earth crust .
29. What is cinnabar ?
30. What is the role of sodium / potassium xanthate in froth–floatation method ?

D. Answer the following question : (Marks - 2)

1. What are the difference between ore and minerals ?
2. Define gangue with example.
3. What is leaching? explain with an example.
4. Explain Froth-floatation method.
5. What is calcination ?
6. What is roasting ?
7. What is flux ? Give example.

8. What is slag ? Give example.
9. How cast iron is different from pig iron ?
10. What is self reduction of copper ?
11. Name some metals extracted by electrolytic refining process.
12. What is zone refining ? Explain with an example.
13. What is Mond process ?
14. What is the role of depressant in froth floatation process ?
15. Out of C and CO, which is a better reducing agent at 673k ?
16. What is the role of cryolite in electrolysis of alumina ?
17. What is the role of graphite rod in electro metallurgy of aluminium ?
18. Can we store $CuSO_4$ solution in aluminium or iron pot ?
19. Define electroplating with example .
20. What is galvanisation ? Give example.
21. Why NaCN is used in extraction of gold ?
22. What is the role of silica in copper metallurgy ?
23. What is blister copper ? How it is formed ?
24. What is anodioation ? Give example.
25. Aluminium cannot be extracted by carbon reduction process - Why ?
26. In iron extraction we use alkaline flux but in case of copper acidic flux is used. Explain why ?
27. Explain the role of flux in extraction of metal.
28. Why zinc cannot be extracted in blast furnace ?
29. Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction ?
30. Write two differences between calcination and roasting.

E. Answer the following questions - (Marks - 3)

1. Name the various steps involved in extraction of pure metals from their ores.
2. (i) What is the role of $CaCO_3$ (lime stone) in the extraction of iron from its oxide Fe_2O_3 .
   (ii) Name one acidic flux .
3. What do you mean by vapour phase refining ? Explain with example.

4. Write down the reaction taking place in different zones in the blast furnace during the extraction of iron.
5. (i) Why anhydrous aluminium chloride cannot be prepared by heating aqueous aluminium chloride.
   (ii) What are the constituents of german silver ? (2+1 =3)
6. Write about Van - Arkel method for refining Zirconium / Titanium.
7. Write chemical reaction taking place in the extraction of zinc from zinc blend.
8. (i) Cu_2O can be reduced with carbon but CaO cannot be reduced with carbon - explain.
   (ii) Among Fe_2O_3 and FeS_2 which one is the ore of iron ? (2+1 = 3)
9. What is the significance of leaching in the extraction of aluminium ?
10. How blister copper is extracted from cupous oxide (copper (I)) oxide ? Write the reaction involved in the process.
11. Write some limitations of Elingham diagram .
12. (i) What is thermit mixture ?
    (ii) Mention about its use. (2 +1 = 3)
13. (i) How ZnS is separated from a mixture of Pbs and ZnS ?
    (ii) Name the group of elements which are purified using chromatography. (2 +1 = 3)
14. (i) In Elingham diagram (C, CO_2) plot is almost horizontal – Why ?
    (ii) What is 18 - 8 steel?
15. (i) Briefly mention about electrochemical principles of metallurgy.
    (ii) Name the compound used as a flux in extraction of iron from hacmatite.
16. Write a shoot note on carbon reduction process.
17. (i) CuO can be reduced by carbon but CaO can’t be reduced by carbon ?
    (ii) Name two important metals present in ‘Anode mud’ at the time of electrical refining of copper.

Answer

A. Select the correct answer (MCQ) : (1 mark each)

1. c 2. c 3. d 4. c 5. b 6. b 7. b 8. d 9. a 10. b 11. b 12. b
13. d 14. b 15. a 16. b 17. d 18. d 19. a 20. a 21. d 22. b 23. a 24. d
25. a

B. Assertion - Reason type questions : (1 marks each)

1. a 2. d 3. a 4. c 5. b 6. d 7. a 8. d 9. a 10. d

Chapter - 7

p- Block Elements

Chapter at a glance :

1. Group-15 elements are collectively called pnictogen. group-15 elements are N, P, As, Sb & Bi.

2. Some improtant physical properties of Gr-15 elements are mentioned in the following table

Element	**Atomic Number**	**Electronic Configuration**	**Atomic Radius**	**Ionisation Enthalpy (IE)**	**Oxidation Number**	**Melting Point (MP)**	**Boiling Point (BP)**	**Covalency**	**Atomicity**	**Conduntance of Heat & Electricity**	**Nature of Bonds**	**Metallic or Non-metallic Nature**	**Density**
N	**7**	ns^2np^3 – [He] $2s^22p^3$	Down a gr. ↑ 70 Pm	Down a gr. ↓ IE_1= 1012 Kj/mol	-3, -2, -1, 0, +1, +2, +3, +4, +5	Down a gr. ↑ 63.29 K	Down a gr. ↑ 77.4 (K)	4	2	Down a gr. ↑	It can form Pπ - Pπ Multiple Bond	Down a gr. ↑ non metal	Down a gr. ↓
P	**15**	[Ne] $3s^23p^3$	110 Pm	IE_1= 947 Kj/mol	-3, to +5			6	4	Poor conductor	It can form Pπ - dπ Multiple Bond	Non metal	
As	**33**	[Ar] $4s^23d^{10}$ $4p^3$	121 Pm	IE_1= 834 Kj/mol	+3, +5			6	4	Semi conductor	It can form Pπ - dπ Multiple Bond	Metalloid	
Sb	**51**	[Kr] $5S^2$ $4d^{10}5p^3$	141 Pm	IE_1= 703 Kj/mol	+3, +5			6	4	Good conductor	It can form Pπ - dπ Multiple Bond	Metal	
Bi	**83**	[Xe] $6s^2$– $4f^{14}5d^{10}$– $6p^3$	148 Pm		+3	544.5 (K)	1833 (K)			Good conductor		Metal	

Some important information about table.

a) ↑ → This sign indicate the increasing.

b) ↓ → Decreasing sing.

c) IE → Ionisation Energy.

d) Down a gr. stability of +3 oxidatin state increases & that of +5 oxidation state decreases.

e) EC → Electronic configuration.

3. Order of different properties of hydrides of Gr-15 elements.

a) Bond angle :- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

b) Boiling Point :- $BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$

c) Solubility :- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

d) Basic character :- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

e) Thermal stability :- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

f) Reducing Character :- $BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$

4. Acidic character of oxide of nitrogen

$N_2O_5 > NO_2 > N_2O_3 > NO > N_2O$

5. NO & N_2O are neutral oxide

6. Acidic character of oxyacid of phosphorous

$H_3PO_2 > H_3PO_3 > H_3PO_4$

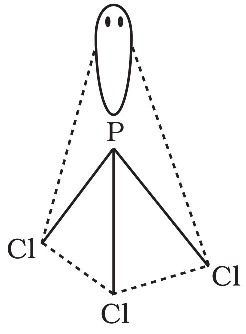
7. Order of basic character of nitrogen halides

$NI_3 > NBr_3 > NCl_3 > NF_3$

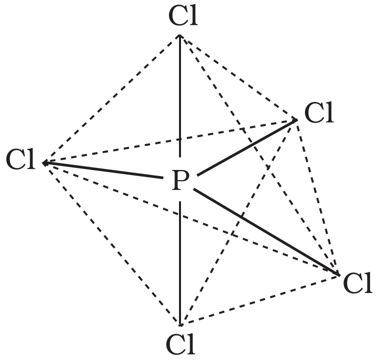
** Note :- NF_3 is stable but NCl_3 is explosive.

8. Structure & Geometry of some important compound.

a) PCl_3 → sp^3 hybridised → Pyramidal shape

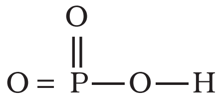


b) PCl_5 → sp^3d hybridised → Trigonal bipyramidal



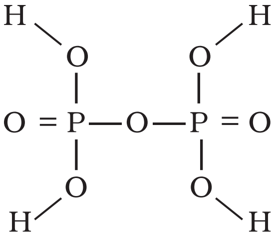
Since in PCl_5 bond angles are different, i.e. 120^0 & 90^0, herce P-Cl bond length are not equal. Axial bond is larger than equatorial bond.

c) HPO_3 (Metal Phosphoric acid) →

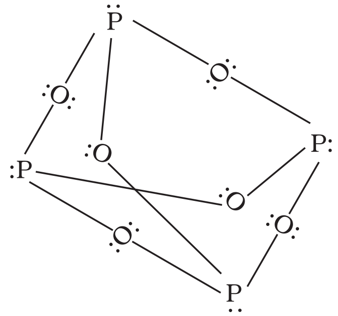


$$O=\overset{\overset{O}{\|}}{P}-O-H$$

d) $H_4P_2O_7$ (Pyrophosphoric acid) →

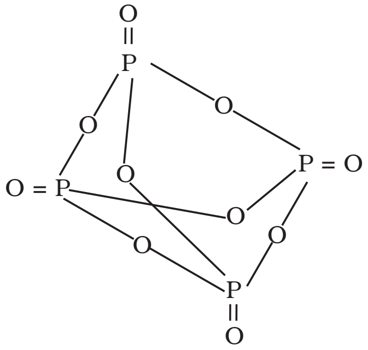


e) P_4O_6 →



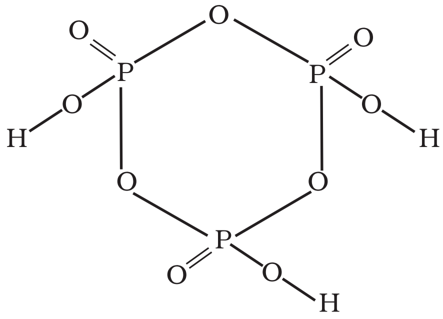
In P_4O_6 molecule No. of P – O – P bonds are six & No. of lp - are sixteen.

f) $P_4O_{10} \rightarrow$

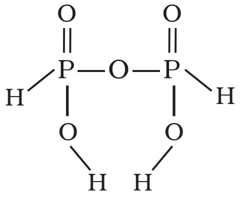


Here also No. of P – O – P bonds are 6.

g) Tnimetaphosphoric acid or cyclometa phosphoric acid $(HPO_3)_3$



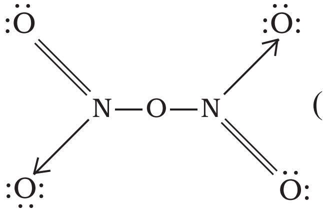
h) Pyrophosphorous acid $(H_4P_2O_5)$



i) Azide ion (N_3^-) :

$\ddot{N} = \overset{+}{N} = \ddot{O}^{(-)}$ (Linear)

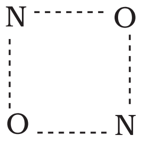
j) N_2O_5 :



(Planar)

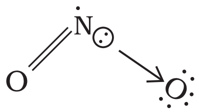
k) $N_2O \rightarrow :N \equiv N: \rightarrow :\ddot{O}:$(Linear)

l) $NO \rightarrow :N \overset{\cdot\cdot\cdot}{\equiv} O:$: or

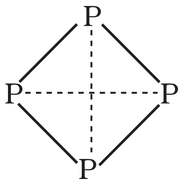


(In liquid state)

m) $NO_2 \rightarrow$



n) Structure of P_4 molecule : Tetrahedral

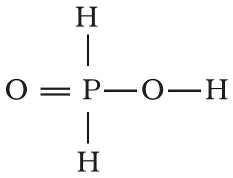


$< P - P - P$ bond angle is 60^o

9. N – N single bond is weaker than P – P single bond.

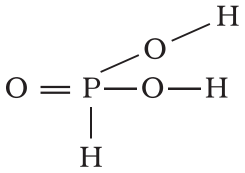
10. Basicity of oxyacid of phosphorous.

$H_3PO_2 \rightarrow$ Monobasic acid

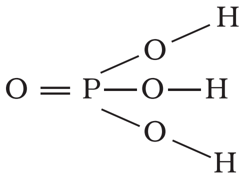


$$O = \underset{H}{\overset{H}{\overset{|}{\underset{|}{P}}}} - O - H$$

$H_3PO_3 \rightarrow$ Dibasic acid



$H_3PO_4 \rightarrow$ Tribasic acid



Chemical properties :

1. Formation of halides :

Nitrogen can form only trihallide where as phosphorous can form trihalide as well as pentahalide due to availability of d- orbital.

$H_2 + 2Cl_2 \rightarrow 2NCl_3$ $N_2 + 3F_2 \rightarrow 2NF_3$

$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 10Cl_2 \rightarrow 4PCl_5$

2. Disproportionation Reaction of Oxyacid of Nitrogen & phosphorous.

$3HNO_2 \rightarrow HNO_5 + 2NO + H_2O$

$H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

$3H_3PO_2 \rightarrow 2H_3PO_3 + PH_3$

3. Hydrolysis reaction of halides :-

NF_3 do not take part in the hydrolysis reaction. Other halides of Gr-15 can take part in the hydrolysis reaction.

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

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

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

$PCl_5 + 4H_2O$ (Hotwater) $\rightarrow H_3PO_4 + 5HCl$

PCl_5 exist as molecule in gas phase but in crystalline solid state it exist as $[PCl_4]^+ [PCl_6]^-$

4. Preparation of some important moleculcs

i) Nitrogen :-

a. Lab. Preparation :-

$NH_4Cl\ (aq) + NaNO_2\ (aq) \rightarrow NH_4NO_2\ (aq) + NaCl\ (aq)$

$NH_4NO_2\ (aq) \rightarrow N_2(g) + 2H_2O(l)$

b. Pure Nitrogen is obtained by heating azide compound.

$Ba(N_3)_2 \rightarrow Ba + 3N_2$

ii) Ammonia (NH_3) :-

a) Lab. Preparation :-

$2NH_4\ Cl\ (aq) + Ca(OH)_2\ (aq) \rightarrow CaCl_2\ (aq) + 2NH_3 + 2H_2O$

b) Ammonia can also be prepared by the hydrolysis of nitride salt.

$Mg_3N_2 + 6H_2O \rightarrow 3Mg\ (OH)_2 + 2NH_3$

c) Haber's process :-

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$\Delta H^0 = -92.2$ KJ/mol

Catalyst :- In Haber's process catalyst is Fe_2O_3 containing small amount of Molybdenum.

Promoter :- Al_2O_3 is used as promoter

Temperature :- 100K is the optimum Temperature

Pressure :- 200 atmosphere.

iii) **Phosphine (PH_3) :-** PH_3 is prepared in the Lab. in an inert atmosphere of CO_2 or coal gas.

$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

PH_3 is prepared along with highly inflammable P_2H_4.

iv) Nitric acid (HNO_3) :-

a) $NaNO_3 + H_2SO_4 \text{ (conc.)} \xrightarrow{475K} NaHSO_3 + HNO_3$

b) Manufacture of HNO_3 by Ostwald process :-

$$4NH_3(g) + 5O_2(g) \xrightarrow[500K,9bar]{Pt\text{-}Catalyst} 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

5. Some important information about the clements of Gr-15 & their compounds.

a) Catenation property of phosphorous is more in Gr-15 elements.

b) Phosphorous can show allotropy white phosphorous in more reactive than red phosphorous. Red phosphorous is used in match box.

c) Among the oxides of Nitrogen N_2O_3 is the most stable oxide. P_2O_5 is thermally more stable but Bi_2O_5 is least stable.

d) NO_2 & NO is paramagnetic and they can form dimer.

e) **Liquor Ammonia :-** Aqueous solution of Ammonia is known as liquor Ammonia. Liquor ammonia bottle should be cooled before opening the cork.

f) **Nitrolim :-** CaNCN or $CaCN_2$ (Calcicum cyanamide)

g) Ammonia is used as good complexing reagent.

h) **Nessler's reagent :** Alkaline solution of K_2HgI_4 (Potasium Mercuric Iodide). It is used to detect NH_3 or NH_4^+ ions.

i) **Laughing gas :-** N_2O It is used as anaesthetic substance

j) **Formula of Brownning :-** $[Fe(H_2O)_5NO]SO_4$ chemical name is hydrated nitrosoferrous sulphate.

k) NO_2 is the mixed anlay dride. $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$

l) Oxides of nitrogen are responsible for acid rain & photochemical smog.

m) **Aqua regia :** It is mixture of 3 vol of conc. HCl & 1 vol of conc. HNO_3

n) Aqua regia can dissolve 'Au' & 'Pt'. Nascent chlorine can dissolve them by formation of $AuCl_3$ & $PtCl_4$.

o) **Holme's signal :-** Mixture of Ca_3P_2 & CaC_2 It gives signal to ships in deep seas & oceans about danger point.

p) **Amatol :-** Mixture of NH_4NO_3 & TNT (TNT → Trinitro Tolune) It is very explosive substance.

q) Among the oxyacid of phosphorous H_3PO_2 is the strongest Redecing agent H_3PO_4 has high visocity & high melting point.

r) Liquid nitrogen is used as a refrigerant to preserve biological specimens.

s) Another name of nitrogen is azote.

t) **Phosphorescence :** White Phosphorus under goes slow combustion in contact with air and glows in dark. We can't feel heat in this glows. This is phosphorescence.

u) **Superphosphate :-** $Ca(H_2PO_2)_2 + 2CaSO_4$

v) **Superphosphate of Lime :-** $Ca(H_2PO_2)_2, H_2O + 2CaSO_4, 2H_2O$

w) **Triple super phosphate of lime :-** $3Ca(H_2PO_2)_2$

Some important reactions :-

1. $NH_2CONH_2 + 2H_2O \rightarrow (NH_4)\,CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$

2. $ZnSO_4(aq) + 2NH_4OH\,(aq) \rightarrow Zn(OH)_2(S) + (NH_4)_2SO_4$

3. $Cu^{2+}(aq) + 4NH_9OH \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

4. $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

5. $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 8H_2O$

6. $Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$ (Metastannic Acid)

7. $S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

8. $Mg + 1\text{-}2\%2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$

9. $Zn + 4HNO_3$ (conc.) $\rightarrow Zn\ (NO_3)_2 + 2NO_2 + 2H_2O$

10. $4Zn + 10\ HNO_3$ (very cold & dilute) $\rightarrow NH_4NO_3 + 4Zn(NO_3)_2$

11. $3Cu + 8HNO_3$ (cold & dil) $\rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O + 3H_2O$

12. $P_4 + 10\ CuSO_4 + 16\ H_2O \rightarrow 10\ Cu + 4\ H_3PO_4 + 10H_2SO_4$

13. $2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$

14. $3CaOCl_2 + 2NH_3 \rightarrow 3CaCl_2 + N_2 + 3H_2O$

15. $2K_2[HgI_4] + NH_3 + 3KOH \rightarrow IHgOHgNH_2 + 7KI + 2H_2O$

Group - 16

Chapter at a Glance :

1. Group - 16 clements are collectively called chalcogen. Gr-16 elements are O, S, Se, Te, Po. Po is a radio active element.

2. Some important physical properties of Gr-16 elements are mentioned in the following Table

Element	Alomic No.	General Electronic configuration	Atomic Radius	Ionisation Energy (IE)	Density	Oxidation No.	Melting Point	Boiling Point	Covalency	Atomicity	Electro Negativity	Multiple Bonding	Metallic & Non Metallic Character
O	**7**	(ns^2np^4) [He] $2s^22p^4$	Down a gr. increases 66 (pm)	Down a gr. decreases 1314KJ/mol	Down a gr. increases	-2, -1, 0, +2	Down a gr. increases -219^{0}C	Down a gr. increases -183^0 C	2	2	Down a gr. decreases 3.5	It can form $P\pi$ -$P\pi$ multiple bond	Non Metal
S	**16**	[Ne] 35^23p^4	104 (pm)	1000 KJ/ Mol		-2 +2 +4 +6	119^{0}C	445^0 C	2 4 6	8	2.44	$P\pi$ - $d\pi$ Multiple bond possible	Non Metal
Se	**34**	[Ar] 45^23d^{10} $4p^3$	117 (Pm)	941 KJ/Mol		-2 +2 +4 +6	217^{0}C	688^0 C	2 4 6		2.48		Non Metallic character more
Te	**52**	[Kr] $5S^2$ $4d^{10}5p^3$	137 (Pm)	869 KJ/ Mol		-2 +2 +4	450^{0}C	990^0 C			2.01		Both Metallic and non metallic
Po	**84**	[Xe] 65^2 $4f^{14}$ $5d^{10}$ $6p^4$	146 (Pm)	813 KJ/Mol							1.76		Metal
Uun	**116**	[Xc] 65^2 $4f^{14}$ $5d^{10}$ $6p^4$											

3. Order of different properties of hydrides of Gr-16

a) Bond angle : $H_2O > H_2S > H_2Se > H_2Te$

b) Boiling Point : $H_2O > H_2Te > H_2Se > H_2S$

c) Thermal Stability : $H_2O > H_2S > H_2Se > H_2Te$

d) Acid Character : $H_2Te > H_2Se > H_2S > H_2O$

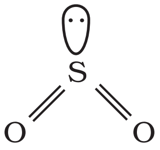
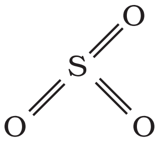
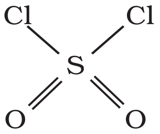
e) Reducing character : $H_2Te > H_2Se > H_2S > H_2O$

f) Volatility : $H_2S > H_2Se > H_2Te > H_2O$

4. Order of Electron affinity of Gr-16 elements are - $S > Se > Te > Po > O$

5. Chemical reaetirity of Gr-16 clements are decreases down a group - $O > S > Se > Te > Po$

6. Number $P\pi$ $P\pi$ & $P\pi$ $P\pi$ bonds in different compounds of sulphur -

Molecule	Structure of the Molecule	$P\pi - P\pi$	$P\pi - d\pi$
SO_2		1	1
SO_3		1	2
$SOCl_2$		0	2

7. Order of acidic character of some compounds -

i) $SO < SO_2 < SO_3$

ii) $H_2SO_3 < H_2SO_4$

iii) $H_2TeO_4 < H_2SeO_4 < H_2SO_4$

8. SO_2 can form additive compound with Cl_2 while SO_3 do not form due to lone pair of central atom. $SO_2 + Cl_2 \rightarrow SO_2Cl_2$ (Sulphuryl/Chloride)

9. **Example of some important oxide -**

Acidic oxide :- Cl_2O_7, SO_3, Mn_2O_7 etc.

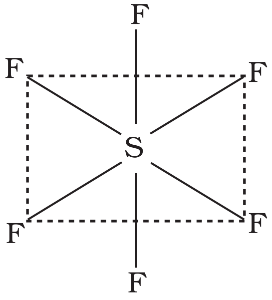
Basic oxide :- Metallic oxides are basic. Na_2O, MgO etc.

Amphoteric oxide :- Al_2O_3, ZnO, PbO, SnO_2, MnO_2, BeO etc.

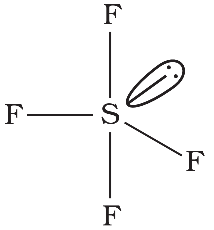
Ncutral oxide :- NO, N_2O, H_2O, CO etc.

10. Structure & Geometry of some important molecule :

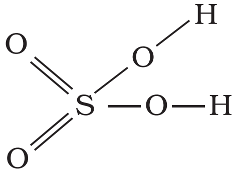
a) SF_6 → Octahcdral →



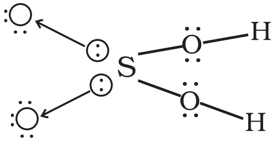
b) SF_4 → Trigonal bipyramidal



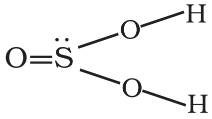
c) H_2SO_4 → (Sulphuric acid)



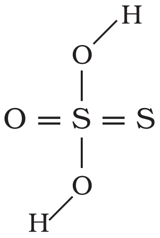
or



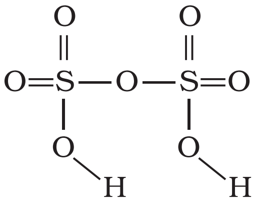
d) H_2SO_3 → (Sulphurous acid)



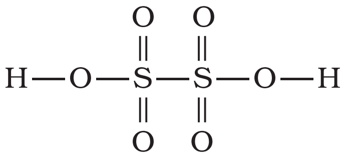
e) $H_2S_2O_3$ (Thiosulphuric acid) →



f) Pyrosulphuric acid ($H_2S_2O_7$) →

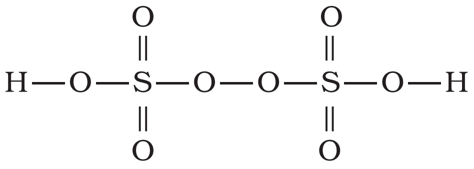


g) Dithionic acid ($H_2S_2O_6$) →



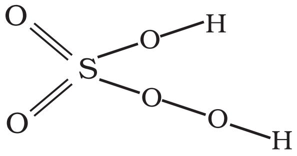
$$H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H$$

h) Peroxo disulphuric acid ($H_2S_2O_8$) →

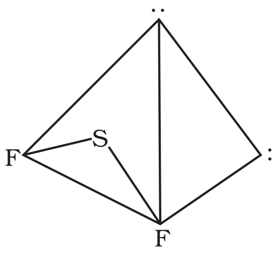


$$H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H$$

i) Peroxo mono sulphuric acid (H_2SO_5) →



j) SF_2 → Tetrahedral →



11. Important information about ozone(O_3) :-

a) 'O_3' is the very strong oxidising agent

b) It is diamagnetic

c) O_3 is the better sterilliser.

d) O_3 can bleach in dry condition.

e) **Tailing of Mercury :-** Mercurry loses its property on contact with O_3 due to formation of Hg_2O.

$2Hg + O_3 \rightarrow Hg_2O + O_2$

f) Ozono-sphere layer is not formed just above the earth surface.

Some important reaction of Gr-16 elements & their compound.

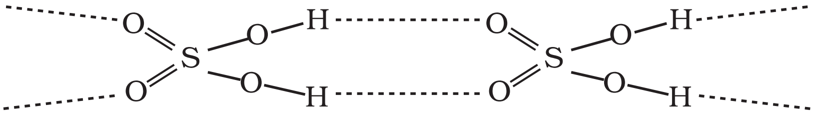
1. Among the allotropes of sulphur alpha– S is the stable allotropes.

2. In vapour state S_8 exist as S_2 and thus become papamagnetic.

3. H_2S is used in qualitative analysis in Laboratory.

4. H_2SO_4 is known as "oil of vitriol" as well as "king of chemicals".

5. BP of H_2SO_4 is very high due to intermolecular H- bonding.



6. SF_6 is not hydrolysed but TeF_6 readily get hydrolysid.

7. Bleaching property of SO_2 is temporary.

8. Sulphur is known as Brim stone.

9. FeS_2 is known as Fool's Gold.

10. During dilution of concentrated H_2SO_4 - water should not be added to conc. H_2SO_4.

11. IUPAC Name of H_2S is sulphane.

12. S_2Cl_2 is used in the vulcanisation of rubber.

Some important reactions of Gr-16 elements & their compound.

1. $2H_2S + SO_2(\text{moist}) \rightarrow 3S + 2H_2O$

2. $4S + 6NaOH \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

3. $\underset{\text{(pink)}}{2KMnO_4} + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + \underset{\text{(Colourless)}}{2MnSO_4} + 5S\downarrow + 8H_2O$

4. $\underset{\text{(Orange)}}{2KMnO_4} + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 3S + 7H_2O$ (Green)

5. $\underset{\text{(Pink)}}{2KMnO_4} + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$ (Colourless)

6. $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

7. $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

8. $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

9. $H_2S + 2HNO_3 \rightarrow S + 2NO_2 + 2H_2O$

10. $H_2SO_4 + PCl_5 \rightarrow SO_2Cl_2 + POCl_3 + H_2O$

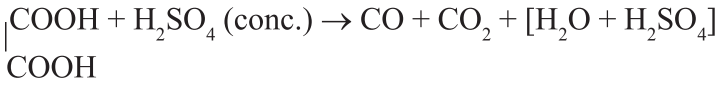
11. $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4$

By this reaction we can produce pure CO.

12. $H_2SO_4 + P_2O_5 \rightarrow SO_3 + 2HPO_3$

13. $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^{-} + 16H^{+} + 10SO_4^{2-}$

14. $2K_4[Fe(CN)_6] + O_3 + H_2O \rightarrow 2K_3[Fe(CN)_6]$

15. 

$$\begin{array}{l} |\text{COOH} \\ \text{COOH} \end{array} + H_2SO_4\ (\text{conc.}) \rightarrow CO + CO_2 + [H_2O + H_2SO_4]$$

Group- 17 / VII - A

Chapter at a Glance :

1. Group-17 elements are collectively known as halogen. Gr-17 elements are F, Cl, Br, I, & At. Among them F_2 & Cl_2 are gaseous, Br_2 is liquid & I_2 & At are solid at ordinary temperature.

2. Some important physical propertics of Gr-17 elements are mentioned in the following table.

Element	**Alomic No.**	**General Electronic configuration (ns^2np^5)**	**Atomic Radius**	**Ionisation Energy (IE)**	**Oxidation No.**	**Melting Point (MP)**	**Boiling Point (BP)**	**Density**	**Electron Affinity**	**Electron Negatirty**	**Solubility**
			Dawan a gr. ↑	Dawan a gr. ↓		Down a gr. ↑	Down a gr. ↑	Down a gr. ↑	Down a gr. ↑ Excep-tion in 'F' & 'Cl'	Down a gr. ↓	
F	**9**	[He] $2s^22p^5$	64 (Pm)	1680KJ/ mol	Only -1 (in comp.)	-220^{0}C	-188^{0}C	0.0017 g/cc	-3.6	4	soluble in H_2O
Cl	**17**	[Ne] $3s^23P^5$	99 (Pm)	1256 KJ/ mol	-1 0 +1 +2 +3 +4 +5 +6 +7	-101^{0}C	-35^{0}C	.0032 g/cc	-3.8	3	soluble in H_2O & in organic solvent
Br	**35**	[Ar] $4s^23d^{10}$ $4p^5$	114 (Pm)	1142 KJ/ mol	-1 0 +1 +2 +3 +4 +5 +6 +7	-7.2^{0}C	58.8^{0}C	3.1028 g/cc	-3.5	2.8	soluble in organic solvent
I	**53**	[Kr] $5s^2$ $4d^{10}5p^3$	198 (Pm)	1008 KJ/ mol	-1 0 +1 +3 +5	114^{0}C	184^{0}C	4.933 g/cc	-3.2	2.5	soluble in organic solvent
At	**85**	[Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^5$									

3. Decreasing order of different propertics of the hydracids of Halogen.

i) Dipole moment : HF > HCl > HBr > HI

ii) Boiling point : HF > HI > HBr > HCl

iii) Thermal stability : HF > HCl > HBr > HI

iv) Acid character : HI > HBr > HCl > HF

v) Reducing character : HI > HBr > HCl > HF

4. Decreasing order of different properties of Halogens

i) Electron gain Enthalpy :-

Cl (g) > F (g) > Br (g) > I (g)

ii) Bond Enthalpy :-

$Cl_2 > Br_2 > F_2 > I_2$

iii) Reactivity order of Halogen :-

$F_2 > Cl_2 > Br_2 > I_2$

5. '-F' is the strongest oxidising agent E^0_{ox} value of 'F' is very high.

6. Fluorine do not form oxoacid because Fluorine is the most electronegative substance. Only HOF can exist.

7. Fluorine do not form polyhalide such as F_3 due to unavailability of d-orbital.

8. Decrcasing order of the different propertics of oxyaid of chlorine.

- **Acidic Character :-** i) $HClO_4 > HClO_3 > HClO_2 > HOCl$
  ii) HOCl > HOBr > HOI
- **Oxidising Character :-** $HOCl > HClO_2 > HClO_3 > HClO_4$
- **Thermal Stability order :-** $HClO_4 > HClO_3 > HClO_2 > HOCl$

9. Colour :- All the halogens are coloured. Fluorine absorbs violet portion & thus appear yellow where as Iodine absorbs yellow & thus appears violet.

10. Interhalogen :- Interhalogen compounds are formed by the combination of two different halogen. such as

$I_2 + Cl_2 \rightarrow 2ICl$

$I_2 + 7F_2 \rightarrow 2IF_7$ etc.

Type of interhalogen compounds are AB type, AB_3 type, AB_5 type & AB type, where A is always bigger atom & B is always smaller afom. Number of 'B' atom incrcascs with in creasing the size of A.

Interhalogen cornpounds are more reactive than halogen because inter halogen compounds are polar order of thermal stability of AB type interhalgen compound are IF > BrF > CIF > ICI etc.

11. **Pseudo halogen & pseudo halide :-** A few ions are known, consisting of two or more electronegative atoms of which at least one atom is nitrogen, are pseudo halide ion.

Such as - cyanide ion → CN^-

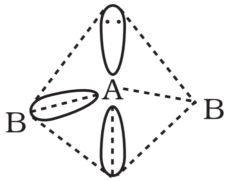
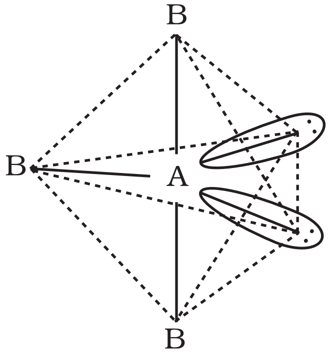
Cyanate ion → OCN^-

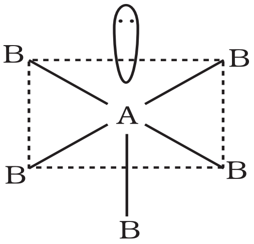
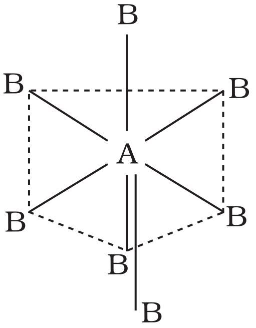
Azide ion → N_3^-

Pseudo halogen are $(CN)_2$ (cyanogen)

$(OCN)_2$ oxycyanogen etc.

12. Some important structure of interhalogen compounds.

Type	Hybridisation	Geometry & actual shape
AB (ICL, ClF etc)	sp^3	 Tetrahedral (linear)
AB_3 (ClF_3, BrF_3 etc)	sp^3d	 Trigonal bipyradial (T-shaped)

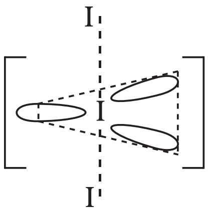
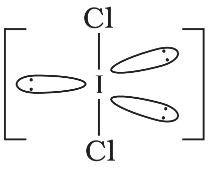
AB_5 (BrF_5, IF_5 etc)	sp^3d^2	 Octahedral, Square pyramidal
AB_7 (IF_7)	sp^3d^3	 Pentagonal bi-pyramidal

13. HF can't be kept in glass container. HF can rcaet with the component of glass

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

This is why HF is kept in the qutta percha bottles or in way bottle.

14. Structure of other important ion :

Ion	**Hybridisation**	**Geometry**	
I_3^-	sp^3d		Trigonal Bipyramidal (Shape-Linear)
ICl_2^-	sp^3d		Trigonal Bipyramidal (Shape-Linear)

15. Some important chemical reactions of halogens & compound of halogens :-

1. $3F_2 + 3H_2O \rightarrow 6HF + O_3$

$2F_2 + 2H_2O \rightarrow 4HF + O_2$

Due to formation of O_3 fishy smell is obtained

2. $2F_2 + 2NaOH\ (dil) \rightarrow OF_2 + 2NaF + H_2O$

$2F_2 + 4NaOH\ (conc.) \rightarrow 4NaF + O_2 + 2H_2O$

since F_2 is the strongest oxidising agent hence if can't form fluorite & fluorate salt.

3. $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

4. $K_2Or_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

5. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

6. $2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + 2MnSO_4 + 2H_2O + Cl_2$

7. $X_2(X_2 = Cl_2, Br_2, I_2) + OH^-\ (dil) \rightarrow {}^-OX + X^- + H_2O$

8. $X_2(X_2 = Cl_2, Br_2, I_2) + OH\text{-}\ (conc.) \rightarrow X\text{-} + XO^-_3 + H_2O$

9. $Cl_2 + Ca(OH)_2$ (dry slaked lime) $\rightarrow Ca(OCl)Cl + H_2O$

10. $Na_2S_2O_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl + S$

11. $SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$

12. $2KI + X_2(X_2 = F_2, Cl_2, Br_2) \rightarrow 2KX + I_2$

13. $2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$

$2KBrO_3 + I_2 \rightarrow 2KIO_3 + Br_2$

14. $CuSO_4 + 2KI \rightarrow CuI_2 + K_2SO_4$

$2CuI_2 \rightarrow Cu_2I_2 + I_2$

15. $Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$

Stain of I_2 can be removed by HYPO - SOl^n ($Na_2S_2O_3$)

This reaction is involved in iodometmic titrations in presence of starch indicator.

Group - 18

1. Elements of Group - 18 are known as inert gascs as well as zero valent elements. Group-18 elements are - He, Ne, Ar, Kr, Xe, Rn & Og. Except Rn & Og these are termed as rare gases of atmosphere.

2. **Some important physical propertics of inertgases are explained in the following :-**

i) **Stable electronic configuration :-**

General electronic configuration ns^2np^6 All the orbitals are doubly occupied. These 'p'-block elements can't form co-valent compound.

ii) **IE (Ionisation Energy) :-**

IE of these elements are more than the rest elements placed in the periodic table. He has highest IE than any orther elements.

iii) **Electron Affinity (EA) :-**

Electron affinity of inert gases are zero.

iv) Inert gases are colourless, odourless & tasteless.

v) **BP & MP :-**

They have low BP and MP. But BP & MP gradually increases down a group.

vi) **Atomic radius :-**

In case of noble gases, the atomic radii correspond to Vander waal's radii which is always greater than the covalent radii. This is why atomic radius of inert gases are exceptionaly high than the Halogens.

vii) **Solubility :-** They are less soluble in water but solubility increases with increasing atomic Number.

viii) These gases have fairly high electrical conductivity. They produced coloured light when on electrical discharge is passed through them at low pressure.

3. **Occurance :-** Argon is the most constituent among the inert gases & rest are in very minute quantities.

4. **Separation of Noble gases :-** Noble gases are scparated by fractional distillation. BP of Noble gases are given below.

He	Ne	Ar	Kr	Xe
-269^0C	-246^0C	-186^0C	-152^0C	-107^0C

5. **Compounds of Nobles gases :-**

i) $XePtF_6$ was the first compound of any Noble gases.

ii) **Clathrates :-** Generally 'He' & 'Ne' do not form clathrates with quinol, because size of cavity is more & size of He & Ne is very small.

6. Some important chemical reactions :

i) $2XeF_2 + 2H_2O \rightarrow 2Xe + 2H_2F_2 + O_2$

XeF_2 act as a strong oxidising agent.

ii) $2XeF_2 + 4^-OH \rightarrow 2Xe + 4F^- + 2H_2O + O_2$

iii) $XeF_2 \quad + 2SbF_5 \quad \rightarrow \quad XeF_2.\ 2SbF_5$

Lewis base Lewis acid Adduct.

iv) $3XeF_4 + 4\ BCl_3 \rightarrow 4BF_3 + 3Xe + 6Cl_2$

v) $2XeF_4 + 3H_2O \rightarrow Xe + XeO_3 + 3H_2F_2 + F_2$

vi) a) $XeF_6 + H_2O \rightarrow XeOF_4 + H_2F_2$

b) $XeOF_4 + H_2O \rightarrow XeO_2F_2 + H_2F_2$

c) $XeO_2F_2 + H_2O \rightarrow XeO_3 + H_2F_2$

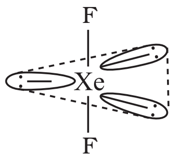
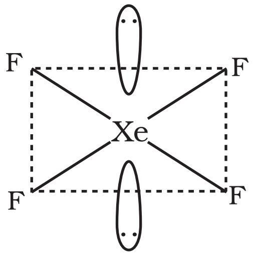
vii) XeF_6 dissolves in HF.

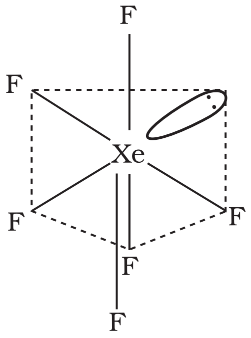
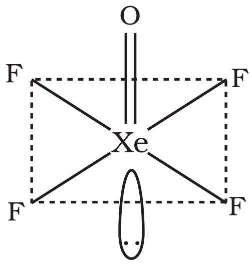
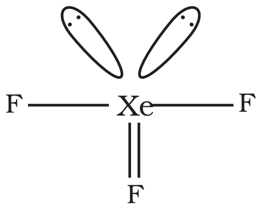
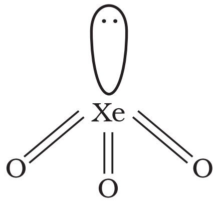
$XeF_6 + HF \rightarrow [XeF_5] + [HF_2^-]$

viii) $LXeF_6 \rightarrow XeF_2 + XeF_4 + 3F_2$

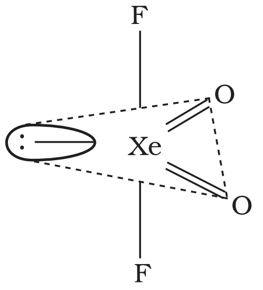
ix) $2XeF_6 + 16^-OH \rightarrow 12F^- + XeO_6^{4-} + Xe + O_2 + 8H_2O$

7. Structure of some important compounds :-

Compound	**Hybridisision**	**Geometry and Shape**
$Xe\ F_2$	sp^3d	**Trigonal bipyramidal**  Linear
XeF_4	sp^3d^2	Octahedral  Square planar

XeF_6	sp^3d^3	Pentagonal bipyramidal  Distorted octahedral
$XeOF_4$	sp^3d^2	Octahedral  Square pyramidal
$XeOF_2$	sp^3d	Trigonal bipyramidal  T- Shape
XeO_3	sp^3	Tetrahedral  Pyramidal

XeO_2F_2	sp^3d	Trigonal bipyramidal



8. Some important uses of Noble gases :-

i) Mixture He & O_2 is used instead of ordinary air by divers for respiration.

ii) He gas is filled in tubes of acroplanc tyres.

iii) Ne-Ar mixture are used in advertising signboard

iv) Rn is used in cancer treatment i.e. in Radio therapy

Group - 15

A. Select the correct answer (MCQ) : (Each carries 1 mark)

1. Pnictogen clements is –

(a) As (b) Si (c) Ge (d) Br

2. Covalency of Nitrogen is N_2O_5 is –

(a) 5 (b) 4 (c) 3 (d) 4.5

3. Among the following which one gives pure nitrogen on heating –

(a) $(NH_4)_2\ Cr_2O_7$ (b) $Ba(N_3)_2$ (c) NH_4NO_3 (d) NH_4NO_2

4. Nitrolim is a mixture of –

(a) $CaCN_2 + C$ (b) $N_2O + C$

(c) $CaC_2 + H_2O$ (d) conc. HCl + conc. HNO_3 (3:1 by vol.)

5. Correct order of thermal stability of Gr-15 Hydrides are –

(a) $NH_3 > PH_3 > AsH_3 > SbH_3$ (b) $SbH_3 > AsH_3 > PH_3 > NH_3$

(c) $AsH_3 > SbH_3 > NH_3 > PH_3$ (d) $PH_3 > NH_3 > AsH_3 > SbH_3$

6. Holme's signal is a mixture –

(a) CaC_2 & Ca_3P_2 (b) $CaSO_4$. $2H_2O$ (c) N_2O & CO_2 (d) Zn + NaOH

7. $P_4 + NaOH + H_2O \rightarrow A + NaH_2PO_2$ The product 'A' is –

(a) NH_3 (b) PH_3 (c) Red P_4 vapour (d) N_2O

8. Mixture of Aqua. regia is –

(a) conc. HCl + dil HNO_3 (3 : 1 by vol.) (b) conc. HCl + dil HNO_3 (3 : 1 by vol.)

(c) dil. HCl + conc. HNO_3 (3 : 1 by vol.) (d) conc. HCl + conc. HNO_3 (3 : 1 by vol.)

9. Among the following Metaphosphoric acid is –

(a) $H_4P_2O_7$ (b) H_3PO_3 (c) HPO_3 (d) H_3PO_2

10. Correct order of BP among the Hydridcs of Gr.-15 –

(a) $SbH_3 > NH_3 > AsH_3 > PH_3$ (b) $SbH_3 > AsH_3 > NH_3 > PH_3$

(c) $PH_3 > AsH_3 > SbH_3 > NH_3$ (d) $NH_3 > SbH_3 > AsH_3 > PH_3$

11. Bismuth does not show penta valency because –

(a) bismuth shows inert pair effect. (b) Bismuth have vacant 'd' orbital

(c) Bismuth is the pnicogen (d) Bismuth is more metauic

12. Among the following which one is does not exist –

(a) BiF_5 (b) PCl_5 (c) PI_5 (d) NCl_3

13. PCl_5 is solid state exist as –

(a) $[PCl_6]^-$ & $[PCl_4]^+$ (b) $[PCl_4]^-$ & $[PCl_6]^+$

(c) $[PCl_5]^+$ $[PCl_5]^-$ (d) None

14. Bond angle is different in the molecule –

(a) PCl_5 (b) $^+NH_4$ (c) $^+PH_4$ (d) SF_6

15. Increasing order of Reducing character of Group-15 Hydrides are –

(a) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$ (b) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

(c) $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ (d) $BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$

16. $I_2 + HNO_3 \rightarrow X + NO_2 + H_2O$. Compound 'X' is –

(a) I_2O_7 (b) HIO_4 (c) I_2O_5 (d) HIO_3

17. Zn + NaOH + $NaNO_3 \rightarrow$ A gas is formed having pungent odour the gas is –

(a) Ammonia gas (b) Phosphinc gas (c) Laughing gas (d) Blue gas

18. Ammonia gas NH_4^+ ion can be detected by –

(a) Nesslar's Reagent (b) Mercurous chlonide

(c) Pungent odour (d) All of these

19. Bond angle of < P – P – P in which phosphorous is –

(a) 60^0 (b) 90^0 (c) 120^0 (d) 150^0

20. Number of P – O – P bonds & number of lone pair in P_4O_6 Molecule is –

(a) 6, 16 (b) 4, 12 (c) 2, 10 (d) None

21. Number of $P\pi - P\pi$ & $P\pi\ ^{-}d\pi$ bonds in $POCl_3$ molecule is/are –

(a) 0, 1 (b) 1, 1 (c) 1, 0 (d) 1, 2

22. The No. of P–O–P bonds in cyclic trimer of metaphosphoric acid is/are –

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

23. Nitrogen is gas but phosphorous is solid, because –

(a) phosphorous do not form $P\pi - P\pi$ bond in between two phosphorous atom

(b) for the completion of octet phosphorous become tetra atomic & tetrahedral

(c) Vanderwaal force of attraction in phosphorous molecules is more

(d) all of these

24. Oxidation No. of 'Fe' in Brown ring is –

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

Group - 16

A. Select the correct answer (MCQ) : (Each carries 1 mark)

1. Incorrect statement is –

(a) Group - 16 elements are known as chalcogen

(b) Catenation property of oxygen is less then sulphur

(c) Rhombic sulphur is the stable allotropic form sulphur

(d) Oxygen & Ozone are not allotropes to cach other

2. Low volatile nature of H_2SO_4 is due to –

(a) strong covalent bond (b) hydrogen bonding

(c) prcsence of co-ordinafe bond (d) none of these

3. In Pyrosulphurous acid, the oxidation state of sulphur atom are –

(a) +6, – 2 (b) 6, 0 (c) 5, 3 (d) 5, -2

4. Increasing order of BP of hydrides of Group-16 elements are –

(a) $H_2S < H_2Se < H_2Te < H_2O$ (b) $H_2S < H_2Te < H_2Se < H_2O$

(c) $H_2Se < H_2Te < H_2S < H_2O$ (d) $H_2Te < H_2Se < H_2S < H_2O$

5. Identify A & B from the following information –

$A + H_2SO_4 \rightarrow B$ (gas) (a colourless & suffocating small)

$B + K_2Cr_2O_7 + H_2SO_7 \rightarrow$ green coloured compound is formed

A & B are

(a) SO_3^{2-}, SO_2 (b) Cl_2, HCl (c) CO_3^{2-}, CO_2 (d) S^{2-}, H_2S

6. Number of $p\pi - p\pi$ & $p\pi - d\pi$ bonds in SO_3 molecule are –

(a) 1, 2 (b) 2, 1 (c) 1, 9 (d) 2, 2

7. When Na_2S is added to alkaline sodium nitroprusside solution then a complex is formed having voilet colour. The formula of the compound is –

(a) $Na_4\,[Fe(CN)_5NOS]$ (b) $[Fe(CN)_5NOS]^{2-}$

(c) $Na_4[Fe(CN)_5NO]$ (d) None

8. The No. of S–S bonds in sulphur trioxide trimer S_3O_9 is –

(a) O (b) 3 (c) 2 (d) 1

9. Which of the following does not have S – linkage ?

(a) $S_2O_8^{2-}$ (b) $S_2O_6^{2-}$ (c) $S_2O_5^{2-}$ (d) $S_2O_3^{2-}$

10. When excess PCl_5 react with conc. H_2SO_4 –

(a) Sulphuryl chloride (b) Sulphurous acid

(c) Chlorosulphonic acid (d) Thionyl chloride

11. The No. of S – S bonds and No. of lp in S_8 mole cules are respectively –

(a) 8, 8 (b) 16, 8 (c) 8, 16 (d) 8, 4

12. O_3 can't oxidise –

(a) KI (b) $FeSO_4$ (c) $KMnO_4$ (d) K_2MnO_4

13. The shape of SF_4 molecule is –

(a) Seasaw (b) Trigonal bipypamidal

(c) Octahedral (d) Trigonal planer

14. Formula of Trailing of mercury –

(a) HgO (b) Hg_2O (c) Hg_2Cl_2 (d) none

15. Bleaching property of SO_2 is Temporary because –

(a) it can bleach the organic coloured substance by nascent Hydrogen

(b) it can bleach the organic coloured substance by nascent oxygen

(c) it can bleach in dry condition

(d) SO_2 can act as only oxidising agent

16. Which of the following statements regarding sulphur is in correct –

(a) S_2 mole cule is paramagnetic (b) the vapour at 200^0C consists mostly S_8 mings

(c) at 600^0C the gas mainly consists of S_2 molecule

(d) the oxidation state of sulphur is never less than +4 in its compound

17. Which of the following is most casily hydrolysed –

(a) SF_6 (b)NF_3 (c) CCl_4 (d) TeF_6

18. Which of the following statements regarding H_2O_2 is correct –

(a) H_2O_2 can act as both oxidising & reducing agent

(b) H_2O_2 can bleach black colour easily

(c) BP of H_2O_2 is more than H_2O

(d) all of these

19. Among the following which is not true about peroxide –

(a) PbO_2 (b)BaO_2 (c) H_2O_2 (d) Na_2O_2

20. Among the following compound which gives carbon with conc. H_2SO_4 –

(a) HCOOH (b) $\begin{array}{l} | CH_2 - COOH \\ CH_2 - COOH \end{array}$ (c) $C_{12}H_{22}O_{11}$ (d) $\begin{array}{l} | COOH \\ COOH \end{array}$

Group - 17

A. Select the correct answer (MCQ) : (Each carries 1 mark)

1. The fifth halogen element is –

(a) ‘At’ (b) ‘Po’ (c) ‘Gc’ (d) Og

2. Among the elements strongest oxidising is –

(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

3. Among the following which one is not correctly matched mentioned in the 1st bracket –

(a) HF > HCl > HBr > HI (Decrcasing order of acidic character)

(b) HF > HI > HBr > HCl (Decrcasing order of BP)

(c) HF < HCl < HBr < HI (mcreasing order of reducing character)

(d) HF > HCl > HBr > HI (Decrcasing order of thermal stalrility)

4. Correct order of Dipolemoment of Halogen hydracids are –

(a) HF > HCl > HBr > HI (b) HI > HBr > HCl > HF

(c) HF > HI > HCl > HBr (d) HCl > HBr > HI > HF

5. In creasing order of Bord energy of halogen are –

(a) $I_2 < Br_2 < Cl_2 < F_2$ (b) $I_2 < F_2 < Br_2 < Cl_2$

(c) $Br_2 < I_2 < F_2 < Cl_2$ (d) $F_2 < Cl_2 < I_2 < Br_2$

6. Correct order of eleetron gain enthalpy of halogen are –

(a) I < Br < Cl < F (b) I < Br < F < Cl (c) Br < I < F < Cl (d) I < Br < F < Cl

7. Among the following the compound does not exist is –

(a) $HClO_3$ (b) HOCl (c) HOF (d) HFO_3

8. $F_2 + NaOH (dil) \rightarrow NaF + X + H_2O$ the compound ‘X’ is –

(a) OF_2 (b) O_2 (c) O_3 (d) O_2F_2

9. Shape of the ClF_3 mole cule is –

(a) trigonal bipyramidal (b) square planar

(c) T-shape (d) sea saw

10. Pscudo halogen is –

(a) $(CN)_2$ (b) $(SCN)_2$ (c) N_3 (d) both 'a' & 'b'

11. Among the following interhalogen compound which is does not exist –

(a) Cl_2 (b) SO_2 (c) O_3 (d) H_2O_2

12. Element can bleach the organic coloured substance is dry condition is –

(a) ClF_3 (b) FCl_3 (d)IF_7 (d) BrF_5

13. Correct increasing order of acid character are –

(a) HOF < HOCl < HOBr < HOI (b) $HOCl < HClO_3 < HClO_4 < HOClO$

(c) $HOCl < HClO_2 < HClO_3 < HClO_4$ (d) $HClO_3 < HIO_3 < HBrO_3 < HOCl$

14. Which of the following is not pseudo halide ion – ?

(a) CNO (b) OCN (c) RCOO (d) N_3

15. Oxyacid of some non metallic element & their respective anhydrides are given. Which is the incorrect comtrination –

(a) $HNO_3 \rightarrow NO_2$ (b) $HClO_2 \rightarrow Cl_2O_3$ (c) $HPO_3 \rightarrow P_2O_5$ (d) $H_2SO_4 \rightarrow SO_3$

16. The halogen that is most readily reduced is –

(a) F_2 (b) Br_2 (c) Cl_2 (d) I_2

17. I_4O_9 is a/an –

(a) Covalent compound (b) Co-ordinate compound

(c) Ionic compound (d) Double salt

18. Which has moximum P^H in aqueous solution –

(a) NaClO (b) NaClO (c) $NaClO_3$ (d) $NaClO_4$

19. Tincture of iodinc is –

(a) Aqueous solution of I_2 (b) Solution of Iodine in aqueous KI

(c) Alcoholic solution of I_2 (d) Aqueous solution of KI

20. Most stable oxide of chlorine is –

(a) ClO_3 (b) Cl_2O (c) Cl_2O_3 (d) Cl_2O_7

21. Interhalogen compounds are more reactive than the halogen because –

(a) their bond energy is less than the bond energy of the halogen molcule

(b) the are more ionic

(c) they carry more encrsy

(d) two halogens are present in place of one

22. Iodine deficiency in diet is known to cause –

(a) Beri-beri (b) Goitre (c) Rickets (d) Night Blindness

23. The acid employed for etching of glass is –

(a) H_2SO_4 (b) $HClO_4$ (c) HF (d) aqua regia

24. $CsBr_3$ on dissociation gives –

(a) Cs^+ & Br_3 — ions (b) Cs^+ & 3Br — ions

(c) Br_2 & lattice CsBr (d) none

25. $HClO_4 + P_2O_5 \rightarrow A + B$ A & B are –

(a) $HClO_3$, H_3PO_4 (b) Cl_2O_7, HPO_3 (c) ClO_2, H_3PO_4 (d) Cl_2O_6, HPO_3

Group - 18

A. Select the correct answer (MCQ) : (Each carries 1 mark)

1. Which is the most casily liquefiable rare gas ?

(a) Ar (b) Ne (c) Xe (d) Kr

2. Among the following one which is does not exist –

(a) XeF_2 (b) XeF_5 (c) XeF_6 (d) XeF_4

3. XeF_6 on complete hydrolysis gives –

(a) Xe (b) XeO_3 (c) $XeOF_4$ (d) XeO_4

4. Bond angle is XeO_3 –

(a) 107^0 (b) 103^0 (c) 119^0 (d) 92^0

5. The colour discharge tube for advertisement mainly cantains –

(a) Xe (b) He (c) Ne (d) Ar

6. Which of the following is not correct statement ?

(a) XeO_3 has four σ and four π bonds

(b) the hybridisation of Xe in XeF_4 is sp^3d^2

(c) among noble gases the occurrence of 'Ar' is highest in air

(d) liquid helium is used as cryogenic liquid

7. The noble gas which shows anomalous behaviour in liquid state & behaves as a superfluid is –

(a) Ne (b) He (c) Ar (d) Xe

8. The 7th noble gas is –

(a) Rn (b) Og (c) Uuo (d) both 'b' & 'c'

9. No. of lp of electrons on 'Xe' afoms in XeF_2, XeF_4, & XeF_6 molecules are respectively –

(a) 3, 2 & 1 (b) 4, 3 & 2 (c) 2, 3 & 1 (d) 3, 2 & 0

10. The element haring highest ionisation potential is –

(a) H_2 (b) O_2 (c) N_2 (d) He

B. Assertion (A) & Reason (R) type questions : (Each carries 1 mark)

1. **A :-** HNO_2 is stronger acid than HNO_3.

R :- IN HNO_3 there are two nitrogen to oxygen bonds where as in HNO_2 there is only one.

2. **A :-** H – N – H Bond angle in $^+NH_4$ is more than NH_3.

R :- 'N' afom of NH_3 is sp^3 hybridised where as in $^+NH_4$ is sp^3d hybridised.

3. **A :-** H_3PO_3 is the tribasic acid.

R :- H_3PO_3 can cat as both oxidising & reducing agent.

4. **A :-** H_3PO_2 is the stronger acid than H_3PO_4.

R :- H_3PO_2 is the mono basic acid.

5. **A :-** Conc. H_2SO_4 can't be used to prepare HBr or HI from KBr or KI.

R :- Conc. H_2SO_4 is the strong oxidising agent and HBr, HI are strong reducing agent.

6. **A :-** SO_3 has a planar structure.

R :- 'S' atom of SO_3 is sp^2 hybridised.

7. **A :-** 'O_3' is the better steriliser than Cl_2.

R :- Ozonosphere layer is not formed just above the carth surface.

8. **A :** SF_6 exist but OF_6 does not exist.

R :- Sulphur has arailable vacant 'd' or bital.

9. **A :-** I_2 can displaces Cl_2 from $KClO_3$.

R :- I_2 is stronger oxidising agent than Cl_2.

10. **A :-** All the halogens are coloured.

R :- Halogens can absorb some wave length from visible light & the eleetrons are promoted to higher energy levels.

11. **A :-** NO_2 dimerises while ClO_2 is not to dimerise.

R :- 'N' atom of NO_2 is sp^2 hybridised while 'Cl' of ClO_2 is sp^3 hybridised.

12. **A :-** Noble gases have highest IE in their respective peroids.

R : The outermost shell of the noble gases is complefely filled.

13. **A :-** Noble gases can combine with fluorime to from respective fluorides under specific conditions.

R :- A number of oxyfluorides of Xenon are known.

14. **A :-** Bond energy of 'Cl_2' is more than 'F_2'

R :- Due to the small size of Fluorine atom large repulsion force are acting between the lp of fluorine atoms.

C. Very short Answer (Each question carries 1 mark)

1. Name the compound of nitrogen which on heating gives laughing gas.

2. An orange colour compound which on heating gives Ammonia gas & Green residue. Name the compound.

3. Are all the five P-Cl bonds in PCl_5 molecule equivalent?

4. What is the basicity of pyrophosphorous acid?

5. Name a nitrate salt which on heating produces firstly pale yellow gas & finally a brown gas?

6. Name of two neutral oxide of nitrogen.

7. Name the gas which is produced along with 'PH_3' in its laboratory preparation whose ignition temp is very low.

8. Name the most reactive allotropes of phosphorous.

9. What is liquor ammonia?

10. Mention the name & type of salt which is formed by the action of one mole of H_3PO_4 & one mole of NaOH.

11. What is the basicity of dithionic acid ?

12. Write down the formula of oleum.

13. Write down the formula of oleum.

14. Name the catalyst which is used in contact process ?

15. Name the gas which can turn the lime water milky and can change the acidified pink colour $KMnO_9$ solution into colourless.

16. An inorganic compound (x) gives a brick red ffame in flame test. Compound 'X' when exposed to air smells of chlorine is obtained. What is the chemical name and formula of X ?

17. Name the Oxyacid of Fluorine ?

18. Name two interhalogen of AB_3 type.

19. Name the product which is formed by the action of I_2 & hypo solution.

20. What is the shape of XeF_6 molecule ?

21. What is the chemical name of Freon ?

22. Name the compound from which 'F_2' gas is obtained at anode.

23. Which was the first noble gas compound synthesized ?

24. Is hydrolysis of XeF_6 be a redox rcaction ?

25. What is the shape of $XeOF_2$ molecule ?

D. Short Answer type questions (Each question carries 2 mark)

1. Why does PCl_3 fume in air?

2. Among red 'P' & white 'P' which ane is more reaetive & Why?

3. Why is ammonia highly soluble in water?

4. Why "He' gas is used in diving apparatus?

5. Why 'PH_3' is prepared in an inert atmosphere of CO_2?

6. Why 'NH_3' is used for refrigeration?

7. Why oxygen is gas but sulphur is solid?

8. Why BP of H_2SO_4 is more?

9. Why HNO_3 is not used to prepare H_2S?

10. Why SO_3 is not directly dissolved in water during the preparation of H_2SO_4 by contact process?

11. Why ozonosphere layer is not formed just above the earth surface?

12. Why F_2 can't be prepared from fluonide salt by oxidation?

13. Why Fluorine does not form F_3^- ion?

14. When a blue litmus is dipped in a solution of HOCl it first turns red & after that red colour is disappeared– why?

15. Mention the name of the product in the following reaction

1. $(NH_4)_2\, Cr_2O_7 \xrightarrow{\Delta}$
2. $Ba(NO_3)_2 \xrightarrow{\Delta}$
3. $NH_3 + O_2 \xrightarrow[\Delta]{\text{Pt (Catalyst)}}$
4. $NH_3 + Cl_2 \longrightarrow$
5. $CuSO_4 + NH_4OH \longrightarrow$
6. $NH_4Cl + NH_4NO_3 \xrightarrow{\Delta}$
7. $Cl + HNO_3$ (dil.) $\longrightarrow$
8. $Zn + HNO_3$ (dil.) $\longrightarrow$
9. $Fe + HNO_3$ (cold & dil.) $\longrightarrow$
10. $I_2 + HNO_3 \longrightarrow$
11. $S_8 + HNO_3 \longrightarrow$
12. $P_4 + HNO_3 \longrightarrow$
13. $H_3PO_3 \xrightarrow{\Delta}$
14. $P_4 + NaOH + H_2O \longrightarrow$

15. $HNO_3 + P_2O_5 \longrightarrow$

16. $PCl_5 + H_2O \longrightarrow$

17. $Zn + NaOH + NaNO_3 \longrightarrow$

18. $CaC_2 + N_2 \longrightarrow ? \xrightarrow{H_2O} ?$

19. $NH_3 + CO_2 \longrightarrow ?$

20. $FeSO_4$ + conc. H_2SO_4 + conc. $HNO_3 \longrightarrow$

21. $H_2SO_4 + PCl_5 \longrightarrow$

22. $P_4 + H_2SO_4 \longrightarrow$

23. $NH_3 + K_2[HgI_4] + KOH \longrightarrow$

24. $Mn_2O_7 + H_2O \longrightarrow$

25. $KI + H_2O + O_3 \longrightarrow$

26. $PbS + H_2O_2 \longrightarrow$

27. $Hg + O_3 \longrightarrow$

28. $MnO_4^- + H^+ + H_2S \longrightarrow$

29. $Cr_2O_7^{2-} + H^+ + H_2S \longrightarrow$

30. $HNO_3 + H_2S \longrightarrow$

31. $KMnO_4 + SO_2 + H_2O \longrightarrow$

32. $K_2Cr_2O_7 + SO_2 + H_2SO_4 \longrightarrow$

33. Zn + conc. $H_2SO_4 \longrightarrow$

34. KI + conc. $H_2SO_4 \longrightarrow$

35. F_2 + NaOH (dil.) $\longrightarrow$

36. F_2 + NaOH (conc.) $\longrightarrow$

37. X_2 (Cl_2, Br_2, I_2) + (dil) $OH^- \longrightarrow$

38. X_2 (Cl_2, Br_2, I_2) + conc.$OH^- \longrightarrow$

E. Long Answer Type Questions : [Each question carries - 3 Marks]

1. a) Why He is not kept in glass container?

b) Name the compound which can absorb Ntric oxide gas?

2. a) Why ‘NO_2’ is called mixed anhydride?

b) NO_2 is the paramagnetic – why?

3. a) Metaphosphoric acid exist but Metaphosphorous acid does not exist – Why?

b) What is the formula of ‘oil of vitriol’?

4. Among HOCl & $HClO_4$ which one is strong oxidising agent & why?

5. a) What is invisible - ink?

b) What is the correct order of basic character of ClO_4, ClO_3, ClO, ClO_2

6. a) HNO_3 can’t be kept in copper container but can be kept in Aluminium container. Why?

b) Name the anhydride of pernitric acid (HNO_4)?

7. a) How will you prove that inert gases are monoatomic?

b) Name the allotropes of phosphorou is used in match boxes.

8. a) Why atomic radius of inert gases are comparatively more?

b) Name the gas which is used for inflating the tyres of aeroplane?

F. Very Long Answer Type Questions : [Each question carries- 5 Marks]

1. a) Maximum compounds of noble gases are made up of ‘Xe’ – Why?

b) H_2O is liquid, but H_2S is gas – Why?

c) Mention the shape of XeF_6 molecule?

2. a) Chlorine water on adding in the starch containing KI solution blue colour is obtained – Why?

b) Why fishy smell is obtained when F_2 gas is passed through the water?

c) Name the substance which can absorb the O_3 gas?

3. a) A colourless inorganic salt (A) containing nitrogen decomposes completely at about 250^0C to give only two products B & C, leaving no residue. C is the better supporter of combustion. White phosphorous burns in excess ‘C’ to produce a strong white dehydrating agent. Mention the balanced equations for the reactions involved in this process & identify A, B & C.

b) Why liquor ammonia bottle should be cooled before opening the cork?

Answer

Group - 15

[A]. Select the correct answer (MCQ) : (Each carries 1 mark)

1. a   2. b   3. b   4. a   5. a   6. a
7. b   8. a   9. c   10. a   11. a   12. c
13. a   14. a   15. d   16. d   17. a   18. a
19. a   20. a   21. a   22. a   23. d   24. c

Group - 16

[A]. Select the correct answer (MCQ) : (Each carries 1 mark)

1. d   2. b   3. a   4. a   5. a   6. d
7. c   8. a   9. a   10. a   11. b   12. c
13. a   14. b   15. a   16. d   17. d   18. a
19. a   20. a

Group -17

[A]. Select the correct answer (MCQ) : (Each carries 1 mark)

1. a   2. a   3. a   4. a   5. b   6. d
7. d   8. b   9. c   10. a   11. c   12. b
13. c   14. c   15. a   16. a   17. c   18. a
19. a   20. d   21. b   22. b   23. c   24. a
25. b

Group -18

[A]. Select the correct answer (MCQ) : (Each carries 1 mark)

1. c   2. b   3. b   4. b   5. c   6. a
7. b   8. b   9. a   10. d

B. Assertion - Reason type questions : (1 marks each)

1. c   2. c   3. d   4. a   5. a   6. a
7. b   8. a   9. c   10. a   11. a   12. a
13. b   14. a

Chapter - 8

The *d* and *f* block elements

Chapter at a glance :

1. The d-block of the periodic table contains the elements of the groups 3-12 in which the d orbitals are progressively filled in each of the four long periods.

   The f -block of the periodic table contains elements where 4f and 5f orbitals are progressively filled in each of the two very long periods of modern periodic table.

2. **d-block elements :** The general electronic configeration of d-block elements is (n–1) d^{1-10} ns^{1-2}. Here (n–1) stands for inner d orbitals.

   Generalisation of properties of these elements has several exceptions mainly due to –

   (i) Very little energy difference between (n–1) d and ns orbitals.

   (ii) half and completely filled sets of orbitals.

3. The very name 'transition' is given to the elements of d block is only because of their position between s- and pP-block elements in the modern periodic table.

   There are three complete rows of transition metals i.e 3d, 4d and 5d. The fourth row of 6d is still imcomplete.

(4) A transition element is defined as the one which has incompletely filled d-orbitals in its ground state or in any one of its oxidation states.

   Zn, Cd, Hg have completely filled d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.

(5) Transition elements with partly filled d-orbitals may exhibit different characteristics properties such as–

   (i) Variety of oxidation states.

   (ii) Formation of coloured ions.

(iii) Foramation of complex ions.

(iv) Catalytic property.

(v) Magnetic property.

(vi) Electronic property etc.

(6) Physical properties of d-block elements :

All the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity, metalic lustre etc.

except Zn, Cd and Hg the transition metals are very much hard and low volatility.

(7) Melting points :

In any row *d* series the melting point rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases. The high melting point of these metals are due to the involvement of greater number of (n–1) d electrons in addition to the ns electrons in the interatomic metalic bonding. Greater the number of valence electron, stronger is the resultant bonding and that is why the pick of the graph rises maximam in the middle of each series.

The enthalpy of atomisation of these metals are very high and melting point increases with increase in enthalpy of atomisation.

8. Atomic and ionic sizes of transition metals :

Shielding effect of d electrons is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases along a series, and the ionic radious decreases along a series.

Along the first (3d) and 2nd (4d) series the atomic size gradually increases but in case of 3rd (5d) series atomic sizes are virtually the same as those of the corresponding members of 2nd (4d) series. This is because in case of 3rd (5d) series 4f orbital must be filled before the 5d series of element begin. This filling of 4f orbital before 5d orbital results in a regular decrease in atomic raddii is called Lanthanoid Contruction.

9. Density :

Density of transition metals along a series increases as the metallic radius decreases with increase in atomic mass of these element.

10. Ionisation enthalpies :

Ionisation enthalpy increase along each series of the transition elements from left to right.

Although the first ionisation enthalpy, in general increases, the magnitude of the increase in the 2nd and 3rd ionisation enthalpies for the successive elements, is much high.

The lowest common oxidation state of these metals is +2. To farm M^{+2} ions from gaseous atoms, the sum of the first and second ionisation energies is required in addition to the enthalpy of atomisation for each element.

The first ionisation enthalpy of Cr and Cu is low because loss of one electron does not disturb d^5 and d^{10} configuration respectively.

The value of second ionisation enthalpy of Zn is correspondingly low as the ionisation consists of the removal of a electron which allows the production of the stable d^{10} configuration.

The third ionisation enthalpy of these element are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}.

11. **Oxidation state :** Transition element can exhibit variable oxidation states ranging from +2 to +7.

Table : Oxidation States of the first row Transition Metals (the most common ones are in bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Oxidation states of the first row transition metals.

The element which give the greatest number of oxidation states occur in or near the middle of the series.

Mn can exhibit all the oxidation states from +2 to +7.

In case of normal elements oxidation states normally differ by a unit of two but oxidation states of transition metals differ from each other by unity eg. V^{II}, V^{III}, V^{IV}, V^{V}.

The only oxidation state of Zn is +2 (no d electron is involved)

Due to inert pair effect the heavier members of P-block elements favours lower oxidation states but in case of d-block elements opposite is true. For example in group-6 Mo(VI) and W(VI) are found to be more stable than Cr (VI). Thus Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent, where as MoO_3 and WO_3 are not.

12. **Electrode Potentials (M^{2+}/M) :** The general trend towards less negative $E^{\ominus}$ values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.

The unique behaviour of Cu, having a positive $E^{\ominus}$ value, accounts for its inability to liberate H_2 from acids.

The high energy to transform Cu (s) to Cu^{+2}(q) is not balanced by its hydration enthalpy. Electrod potential (M^{2+}/M) also depends on enthalpy of atomisation (Δ aH$^{\ominus}$). Greater the value of ΔaH$^{\ominus}$ lower is the electrode potential (E$^{\ominus}$).

13. **Electrode Potential (M^{3+}/M^{2+}) :** Electrode potential (M^{3+}/M^{2+}) for transition metal depends upon the electronic configuration after the transformation. Low value indicates that after transformation a stable configuration is attained. The low value of Sc and Fe reflects the stability of Sc^{3+} and Fe^{3+}(d^5).

14. **Stability of higher oxidation states :** In the first 3d series the highest oxidation numbers are achived in TiX_4 (tetrahalides), VF_5 and CrF_6 .

 The +7 state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn no metal has a trihalide except FeX_3 and CoF_3.

 The ability of fluirine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3 or higher bond enthalpy terms for the higher covalent compounds e.g VF_5 and CrF_6 .

 All Cu^{2+} hallidas are known except the iodine. In this case Cu^{2+} oxidises I^- to I_2

$$2\ Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$$

 Cu (I) compounds are unstable in aquous solution and undergo disproportionation,

$$2\ Cu^+ \rightarrow Cu^{2+} + Cu$$

 The highest oxidation number in the oxides of first transition series is coincides with the group number. Beyond GP-7, no higher oxides of Fe above Fe_2O_3 are possible.

 The ability of oxygen to stabilise high oxidation states exceeds that of flurine. That is why the highest Mn fluride is MnF_4 whereas the highest oxide of Mn is Mn_2O_7.

15. **Chemical reactivity and E$^{\ominus}$ values :**

 Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble' – that is they are uneffected by single acids.

 The E$^{(-)}$ values for M^{2+}/M indicate a decreasing tendency to form divalent cations across the series. This is due to the increase in the sum of the first and second ionisation enthalpies.

 E$^{(-)}$ values for the radox couple M^{3+}/M^{2+} shows that Mn^{3+} and Co^{+3} ions are the strongest oxidising agents in aquous solution.

 The ions Ti^{2+} , V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from dilute acid. e.g. $2Cr^{2+}(aq) + 2H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + H_2(g)$

16. **Magnetic properties :** For the compounds of the first series of transition metal the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula i.e. $\mu = \sqrt{n(n+2)}$

Where n is the number of unpaired electrons.

No. of unpaired electron	Calculated magnetic moments
1	1.73 BM
2	2.84 BM
3	3.87 BM
4	4.90 BM
5	5.92 BM

17. **Formation of Coloured ions :** Due to the presence of unpaired electrons in d-orbitals transition metals absorbs light frequency lies in visible region and undergo d-d transition. The colour observed corresponds to the complementary colour of light absorbed. The frequency of light absorbed is determined by the nature of the ligand.

18. **Formation of complex compounds :** The transition metals form a large number of complex compounds. This is due the comparatively smaller sizes of the metal ions, their high ionic charges and availability of d - orbitals for bond formation.

    A few examples are – $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, $[PtCI_4]^{2-}$ etc.

19. **Catalytic properties :** Transition metal ions can change their oxidation states and become more effective as catalysts. First row transition metals utilise 3d and 4s electrons for the formation of bonds between reactant molecules and atoms of the surface of the catalyst. Thus concentration of the reactants at the catalyst surface increases and the bonds in the reacting molecules become weak.

20. **Formation of Interstitial compounds :**

    Interstitial compounds are those which are formed when small atoms like H, C and N are trapped inside the crystal lattices of metals. For example – TiC, Mn_4N, Fe_3N, $VH_{0.56}$, $TiH_{1.7}$ etc. Some characteristics of these type of compounds are –

    (i) They have high melting points, higher than those of pure metals.

    (ii) They are very hard, some borides approach dimond in hardness.

    (iii) They retain metalic conductivity.

    (iv) They are chemically inert.

21. **Alloy formation :**

    Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.

    Transition metals can form alloys with other transition metals. e.g. ferrous alloys. Again they can form alloys with other non - transition metals too. eg. brass (Cu - Zn), bronze (Cu - tin) etc.

22. **Oxides and oxoanions of transition metals :**

Oxides of transition metals are generally formed at high temperature. All the metals except

Sc form MO type which are ionic. Besides the oxides, the oxocations stabilise V^V as VO_2+, V^{IV} as Vo^{2+} and Ti^{IV} as TiO^{2+}. As the oxidation number increases, ionic character of these compounds decreases.

In case of higher oxides, the acidic character is predominant. $HMnO_4$, H_2CrO_4, $H_2Cr_2O_7$ is acidic in nature. V_2O_5 is however amphoteric and it gives VO_4^{3-} as well as VO_2^+ salts. CrO is basic but Cr_2O_3 is amphoteric.

23. **Potassium dichromate, $K_2Cr_2O_7$:**

$K_2Cr_2O_7$ is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds.

$K_2Cr_2O_7$ is less soluble than $Na_2Cr_2O_7$. That is why $K_2Cr_2O_7$ is prepared by treating the solution of $K_2Cr_2O_7$ with KCl.

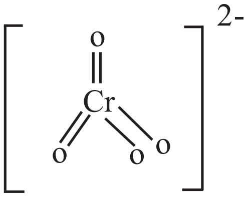
$$\underset{\text{(orange solution)}}{Na_2Cr_2O_7} + 2KCl \rightarrow \underset{\text{(orange crystals)}}{K_2Cr_2O_7} + 2NaCl$$

The chromates and dichromates are interconvertible in aquous solution depending upon P^H of the solution.

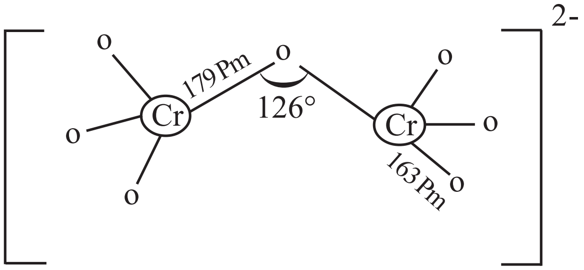
$$2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

Structure of chromate ion –



Structure of dichromate ion –



In acid solution its oxidising action can be represented as follows :

$$Cr_2O_7^{2-} + 14H^+ + 6\,e^- \rightarrow 2Cr^{+3} + 7H_2O\ (E^{(-)} = 1.33v)$$

Acidified $K_2Cr_2O_7$ oxidises Iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

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

$$3H_2S \rightarrow 6H^+ 3S + 6e^-$$

$$3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$$

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

24. **Potassium permanganate ($KMnO_4$)** :

$KMnO_4$ is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3 .

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

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO^-_4 + MnO_2 + 2H_2O$$

Commercial process :

$KMnO_4$ is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of MnO_4^{2-} .

$$MnO_2 \xrightarrow[\text{Oxidised with air or KNo}_3]{\text{Fused with KOH}} MnO^{2-}{}_4$$

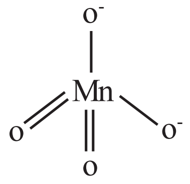
$$MnO^{2-}{}_4 \xrightarrow[\text{Oxidation in alkaline solution}]{\text{Electrolytic}} MnO^-{}_4$$

Labratory process : A manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

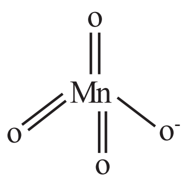
$$2\ Mn^{2+} + 5\ S_2O^{2-}_8 + 8\ H_2O \rightarrow 2MnO^-_4 + 10SO^{2-}_4 + 16H^+$$

$KMnO_4$ is isostructural with $KClO_4$. When heated at 513K it decomposes and produce K_2MnO_4

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$



Structure of managanate ion : (green)



Structure of permanganate ion : (purple)

A few important oxidising reactions of $KMnO_4$ are given below :

In acid solution :

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

(b) $5Fe^{2+} + MnO^-_4 + 8\ H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(c) $5C_2O^{2-}_4 + 2MnO^-_4 + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(d) $5S^- + 2MnO^-_4 + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$

(e) $5SO_3^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

(f) $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

In neutral or faintly alkaline solutions :

(a) $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

(b) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(c) $2MnO_4^- + 3Mn^{2+} + 3H_2O \rightarrow 5MnO_2 + 4H^+$

Use of $KMnO_4$: (a) It is a used as an oxidising reagent.
(b) For bleaching of wool, cotton, silk etc.
(c) For the decolourisation of oils.

25. The Inner Transition Elements (f-block)

The f-block consists of two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinum).

Lanthanoids : The general symbol of Lanthanoids is Ln. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. Lanthanoids have only one stable oxidation state.

The general electronic configuration of lanthanoids is $4f^{1-14} 5d^{0-1} 6s^2$.

Properties :

(a) Atomic size and ionic size :

Atomic and ionic radii decreases fairly with increasing atomic number from Lanthanum to Lutetium. The decrease in atomic or ionic radii is due to the poor sheilding capacity of f-electron. This is called lanthanoid construction and due to this the radii of the member of 3rd transition series is vey much similar.

Radii of Zr (160 pm) and Hf (159 pm) is almost identical.

(b) Oxidation state : In the lanthanoids Ln (II) and Ln (III) compounds are predominant. Occationally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity arises mainly from the extra stability of empty, half filled or filled f-subshell.

The E° value for Ce^{4+}/Ce^{3+} is +1.74 V, which suggests that it can oxidise water (H_2O). Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2.

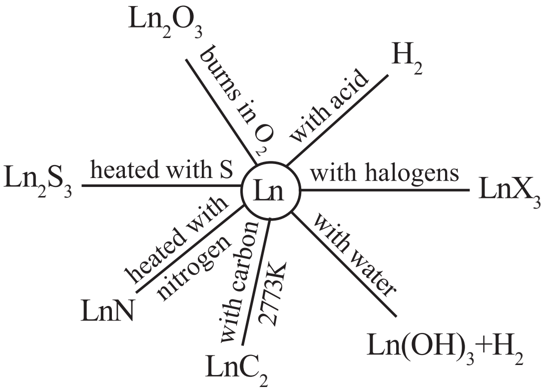
Eu^{2+} is a strong reducing agent and the behaviour of Samarium is very much like Europium, exhibiting both +2 and +3 oxidation states.

(c) General characteristics :

(i) All the lanthanoids are silvery white soft metals and turnish rapidly in air. Their melting points ranges between 1000 to 1200K but samarium melts at 1623K. They are good conductor of heat and electricity. Many trivalent lanhanoid ions are coloured both in solid state and in aquous solutions. The lanthanoid ions other than the f° type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.

The first and second ionisation enthalpies of lanthanoids are around 600 KJ mol^{-1} and 1200 KJ^{-1} respectively. The third ionisation enthalpy of lanthanum, gadolinium and lutetium are abnormally low and this is due to the degree of stability to empty, half - filled and completely filled f-orbitals respectively.

(ii) Chemical reactions of the lanthanoids :



26. **The actinoids :**

The actinoids include the fourteen elements from Th to Lr.

The actinoids are radioactive elements and their half-lives are relatively low, ranging from a day to 3 minutes for lawrencium (z = 103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

(a) Electronic configuration :

The general electronic configuration of actinoid is $5f^{1-14}\,6d^{0-1}\,7s^2$.

The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f°, f^7 and f^{14} occupancies of the 5f orbitals.

Am (z = 95) – [Rn] $5f^7\,7s^2$

Cm (z = 96) – [Rn] $5f^7\,6d^1\,7s^2$

(b) Ionic sizes : There is a general decrease in the size of atoms or M^{3+} ions across the series. This is due to the poor shielding capacity of 5f electrons. This is known as actinoid contraction.

(c) Oxidation states : The actinoids show greater range of oxidation states but in general show the +3 oxidation state.

The actinoids resembles the lanthanoids in having more compounds in +3 state than in the +4 state. However +3 and +4 ions tends to hydrolyse.

27. General characteristics of actinoids :

(i) The actinoids metals are all silvery in appearance.

(ii) Actinoids are highly reactive metals, especially when finely divided.

(iii) With boiling water they produce a mixture of oxide and hydride.

(iv) HCl attacks all these metals but most are slightly affected by HNO_3 due to the formation of a protective oxide layer.

(v) Their ionisation enthalpies are lower in comparison to lanthanoids. This is because 5f electrons will penetrate less into the inner core of electrons. As the outer electrons are less firmly held, they are available for bonding in the actinoids.

28. Application of d and f block elements :

(i) TiO is used in pigment industry.

(ii) MnO_2 is used in dry battery cells.

(iii) Zn and Ni/Cd are also used in battery industry.

(iv) Cu, Ag and Au are used in coins.

(v) The 'silver' Uk coins are a Cu/Ni alloy.

(vi) Many of these metals or metal compounds are used as catalysts in the chemical industry.

e.g. (a) V_2O_5 catalyses the oxidation of SO_2 in the manufacture of H_2SO_4.

(b) $TiCl_4$ with $Al(CH_3)_3$ farms the basis of the ziegler catalysts used to manufacture polythene.

(c) In the Wacker process of oxidation of ethyne to ethanal is catalysed by $PdCl_2$.

(d) AgBr is used in photographic reels.

(e) They have several use is organic synthesis.

A. Select the correct answer (MCQ) : (1 mark each)

1. Whic one of the following is a d-block elements ?

   a) Gd b) Hg c) Es d) Cs

2. Whic of the following has maximum number of unpaired d-electrons ?

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

3. The maximum oxidation state shown by Mn in its compounds is

   a) +4 b) +5 c) +6 d) +7

4. Which one of the following transition metal ions is colourless in aqueous solution ?

   a) Ti^{+4} b) V^{+4} c) Mn^{2+} d) Fe^{3+}

5. Magnetic moment μ, of transition metals is related to the number of unpaired electrons n an

   a) $\mu = n\,(n+2)^2$ b) $\mu = n^2\,(n+2)$

   c) $\mu = \frac{n}{(n+2)}$ d) $\mu = \sqrt{n(n+2)}$

6. When dil.H_2SO_4 is added to aqueous solution of potassium chromate, yellow colour of solution forms to orange colour. It indicates

   a) Chromate ions are reduced

   b) Chromate ions are oxidised

   c) monocentric complex is converted into dicentric complex

   d) Oxygen gets removed from chromate ions.

7. General electronic configuration of Lanthanoids are

   a) $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$ b) $(n-2)f^{10-14}\,(n-1)d^{0-1}\,ns^2$

   c) $(n-2)f^{0-14}\,(n-1)d^{10}\,ns^2$ d) $(n-2)f^{0-1}\,(n-1)d^{1-14}\,ns^2$

8. Europium is a–

   a) s-block element b) p- block element c) d-block element d) *f*-block element

9. The lanthanoid contraction relates to

   a) atomic radius b) atomic as well as M^{3+} radii

   c) valence electrons d) Oxidation states.

10. Reason of Lanthanoid contraction is

    a) negligible secreening effect of *f- orbitals* b) increasing nuclear charge

    c) decreasing nuclear charge d) decreasing screening effect

11. Across the lanthonid series, the basicity of the lanthanide hydroxides

a) increase　　b) decreases

c) first increase and then decreases　　d) first decrease and then increase

12. Most basic hydroxide among the following is

a) $Lu(OH)_3$　　b) $Eu(OH)_3$　　c) $Yb(OH)_3$　　d) $Ce(OH)_3$

13. Which of the following oxidation state is the most common among the lanthanoids ?

a) +3　　b) +4　　c) +2　　d) +5

14. Whic one of the following species is the most stable in aqueous solution ?

a) Mn^{3+}　　b) Cr^{3+}　　c) V^{3+}　　d) Ti^{3+}

15. Which of the following is amphoteric oxide ?

a) V_2O_5, Cr_2O_3　　b) Mn_2O_7, CrO_3　　c) CrO, V_2O_5　　d) V_2O_5, V_2O_4

16. Which of the following statement is not correct ?

a) Copper liberates hydrogen from acids.

b) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.

c) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution.

d) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution.

17. Transition elements are coloured

a) due to unpaired d-electrons

b) due to small size

c) due to metallic nature

d) All of the above.

18. Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?

a) Both HCl and $KMnO_4$ as oxidising agents.

b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent.

c) $KMnO_4$ is a weaker oxidising agent then HCl .

d) $KMnO_4$ acts as a reduring agent in the presence of HCl.

19. Which one of the following acts as an oxidising agent ?

a) Np^{+4}　　b) Sm^{+2}　　c) Eu^{+2}　　d) Yb^{+2}

20. Atomic number of gadoliniuom is 64. Which of the following is the correct electronic contiguration of gadolinium.

a) $[xe]\ 4f^7\ 5d^1\ 6s^2$　　b) $[xe]\ 4f^6\ 5d^2\ 6s^2$　　c) $[xe]\ 4f^8\ 6d^2$　　d) $[xe]\ 4f^9\ 5s^1$

21. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?

    a) U b) Np c) Tm d) Fm

22. Arrange Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} in increasing order of their ionic radii.

    a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$ b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$

    c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$ d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

23. Which of the following is correct ?

    a) Duralumin : Al+Cu+Mg+Ag b) German Silver : Cu + Zn + C

    c) Gun metal : Cu + Zn + Sn d) Solder : Pb + Al

24. Transuranic elements begins with

    a) Np b) Cm c) Pu d) U

25. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because.

    a) it has variable ionisation enthalpy.

    b) it has variable oxidation state.

    c) it has tendency to attain f^0 configuration.

    d) it resembles Pb^{4+}

B. Assertion - Reason type questions : (1 marks each)

Direction each of these questions contains two statements. Assertion and Reason. Each of these questons also has four laternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d).

a. Assertion is true, Reason is true, Reason is a correct explanation for Assertion.

b. Assertion is true, Reason is true, Reason is not a correct explanation for Assertion.

c. Assertion is true, Reason is false.

d. Assertion is false, Reason is true.

1. Assertion : Cu^{2+} iodide is not known.

   Reason : Cu^{2+} oxidises I^- to iodine.

2. Assertion : Separation of Zr and Hf is difficult.

   Reason : Zr and Hf lie in the same group of the periodic table.

3. Assertion : Actinoids form relatively less stable complexes as compared to lanthanoids.

   Reason : Actinoids can utilise their 5f orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.

4. Assertion : Cu cannot liberate hydrogen from acids.
   Reason : It has positive electrode potential.
5. Assertion : The highest oxidation state of Osmium is +8.
   Reason : Osmium is a 5d block elements.

(C) Answer in one word or one sentences : (Each questions 1 marks)

1. Which of the d-block elements are not considered as transition element ?
2. Why are the transition elements called so ?
3. Name the elements in the first transition series that exhibits +1 oxidation state.
4. Name a transition element which does not exhibit veriable oxidation states.
5. What is the highest oxidation state of Chromium ?
6. Write the general electronic configuration of d-block elements ?
7. Name the highest and heaviest transition element.
8. Name the compound that evolves as vapour when NaCl is heated with $K_2Cr_2O_7$ and H_2SO_4.
9. Which element is used as a 'bone nail' in surgery ?
10. Why transition metal ions have high hydration enthalpy ?
11. Calculat Spin only magnetic moment of Fe^{3+} ion.
12. Why is Fe^{3+} ion paramagnetic ?
13. Arrange the following in increasing order of acidity : CrO_3, CrO, Cr_2O_5
14. Which first row transition element has positive $E^o_{M^{2+}/M}$ value ?
15. Name a lanthanoid that exhibits +4 oxidation state.

(D) Short answer type questions : (Each question 2 marks)

1. Why is copper considered to be transition elements but zinc is not ?
2. Why do transition metals show variable oxidation states ? Mention the highest oxidation state shown by transition elements.
3. Why do transition elements act as a good catalyst ?
4. Transition elements form coloured compounds. Why ?
5. Which of the following is more paramagnetic ? Fe^{2+} Or Fe^{3+}
6. Why do transition metals form alloys easily ?
7. Transition elements form interstitial compunds. Why ?

8. Atomic radius of the transition elements do not decrease significatnly, with increase in atomic number. Give reason.

9. Which of the following has highest magnetic moment ?

   Ti^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}

10. Cu^{2+} is more stable than Cu^{+} in aqueous. medium –explain.

(E) Short answer type questions : (Each question 3 marks)

1. Write all reactions involved in the preparation of potassium dichromate ($K_2Cr_2O_7$) from chromite orc.

2. Complete the following equations :

   a) $Cr_2O_7^{2-} + Fe^{2+} + H^{+} \rightarrow ?$

   b) $MnO_4^{-} + C_2O_4^{2-} + H^{+} \rightarrow ?$

   c) $MnO_4^{-} + S_2O_3^{2-} + H_2O \rightarrow ?$

3. What is lanthanoid contraction ? What are the consequences of lanthanoid contraction.

4. **Give reason :**

   a) La $(OH)_3$ is the most basic and $Lu(OH)_3$ is the least.

   b. Actinoid contraction is more prominent than lanthanoid contraction.

   c. Fe^{2+} has a greater tendency to attain the +3 oxidation state as compared to Mn^{2+}

5. **Explain –**

   a) The transition elements of the 5d-series have higher ionisation enthalpy as compared to the 3d series.

   b) Cr^{2+} is reducing and Mn^{3+} is oxidising though both have d^4 configuration.

   c) Elements of chromium group have high melting point.

6. a) Why the second and third transition series have almost similar atomic radii ?

   b) Why Sc^{3+} and Zn^{2+} salts are colourless ?

   c) Name an important alloy which contain some of the lanthanoid metals.

7. Compare the chemistry of actinoids with that of the lanthanoids with special reference to

   a) electronic configuration (b) atomic and ionic sizes (c) Oxidation state (d) chemical reactivity.

8. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with :

   (a) Iodide solution (b) Iron (II) solution (c) H_2S

9. Compare the chemistry of the actinoids with that of lanthanoids with reference to :

   (i) electronic configuration (ii) oxidation state and (iii) chemical reactivity

10. What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

11. Give examples and suggest reasons :
    - (i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
    - (ii) A transition metal exhibits highest oxidation state in oxides and flurides.
    - (iii) The highest oxidation state is exhibited in oxoanions of a transition metal.

12. Predict which of the following will be coured in aqueous solutions? Ti^{3+}, Sc^{3+}, Fe^{3+}. Give reason for each.

13. What are alloys? Name an important alloy which contains some of the lanthanoid metals. mention its use.

14. On the basis of lanthanoid contruction, explain the following :
    - (i) Nature of bonding in La_2O_3 and Lu_2O_3.
    - (ii) Stability of the complexes of lanthanoids.
    - (iii) Trends in acidic character of lanthanoid oxides.

15. Answer the following questions :
    - (i) Which element of the first transition series has highest second ionisation enthalpy?
    - (ii) Which element of the first transition series has highest third ionisation enthalpy?
    - (iii) Which element of the first transition series has lowest enthalpy of atomisation?

(F) Long answer type questions : (Each question marks 5)

1. Explain giving reasons :
- (i) Transition metal and many of their compounds show paramagnetic behaviour.
- (ii) The enthalpy of atomisation of transition metals are high.
- (iii) The transition metals generally form coloured compounds.
- (iv) Transition metals and their many compounds act as good catalyst.
- (v) There are irregularities in the electronic configuration of actinoids.

2. (a) Write balanced equations to represent what happens when –
    - (i) Acidified $KMnO_4$ solution reacts with iron (II) ions.
    - (ii) Pyrolusite is fused with KOH in the presence of air.

   (b) Give reason for each of the following :
    - (i) Size of trivalent lanthanoid cations decreases with increase in atomic number.

(ii) Transition metal flurides are ionic in nature, whereas bromides and chlorides are usualy covalent in nature.

(iii) Chemistry of lanthanoids is quite similar.

3. Answer the following questions:

(i) Which element in the first transition series does not exhibit variable oxidation states and why?

(ii) Why do actinoids, in general, exhibit a greater range of oxidation states than the lanthanoids.

(iii) What are inner-transition elements? Write their general electronic configurations.

4. Complete the following chemical equations :

(i) $MnO^{-}_{4} + C_2O^{2-}_{4} + H^{+} \longrightarrow$

(ii) $KMnO_4 \xrightarrow{heated}$

(iii) $Cr_2O_7^{2-} + H_2S + H^{+} \longrightarrow$

(iv) $Cr_2O_7 (aq) + Fe^{2+} (aq) + H^{+} (aq) \longrightarrow$

(v) $MnO^{-}_{4} + SO_3^{2-} + H^{+} \longrightarrow$

5. (a) Describe the general characteristics of the transition elements with special reference to the following:

(i) enthalpy if atomisation .

(ii) variable oxidation states.

(iii) interstitial compounds.

(b) Assign reasons for the following :

(i) Co^{2+} has higher magnetic moment than Ni^{2+} .

(ii) Zn^{2+} salts are white, while Cu^{2+} salts are blue.

Answer

A. Select the correct answer (MCQ) : (1 mark each)

1. (b) 2. (b) 3. (d) 4.(a) 5.(d) 6. (c) 7. (a)
8. (d) 9. (d) 10. (a) 11. (d) 12. (d) 13. (a) 14. (d)
15. (a) 16. (a) 17. (a) 18. (b) 19. (a) 20. (a) 21. (c)
22. (a) 23. (c) 24. (a) 25. (c)

B. Assertion - Reason type questions : (1 marks each)

1. (a) 2. (b) 3. (d) 4. (a) 5. (b)

C. Very short answer type questions : (1 mark each)

1. Zn, Cd, Hg :
2. Transition elements are so called because their properties are in between those of S-block and p-block elements.
3. Copper (Cu)
4. Scandium (Sc)
5. 6
6. $(n-1)d^{1-10}ns^{1-2}$
7. Lightest : Scandium (Sc), Heaviest : Iridium (Ir)
8. Chromyl chloride (CrO_2Cl_2)
9. Tantallum (Ta)
10. Due to high charge density.
11. Fe^{3+} ion has 5 unpaire electrons.
12. As Fe^{3+} ion has 5 unpaired electrons.
13. $Cr<Cr_2O_3<CrO_3$
14. Copper (Cu)
15. Cerium (Ce)

Chapter - 9

Coordination Compounds

Chapter at a glance :

1. The transition metals form a large number of complex compounds. In modern terminolodgy such compound are called coordination compounds. Chlorphyll, hemoglobin and vitamin B-12 are coordanation compounds of megnasium, iron and cobalt respectively.

2. **Werner Theory of coordination compounds :**

   Werner in 1898, propounded his theory of coordination compound. The main postulates are -

   (a) In cordination compounds metals show two types of linkages (valencys), primary and secondary.

   (b) The primary valencies are normally ionisable and are satisfied by negative ions.

   (c) The secondary valances are non-ionisable. These are satisfied by natural moleeules or negative ions. The secondary valance is equal to the coordination number and is fixed for a metal.

   (d) The ions/ groups bound by the secondary linkages to the metal have charcteristic spacial arrangements corresponding to diffarent coordination numbers.

3. He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Some examples are-

   Octahedral → $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$, $[CoCl_2(NH_3)_4]^+$

   tetrahedral → $[Ni(CO)_4]$

   squareplanner → $[PtCl_4]^{2-}$

   The speacial arrangements corresponding to different coordination numbers enclosed in square bracket are called coordination polyhedra and the ions outside the square bracket are called counter ions.

4. **Double Salt :**

Double salts are formed by the combination of two or more stable compounds in stoichiometric ratio. Double salt when disolved in water completely dissociate into simple ions. Some examples of double salts are-

Carnallite	→	$KCl. MgCl_2. 6 H_2O$
Mohr's salt	→	$FeSO_4.(NH_4)_2SO_4. 6 H_2O$
Potash allum	→	$K_2SO_4 . Al_2 (SO_4)_3 . 24 H_2O$

5. Complex ions such as $[Fe(CN_6)]^{4-}$ of $K_4[Fe(CN_6)]$ do not dissociate into Fe^{2+} and CN^- ions. In aqueous solution only secondary valanceis are dissociate but primary valenceies does not dissociate for a complex compounds.

6. **Some important terms :**

a) Coordination entity :

A coordination entity constitutes a central metal atom or ion bounded to a fixed number of ions or molecules. For exemple the cordination entity of $K_4[Fe(CN_6)]$ is $[Fe(CN_6)]^{4-}$.

b) Central atom/ ion :

The metal atom or ion present in a coordination entity is called central atom. These are also referred to as Lewis acids. In $[Fe(CN_6)]^{3-}$ the central ion is Fe^{3+}.

c) Ligands :

The ions or molecules bound to the central atom/ ion in the coordination entity are called ligands.

Depending upon the number of donar atom present in a ligand, they can be classified into three groups .i.e unidentate, bidentate/ didantate and polydantate ligands.

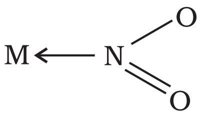
Unidantate ligands	→	Cl^-, H_2O, NH_3 etc.
bidantate ligands	→	$H_2N CH_2 CH_2 NH_2$, $C_2O_4^{2-}$ etc.
Polydantate ligands	→	$N (CH_2 CH_2 NH_2)_3$, $(EDTA)^{4-}$ etc.

d) Chelate ligands :

When a di or poly dantate ligand uses its two or more donour aroms to bind a single metal ion, it is said to be a chelate ligends. The number of such ligating groups is called the denticity of the ligands.

e) Ambident ligands :

Ligand which can ligate through two different atoms but in the formation of complex it can use only one donour atom is called ambidant ligand. e.g NO_2^- SCN^- ions etc.



$M \leftarrow O - N = O$

nitrito-N nitrito-O

$M \leftarrow SCN$ $M \leftarrow NCS$

(thiocyanato-S) (isothiocyanato)

f) Coordination number :

The number of ligand donor atoms to which the metal is derectly bonded is called the coordination number (CN) of a metal ion in a complex.

Only the sigma bonds are counted for the calculation of coordination number not the Pie(π) bonds.

Complex ions	**Coordination number**
$[Pt\,Cl_6]^{2-}$	6
$[Ni\,(NH_3)_4]^{2+}$	4
$[Fe(C_2O_4)_3]^{3-}$	6
$[Co\,(en)_3]^{3+}$	6

g) Oxidation number of central atom :

The charge on the metal ion in a complex, if all the ligands are removed along with the electron pairs that are shared with the centrel atom is called the oxidation number of the central atom. For example, in $[Cu(CN)_4]^{3-}$ the oxidation number of Cu is +1 and it is written as Cu (I).

h) Homolaptic and heteroleptic complexes :

Complexes in which a metal is bound to only one kind of donor groups e.g. $[Co\,(NH_3)_6]^{3+}$ are called homoleptic complexes.

Complexes in which a metal is bound to more then one kind of donor groups .e.g $[Co(NH_3)_4Cl_2]^+$ are called heteroleptic complexes.

7) Formulas of Mononuclear Coordination entities :

Mononucleas coordination entities contain a single central metal atom. Following are the IUPAC rules followed while writing the formula of a complex compound.

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order.

(iii) Polydantate ligands are also listed alphabatically. In case of abbreviated ligand the first letter of the abbriviation is used to determine the alphabatical order.

(iv) The formula of the entire coordination entity is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in perentheses. Ligand abbreviations are also enclosed in parentheses.

(v) there should be no space between the ligands and metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written with out that of the counter ion, the charge is indicated out side the square bracket as a right superseript with the number before the sign. For example $[Co(CN)_6]^{3-}$ etc.

(vii) The Charge of the cation (s) is balanced by the charge of the anion (s).

8) Naming of Mononuclear Coordination Compounds :

The following IUPAC rules are used when naming coordination compounds.

(i) The cation is named first in both positivety and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula)

(iii) Names of anionic ligands end in- o, those of neutural and cationic ligands are the same except aqua for H_2O, ammine for NH_3, Carbonyl for CO and nitrosyl for NO. These are placed within enclosing marks () when written in the formula of coordination entity.

(iv) Prefixes mono, di, tri etc. are used to indicate the mumber of the ligands include a numerical prefix, then the term bis, tris, tetrakis are used, the ligand to which they refer being placed in perendtheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichlorobis (triphenyl phosphine) nickel (II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parentheses.

(vi) If the complex ion is a cation, the metal is named same as the element. But if the complex ion is anion, the name of the metal end with the siffix 'ate'. For example Co in complex cation is called cobalt and Co in complex anion is called cobaltatre. For some metals the Latin names are used in the complex anions. e.g ferrate for Fe.

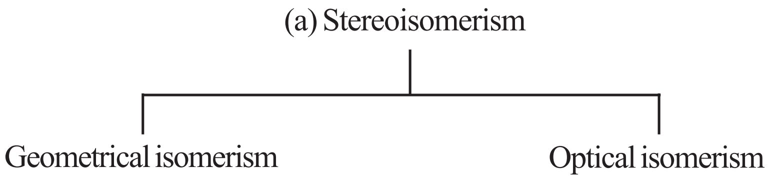
(vii) The neutral complex molecule is named similar to that of the complex cation.

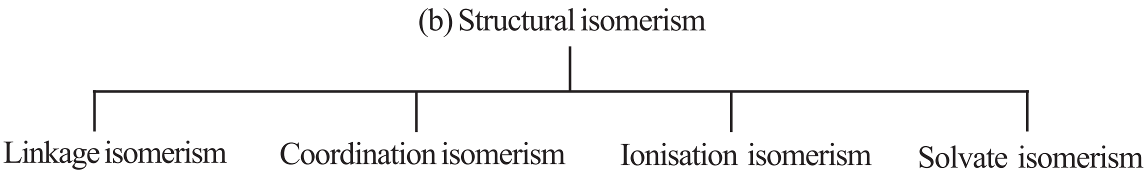
9) IUPAC Names of some important complex compounds.

Complex Compound	**IUPAC Name**
1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$	Triammine triaqua Chromium (III) Chloride.
2. $[Co(H_2NCH_2CH_2NH_2)_3]_2(So_4)_3$	Tris (elhane- 1,2, diammine) cobalt (III) Sulphate.
3. $[Ag(NH_3)_2][Ag(CN)_2]$	Diammine silver (I) dicyamine argentate (I).
4. $[Ni(CO)_4]$	Tetracarbonylnikel (o).
5. $[CoCl_2(en)_2]^+$	Dichlorobis (ethane- 1, 2- diammine).
6. $K_3[Al(C_2O_4)_3]$	Potassium trioxalato aluminate (III).
7. $[Co(NH_3)_4(H_2O)Cl]Cl_2$	Tetra aminine aqua chlorido codalt (III) Chloride.
8. $K_2[Zn(OH)_4]$	Pottasium tetra hytrahydroxidoxincate (III).
9. $Hg[Co(SCN)_4]$	Mercury (I) tetrathiocyanato cobaltate (III).
10. $[P+(NH_3)_2Cl(No_2)]$	Diammine Chloridonitrito - N - Platinum.
11. $[Ni(NH_3)_4]$ $[Ni\ Cl_4]$	Tetrammine nickel (II) tetra chloronickelate (II).
12. $[Co(NH_3)_6]\ Cl_3$	Hexammine cobalt (III) chloride
13. $[Co(NH_3)_5Cl]\ Cl_3$	Pentaammine chlorido cobalt (III) chloride
14. $K_3[Fe(CN)_6]$	Pottasiumhexa cyanidoferrete (III)
15. $K_3[Fe(C_2O_4)_3]$	Pottasium tri oxalatoferrate (III)
16. $K_2[PdCl_4]$	Pottasium tetra chloridopaladate (II)
17. $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$	Diamminchloride (methanammine) platinum (II) chloride
18. $[Cr(en)_3]Cl_3$	Tris (ethan- 1, 2 - diammine) chromium (III) chloride
19. $Fe_4[Fe(CN)_6]_3$	Iron (III) hexacyanidoferrate (II)
20. $[Pt\ Cl_2\ (en)_2]\ (NO_3)_2$	Dichlorido bis (ethane-1,2-diammine) platinum (IV) nitrate

10) Isomerism in Coordination Compounds :

Two principal types of isomerism are known among coordination compound. Each of which can farther be subdivided.

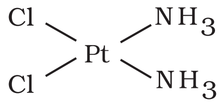




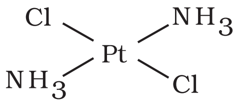
11) Geometrical isomerism :

Generally heteroleptic complexes with coordination number 4 and 6 shows this type of isomerisom.

Square planar complexes of formula $[MX_2L_2]$ (X and L are both unidentate) may be arranged adjecent to each other in a cis isomer or opposite to each other in a trans isomer.



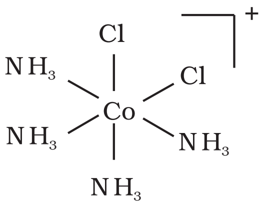
cis



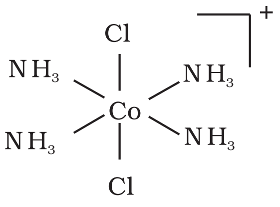
trans

Square planar complexes of the type MABXL (where A, B, X, L are unidantates) shows two cis isomers and one trans isomer.

Octahedrel complexes of formula $[MX_2L_4]$ also shows cis and trans isomers.

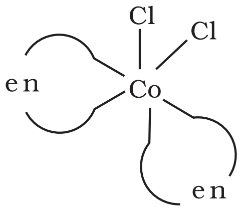


cis

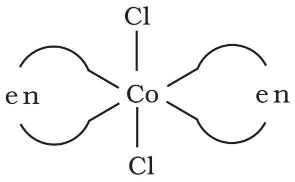


trans

Complexes of formula $[MX_2(L\text{-}L)_2]$ with didentate ligands also shows cis and trans isomers.

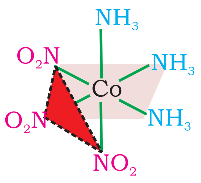


(cis)

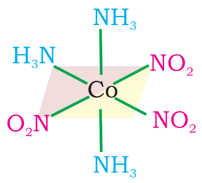


(trans)

Octahedral coordination entities of the type $[Ma_3b_3]$ for example $[Co(NH_3)_3(NO_2)_3]$ shows another type of geometrical isomerism. If three donar atoms of the some ligands occupy adjecent positions at the corners of an octahedral face, we have the facial (fac) isomer. when the positions are at the meridian of the octahedron, we get the meridional (mer) isomer.



fac–

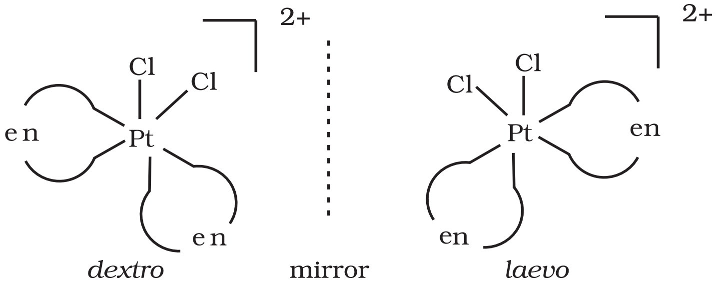


mer–

12) Optical isomerism :

Optical isomers are mirror images that cannot be superimposed on one another. These are called dextro (d) and laevo (l). The molecules or ions that cannot be superimposed are called **chiral**.

In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the cis isomer shows optical activity.



13) Linkage isomerism :

Linkage isomerism arises in a coordination compound containing ambidedentate ligand. Jrgenson discovered such behabiour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$. When nitrite ligand is bound through oxyzen (-ONO) it is obtained as the red form. But when nitrite legand is bound through nitrogen (-N) it is obtained as yellow form.

14) 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 is $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$

15) Ionisation isomerism :

This type of isomerism arises when the counter ion in a complex salt is itself a ligand and can displace a ligand which can then become the counter ion. An example is

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

16) Solvate isomerism :

This is similar to ionisation isomerism. This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvant. An example is $[Cr(H_2O)_6]$ Cl_3 (violet) and $[Cr(H_2O)_5Cl]$ $Cl_2.H_2O$ (grey-green).

17) Bonding in coordination aompounds :

Many approaches have been put forth to explain the nature of boanding in coordination compounds viz. Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT), and Molecular Orbital Theory (MOT).

18) Valence Bond Theory (VBT) :

According to this theory, the metal atom or ion under the influence of ligands can use its (n-1) d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry. These hybridised orbitals are allowed to overlap with ligands that can donate electron pairs for bonding.

Co-ordination number	Types of hybridasation	Distribution of hybrid orbitals in space or geometry of orbitals
4	Sp^3	Tetrahetral
4	dsp^2	Square planar
5	Sp^3d	Trigonal bipyramidal
6	Sp^3d^2	Octahedral
6	d^2Sp^3	Octahedral

Hybridisation in $[Co(NH_3)_6]^{3+}$

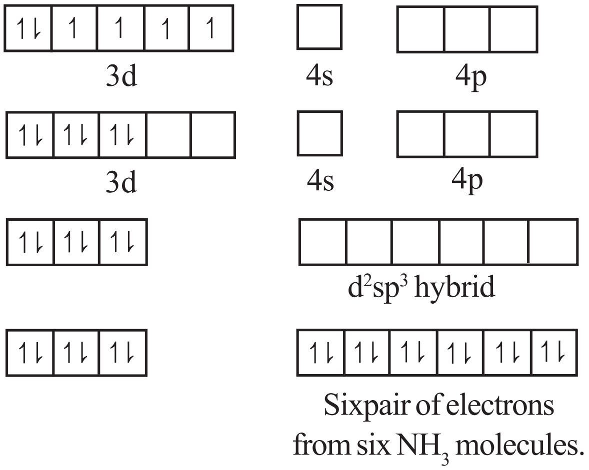
Here co ion is in +3 oxidation state.

orbitals of Co^{3+} ion

Orbitals of Co^{3+} ion under the influence of NH_3 ligand

d^2sp^3 hybridised orbitals of Co^{3+}

Orbitals of Co^{3+} ion in $[Co(NH_3)_6]^{3+}$ (inner orbital or low spin complex)



Thus $[Co(NH_3)_6]^{3+}$ has octahedrel geometry and diamagnetic because of the absence of unpaired electron.

Since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called inner orbital or low spin or spin paired complex.

Hybridisation in $[Co F_6]^{3-}$

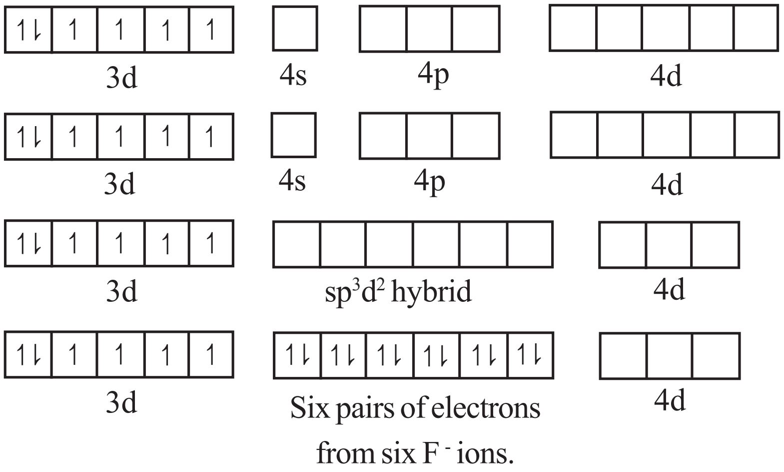
Here Co ion is in +3 oxidation state.

orbitals of Co^{3+} ion

Orbitals of Co^{3+} ion under the influence of F^- ligand

sp^3d^2 hybridised orbitals of Co^{3+}

Orbitals of Co^{3+} ion in $[Co F_6]^{3-}$ (outer orbital or high spin complex)



Thus $[Co F_6]^{3-}$ has octahedral geometry and paramagnetic because of the presence of 4 Nos. unpaired electrons.

Since the outer d orbital (4d) is used in hybridisation, the complex $[Co F_6]^{3-}$ is called outer orbital or high spin or spin free complex.

Hybridisation in $[NiCl_4]^{2-}$

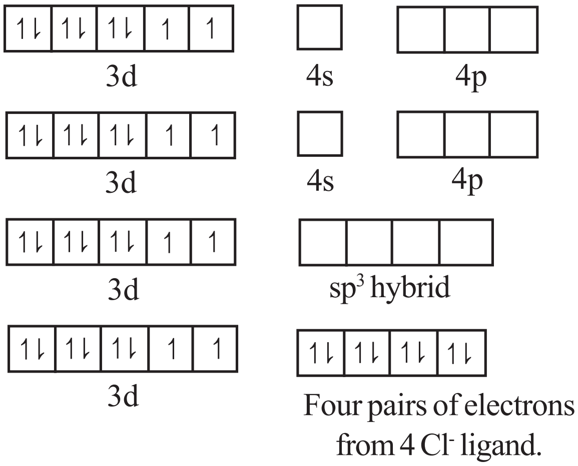
Here Ni ion is in +2 oxidation state.

orbitals of Ni^{2+} ion

Orbitals of Ni^{2+} ion under the influence of Cl^- ligand

sp^3 hybridised orbitals of Ni^{2+}

Orbitals of Ni^{2+} ion in $[NiCl_4]^{2-}$(high spin complex)

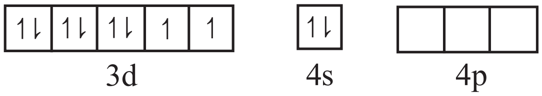


Thus $[NiCl_4]^{2-}$ has tetrahedral geometry and paramegnetic because to the prescnce of 2 Nos. unpaired electrons.

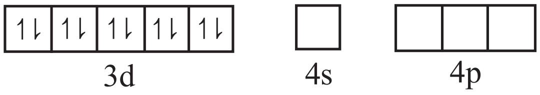
Hybridisation in [Ni (Co)$_4$]

Here Ni ion is in 0 oxidation state.

Orbitals of Ni

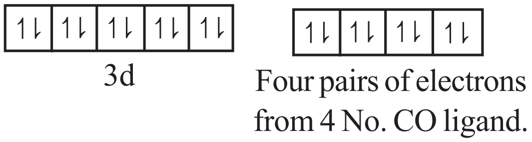


Orbitals of Ni under the influence of CO ligand



sp^3 hybridised orbitals of Ni

Orbitals of Ni in $[Ni(CO)_4]$ complex (low spin complex)

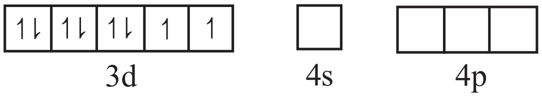


Thus $[Ni(CO)_4]$ has tetrahedral geometry and diamegnetic because of the abscnce of unpaired electrons.

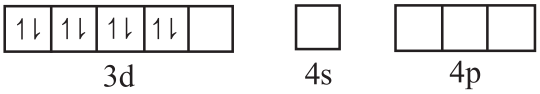
Hybridisation in [Ni (CN)$_4$]$^{2-}$

Here Ni ion is in +2 oxidation state.

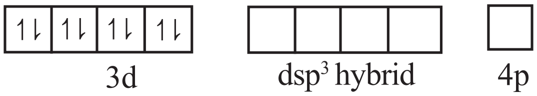
Orbitals of Ni^{2+} ion



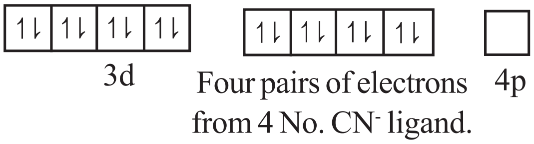
Orbitals of Ni^{2+} under the influence of (CN) ligand



dsp^2 hybridised orbitals of Ni^{2+}



Orbitals of Ni in $[Ni(CN)_4]$ complex



Thus $[Ni (CN)_4]^{2-}$ has square planar geometry and diamagnetic because of the absence of unpaired electron.

19. Magnetic properties of coordination compound :

By measuring the magnetic moment of coordination compounds we can obtain information about structures adopted by metal complexes.

Configaration	Unpaired electrons	Magnetic moments in BM unit
$3d^0$	0	0
$3d^1$	1	1.73
$3d^2$	2	2.84
$3d^3$	3	3.87
$3d^4$	4	4.90
$3d^5$	5	5.92
$3d^6$	4	4.90
$3d^7$	3	3.87
$3d^8$	2	2.84
$3d^9$	1	1.73
$3d^{10}$	0	0

For example, the calculated magnetic moment of $[Ni(CO)_4]^{2-}$ is zero. It means it has no unpaired electrons.

Here the coordination number of Ni^{2+} ion is 4. So it will either tetrahedral or square planar.

As number of unpaired electron is zero so it is a low spin complex and favour square planar geometry ruther than tetrahedral geometry.

For metal ions with upto three electrons in the d-orbitals, like Ti^{3+} (d^1), V^{3+} (d^2), Cr^{3+} (d^3) - two vacant d-orbitals are available for octahedral hybridisation with 4s and 4p orbitals. But for d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6 (Fe^{2+}, Co^{3+}) cases, a vacant pair of d-orbitals results only by pairing of 3d electrons, which leaves two, one or zero unpaired electrons respectively.

However with species containing d^4 and d^5 ions there are complications. $[Mn(CN)_6]^{3-}$ has magnetic moment of unpaired electron while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired elecctrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of two unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment with four unpaired elctrons. This apparent anomaly is explained by VBT in terms of formation of inner orbital and outer orbital complexes involving d^2sp^3 and sp^3d^2 hybridisation respectively.

$[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ are inner orbital complexes.

and $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ are outer orbital complexes.

20) Limitations of VBT :

VBT suffers from the following limitations-

i) It involves a number of assumptions.

ii) It does not give quantitative interpretation of magnetic data.

iii) It does not explain the colour exhibited by coordination compounds.

iv) It does not give a quantitative interpritation of the thermodynamic or kinetic stabilities of coordnation compounds.

v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4 cordinate complexes.

vi) It does not distinguish between week and strong ligands.

21) Crystal Field Theory (CFT) :

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules.

The five d- orbitals in an isolated gaseous metal atom/ ion have same energy i.e. they are degenerate. due to presence of ligands in a complex, d-orbitals becomes asymmetrical and the degeneracy of the d-orbitals is lifted.

a) Crydsfal field splitting in octahedral coordination entities :

In an octahedral coordination entity with six ligands surrounding the metal atom/ ion, there will be repulsion between the electrons in metal d-orbital and the electrons (or negative changes) of the ligands.

The $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experince more repulsion and will be raised in energy. But the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. This splitting of d-orbitals will yield there orbitals of lower energy, t_{2g} set and two orbitals of higher energy, eg set.

The energy separation is donoted by Δ_0 (the subscript 0 is for octahedral). Thus the energy of the two eg orbitals will increase by $(3/5)\ \Delta_0$ and that of the three t_{2g} will decrease by $(2/5)\ \Delta_0$.

The crystal field splitting, Δ_0, depands upon the field produced by the ligand and charge on the metal ion.

Ligands can be arranged in a series in the order of increasing field strength as given below :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

This series is also known as spectro-chemical series of ligands.

In d^1, d^2 and d^3 coordination entities, the d-electrons occupies one of the lower energy t_{2g} orbitals in accordance with the Hund's rule.

For d^4 ions, two possible patterns of electron distribution is arises,

(i) the fourth electron could either enter the t_{2g} level and pair with an existing electron or

(ii) the fourth electron may enter in the eg level.

Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_0 and the pairing energy, P.

The two options are -

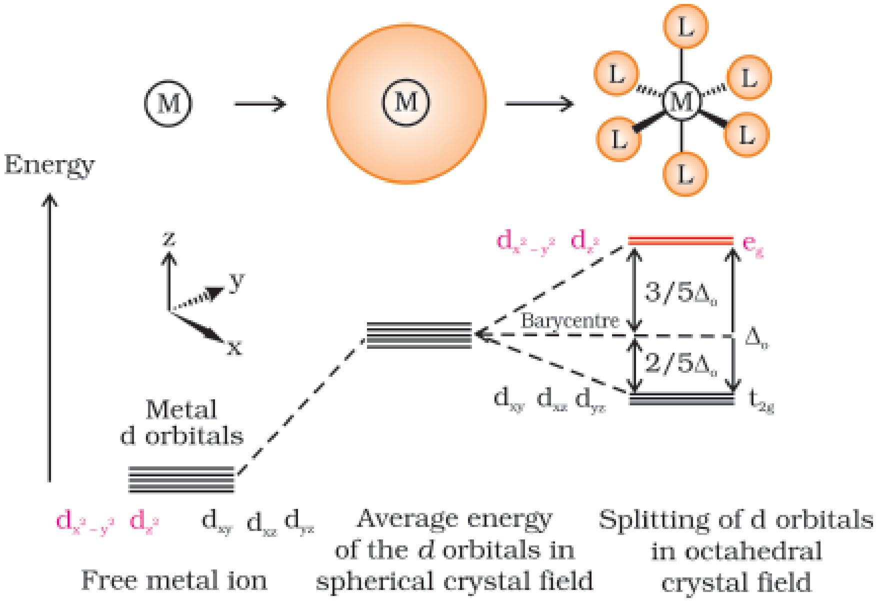
(i) If $\Delta_0 < P$, the fourth electron enters one of the eg orbitals giving the configuration $t_{2g}^3 e_g^1$

Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

(ii) If $\Delta_0 > P$, the fourth electron enters one of the t_{2g} orbitals giving the configaration $t_{2g}^4 e_g^0$

Ligands for which $\Delta_0 > P$ are known as strong field ligands and form low spin complexes.

Calcutions show that d^4 and d^7 coordination entities are more stable for strong field as compared to weak field cases.



b) Crystal field splitthing in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d- orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that, $\Delta_t = \frac{4}{9}\Delta_0$

Consequentty, the orbital splitting energies are not sufficiency large for forcing pairing and therefore law spin configuration are rarely observed in tetrahedral coordination entities.

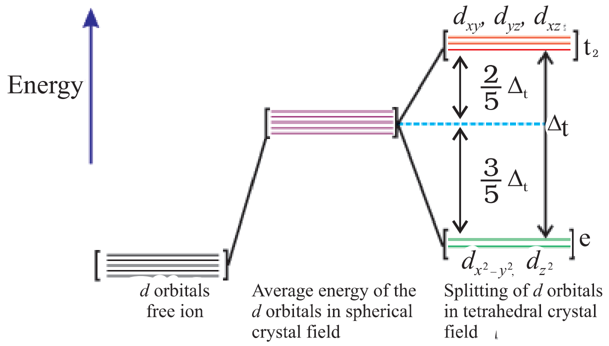


Fig. : d orbital splitting in a tetrahedral crystal field.

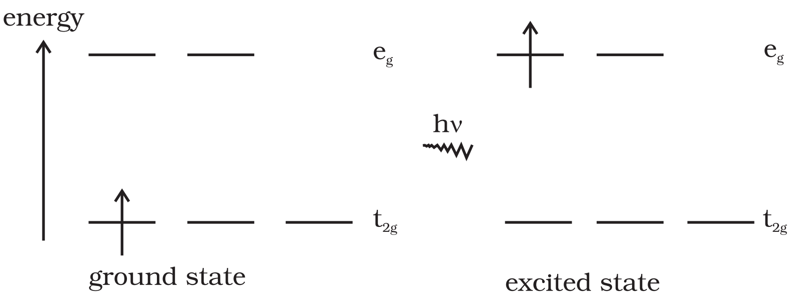
22) Colour in coordination compounds:

One of the most distinctive properties of transition metal complexes is their wide range of colours. The colour of the complex is complimentary to that which is absorbed. The complimenntary colour is the colour genatated from the wavelength left over.

Table : Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

Coordinaton entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow 🟨	Violet 🟪
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green 🟩	Red 🟥
$[Co(NH_3)_6]^{3+}$	475	Blue 🟦	Yellow Orange 🟧
$[Co(CN)_6]^{3-}$	310	Ultraviolet Not in visible region	Pale Yellow 🟨
$[Cu(H_2O)_4]^{2+}$	600	Red 🟥	Blue 🟦
$[Ti(H_2O)_6]^{3+}$	498	Blue Green 🟩	Violet 🟪

The colour of the coordination compounds can be readily explained in terms of crystal field theory. The crystal field theory attributes the colour of the coordination compounds to d-d transition of electrons i.e transition to t_{2g} level to eg level.



Transition of an electron in $[Ti(H_2O)_6]$

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colorless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ and $CuSO_4.5H_2O$ on heating renders them colourless.

d-d transition can also be observed in some Gem stone that occurs frequently in everyday life. For example, Ruby is aluminium oxide (Al_2O_3) containing about 0.5-1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+}. In emerald Cr^{3+} ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$).

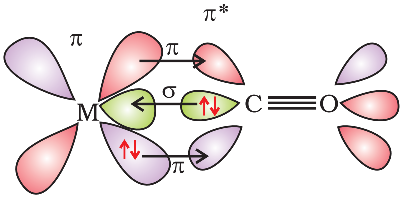
23) Limitations of Crystal Field Theory :

According to crystal field theory ligands are considered as point charges. So the anionic ligands should exert the greatest splitting effect. But actually the anionic ligands are found at the low end of spectrochemical series.

Moreover crystal field theory does not take into account the covalent character of bonding between the ligand and the central metal atom/ ion.

24) Bonding in metal corbonyls :

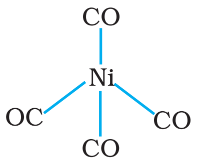
The metal-carbon bond in metal carbonyls possess both δ and π character. The M-C sigma (δ) bond is formed by the donation of lone pair of electrons on the metal. The M-C pi (π) bond is formed by the donation of a pair of electrons from filled d-orbital of metal into the carbonyl carbon into a vacant d-orbital of the vacant antibonding π orbital of carbon monooxide. The metal to ligand bonding creates a siynergic effect which strenthens the bond between CO and the metal.



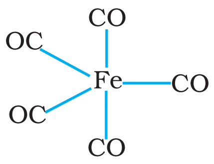
Synergic bonding

Fig. : Example of synergic bonding interactions in a carbonyl complex.

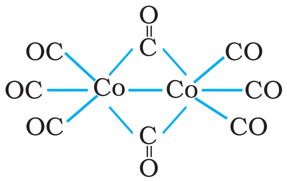
Structures of some homoleptic metal carbonyls



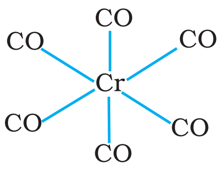
$Ni(CO)_4$
Tetrahedral



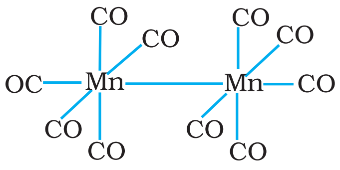
$Fe(CO)_5$
Trigonal bipyramidal



$[Co_2(CO)_8]$



$Cr(CO)_6$ Octahedral



$[Mn_2(CO)_{10}]$

25) Stability of coordination compounds :

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium.

For a reaction of the type :

$$M+4L \rightleftharpoons ML_4$$

The stepwise stability constants are as follows:

$$\begin{array}{lllllll}
M & + & L & \rightleftharpoons & ML & K_1 = & [ML]/[M][L] \\
ML & + & L & \rightleftharpoons & ML_2 & K_2 = & [ML_2]/[ML][L] \\
ML_2 & + & L & \rightleftharpoons & ML_3 & K_3 = & [ML_3]/[ML_2][L] \\
ML_3 & + & L & \rightleftharpoons & ML_4 & K_4 = & [ML_4]/[ML_3][L] \\
\hline
ML_{(n-1)} & + & L & \rightleftharpoons & ML_n & K_4 = & [ML_n]/[ML_{(n-1)}][L]
\end{array}$$

Where K_1, K_2, K_3, K_4 etc are called stepwise stability constants.

But $M + 4L \rightleftharpoons ML_4$ for this reaction the Overall stability constant $\beta_4 = [Cu(NH_3)_4{}^{2+}]/[Cu^{2+}][NH_3)^4$

so $\quad \beta_4 = K_1 \times K_2 \times K_3 \times K_4$

or $\quad \beta_n = K_1 \times K_2 \times K_3 \times K_4 \text{ ....} K_n \qquad \beta = [ML_n]/[M][L]^n$

For most formation constant, the successive stability constants are genearlly decreases.

The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of formation constant.

26) Application of coordination compound :

coordination compounds play many important functions in the area of analytical chemistry, melallurgy, biological systems, industry and medicine.

(i) The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. Hardness of water is estimated by simple titration with Na_2 EDTA.

(ii) Gold (Au) combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of Zn.

(iii) Chlorophyll, haemoglobin and vitamin B-12 are coordination compounds of magnesium, iron and cobalt respectively.

(iv) Rhodium complex, $[(Ph_3 P)_3 Rh Cl]$, a Wilkinson catalyst is used for the hydrogenation of alkenes.

(v) $[Ag (CN)_2]^-$ and $[Au (CN)_2]^-$ are used for smooth and evenly electroplating.

(vi) In black and white photography hypo solution dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

(vii) EDTA is used in the treatment of lead poising.

(viii) Cis-platin and related compounds effectively inhibit the grouth of tumours.

(ix) Excer of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime-B in chelate therapy.

A. Select the correct answer (MCQ) : (Each one carries one mark)

1. The oxidation number of cobalt in $K[Co(CO)_4]$ is -

a) +1 b) +3 c) -1 d) -3

2. Which of the follwing species is not expected to be a ligand ?

a) Co b) NH_4^+ c) $NH_2CH_2CH_2NH_2$ d) CN^-

3. Which of the following is the most stable complex species ?

a) $[Fe(CN)_6]^{3-}$ b) $[Fe(CN)_6]^{4-}$ c) $[Fe(C_2O_4)_3]^{3-}$ d) $[Fe(H_2O)_6]^{3+}$

4. Oxidation state of Ni in $[Ni(CO)_4]$ is -

a) 0 b) +1 c) +2 d) +4

5. The compounds $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$ represent -

a) Linkage isomerism b) ionisation isomorism

c) Coordination isomerism d) solvate isomerism

6. The compounds $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ represent -

a) linkage isomerism b) ionisation isomerism

c) coordination isomerism d) solvate isomerism

7. Coordination number of Fe in $[Fe(C_2O_4)_3]^{3-}$ is -

a) 4 b) 6 c) 0 d) None of these

8. Indicate the complex ion which shows geometrical isomerism.

a) $[Cr(H_2O)_4Cl_2]^+$ b) $[Pt(NH_3)_3Cl]$ c) $[Co(NH_3)_6]^{3+}$ d) $[Fe(CN)_6]^{3-}$

9. Which of the following octahedral complexes will not show geometrical isomerism?

(A and B are monodantate ligand)

a) MA_2B_4 b) MA_3B_3 c) MA_5B d) MA_4B_2

10. The number of unpaired electron in $[Ni(CO)_4]$ is -

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

11. Which of the following complexs will give white precipitate with $BaCl_2$ solution?

a) $[Co\ (NH_3)_5SO_4]Br$ b) $[Co\ (NH_3)_5Br]\ SO_4$

c) $[Co\ (NH_3)_4(SO_4)_2]\ Br$ d) $[Co\ (NH_3)_4Br(SO_4)]$

12. $[Co\ (NH_3)_6]^{3+}$ is -

a) Paramagnetic and undergoes sp^3d^2 hybridisation.

b) Diamagnetic and undergoes sp^3d^2 hybridisation.

c) Paramagnetic and undergoes d^2sp^3 hybridisation.

d) Diamagnetic and undergoes d^2sp^3 hybridisation.

13. $Ni\ (CO)_4$ is -

a) Paramagnetic and undergoes sp^3 hybridisation.

b) Diamagnetic and undergoes sp^3 hybridisation.

c) Paramagnetic and undergoes dsp^2 hybridisation.

d) Diamagnetic and undergoes dsp^2 hybridisation.

14. Among the following which is ambident ligand -

a) $H_2NCH_2CH_2NH_2$ b) $C_2O_4^{2-}$

c) NO_2^- d) Cl^-

15. Which of the following complex will heve tetrahedral shape -

a) $[Ni(CO)_4]$ b) $[Ni\ (CN)_4]^{2-}$ c) $[PdCl_4]^{2-}$ d) $[Pd\ (CN)_4]^{2-}$

16. The ligand $N\ (CH_2CH_2NH_2)_3$ is -

a) Bidentate b) Tridentate c) Tetradentate d) Pentadentate

17. The metal present in vitamine- B_{12} is -

a) Fe b) Mg c) Cr d) Co

18. The spin-only magnetic moment value of $[NiCl_4]^{2-}$ is -

    a) 2.84 B.M b) 1.73 B.M c) 3.87 B.M d) 0

19. $CuSO_4$, $5H_2O$ is blue in colour while anhydrous $CuSO_4$ colourless due to -

    a) Anhydrous $CuSO_4$ undergoes d-d transition

    b) Absence of water d-d transition are not possible in $CuSO_4$.

    c) Colour is lost due to lose of unpaired electrons.

    d) Presence of strong field ligand in $CuSO_4$, $5H_2O$.

20. Which of the following ligand will not show chelation?

    a) $H_2N\ CH_2CH_2NH_2$ b) $N\ (CH_2CH_2NH_2)_3$

    c) SCN^- d) $(EDTA)^{4-}$

21. The Correct increasing order of ligand field strength is -

    a) $I^- < SCN^- < H_2O < C_2O_4^{2-}$ b) $I^- < SCN^- < C_2O_4^{2-} < H_2O$

    c) $SCN^- < I^- < C_2O_4^{2-} < H_2O$ d) $I^- < H_2O < SCN^- < C_2O_4^{2-}$

22. The IUPAC name of $[Ni(NH_3)_4][Ni\ Cl_4]$ is -

    a) Tetrachloronickel (II) tetraamminenickel (II)

    b) Tetraamminenickel (II) tetrachloronickel (II)

    c) Tetraamminenickel (II) tetrachloronickelate (II)

    d) Tetrachloronickel (II) Tetraamminenickelate (0)

23. Formula of triamminetriaqua chromium (III) chloride is -

    a) $[Cr\ (NH_3)_3(\ H_2O)_3]Cl$ b) $[Cr\ (NH_3)_3(\ H_2O)_3]Cl_2$

    c) $[Cr\ (NH_3)_3(\ H_2O)_3]Cl_3$ d) $[Cr\ (NH_3)_3(\ H_2O)_2]Cl_3$

24. Among the following ions which one has the highest magnetic moment value ?

    a) $[Cr\ (H_2O)_6]^{3+}$ b) $[Fe\ (H_2O)_6]^{2+}$

    c) $[Zn\ (H_2O)_6]^{2+}$ d) $[Co\ (H_2O)_6]^{3+}$

25. How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

    a) 2 b) 3 c) 4 d) 6

B) Assertion Reason type Question : (Each question carries 1 mark)

In the following questions a statement of assertion is followed by a statement of reason. Mark the correct choice from,

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but the reason is not the correct explenation of assertion.

c) Assertion is a true, but reasone is false.

d) Reason is true but assertion is false..

1. Assertion : $[Fe(H_2O)_6]^{2+}$ is sp^3d^2 hybridised and paramagnetic complex ion.
   Reason : It has four unpaired electrons.
2. Assertion : $[Fe(H_2O)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
   Reason : Because it has d^2sp^3 type of hybridisation.
3. Assertion : Toxic metal ions are removed by the chelating ligand.
   Reason : Chelate complex tend to be more stable.
4. Assertion : $[Co(NH_3)_5Cl]^{2+}$ do not show geometrical isomerism.
   Reason : Geometrical isomerism is shown by complexes with coordination number 4.
5. Assertion : According to crystal field theory during complex formation, the d-orbitals split and from two sets of orbitals t_{2g} and e_g.
   Reason : Spliting of d-orbitals occurs only in case of strong field ligands.
6. Assertion : $[Co(NH_3)_5Br]SO_4$ gives white precipitate with $BaCl_2$ solution.
   Reason : The complex dissociates in solution to give SO_4^{2-} ion.
7. Assertion : $[Co(NH_3)_5Cl]Cl_2$ gives white precipitate with $AgNO_3$ solution.
   Reason : The complex dissociates in solution to give three number of Cl^- ions.
8. Assertion : $[Fe(CN)_6]^{4-}$ dissociates into Fe^{2+} and CN^- ions in aquons solution.
   Reason : In aquous solutions only secondary valancies dissociates for a complex compound.
9. Assertion : Optical isomers are mirror images that cannot be superimposed on one another.
   Reason : Optical isomers are enantiomers.
10. Assertion : $[Co(NH_3)_6]^{3+}$ has octahedral geometry and diamagnetic in nature.
    Reason : It is an inner orbital or low spin complex.

C) Very short answer type Questions : (Each question carries 1 mark)

1. Name a coordination compound in which the central metal atom is magnesium.
2. Write the name and formula of a double salt.
3. Which type of valency of a coordinate entity does not dissociates in aqueous solution?
4. Identify the coordinate entity present in $K_4[Fe(CN)_6]$?
5. Give an example of chelate ligand?
6. Why NO_2^- is considered as ambident ligand?
7. What is the oxidation number of Cu in $[Cu(CN)_4]^{3-}$?
8. Write the IUPAC name of the complex $[NiCl(PPh_3)_2]$?
9. Write the formula of the complexes potassiumtri- oxalatoaluminate (III).
10. Why homolepetic complexes does not show geometrical isomerism?
11. Draw the structure of cis $[Co(NH_3)_4Cl_2]^+$.
12. Which isomer of $[PtCl_2(en)_2]^{2+}$ is optically active?
13. When a ligand is displaced by the counter ion of a complex, which type of isomerism arises?
14. Given an example of hydrate isomerism.
15. Which type of hybridisation is required for octahedral geometry?
16. What is the number of unpaired electrons present in the coordination entity $[CoF_6]^{3-}$?
17. What is the value of spin-only magnetic moment of the coordination entity $[NiCl_4]^{2-}$?
18. According to crystal field theory d-orbitals are assumed as degenerate - why?
19. Name the ligand which can form chelate complex that is used in the treatment of lead poisoing?
20. Write the formula of the coordination isomer of $[Cr(en)_3][Co(CN)_6]$?

D. Short Answer Questions : (Each one carries 2 marks)

1. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aquous ammonia in 1:4 molar ratio does not give the test of Cu^{+2} ion. Explaine why?
2. What is meant by ambident ligands? Give two examples.

3. Specify the oxidation numbers of metls in the following coordination entities:

   i) $[CoBr_2(en)_2]^+$ ii) $[Cr(NH_3)_3Cl_3]^+$

4. Using IUPAC norms write the formulas for the following:

   i) Potassiumtetrachloridopalladate

   ii) Hexaammineplatinum (iv)

5. Using IUPAC norms write the systematic names of the following:

   i) $[Co(NH_3)_4Cl(NH_2)]Cl$

   ii) $[Ni(NH_3)_6]Cl_2$

6. How many geometrical isomers are possible in the following coordination entities?

   i) $[Cr(C_2O_4)_3]^{3-}$

   ii) $[Co(NH_3)_3Cl_3]$

7. Draw the structures of optical isomers of:

   i) $[PtCl_2(en)_2]^{2+}$

   ii) $[Cr\,(NH_3)_2Cl_2(en)]^+$

8. Discuss the nature of bonding for the coordination entity $[FeF_6]^{3-}$ on the basis of Valence Bond Theory.

9. What is meant by chelate effect? Give an example.

10. $[Fe\,(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution. Why?

11. Discuss the nature of bonding in metal carbonyls.

12. What is spectrochemical series? Explain the difference between weak field ligand and strong field ligand.

13. Draw figure to show the splitting of d-orbitals in an octahedral crystal field.

14. What is meant by stability of a coordination compound is solution? State the factors which govorn stability of complexes.

15. Give the oxidation state and coordination number of the central metal ion in the following complexes:

   i) $[Mn\,(H_2O)_6]SO_4$

   ii) $K_3[Co\,(C_2O_4)_3]$

16. What is meant by coordination number? Write the correct coordination number of the central metal ion in the complex $(NH_4)_2[CoF_4]$.
17. Transition metals form complex compound. Why?
18. NH_3 takes part in the formation of complex compound but NH_4^+ can not. Why?
19. Differentiale between $[Co\,(NH_3)_5Br]SO_4$ and $[Co\,(NH_3)_5SO_4]Br$ by proper chemical experiment. Name the type of isomerism they will produce.
20. Transition metals can form π-complexes. Explain why?
21. Draw the possible structures of isomer of $[Co\,(NH_3)_3(NO_2)_3]$
22. According to valance Bond theory what will be the structure (geometry) and magnetic property of $[Ni(CN)_4]$ coordination entity?
23. Among the ligands H_2O and CO which is the batter ligand for the formation of complex entities? Give reason in support your answer?
24. The colour of blue vitriol is blue but that of anhydrous $CuSO_4$ is colourless. Explain why?
25. Ni does not have any low spin octahedral complex. why?

E. Long Answer Questions : (Each question carries 3 marks)

1. Explain with two examples each of the following:
   i) Coordination entity
   ii) Coordination number
   iii) Coordination polyhedron
2. List various types of isomerism possible for coorination compounds, giving an example of each.
3. Write all the geometrical isomers of $[Pt\,(NH_3)\,(Br)\,(Cl)\,(Py)]$ and how many of these will exhibit optical isomers?
4. Aqueous copper sulphate solution (blue in colour) gives:
   i) A green precipitate with aquous protassium fluride and
   ii) A bright green solution with aquous potassium cholride.
   Explain these experimental results.
5. Discuse briefly giving an example in each case the role of coordination compounds in:
   i) Biological systems
   ii) Medicinal chemistry
   iii) Extraction/ metallurgy of metals.
6. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is dianagnedtic. Explain why?
7. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Why?

8. What is crystal field splitting energy? How does the magnitude of Δ_0 decide the actual configuration of d-orbitals in a coordination entity?
9. Give an example of each with IUPAC name for the following?
   - i) Cationic complex
   - ii) Anionic complex
   - iii) Neutral complex
10. State the geometrical structure, oxidation state of central metal ion and magnetic property of the following:
    - i) $[Co(NH_3)_6]^{3+}$
    - ii) $[Ni(CN)_4]^{2-}$

Answers

A. Select the correct answer (MCQ) : (Each one carries one mark)

1. (c) 2. (b) 3. (c) 4.(a) 5.(b) 6. (c) 7. (b)

8. (a) 9. (c) 10. (b) 11. (b) 12. (d) 13. (b) 14. (c)

15. (a) 16. (c) 17. (d) 18. (a) 19. (b) 20. (c) 21. (b)

22. (c) 23. (c) 24. (b) 25. (b) 26. (c)

B) Assertion Reason type Question :

1. (a) 2. (d) 3. (c) 4. (c) 5. (c) 6. (a) 7. (c)

8. (d) 9. (b) 10. (a)

C) Very short answer type Questions : (Each question carries 1 mark)

1. Chlorophyll 3. Primary Valency 4. $[Fe(CN)_6]^{2-}$ 7. +1

9. $K_3[Al(C_2O_4)_3]$ 12. cis isomer 13. ionisation isomer 15. d^2sp^3/sp^3d^2

16. 4 17. 2.84 BM 18. degenerate 19. EDTA

20. $[Co(en)_3][Cr(CN)_6]$

Chapter - 10

Haloalkanes and Haloarenes

Chapter at a glance :

The replacement of one or more hydrogen atom(s) in a hydrocarbon (aliphatic or aromatic) by same number of halogen atom(s) gives alkyl halide (haloalkane) and aryl halide (haloarenes) respectively

In haloalkanes halogen atom(s) are attached to sp^3 hydridised carbon atom(s) of an alkyl group. In haloarenes halogen atom(s) are attached to sp^2 hybridised carbon atom(s) of an aryl group.

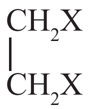
Haloalkanes and haloarenes have wide applications in industry as well as in day-to-day life. For example chloramphenical is used in the treatment of typhoid fever, deficiency of thyroxine in our body causes goiter disease. Synthetic halogen compounds viz. chloroquine is used far the treatment of malaria; halothane is used as an anaesthetic during surgery.

Haloalkanes and haloarenes are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds.

1) **Classification :** Depending on the presence of halogen atom they are classified into mono, di or polyhalogen (tri, tetra etc) compounds.

C_2H_5X

Monohaloalkane

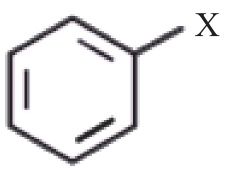


$$\begin{array}{l} CH_2X \\ | \\ CH_2X \end{array}$$

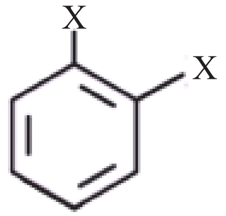
Dihaloalkane

$$\begin{array}{l} CH_2X \\ | \\ CHX \\ | \\ CH_2X \end{array}$$

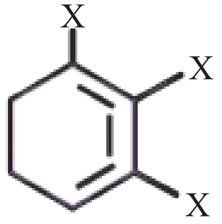
Tri halolkane



Monohaloarene



Dihaloarene



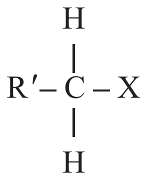
Tri haloarene

Monohalo compounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded.

a) Alkyl halides or haloalkanes (R–X) :

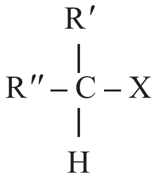
In this class halogen atom is bonded to an alkyl group (R). They farm a homologous series represented by Cn $H_{2n+1}X$.

They are further classified into primary (1°), secondary (2°) or tertiary (3°) alkyl halides.



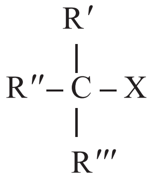
$$\begin{array}{c} H \\ | \\ R'-C-X \\ | \\ H \end{array}$$

primary (1°),



$$\begin{array}{c} R' \\ | \\ R''-C-X \\ | \\ H \end{array}$$

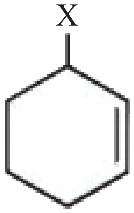
secondary (2°)



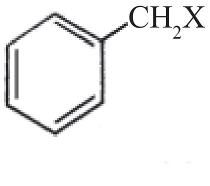
$$\begin{array}{c} R' \\ | \\ R''-C-X \\ | \\ R''' \end{array}$$

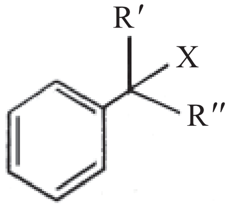
tertiary (3°)

b) Alylic Halides :



c) Benzylic halides :





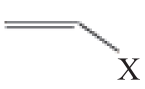
$R' = CH_3, R'' = H$ (2°)

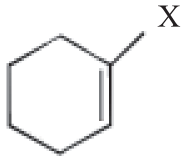
$R' = R'' = CH_3$(3°)

2) **Haloalkanes and aloarenes containing**

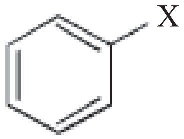
sp^2 C–X bonds :

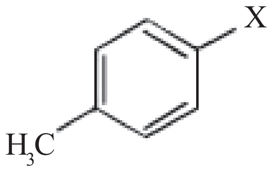
a) Vinylic halides :



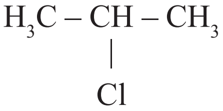
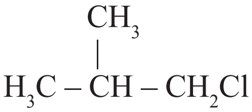


b) Aryl halides :

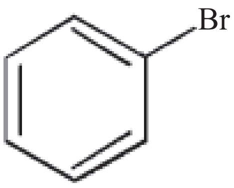
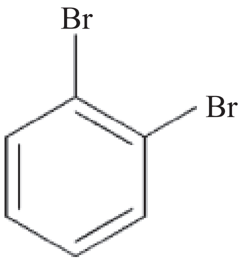
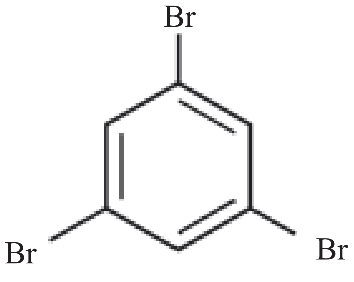




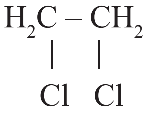
3) **Nomenclature :** The common names of alkylhalides are derived by naming the alkyl group followed by the halide. In the IUPAC system of nomenclature alkylhalides are concidered as halosubstituted hydrocarbons.

	$CH_3CH_2CH_2Br$	 $H_3C-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_3$	 $H_3C-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}-CH_2Cl$
Common name :	n – propylbromide	Isopropyl chloride	Isobutyl chloride
IUPAC name :	1– Bromopropane	2 – chloropropane	1-Chloro-2– methyl propane

Haloarenes are commmon as well as IUPAC names of aryl halides

			
Common name :	Bromobenzene	m-dibromobenzene	sym- Tribromobenzene
IUPAC name :	Bromobenzene	1,3 dibromobenzene	1,3,5 Tribromobenzene

The dihalo compounds having same type of halogen atoms are further classified as geminal (as gem) dihalides and vicinal (or vic) di halides.

	$H_3C-CHCl_2$	 $\underset{Cl}{H_2C}-\underset{Cl}{CH_2}$
Common name :	Ethylidene chloride (gem-dihalide)	Ethylene dichloride (vic-dihalide)
IUPAC name :	1,1- dichloroethane	1,2- dichloroethane

4) **Nature of C–X bond :** The carbon-halogen bond of alkylhalide is polarised. The carbon atom bears a partial +Ve charge whereas the halogen atom bears a partial –Ve charge

Since the size of the halogen increases in the order F<Cl < Br<I the carbonhalogen bond (C–X) length also increase from C–F to C–I.

5) **Some important methods of preperation :**

a) From alcohols :

$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$

$R-OH + NaBr + H_2SO_4 \longrightarrow R-Br + NaHSO_4 + H_2O$

$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$ [X = Cl, Br]

$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$

$R-OH \xrightarrow[X_2=Br_2, I_2]{red\ P/X_2} RX$

$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$

The order of reactivity of alcohols with a given haloacid is $3^o > 2^o > 1^o$.

The above methods are not applicable for the preparation of aryl halides beccause the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break.

b) From hydrocarbons : (Free radical halogenation)

$CH_4 (g) + Cl_2 (g) \xrightarrow[or\ heat]{Uv\ light} CH_3Cl (g) + HCl (g)$

(excess)

$CH_3Cl (g) + Cl_2 (g) \longrightarrow CH_2Cl_2 (g) + HCl (g)$

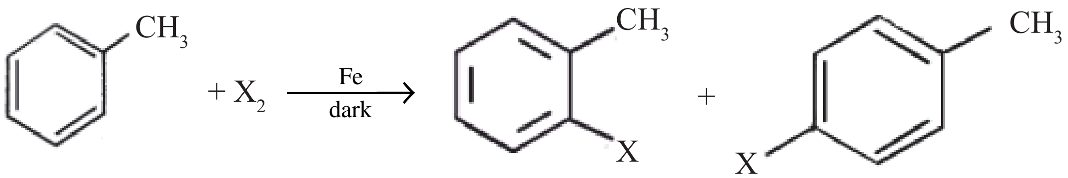
$CH_2Cl_2 (g) + Cl_2 (g) \longrightarrow CHCl_3 (g) + HCl (g)$

$CHCl_3 (g) + Cl_2 (g) \longrightarrow C\,Cl_4 (g) + HCl (g)$

Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono– and polyhaloalkanes, which is difficult to separate as pure compounds.

$CH_3CH_2CH_2CH_3 \xrightarrow[or\ heat]{Cl_2/Uv\ light} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CH(Cl)\,CH_3$

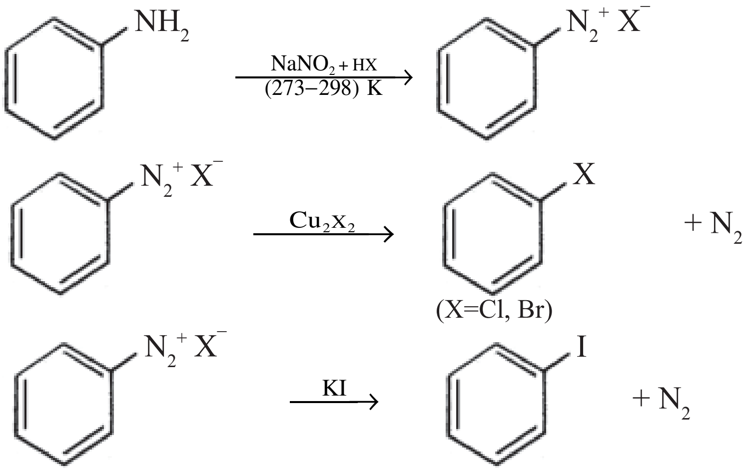
c) By electrophilic substitution :



(ortho) (para)

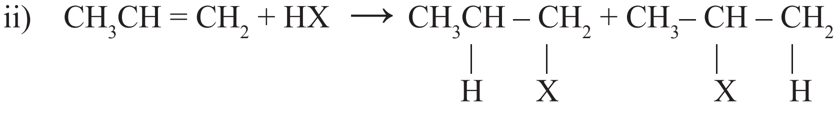
Fluoro compounds are not prepared by this method due to high reactivity of fluorine

d) From Primary amines (Sandmeyer's reaction) :



e) From alkenes :

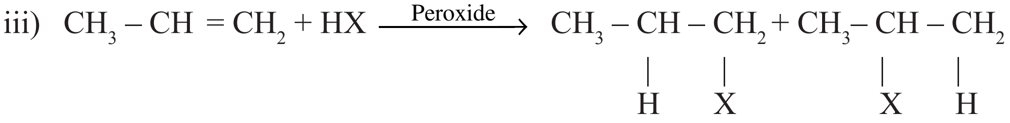
i) $CH_2 = CH_2 + HX \longrightarrow CH_3CH_2 - Cl$



ii) $CH_3CH = CH_2 + HX \longrightarrow \underset{\displaystyle H}{\underset{|}{CH_3CH}} - \underset{\displaystyle X}{\underset{|}{CH_2}} + CH_3 - \underset{\displaystyle X}{\underset{|}{CH}} - \underset{\displaystyle H}{\underset{|}{CH_2}}$

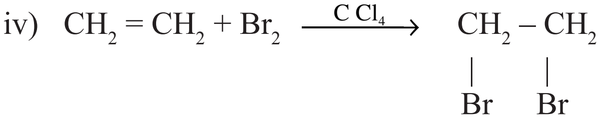
(minor) (major)

Addition of haloacids (HX) follows Markovnikovs



iii) $CH_3 - CH = CH_2 + HX \xrightarrow{\text{Peroxide}} CH_3 - \underset{\displaystyle H}{\underset{|}{CH}} - \underset{\displaystyle X}{\underset{|}{CH_2}} + CH_3 - \underset{\displaystyle X}{\underset{|}{CH}} - \underset{\displaystyle H}{\underset{|}{CH_2}}$

(major) (minor)



iv) $CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\displaystyle Br}{\underset{|}{CH_2}} - \underset{\displaystyle Br}{\underset{|}{CH_2}}$

(vic-dibromide)

f) By halogen exchange :

$RX + NaI \longrightarrow R-I + NaX$

(X = Cl, Br)

$H_3C-Br + AgF \longrightarrow H_3C-F + AgBr$

(Swarts reaction)

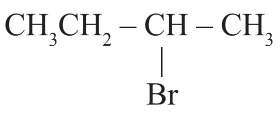
6) **Physical properties :** Alkyl halides all colourless when pure. Many volatile halogen compounds have sweet smell.

Due to greater polarity of C–X bond boiling points of chlorides, bromides and iodides are considerably higher than those of hydrocarbons of comparable molecular mass.

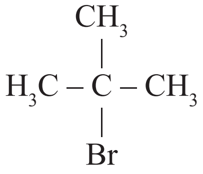
For the same alkyl groups the boiling points of alkyl halides decreases in the order, RI>RBr>RCl>RF.

The boiling points of isomeric haloalkanes decreases with increase in branching.

$CH_3CH_2CH_2CH_2Br$



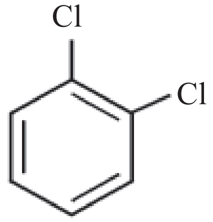
$CH_3CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$

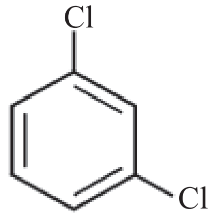


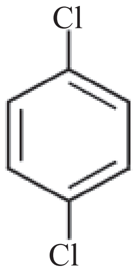
$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$

b.p/k	375	364	346

The symmetry of para isomers fits in crystal lattice than that of ortho– and metaisomers and that is why the melting point of para-isomers are comparatively high.







b.p/k	453	446	448
m.p/k	256	249	323

Density of haloalkanes increases with increase in number of carbon atoms, halogen atoms and atomic mass of halogen atoms.

Haloalkanes are very slightly soluble water.

7) **Chemical Reactions :**

a) Nucleophilic substitution reaction :

It is one of the most useful type of reaction of alkylhalides in which halogen is bonded to sp^3 hybridised carbon.

$$R-X + Nu^- \longrightarrow R-Nu + X^-$$

$R - X + NaOH / KOH \longrightarrow R - OH + NaX / KX$

$R - X + H_2O \longrightarrow R - OH + HX$

$R - X + NaOR' \longrightarrow R - OR' + NaX$

$R - X + I^- \longrightarrow R - I + X^-$

$R - X + NH_3 \longrightarrow R - NH_2 + HX$

$R - X + KCN \longrightarrow R - CN + KX$

$R - X + AgCN \longrightarrow R - NC + AgX$

$R - X + AgNO_2 \longrightarrow R - NO_2 + AgX$

$R - X + LiAlH_4 \longrightarrow R - H$

Cyanides and nitrites group possess two nucleophilic centres and are called ambident nucleophiles. Ambident mucleophile is a group which can act as a nucleophile in two different ways.

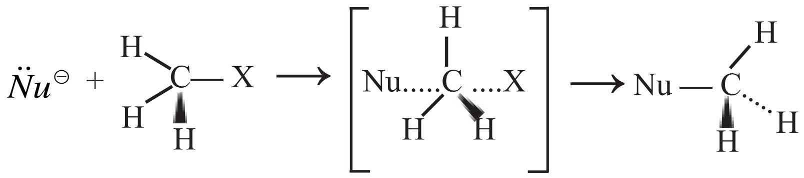
$$\left[{}^{\ominus}C \equiv N \leftrightarrow : C = N^{\ominus}\right]$$

$$\left[{}^{-}O - \ddot{N} = O\right]$$

These substitution reactions has been found to proceed by two different mechanisms.

i) Substitution nucleophilic bimolecular (S_N2) :

These type of reaction follows second order kinetics i.e the rate of the reacion depends upon the concentration of both the reactants. The incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break while forming a new carbon–OH bond. These two processes take place simultaneously in a single step and no intermidiate is formed. As this happens the configuration of carbon atom under attack inverts and that is why this process is called as inversion of configuration.



The order of reactivity followed as :

Primary halide > Secondary halide > Tertiary halide.

ii) Substitution nucleophilic unimolecular (S_N1) :

S_N1 reactions are genearlly carried out in polar protic solvents (like water, alcohol, acetic acid etc.) These type of reactions follows first order kinetics i.e the rate of the reaction depends upon the concentration of only alkylhalide.

It occurs in two steps. In step-I, the polarised C–X bond undergoes slow cleavage to produce a carbocation and a halide ion . In step-II, the carbocation is attacked by nucleophile to complete the reaction.

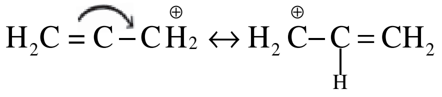
$$(CH_3)_3C-X \xrightleftharpoons{\text{Step-I}} (CH_3)_3\ C^{\oplus} + X^{\ominus}$$

$$(CH_3)_3C^{\oplus} + \ddot{N}u^{\ominus} \xrightarrow{\text{Step-II}} (CH_3)_3CNu$$

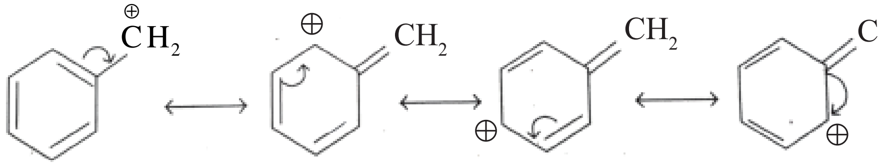
Step-I is slowest and reversible. Rate of reaction depends on step-I as it is slowest step. The order of reactivity follows as :

Tertiary halide> Secondary halide> Primary halide.

Allylic and benzylic halides show high reactivity towards S_N1 reaction. The carbocation thus formed gets stabilised through rasonance as shown bellow :



$$H_2C=C-\overset{\oplus}{C}H_2 \leftrightarrow H_2\overset{\oplus}{C}-\underset{H}{C}=CH_2$$



For a given alkyl group, the reactivity of the halide, R–X, follows the same order in both the mechanisms, R–I > R – Br > R – Cl > R – F

iii) Stereochemical aspects of nucleophilic substitution reactions :

Some basic stereochemical principles and notations are :

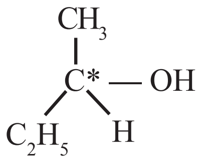
Optical activity : The compounds which can rotate plane polarised light when it is passed through their soluions are called optically active copounds.

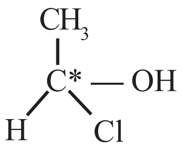
If the compound rotates the plane polarised light clockwise i.e. to the right side, it is called dextrorotatory or the *d* form and is indicated by placing a positive (+) sign before the degree of rotation.

If the light is rotated anticlockwise i.e to the left side, the compound is called leavorotatory or the *l* form and *a* negative (–) sign is placed before the degree of rotation. Such (+) and (–) isomers of a compound are called optical isomers and the phenomenon is termed as optical isomerism.

Chirality : An object or molecule which is non-superimposable on its mirror image is called chiral object or molecule and the property is known as chirality. While the objects which are superimposable on their mirror images are called achiral.

Asymmetric carbon : If all the four groups or atoms attached to a tetrahedral carbon are different, the carbon atom is called asymmetric carbon.



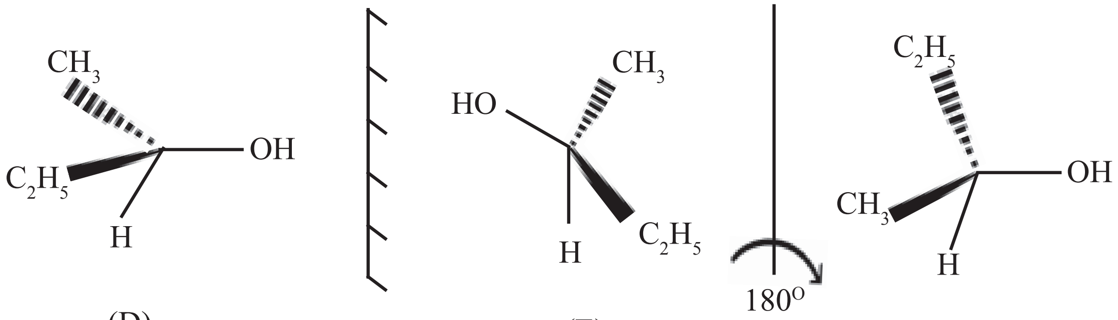


Asymmetric carbon is generally indicated by asterisk as C*.

Asymmetric carbons present in a molecule is called stereocentre also.

The stereo-isomers which are non superimposable mirror images are called enantiomers.

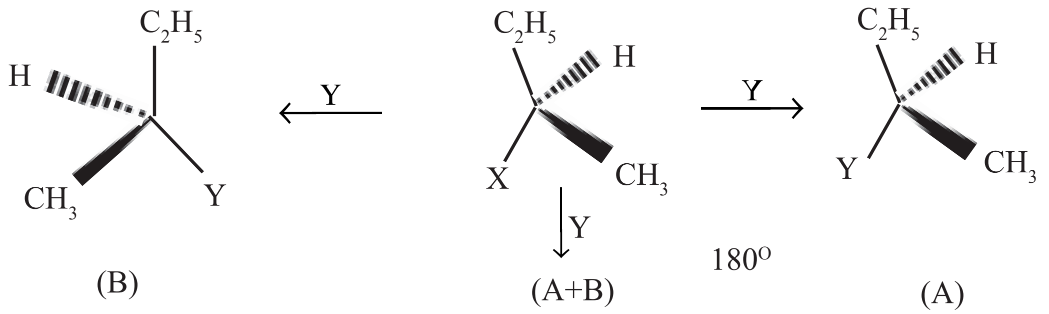
Enantiomers possess identical physical properties namely melting point, boiling point, refractive index etc. They only differ with respect to the rotation of plane polarised light.



(D) (E) (F)

1. **Inversion, retention racemisation :**

There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by group Y in the following reaction.



If (A) is the only compound obtained, the process is called retention of configuration.

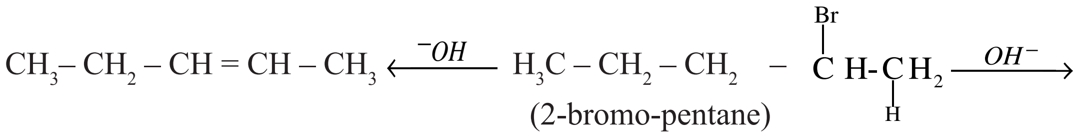
If (B) is the only compound obtained, the process is called inversion of configuration.

If a 50 : 50 mixture of A and B is obtained, the process is called racemisation and the product is optically inactive.

2. **Elimination reactions :**

When haloalkanes with β-hydrogen atom is heated with alcoholic KOH solution, there is elimination of H-atom from β - carbon and a halogen (X) atom from α - carbon atom. As result an alkene is formed. It is often called β - elimination,

β - elimination follows Saytzeff rule.



$$CH_3-CH_2-CH=CH-CH_3 \xleftarrow{^{-}OH} H_3C-CH_2-CH_2 - \overset{Br}{C}H-\underset{H}{C}H_2 \xrightarrow{OH^-}$$

(2-bromo-pentane)

$H_3C-CH_2-CH=CH-CH_2+ \ H_3C-CH_2\ CH_2-CH=CH_2$

(Pent - 2 - ene) 81% (major)   (Pent - 1 - ene) 19% (minor)

3. **Reaction with metals :**

i) Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds and are known as organo-metallic compounds. Victor Grignard in 1900 discovered alkyl magnesium halide, RMgX reffered as Grignard Reagents.

$CH_3CH_2\ Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2\ Mg\ Br$ (Grignard reagent)

In Grignard reagent the carbon-magnesium bond is covalant but highly polar and that is why Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons.

$$RMgX + H_2O \longrightarrow R{-}H + Mg\,(OH)\,X$$

ii) Wurtz reaction : Alkyl halides react with sodium metal in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.

$$2\,RX + 2\,Na \xrightarrow{\text{dry ether}} R{-}R + 2\,NaX$$

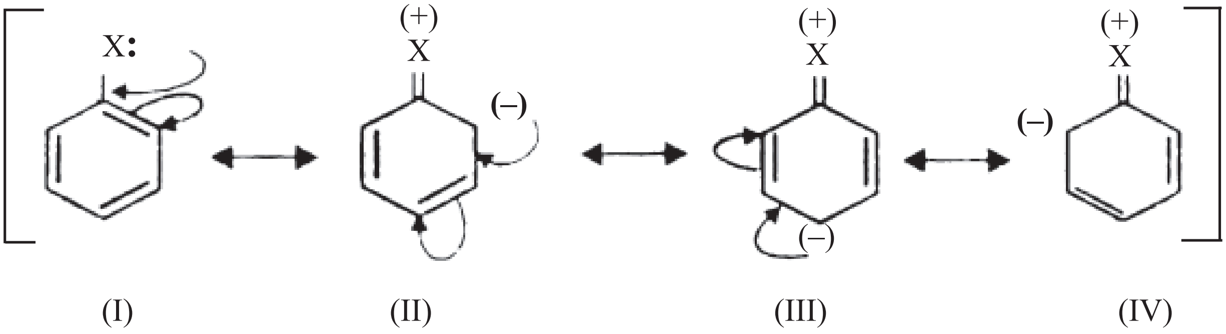
8) **Reaction of haloarenes :**

In haloarenes the halogen atom is bonded to sp^2 hybridised carbon and that is why haloarenes are less reactive than haloalkanes.

Reactivity of C–X bond is haloarenes decreases due to :

i) Hybridisation : Single bond length between sp^2 carbon atom and halogen atom is shorter than that of sp^3 carbon atom and halogen single bond.

ii) Resonance : The C–X bond in haloarenes acquires a partial double bond character as haloarenes are resonance hybrid of various resonating structures :



iii) Polarity of C–X bond : C–X bond in haloarenes are less polar than that of haloalkanes.

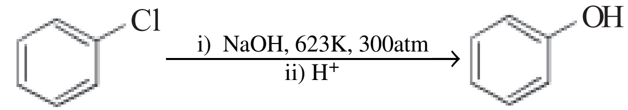
iv) Instabilty of phenyal cation : By self ionisation of haloarenes phenyal cation is formed, which will not be stabilised by resonance and therefore S_N1 mechanisam is ruled out.

v) Electron rich nucleophile cannot approach electron rich haloarenes due to high repulsion.

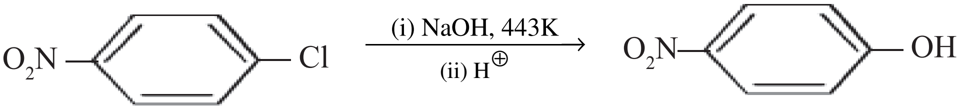
The reactivity towards nucleophiles is enhanced in presence of electron withdrawing substituents on the benzene ring at ortho and para-position.

a) Nucleophilic substitution :

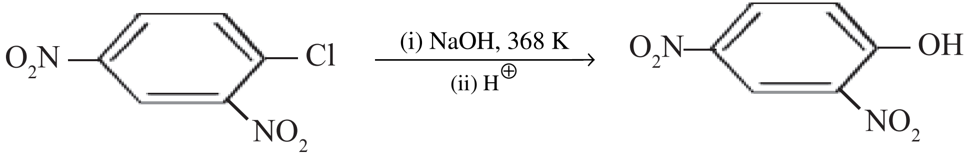
Some important reactions are :



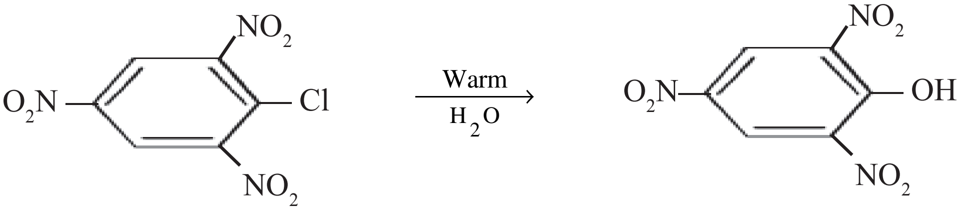
(Chlorobenzene) (Phenol)



(para chloronitrobenze) (p-nitrophenol)



(2, 4, dinitrochlorobenze) (2, 4, dinitrophenol)

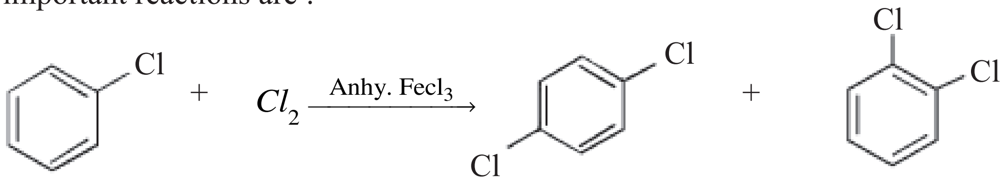


(2, 4, 6, trinitrochlorobenze) (2, 4, 6, trinitrophenol)

2) **Electrophilic Substitution reactions :**

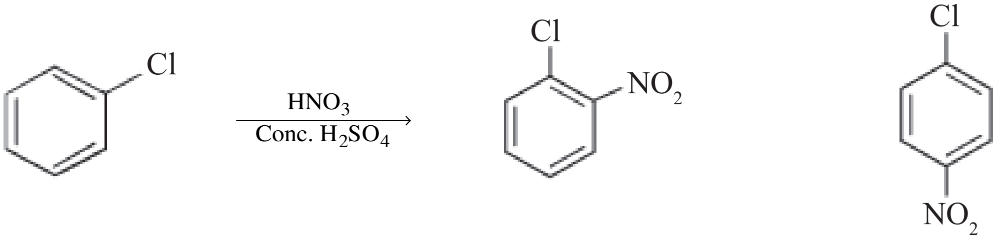
Some important reactions are :

(i)



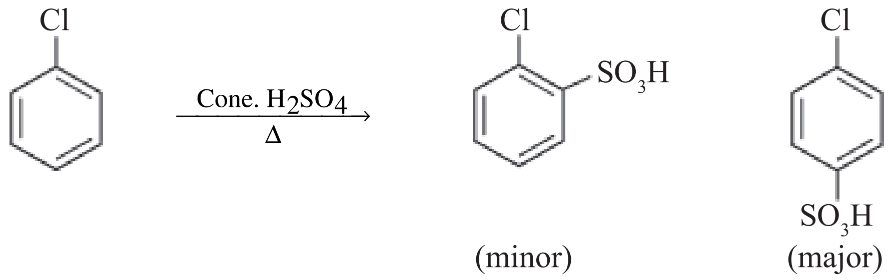
(chlorobenzene) (p-dichlorobenze) (major) (orthodichloobenzene) (minor)

(ii)

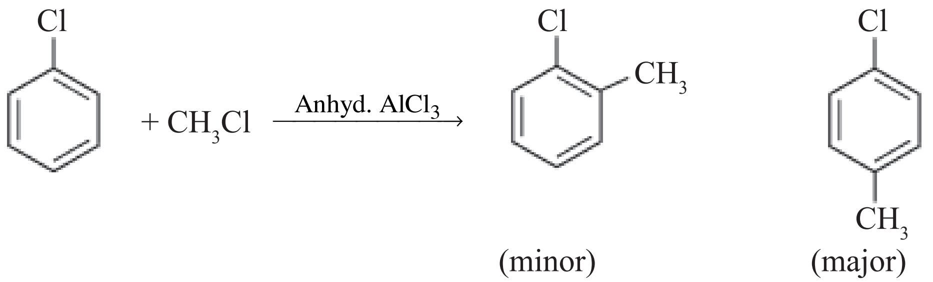


(minor) (major)

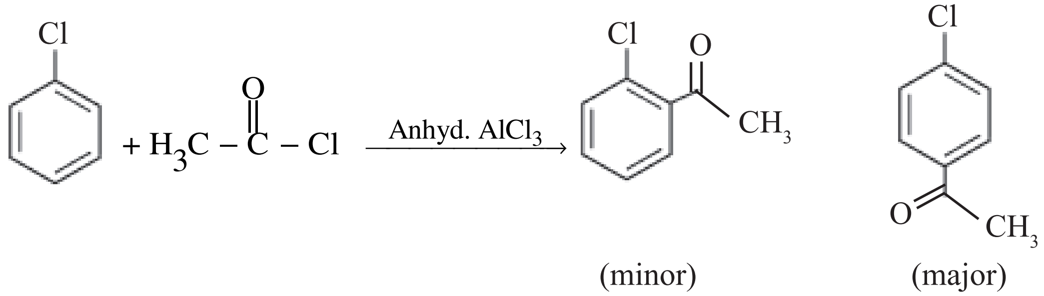
(iii)



(iv) Friedel Crafts alkylation :

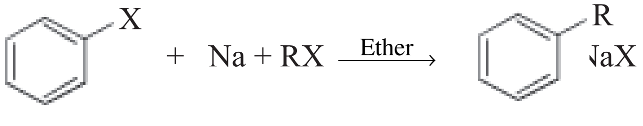


(v) Friedel Crafts acylation :

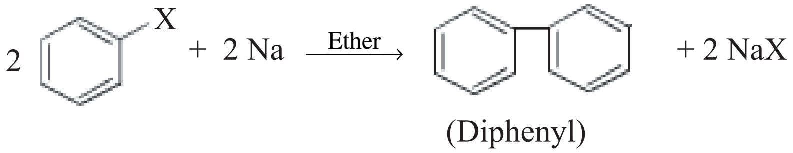


3. **Reaction with metals :**

i) Wurtz Fitting reaction :



ii) Fitting reaction :



9) **Polyhalogen compounds :**

Some important polyhalogen compounds are :

a) Dichloromethane (CH_2Cl_2) : It is widely used as a point remover, as propellant in aerosols, as a process slvant in the manufacture of drugs, as a metal cleaning and finishing solvant.

Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numness in the finger and toes.

b) Trichloromethane (Chloroform) : Chemically Chloroform is employed as a solvant far fats, alkanoids, iodine and other substances. It is also used to prepare refrigerant freon-22.

Chloroform is slowly oxidised by air in the presence of light to an extremly poisonous gas, carbonyl chloride also known as phosgene.

$$2\ CHCl_3 + O_2 \xrightarrow{\text{light}} 2\ COCl_2 + 2\ HCl$$

(chloroform) (phosgene)

c) Triiodomethane (Iodoform) : It was used earlier as an antiseptic but due to its objectionable smell, it has been replaced by other formulation containing iodine.

d) Tetrachloromethane (Carbontetrachloride) : It is used as solvent, as feedstock in the synthesis of CFC's and other chemicals. There is some evidence that exposure to CCl_4 causes liver cancer in human, can make the heart beat irregularly or stop.

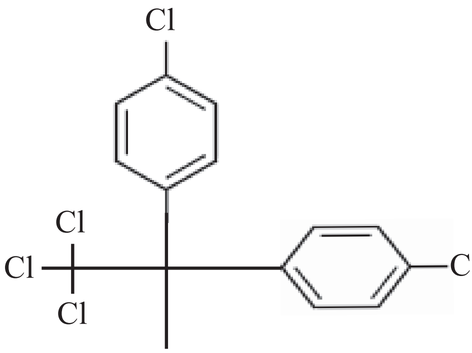
e) Freons : The chlorofluorocarbn compounds of methane and ethane are collectively known as freons.

They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.

Freon-12 (CCl_2F_2) is manufactured from tetrachloromethane by swarts reaction.

Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere Freon is able to initiate radical chain reactions that can upset the natural ozone balance.

f) p,p′-Dichlorodiphenyl-trichloro ethane (DDT) : It is the first chlorinated organic insecticide. After world War II its use was enormously increased to kill mosquito which spreads malaria and lice which carry typhus. DDT is extremely stable compound and is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. The use of DDT was banned in the United States in 1973.



(DDT)

A) Choose the correct answer (MCQ) : [Each quesion carries 1 mark]

1) Which halaogen compound would undergo S_N2 reaction faster?

a) 

b) 

c) 

d) 

2) The IUPAC name of $CH_2 = CHCH_2Br$ is

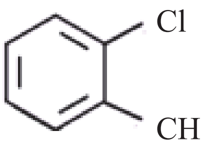
a) 1- bromopropane

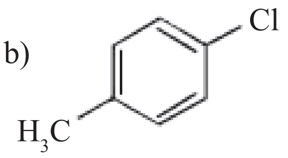
b) 3- bromopropane

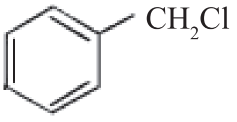
c) 1- propene-3 bromide

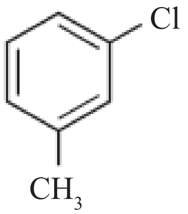
d) 3- bromo-1-ene

3) Structure of Chlorophenylmethane is

a) 

b) 

c) 

d) 

4) Which one is a 3° haloalkane ?

a) $(CH_3)_2\ C(Br)\ CH_2CH_3$ b) $(CH_3)_2\ CHCH(Br)\ CH_3$

c) $CH_3CH_2CH\ (Br)\ CH_3$ d) $(CH_3)_3\ C\ CH_2\ Br$

5) The halogenated compound used in the treatment of typhoid fever is

a) chloramphenicol b) chloroquine

c) halothane d) chloroethane

6) The major product X in the following reaction is–

$$CH_3CH_2\ CH = CH_2 \xrightarrow[\text{Peroxide}]{\text{HI}} X$$

a) $CH_3CH_2CH\ I\ \ CH_3$ b) $CH_3CH_2CH_2CH_2\ I$

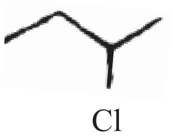
c) $I\ CH_2CH =\ CH_2$ d) $CH_3\ CH\ I\ \ CH_2CH_3$

7) Chlorobezene can be obtained from benzene diazonium chloride by

a) Wurtz reaction b) Fittig reaction

c) Gatterman's reaction d) Swarts reaction

8) In the following halogen compounds which compound undergoes S_N1 reaction faster?

a)


b)


c)


d)


9) C – X bond is strongest in which of the following compounds?

a) CH_3F b) CH_3Br

c) CH_3I d) CH_3Cl

10) The correct decreasing order of dipole moment is–

a) CH_3F, CH_3Cl, CH_3Br, CH_3I b) CH_3Cl, CH_3Br, CH_3I, CH_3F,

c) CH_3I, CH_3Br, CH_3Cl, CH_3F d) CH_3Cl, CH_3F, CH_3I, CH_3Br

11) The IUPAC name of ethylidene chloride is–

a) Ethane-1, 2 – dichloride   b) 1,2 - dichloroethane

c) 1, 1- dichloroethane   d) 2, 2 - dichloroethane

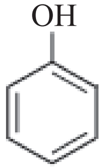
12) The boiling points of haloalkanes follow the order

a) RCl > R Br > RI   b) RI > RBr > RCl

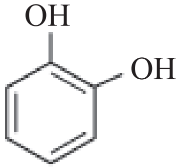
c) RI > RCl > RBr   d) RBr > RI > RCl

13) Chlorobenzene on heating with aqueous sodium hydroxide solution at 623 K and pressure of 300 atomospheres yields.

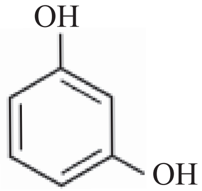
a)



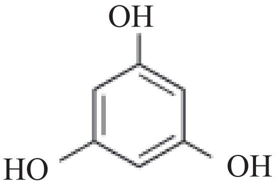
b)



c)



d)



14) The reaction :

$Ph{-}X + Na + RX \xrightarrow{\text{Ether}} Ph{-}R + NaX$ is called

a) Fittig reaction   b) Wurtz reaction

c) Wurtz - Fittig reaction   d) Swarts reaction

15) The reaction :

$RX + NaI + RX \xrightarrow[\text{Reflux}]{\text{Acetone}} RI + NaX$ is called

a) Finkelstein reaction   b) Gatterman reaction

c) Mendius reaction   d) Swarts reaction

16) Which reagent will you use for the following reaction ?

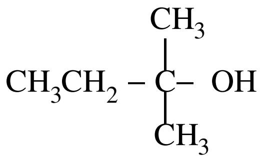
$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHCl\,CH_3$

a) Cl_2 gas in dark   b) Cl_2 gas in the presence of iron in dark

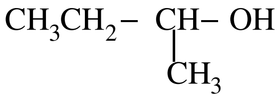
b) $NaCl + H_2SO_4$ d) Cl_2 / Uv light

17) Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

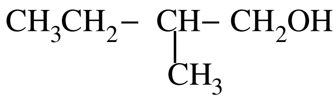
a) $CH_3CH_2CH_2OH$

b) 

$CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH$

c) 

$CH_3CH_2-\underset{CH_3}{CH}-OH$

d) 

$CH_3CH_2-\underset{CH_3}{CH}-CH_2OH$

18) Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is–

a) Electrophilic elemination reaction

b) Nucleophilic substitution reaction

c) Free radical addition reaction

d) Electrophilic substitution reaction

19) A primary alkyl halide would prefer to undergo–

a) S_N^1 reaction b) S_N^2 reaction

c) Recemisation d) α-Elemination

20) Ethylidene chloride is an–

a) gemdihalide b) vicdihalide

c) allylic halide d) vinylic halide

B) Very short answer type questions : (Each question carries 1 mark)

1) Why is chloroethane insoluble in water?

2) Which alkyl halide has the highest density?

3) An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure?

4) Arrange the following in order of increasing reactivity in nucleophilic substitution reaction.

CH_3F, CH_3I, CH_3Br, CH_3Cl

5) Out of ethylbromide and bromobenzene which can be more easily hydrolysed?

6) What is racemization?

7) Give one example of Wurtz-Fittig reaction

8) What is BHC? Give one use.

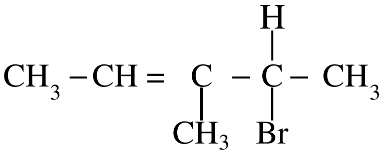
9) What is DDT? Give one use.

10) What effect should the following resonance of vinylchloride have on its dipole moment?

$$CH_2{=}CH{-}Cl \leftrightarrow {}^{\ominus}CH_2{-}CH{=}Cl^{\oplus}$$

11) Give two examples of chloro insectisides.

12) Give IUPAC name of the following organic compound.



$$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_3$$

13) What is the function of anhydrous $AlCl_3$ in chlorination of benzene?

14) Out of chlorobenzene and chloromethane, which one is more reactive towards nucleophilic substitution reactions?

15) A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon.

16) What is phosgene? How do you obtain it?

17) What are ambident nucleophiles?

18) Give one chemical test to distinguish between C_2H_5Br and PhBr.

19) What happens when CH_3Br is treated with KCN?

20) What product is obtained when toluenc is treated with Cl_2 in presence of light?

C) **Assertion and Reason type questions : (each question 1 mark)**

The questions given bellow consist of an Assertion and the Reason. Use the following key to choose the approprite answer.

a) Both assertion and reason are CORRECT and reason is the correct explanation of the assertion.

b) Both assertion and reason are CORRECT but the reason is non the correct explanation of the assertion.

c) Assertion is correct but reason is incorrect.

d) Assertion is incorrect but reason is correct.

1. Assertion : S_N^2 reaction proceeds with inversion of confioguration.

   Reason : S_N^2 reaction occur in one step.

2. Assertion : Ethanol gives iodoform test while methanol does not.

   Reason : Ethanol is less reactive than methanol towards nucleophilic addition reactions.

3. Assertion : The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.

   Reason : Vinyl group is electron donating group.

4. Assertion : Ethyl bromide can easily be hydrolysed than bromobenzene.

   Reason : Ethyl bromide is an haloalkane.

5. Assertion : Chloroethane is insoluble in water.

   Reason : Chloroethane can't form hydrogen bond with water.

6. Assertion : Haloalkane react with KCN to form alkyl cyanides.

   Reason : KCN is mainly covalent in nature.

7. Assertion : Grignard reagents should be prepared under dry condition.

   Reason : Grignard reagents easily undergo hydrolysis to farm alkanes.

8. Assertion : H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide.

   Reason : H_2SO_4 converts KI to corresponding HI and than oxidises it to I_2.

9. Assertion : Chloroform is used as an anaesthetic

   Reason : On reduction chloroform produces phosgene, which is potentially fatal.

10. Assertion : CH_3CHCl_2 gives yellow ppt. in 2, 4 - DNP test.

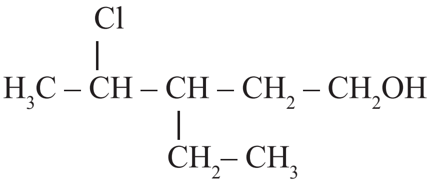
    Reason : CH_3CHCl_2 is a geminal dihalide.

D) Short answer type questions : (Each question carries 2 marks)

1) Write IUPAC names of the following compounds.

i) 

$BrCH_2 - \underset{OH}{\underset{|}{CH}} - CH_2 - CH_2Cl$

ii) 

$H_3C - \overset{Cl}{\overset{|}{CH}} - \underset{CH_2-CH_3}{\underset{|}{CH}} - CH_2 - CH_2OH$

2) Write the structures of the following compounds

i) 4-Bromo-3-methylpent-2-ene

ii) 1, 4-D Dibromobut -2-ene

3) Which one of the following has the highest dipole moment? Why?

a) CH_2Cl_2 b) $CHCl_3$ c) CCl_4

4) What are ambident nucleophiles? Explain with an example.

5) Explain why–

i) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

ii) Grignard reagents should be prepared under anhydrous condition?

6) Arrange the compounds of each set in order of reactivity towards S_N^2 displacement.

i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane.

7) Arrange the following in the order of increasing density :

i) $CHCl_3$, CH_2Cl_2, CCl_4, CH_3Cl

i) C_2H_5Cl, C_2H_5I, C_2H_5Br

8) Arrange the following in the order of increasing boiling points

i) bromobenene, chlorobenzene, iodobenzene

ii) n-pentylchloride, iso-pentylchloride, neo-pentylchloride.

9) What is enantiomer? Draw structures of possible enantiomers of 3-methylpent-1-ene.

10) State whether the following statements are true or false. Justify your answer.

   i) A molecule can be optically inactive despite having centres of chirality.

   ii) A racemic mixture cannot rotate the plane of plane polarized light.

11) Explain why–

   i) Haloalkanes are more reactive towards nucleophilic substitution reactions than haloarenes.

   ii) Alkylhalides, though polar, are immiscible with water.

12) Write the structure of major organic product in each of the following reactions.

   i) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$

   ii) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow$

13) How will you bring about the following conversions?

   i) Benzene to biphenyl

   ii) Bromomethane to propanone.

14) Give reagents, inorganic or organic, needed for the following conversions.

   i) Benzyl bromide to benzyl alcohol.

   ii) Benzyl bromide to benzyl cyanide.

15) What happens when

   i) A mixture of chloral and chlorobenzene is heated in the presence of concentrated H_2SO_4.

   ii) Ethyl chloride is treated with aqueous KOH.

16) The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are the major products. Explain.

17) Para-Dichlorobenzene has higher melting point than those of ortho and meta isomers. Discuss.

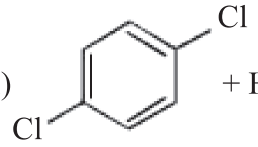
18) Out of chlorobenzene and ethylchloride which one is more reactive and why?

19) Account for the following

Nucleophilic substitution in aryl halides are facilitated by electron withdrawing groups while electrophilic substitutions are facilitated by electron releasing groups.

20) Write the structure of the major organic product in each of the following reaction.

i) $(CH_3)_3CBr + H_2O \xrightarrow{heat}$

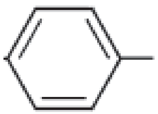
ii) 

$+ HNO_3 \xrightarrow{H_2SO_4}$

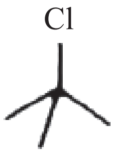
21) Write the reactions involved in–

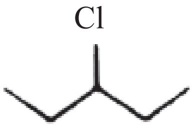
a) isocyanide test b) iodoform test.

22) Identify A and B in the following reaction.


$Br + Mg \xrightarrow{dry\ ether} A \xrightarrow{H_2O} B$

23) In the following pair of halogen compounds which compound undergo faster S_N1 reaction?



and


24) Write structures of different dihalogen derivatives of propane.

25) Write the equations for the preparation of 1-iodobutane from

a) 1 - butanol b) but - 1 - ene

26) Give the uses of–

Freon-12, DDT, Carbontetrachloride and iodoform.

E) Short answer type questions : (Each questions 3 marks)

1) Explain the following :

a) Vinylchloride is unreactive in nucleophilic substitution reaction.

b) Allylchloride is hydrolysed more readily than n-propylchloride.

2) Write short notes.

a) Gatterman reaction

b) Wurtz Fittig reaction.

3) What happens when,

   a) a haloalkane is boiled with alcoholic KOH

   b) a haloalkane is heated with Na-metal

   c) a haloalkane is treated with alcoholic potassium cyanide.

4) Write structures of the following compounds

   a) 4 - tert - butyl - 3 - iodo heptane

   b) 1 - Bromo - 4 - Sec - butyl - 2 - methylbenzene

   e) 2 - Bromo - 2 - methylbutane.

5) Among the isomeric alkanes of molecular farmula C_5H_{12}, identify the one that on photochemical chlorination yields,

   (i) A single monochloride.

   (ii) Three isomeric monochlorides.

   (iii) Four isomeric monochlorides.

6) Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanides as the chief product. Explain.

7) Although chlorine is an electron - withdrawing group, yet it is ortho–, para - directing in electrophilic aromatic substitution reaction. Why?

8) Write the isomers of the compound having farmula C_4H_9Br.

9) Which one of the following has highest dipole moment? Why

   a) CH_2Cl_2 b) $CHCl_3$ c) CCl_4

10) a) Explain the following reactions.

   $$\text{n- BuBr} + \text{KCN} \xrightarrow{\text{EtOH-H}_2\text{O}} \text{n BuCN}$$

   b) Convert ethylchloride into propanoic acid.

11) How the following conversions can be carried out?

   a) 1- Bromopropane to 2 - Bromopropane

   b) Benzene to 4 - Bromoinitrobenzene

   c) Aniline to Phenylisocyanide.

12) Write short notes on–

a) Sandmeyer's reaction

b) Wurtz reaction.

13) a) Haloalkanes and haloarenes are insoluble in water though they contain a polar C–X bond. Explain.

b) Convert 2 - methyl - 1 - propene into 2 - chloro - 2 - methyl propane.

14) Write the structure of major organic product in each of the following reactions.

a) $CH_3CH\,(Br)\,CH_2CH_3 + NaOH \xrightarrow{\text{Water}}$

b) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

c) $C_6H_5CH_2Cl + C_2H_5ONa \longrightarrow$

15) A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

16) Write chemical reactions for the preparation of the followings–

a) D.D.T from chlorobenzene

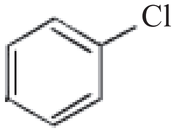
b) Freon - 12 from carbontetrachloride.

17) a) Why is trichloromethane stored in dark coloured bottles? Give reason with related equation.

b) Haloarenes undergo electrophilic substitution reaction at ortho– and para– position. Explain.

18) Identify A and B.

a) $CH_3CH = CH_2 \xrightarrow{\text{HBr}} A \xrightarrow{\text{aq. KOH}} B$

b) 

$\xrightarrow{\text{HBr}} A \xrightarrow{\text{aq. KOH}} B$

19) a) Complete the reaction

$CH_3CH_2Br + KOH\ (alc.) \longrightarrow$

b) Explain why the use of chloroform as anaesthetic is decreasing.

c) What happens when bromobenzene is treated with magnesium in the presence of dry ether?

20) Give Reasons :

a) C – Cl bond length in chlobenzene is shorter than the C – Cl bond length in $CH_3 – Cl$.

b) The dipole moment of chlorobenzene is lower than that of cyclohexylchloride.

c) S_N1 reactions are accompanied by racemization in optically active alkyl halides.

Answer

[A] Choose the correct answer (MCQ) :

(1) – c
(2) – b
(3) – c
(4) – a
(5) – a
(6) – b
(7) – c
(8) – c
(9) – a
(10) – d
(11) – c
(12) – a
(13) – a
(14) – c
(15) – a
(16) – d
(17) – b
(18) – d
(19) – b
(20) – a

[C] Assertion and Reason :

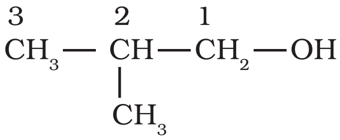
(1) – b
(2) – b
(3) – c
(4) – a
(5) – a
(6) – c
(7) – d
(8) – a
(9) – c
(10) – a

Chapter - 11

Alcohol, Phenol & Ether

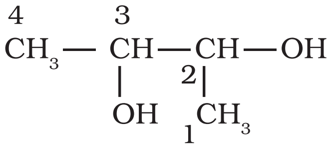
Chapter at a glance :

1. **IUPAC Nomenclature :**



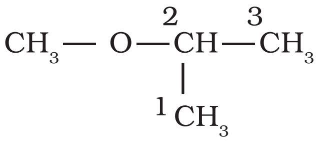
$$\overset{3}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_2}-OH$$

2- Methlyl Propanol



$$\overset{4}{CH_3}-\underset{OH}{\overset{3}{CH}}-\underset{\overset{1}{CH_3}}{\overset{2}{CH}}-OH$$

Butane-2, 3-di-ol



$$CH_3-O-\underset{\overset{1}{CH_3}}{\overset{2}{CH}}-\overset{3}{CH_3}$$

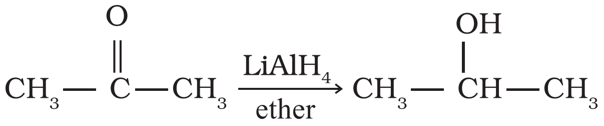
2-Methoxy butane

2. **Preparation of 1°2° & 3° alcohol from alkene, aldehyde, ketone and carboxylic acid. Preparation of phenol & ether.**

(a) $CH_2=CH_2 \xrightarrow{H_2O/H^+} CH_3CH_2OH$

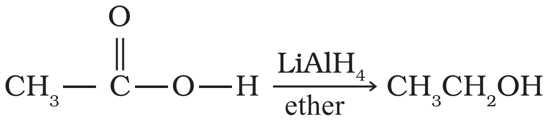
(b) $CH_2CHO \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2OH$

(c)



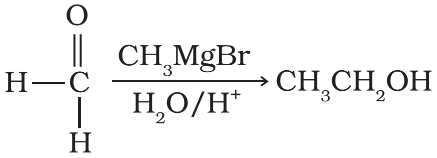
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{ether}]{LiAlH_4} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3$$

(d)



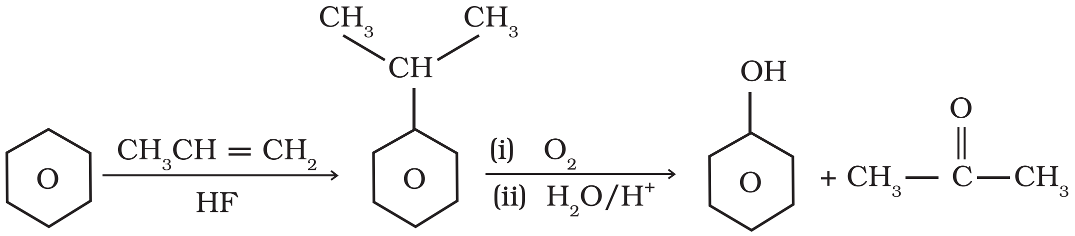
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2OH$$

(e)

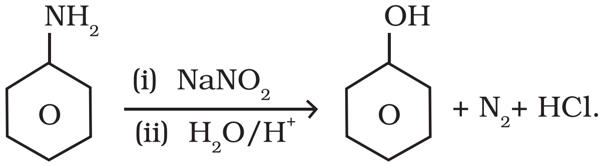


$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} \xrightarrow[H_2O/H^+]{CH_3MgBr} CH_3CH_2OH$$

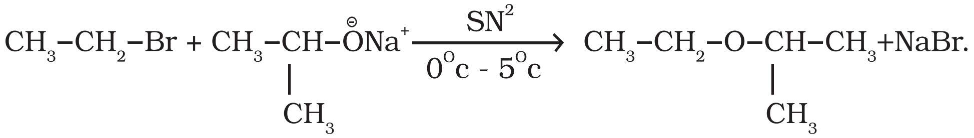
(f)



(g)



(h)



$$CH_3-CH_2-Br + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\ominus}{O}Na^+ \xrightarrow[0^{\circ}c\ -\ 5^{\circ}c]{SN^2} CH_3-CH_2-O-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3 + NaBr.$$

(i) $CH_3CH_2OH \xrightarrow[140^{\circ}C]{\text{conc. } H_2SO_4} CH_3CH_2\ O\ CH_2CH_3$

(j) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$

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

3. Chemical Reactions of Alcohol, Phenol & Ether :

(a) Aliphatic alcohol take part in the two types of chemical reaction.

1. Elimination Reaction
2. Nucleophilic Substitution Reaction

(b) Nucleophilic substitution reaction of phenol is comparatively difficult.

But Phenol can take part in the electrophilic substitution reaction.

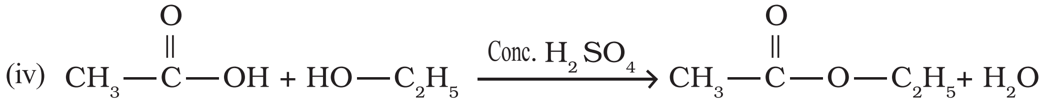
(c) Ether can take part in the nucleophilic Substitution Reaction.

- Some-important reactions of aliphatic alcohol are-

(i) $CH_3CH_2OH \xrightarrow[170^{O}C]{Conc.\ H_2SO_4} CH_2{=}CH_2 + H_2O$ (Elimination Reaction)

(ii) $CH_3CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$ (Nucleophilic Substitution)

(iii) $2CH_3CH_2OH + 2Na \longrightarrow 2CH_3{-}CH_2{-}O{-}Na + H_2$ (Reaction showing acidic nature)

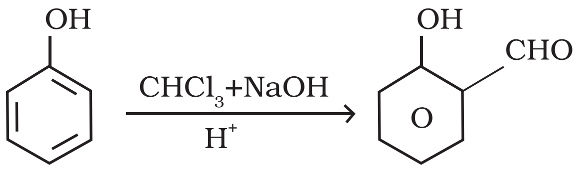
(iv) 

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + HO-C_2H_5 \xrightarrow{Conc.\ H_2SO_4} CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5 + H_2O$$

(Esterification Reaction)

- **Some important reactions of phenol**

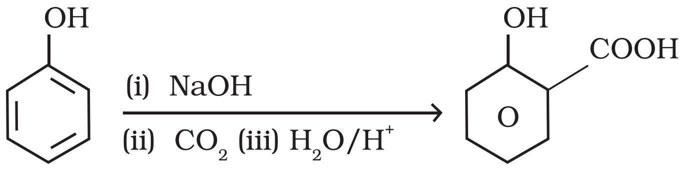
(i) Reimer Tiemann Reaction



Salicylaldehyde

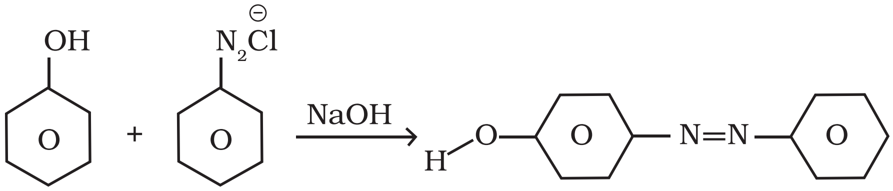
It is electrophilic subbstitution. Name of the electrophile is dichloro carbene ($:CCl_2$)

(ii) Kolbe Reaction.



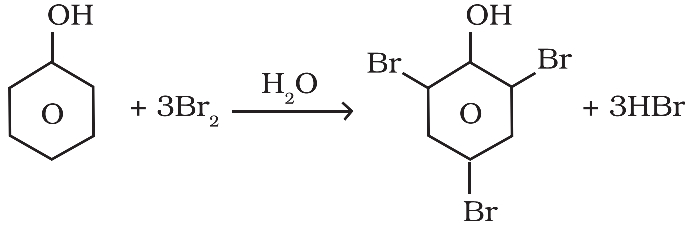
Electrophile is CO_2.

(iii) Coupling Reaction :



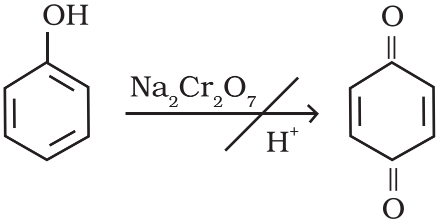
Electrophile is diazonium ion.

(iv)



white precipitate

(v)

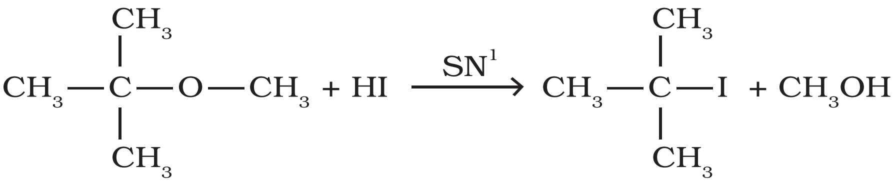


Alcohol, Phenol & Ether

- **Some important Reactions of ether.**

(i) $CH_3—CH_2—O—CH_3 \xrightarrow{SN^2} CH_3I + CH_3CH_2OH$

(ii)

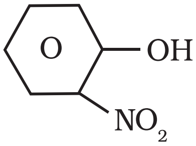
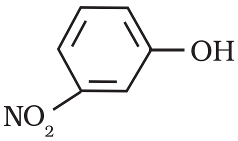
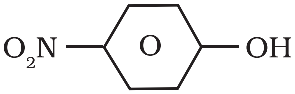


$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—O—CH_3 + HI \xrightarrow{SN^1} CH_3—\underset{CH_3}{\overset{CH_3}{C}}—I + CH_3OH$$

(iv) The mixture of anhydrous $ZnCl_2$ and conc. HCl is called Lucas reagent.

Primary alcohol does not react at room temperature.

A. Select the correct option (MCQ) : (Each question carries 1 mark)

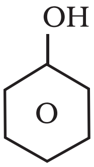
1. (i), Phenol (ii),  (iii),  (iv), 

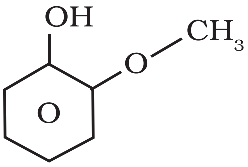
Correct order of acid character among the above compounds are-

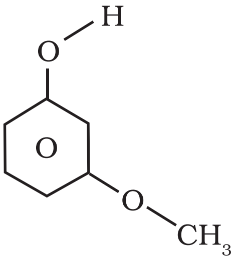
a) i > ii > iii > iv b) iv > ii > iii > i

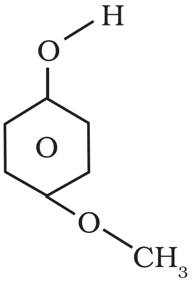
c) ii > iv > iii > i d) iii > iv > ii > i

2. Which of the following has the lowest pK_a value?

a) 

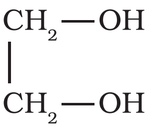
b) 

c) 

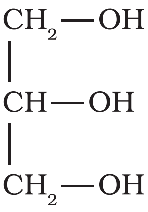
d) 

3. Maximum Boiling Point will be Shown by -

a) CH_3CH_2OH

b) 

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

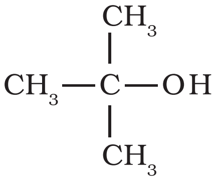
c) 

$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

d) $CH_3CH_2CH_2OH$

4. Out of following which one is more soluble in water -

a) $CH_3CH_2CH_2CH_2OH$

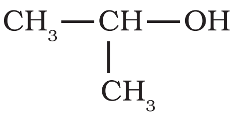
b) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$

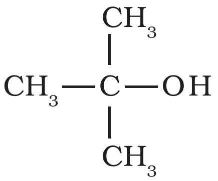
c) $CH_3CH\ (CH_3)\ CH_2OH$

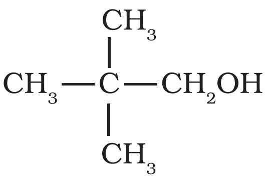
d) $CH_3CH_2CH_2OH$

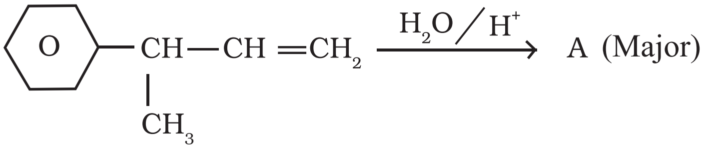
5. Maximum Reactirity of alcohol towards Sodium in the following is-

a) CH_3CH_2OH

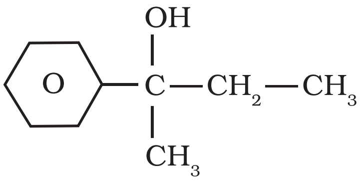
b) 
$CH_3-\underset{CH_3}{CH}-OH$

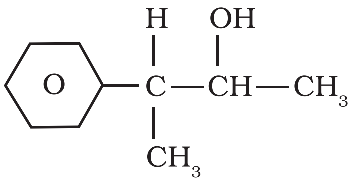
c) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$

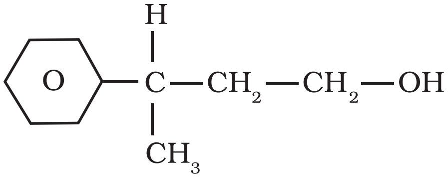
d) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$

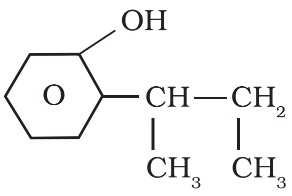
6. 

Product 'A' is -

a) 

b) 

c) 

d) 

7. 
$CH_3-CH=CH_2 \xrightarrow[\text{dil. } H_2SO_4]{} CH_3-\underset{OH}{CH}-CH_3$

The type of Reaction is-

a) Electrophilic addition Reaction

b) Nucleophilic addition Reaction

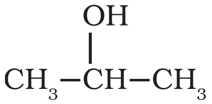
c) Electrophilic Substitution

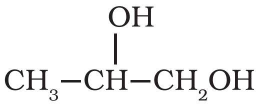
d) Nucleophilic Substitution

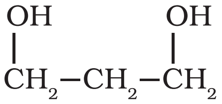
8. $CH_3 - CH = CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6}$ 'X'

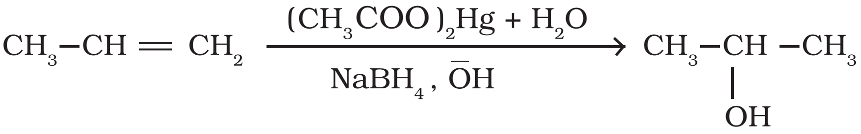
The Product 'X' is -

a) $CH_3CH_2CH_2OH$

b) 
$CH_3-\underset{}{\overset{OH}{\overset{|}{C}H}}-CH_3$

c) 
$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2OH$

d) 
$\overset{OH}{\overset{|}{C}H_2}-CH_2-\overset{OH}{\overset{|}{C}H_2}$

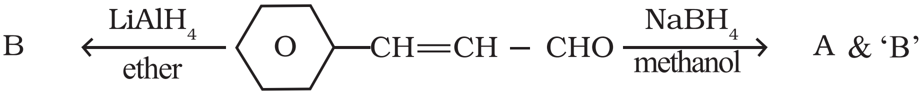
9. 
$CH_3-CH = CH_2 \xrightarrow[NaBH_4,\ \overline{O}H]{(CH_3COO)_2Hg + H_2O} CH_3-\underset{OH}{\underset{|}{C}H}-CH_3$ The Process is Known as -

a) Oxymercuration & Demercuration

b) Hydroboration

c) Hydration

d) None

10. 

A & B are-

a) 

b) Ph-CH=CH - CH_2OH & Ph-CH_2-CH_2-CH_2OH

c) Ph-CH_2-CH_2-CHO & Ph-CH_2CH_2CHO

d) Ph-CH=CH - CH_2OH (Both 'A' & 'B')

11. During the fermentation of cane-sugar it seerns to be boi ling -because

a) Brisk effervescence of $CO_2\uparrow$

b) O_2 gas is evolved out

c) Inert gas is liberated

d) Actually fermentation of Sugar is not Possible

12. Power alcohol is the mixture of

a) $C_2H_6 + C_2H_5OH$ + Petrol

b) CH_3 OH + Petrol

c) $C_6H_5CH_3 + C_2H_5OH$ + Petrol

d) $CHCl_3 + C_2H_5$-OH + Petrol

13. Grain alcohol is -

a) CH_3CH_2OH b) CH_3OH

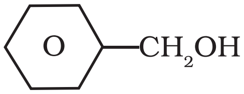
c) $(CH_3)_2CH\,OH$ d) $(CH_3)_3COH$

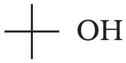
14. Lucas reagent is

a) $ZnCl_2 + HCl$ b) Anhydrous $Zncl_2$ & Concentrated HCl

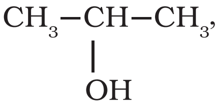
c) $HCl + POCl_3$ d) Concentrated H_2SO_4 Anhydrous HCl

15. The alcohol which responds in the Lucas test

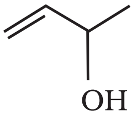
a) 

b) 

c) $CH_2{=}\,CH - CH_2 - OH$ d) All of these

16. (I) CH_3CH_2OH, (II) 

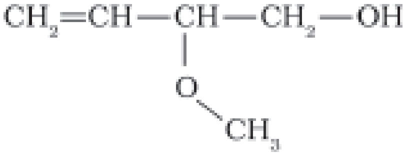
$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$,

(III)  , (IV) 

Correct order of rate of dehydration among -

a) III > II > I > IV b) III > IV > II > I

c) I > II > III > IV d) III > IV > I > II

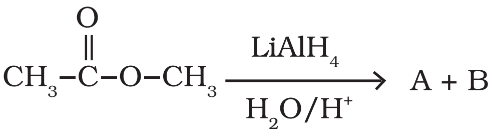
17. 

$CH_2{=}CH{-}\underset{\underset{\displaystyle O{-}CH_3}{|}}{CH}{-}CH_2{-}OH$

IUPAC name of the compound is -

a) But -2- ene -2- methoxy-1-ol *b) 2- Methoxy -2- butenol*

c) 2- Methoxy -3- butenol *d) None*

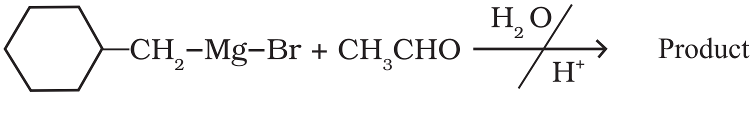
18. 

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_3 \xrightarrow[H_2O/H^+]{LiAlH_4} A + B$$

Products A & B are -

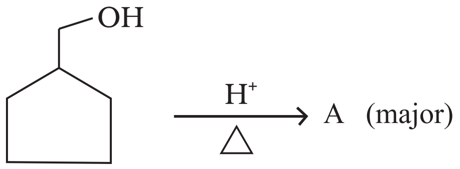
a) CH_3CH_2OH (Both A & B) b) CH_3CH_2OH and CH_3OH

c) CH_3CHO and CH_3OH d) CH_3CH_2OH and HCHO

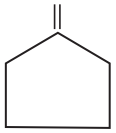
19. 

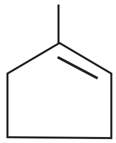
a) 1° alcohol (Primary alcohol) b) 2° alcohol (Secondary alcohol)

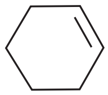
c) 3° alcohol (Tertiary alcohol) d) Allyl alcohol

20. 

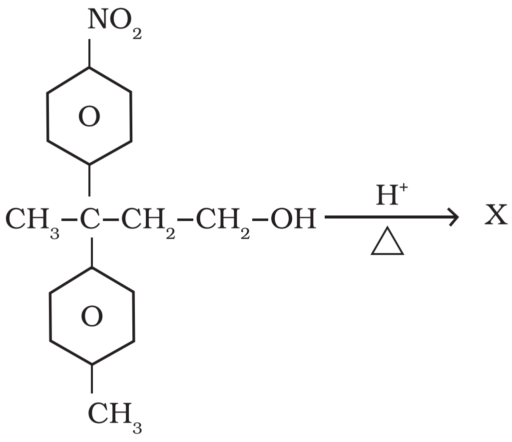
Product A is-

a) 

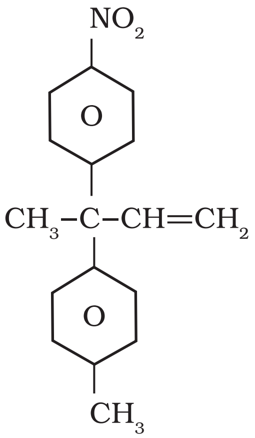
b) 

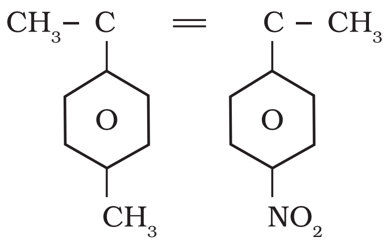
c) 

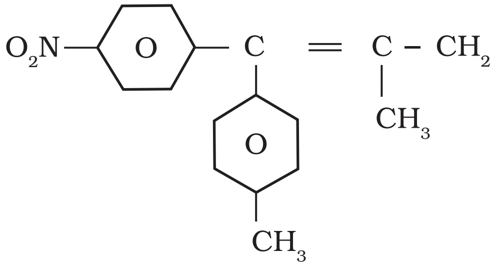
d) None.

21. 

Product ‘X’ is -

a) 

b) 

c) 

d) None.

22. Among the following alcohol which one is not get easily oxidised

a) CH_3CH_2OH b) $(CH_3)_2CHOH$

c) $(CH_3)_3COH$ d) $CH_2=CH-CH_2=OH$

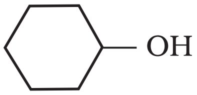
23. Correct order of esterification reaction among the alcohol are-

(i) CH_3OH , (ii) CH_3CH_2OH , (iii) $(CH_3)_2CHOH$, (iv) $(CH_3)_3COH$

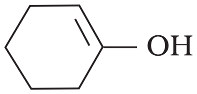
a) iv > iii > ii > i b) iii > iv > ii > i

c) i > ii > iii > iv d) iv > ii > iii > i

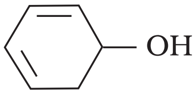
24. The correct order of ease of dehydration of the following is-



I



II



III

a) i > ii > iii b) iii > ii > i

c) i > iii > ii d) iii > i > ii

25. The correct order of reactivity of following alcohol with HBr is-

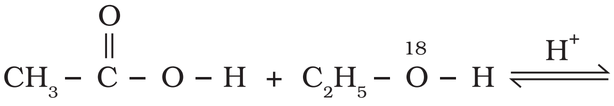
i) 1- Phenyl Propan -1-ol, ii) 1- Phenyl Propan -2-ol, iii) 3- Phenyl Propan -1-ol

a) iii > ii > i b) ii > iii > i

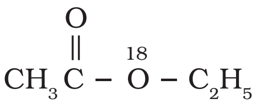
c) i > ii > iii d) ii > i > iii

26. A Polyhydric alcohol (molecular mass = 180) Polyhydric alcohol when react with acetic anhydride in presence of sodium acetate an ester is formed whose molecular weight is 390. Number of OH group in the poly hydric alcohol are -

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

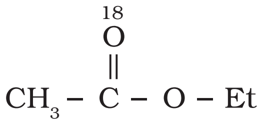
27. 

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + C_2H_5-\overset{18}{O}-H \overset{H^+}{\rightleftharpoons}$ ester Formula of ester is

a) 

$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{O}-C_2H_5$

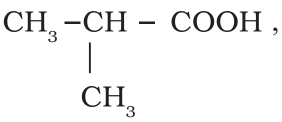
b) CH_3 COO Et

c) 

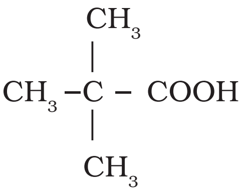
$CH_3-\overset{\overset{\displaystyle \overset{18}{O}}{\|}}{C}-O-Et$

d) None.

28. Reactivity order of correct scquence of mono carboxylic acids among the following towards a definite alcohol-

(i) HCOOH, (ii) CH_3COOH, (iii) 

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-COOH$,

(iv) 

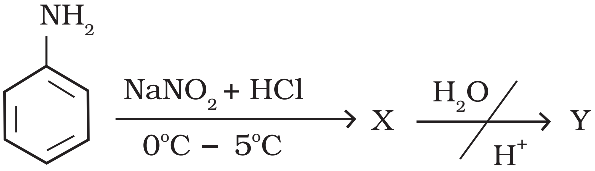
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-COOH$

a) i > ii > iii > iv

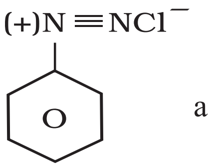
b) iii > iv > ii > i

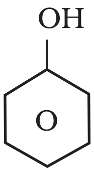
c) ii > iii > iv > i

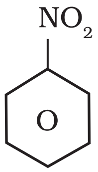
d) i > iii > ii > iv

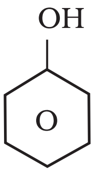
29. 

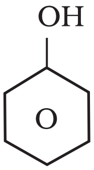
x and y are ...

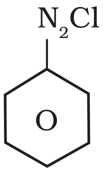
a) 

and 

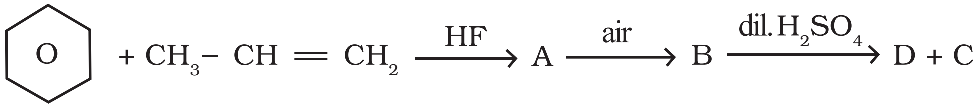
b) 

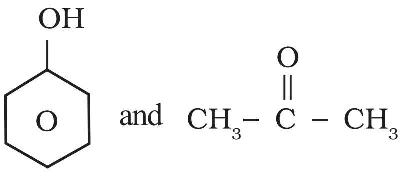
and 

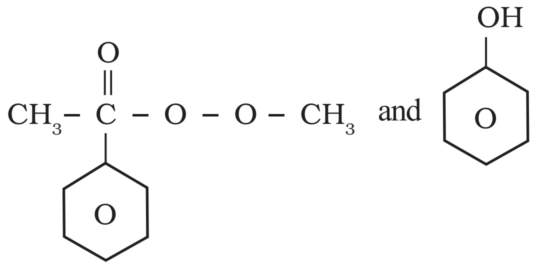
c) 

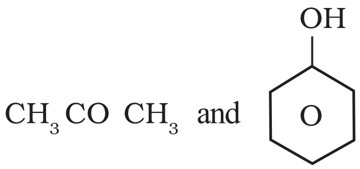
and 

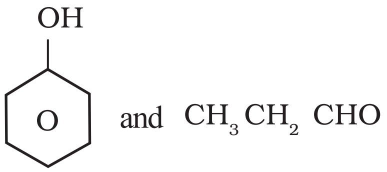
d) None.

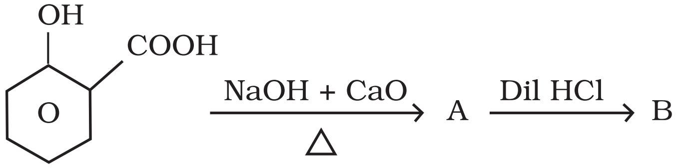
30. 

a) 

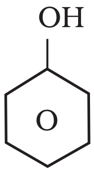
b) 

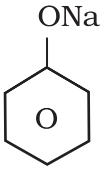
c) 

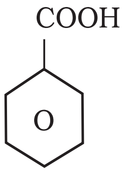
d) 

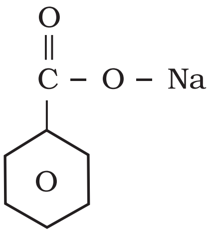
31. 

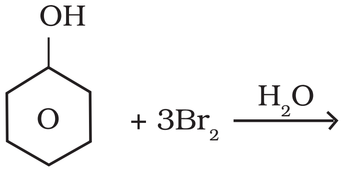
Final product 'B' is

a) 

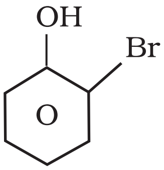
b) 

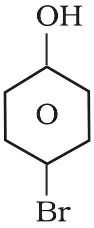
c) 

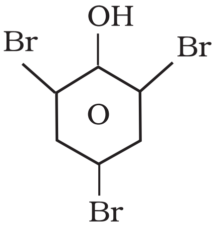
d) 

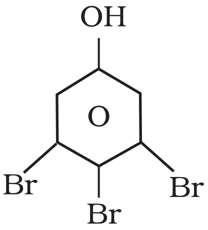
32. 

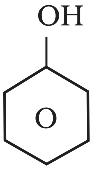
A white ppt is formed. White ppt is-

a) 

b) 

c) 

d) 

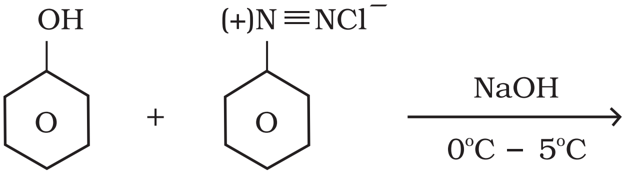
33.  + conc. HNO_3 + conc. $H_2SO_4 \rightarrow$ An acid stronger than phenol is formed. Stronger acid is-

a) o - Nitro Phenol

b) p - Nitro Phenol

c) m - Nitro Phenol

d) Picric acid

34.  An orange coloured azo compound is formed.

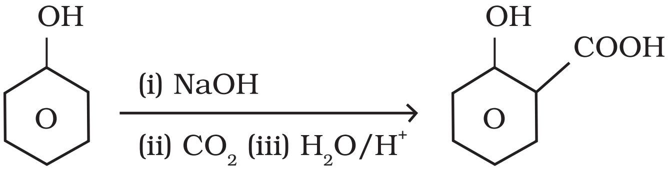
Name of the azo compound is

a) p - Hydroxy azobenzene

b) o - Hydroxy azobenzene

c) m - Hydroxy azobenzene

d) o- Amino Phenol.

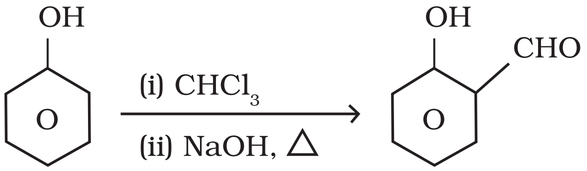
35.  Name of the electrophile in the above reaction is -

a) H^+

b) Na^+

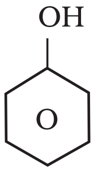
c) CO_2

d) H_3O^+

36. 

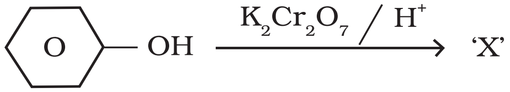
Name reaction is -

a) Kolbe Schimdt Reaction
b) Reimer tiemann Reaction
c) Coupling Reaction
d) Claisen Schimdt Reaction

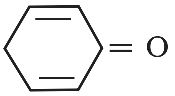
37. 

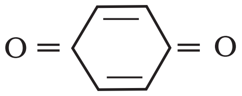
+ $FeCl_3$ (soln.) → A coloured complex will form. Colour of the complex is -

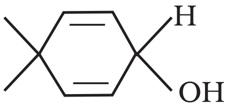
a) Pink
b) Violet
c) Red
d) Orange

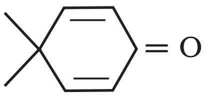
38. 

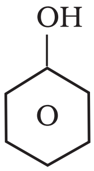
'X' is-

a) 

b) 

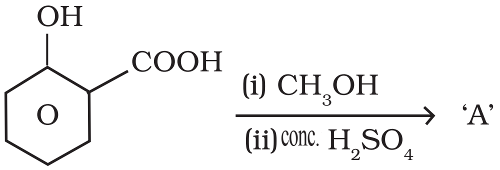
c) 

d) 

39. 

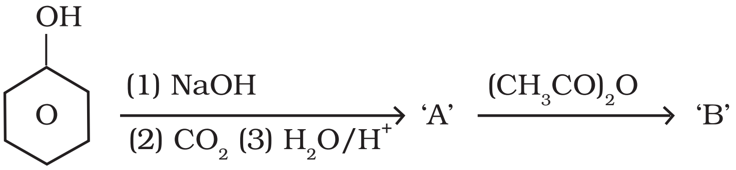
+ Pthalic anhydride → An indicator is formed, Name of the indicator is

a) Methyl orange
b) Methyl red
c) Phenol Phthalein
d) Red litmus paper.

40. 

Compound 'A' is -

a) Oil of winter green
b) Methyl Salicylate
c) Of characteristics smell of iodex
d) All the above.

41. 

compound 'A' & ' B' are -

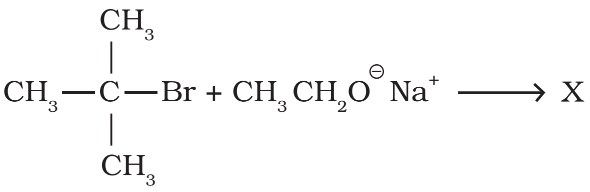
a) Salicylic acid and Aspirin
b) Salicylic aldehyde and Aspirin
c) Salicylic acid and Salol
d) Pthalic acid & Salol.

42. IUPAC name of the compound CH_3- O - CH_2- CH_2- OCH_3 is -

a) 1, 2- Diethoxy ethane
b) Dimethyl ether
c) Ethyl methyl ether
d) None

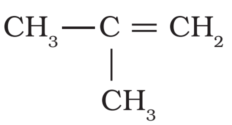
43. $CH_3CH_2OH \xrightarrow[\text{low temp.}]{H^+} CH_3CH_2-O-CH_2-CH_3$ The Type of reaction is -

a) Elimination Reaction
b) Nucleophilic Substitution
c) Electrophilic addition
d) Electrophilic Substitution

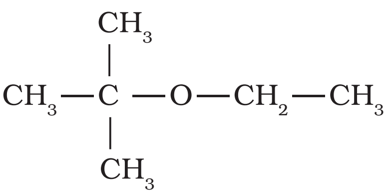
44. 

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + CH_3CH_2O^{\ominus}Na^{+} \longrightarrow X$

Major product 'X' is -

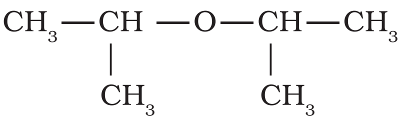
a) 

$CH_3-\underset{CH_3}{C}=CH_2$

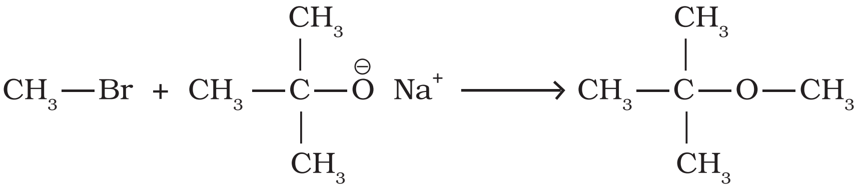
b) 

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_2-CH_3$

c) $CH_2 = CH_2$

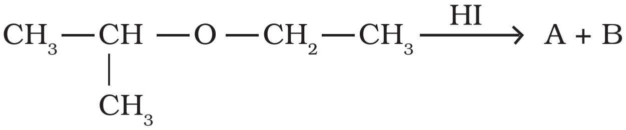
d) 

$CH_3-\underset{CH_3}{CH}-O-\underset{CH_3}{CH}-CH_3$

45. 
$CH_3-Br + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\ominus}{O}\ Na^+ \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3$

The Type of reaction is -

a) SN^1 b) SN^2 c) E^1 d) E^2

46. 
$CH_3-\underset{CH_3}{CH}-O-CH_2-CH_3 \xrightarrow{HI} A + B$

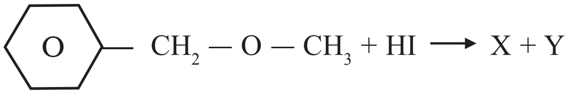
The Product 'A' & 'B' are -

a) $(CH_3)_2\ CH-I$ and CH_3CH_2OH

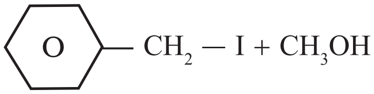
b) $(CH_3)_2CH-OH$ and CH_3CH_2I

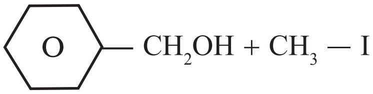
c) $CH_3\text{-}CH = CH_2$ and CH_3CH_2OH

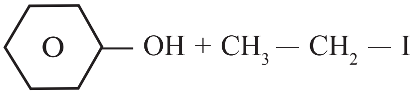
d) $(CH_3)_2CHOH$ and $CH_2 = CH_2$

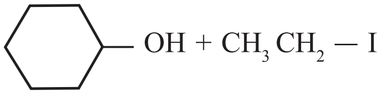
47. 

Product X & Y are -

a) 

b) 

c) 

d) 

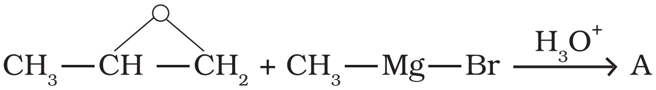
48. Ether is used as solvent in the preparation of grignard reagent because -

a) Ether is inert solvent

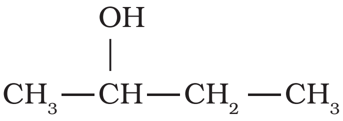
b) Grignard reagent form complex with ether

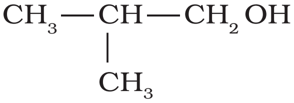
c) Produced complex is soluble in ether

d) All the above are correct.

49. 

Main product 'A' is -

a) 
$CH_3-\overset{OH}{CH}-CH_2-CH_3$

b) 
$CH_3-\underset{CH_3}{CH}-CH_2OH$

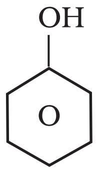
c) $CH_3-CH = CH-CH_3$

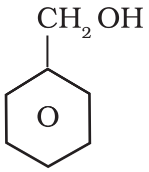
d) $CH_3\ CH_2\ CH_2\ CH_2OH$

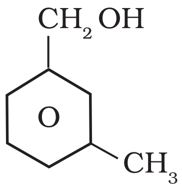
50. How many alcohols with molecular formula C_4H_0O are chiral in nature-

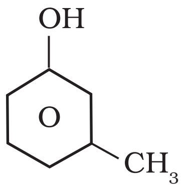
a) 1 b) 2 c) 3 d) 4

51. Which of the following compounds is aromatic alcohol ?


(I)

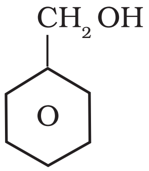

(II)

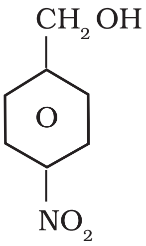

(III)

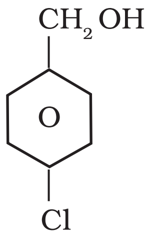

(IV)

a) i, ii, iii, iv b) i & iv c) ii & iii d) Only i

52. Arrange the following compounds in the increasing order of reactirity towards HBr

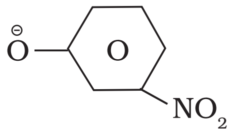
(I)


(II)


(III)


a) iii, ii, i b) ii, iii, i c) i, ii, iii d) ii, i, iii

53. Which of the following species is the stromgest base?

a) $^{\ominus}OH$ b) $^{\ominus}OR$ c) $^{\ominus}OC_6H_5$ d)


54. Mono Chlorination of Toulene in sunlight followed by hydrolysis with aq NaOH produces-

a) o- Cresol b) m - cresol

c) 2, 3- Dihydroxy Toilene d) Benzyl alcohol

55. Which of the following will not be soluble in $NaHCO_3$?

a) 2, 4, 6 - Trinitro Phenol b) Benzoic acid

c) o - Nitro Phenol d) Benzene sulphonic acid

56. Number of isomeric alcohols of molecular formula $C_6H_{14}O$ which can give positive iodoform test is/ are-

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

57. When Glycerol is treated with excess of HI, it produces

a) 2- iodopropane b) Allyl iodide c) Propene d) Glycerol tri iodide

58. How many isomers of $C_5H_{11}OH$ will be primary alcohols?

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

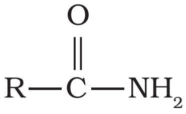
59. Ethyl chlonide is converted into diethyl ether by-

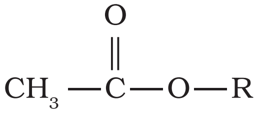
a) Perkins reaction b) Grignard reaction

c) Wurtz reaction d) Wailliamson's synthesis

60. Which one of the following compounds is resistant to nuclcophilic attack by hydroxyl ions?

a) R-O-R b) R-C≡N

c) 
$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

d) 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-R$

61. In the following sequence of reactions $CH_3-Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow{LiAlH_4} C$

The end product 'C' is -

a) Acetone b) Methane c) Acetaldehyde d) Ethyl alcohol

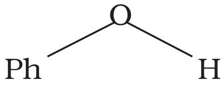
62. $HO\,CH_2CH_2OH$ on heating with per-iodic acid gives -

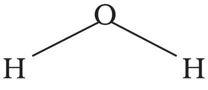
a) 2 HCOOH

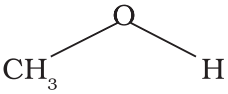
b) 
$\begin{array}{c} CHO \\ | \\ CHO \end{array}$

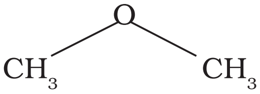
c) 2HCHO d) $2CO_2$

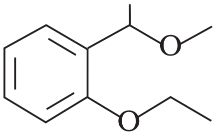
63. The compound that is most difficult to Protonate is -

a) 

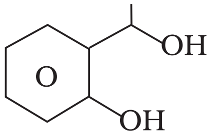
b) 

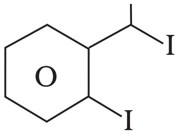
c) 

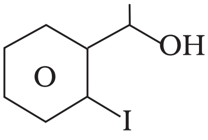
d) 

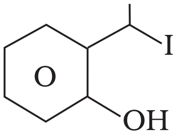
64. 

$\xrightarrow[\text{heat}]{\text{HI}}$ The major product formed in the following reaction is -

a) 

b) 

c) 

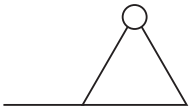
d) 

65. In the Victor Meyer's test, the colour given by 1°, 2° & 3° alcohols are respectively
    - a) Red, Colourless, blue
    - b) Red, blue, colourless
    - c) Colourless, Red, blue
    - d) Red, blue, violet

B) Assertion Reason type Question : (Each question carries 1 mark)

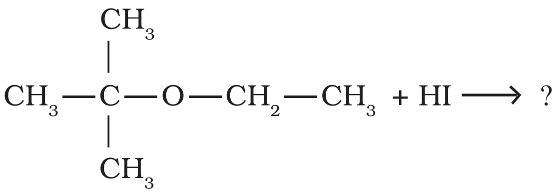
a) Assertion (A) and Reason (R) both are correct and Reason is the proper explanation of Assertion.
b) 'A' & 'B' both are correct but 'R' is not the Proper explenation of 'A'
c) 'A' is a correct, but 'R' is wrong.
d) 'A' is wrong but 'R' is correct.

1. Assertion : Addition Reaction of water to but-1-ene in acidic medium yields butan-2-ol as major product.
   Reason : Addition of water procceds through the formation of 2° carbo cation
2. Assertion : o-Nitro phenol is more acidic than p- nitrophenol.
   Reason : o-Nitro phenol can form intra molecular H bonding.
3. Assertion : Phenol gives 'o' & 'p' nitro phenol with concentrated HNO_3 & Concentrated H_2SO_4.
   Reason : In nitration reaction $\overset{(+)}{N}O_2$ is the electrophile.
4. Assertion : 2, 4- Dinitrophenol can produce effervescence of carbondioxide with $NaHCO_3$
   Reason : Phenol do not form CO_2 with $NaHCO_3$
5. Assertion : During dehydration reaction of alcohol always carbocation is formed as intermediate.
   Reason : Stability order of carbocation are $3°C^+ > 2°C^+ > 1°C^+$
6. Assertion : Phenol form white ppt of 2,4,6- toribromo Phenol with Bromine water.
   Reason : Polar Solvent water activate the berzene ning.
7. Assertion :



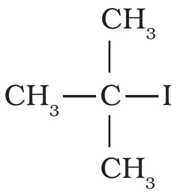
$+ CH_3MgBr \xrightarrow{H_2O / H^+}$ Product is Butan -2-ol.

   Reason : $\overset{\ominus}{C}H_3$ of CH_3MgBr will attack less strically hindered carbon atom.
8. Assertion :



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_2-CH_3 + HI \longrightarrow ?$$

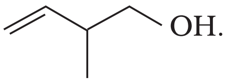
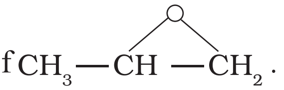
Major product is



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-I$$

   Reason : Reaction proceeds throush SN^1 mechanism.

C) Very short answer type Questions : (Each question carries 1 mark)

1. Name a Praimary alcohol which can respond in the lucas reagent.
2. Name a trihydric alcohol which is used in our daily life in winter season.
3. Among n- butanol and t-butanol which one is more soluble in water ?
4. Which one is more volatile among the O- nitro phenol and P- nitro phenol ?
5. Write downn the structure of But-3-ene-1-ol.
6. What is the IUPAC name of 
7. Name the functional isomers of $C_4H_{10}O$.
8. Is it possible to get the chain isomer having molecular formula of C_3H_8O.
9. What is the IUPAC name of  $CH_3—CH—CH_2$.
10. What is the reaction between diethyl ether and methyl isopropyl ether.
11. Name the alkene which gives only primary alcohol during hydration reaction.
12. Name the intermediate which is formed during dehydration of alcohol.
13. $CH_3—CH = CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } BH_3}$ An alcohol is formed. What is the name of the alcohol ?
14. $CH_3—CH = CH_2 \xrightarrow[CH_3COOH,\ THF]{\text{(i) } (CH_3COO)_3Hg} A \xrightarrow[OH^-]{NaBH_4} B$

    Name A and B
15. i) $CH_3CH_2OH + SO_2Cl_2 \rightarrow CH_3CH_2 - Cl + SO_2 + HCl$

    ii) $CH_3CH_2OH + PCl_3 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$

    Which one is better process for the preparation of ethyl chloride ?
16. Name the carbonyl compound which can produce 2° alcohol with Grignard reagent.
17. Name the reagent of victor mayer test.
18. Which one is more acidic in between phenol & ethanol ?

19. What is absolute alcohol ?

20. What is denatured alcohol ?

21. What is wood spirit ?

22. Name the product which is for need by the action of ethyl alcohol and sodium.

23. What is Rectified spirrit ?

24. What is the chemical name of carbolic acid ?

25. Write the structure of the molecule whose IUPAC name is 1- phenyl propan-2-ol.

D. Short Answer Questions : (Each question carries 2 mark)

1. How will you carry out the following corversion-

a) Propan-1-ol ⟶ Propan-2-ol

b) Ethanol ⟶ Propanol

c) Benzene ⟶ Phenol

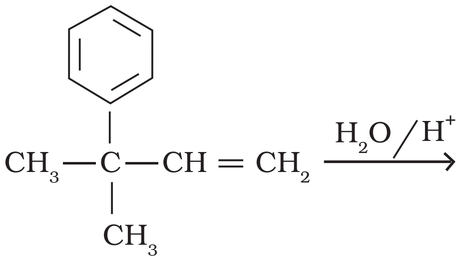
d) Phenol ⟶ Aspirin

e) Ethanol ⟶ Tertiary butyl alcohol

f) Butan-2-ol ⟶ Propan-1-ol

g) CH_3-CH_2-Cl ⟶ Tert butyl ethyl ether

h)

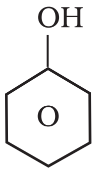


Name the Product.

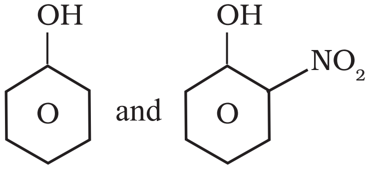
2. How can you distinguish the following pair -

i) CH_3-CH_2-OH & CH_3OH

ii) CH_3-CH_2-OH &



iii) CH_3-CH_2-OH & $(CH_3)_2$ CHOH

iv) 

3. Explain-
   i) Why phenol is more acidic than Ethyl alcohol ?
   ii) Why boiling point of p - nitro phenol is more than o - nitro phenol ?
   iii) Out of 2-Chloro ethanol and cthanol which is more acidic and why?
   iv) The carbon oxygen bond in phenol is slighfly stronger as well as shorter than that in methanol why?
   v) Why alcohol and ether of comparable molecular mass have different boiling point?
   vi) Dipole moment of phenol is less than ethanol why ?
   vii) Why nuclcophilic substitution of phenol is difficult than ethanol ?
   viii) Why primary alkyl halide is used in the preparation of ether by williamson systhesis ?
   ix) Why is O = C = O non polar?

       While R - O - R is polar?
   x) In kolbe's reaction phenoxide ion is reacted with carbondi oxide instead of phenol why ?
4. Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.
5. What happens when benzene diazonium chloride is heated with water?
6. Suggest the reaction mechanism of ethanol to ethene by using concentrated H_2SO_4 at higher temperature?
7. Draw the aromatic isomer having molecular formula C_7H_8O.

D. Long Answer Questions : (Each question carries 5 mark)

1. (a) Name the starting material used in the industrial preparation of phenol.

   (b) Write the complete reaction for the bromination of phenol in aqueous & non aqueous medium.

   (c) How will you produce o- nitro phenol and p - nitro phenol from phenol. 1+2+2=5

2. (a) Write the structure of aspirin?

   (b) Suggest the suitable mechanism in the reaction between HI and methoxy benzene.

   (c) Why boiling point of ether is less than alcohol having comparable molecular mass ?

3. An alcohol 'A' ($C_4H_{10}O$) on dehydration reaction gives an alkene B (C_4H_8). 'B'- on treatment with HBr gives 2-Bromo-2-methyl propane as major product. Alcohol 'A'is a tertiary alcohol. B-on reductive ozonolysis produces C (C_3H_6O) & D (CH_2O). Compound 'C' can respond in Haloform reaction. Identitfy the A, B, C & D -with proper reason.

Answer

A. Select the correct option (MCQ) : (Each question carries 1 mark)

1. b 2. c 3. c 4. b 5. a 6. a 7. a 8. a
9. a 10. b 11. a 12. a 13. a 14. b 15. d 16. b
17. c 18. b 19. b 20. c 21. d 22. c 23. c 24. b
25. c 26. c 27. a 28. a 29. a 30. a 31. a 32. c
33. d 34. a 35. c 36. b 37. b 38. b 39. c 40. b
41. a 42. a 43. b 44. a 45. b 46. b 47. a 48. c
49. a 50. b 51. b 52. d 53. b 54. d 55. c 56. a
57. a 58. b 59. d 60. a 61. d 62. c 63. a 64. a
65. c

B. Assertion Reason type Question : (Each question carries 1 mark)

1. a 2. d 3. d 4. b 5. b 6. a 7. a 8. a

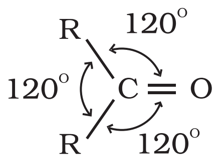
Chapter - 12

Aldehydes, Ketones & Carboxylic Acids

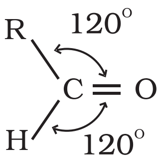
Chapter at a glance :

1. **Structure:**

Carbon of aldehyde & ketone are sp^2 hybridised.



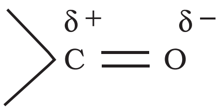
Ketone



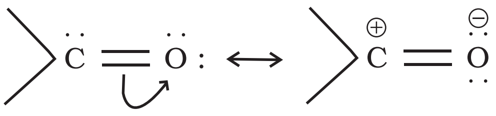
Aldehyde

Molecular shape is trigonal Planar.

Aldehyde & Ketone both are polar molecule.



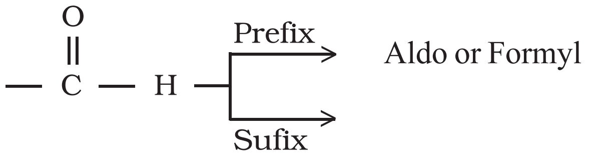
Polarity due to I effect

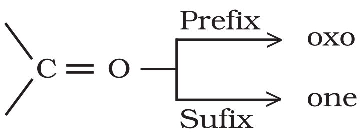


Polarity due to resonance

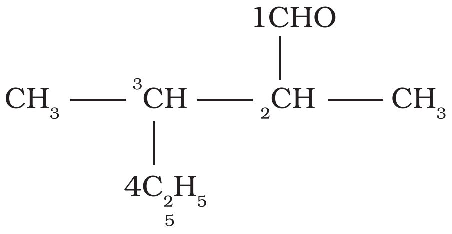
Generally ketone are more polar than aldehyde.

2. **IUPAC Nomen clature :**





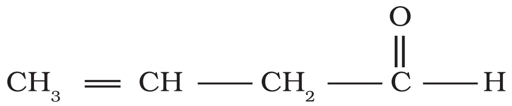
1.



$$\mathrm{CH_3 - \underset{\substack{|\\ 4C_{\substack{2\\5}}H_5}}{{}^3CH} - \overset{\substack{1CHO\\|}}{{}_2CH} - CH_3}$$

2, 3 - Dimethyl Pentanal

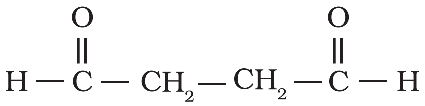
2.



$$\mathrm{CH_3 = CH - CH_2 - \overset{\substack{O\\\|}}{C} - H}$$

3 - Butenal

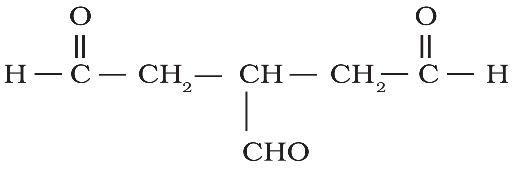
3.



$$\mathrm{H - \overset{\substack{O\\\|}}{C} - CH_2 - CH_2 - \overset{\substack{O\\\|}}{C} - H}$$

Butane - 1,4 - dial

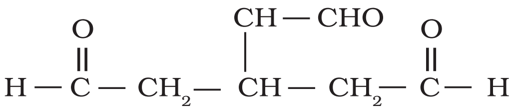
4.



$$\mathrm{H - \overset{\substack{O\\\|}}{C} - CH_2 - \underset{\substack{|\\CHO}}{CH} - CH_2 - \overset{\substack{O\\\|}}{C} - H}$$

Propane - 1, 2, 3 tri carbaldehyde

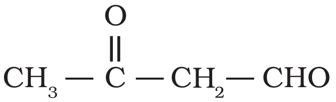
5.



$$\mathrm{H - \overset{\substack{O\\\|}}{C} - CH_2 - \overset{\substack{CH - CHO\\|}}{CH} - CH_2 - \overset{\substack{O\\\|}}{C} - H}$$

3- (Aldomethyl) Pentane - 1, 5 - dial.

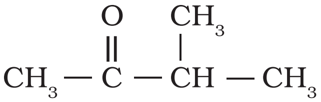
6.



$$\mathrm{CH_3 - \overset{\substack{O\\\|}}{C} - CH_2 - CHO}$$

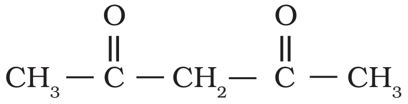
3- oxo butanal

7.



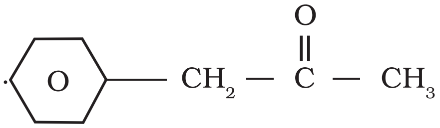
$$\mathrm{CH_3 - \overset{\substack{O\\\|}}{C} - \overset{\substack{CH_3\\|}}{CH} - CH_3}$$

3- Methyl butan-2-one/ 3- Methyl butanone

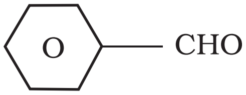
8. 

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Pentane- 2, 4- di one.

9. 

1- Phenyl -2- Propanone

10.  Benzene Carbaldehyde.

3. **Isomer:**

i) Aldehyde do not form position isomer.

ii) Aldehyde & Ketone are functional group isomer to each other.

iii) Ketone can form position isomer.

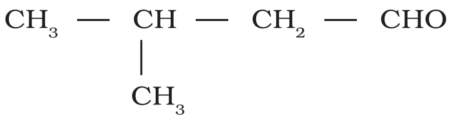
iv) Ketone can form metamer.

v) Aldehyde & Kertone both can form Tautomer.

Name the isomer of compound having molecular formula $C_5H_{10}O$

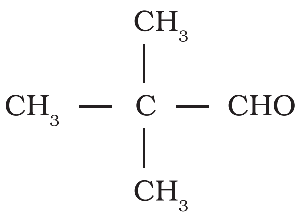
1. $CH_3-CH_2-CH_2-CH_2-CHO$

Pentanal

2. 

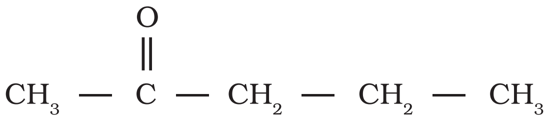
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CHO$$

3- Methyl butanal

3. 

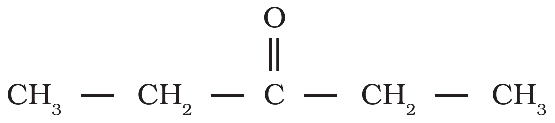
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO$$

2, 2- Dinethyl Propanal

4. 

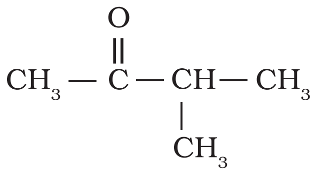
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

Pentan-2-one

5) 

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

Pentan-3- one

6) 

$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

3 - Methyl butan-2-one

Relation between the isomers are

(1) & (2) (2,3) & (1,3) are chain isomers to each other

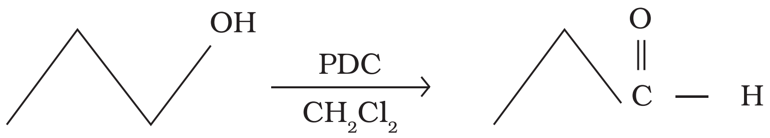
(1,4), (1,5), (1,6) are functional group isomer to each other

(4,5) Position isomer as well as metamer to each other

(4,6) Chain isomer as well as metamer to each other.

4. **Preparation of Carbonyl Compound:**

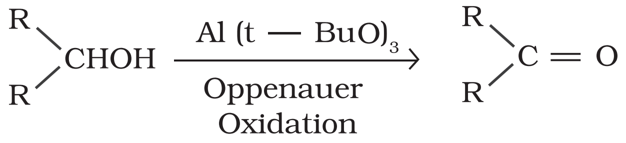
(i) By oxidation of 1° & 2° alcohol

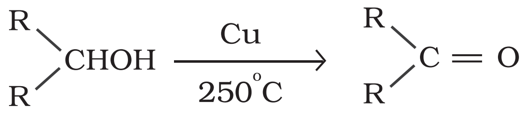


Note: PCC (Pyridinium chloro chromate) may also be used in stead of Pyridinium dichromate (PDC).

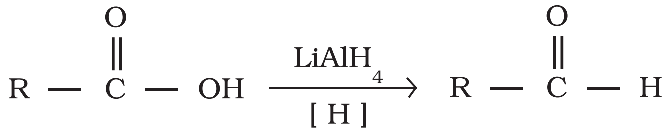
Advantages of PCC & PDC, further oxidation of aldehyde is not possible.

Jone's reagent may also be used. Solution of chromic anhydride in water, acetone & H_2SO_4 is the Jone's reagent.



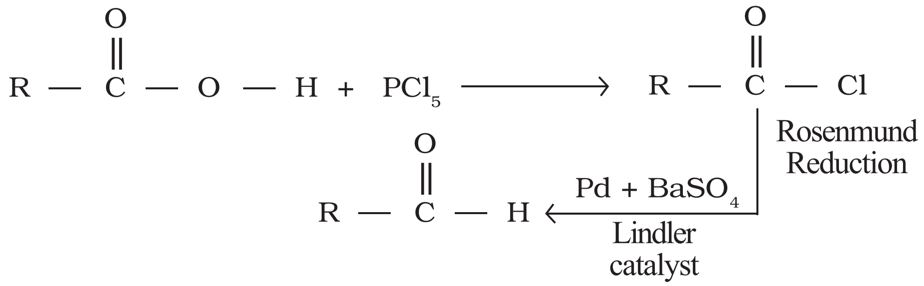


(ii) Aldehyde not ketone can be formed by the reduction of carboxylic acid chloride, ester & nitrile.

(a) 

$$R-\overset{\overset{O}{\|}}{C}-OH\xrightarrow[{[H]}]{LiAlH_4}R-\overset{\overset{O}{\|}}{C}-H$$

(b)

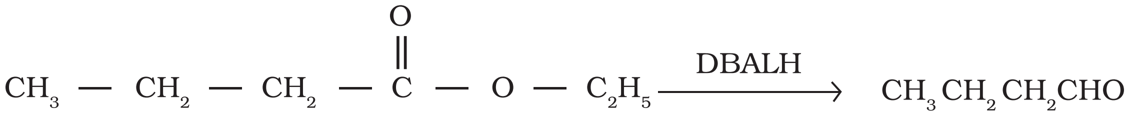


$$R-\overset{O}{\overset{\|}{C}}-O-H + PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Lindler catalyst}]{Pd + BaSO_4} R-\overset{O}{\overset{\|}{C}}-H$$

This Process is also known as Rosenmund reduction.

Note: The two important reducing agent, LBAH (Lithium tri tert butoxyaluminium hydride), DBAH (Di isobutyl aluminium hydride), are less reducing agent than $LiAlH_4$

(c)

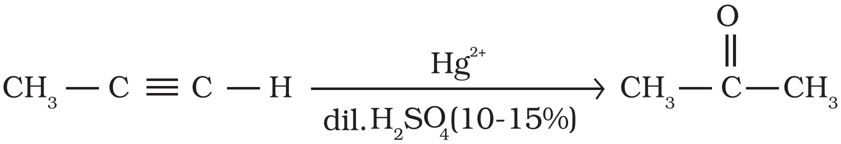


$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{DBALH} CH_3CH_2CH_2CHO$$

(d) $CH_3-CH_2.CH_2.C\equiv N \xrightarrow{DBALH} CH_3CH_2CH_2CHO$

(iii) Aldehyde (Specially acetaldehyde) & Ketone can be Prepared by hydration of alkyne.

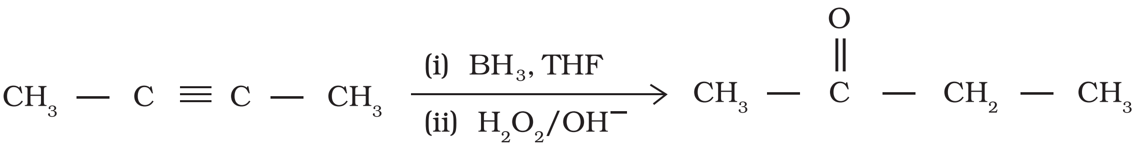
$$H-C\equiv C-H \xrightarrow[\text{dil.}H_2SO_4(10\text{-}15\%)]{Hg^{2+}} CH_3CHO$$



$$CH_3-C\equiv C-H \xrightarrow[\text{dil.}H_2SO_4(10\text{-}15\%)]{Hg^{2+}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

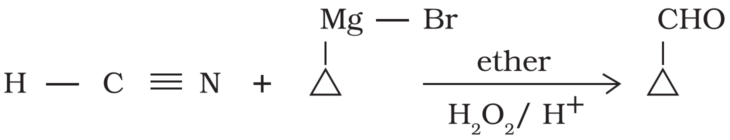
(iv) Aldehyde & Ketone both can be prepared by hydroboration reaction of alkyne.

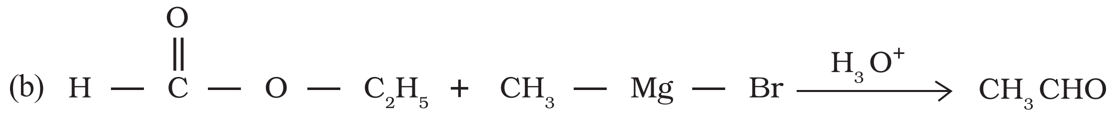
$$CH_3-C\equiv C-H \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } BH_3,\ THF} CH_3-CH_2-CHO$$



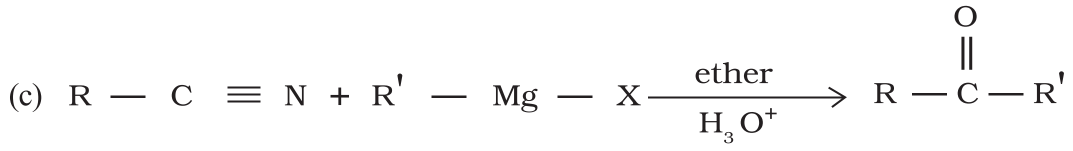
$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } BH_3,\ THF} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

(v) (a)

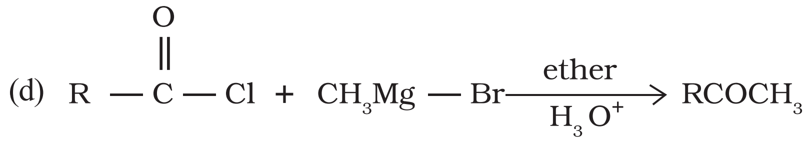


(b) 

$$H-\overset{\overset{O}{\|}}{C}-O-C_2H_5 + CH_3-Mg-Br \xrightarrow{H_3O^+} CH_3CHO$$

(c) 

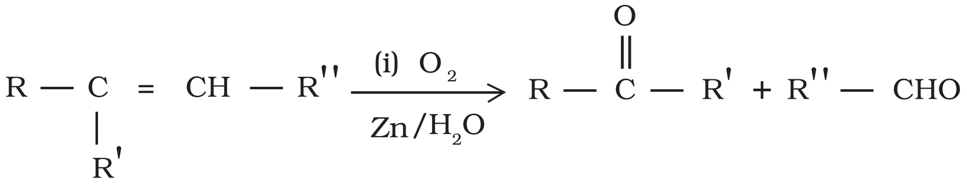
$$R-C\equiv N + R'-Mg-X \xrightarrow[H_3O^+]{ether} R-\overset{\overset{O}{\|}}{C}-R'$$

(d) 

$$R-\overset{\overset{O}{\|}}{C}-Cl + CH_3Mg-Br \xrightarrow[H_3O^+]{ether} RCOCH_3$$

(vi) Ozonolysis of alkene :

$$R-CH=CH_2 \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_2} R-CHO + HCHO$$

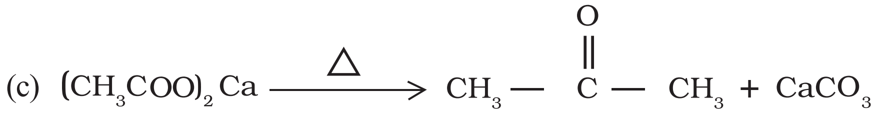


$$R-\underset{\underset{R'}{|}}{C}=CH-R'' \xrightarrow[Zn/H_2O]{\text{(i) } O_2} R-\overset{\overset{O}{\|}}{C}-R' + R''-CHO$$

(vii) Dry distillation of calcium salts of fatty acid :

(a) $(HCOO)_2Ca \xrightarrow{\triangle} HCHO + CaCO_3$

(b) $(HCOO)_2Ca + (CH_3COO)_2Ca \xrightarrow{\triangle} 2CH_3CHO + 2CaCO_3$

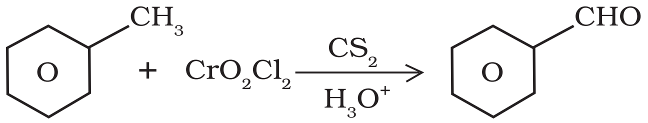
(c) 

$$(CH_3COO)_2Ca \xrightarrow{\triangle} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CaCO_3$$

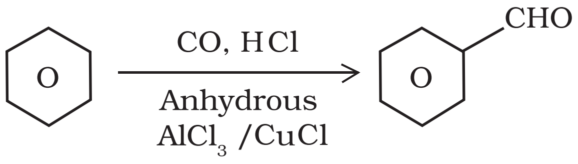
(viii) Stephen Reduction :

$$R-CN + SnCl_2 + HCl \longrightarrow R-CH=NH \xrightarrow{H_2O^+} R-CHO$$

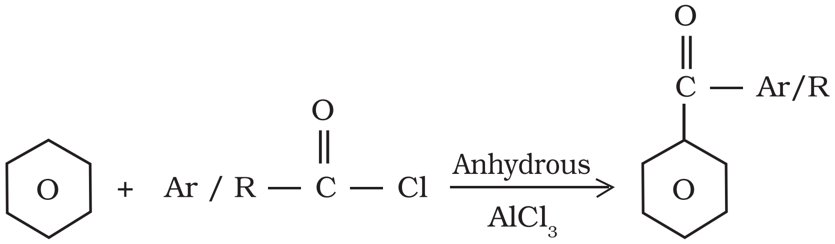
(ix) Etard Reaction :



(x) Gatterman koch reaction



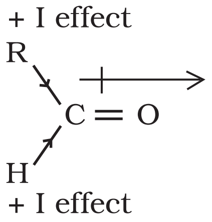
(xi) Friedal Craft Reaction

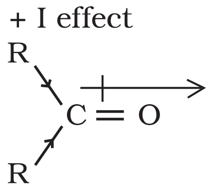


Propertics of carbonyl compound

(i) Physical Properties :

(a) Dipolemoment :



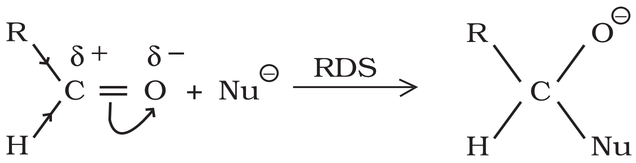


Ketone has more dipole moment than aldelyde.

(b) Boiling Point: BP of Ketone compound is more than aldehyde.

(ii) Chemical Propertice:

Aldehyde & ketone always take part in the Nucleophilic addition reaction.

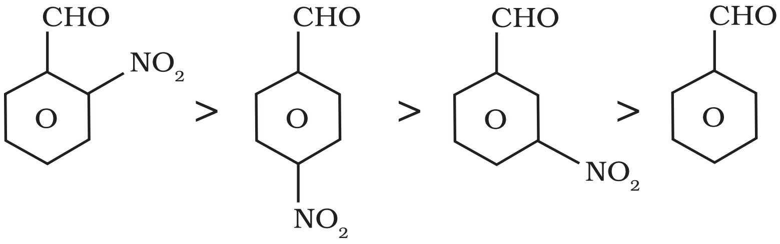


(RDS = Rate determining step)

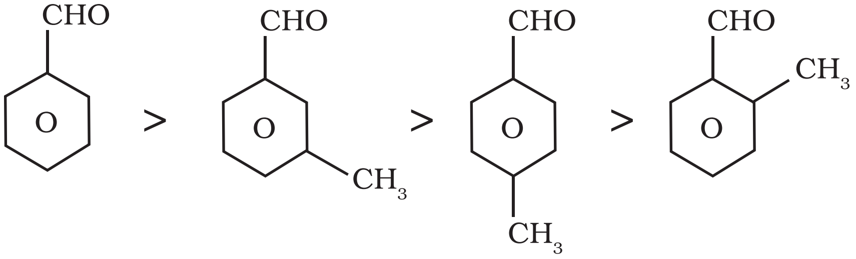
a) Relative reactivity of aldehyde & ketones towards nuclcophilic addition :

1) $HCHO > CH_3CHO > CH_3CO\ CH_3$
2) $O_2NCH_2CHO > HCHO > CH_3CHO > CH_3CO\ CH_3$

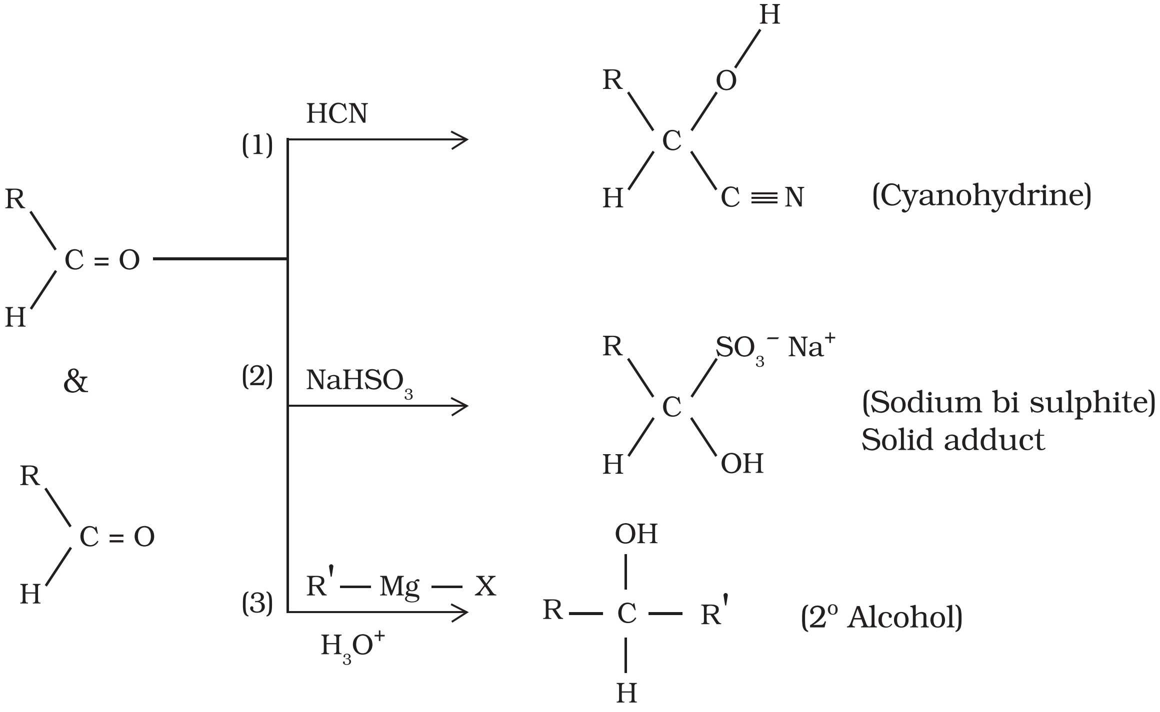
3)



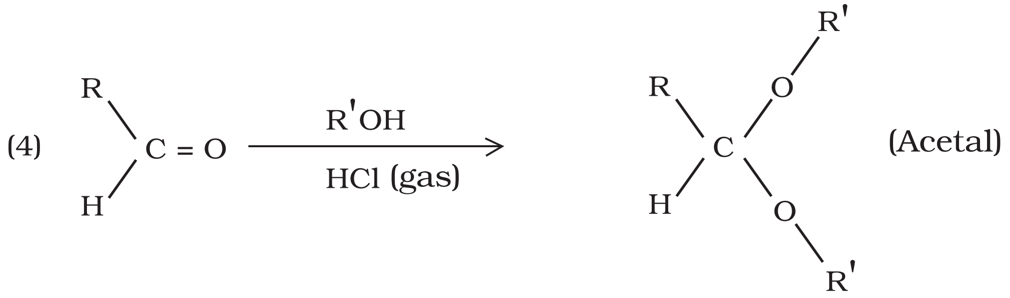
4)



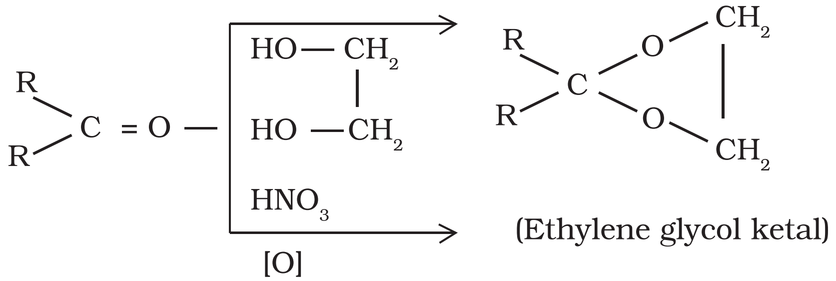
b) Some important reactions :

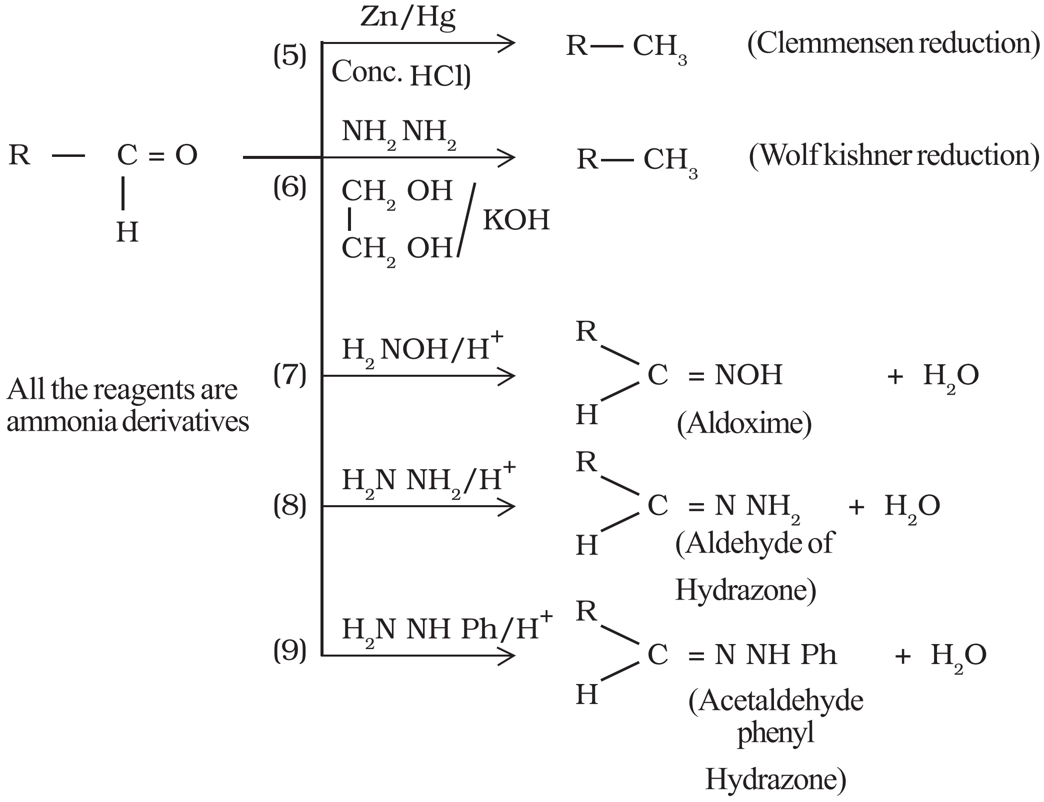


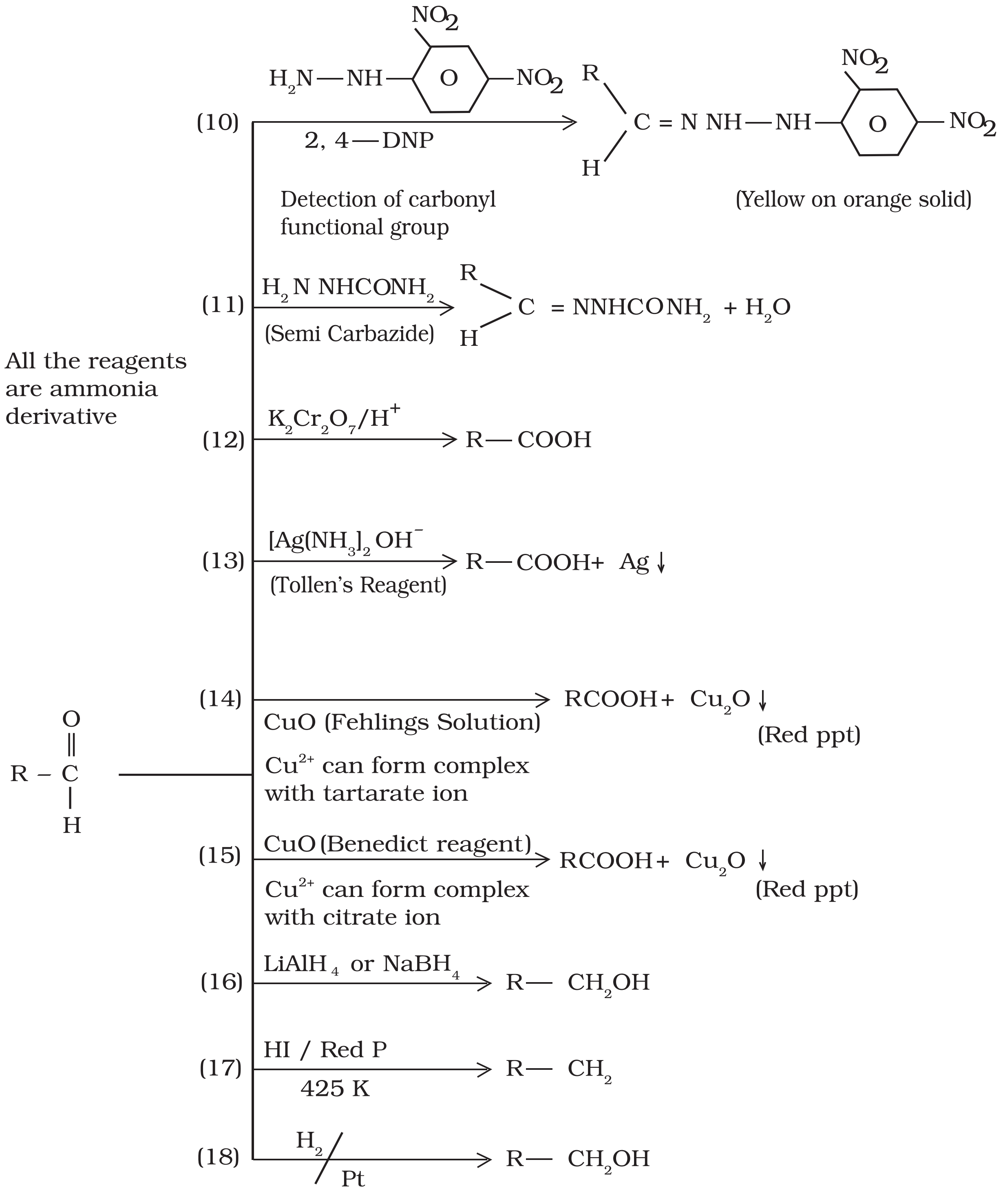
(Ketone gives 3° Alcohol)



Ketone do not react with monohydric alcohol, but with dihydric alcohol to form cyclic acetal,







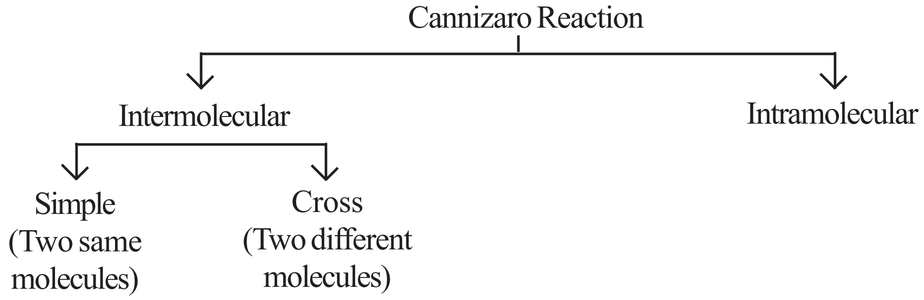
Note: ketone do not react with Tollen's reagent, Fehlings solution & Benedict reagent.

Some important name reactions :

1. **Cannizaro reaction :**

Carbonyl compound having No α - H can take part in the Cannizaro reaction.

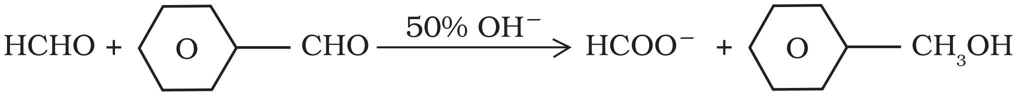
This reaction is carried out in presence of conc. alkali medium.



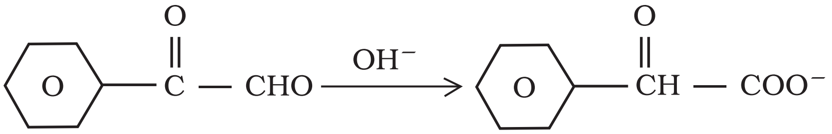
Simple :

$$HCHO + HCHO \xrightarrow{50\%\ OH^-} H\,COO^- + CH_3OH$$

Cross :



Intra :



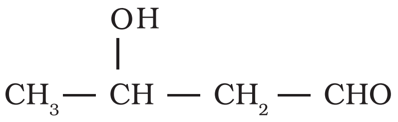
Note: CCl_3CHO (Chloral) do not take part in the Cannizaro reaction.

2) **Aldol Condensation :**

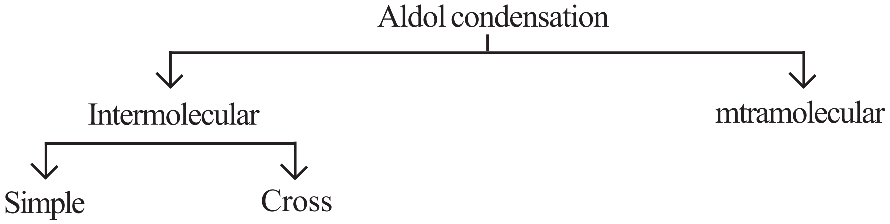
Carbonyl compound having α -H Can take part in the aldol condensation.

Reaction is carried out in presence of dil alkali medium or acid medium or Na_2CO_3 solution.

Aldol : β - Hydroxy aldehyde

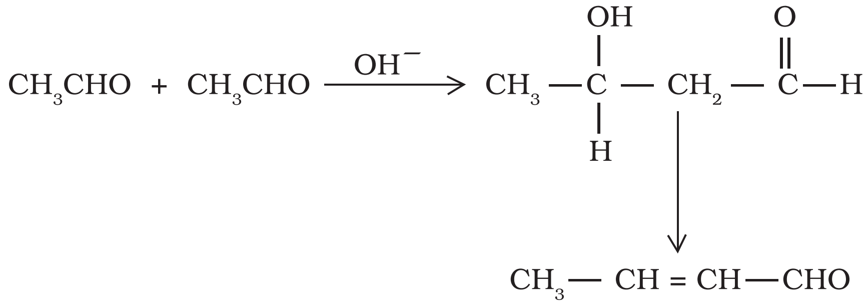


$$CH_3 - \overset{\overset{\large OH}{|}}{CH} - CH_2 - CHO$$



Intermolecular Aldol condensation :

Simple

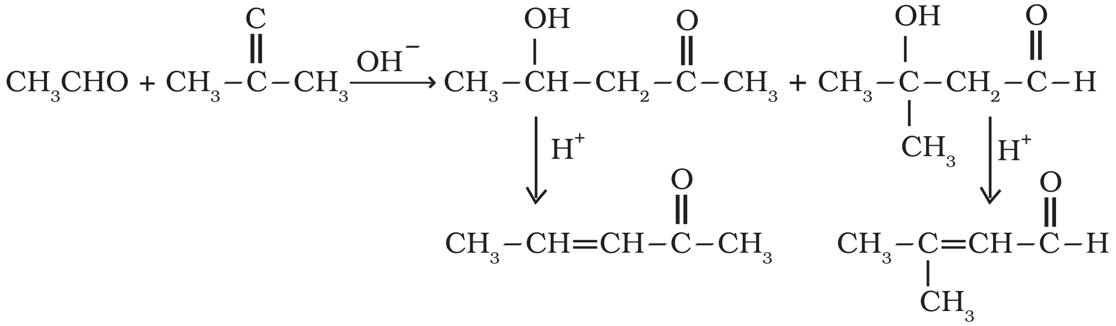


$$CH_3CHO + CH_3CHO \xrightarrow{OH^-} CH_3-\underset{H}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H \;\downarrow\; CH_3-CH=CH-CHO$$

(Chrotonaldehyde)

Cross Aldol condensation :

In cross Aldol condensation number of products will be 4.



$$CH_3CHO + CH_3-\overset{C}{\overset{\|}{C}}-CH_3 \xrightarrow{OH^-} CH_3-\overset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

$$\downarrow H^+ \qquad\qquad \downarrow H^+$$

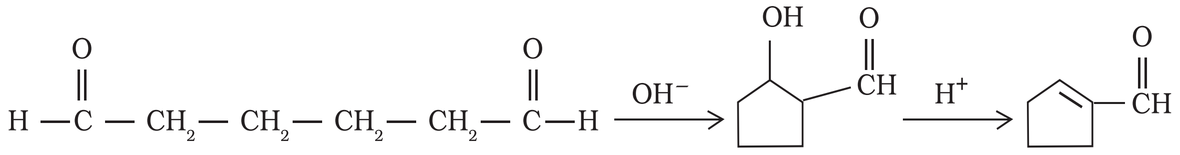
$$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 \qquad CH_3-\underset{CH_3}{C}=CH-\overset{O}{\overset{\|}{C}}-H$$

Another two products are formed by simple aldol condensation in between-

(i) CH_3CHO & CH_3CHO

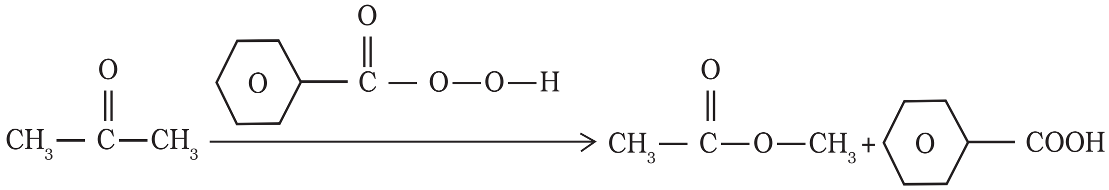
(ii) CH_3COCH_3 & CH_3COCH_3

Intramolecular aldol condensation :

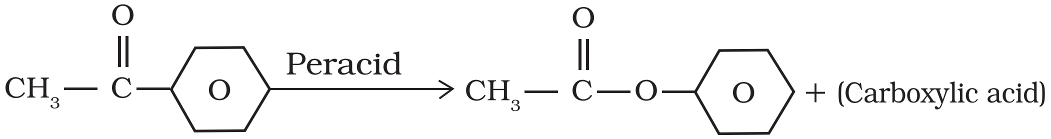


Bayer villiger oxidation

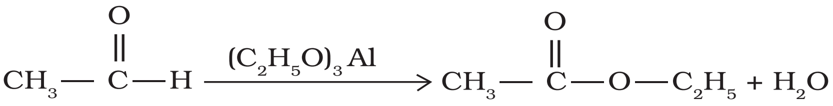
(i)



(ii)

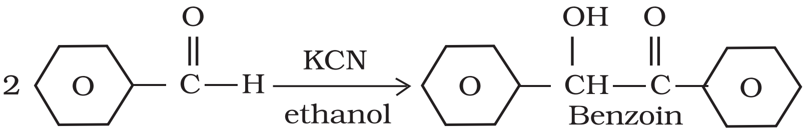


Tischenko Reaction

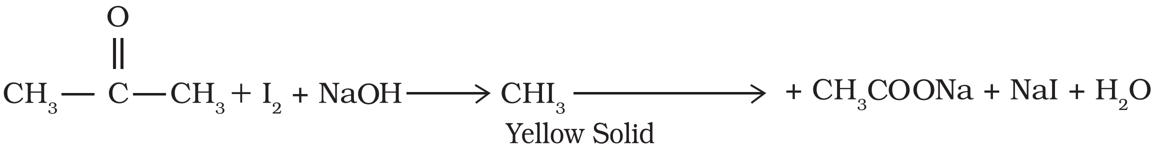


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{(C_2H_5O)_3Al} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5 + H_2O$$

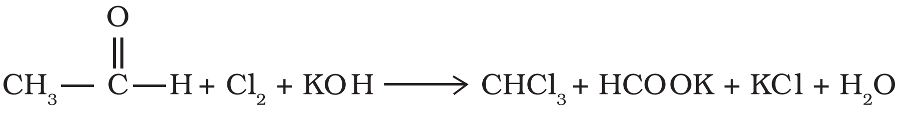
Benzoin cardontsation



5. **Haloform Reaction :**



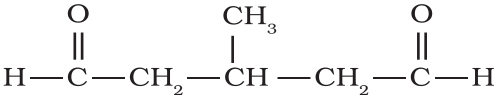
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + I_2 + NaOH \longrightarrow \underset{\text{Yellow Solid}}{CHI_3} \longrightarrow + CH_3COONa + NaI + H_2O$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + Cl_2 + KOH \longrightarrow CHCl_3 + HCOOK + KCl + H_2O$$

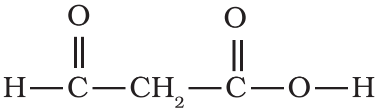
Compound those have ketomethyl group or on oxidation ketomethyl group is formed they can take part in the haloform reaction. Ketomethyl group must contain either ‘C’ or ‘H’.

A. Select the correct answer (MCQ) : (Each question carries 1 mark)

1.  $H-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$ has its IUPAC name as

a) 3- Aldomethyl pentone -1,5- dial b) 1, 2, 3 - Propane tri carbaldehyde

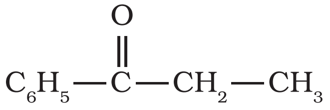
c) 3- Methyl Pentane - 1,5 dial d) None

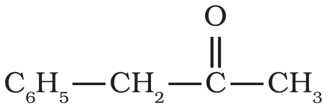
2.  $H-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-H$ IUPAC name of the compound is

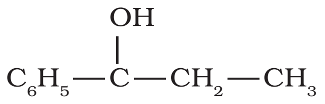
a) 2- Aldo ethanoic acid b) 3- Oxo Propanoic acid

c) Both (a) & (b) d) None

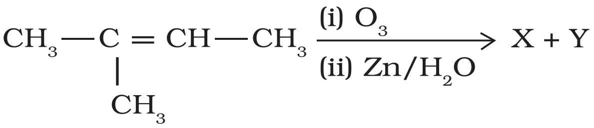
3. $C_6H_5-C\equiv C-CH_3 \xrightarrow[H^+]{Hg^{2+}/} A$ Here 'A' is

a)  $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

b)  $C_6H_5-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

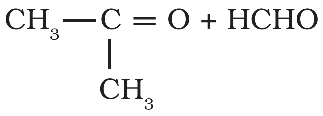
c)  $C_6H_5-\overset{\overset{OH}{|}}{C}-CH_2-CH_3$

d) None

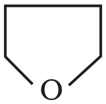
4.  $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3 \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} X + Y$

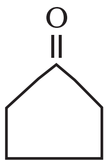
'X' & 'Y' are

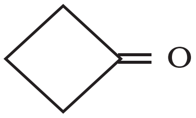
a) $(CH_3)_2C = O$ & CH_3CHO b) CH_3CHO & $HCHO$

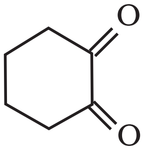
c)  $CH_3-\underset{\underset{CH_3}{|}}{C}=O + HCHO$ d) CH_3CHO & $HCHO$

5. Dry distillation of calcium salt of adipic acid gives

a) 

b) 

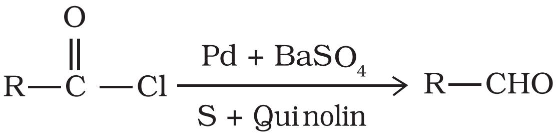
c) 

d) 

6. Relation between 2- methyl butanal and pentan -3- one are

a) Functional isomer b) Chain isomer

c) Both (a) & (b) d) None

7. 

$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[S + Quinolin]{Pd + BaSO_4} R-CHO$ The above reaction is the-

a) Rosenmund reaction b) Clemmenson reaction

c) Benzoin condensation d) Cannizaro reaction

8.  $\xrightarrow[\text{(ii) } H_2O_2 / OH^-]{\text{(i) } BH_3} X$

Product ‘X’ is the

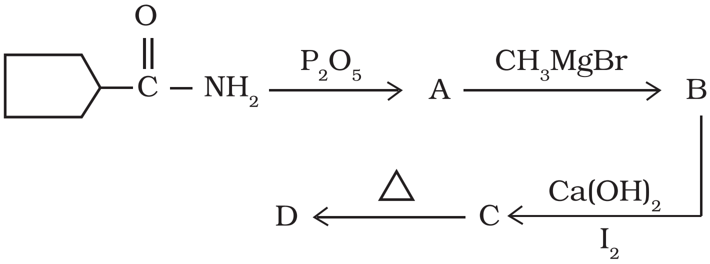
a) Ketone b) Acetophenone

c) Aldehyde d) Acetic acid

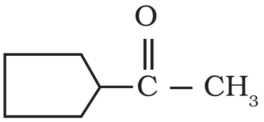
9. $.CH_3-C\equiv N \xrightarrow[\text{(ii) } H_2O / H^+]{\text{(i) } CH_3MgBr} A$ Product ‘A’ is the

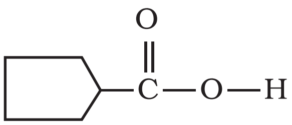
a) Acetone b) Alcohol

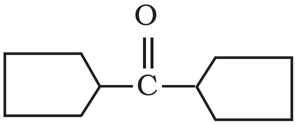
c) Acetonitmile d) Acetal

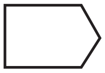
10. 

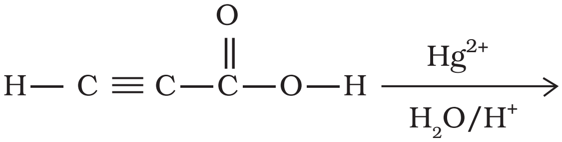
D is-

a) 

b) 

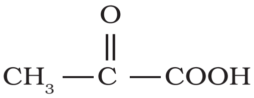
c) 

d) 

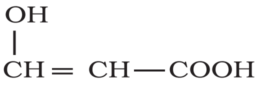
11. 

$$H-C\equiv C-\overset{\overset{O}{\|}}{C}-O-H \xrightarrow[H_2O/H^+]{Hg^{2+}} ?$$

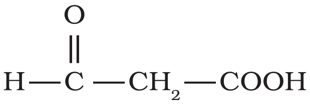
The product is-

a) 

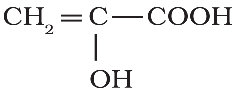
$CH_3-\overset{\overset{O}{\|}}{C}-COOH$

b) 

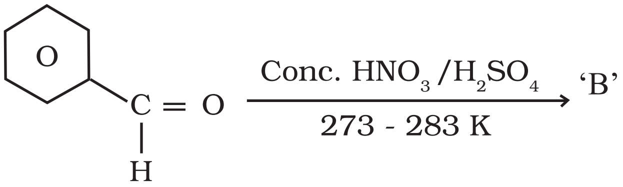
$\overset{\overset{OH}{|}}{CH}=CH-COOH$

c) 

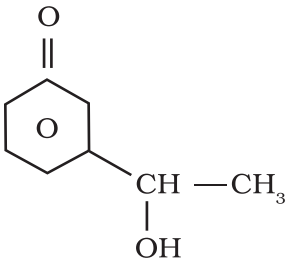
$H-\overset{\overset{O}{\|}}{C}-CH_2-COOH$

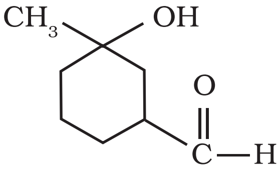
d) 

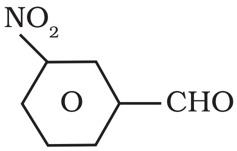
$CH_2=\underset{\underset{OH}{|}}{C}-COOH$

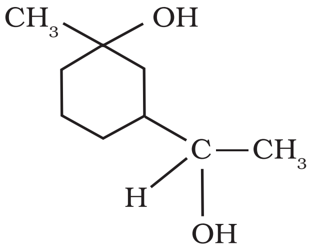
12. 

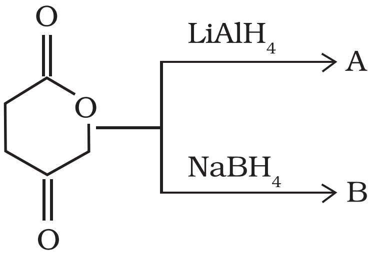
'B' is -

a) 

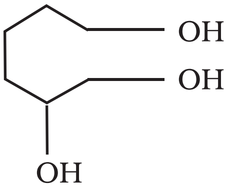
b) 

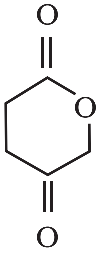
c) 

d) 

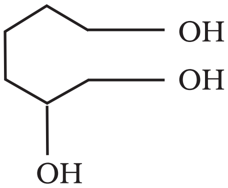
13. 

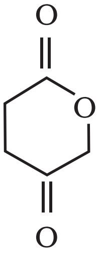
A & B are

a) 

and 

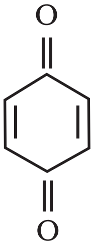
compound- A compound- B

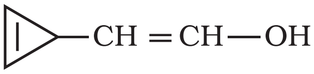
b) 

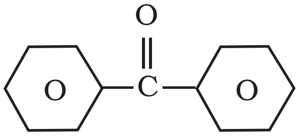
c) 

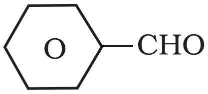
d) None

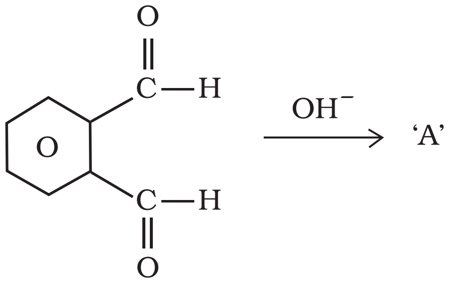
14. Tautomerism is exibited by

a) 

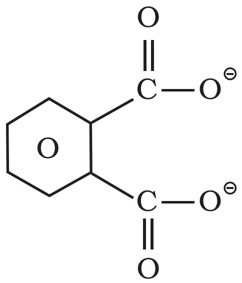
b) 

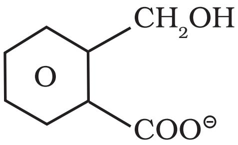
c) 

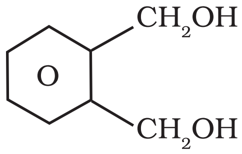
d) 

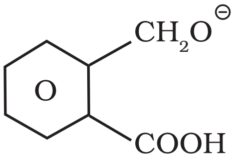
15. 

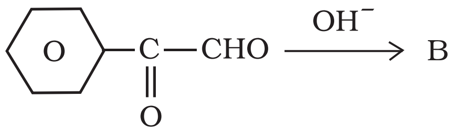
'A' The product 'A' is -

a) 

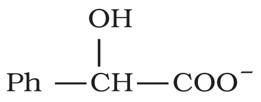
b) 

c) 

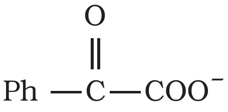
d) 

16. 

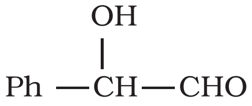
The product 'B' is -

a) 

$Ph-\overset{OH}{\overset{|}{C}H}-COO^-$

b) 

$Ph-\overset{O}{\overset{\|}{C}}-COO^-$

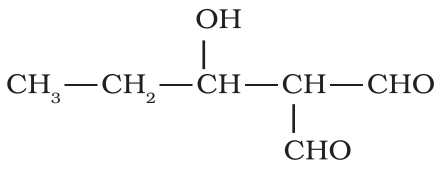
c) 

$Ph-\overset{OH}{\overset{|}{C}H}-CHO$

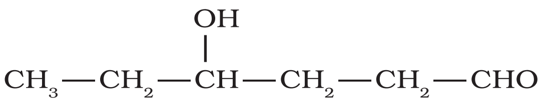
d) None

17. $CH_3-CH_2-CHO \xrightarrow[\text{(ii) Acid Catalyst}]{\text{(i) Base Catalyst}} A$

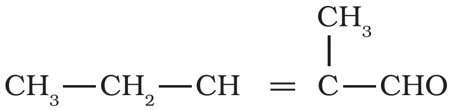
'A' is

a) 

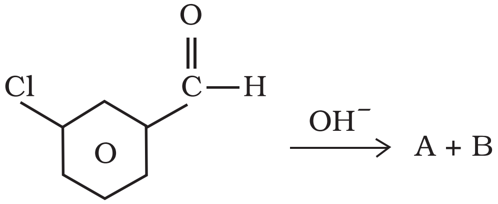
$CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-\underset{CHO}{\underset{|}{C}H}-CHO$

b) 

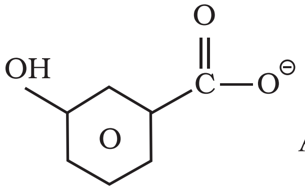
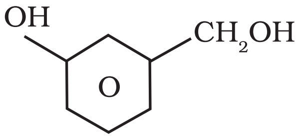
$CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-CH_2-CHO$

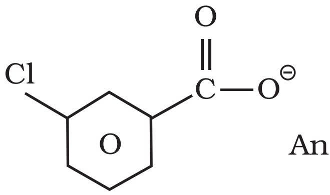
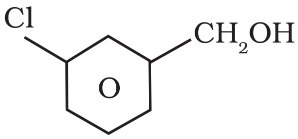
c) 
$CH_3-CH_2-CH=C(CH_3)-CHO$

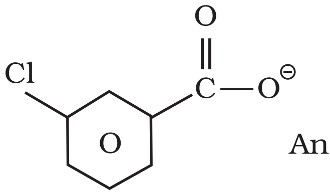
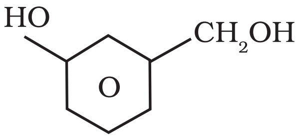
d) None

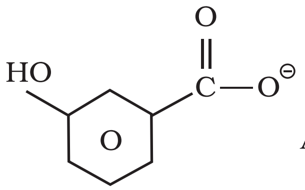
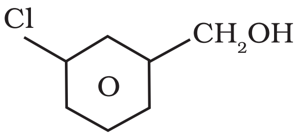
18. 

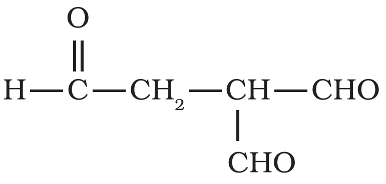
Product 'A' & 'B' are-

a)  And 

b)  And 

c)  And 

d)  And 

19.  IUPAC Name of the compound is
$H-C(=O)-CH_2-CH(CHO)-CHO$

a) 1, 1, 2 - Ethane tricarbaldehyde

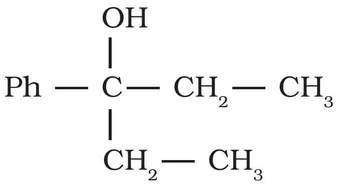
b) Ethane 1, 2, 2 tricarbaldehyde

c) Ethane - 1, 1, 2 tricarbal dehyde

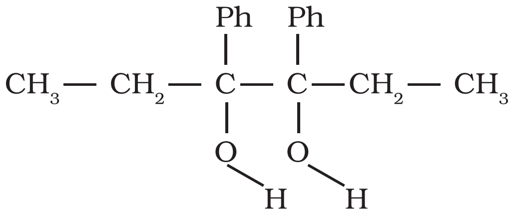
d) None

20. $C_6H_6 + CH_3CH_2COCl \xrightarrow{AlCl_3} A \xrightarrow[H_3O^+]{KMnO_4/KOH} B$ Final product is-

a) $C_6H_5\ COCH_2CH_3$

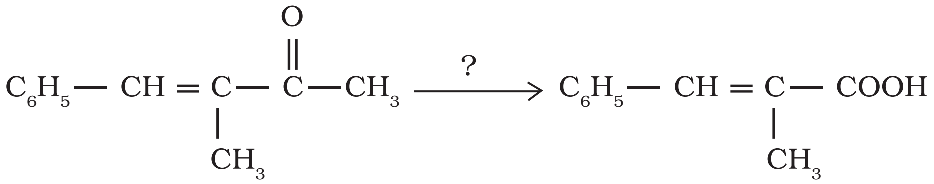
b) 

$Ph-\overset{OH}{\underset{CH_2-CH_3}{C}}-CH_2-CH_3$

c) 

$CH_3-CH_2-\overset{Ph}{\underset{OH}{C}}-\overset{Ph}{\underset{OH}{C}}-CH_2-CH_3$

d) Ph – COOH

21. 

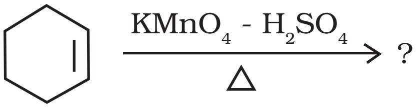
$C_6H_5-CH=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{?} C_6H_5-CH=\underset{CH_3}{C}-COOH$

a) Alkaline $KMnO_4$

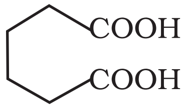
b) Conc. HNO_3

c) NaOI, H^+

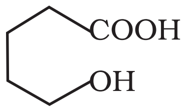
d) Any of the three.

22. 

Product 'X' is

a) 

b) No reaction

c) 

d) Both (a) and (c)

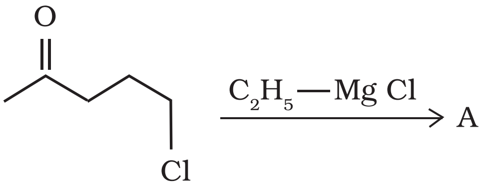
23. $CH_3CHO + CH_3CH_2CHO \xrightarrow[\text{(ii) Acid Catalyst}]{\text{(i) Base Catalyst}} ?$ Number of products are-

a) 2

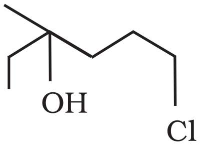
b) 3

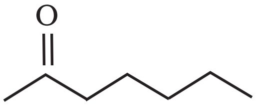
c) 4

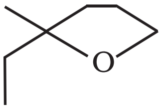
d) None

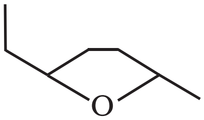
24. 

Product A is-

a) 

b) 

c) 

d) 

25. Which of the following will undergo hydration most readily ?

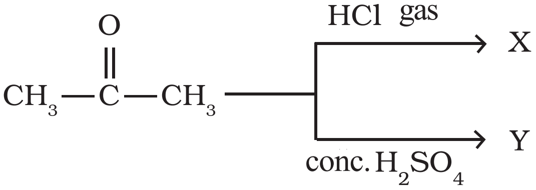
a) CH_3COCH_3 b) CH_3COCCl_3

c) CCl_3COCCl_3 d) CF_3COCF_3

26. Cannizzaro's reaction involves the intermolecular shift of -

a) H^+ b) H-atom

c) H^--ion d) H_3O^+

27. 

X & Y are respectively

a) Mesityl oxide, Phorone b) Phorone, mesityl oxide

c) Phorone, isophorone d) Isophorone, mesityl oxide

28. The order of reactivity towards nucleophilic addition among HCHO (i), CH_3CHO (ii), CH_3COCH_3 (iii) & O_2NCH_2CHO (iv) are

a) iv > i > ii > iii b) i > iv > iii > ii

c) iv > i > iii > ii d) i > ii > iii > iv

29. The order of reactivity towards nucleo Philic addition among Benzaldehyde (i), o-Nitro Benzaldehyde (ii), m - nitro Benzaldehyde (iii) & p -nitro Benzaldehyde (iv) are

a) i > ii > iii > iv b) ii > iv > iii > i

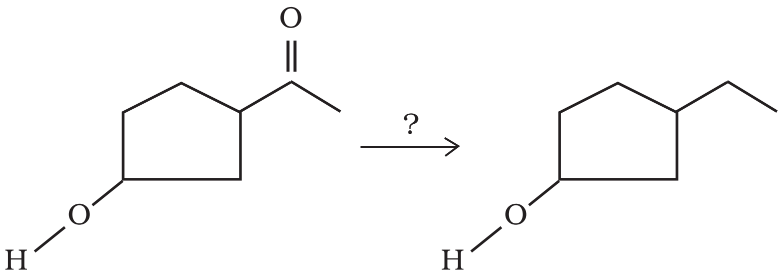
c) ii > i > iii > iv   d) iv > i > ii > iii

30. Which one is the best method for reducing -3- Bromo Propanol to 1- bromo propane

a) Wolf Kishner reduction   b) Clemmensen reduction

c) Both ‘a’ & ‘b’   d) None

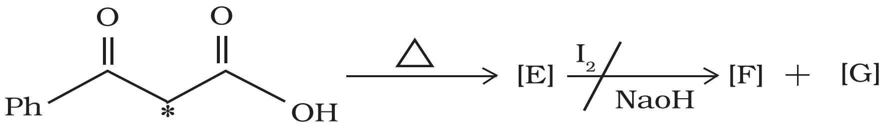
31. The appropriate reagent for the following transformation is -

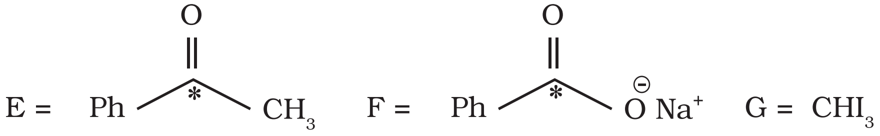


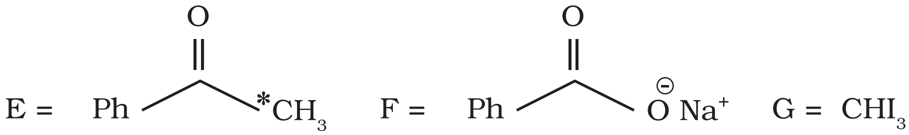
a) Zn/ Hg, HCl (conc.)   b) NH_2NH_2,OH^-

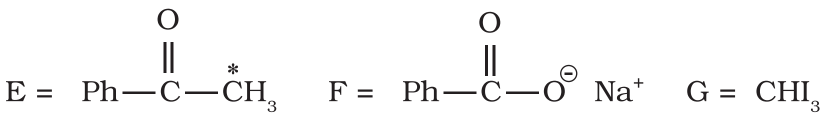
c) H_2/ Ni   d) $NaBH_4$

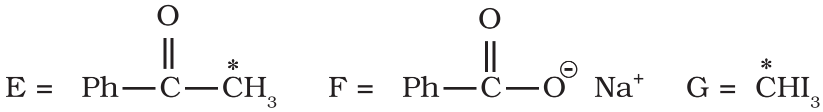
32. In the following reaction sequence, the correct structures of E, F & G are



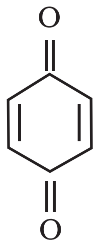
a)


b)


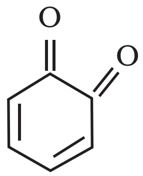
c)

E = $Ph-\overset{O}{\overset{\|}{C}}-\overset{*}{C}H_3$ F = $Ph-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ Na^+$ G = CHI_3

d)

E = $Ph-\overset{O}{\overset{\|}{C}}-\overset{*}{C}H_3$ F = $Ph-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ Na^+$ G = $\overset{*}{C}HI_3$

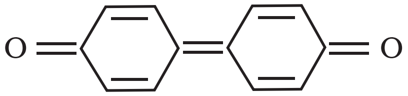
33. The correct stability order of the following three quinones is -



I



II



III

a) i > iii > ii

b) i = iii > ii

c) i = ii > iii

d) iii > i > ii

34. A new carbon carbon bond is formed in -

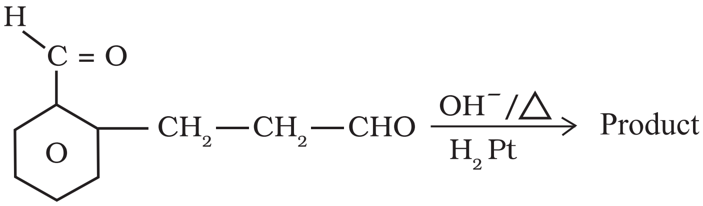
Aldol condensation (i), Kolbe's reaction (ii), Reimer Tiemann reaction (iii), Wurtz Fitting reaction (iv)

a) i, iii

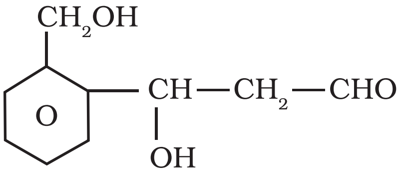
b) ii, iii

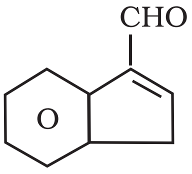
c) i, iii, iv

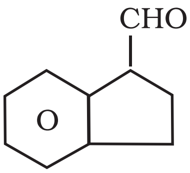
d) All the four

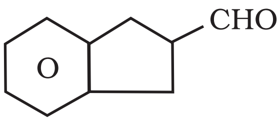
35. 

Product is

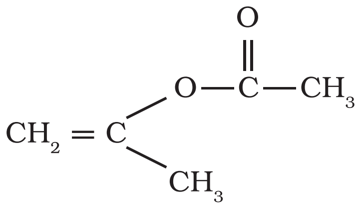
a) 

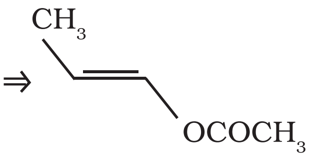
b) 

c) 

d) 

36. The product of acid hydrolysis of P & Q can be distinguished by -

P ⇒ 

Q ⇒ 

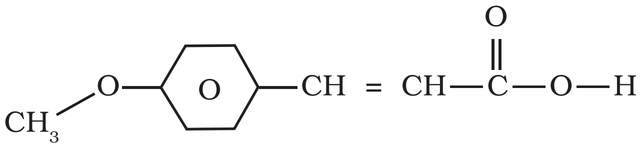
a) Lucas reagent

b) 2, 4- DNP

c) Fehling's solution

d) $NaHSO_3$

37. 



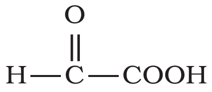
('A')

The compound X is-

a) CH_2COOH

b) $Br - CH_2 - COOH$

c) $(CH_3CO)_2O$

d)  $H-\overset{\overset{O}{\|}}{C}-COOH$

38. The correct order of acid character among Benzoic acid (i), Formic acid (ii), Acetic acid (iii), Mononitro acetic acid (iv) are

a) iv > ii > i > iii

b) ii > iv > i > iii

c) iv > i > ii > iii

d) iii > ii > i > iv

39. The correct order of acid character among Benzoic acid (i), o- Methyl benzoic acid (ii), p- Methyl benzoic acid (iii), m - Methyl benzoic acid (iv) are

a) ii > i > iv > iii

b) i > iv > iii > ii

c) i > ii > iii > iv

d) iv > ii > iii > i

40. The correct order of acid character among Benzoic acid (i), o- Nitro benzoic acid (ii), p- Nitro benzoic acid (iii), m - Nitro benzoic acid (iv) are

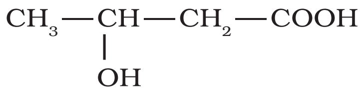
a) ii > iii > iv > i

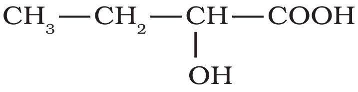
b) ii > iii > i > iv

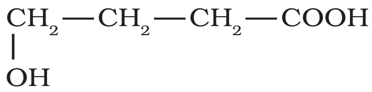
c) i > ii > iii > iv

d) iii > ii > i > iv

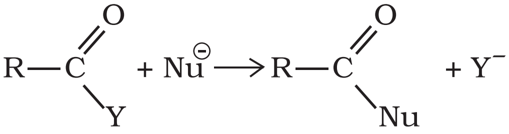
41. Which of these hydroxy carboxylic acid on heating gives unsaturated acid ?

a) 
$CH_3-CH(OH)-CH_2-COOH$

b) 
$CH_3-CH_2-CH(OH)-COOH$

c) 
$CH_2(OH)-CH_2-CH_2-COOH$

d) $C_6H_5\,CH_2\,COOH$

42. The reaction  is fastest when Y is

a) $-Cl$

b) $-NH_2$

c) $-O-C_2H_5$

d) $-OCOR$

43. Which of the following compounds is amphoteric in nature

a) CH_3COCl

b) CH_3CONH_2

c) $CH_3COOC_2H_5$

d) $(CH_3CO)_2O$

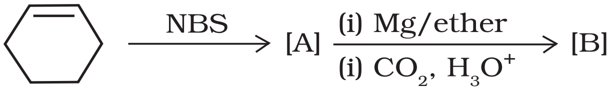
44. When propionic acid is treated with aqueous $NaHCO_3$, CO_2 comes from

a) - CH_3 gr

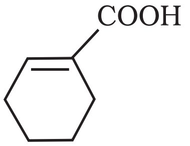
b) - COOH gr

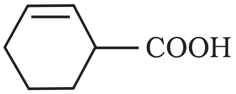
c) > - CH_2 gr

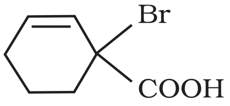
d) - HCO)$_3$ gr

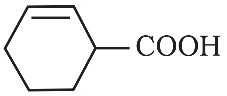
45. 

Here 'B' is

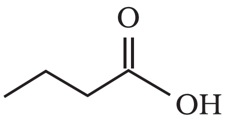
a) 

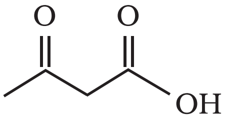
b) 

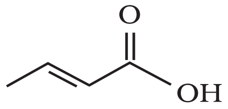
c) 

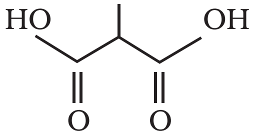
d) 

46. Which of the following is most difficult to decarboxylate

a) 

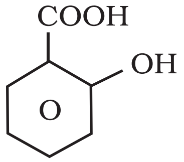
b) 

c) 

d) 

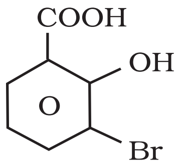
47. Arrange the following is increasing order of their pKa values CH_3COOH (i), Me_3CCH_2COOH (ii), $Me_3N^+CH_2COOH$ (iii)

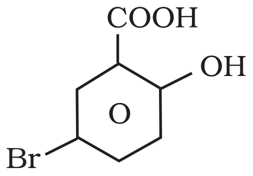
a) i < ii < iii
b) ii < i < iii
c) iii < ii < i
d) iii < i < ii

48. 

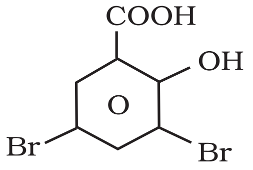
$+ Br_2$ (in acetic acid) $\longrightarrow$ 'X'

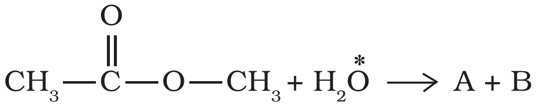
Here 'X' is

a) 

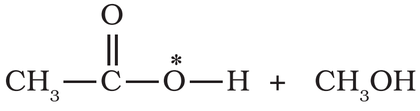
b) 

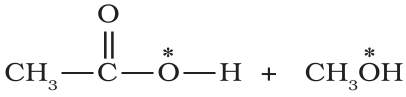
c) both (a) & (b)

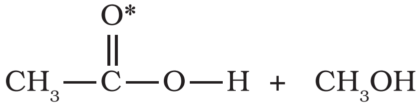
d) 

49. 
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + H_2\overset{*}{O} \longrightarrow A + B$

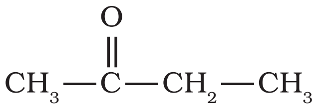
Products A & B are

a) 
$CH_3-\overset{\overset{O}{\|}}{C}-\overset{*}{O}-H + CH_3OH$

b) 
$CH_3-\overset{\overset{O}{\|}}{C}-\overset{*}{O}-H + CH_3\overset{*}{O}H$

c) 
$CH_3-\overset{\overset{O^*}{\|}}{C}-O-H + CH_3OH$

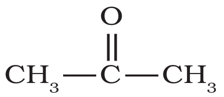
d) None

50. 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3 \xrightarrow{HNO_3}$ Major Product is/ are

a) CH_3COOH b) CH_3CH_2COOH

c) $HCOOH$ d) CH_3CH_2COOH & $HCOOH$

B) Very Short Answer Question : (Each question carries 1 mark)

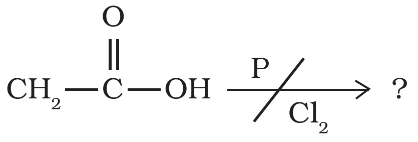
1. Name a Mono carboxylic acid which can respond in the Tollen's reagent test ?
2. Which aldehyde do not respond in the Fehlings Solution ?
3. Name the product which is formed by the action of phenol & Bromine water ?
4. Name the functional isomer of propionaldehyde.
5. How many metamer are possible having molecular formula $C_5H_{10}O$?
6. Among CH_3CH_2CHO & CH_3COCH_3 which one has more DM ?
7. Name the alkync which gives only CH_3CHO on hydration ?
8. Name the alkyne which gives only CH_3COCH_3 on ozonolysis reaction ?
9. Name the monocaeboxylate salt of calcium which gives CH_3COCH_3 on dry distillation.
10. Name the cyanide compound which gives CH_3CHO with grignand reagent ?
11. Which ketone compound can give 3° Butyl alcohol with Grignard reagent ?
12. What is Brady's reagent ?
13. What is Tollen's reagent ?
14. What is Fehling's reagent ?
15. 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{C_6H_5COOOH}$ 'A'

    What is name of the product A?
16. What is aldol ?
17. $HCHO \xrightarrow{50\%\ OH^-} A + B$

    What are the products A & B ?

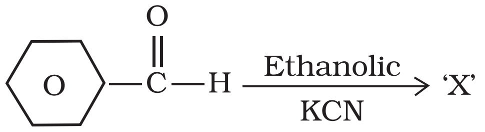
18. $CH_3CHO \xrightarrow{(C_2H_5O)_3\ Al} X + Y$

    What are the Products X & Y ?

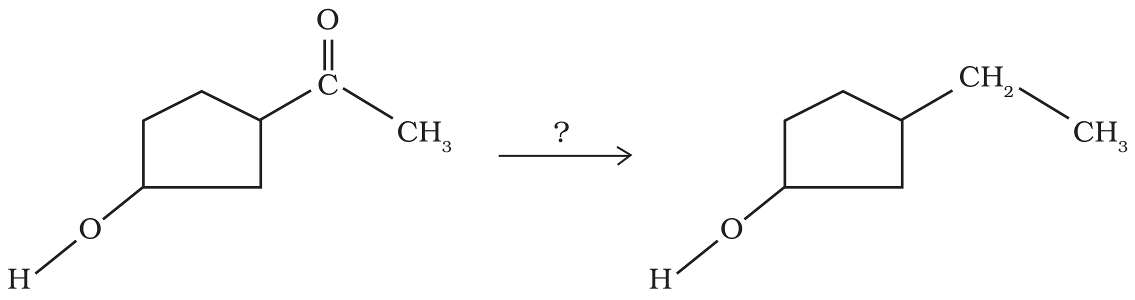
19. What is formalin ?
20. What is mesitylene ?
21. What is Phorone ?
22. What is paraldehyde ?
23. Which one has more dissociation constant among HCOOH & CH_3COOH ?
24. 

    $CH_2-\overset{\overset{O}{\|}}{C}-OH \cancel{\xrightarrow[Cl_2]{P}} ?$

    What is the name of the Product ?

25. What is glacial acetic acid ?
26. Name a chemical compound having no α– H but can't respond in the Cannizaro reaction.
27. 

    What in the structure of the compound X ?

28. 

    Among clemmensen reduction & Wolf kishner reduction which one is better for the abore conversion?

29. Which one gets easily hydrolysed among Acetyl chloride and acetamide.
30. $CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + CO_2 + AgBr$

    What is the name reaction ?

C) Short answer type Questions : (Each question carries 2 marks)

1. a) What Boiling point of CH_3COCH_3 is more than propanal?

   b) What is mesityl oxide?

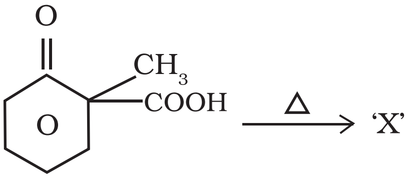
2. a) Why Formic acid respond in the tollen's reagent Test ?

   b) Why boiling point of HCOOH acid is more than CH_3CH_2OH thought their molecular weight is same?

3. a) What is metaldehyde ?

   b) $$CH_3-C\equiv C-H \xrightarrow[\text{(i) } H_2O_2/OH^-]{\text{(i) } B_2H_6} \text{'A'}$$

   What is the name of the product A ?

4. a) 

   What is the name of the product X?

   b) The pKa Value of HCOOH acid is less than CH_3COOH why ?

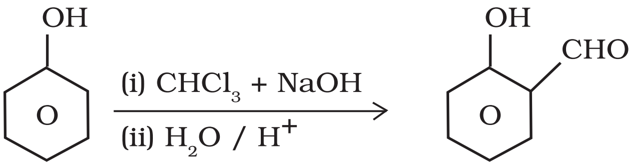
5. a) $$CH_3\,CHO + HCHO\ \text{(excess)} \xrightarrow[\text{(conc.)}]{\text{NaOH}} \text{'A' ?}$$

   What is the name of the compound A ?

   b) Write the Etard's reaction?

6. a) $$CH_3-CHCl_2 \xrightarrow[\text{KOH}]{\text{Aqueous}} \text{'A'}$$

   What is A ?

   b) 

   Name the electrophile in the above reaction ?

7. a) How can you separate the component from the following mixture CH_3CH_2OH, CH_3COCH_3, CH_3COOH

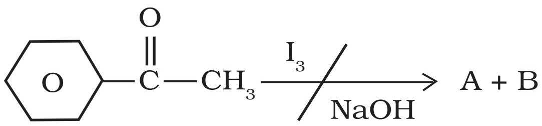
8. Why P^H value should be controlled in the reaction between carbonyl compound and ammonia derivative?

9. How can you distinguish between the following pair

   (i) HCHO and CH_3CHO or CH_3COCH_3 and CH_3CHO

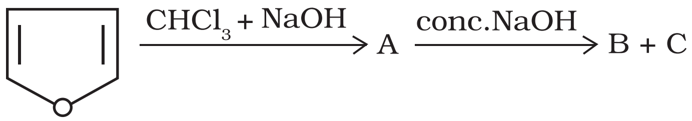
   (ii) HCOOH and CH_3COOH or CH_3COCl and $CH_3CO)_2O$

10. a)



B is the yellow precipitate having characteristic smell. Identify A & B

b)



Identify 'B' & 'C' ?

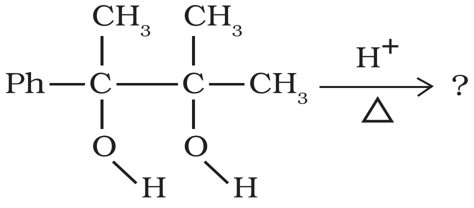
11. a) $C_6H_5CHO + CH_2(COOH)_2 \xrightarrow[\Delta]{H^+} X$

What is the name the compound 'X'?

b) Write the Tischenko reaction ?

12. a) What is Urotropin ?

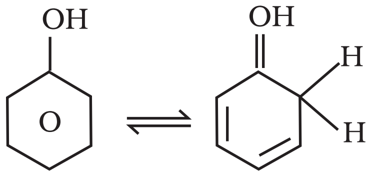
b)



$$Ph-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[\Delta]{H^+} ?$$

What is the name of the product ?

13. a)



I II

Among the two tautomer (i) & (ii) which one is more stable & why?

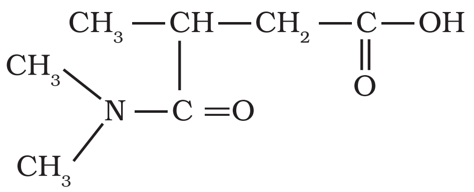
b) Name a compound having ketomethyl group but do not respond in the haloform test?

14. a) What is the IUPAC name of crotonaldehyde?
    b) Name the nucleophile which is used in the cannizaro reaction?
15. a) Write the HVZ reaction ?
    b) Among Na_2CO_3 and $NaHCO_3$ Which one is better reagent to detect the carboxylic group?

D) Long Answer Type Questions : (Each question carries 3 mark)

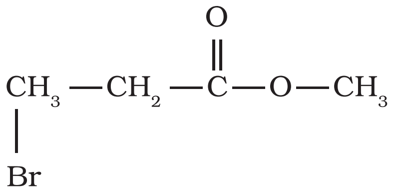
1. a) Write short note on aldol condensation.
   b) How can you distiguish between CH_3COOH & CH_3CH_2OH ?
2. a) Why Boiling point of amide is more than carboxylic acid?
   b) Write dawn the IUPAC Name of fhe following

(i)



(ii) $(CH_3CO)_2O$

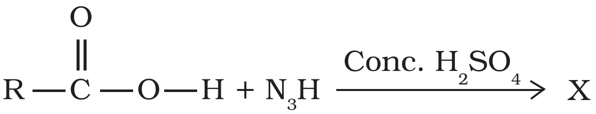
(ii)



$CH_3(Br)-CH_2-C(=O)-O-CH_3$

3. a) Write short note on Holfmann degradation
   b) Why 2° & 3° amide can't take part in the Holfmann degradation
   c) Give the example of a compound which can not take part in the claisen condensation ?

4. a)



$R-\overset{O}{\overset{\|}{C}}-O-H + N_3H \xrightarrow{Conc.\ H_2SO_4} X$

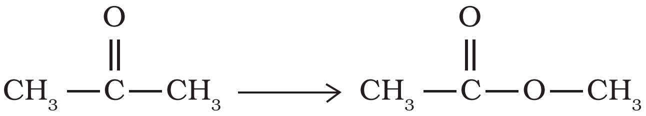
What is the name of the product 'X'? Also mention the name reaction?

   b) Convert the following
      (i) HCOOH ⟶ CH_3COOH
      (ii) HCHO ⟶ CH_3CHO
      (iii) CH_3CHO ⟶ CH_3COCH_3

5. How will you carry out the following conversion

(i) $CH_3COOH \longrightarrow HCOOH$

(ii) $HCHO \longrightarrow CH_3OH$ (Without using reducing agent)

(iii) 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$

(iv) $CH_3COOH \longrightarrow CH_3COCOOH$
(Pyruvic acid)

(v) $CH_3CHO \longrightarrow CH_3-CH=CH-CHO$

(Crotonal dehyde)

Answers

A. Select the correct answer (MCQ) : (Each question carries 1 mark)

1. c	2. b	3. a	4. a	5. b	6. a	7. a
8. c	9. a	10. d	11. b	12. c	13. a	14. b
15. d	16. b	17. c	18. b	19. c	20. d	21. d
22. a	23. c	24. a	25. d	26. a	27. a	28. a
29. b	30. b	31. b	32. d	33. d	34. d	35. d
36. c	37. c	38. a	39. a	40. a	41. c	42. a
43. b	44. b	45. b	46. c	47. b	48. b	49. a
50. b	51. b	52. d	53. b	54. d	55. c	56. a

Chapter - 13

Amines

Chapter at a glance :

1. Amines are derivatives of ammonia (NH_3) obtained by replacement of one, two or all the three hydrogen atoms by alkyl (R-) and or aryl (Ar-) groups.

   eg : $R-\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$

   $Ar-\ddot{N}H_2$, $Ar\ddot{N}HR$, $Ar\ddot{N}HR_2$

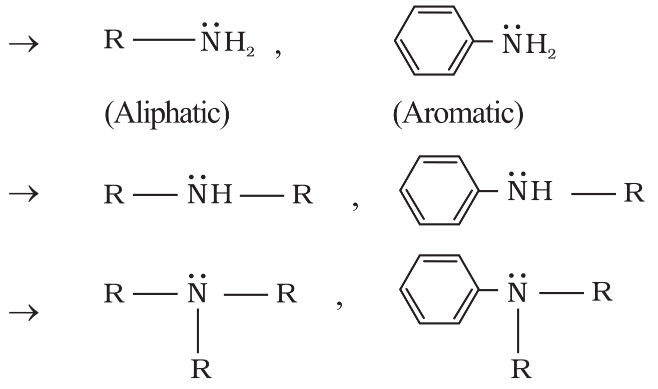
2. Like ammonia $\ddot{N}H_3$, nitrogen atom of amines is trivalent and carries a lone pair of electrons. Central *N* atom is sp^3 hybridised and geometry of amines is pyramidal.

3. Amines are classified as primary (1°), Secondary (2°) and Tertiary (3°) as shown below :

Primary (1°) →

Secondary (2°) →

Tertiary (3°) →



4. Common name of amines : Alkyl amine (Aliphatic) and Aryl amine (Aromatic)

   IUPAC name of amines : Alkanamine

   eg: i) $CH_3-CH_2-NH_2$ (1° amine)

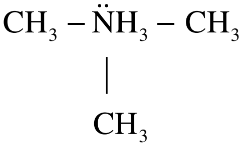
   Common name : Ethyl amine

   IUPAC : Ethanamine

ii) $CH_3 - \ddot{N}H - CH_3$ (2° amine)

Common name : Dimethyl amine

IUPAC : N- Methylmethanamine

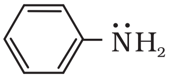
iii) 

$$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{\ddot{N}H_3} - CH_3$$

(3° amine)

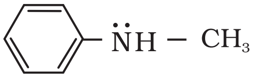
Common name : Trimethyl amine

IUPAC : N,N- dimethyl methanamine

iv) 

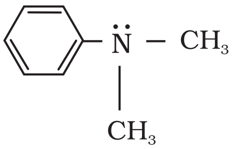
(Aromatic 1° amine)

IUPAC : Aniline

v) 

(Aromatic 2° amine)

IUPAC : N - Methyl aniline

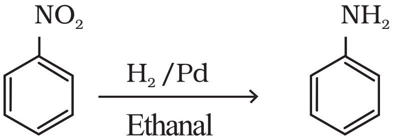
vi) 

(Aromatic 3° amine)

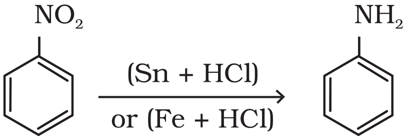
IUPAC : N,N- dimethyl aniline

5. Amines are prepared by the following method :

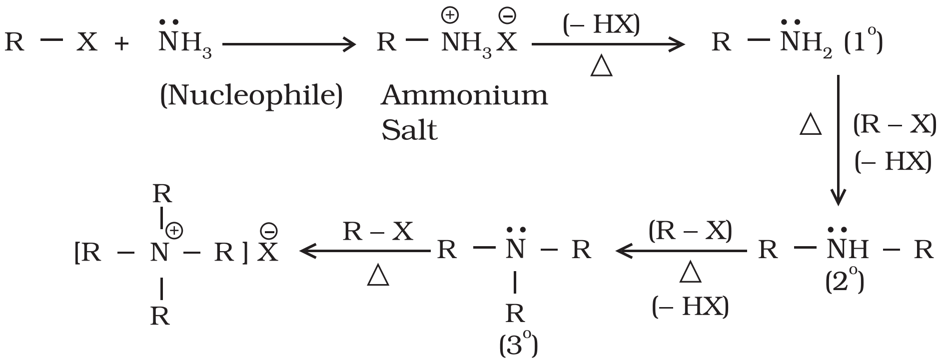
i) By reduction of nitro compounds:



Nitrobenzene Aniline (1° amine)



ii) By ammonolysis of alkyl halides (RX) :



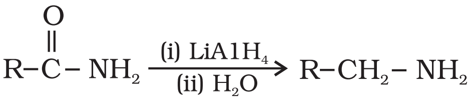
Quaternary ammonium salt.

The order of reactivity of alkyl halides with amines is R-I> R-Br> R-Cl

iii) By reduction of nitriles :

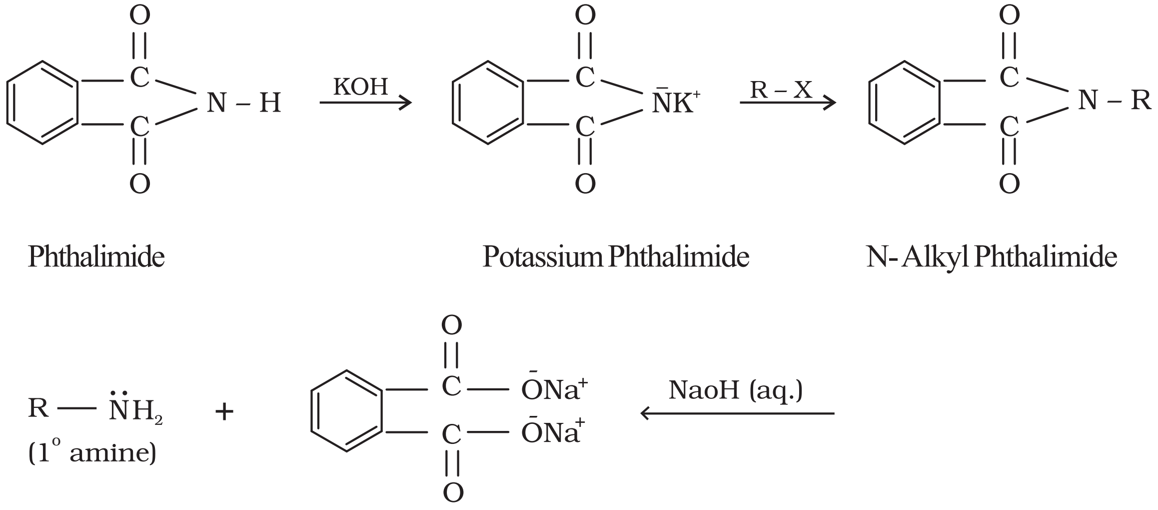
$$R-C\equiv N \xrightarrow[\text{or } Na/C_2H_5OH]{H_2/Ni} R-CH_2-\ddot{N}H_2$$

iv) By reduction of amides



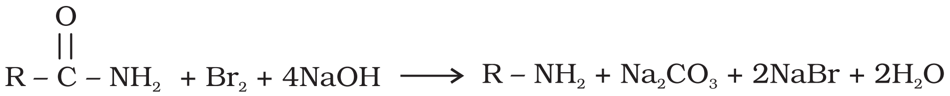
$$R-\overset{\overset{\large O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiA1H_4} R-CH_2-NH_2$$

v) By Gabriel Phthalimide syhthesis :



2^{o} & 3^{o} amine can't be produce by Gabricl pthalimide synthesis.

vi) By Hoffmann Bromamide degradation reaction :



$$R-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

2° & 3° amide do not form 1°– amine

6. Physical properties of amines :

i) Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water moleeules. Solubility decreases with increase in molar mass due to increase in size of the hydrophobic alkyl part.

ii) The order of boiling in more in primary amines than in secondary amines are :

Primary > Secondary> Tertiary

Reason : Intermolecular H-bondind is more in primary amines than in secondary amines, while is tertiary amines these is no H-bording due to absence of H-atom for H bording.

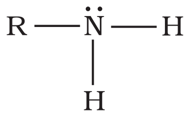
iii) Boiling points of amines alcohols and alkanes of comparable melecular masses are :

Alkane < 3° Amine < 2° Amine < 1° Amine < Alcohol

Boiling Point increases because of intermolecular H– bonding

7. Chemical Properties of amines :

i). Amines are reactive due to electronegativity difference between nitrogen and hydrogen atoms and also the preference of a lone pair of electrons on Nitrogen atom.

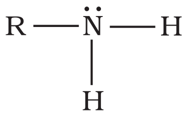


$$R-\underset{\underset{H}{|}}{\ddot{N}}-H$$

(1° Amine)

$R-\ddot{N}H-R$

(2° Amine)



$$R-\underset{\underset{H}{|}}{\ddot{N}}-H$$

(3° Amine)

ii). Amines are basic in nature due to presence of a lone pair of electrons on N- atom. Basic strength depends on the availability of lone pair of electrons for protonation and the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

iii) In aliphatic amines, due to the electron releasing nature (+I) of alkyl group, it (R) Pushes electrons towards nitrogen and thus makes the lone pair of electrons more avalable for protonation. Hence alkyl amines are stronger bases than ammonia (NH_3).

iv) The basic nature of aliphatic amines (In gaseous phase) increases with the increase of the number of alkyl groups (+I effect).

$$\underset{R_3\ddot{N}}{3^{\circ}\text{ amine}} > \underset{R_2\ddot{N}H}{2^{\circ}\text{ amine}} > \underset{R\ddot{N}H_2}{1^{\circ}\text{ amine}} > \ddot{N}H_3$$

Basic strength increases in geseous phase

v) Basic character of amines in aqueous medium:

Amines, being basic is nature, absorbs a proton from water to form ammonium cations.

$$R-\ddot{N}H_2 + H_2O \rightleftharpoons R-\overset{\oplus}{N}H_3 + \overset{\ominus}{O}H$$

$$K = \frac{[R\overset{\oplus}{N}H_3]\ [\overset{\ominus}{O}H]}{[RNH_2]\ \ [H_2O]}$$

$$\text{or,}\quad K.[H_2O] = \frac{[R\overset{\oplus}{N}H_3]\ [\overset{\ominus}{O}H]}{[RNH_2]}$$

$$\text{or,}\quad K_b = \frac{[R\overset{\oplus}{N}H_3]\ [\overset{\ominus}{O}H]}{[RNH_2]}$$

$$\therefore\ pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

vi) In the aqueous phase, the basic strength of amine depends on following factors :

(a) The stability of substituted ammonium cations by electron releasing effect (+I) of alkyl groups (R). The order of stability of ions are.

3°> 2°> 1°

(b) The stability of substituted ammonium cations by solvtion (H-bonding) with water rolecules. The order of H-bonding in water and order of stability of ions by solvation are-

1°> 2°> 3°

Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base.

(c) The stability of substituted ammonium cations by H-bonding is affected by steric hindrance of alkyl groups (R). If the alkyl group is small ($-CH_3$), there is less steric hindrance to H-bonding. But for bigger alkyl group (like-C_2H_5), there will be steric hindrance to H-bonding.

Thus there is a subtle interplay of the inductive effect, solvation effect and steric hindrance of the alkyl groups which decides the basic strength of alkyl amines in the aqueous state.

→ The order of basic strength in case of methyl substituted amines are -

$$(CH_3)_2\,NH > CH_3\,NH_2 > (CH_3)_3\,N > NH_2$$

$$2^\circ \quad > \quad 1^\circ \quad > \quad 3^\circ$$

→ The order of basic strength in case of ethyl or bigger alkyl groups substitited amines are–

$$R_2\,NH > R_3N > RNH_2 > NH_3$$

$$2^\circ > 3^\circ > 1^\circ$$

eg. $\underleftarrow{(C_2H_5)_2\,NH > (C_2H_5)_3\,N > C_2H_5NH > NH_3}$

Basic stranght increases

K_b Value increases

pK_b Value decreases

vii) In the aromatic amines, the - NH_2 group is attached directly to the benzene ring. It results in the lone pair of electrons on hydrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. Hence aromatic amines (like aniline) are weaker base (less K_b value i.e high pk_b value) as compared to ammonia or aliphatic amines.

In case of substituted aniline, it is observed that electron releasing groups like - OCH_3, - CH_3 increase basic strength whereas electron withdrawing groups like of - NO_3, - SO_3H, COOH, - X decrease basic strength.

viii) Alkylation of amines :

Amines under go alkylation on reaction with alkyl halides.

$$R - \ddot{N}H_2 \xrightarrow[(-HX)]{R-X} R_3\ddot{N}H \xrightarrow[(-HX)]{R-X} R_3\ddot{N} \xrightarrow[R_4\overset{\oplus}{N}\overset{\ominus}{X}]{R-X}$$

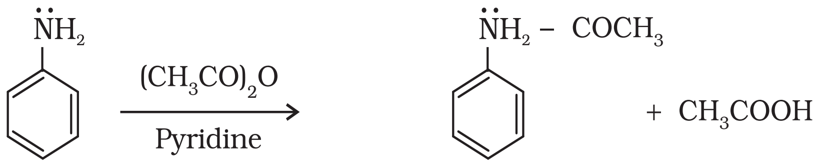
ix) Acylation of amines :

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and ester by nucleophilic substitution reaction. this reaction is known as acylation.

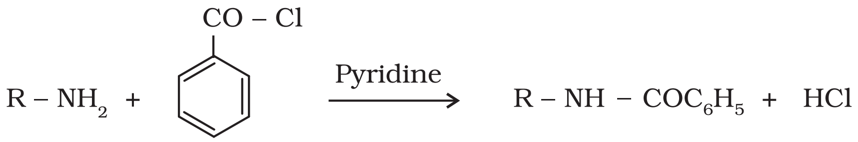
The reaction is carried out in presence of base like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.

$$R - \ddot{N}H_2 \xrightarrow[\text{Pyridine}]{CH_3COCl} R - \ddot{N}H - COCH_3 + HCl$$

$$R_2 - \ddot{N}H \xrightarrow[\text{Pyridine}]{CH_3COCl} R_2 . \ddot{N} - COCH_3 + HCl$$

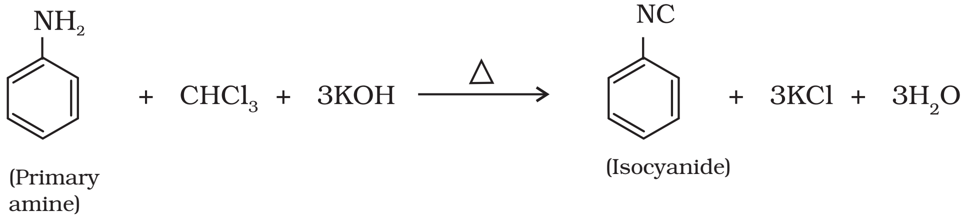


Amines when react with benzoyl chloride, the reaction is known as benzoylation.



x) Carbylamine reaction :

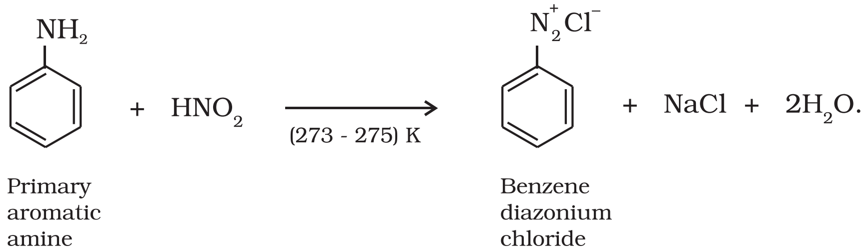
$$\underset{\text{(Primary amine)}}{R - NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{(Isocyanide) or Carbylamine) Foul smelling subtancy}}{R - NC} + 3KCl + 3H_2O$$



Secondary and Tertialy amines do not show carbylamines reaction. This reaction is used as a test for primary amines (Aliphatic and Aromatic both).

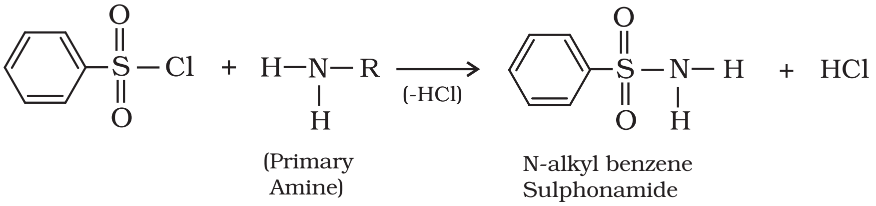
xi) Reaction with nitrous acid (HNO_2)

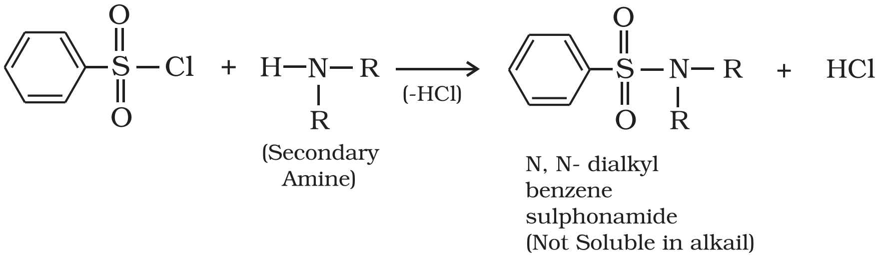
$$\underset{\text{(Primary amine)}}{R - NH_2} + HNO_2 \xrightarrow[0^{o} - 5^{o}C]{(NaNo_2 + HCl} \underset{\text{Unstable}}{[R - \overset{+}{N_2} Cl^{-}]} \xrightarrow{H_2O} R - OH + N_2 + HCl$$



xii) Reaction with arylsulphonyl chloride :

Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is known as Hinsberg's reagent. It reacts with primary and secondery amines to form sulphonamides.





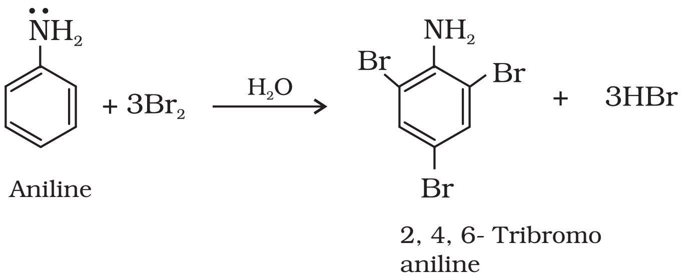
Tertiary amines do not react with benzene sulphonyl chloride.

Hence Hinsberg test can be used to distinguish between 1°> 2°> and 3° amines.

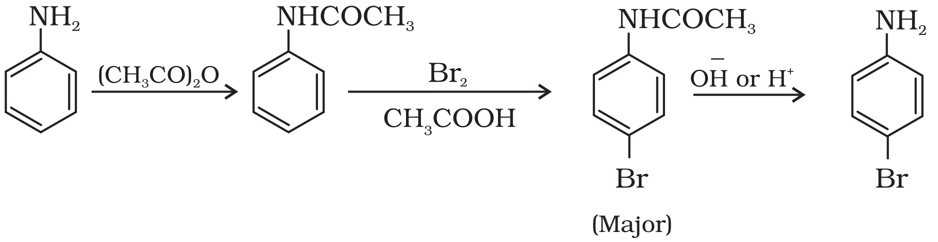
xiii) Electrophilic substitution reaction :

Due to '+R' effect -NH_2 group is ortho and para directing to wards S_E reaction is aromatic amines like ariline. -NH_2 group is a powerful activating group.

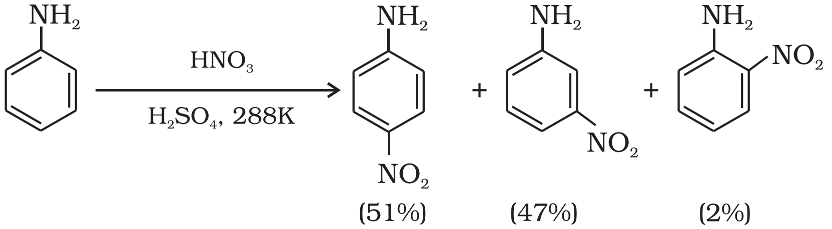
a) Bromination :

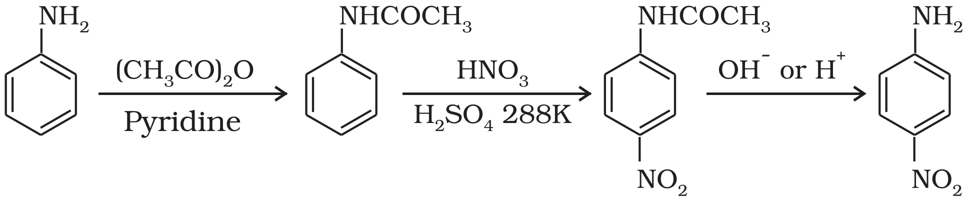


To prepare monosubstituted aniline derivative, we have to protect the -NH_2 group by acetylation.



b) Natration :

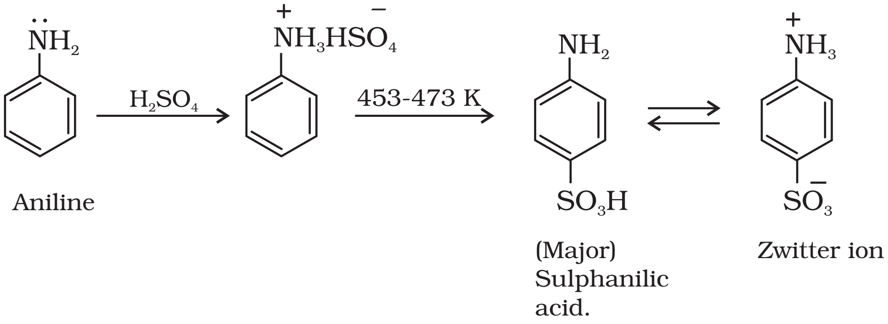




-NH_2 group is ortho and para directing towards S_E, but in acidic medium, it form anilinium ion which is meta directing. So a mixture of ortho, meta and para derivatives are formed. However, by protecting -NH_2 group by acetylation followed by nitration given 4-nitroaniline.

c) Sulphonation :

Aniline reacts with concentrated sulphuric acid to form anilinium hydrogen sulphate which on heating with sulphuric acid at 453-473 K produces 4- amino benzene sulphonic acid (sulphanilic acid) as major product.



Aniline does not undergo Friedel-crafts reaction due to salt formation with $AlCl_3$, the lewis acid, used as catalyst.

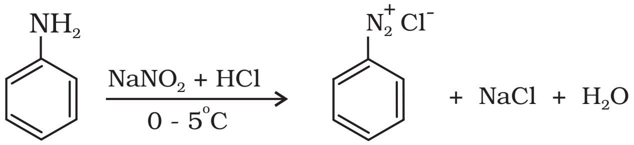
xiv) Benzene diazonium salts :

The diazonium salt have the general formula $RN_2^+X^-$, where R stands for an alkyl group or an aryl group.

Primary aliphatic amines form highly unstable alkyl diazonium salts on treatment with HNO_2, where as primary aromatic amines form stable arene diazonium salts at law temperature (273-278 K).

$$R - NH_2 \xrightarrow[O°C]{HNO_2} \underset{\text{Vesy unstable}}{\left[R - \overset{+}{N_2}\,Cl^-\right]} \xrightarrow{H_2O} R - OH + N_2 + HCl$$

Preparation of behzene diazonium chloside by diazotisation reaction :



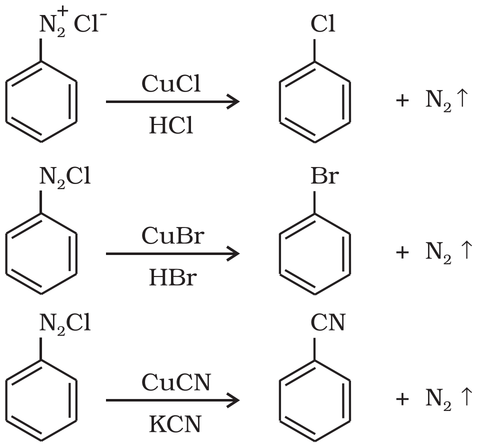
Aniline

xv) Chemical reactions of diazonium slats :

Reaction involving displacement of nitrogen :

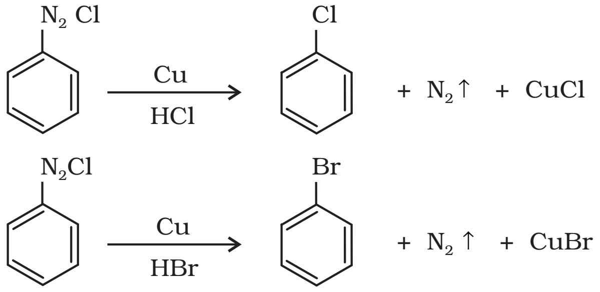
Diazonium group is a good leaving group :

a)



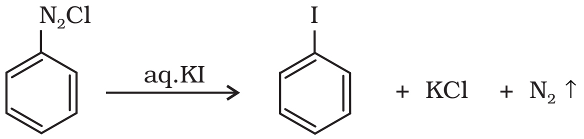
This reaction is called Sandmeyer reaction.

b)

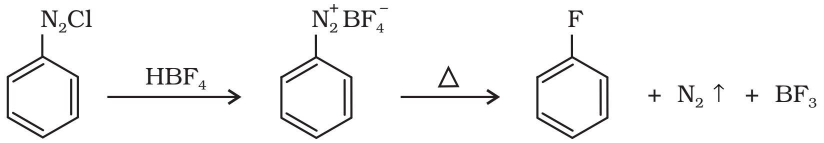


This reaction is called Gatterman reaction.

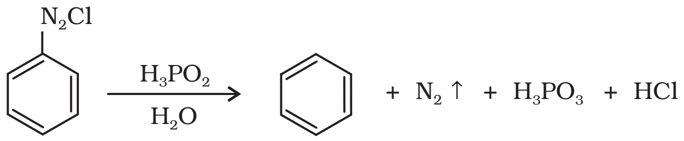
c)



d)



e)



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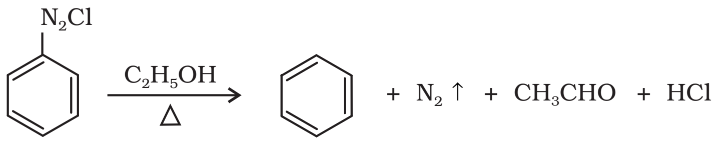
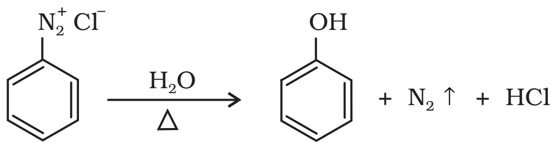
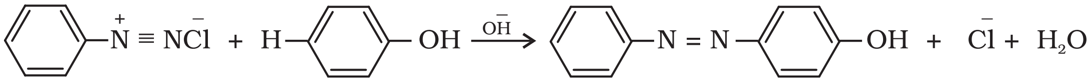


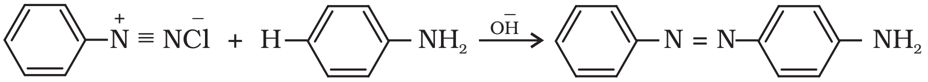
g)



Reaction involving retention of diazo group :



P - hydroxy azo benzene
(orange dye)

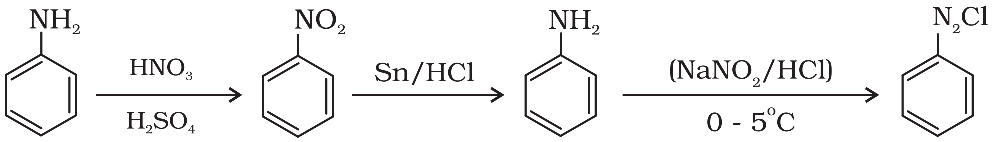


P - Amino azobenzene
(yellow dye)

This reaction is called coupling reaction.

xvi) Importance of diazonium salts in aromatic compound synthesis :

Diazonium salts are very good intermediate for the introduction of -F, -Cl, -Br, -I, -CN, -OH groups into the aromatic ring. Thus, the replacement of diazo group by other groups in helpfull in the synthesis of aromatic compounds which can not be prepared by direct substance in benzene or substituted benzene. So, benzene is converted to diazonium salt for synthesis of other aromatic compounds through the following route:



A. Select the correct option (MCQ) : Each question carries 1 mark

1. The amine that does not react with acetyl chloride is -

   a) CH_3NH_2 b) $(CN_3)_2NH$

   c) $(CN_3)_3N$ d) None of these

2. Which is most basic ?

   a) $C_6H_5NH_2$ b) $(C_6H_5)_2NH$

   c) CH_3NH_2 d) $(CH_3)_2NH$

3. The hybrid state of N in R_2NH is-

   a) sp^3 b) sp^2

   c) sp d) dsp^3

4. Which of the following does not react with hinsberg reagent?

   a) Ethylamine b) $(CH_3)_2NH$

   c) $(CH_3)_3N$ d) Propar -2-alnine

5. $C_2H_5NH_2 \xrightarrow{NaNO_2,HCl}$ Ⓧ $\xrightarrow[P]{Br_2}$ Ⓨ $\xrightarrow[\text{(Excess)}]{NH_3}$ Ⓩ

   a) Cyahoethare b) Ethanamide

   c) Methanamine d) Ethanamine

6. Oxidation of aniline with $K_2Cr_2O_7/H_2SO_4$ gives-

   a) Phenylhydroxylamine b) P-benzoquinone

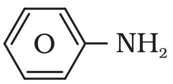
   c) Nitrosobenzene d) Nitrobenzene

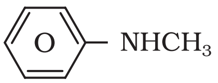
7. Which of the following cannot couple with benzene diazorium chloside?

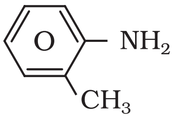
   a) Aniline b) Phenol

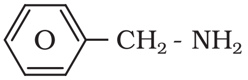
   c) β - Naphthol d) Benzyl alcohol

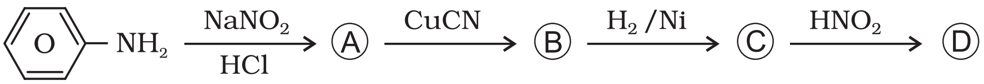
8. Which of the following is the strongest base?

a)


b)


c)


d)


9.


The structure of 'D' would be-

   a) $C_6H_5CH_2OH$ b) $C_6H_5CH_2NH_2$

   c) C_6H_5NHOH d) $C_6H_5NHCH_2CH_3$

10. The correct order of increasing basic nature is-

   a) $CH_3NH_2 < (CH_3)_2NH < NH_3$

   b) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

   c) $(CH_3)_2NH < NH_3 < CH_3NH_2$

   d) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

11. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives-

   a) Diphenyl ether b) P-hydroxy azobenzene

   c) Chlorobenzene d) Benzene

12. Identify the product in the following :

3,4,5,- tribromo aniline $\xrightarrow[\text{(ii) } H_3 PO_2]{\text{(i) } HNO_2 /O^{o}C}$?

a) 3,4,5 - tribromo benzene b) 1,2,3 - tribromo benzene

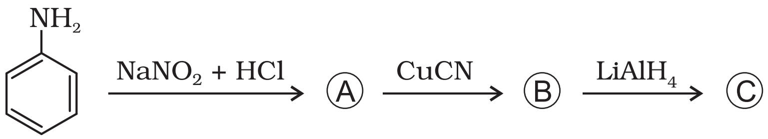
c) 2,4,6 - tribromo benzene d) 3,4,6 - tribromo benzene

13. Which will not take part in the diazotisation?

a) C_6H_5NH b) $C_6H_5CH_2NH_2$

c) $H_2N - C_6H_4 - CH_3$ d) $H_2N - C_6H_4 - NO_2$

14.



The product ‘C’ is-

a) Benzonitrile b) Benzaldehyde

c) Benzoic acid d) Benzyl amine

15. Reaction of aniline with benzaldehyle is -

a) Poly merisation b) Condensation

c) Addition d) Substitution

16. Which of the following statements about primary anines is false?

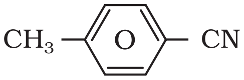
a) Alkyl amines are stronger bases than aryl amines.

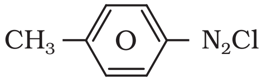
b) Alkyl amines react with nitrous acid to produce phenols.

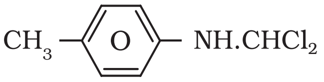
c) Aryl amines react with nitrous acid to produce phenols.

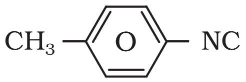
d) Alkyl amines are stronger bases than ammonia.

17. The reaction of chloroform with alcoholic KOH and P-toluidine forms-

a) 

b) 

c) 

d) 

18. In the following reaction :

$$\textcircled{X} \xrightarrow{\text{Bromination}} \textcircled{Y} \xrightarrow[\text{+ HCl}]{NaNO_2} \textcircled{Z} \xrightarrow[C_2H_5OH]{\text{Boiling}} \text{Tribromobenzene}$$

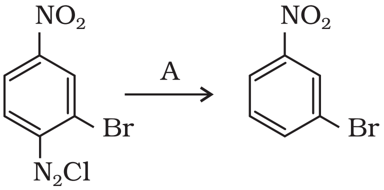
The compound ‘x’ is-

a) Benzoic acid
b) Salicylic acid
c) Phenol
d) aniline

19. Which of the following compounds will hot undergo friedel craft’s reaction easily?

a) Xylene
b) Nitrobenzene
c) Toluene
d) Cumene

20.



A is -

a) Cu_2Cl_2
b) H_3PO_2 and H_2O
c) H^+/H_2O
d) $HgSO_4$ / H_2SO_4

21. Among the following conpounds, the one that is most reac tive towards electrophilic nitration is-

a) Benzoic acid
b) Nitro benzene
c) Toluene
d) Benzene

22. Some meta directing substituents in aromatic substituting are given below. Which one in most deactivating?

a) $-SO_3H$
b) $-COOH$
c) $-NO_2$
d) $-C \equiv N$

23. Which one of the following or reduction with $LiAlH_4$ yields a secondary amine?

a) Methyl isocyanide
b) Acetamide
c) Methyl cyanide
d) Nitro ethane

24. Phenyl isocyanide prepared by which of the following reaction?

a) Reimer- Tiemann reaction
b) Carbylamine reaction
c) Rosenmund’s reaction
d) Wurtz reaction

25. Which product is formed, when acetonitrile is hydrolysed partially with cold concentrated alkali?

a)	Methyl cyanide	b)	Acetic anhydride
c)	Acetic acid	d)	Acetamide

B. Assertion Reason type Question : (Each question carries 1 mark)

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given.

Choose the correct answer out of the following choices.

a) Both assertion and reason are correct and reason is the correct explanation of assertion.

b) Both assertion (A) and reason (R) are correct but the reason is not the correct explanation of assertion.

c) Assertion (A) is a correct statement, but the reason (R) is a wrong statement.

d) Assertion is wrong but reason is correct.

1. Assertion : Acylation of amines gives a mono- substituted product whereas alkylation of amine gives a poly substituted product.

   Reason : Acyl group sterically hinders the approach of further acyl groups.

2. Assertion : Aromatic 1° amines can be prepared by Gabriel phthalimide synthesis.

   Reason : Acyl halides undergo nucleophilic substitution reaction with anion formed by phthalimide.

3. Assertion : Acetanillide is less besic than aniline.

   Reason : Acetylation of aniline results in a decscase of electron density on nitrogen.

4. Assertion : Hoffmann's bromamide reaction is used to prepare primary amines.

   Reason : Primary amines are more basic than secondary amines.

5. Assertion : N-Ethyl benzene sulphonamide is soluble in alkali.

   Reason : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

6. Assertion : A primary amine has higher boiling point than any tertiary amine.

   Reason : A tertiary amine has greater number of N-H bords for H-bonding

7. Assertion : Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

Reason : $FeCl_2$ formed gets hydsolysed to release HCl during the reaction.

8. Assertion : Amines are basic in nature.

Reason : Amines have lone pair of electrons on nitrogen atom.

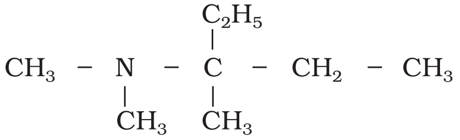
9. Assertion : Nitration of aniline can be conveniently done by protecting the amino group by acetylation.

Reason : Acetylation increases the electron density in the benzene sing.

10. Assertion : Aniline does not undergo Friedel crafts reaction.

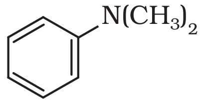
Reason : $-NH_2$ group of aniline reacts with $AlCl_3$ to give acid-base reaction.

C. Very short answer type Questions : (Each question carries 1 mark)

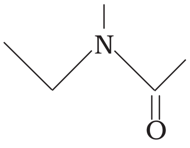
1. Give the IUPAC name of 

$CH_3 - \underset{CH_3}{N} - \overset{C_2H_5}{\underset{CH_3}{C}} - CH_2 - CH_3$

2. Write down the structural formula and IUPAC name of iso butyl amine.

3. Write down the IUPAC name of 

4. Write the structural formula and IUPAC name of allylamine.

5. Give IUPAC name of 

6. What is Hinsberg's reagent?

7. Arrange the followings in decreasing order of their basic strength in aqueous aolutions :

CH_3-NH_2, $(CH_3)_2$-NH, $(CH_3)_3$-N and NH_3

8. Why is alkylamine more basic than ammoria?

9. What is diazotisation?

10. Explain why n-propylamine has higher boiling point than trimethyl amine?

11. Why is NH_2 group of aniline acylated before carrying out nitration?

12. Explain why diazonium salt of aromatic amines are more stable than those of aliphatic amines?
13. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?
14. Direct nitration of aniline is not carrired out. Explain
15. Why aromatic primary amines can not be prepared by gabriel phtha limide synthesis?
16. Arrange the following in decreasing order of their basic strergth :

    $C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3
17. How will you convert aniline into benzene?
18. Arrange the following in the decreasing order of boiling point:

    $(C_2H_5)_2NH$, $C_4H_9NH_2$, $C_2H_5N(CH_3)_2$
19. What is the best reagent to convert nitrile to primary amine?
20. Why do amines behave as nucleophiles?
21. For a amine RNH_2 Write the expression for K_b to indicate its basic strength.
22. What is the role of pyridine in the acylation reaction of amines?
23. Mention the chief use of quaternary ammonium salts derived from long chain amines.
24. Mention two inportant uses of sulphanilic acid.
25. Why is benzene diazonium chloride not stored & is used immediately after its preparation?
26. Arrange the following compounds in increasing order of solubility in water :

    $C_6H_5NH_2$, $C_2H_5N(CH_3)_2$, $(C_6H_5)_2NH$ & CH_3NH_2
27. Convert : Aniline into p-Nitroaniline.
28. Which one is more basic and why? CH_3NH_2 or NH_3
29. How will convert : Benzene into aniline.
30. Write the chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

D. Short Answer Questions : (Each question carries 1 mark) 3)

1. Illustrate the following reactions giving a suitable example for each :

    i) Hoffmann bromamide reaction.

ii) Carbylamine reaction.

iii) Gatterman reaction.

2. Complete the following reactions :

i) $$CH_3 - CO\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\triangle} \textcircled{A} \xrightarrow[\triangle]{Br_2 / KOH} \textcircled{B} \xrightarrow[Pyridine]{CH_3COCl} \textcircled{C}$$

ii) $$C_6H_5\overset{+}{N_2}\overset{-}{BF_4} \xrightarrow{NaNO_2} \textcircled{A} \xrightarrow{Sn / HCl} \textcircled{B} \xrightarrow[\triangle]{CHCl_3 + KOH\ (alc)} \textcircled{C}$$

3. Write the chemical equation involved when $C_6H_5NH_2$ is treated with the following reagents :

i) CH_3COCl/ Pyridine

ii) $C_6H_5SO_2Cl$

iii) $CHCl_3$+KOH

4. Arrange the following:

i) In increasing order of their basic strength : C_6H_5-NH_2, CH_3-CH_2-NH_2, CH_3-NH-CH_3.

ii) In increasing order of solubility in water : CH_3-NH_2, $(CH_3)_3N$, $(CH_3)_2NH$.

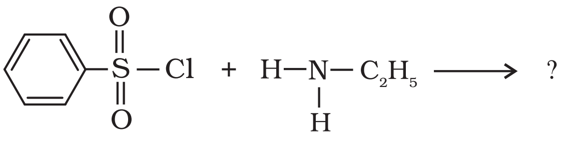
5. Give the structures of A,B,C in the following reaction :

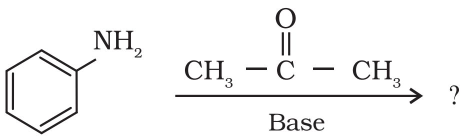
i) $$C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{CuCN} \textcircled{A} \xrightarrow{H_2O / H^+} \textcircled{B} \xrightarrow[\triangle]{NH_3} \textcircled{C}$$

ii) $$C_6H_5NO_2 \xrightarrow{Sn/HCl} \textcircled{A} \xrightarrow[HCl]{NaNO_2} \textcircled{B} \xrightarrow[H^+]{H_2O} \textcircled{C}$$

6. Write the main products of the following reaction

i) $$CH_3CH_2NH_2 \xrightarrow[0^oC]{HNO_2} ?$$

ii) 

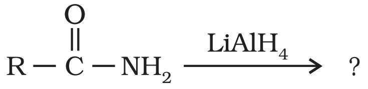
iii) 

7. Give the structures of A, B, C in the followings

i) $CH_3CH_2I \xrightarrow{NaCN} Ⓐ \xrightarrow[\text{Partial hydrolysis}]{OH^-} Ⓑ \xrightarrow[HCl]{NaOH + Br_2} Ⓒ$

ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} Ⓐ \xrightarrow{NaOBr} Ⓑ \xrightarrow[HCl]{NaNO_2} Ⓒ$

8. Complete the following equation :

i) 

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} ?$

ii) $C_6H_5\text{-}N_2Cl + H_3PO_2 + H_2O \longrightarrow ?$

iii) $C_6H_5NH_2 + Br_2(aq.) \longrightarrow ?$

9. How will you convert ?

i) Methyl amine into ethylamine

ii) Aniline into p-bromo aniline.

iii) Aniline into 1,2,3 - tribromobenzene.

10. Account for the following :

i) Although amino group is o-& p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

ii) Aniline does not undergo friedel -Crafts reaction.

iii) Ethylamine is soluble in water, whereas aniline is not.

11. State reasons for the following :

i) pK_b value for aniline is more than that for methylamine

ii) Primary amines have higher boiling points than tertiary amines

12. Account for the following:

i) Silver chloride dissolves in aqueous methylamine solution.

ii) Electrophilic substitution in case of aromatic amines takes place more readily than in benzene.

iii) Ammonolysis of alkyl halides does not give the corresponding amine in pure state.

13. i) How can you convert an amide into an amine having one carbon less than the starting compound?

ii) What is the name reaction?

iii) Give the IUPAC name & structure of the amine obtained by the above method if the amide is 3- chlorobutanamide.

14. How are the following conversions carried out?

    i) Aniline to Fluorobenzene

    ii) Benzene diazonium chloride to benzene

    iii) Methyl chloride to ethylamine.

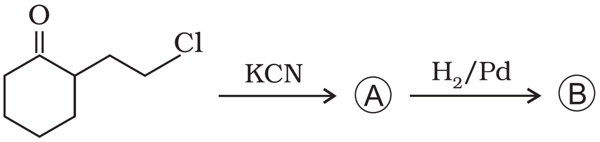
15. Give one chemical test to distinguish between the following pairs of amines:

    i) Methylamine and dimethylamine.

    ii) Ethylamine and aniline.

    iii) Aniline and benzylamine.

16. Identify A and B in the following reaction :



17. Give reasons for the following :

    i) Aniline does not undergo Friedel crafts reaction.

    ii) p- Methylaniline is more basic than p- nitroaniline.

    iii) Acetylation of $-NH_2$ group in done is aniline before preparing its ortho and para compounds.

18. Complete the following reaction

    i) $C_6H_5COOH \xrightarrow{NH_3}$ Ⓐ $\xrightarrow{\Delta}$ Ⓑ $\xrightarrow{Br_2\ /\ KOH}$ Ⓒ

    ii) $C_6H_5 - NO_2 \xrightarrow{Fe/HCl}$ Ⓐ $\xrightarrow[+\ HCL\ (273 - 278)\ K]{NaNO_2}$ Ⓑ $\xrightarrow{CuCN}$ Ⓒ

    iii) $CH_3 - Cl \xrightarrow{KCN}$ Ⓐ $\xrightarrow{LiAlH_4}$ Ⓑ $\xrightarrow[273\ K]{HNO_2}$ Ⓒ

19. Arrange the following compounds in the order of property indicated :

    i) NH_3, RNH_2, R_2NH, R_3N (increasing basic strength in aqueoen solution)

    ii) $CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH (increasing order of dipole moment)

    iii) p- toluidine, N,N- dimethyl -p-toluidine, p-Nitroaniline, aniline (increasing basicity)

20. How will you convert :

    4- nitrotoluene to 2- bromobenzoic acid.

21. Account for the following :
    - i) Tertiary amines do not undergo acylation reaction.
    - ii) Benzylamine is more basic than aniline.
    - iii) pK_b of aniline is more than that of methylamine.

22. How are the following conversions carried out?
    - i) Benzamide to toluene.
    - ii) Benzene to p- nitro aniline
    - iii) Ethylamine to methylamine

23. Describe Hinsberg method for the identification of primary, secondary and tertiary amines. Also write the equation of the reaction involved.

24. Write the structures of main products when aniline reacts with the following reagents :
    - i) Br_2 water
    - ii) HCl
    - iii) $(CH_3CO)_2O$ in pyridine

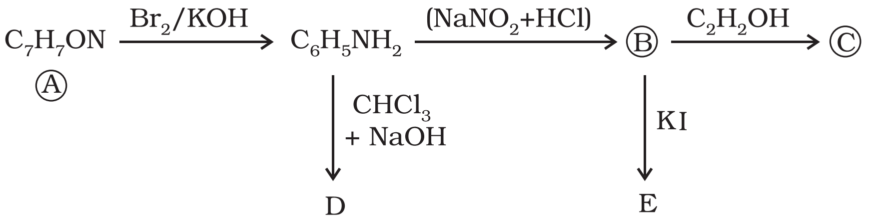
25. Give a simple chemical test to distinguish between the followings :
    - i) $(CH_3)_2$ NH and $(CH_3)_3$ N
    - ii) Aniline and N- methyl aniline
    - iii) Ethylamine and aniline

26. Write chemical equation for the following Conversions :
    - i) Nitrobenzene to benzoic acid.
    - ii) Benzyl chloride to 2- phenylethanamine
    - iii) Aniline to benzyl alcohol.

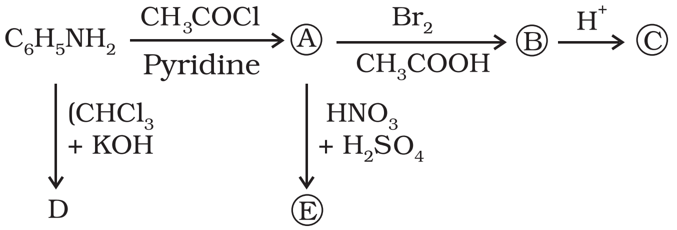
27. Give possible explanation for each of the following :
    - i) The Presence of a base is needed in the ammonolysis of alkyl halides
    - ii) Amides are more acidic than amines.
    - iii) Aniline gets coloured on standing in air for a long lime.

E. Long Answer Questions : (Each question carries 5 mark)

1. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reaction :



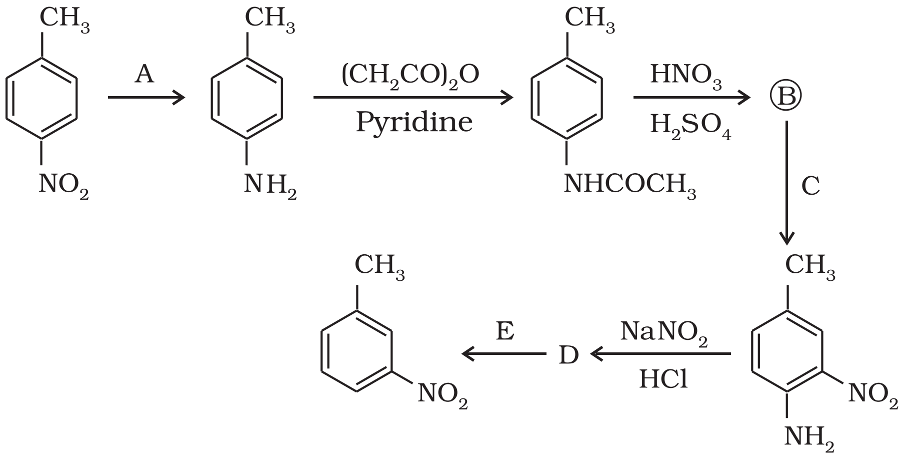
2. Write the structures of A, B, C, D and E in the following reaction :



3. An aromatic compound 'A' on treatment with aqueous ammonia and heating form compound 'B' which on heating with Br_2 and KOH form a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of the compounds A, B and C.

4. A hydrocarbon 'A' (C_4H_8) on reaction with HCl gives a compound 'B' (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C' yields an optically active alcohol, 'D' Ozonolysis of 'A' gives to mole of acetaldehyde. Identify the compounds 'A' to 'D'. Explain the reaction involved.

5. Predict the reagents or the products in the following reaction sequence :



Answers

A. MCQ : (Answer key)

1. (c) 2. (d) 3. (a) 4. (c) 5. (d) 6. (b)
7. (d) 8. (d) 9. (a) 10. (d) 11. (b) 12. (b)
13. (b) 14. (d) 15. (b) 16. (c) 17. (d) 18. (d)
19. (b) 20. (b) 21. (c) 22. (c) 23. (a) 24. (b) 25. (d)

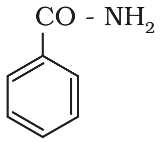
B. Assertion and Reason tpye question: (Answer key)

1. (c) 2. (a) 3. (a) 4. (c) 5. (a) 6. (c) 7. (d)
8. (a) 9. (c) 10. (a)

E. Answers of Long Answer Questions : (Mark- 5)

1.

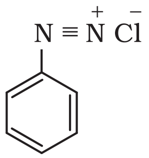
A =



Benzamide

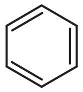
,

B =



Benzanediazonium
Chloride

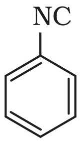
C =



Benzene

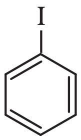
,

D =



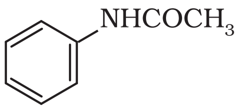
Phenyl Isocyanide

E =



Iodo benzene

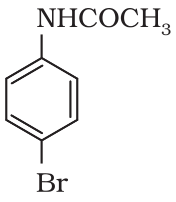
2. A =



Acetanilide

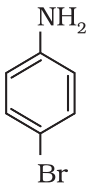
,

B =



P- Bromo acetanilide

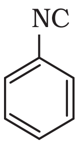
C =



P- Bromoaniline

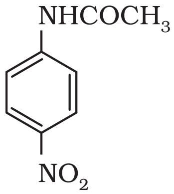
,

D =



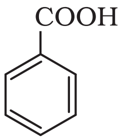
Phenyl isocyanide

E =



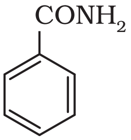
P- Nitroacetanilide

3. A =



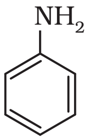
Benzoicacid

, B =



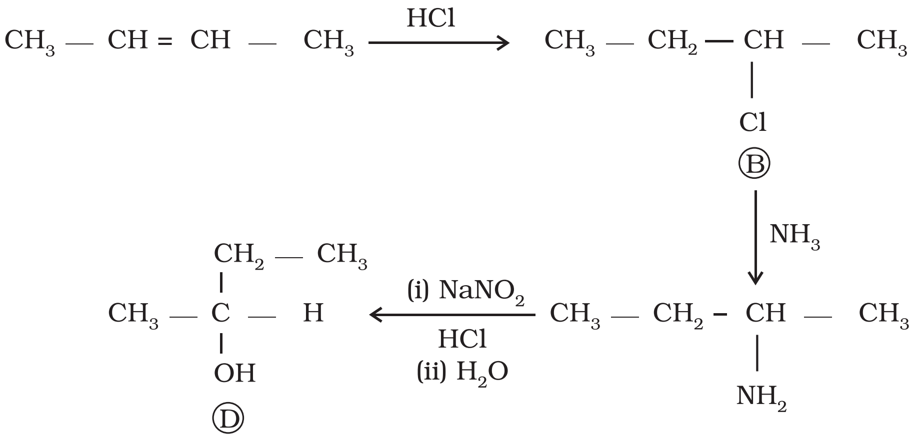
Benzamide

, C =



Aniline

4.

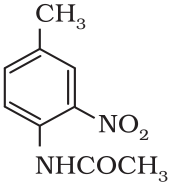


$$CH_3-CH=CH-CH_3 \xrightarrow{HCl} CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3 \ \text{Ⓑ}$$

$$\text{Ⓑ} \xrightarrow{NH_3} CH_3-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } NaNO_2,\ HCl} CH_3-\overset{\overset{CH_2-CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-H \ \text{Ⓓ}$$

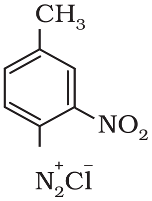
5. A = Sn - HCl (Conc)

B =



C = H_2O / H^+

D =



C = H_3PO_2 / H_2O

Chapter - 14

Biomolecules

Chapter at a glance :

(1) Living systems are made up of various complex biomolecules like carbohydrates, proteins, nuclic acids, lipids etc. The persuit of knowledge of what goes on chemically within a living system falls in the domain of biochemistry.

(2) Carbohydrates : Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis.

Most of them have a general formula, $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived.

But all the compounds which fit into this formula may not be classified as carbohydrates. For example general formula of acetic acid is $C_2(H_2O)_2$ but it is not a carbohydrate. Similarly rhamnose, $C_6H_{12}O_5$ is a carbohydrate but does not fit is this definition.

Some of the carbohydrates which are sweet in test, are also called sugars. For example sucrose, lactose etc.

Carbohydrates are also called saccharides (Greek : sakcharon means sugar)

(3) Classification of carbohydrates :

On the basis of their behaviour on hydrolysis carbohydrates are classified into following three groups.

(i) Monosaccharides : A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or keton is called a monosaccharide. Examples are glucose, fructose, ribose etc.

(ii) Oligosaccharides : Carbohydrates that yeild 2 - 10 monosaccharide units, on hydrolysis, are called oligosaccharides.

They are further classified as disaccharides, trisaccharides, tetra saccharides etc, depending upon the number of monosaccharide, they provide on hydrolysis.

For examples sucrose, maltose, lactose etc.

(iii) Polysaccharides : Carbohydrates which yield more than 10 number of monosaccharide unit on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums etc.

(4) On the basis of action on Fehling's solution and Tollen's reagent carbohydrates may also be classified into reducing and non-reducing sugar's. The carbohydrates which reduces Fehling's solution and Tollen's reagent are called reducing sugars. All monosaccharides are reducing sugars. The carbohydrates which can't reduce Fehling's solution and Tollen's reagent are called non reducing sugars. For example maltose lactose, sucrose etc.

(5) Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them.

Different types of monosaccharides

No. of carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

(6) Preparation of Glucose :

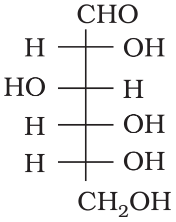
(i) From cane sugar : The carbohydrate present in cane sugar is sucrose. If sucrose is boiled with dilute HCl or H_2SO_4 on alcoholic solution glucose and fructose are obtained in equal amounts.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H+} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

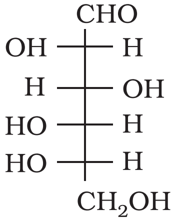
(ii) Commercial process : Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393K under pressure.

$$\underset{\text{(Starch)}}{(C_6H_{10}O_5)n} + nH_2O \xrightarrow[393K,2-3atm]{H+} \underset{\text{(Glucose)}}{nC_6H_{12}O_6}$$

(7) Structure of glucose : Glucose is an aldohexose and is also known as dextrose. The open or free chain structure of glucose is :



D (+) glucose



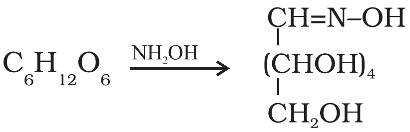
L(-) glucose

This structure of glucose was assigned on the basis of following evidences :

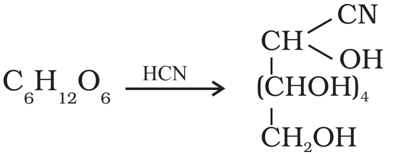
1. The molecular formula of glucose was found to be $C_6H_{12}O_6$
2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.

$$C_6H_{12}O_6 \xrightarrow{HI,\ \Delta} \underset{(n\text{-Hexane})}{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

3. Glucose reacts with hydroxylamine to form an oxim and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirms the presence of a carbonyl group ($> C = 0$) in glucose.

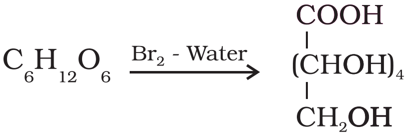


$$C_6H_{12}O_6 \xrightarrow{NH_2OH} \begin{array}{c} CH{=}N{-}OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \quad \text{(Oxime)}$$



(Cyanohydrin)

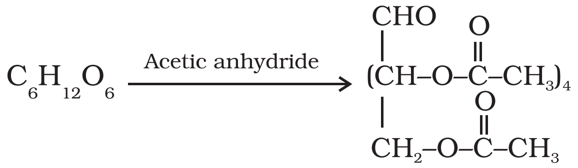
(iv) Glucose on reduction with mild oxidising agent like bromine water gets oxidised to gluconic acid, a six carbon carboxylic acid. This indicates that the carbonyl group is present as an aldehydic group.



$$C_6H_{12}O_6 \xrightarrow{Br_2\text{ - Water}} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

(Gluconic acid)

(v) Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of 5(five) – OH groups

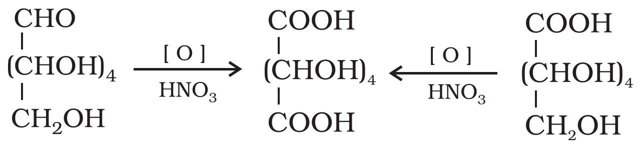


$$C_6H_{12}O_6 \xrightarrow{\text{Acetic anhydride}} \begin{array}{l} CHO \\ | \\ (CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3)_4 \\ | \\ CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \end{array}$$

(Glucose pentaacetate)

(vi) On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccaaric acid.

This indicates the presence of a primary alcoholic (– OH) group in glucose.



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow[HNO_3]{[\,O\,]} \begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array} \xleftarrow[HNO_3]{[\,O\,]} \begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

(Glucose) (Saccharic acid) (Gluconic acid)

(8) Cyclic structure of glucose :

The following reactions and facts could not be explained by the open chain structure of glucose :

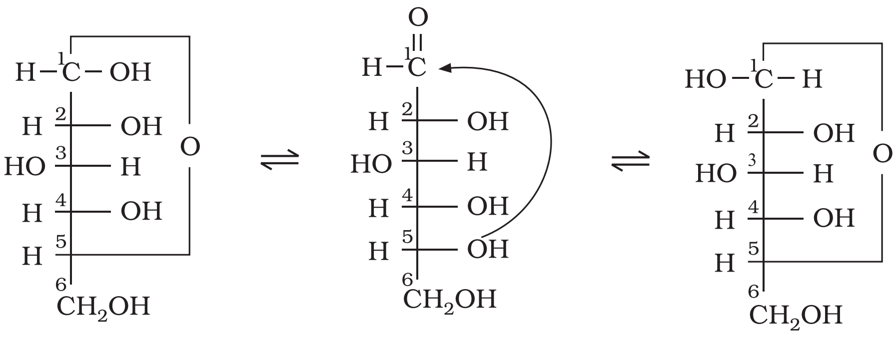
(1) Despite having the aldehyde group, glucose does not give Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.

(2) The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free – CHO group.

(3) Glucose is found to exist in two different crystalline forms which are named as α and β glucose.

It was proposed that the – OH group at C_5 is involved in ring formation and add to the –CHO group to form a cyclic hemiacetal structure.

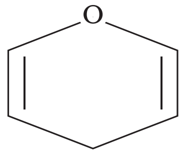
These two cyclic forms exist in equlibrium with open chain structure.



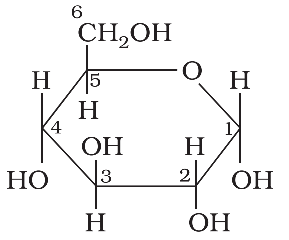
α – D – (+) – Glucose D (+) – Glucose β – D– (+) – Glucose

Such isomers i.e α form and β form are also called anomers.

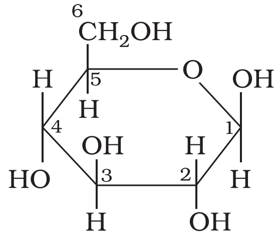
The six membered cyclic structure of glucose is called pyranose structure (α or β), in anology with pyran.



(Pyran)



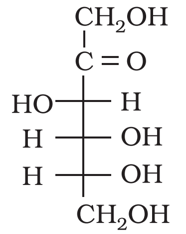
α – D (+) Glucopyranose



β – D – (+) – Glucopyranose

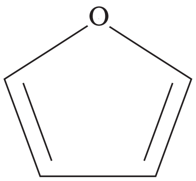
(9) Structure of Fructose : Fructose is a ketohexose and its molecular formula is $C_6H_{12}O_6$.

The open chain structure of fructose is :

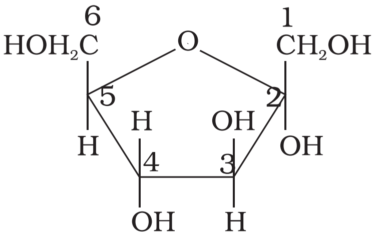


D – (–) – Fructose

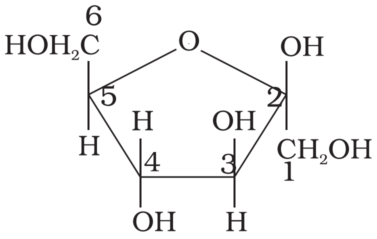
The Furanose structure of fructose are :



(Furan)



α – D – (–) – Fructofuranose

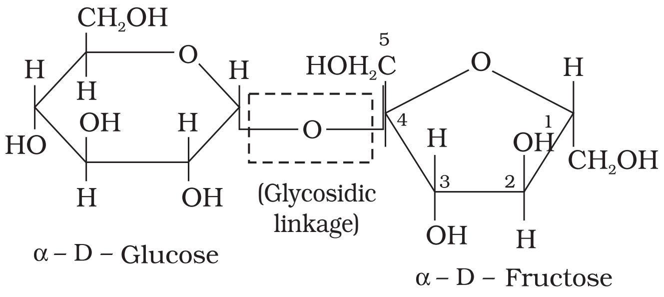


β – D – (–) – Fructofuranose

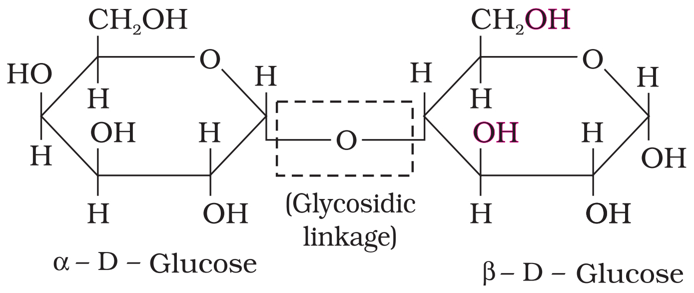
(10) Disaccharides : Disscharides on hydrolysis with dilute acid or enzymes yield two molecules of either the same or different monosaccharides. In otherword two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule to form a disaccharide. Such linkage thorough oxygen atom is called glycosidic linkage.

Examples of disaccharides re sucrose, maltose, lactose etc.

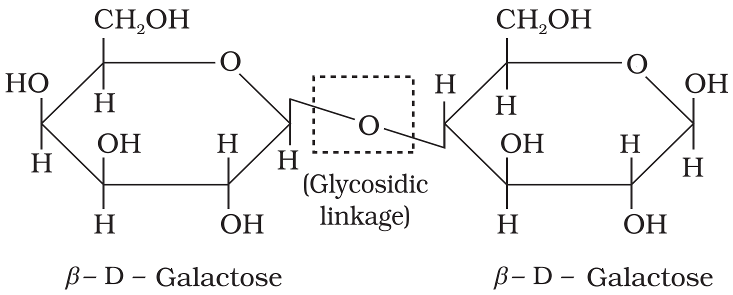
Glycosidic linkage in sucrose :



Glycosidic linkage in maltose :



Glycosidic linkage in Lactose :



(11) Polysaccharides : Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. Starch, cellulose, glycogen are some examples of polysaccharides. Polysaccharides mainly act as the food storage or structural materials.

(i) Starch : Starch is the main storage polysaccharide of plants. 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 a unbranched chain polymer and is soluble in water but Amylopectin is a branched chain polymer and insoluble in water.

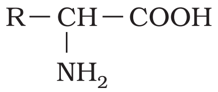
(ii) Cellulose : Cellulose occurs exclusively in plants and it is the most abundent organic substance in plant kingdom. It is a predominent constituents of cell wall of plant cells.

(iii) Glycogen : The carbohydrates are stored in animal body as glycogen. It is also known as animal starch because its structure is similar to amylopectin. It is present in liver, muscles and brain. When the body needs glucose, enzymes breaks the glycogen down to glucose. Glycogen is also found in yeast and fungi.

(12) Importance of Carbohydrates : Carbohydrates are used as storage molecules as starch in plants and glycogen in animals. Carbohydrates provide raw materials for many important industries like textiles, paper, lacquer and breweries. D - ribose and 2 – deoxy – D – ribose are present in nucleic acids. Carbohydrates are found in bio – system in combination with many proteins and lipids.

(13) Proteins : Proteins are polymers of α - amino acids. Protein occur in every part of the body and form the fundamental basis of structure and functions of life.

(14) Amino Acids : Amino acids contain amino ($-NH_2$) and carboxyl ($-COOH$) group. They may contain other functional groups also. Depending upon the relative position of amino group with respect to carboxyl group, the amino acid may be classified as α, β, γ, δ and so on. Only α-amino acids are obtained on hydrolysis of proteins.

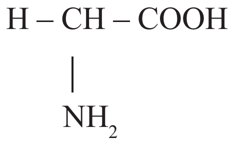
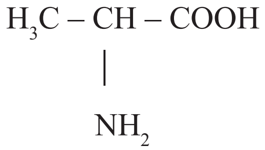
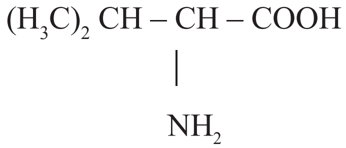


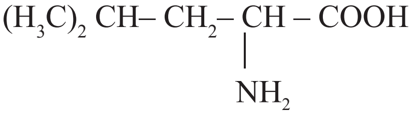
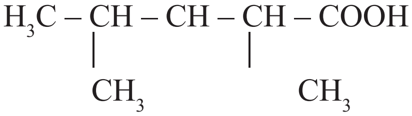
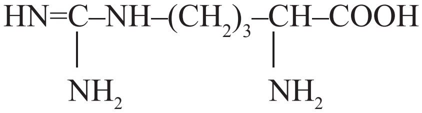
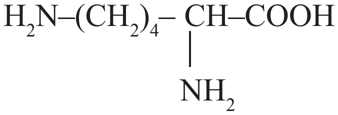
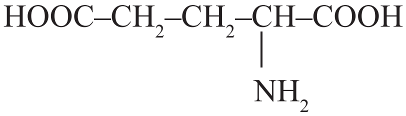
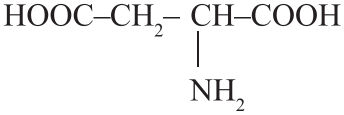
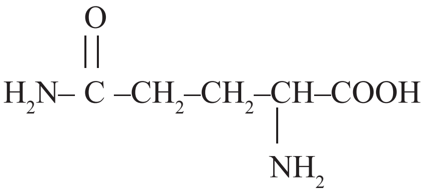
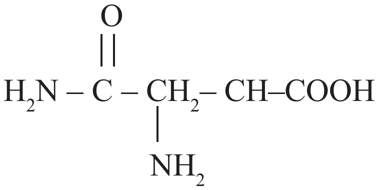
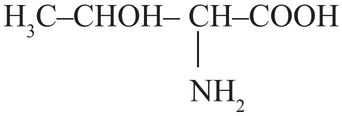
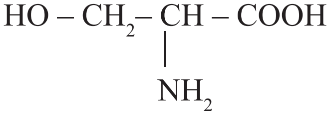
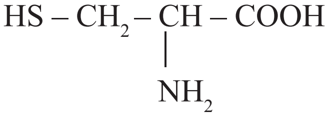
$$\mathrm{R-\underset{\underset{NH_2}{|}}{CH}-COOH}$$

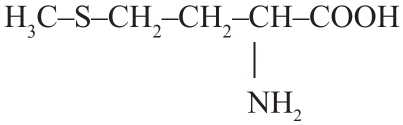
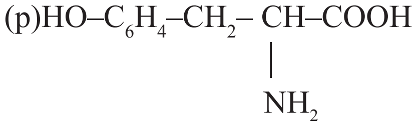
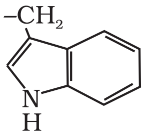
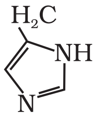
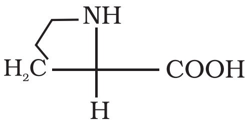
α - amino acid
(R = side chain)

Amino acids are generally represented by a three letter symbol, sometimes one letter symbol is also used.

Structures and symbols of some commonly occuring amino acids are given below :

	Name of the amino acids	**Structure of amino acid**	**Three letter symbol**	**One letter symbol**
1.	Glycine	 $\mathrm{H-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$	Gly	G
2.	Alanin	 $\mathrm{H_3C-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$	Ala	A
3.	Valine*	 $\mathrm{(H_3C)_2\,CH-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$	Val	V

4.	Leucine*	 $(H_3C)_2\,CH-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Leu	L
5.	Isoleucine*	 $H_3C-\underset{CH_3}{\underset{\vert}{CH}}-CH-\underset{CH_3}{\underset{\vert}{CH}}-COOH$	Ile	I
6.	Arginine*	 $HN{=}\underset{NH_2}{\underset{\vert}{C}}-NH-(CH_2)_3-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Arg	R
7.	Lysine*	 $H_2N-(CH_2)_4-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Lys	K
8.	Glutamice acid	 $HOOC-CH_2-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Glu	E
9.	Aspartic acid	 $HOOC-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Asp	D
10.	Glutamine	 $H_2N-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Gln	Q
11.	Asparagine	 $H_2N-\overset{O}{\overset{\Vert}{C}}-\underset{NH_2}{\underset{\vert}{CH_2}}-CH-COOH$	Asn	N
12.	Threonine*	 $H_3C-CHOH-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Thr	T
13.	Serine	 $HO-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Ser	S
14.	Cysteine*	 $HS-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Cys	C

15.	Methionine*	 $H_3C-S-CH_2-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Met	M
16.	Phenylalanine*	$C_6H_5-CH_2-CH-COOH$	Phe	F
17.	Tyrosine	 $(p)HO-C_6H_4-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	Tyr	Y
18.	Tryptophan*		Trp	W
19.	Histidine*		His	H
20.	Proline		Pro	P

* essential amino acid

(15) Classification of amino acids : Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecules.

Neutral amino acids : Glycine, Alanine

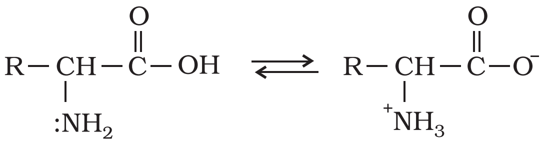
Acidic amino acids : Glutamic acid, Aspartic acid

Basic amino acids : Glutamine, Asparagine

The amino acids which cannot be synthesised in our body and must be obtained through diet are called essential amino acids. For example valine, Leucine, Lysine, Phenylalanine, Histidin etc.

Amino acids are water soluble, high melting solids. Due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule they behave like salts.

In aquous solution the carboxylic group can lose a proton (H^+) and amino group can accept a protoin, giving rise to a dipolar ion known as zwitter ion.

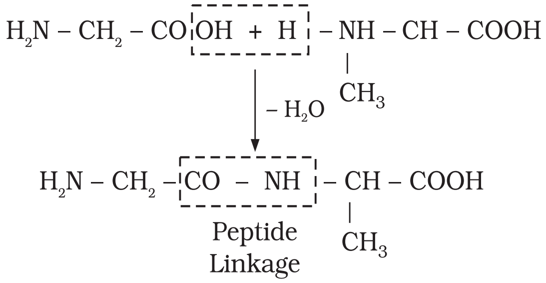


$$R-\underset{:NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons R-\underset{^{+}NH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^-$$

(zwitter ion)

Except glycine, all other naturally occurring α-amino acids are optically active. Most naturally occurring amino acids have L-configuration.

(16) Structure of proteins : Proteins are the polymers of α-amino acids and connected to each other by peptide bond. When two same or different molecule of amino acids combines, one water molecule eleminates and a peptide bond [– CO – NH –] is formed. For example when glycine combines with alanine we get a dipeptide, glycylalanine.



$$H_2N-CH_2-CO\boxed{OH + H}-NH-\underset{CH_3}{\underset{|}{CH}}-COOH \xrightarrow{-H_2O} H_2N-CH_2-\underset{\text{Peptide Linkage}}{\boxed{CO - NH}}-\underset{CH_3}{\underset{|}{CH}}-COOH$$

Gly calaline (Gly-Ala)

Similarly tripeptide, tetrapeptide, pentapeptide etc are formed. When the number of such amino acid is more than ten (10), then the products are called polypeptides. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u is called a protein.

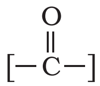
(17) Classification of proteins : Proteins can be classified into two types on the basis of their molecular shape.

(a) Fibrous proteins : When polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre like structure is formed. Fibrous proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles) etc.

(b) When chains of polypeptides coil around to give a spherical shape we get globular proteins. These are usually soluble in water. Insuline and albumins are common examples of globular proteins.

Structure and shape of proteins can be studied at four different levels i.e. primary, secondary, tertiary and quartarnary.

(i) Primary structure of proteins : Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that it said to be the primary structure of that protein.

(ii) Secondary structure of proteins : Secondary structures arises due to the regular folding of primary structure (backbone) of the polypeptide chain due to hydrogen bonding between  $[-\overset{\displaystyle O}{\overset{\|}{C}}-]$ and [– NH–] groups of the peptide bond.

A protein may assume α-helix structure or β-pleated structure. The α-helix structure results due to regular coiling of polypeptide chain. In β-pleated sheet structure, all peptide chains are streched to nearly maximum extention and then laid side by side.

(iii) Tertiary structure of proteins : Tertiary structure of proteins are formed due to further folding of secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. Hydrogen bonds, disulphide linkage, van-der-wall and electrostatic forces of attractions are the main forces which stabilises the 2° and 3° structure of proteins.

(iv) Quarternary structure of proteins : Some proteins are composed of two or more polypeptide chains and the special arrangement of these different polypeptide chains with respect to each other is known as quarternary structure.

(18) Denaturation of proteins : When a protein in its native form, is subjected to physical change like change in temparature or chemical change like change in PH, the hydrogen bonds are disturbed. Due to this globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

During denaturation 2° and 3° structures are destroyed but 1° structures remains intact. The coagulation of egg white on boiling, cardling of milk are some common examples of denaturation at proteins.

(19) Enzymes : Enzymes are essential biological catalysts which are required in small quantities to catalyse biological reaction in living organism. All most all the enzymes are globular proteins.

Enzymes are named after the compound or class of compounds upon which they work.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\textit{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

The ending of the name of an enzyme is–ase.

The enzymes which catalyses the oxidation of one substrate with simultaneous reduction of another substrate are named as oxidoreductase enzymes.

Enzymes are very specific for a pariticular reaction and for a particular substrate.

(20) Vitamins : Vitamins are the organic compounds required in the diet in small amounts to perform specific biological functions for normal maintanance of optimum growth and health of the living organisms.

vitamins are designated by alphabets A, B, C, D etc. Some of them are further named as sub groups e.g. B_1, B_2, B_6, B_{12} etc.

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) Examples of fat soluble vitamins are vitamins A, D, E and K.

(ii) Examples of water soluble vitamins are B-group viamins and vitamin-C.

Sl. No.	Name of Vitamins	Sources	Deficiency diseases
1.	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2.	Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
3.	Vitamin B_2 (Riboflavin)	Milk, eggwhite, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5.	Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6.	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
7.	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
8.	Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
9.	Vitamin K	Green leafy vegetables	Increased blood clotting time

(21) Nucleic Acids : The particles in the nucleus of the cell, responsible for heredity, are called chromosomes. Chromosomes are made up of proteins and another type of biomolecules called nucleic acids.

Nuclic acids are mainly of two types –

(i) Deoxyribonucleic Acid (DNA) and

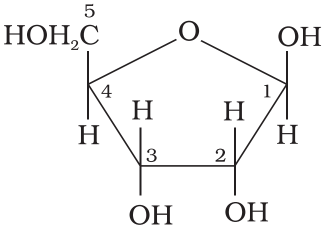
(ii) Ribonucleic Acid (RNA)

Nucleic Acids are long chain polymers of nucleotides and are also called polymucleotides.

James Dewey Watson is best known for his discovery of the structure of DNA and proposed that DNA molecule takes the shape of a double helix.

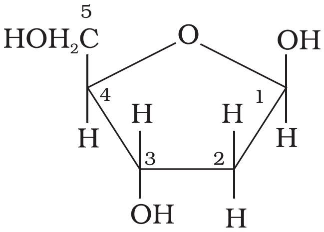
(22) Chemical composition of Nucleic acids : On hydrolysis DNA and RNA both yields a pentose sugar, phosphoric acid and nitrogen containing hetrocyclic compounds (called bases).

The sugar moiety of DNA molecules is –



β–D– ribose

The sugar moiety of RNA molecule is –

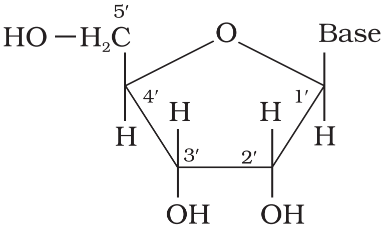


β–D–2– deoxyribose

Bases of DNA:	Adenine(A)	Guanine(G)	Cytosine(C)	Thymine(T)
Bases of RNA:	Adenine(A)	Guanine(G)	Cytosine(C)	uracil (u)

(23) Structure of Nucleic Acids :

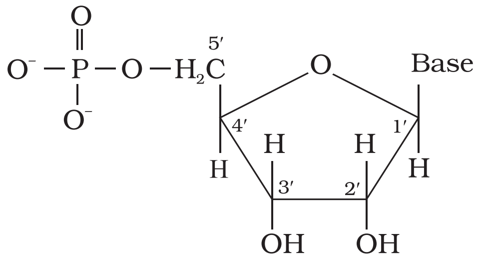
When a nitrogeneous base (A, G, C, U, T) is combined with a pentose sugar at 1′ position of the sugar a nucleoside is formed.



Structure of Nucleoside

Nucleoside = Sugar + Base

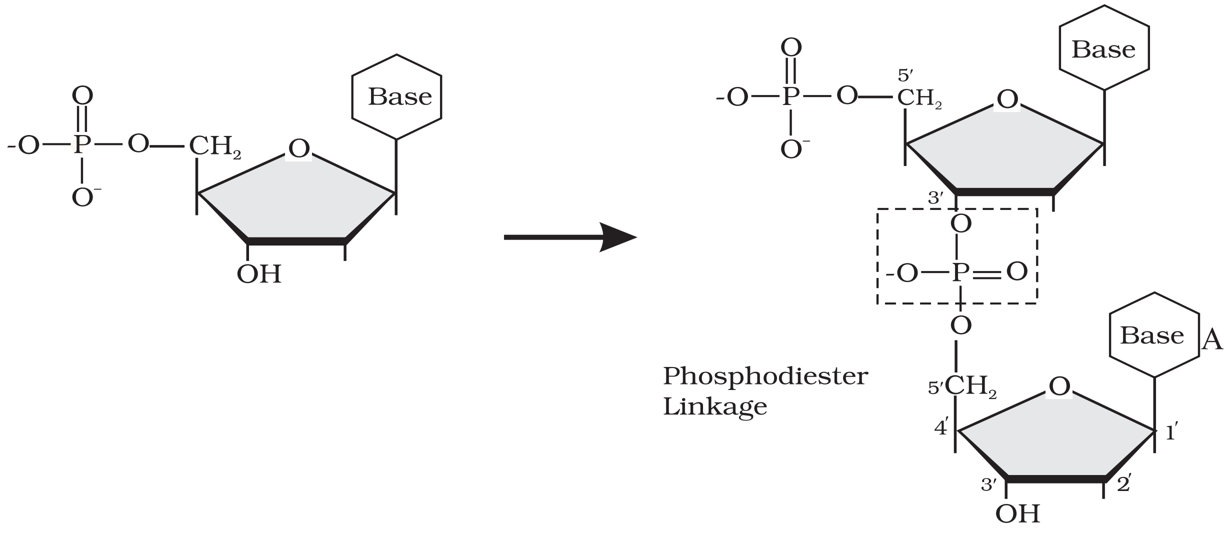
When a nucleoside is combined with a phosphoric acid at 5′ position of sugar moiety a nucleotide is formed.



(Structure of Nucleotide)

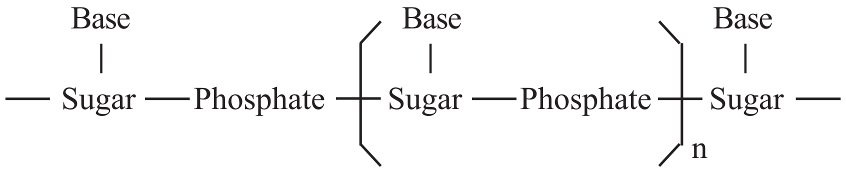
Nucleotide = One pentose sugar + One hetrocyclic base + One phosphate group

Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar.



(Formation of a dinucleotide)

A simple version of nucleic acid chain is as shown below :



$$-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}-\left(\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}\right)_n-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-$$

Differences between Nucleoside and Nucleotide

Nucleotide	Nucleoside
1. It is the structural unit of DNA or RNA. 2. It is formed of pentose sugar, nitrogeneous base and phospate group. 3. Chemically acidic.	1. Nucleoside combines with a phosphoric acid to form a nucleotide. 2. It is formed of pentose sugar and nitrogeneous base. 3. Chemically basic.

Structures of nucleic acid are as follows :

(i) Primary structure : Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure.

(ii) Secondary structure : When two nucleic acid chains are held together by hydrogen bonds between pairs of bases we get the secondary structure. It is a double strand helix structure.

Secondary structure of RNA :

In secondary structure of RNA only single strand helices are present. RNA molecules are of three types and they performed different functions.

(i) Messenger RNA (m – RNA) : It carries genetic information and takes part in protein synthesis.

(ii) Ribosomal RNA (r – RNA) : It helps in the attachment of m – RNA to ribosomes and thus forming a polysome.

(iii) Transfer RNA (t – RNA)) : During protein synthesis it sends a particular amino acid to the specified location to construct the correct sequence of amino acid.

Differences between DNA and RNA :

DNA	RNA
1. It is located in chromosome	1. It is located in the cyloplasm.
2. It's sugar base is β–D–2–deoxy ribose.	2. It's sugar base is β–D–ribose.
3. It has double strained helical shape.	3. It has a single strained shape.
4. It carries the heriditary information.	4. It helps in protein synthesys.
5. DNA is formed from RNA.	5. RNA can't be formed from DNA.

(25) DNA fingerprinting: Every individuals has unique fingerprints. These occur at the tips of the fingers and have been used for identification as the sequences of bases of DNA of an individual is unique. DNA fingerprinting is used in –

(i) forensic laboratories
(ii) determining peternity of an individual.
(iii) identifing the dead bodies by comparing the DNA's of parents or children.
(iv) identifing racial groups to rewrite biological evolution.

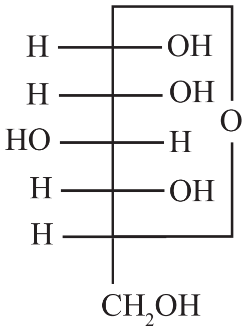
A. Choose the correct answer (MCQ) : (Each question marks – 1)

(1) Which of the following polymer is stored in the liver of animals ?
(a) Amylose (b) Cellulose (c) Amylopeclin (d) Glycogen

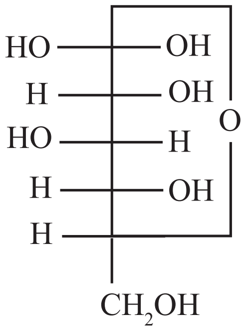
(2) Sucrose (cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives –
(a) 2 molecules of glucose
(b) 2 molecules of glucose + 1 molecules of fructose
(c) 1 molecules of glucose + 1 molecules of fructose
(d) 2 molecules of fructose

(3) Which of the following reactions of glucose can be explained only by its cyclic structure?
(a) Glucose forms pentaacetate.
(b) Glucose reacts with hydroxylamine to form an oxim.
(c) Pentaacetate of glucose does not react with hydroxylamine.
(d) Glucose is oxidise by nitric acid to gluconic acid.

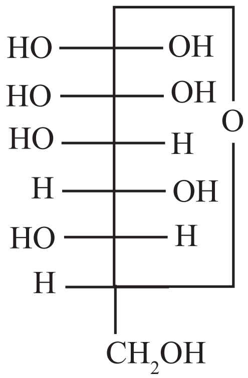
(4) Three cyclic structures of monosaccharides are given below. Which of these are anomers?



(I)



(II)



(III)

(a) I and II (b) II and III
(c) I and III (d) III is anomer of I and II

(5) Which of the following acids is a vitamin ?
(a) Aspartic acid (b) Ascorbic acid (c) Adipic acid (d) Saccharic acid

(6) Nucleic acid are the polymers of –
(a) Neocleosides (b) Neocleotides (c) Bases (d) Sugars

(7) Which of the following statements is not true about glucose ?

(a) It is an aldohexose.
(b) On heating with HI it forms n–hexane.
(c) It is present in furanose form.
(d) It does not give 2, 4 - DNP test.

(8) DNA and RNA contain four bases each. Which of the following bases is not present in RNA ?

(a) Adenine (b) Uracil (c) Thymine (d) Cytosine

(9) Which of the following bases is not present in DNA ?

(a) Adenine (b) Cytosine (c) Thymine (d) uracil

(10) Which of the following B-group vitamins can be stored in our body ?

(a) Vitamin B_1 (b) Vitamin B_2 (c) Vitamin B_6 (d) Vitamin B_{12}

(11) Which one of the following is not a constituent of nucleic acid ?

(a) uracil (b) Guanidine (c) Phosphoric acid (d) Ribose sugar

(12) In acquous solution, glucose remains as –

(a) only in open chain form.
(b) only in pyranose form.
(c) only in furanose form.
(d) In all three forms in equilibrium.

(13) Which of the following vitamin is soluble in water ?

(a) Vitamin – C (b) Viamin – D (c) Vitamin – E (d) Vitamin – K

(14) Which of the following substances can be identified by Molisch's test ?

(a) Sugars (b) Amines (c) Ketones (d) Nitro compound

(15) The end product of protein metabolism is –

(a) Peptide (b) Peptone (c) Proton (d) α - amino acid

(16) Which of the given below is a non-reducing sugar ?

(a) Sucrose (b) Maltose (c) Lactose (d) Glucose

(17) The sequence in which amino acids are arranged in a protein is called –

(a) Primary structure
(b) Secondary structure
(c) Tertiary structure
(d) Configuration

(18) Which of the following is not a class of proteins ?

(a) Enzymes (b) Hormones (c) Antibodies (d) Lipids

(19) All proteins on hydrolysis gives –

(a) α - amino acid (b) peptides

(c) aminos and carboxylic acid (d) enzymes

(20) Which of the following statement is not correct ?

(a) Amino acids exist in zwiter ions.

(b) All naturally occuring α - amino acids have $-NH_2$ group on the right.

(c) Except glycine, all other naturally occuring α - amino acids have a chiral carbon atom.

(d) The basic character in α - amino acids is due to the $-COO^-$ group.

(21) Which of the following monosaccharides are present as five membered cyclic structure (furamose structure) ?

(a) Glucose (b) Fructose (c) galactose (d) Maltose

(22) Glucose when reduced with HI and red phosphorus gives –

(a) n – hexane (b) n – heptane (c) n – pentane (d) n – octane

(23) Which of the following enzymes helps in digestion of protein ?

(a) Invertase (b) Trypsin (c) Thyrosinase (d) ureas

(24) Which of the following is an essential amino acid ?

(a) Cysteine (b) Serine (c) Tyrosine (d) Isoleucine

(25) The two functional group's present in a typical carbohydrate are –

(a) – OH and – COOH (b) – CHO and – COOH

(c) >C = O and – OH (d) – OH and – CHO

(26) Deficiency of vitamin B_1, causes the disease –

(a) convulsions (b) beri – beri (c) cheilosis (d) sterility

(27) In aqueous solution, an amino acid exists as

(a) cation (b) anion (c) zwitter ion (d) neutral molecule

(28) Which one of the following forms the constiuent of cell wall of plant cells ?

(a) starch (b) cellulose (c) Glycogen (d) Amylose

(29) Which one is not a constituent of necleic acid ?

(a) uracil (b) Guanidine (c) Phosphoric acid (d) Ribose sugar

(30) The letter 'D' in D-glucose signifies

(a) configuation at all chiral carbons
(b) dextrorotary
(c) that it is a monosaccharide
(d) configuration at a particular chiral carbon

B. Assertion and Reason type question : (Marks - 1)

The following questions consist of an Assertion and Reason. Use the following key to choose the appropriate answer.

(a) Both assertion and reason are correct and the reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct and the reason is not the correct explanation of the assertion.

(c) Assertion is correct but reason is incorrect.

(d) Assertion is incorrect but reason is correct.

1. Assertion : D (+) glucose is dextrorotatory in nature
Reason : 'D' represents its dextrorotatory nature.

2. Assertion : Vitamin D can be stored in our body.
Reason : Vitamin D is fat soluble vitamin.

3. Assertion : β - glycosidic linkage is present in maltose.
Reason : Maltose is composed of two glucose units in which c-1 of one glucose unit is linked to c-4 of another glucose unit.

4. Assertion : In presence of enzymes, substrate molecule can be attacked by the reagent effectively.
Reason : Active sites of enzymes hold the substrate molecule in a suitable position.

5. Assertion : All naturally occuring α-amino acids except glycine are optically active.
Reason : Most naturally occuring amino acids have L– configuration.

6. Assertion : Glycosides are hydrolysed in acidic conditions.
Reason : Glycosides are acetals.

(7) Assertion : Uracil is present in DNA.
Reason : DNA undergoes replication.

(8) Assertion : Cellulose is not digested by human beings.
Reason : Cellulose is a polymer of β – D – glucose.

(9) Assertion : Fats and oils are one of the main sources of food for all living organism.
Reason : Lipids act as energy reservers..

(10) Assertion : Insulin is a globular protein.
Reason : Globular proteins are water soluble.

C. Very short answer type questions : (Each questions marks - 1)

1. What are reducing sugars ?
2. What are monosaccharides ?
3. Why are carbohydrates generally optically active ?
4. What are anomers ? Give one example .
5. What is meant by inversion of sugar ?
6. What is mutarotation ?
7. What are oligosaccharides ?
8. What are meant by polysaccharides ? Gives one example.
9. What do you understand by glycosidic linkage ?
10. Name two components of α – glucose which constitude starch.
11. State two main function of carbohydrates.
12. What is peptide linkage ?
13. What is the basic difference between starch and cellulose ?
14. Which of the two components of starch is water soluble ?
15. Name the vitamin whose defficiency causes the disease beri – beri.
16. Which sugar molecule is present in DNA molecule ?
17. Write the chemical name of vitamin B–12.
18. Which sugar molecule is present in RNA molecule ?
19. Name the products of hydrolysis of sucrose.
20. What is the basic difference between proteins and polypeptides ?
21. Name the purines present in DNA.
22. Give one example of denaturated protein.
23. What type of bonding helps in stabilising the α-helix structure of proteins.
24. Explain why vitamin–C can not be stored in human body.
25. What is nucleoside ?
26. What is nucleotide ?
27. Out of lysine and leucine which one is a basic amino acid ?
28. Draw the open chain or free structure of D (+) glucose.

29. Draw the cyclic form of α – D (+) glucose.
30. Name the protein which is present in our hair.
31. Draw the cyclic structure of β – D – ribose.
32. Name the sugar moiety of RNA molecule.
33. Which type of RNA molecule carries genetic information ?
34. Which type of RNA molecule forms polysome ?
35. Which type of RNA molecule construct the correct structural sequence of amino acids ?

D. Short answer type questions : (Each questions marks -2)

1. Why does glucose show mutarotation ?
2. Justify the formation of zwitter ion of α-amino acid with a suitable example.
3. What do you mean by N–terminal and C– terminal amino acid ?
4. Distinguish between nucleoside and nucleotide with example.
5. Define glycosidic bond. Explain it with the help of an example.
6. State the major differences between fibrous and globular proteins.
7. What happens when
   (i) Glucose is oxidised by bromin water.
   (ii) Glucose is reduced by red P/HI.

8. What happens when
   (i) Glucose reacts with HNO_3
   (ii) Glucose reacts with HIO_4

9. Define reducing and non – reducing sugars ? Give example.
10. How will you prove that six carbon atoms of glucose are linked by an unbranched chain ?
11. How will you prove the presence of one carbonyl (>C = 0) group in glucose.
12. How will you prove the presence of one –CHO group at the terminal position of glucose.
13. Explain with example –
    (i) Acidic amino acids.
    (ii) Basic amino acids.
14. Explain what is meant by –

(i) A peptide linkage.

(ii) A glycosidic linkage.

15. Write any two reactions of glucose which can't be explained by the open chain structure of glucose.

16. Write down the differences between DNA and RNA.

17. What is glycogen ? Why is it called animal starch ?

18. What is denaturation of proteins ? What type of bond hold a DNA double helix together ?

19. Write one function and two sources of Vitamin - D.

20. What are enzymes ? How do enymes differ from ordinary chemical catalysts ?

21. Comment on the specificity of enzymes action. What is the most important reason for their specificity?

22. What type of forces are responsible for the formation of –

    (a) Cross linking of polypeptide chains.

    (b) α-helix formation.

23. Name two components of starch. How do they differ from each other structurally ?

24. What are nucleic acids ? Mention their two important biological functions.

25. What do you mean by 'Gly – Ala' ? Write its structural formula.

E. Long answer type questions : (Each questions marks - 3)

1. (i) Enumarate the reactions of D - glucose which can not be explained by its open chain structure.
   (ii) What are the hydrolysis products of lactose ?
2. (i) What is glycogen ? How it different from starch ?
   (ii) Why can not vitamin-C be stored in our body ?
3. (i) Why vitamin-A and vitamin-C are essential to us ?
   (ii) Defficiency of which vitamin causes xerophthalmia disease ?
4. Answer the following question briefly .
   (i) What are two good souces of viamin - A ?
   (ii) What are nucleosides ?
   (iii) Give an example of simple lipid .
   (iv) Define enzymes .
5. Define the following terms :

(i) Glycosidic linkage
(ii) Invert sugar
(iii) Oligosaccharides

6. What is essencially the difference between α-glucose and β-glucose ? What is meant by pyronose structure of glucose ?

7. (i) Among starch, maltose, fructose which one is a polysachharide ?
(ii) What is the differences between native protein and denatured protein ?
(iii) Write the name of the vitamin responsible for the coagulation of blood .

8. Define the following :
(i) Nucleotide
(ii) Anomers
(iii) Essential amino acids.

9. (a) Name two water soluble vitamins, their sources and the disease caused by their defficiency in diet.
(b) Name the four bases present in DNA. Which one of these is not present in RNA ?

10. (a) Name two fat soluble vitamins, their sources and the diseases caused by their defficiency in diet.
(b) What type of linkage is present in nucleic acids?

Solutions

A. Choose the correct answer (MCQ)

(1) d (2) c (3) c (4) a (5) b (6) b (7) c (8) c
(9) d (10) d (11) b (12) d (13) a (14) a (15) d (16) b
(17) a (18) d (19) b (20) b (21) b (22) a (23) b (24) d
(25) c (26) b (27) c (28) b (29) b (30) d

B. Assertion and Reason type question :

(1) c (2) a (3) d (4) a (5) b
(6) a (7) d (8) b (9) a (10) a

Chapter - 15

Polymers

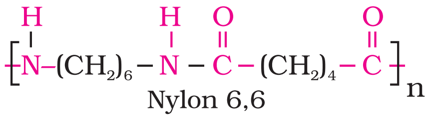
Chapter at a Glance :

The polymer is defined as very large molecule or macromolecules having high molecular mass (10^3 - 10^7u). Polymers are formed by repeating struetural units known as monomers linked to each other by covelent bonds. This process of formation of polymers from respective monomers is called polymerisation.

Example :

(i) $$nCH_2 = CH_2 \xrightarrow{\text{Polymerisation}} n\left[CH_2-CH_2\right] \longrightarrow \left[CH_2-CH_2\right]_n$$

Ethene — Repeating unit — Polythene polymer



(ii) $$nNH_2(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \xrightarrow{\text{Polymerisation}} \left[\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}\right]_n$$

Hexamethylene diamine — Adipic acid — Nylon 6,6

Classification of Polymers

Based of Source :

1. Natural Polymers- Protein, Cellulose, Starch, Resin, Rubber.
2. Semi-Synthetic Polymer- Rayon, Cellulose nitrate.
3. Synthetic Polymer- Nylon-6, 6, Buna-S.

Based on mode of Polymerisation :

1. Addition Polymer
   - Polythene
   - Polypropene
   - Buna-s.
   - Buna-N
2. Condensation Polymer :
   - Terylene
   - Nylon-6, 6.
   - Nylon-6.

Based on Growth Polymerisation :

1. Addition or Chain Growth Polymerisation
   - Polythene (LDPE, HDPE)
   - Teflon, Polyacrylonitrile
2. Condensation or Step Growth Polymerisation
   - Terylene or Dacron
   - Nylon-6, 6, Nylon-6.
   - Polyesters, Bakelite, Melamine-Formaldehyde

Based on structure :

1. Linear Polymer : HDPE, PVC
2. Branched Polymer : LDPE
3. Cross-linked Polymer : Bakelite, Melamine.

Based on Molecular Forces :

1. Elastomer– Buna-S, Buna-N, Neoprene.
2. Fibres– Nylon-6, 6, Polyesters.
3. Thermoplastic– Polythene, Polystyrene, Polyvinyl.
4. Thermosetting Plastic– Bakelite.

Homopolymers : Addition polymers by single monomeric speeies. Example - polythene

$$nCH_2 = CH_2 \rightarrow \quad -(CH_2 - CH_2)_n-$$

Ethene Polythene

Copolymers : Addition polymerisation from two different monomers, Example - Buna-S, Buna-N

$$n\,CH_2=CH-CH=CH_2+n\,C_6H_5CH=CH_2 \longrightarrow -\!\left(CH_2-CH=CH-CH_2-\overset{C_6H_5}{\overset{|}{C}H}-CH_2\right)_n\!-$$

1, 3-Butadiene Styrene Butadiene-styrene copolymer (Buna - S)

Preparation of Nylon 6, 6 :

$$n\,H_2N\,(CH_2)_6\,NH_2+n\,HOOC\,(CH_2)_4\,COOH$$

$$\longrightarrow \;-\!\left[NH\,(CH_2)_6\,NHCO(CH_2)_4CO\right]_n\!- \;+\,n\,H_2O$$

Nylon 6, 6

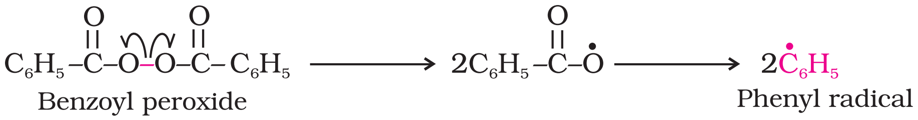
Hexamethylene diamine + Adipic acid → Nylon 6, 6

Thermoplastic polymer	Thermosetting polymer
1. Linear or slightly branched	1. Cross linked or heavily branched
2. Softens or heating and harden on cooling	2. Infusible
3. Can be reused	3. Can't be reused
4. Polythene, PVC etc.	4. Bakelite, Urea-formaldehyde etc.

Addition polymerisation by free redical Mechanism :

Formation of Polythene :

i) Chain initiation steps :



$$C_6H_5-\overset{O}{\overset{||}{C}}-O-O-\overset{O}{\overset{||}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{||}{C}}-\dot{O} \longrightarrow 2\dot{C}_6H_5$$

Benzoyl peroxide Phenyl radical

$$\dot{C}_6H_5+CH_2=CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$

ii) Chair propagation step :

$$C_6H_5-CH_2-\dot{C}H_2+CH_2=CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\downarrow$$

$$C_6H_5\left(CH_2-CH_2\right)_nCH_2-\dot{C}H_2$$

iii) Chain termination step :

$$\left.\begin{array}{l} C_6H_5 \left(CH_2 - CH_2 \right)_n CH_2 - \dot{C}H_2 \\ C_6H_5 \left(CH_2 - \overset{+}{C}H_2 \right)_n CH_2 - \dot{C}H_2 \end{array}\right. \longrightarrow C_6H_5 \left(CH_2 - CH_2 \right)_n CH_2 - CH_2 - CH_2 \left(CH_2 - CH_2 \right)_n C_6H_5$$

Polythene

Ziegler Natta catalyst :

Triethyl aluminium and Titanium tetra chloride.

$$nCH_2 = CH_2 \xrightarrow{\text{Ziegler Natta catalyst}} -(CH_2 - CH_2)_n$$

Ethene Polythene

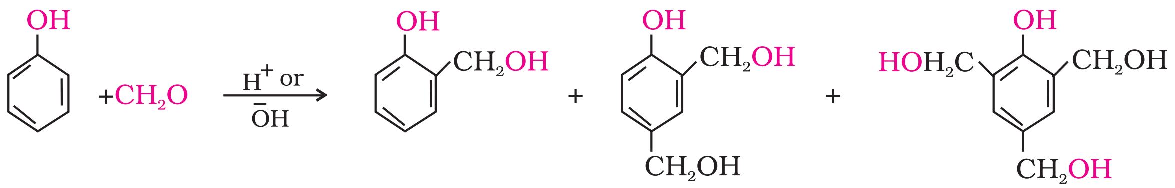
Terylene or dacron

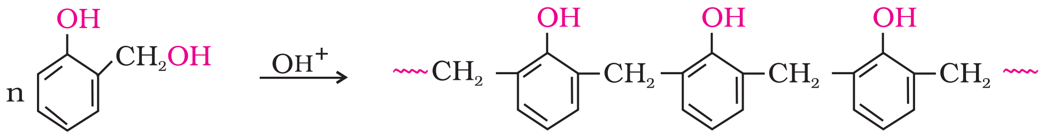
Ethylene glycol (Ethane-1, 2 - diol)

Terephthalic acid (Benzene-1,4 - di carboxylic acid)

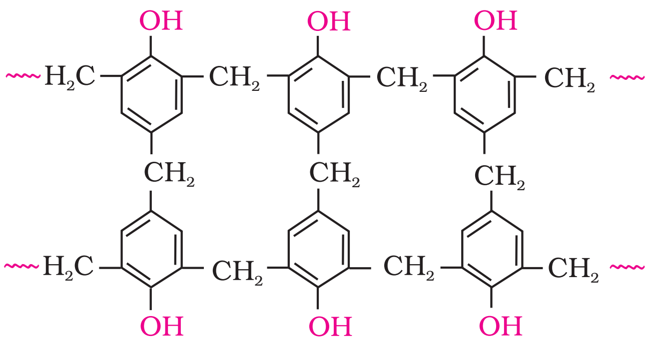
Terylene or dacron

Preparation of Bakelite :





Novolac

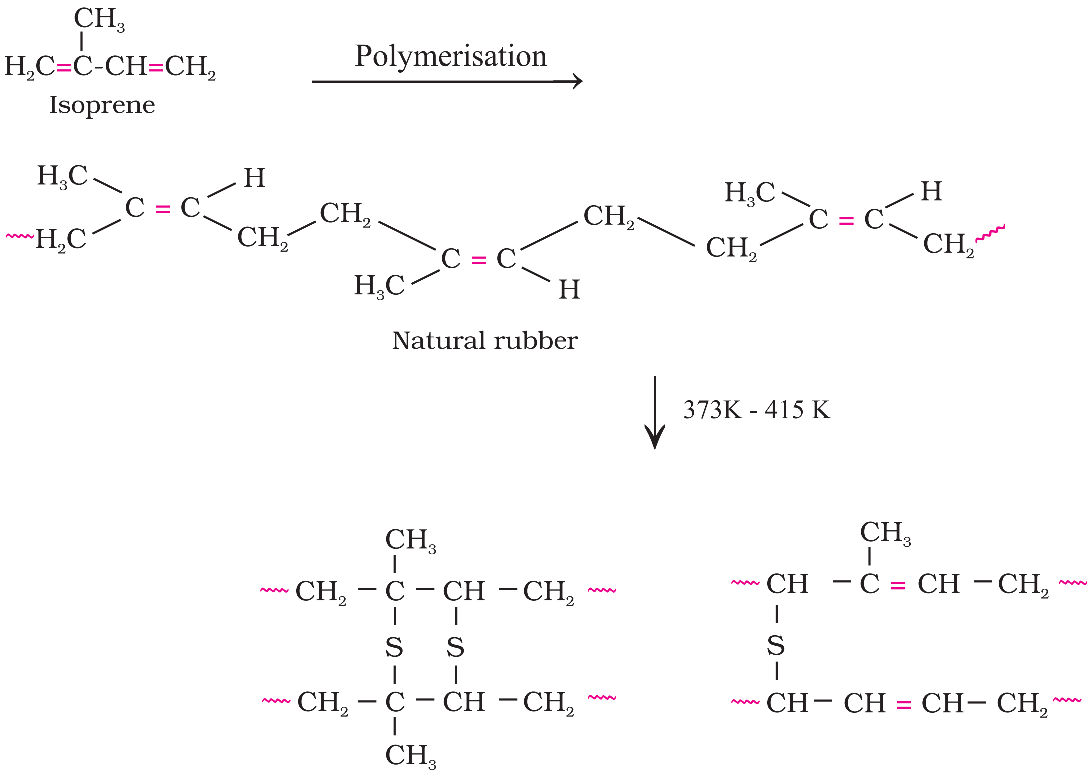


Bakelite

Melamine :


Melamine Formaldehyde Resin intermediate

Isoprene :


Isoprene

Natural rubber

Biodegradable Polymers :

1. Poly β hydroxy butyrate-co β valerate (PHBV)
2. Nyton 2 - nylon 6

Commercially Important Polymers :

1. Bakelite – For making combs, electrical switches, handles of utensils, computer discs.
2. PVC – For making rain coats, hand bags, vinyl flooring water pipes.
3. Poly propene – For making ropes, toys, pipes, fibres.
4. Glyptal – For making paint and varnishes.

A. Select the correct option (MCQ) : (Each carries 1 mark)

1. Which one is natural polymer –

(a) Protein (b) PVC (c) Nylon 6, 6 (d) Teflon

2. Which one is synthetic polymer –

(a) Protein (b) Cellulose (c) Starch (d) Buna-S

3. Which one is Co-polymer –

(a) Buna-S (b) Polypropene (c) PVC (d) Teflon

4. Which one is homo polymer ?

(a) Buna-N (b) Polythene (c) Nylon 6, 6 (d) Terylene

5. Due to vulcanization, rubber becomes –

(a) Soft (b) Hard (c) Less elastic (d) Soluble in water

6. Natural rubber is a polymer of –

(a) Acrylic acid (b) isoprene (c) 1, 3 butadiene (d) ethylene

7. Natural Silk is –

(a) Polyester (b) Polyamide (c) Polyacid (d) Poly saccharide

8. Which one of the following is not a biopolymer ?

(a) Proteins (b) Nucleic acids (c) Neoprene (d) cellulose

9. Select the one that is a Condensation homopolymer ?

(a) Nylon 6, 6 (b) Nylon - 6 (c) Nylon 6, 10 (d) Daoon

10. Thermoplastics are –

(a) Soften or melt on heating

(b) linear polymers

(c) molten polymer can be moulded in desired shape

(d) all the above are correct

11. Select the one that is thermosetting polymer –

(a) Polythene (b) PVC (c) Bakelite (d) Neoprene

12. The monomeric unit of orlon molecule is –

(a) $CH_2 = CH - Cl$ (b) $CH_2 = CHCN$

(c) $C_6H_5 - CH = CH_2$ (d) $CF_2 = CF_2$

13. Bakelite is a polymer of –

(a) Phenol and Benzaldehyde (b) Phenol and Acetaldehyde

(c) Phenol and formaldehyde (d) Formaldehyde and Benzylalcohol

14. The catalyst used for polymerisation of ethene is –

(a) Wilkinson Catalyst (b) Ranny-nickel catalyst

(c) Ziegber-Natta catalyst (d) None of thase

15. Which of the following is a semi-synthetic polymer ?

(a) Starch (b) Rayon (c) Resins (d) Polythene

16. Teflon, starch and neoprene are all –

(a) Copolymers (b) Condensation polymers

(c) monomers (d) homopolymers

17. The commercial name of polyaerylonitrile is –

(a) Dacron (b) Orlon (acrilan) (c) PVC (d) Bakelite

18. Which one of the following s used to make 'non-strick' cookware?

(a) Polyethylene terephthalate (b) Teflon

(c) PVC (d) Polystyrene

19. Which of the following is a bio-degradable polymer –

(a) Cellulose (b) Polythene (c) Polyvinyl chloride (d) Nylon - 6

20. The polymer used for making contact lenses for eyes is –

(a) Polymethyl methacrylate (b) Polyethylene

(c) Polyethyl acrylate (d) Nylon - 6

21. Which of the following fibers is made of polyamide –

(a) Dacron (b) Orlon (c) Nylon (d) Rayon

22. Which of the following is used in paint ?

(a) Nylon 6, 6 (b) Ethylacrylate (c) Glyptal (d) Acrylonilrile

23. Which of the following has an ester linkage ?

(a) Nylon (b) Bakelite (c) Terylene (d) PVC

24. Which of the following frbres is made of polyamide ?

(a) Dacron (b) Orlon (c) Nylon (d) Rayon

25. Which of the following is a chain growth polymer ?

(a) Starch (b) Nucleic acid (c) Polyestyrene (d) Protein

26. Treatment of rubber with sulphur is called –

(a) Annealing (b) Vulanisation (c) Quenching (d) Name of these

27. Which one is a correct example of condensation polymer?

(a) Nylon, Buna-S (b) Teflon, Buna-N

(c) Nylon 6, 6 (d) Door Neoprene, Buna-S

28. Cellulose is polymer of –

(a) Glucose (b) Fructose (c) Ribose (d) Sucrose

29. Which of the following statement is false ?

(a) Artificial silk is derived from cellulose

(b) Nylon 6, 6 is an example of elastomer

(c) The monomer of natural rubber is isoprene

(d) Both starch and cellulose are polymers of glucose

30. Caprolactum is the monomer of –

(a) Nylon-6 (b) glyptal (c) dacron (d) melamine

31. The common acid used in the mannfacture of rayon and plastics is –

(a) methanoic acid (b) ethanoic acid (c) propanoic acid (d) butanoic acid

32. The catalyst used in ziegler process for polythylene manufacture –

(a) consists of aluminium chloride and titanium dioxide

(b) vanadium pentoxide

(c) aluminium triethyl and titanium tetrachloride

(d) finely divided nickel.

33. Three dimensional molecules with cross links are formed in case of a –

(a) Thermoplastic (b) Thermosetting plastic

(c) both (d) none

34. The monomer of polystyrene is –

(a) C_2H_5 - CH = CH_2 (b) CH_2 - CH = CH_2

(c) C_6H_5 - CH = CH_2 (d) CH_2 - CH = CHCl

35. Which of the polymer is hard ?

(a) Linear (b) Branched chain (c) Thermoplastic (d) corss-linked

36. Nylon 6, 6 is made by using –

(a) Succinic acid (b) Benzal dehyde

(c) Adipic acid (d) Benzyl chloride

37. Bakelite is prepared from –

(a) Urea and HCHO (b) Ethylene glycol

(c) Phenol and HCHO (d) Tetramethylene glycol

38. An example of addition polymer is –

(a) PVC (b) Bakelite (c) cellulose (d) Nylon 6, 6

39. Which one is copolymer –

(a) PVC (b) Nylon 6, 6 (c) Teflon (d) Polybutadiene

40. The inter-particle forces between linear chains in Nylon-6, 6 are –

(a) Ionic-bonds (b) Covalent bond (c) Hydrogen bond (d) None of these

41. The monomer of acrilon is –

(a) Vinyl cyanide (b) Vinyl chloride (c) Vinyl bromide (d) Vinyl alcohol

42. Nylon - 6, 6 is an example of –

(a) Polystyrene (b) Polypropylene (c) Polyamide (d) Polyisoprene

43. Natural silk is –

(a) Polyester (b) Polyamide (c) Polyacid (d) Polysaccharide

44. Low density polythene is –

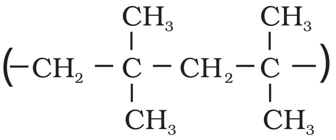
(a) Tough (b) Hard

(c) Poor conductor of electricity (d) Highly branched structure

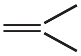
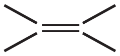
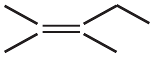
45. Buna-S is formed by the condensation of –

(a) Sodium and Styrene (b) Styrene and Ethene

(c) Sodium and Butadiene (d) Butadiene and Styrene

46. 

$\left(-CH_2 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - \underset{CH_3}{\overset{CH_3}{C}} - \right)$ is a polymer having monomer units –

(a)  (b)  (c)  (d) 

47. Polymer used to prepare squeeze bottle is –

(a) Polystyrene (b) Teflon

(c) Polypropene (d) Low Density Polythene

48. Which alkene is most active in cationic polymerisation

(a) $H_2C = CH\ CH_3$ (b) $CH_2 = CH_2$ (c) $H_2C = CHCN$ (d) $H_2C = CHC_6H_5$

49. Repeating unit in case of PTEE is –

(a) $Cl_2CH - CH_3$ (b) $F_2C = Cl_2$ (c) $F_3C - CF_3$ (d) $FCl\ C = CF_2$

50. Which polymer acts as lubricator and insnlator –

(a) SBR (b) PVC (c) PTEE (d) PAN

B. **Assertion Reason type question : (Each carries 1 mark)**

The Question given below consist of an assertion and the reason. Use the following key to choose the appropriate answer.

a. Both assertion and reason are corect and reason is the correct explanation of the assertion.

b. Both assertion and reason are correct but the reason is not the correct explanation of the assertion.

c. Assertion is correct but reason is incorrect.

d. Assertion is incorrect bat reason is correct.

1. Assertion : Polyghylolic acid (PGA) is a biodegradable polymer.

Reason : When PGA is buried as waste, miroorganism present in the soil can degrade the polymer.

2. Assertion : Due to vulcanisation, intermoleenlar movement of rubber springs is prevented resulting in change of physical characeter of rubber.

Reason : During vulcanization sulphur reacts with polymer forming a cross-linked network. The cross liking gives mechanical strength.

3. Assertion : Nyton 6, 6 is a addition polymer.

Reason : Hexamethylene diamine and adipic acid on heating under pressure gives Nylon 6, 6.

4. Assertion : Nylon makes good fiber.

Reason : In Nylon hydrogen bonding can occur between polymer chains which provide strength to the fibers.

5. Assertion : Bakelite is a thermoplastic.

Reason : It can be melted many times again and again withont any change.

6. Assertion : Most of the synthetic polymers are not biodegredable.

Reason : Because of polymerization toxic character is generated in organic molecule.

7. Assertion : Network polymers are thermoplastics

Reason : Network polymers make high molecular mass.

8. Assertion : LDPE has low density (0.92 gcm^3) and low melting point.

Reason : LDPE has a highly branched structure and therefore do not pack well.

C. Very Short Answer Type Question : (Each carries 1 mark)

1. What are monomers ?

2. Give example of Natural polymers.

3. Give example of synthetic polymer.

4. What is a homo polymer ?

5. What are the copolymer of Buna-S

6. Define polymerization.

7. Give example of cross linked polymer.

8. Give example of addition polymers.

9. What type of compounds under go chain growth polymerization.

10. What is the difference between Nylon 6, and Nylon 6, 6.

11. What is gutta percha ?

12. Name the monomers of Nylon 6, 6.

13. What is teflon ?

14. Is $[CH_2 - CH - C_6H_5]_n$ a homopolymer or copolymer ?

15. Give example of cross linked or Network polymer.

16. Give two example of thermoplastic polymer.

17. What is PHBV?

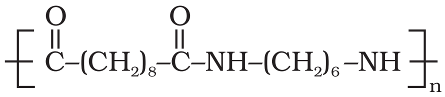
18. Name the monomers of Glyptal.

19. Is $(NHCHR\text{-}CO)_n$ a homopolymer or copolymer ?

20. Give two uses of Bakelite.

21. What is the main purpose of Vulcanisation of rubber ?

22. Identify the monomer in the following polymeric strnctnres -



$$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH \right]_n$$

23. Give example of Biodegradable polymer.

24. What is Zieglar-Natta catalyst ?

25. What is orlon ?

26. Which polymer is used to prepare squeeze bottle ?

27. Give an example of polyester.

28. What is PLA ?

29. Give two uses of PHBV.

30. Name the constituent used in vulcanisation of rubber.

D. Short Answer Type Question : (Each carries 2 marks)

1. What do you mean by homopolymer and copolymer ? give example.

2. Discuss the main purpose of vulcanisation of rubber.

3. Define thermoplastics and give example.

4. In which classes, the polymers are classified on the basis of molecular forces ?

5. Explain the difference between Buna-N and Buna-S.

6. Write the monomers of PHBV. Mention about its use.

7. How Buna-N is prepared ?

8. What is melamine ? How it is prepared ?

9. What is the structure of Bakelite ? Mention some of its uses.

10. How Dacron is prepared ?

11. What is step growth polymerisation ?

12. What is polyacrylonitrile ? Mention about its use.

13. Write the monomers of PVC ? Give two uses of PVC.

14. Name the polyester used to manufacture water bottle, write it's structure.

15. How polypropylene is prepared ?Mantion some uses of polypropylene.

16. Give two differences between linear polymers and branched chain polymers.

17. How tefon is prepared ? Give its use.

18. What is a plasticizer ? Give example.

19. What do you mean by degree of polymerization ?

20. What is Nylon 6, 6 ? Write the names of it's monomers.

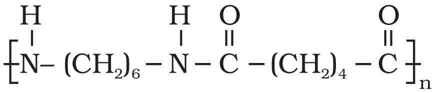
E. Short Answer Type Question : (Each carries 2 marks)

1. How polymers are classified based on the structure? Give example of each.

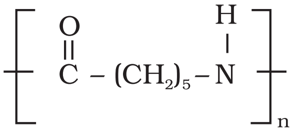
2. Explain different steps of addition or chain growth polymerisation with example.

3. What do you mean by condensation polymerisation or step growth polymerisation? Explain.

4. Write the monomers of following polymers –

(i) 

$$\left[\overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - (CH_2)_4 - \overset{\overset{O}{\|}}{C} \right]_n$$

(ii) 

$$\left[\overset{\overset{O}{\|}}{C} - (CH_2)_5 - \overset{\overset{H}{|}}{N} \right]_n$$

(iii) $\left[CF_2 - CF_2 \right]_n$

5. How will you prepare the following :

(i) Nylon 6, 6 (ii) Buna-S (iii) Bakelite

6. What is vulcanisation? Why it is done? Why is diphenyl added to rubber ?

7. What type of polymerization takes place when a polyester is formed ? Give one example of a polyester and name the monomers from which it is formed.

8. What is free radical governed addition or chain growth polymerisation ? Explain with example.

9. Briefly describe ionic polymerisation with example.

10. What is the role of berzoyl peroxide in addition polymerization of alkenes? explain with an example.

11. Give the differences between thermoplastic and thermosetting polymers.

12. How Nylon 6, 6 is prepared ? Give Mention about its use.

13. How will you elassify polymers on the basis of molecular forces ?

14. How bakelite is prepared? Give its use.

15. How dacron is obtained from ethylene glycol and terephthalic acid ?

Answer Key

A. Select the correct option (MCQ) :

1. a 2. d 3. a 4. b 5. b 6. b 7. b 8. c 9. b 10. d 11. c 12. b
13. c 14. c 15. b 16. d 17. b 18. b 19. a 20. a 21. c 22. c 23. c 24. c
25. c 26. b 27. c 28. a 29. b 30. a 31. b 32. c 33. b 34. c 35. d 36. c
37. c 38. a 39. b 40. c 41. a 42. c 43. b 44. d 45. d 46. a 47. d 48. a
49. b 50. c

B. Assertion & Reasoning :

1. a 2. a 3.d 4.a 5. d 6. b 7. d 8. a

Chapter - 16

Chemistry in Everyday Life

Chapter of a glance

Chemistry is very important to the humanity in every aspect of life. There is hardly any field of our life where chemistry does not have an impact - it may be medicines, drugs, food preservatives, soaps, detergents, shampoos, creams etc.

Medicines : The chemicals used in diagnosis, prevention and treatment of diseases, ease symptoms are called medicines. Medicines almost have no side effects, do not cause addiction and are safe for human body.

Drugs : The chemicals used for diagnosis, prevention, control and treatment of diseases are called drugs. Drugs have side effects, may cause addiction and are not safe if not consumed in proper dosage.

The treatment of disease by chemical compound which destroy the mieroorganism without attacking the tissue of human body is called chemotherapy and the chemicals are called chemotherapeutic agent.

Various types of medicinal compounds :

a. **Antacids :** The chemical substances which can reduce or neutralise the acidity in stomach and raise the PH to some appropriate level are called antacids.

Sodium hydrogencarbonate or a mixture of aluminium and magnesium hydroxide, cimetidine (tegament) rantidine (zantac) are some antacids. Omeprazole and lansoprazole are used for treatment of hyperacidity.

b. **Antihistamines :** The drugs which combat the effects of histamine, a chemical released by certain cells of the body (most cells) during an allergic reaction are called antihistamines.

Some commonly used antihistamines are diphenhydramine (Benadryl), Fexofenidine (Allegra), Cetrizine (Zrytect) etc.

c. **Tranquilizers :** The drugs given to the patients suffering from anxiety and mental tension. The two antidepressant drugs that are commonly used are phenelzine and iproniazid.

d. **Analgesic :** The drugs which reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordiuation or paralysis or some other disturbances of nervous system are called analgesic.

   i) Non-norcatic analgesic : There are effective in relieving skeletal pain, reducing fever (antipyretic) and preventing blood clothing. Aspirin is used in prevention of heart attacks.

   ii) Narcotic analgesic : The analgesic which produce sleep and unconsciousness are called narcotics. But these are addictive, produce stupor, coma, convulsions and ultimately death. These are used for the relief of postoperative pain, cardiac pain and pains of terminal cancer and in child birth. For example - Morphine, Heroin, codeine.

e. **Antimicrobials :** The chemicals which kills or destroy micro-organisms, are called antimicrobials. These are used to treat disases caused by microbes like bacteria, virus, fungus. eg. - salvarsan, prontosil & sulphadrugs etc.

f. **Antiseptics :** The chemicals which prevent the growth of micro-organims, may also kill them but do nto harm the living tissues are called antiseptic. eg. - Iodoform, dettol, tincture of Iodine etc.

g. **Disinfectants :** The chemicals which kill microorganimrs but are not safe for contact with living tissues are kuown as disinfectants. These are uesd only on nonliving (washroom, drain, floor) objects. eg. - Phenyl, Formaldelyde (gaseous) Lisol etc.

h. **Antibiotics :** The chemicals produced by micro-organims (bacteria, fungi, moulds) that can inhibit the growth or even destroy other microorganims are called antibiotics.

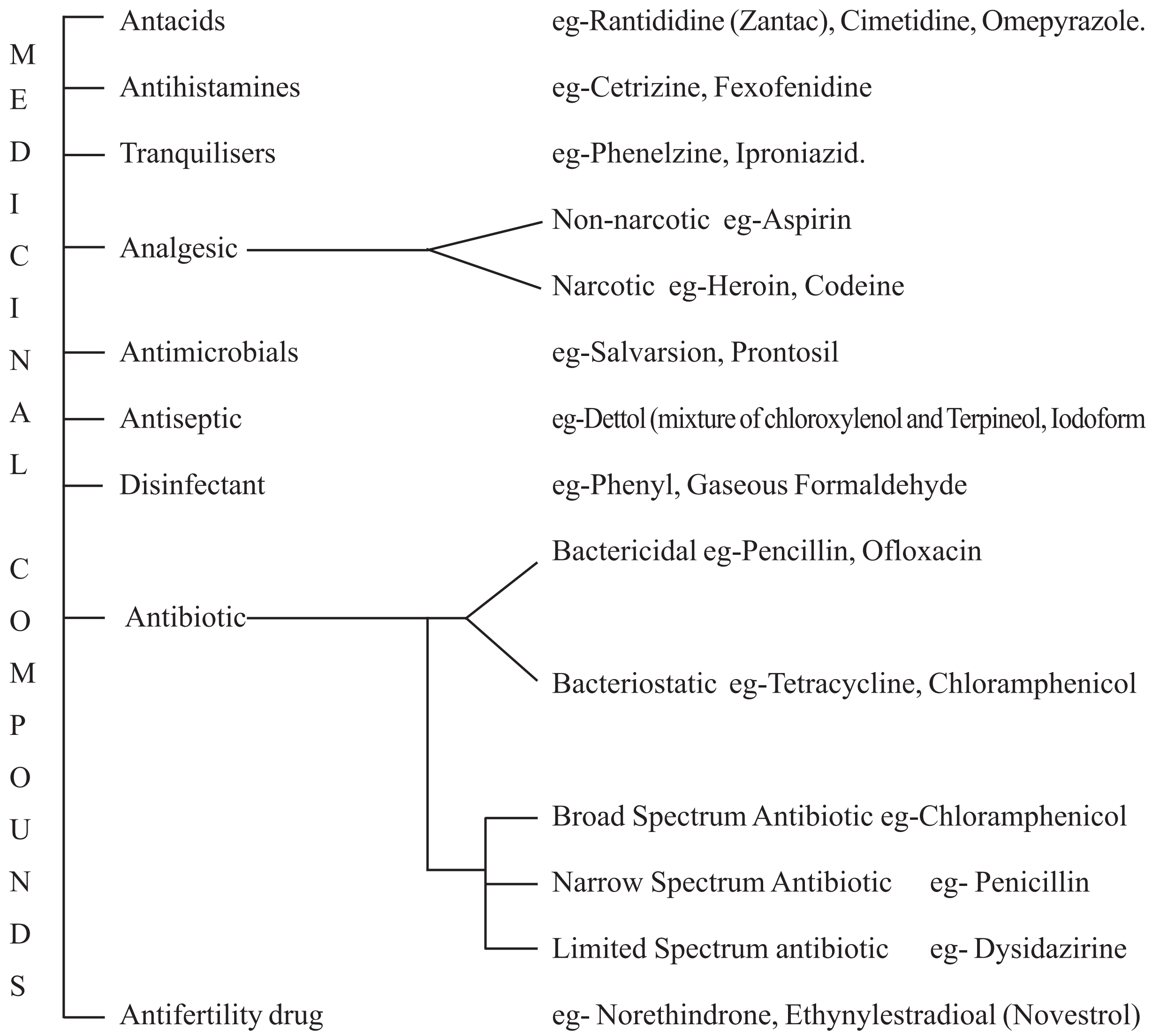
Antibiotics have either

i) cidal (killing) effect on microbes and are called bactericidal or

ii) a static (inhibitory) effect on microbes and are called bacteriostatic.

The range of microorganisms affected by a certain antibiotic is expressed as its spectrum of action. Based on this factor autibotics are classified as broad spectrum antibiotics, narrow spectrum antibiotics and limited spectrum antibiotics.

Antifertility druges - The chemicals which are used for birth control are called antifertility drugs. These are mostly hormonal contraceptives. eg. - Norethindrone, Ethynylestradiol (Novestrol).



Chemicals in Food

Chemicals are added to food for (i) their preservation (ii) enhancing their appeal (iii) adding nutritive value in them. Some food additives which add colour of food are carotenoid, indigoid, flavonoid, coupounds like Monosodium glutamate (MSG) add flavour to food ileuss.

Artificial sweetener : Artificial sweetener or sugar substitutes are chemicals added to some foods & beverages to make them taste sweet. eg. - Saccharin, Aspartame

Food preservatives : These prevent spoilage of food due to microbial growth. common salt, vegatable oils (natural) and sodium Benzoate, Epoxide (artificial) are some food preservatives.

Antioxidant : these prevent the food items which contain unsaturated fats & oils. eg. - BHA, BHT.

Cleansing Agents

Soaps - Soaps are the sodium or potassium. salts of higher fally acids like stearic, oleic and palmitic acid Soaps are cleansing ageats.

Detergents : Synthetic detergents are cleansing agents which act equally well in both soft and hard water.

Synthetic detergeats are of three types -

i) **Anionic detergeats -** are sodium salts of sulphonated long chain alcohols or hydrocarlrons. eg.- sodium laurylsulphate, sodium dodecylbenzenesulphonate.

ii) **Cationic detergeats -** are quarternary ammouium salts of amines with acetates, chlorides, beromides as anions eg.- cetyltrimethle ammonium beromide

iii) **Non-ionic detergents -** These do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethyleneglycol. eg.- Liquid dishwashing detergents are such detergents.

A. Select the correct option (MCQ) : (Each carries 1 mark)

1. Which of the following produces soapy foam ?

   a) Sodium bicarbonate   b) Sodium Rhodinate

   c) Sodium stearate   d) Trisodium phosphate

2. Which of the follwing is not used as a food preservative ?

   a) Table salt   b) Sodium Bicarbonate

   c) Epoxide   d) sodium Benzoate

3. Which of these is not a drug target

   a) Carbohydrate   b) Lipid

   c) Vitamin   d) Protein

4. Chloramine - T is a/ an

   a) Disinfectant   b) Antiseptic

   c) Analgesic   d) Antipyretic

5. Interferon is associated with

   a) Tonic b) Virus

   c) Carbohydrate d) Antipyretic

6. Which is Hypotic drug ?

   a) Luminal b) Salol

   c) Catechol d) Chemisol

7. Which is not used as an antacid ?

   a) $NaHCO_3$ b) $Mg(OH)_2$

   c) Na_2CO_3 d) $Al(OH)_3$

8. The drug used in Iodex is -

   a) Methyl salicylate b) Ethyl salicylate

   c) Acetyl salicylic acid d) Ortho hydroxy benzoic acid

9. Which is cationic detergent ?

   a) Sodium lauryl Sulphate b) Cetyltrimethyl ammonium bromide

   c) Sodium Doecylbenzenesulphonate d) Sodium stearate

10. Insulin belongs to which group ?

    a) Hormone b) Enzyme

    c) Receptor d) Agonist

11. Narcotic Analgesic is

    a) Aspirin b) Paracetamol

    c) Codeine d) Cimetidine

12. Which is an antidepressant ?

    a) Phenelzine b) Rantidine

    c) Aluminium hydroxide sol d) Cimetidine

13. Which is used to releive mental stress-

    a) Analagesic b) Antiseptic

    c) Antihistamine d) Tranquilizer

14. Salt of sorbic acid and propanoic acid is used as

    a) Antioxidant b) Flavouring agent

    c) Food Preservative d) Nutritional supplement

15. Which contains - COOH group as functional group -

    a) Picric acid b) Barbituric acid

    c) Ascorbic d) Aspirin

16. Which is used in hair conditioner ?

    a) Sodium dodecyl bewzene sulphonate b) Cetyl Trimethyl ammonium bromide

    c) Tetramethyl ammonium bromide d) Sodium lauryl sulphate

17. Which is an antihistamine drug ?

    a) Terfenadine b) Rantidine

    c) Adrenaline d) Epinidrine

18. Which is strong analgesic ?

    a) Noradrenaline b) Heroin

    c) Chlodiazepoxide d) Phenelzine

19. Aspirin is

    a) Methyl salicylic acid b) Acetyl salicylic acid

    c) Phenyl salicylate d) Acetyl salicylate

20. Which is used for treatment of fever?

    a) Tranquiliser b) Antibiotic

    c) Antipyretic d) Analgesic

B) Assertion and Reasoning type question : (Each carries 1 mark)

The questions given below consist of an assertion (A) and Reason (R). Use the following key to choose the appropriate answer.

a) Both A and R are correct and R is the correct explanation of A.

b) Both A and R correct, but R is not the correct explenation of A.

c) A is correct but R is not.

d) A is incorrect but R is correct.

1. Assertion : Rantidine is an antihistamine drug which is used in treatment of hyperacidity.
   Reason : Rantidine neutralises the excessive acid released by stomect.
2. Assertion : In the level of noradrenaline is low for some reasons, the person suffers from depression.
   Reason : In such situations, the antidepressant drugs used inhibit the enzymes which catalyse the degradation of noradrenaline.
3. Assertion : Artificial sweeteners are used in preparing sweets to control calorie intake in our body.
   Reason : These appear to be entirely inert and harmless when taken.
4. Assertion : Saccharin is the first popular artificial sweetening agent.
   Reason : It is 100 times as sweet as cane sugar
5. Assertion : Tetracycline is a becteriostatic antibiotic.
   Reason : It Prevents the growth of microorganisms.
6. Assertion : Receptors are proteins
   Reason : These are crucial to body's communication process.
7. Assertion : Detergents with branched chains are biodegradable.
   Reason : Bactetia cannot degrade branched chain detergents, so these cause water pollution.
8. Assertion : Some substances (like phenol) can act as an antiseptic as well as disinfectant.
   Reason : Because antiseptics & disinfectants act in the same way on different bodies.
9. Assertion : Drugs that bind to the receptor site and inhibit its natural function are called agonists
   Reason : Agonists are useful when there is lack of natural chemical messenger.
10. Assertion : Receptors are the proteins that are crucial to body's communication process.
    Reason : Carrier proteins carry polar molecules across the cell membrane.

C) Very short answer type questions : (Each carries 1 mark)

1. Name the antibiotic used for treatment of Tuberculosis ?
2. Name the type of drug to which chloramphenicol belong ?
3. Name a medicine used for psychiatric patient ?
4. Name the analgesic used for releif of pain of heart ?
5. Name a sulphadrug ?
6. Name the macromolecules that are chosen as drug targets ?

7. Where are the receptors found ?
8. What is the essential component of sleeping pills ?
9. What is the main component of Dettol ?
10. Name a sweetner used in making sweets for diabetic patients ?
11. Which type of detergent is used in toothpastes ?
12. Which type of medicines are used as hypnotics ?
13. Name the artificial sweetner which is 100 times sweeter than sugar ?
14. Which compounds are used as frothing agent in soaps ?
15. Name two chemical messengers ?
16. Name a broad spectrum antibiotic ?
17. What is tincture of iodine ?
18. Why is ethanol added to soap ?
19. Why is glycerol added to the soaps used for shaving ?
20. What do you mean by pathogen ?
21. Name two narcotics used as analgesic ?
22. Name a drug which is used as both antipyretic and analgesic ?
23. What is bacteriostatic drug ?
24. What are the diffrences between toilet soaps and laundry soaps ?
25. What is antipyretic ?
26. Name the antioxidant used in wine and beer ?
27. What do you mean by soft soap ?
28. Name two α - amino acids which are dipeptide and 100 times sweeter than cane sugar ?
29. What is heroin ?
30. What is the percentage of phenol in disinfactants ?

D) Answer in short : (each carries 2 marks)

1. Why is Rantidine used as an antacid ?
2. Why do we use artificial sweetening agents ?
3. Why do we need to classify drugs in different groups ?
4. Name the macromolecules that are chosen as drug targets ?
5. Define the term chemotherapy ?
6. What is meant by the term ‘broad spectrum antibiotics’ ? explain.
7. Why should not medicines be taken without consulting dortors ?
8. Why do soaps not work in hard water ?

9. Which type of medicines are used to treat hyperacidity ?
10. What are the side effects of excessive intake of antacids ?
11. Name a medicine used in controlling depression and hypertension ?
12. Write the structures of aspirin and paracitamol ?
13. Why should aspirin not be taken in empty stomach ?
14. Why aspirin finds use in prevention of heart attacks ?
15. What are antioxidants. Give examples .
16. How do antiseptics differ from disinfectants ?
17. Name the constituents of birth controll pills ?
18. Define - (a) Receptor (b) Enzyme.
19. What are antagonists ? How are they useful ?
20. Define with examples - (a) antibiotic (b) antiseptic.
21. What do you mean by biodegradable and non-biodegradable detergents ?
22. Why do some drugs prevent the catalytic function of enzymes ?
23. (a) How are the transparent soaps made ?
    (b) What are the harmful affects of hyper acidity ?
24. How are synthetic detergents better than soaps ?
25. What problem arises in using alitame as artificial sweetener ?

Answers

A. Answer key (MCQ) :

1-a 2-b 3-c 4-a 5-b 6-a 7-c 8-a
9-b 10-a 11-c 12-a 13-d 14-c 15-d 16-b
17-b 18-b 19-b 20-c

B. Assertion Reasoning :

1 - c 2- a 3 - a 4 - c 5 - a 6 - b 7 - d 8 - c
9 - d 10 - b

C. Very short answer type :

1. Streptomycin & chloramphenicol
2. Antibiotic
3. Veronal

4. Aspirin
5. Sulphapyridine
6. Nucleic acid, Protein, Carbohydrate and lipid.
7. On the outer surface of cell membrane.
8. Tranquilizer.
9. Chlorooxylenol and α - terpineol.
10. Ortho - Sulphobenzymide or Saccharin.
11. Anionic detergent.
12. Barbiturate.
13. Aspartame.
14. Rosin.
15. Neurotransmitters and hormones.
16. Chloramphenicol.
17. 2-3% solution of iodine in alcohol - water mixture.
18. To make it transparent.
19. To prevent rapid drying.
20. Organism causing diseases to its host.
21. Morphine and Aspirin.
22. Aspirin.
23. The antibiotics which prevent the growth of micro organisms.
24. Bathing soaps (toilet soaps) are potassium salts of long chain fatty acid & Laundry soaps are sodium salts of long chain fatty acids.
25. Medicines used to reduce fever.
26. Sodium sulphite and sodium metabisulphide.
27. Potassium salts of long chain fatty acids line oleic acid, palmitic acid, stearic acid etc.
28. Aspartame and phenyl alanine.
29. Morphine diacetate.
30. 1% Phenol.

NOTE

NOTE