JEE-2022 Aspirants

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JEE ADVANCED 2021

द्वितीय वर्ष में अद्वितीय परिणाम

7 IN TOP 200 · **19** IN TOP 500 · **34** IN TOP 1000

AIR **67**

ANKAN SARKAR
Roll No. : 20771420 | CCP

ALL STUDENTS WERE ENROLLED IN
CLASSROOM COACHING PROGRAM SINCE INCEPTION


AIR **109**
KUSHAGRA GUPTA
Roll No. : 20975433 | CCP


AIR **118**
MONIL LODHA
Roll No. : 20771425 | CCP


AIR **132**
UJJAYAN PAL
Roll No. : 20771408 | CCP


AIR **149**
HARSH BIHANY
Roll No. : 20771419 | CCP


AIR **155**
SWASTIK SINGHAL
Roll No. : 20770487 | CCP


AIR **186**
AKSHAT RAJANI
Roll No. : 20771411 | CCP


AIR **254**
HARSH VARDHAN
Roll No. : 20770555 | CCP


AIR **255**
VISHWAJEET SOLANKI
Roll No. : 20770578 | CCP


AIR **259**
ARNAV PATI
Roll No. : 20771417 | CCP


AIR **305**
NAVNEET RAJ
Roll No. : 20771638 | CCP


AIR **306**
ADITYA RAJ
Roll No. : 20770366 | CCP


AIR **350**
ADITYA THOMAS
Roll No. : 20771415 | CCP


AIR **360**
PARTH K. SAKALKALE
Roll No. : 20770379| CCP


AIR **362**
ANKIT CHAUDHARY
Roll No. : 20770495| CCP


AIR **408**
ARYAN BIBHUTI
Roll No. : 20771405 | CCP


AIR **467**
PRANAV JAIN
Roll No. : 20771421 | CCP


AIR **493**
BEDANTA BHAUMIK
Roll No. : 20770392 | CCP


AIR **500**
HARSH KATARA
Roll No. : 20770468 | CCP


OUR CATEGORY TOPPER
AIR **12** (SC)
AIR **802** (GEN)
MEGH H. GOHIL
Roll No. : 20770866 | CCP

JEE MAIN 2021

AIR
72
KUSHAGRA GUPTA
CCP
100 %ile in PHYSICS

AIR
92
ANKAN SARKAR
CCP
100 %ile in MATHS


AIR **120**
ANKIT CHAUDHARY
CCP
100 %ile in PHYSICS & MATHS


AIR **120**
JENISH JAIN
Roll No. : 20771425 | CCP
100 %ile in PHYSICS & MATHS


AIR **123**
PRANAV JAIN
Roll No. : 20771408 | CCP
100 %ile in MATHS


AIR **141**
UJJAYAN PAL
Roll No. : 20771419 | CCP
100 %ile in PHYSICS


AIR **184**
ARNAV PATI
Roll No. : 20770487 | CCP
100 %ile in MATHS


AIR **186**
NAVNEET RAJ
Roll No. : 20771411 | CCP
99.98%ile

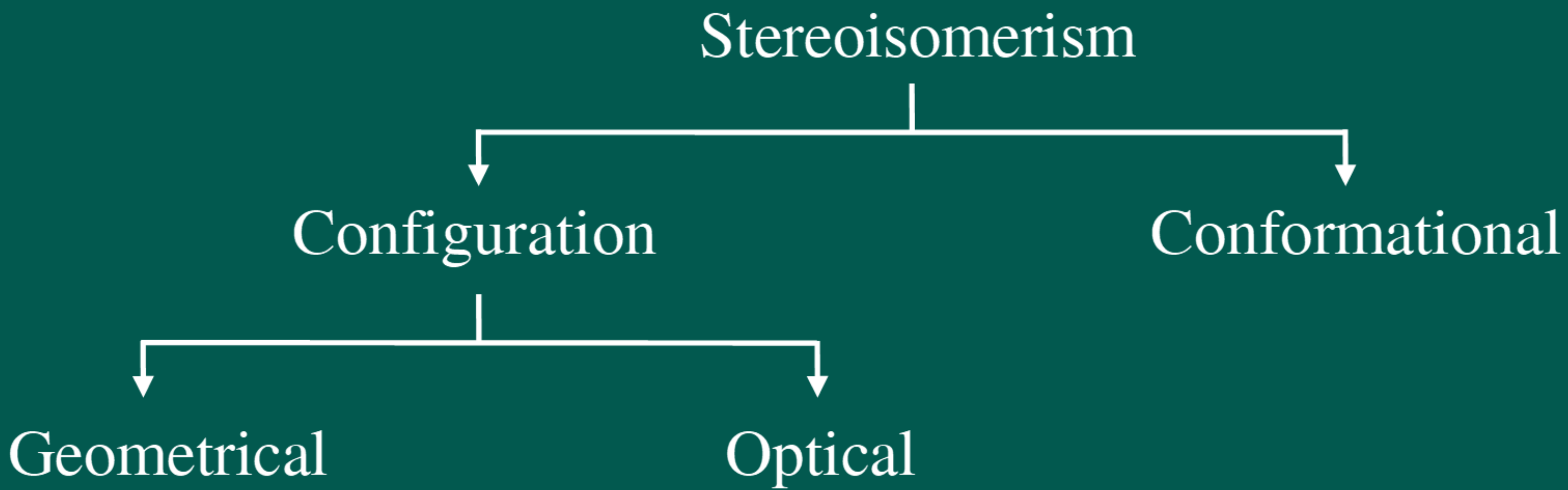

OUR CATEGORY TOPPER
AIR **4** (SC)
MEGH H. GOHIL
CCP
100 %ile in PHYSICS & MATHS

2 IN TOP 100 · **8** IN TOP 200 · **20** IN TOP 500

77.79% Students Qualified for JEE Advanced 2021

All Students were Enrolled in Classroom Coaching Program Since Inception

STEREOISOMERISM



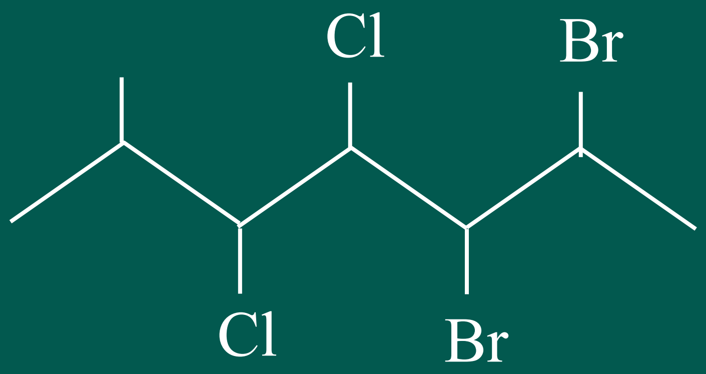
Stereoisomerism

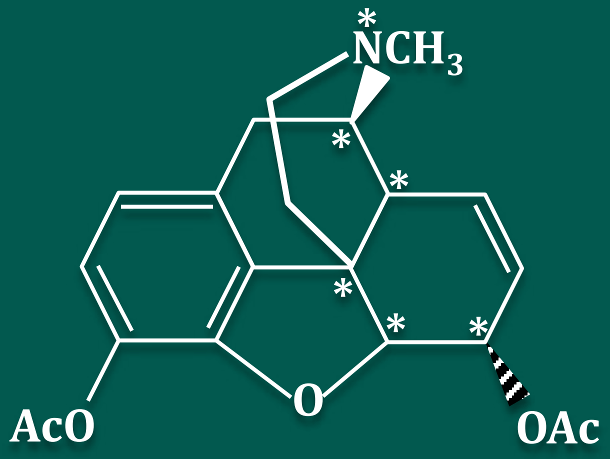
Configuration

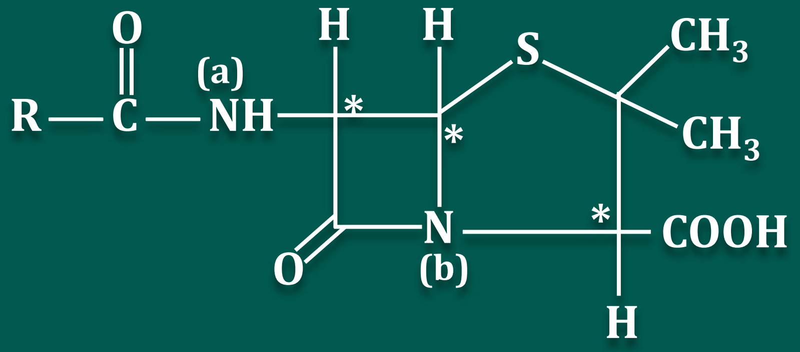
Conformational

Geometrical

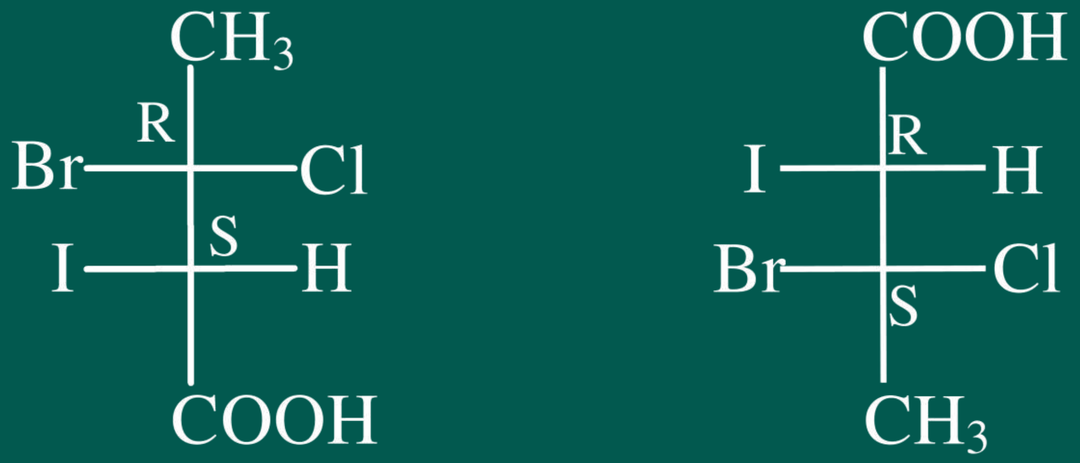
Optical


Cl
Br
Cl
Br

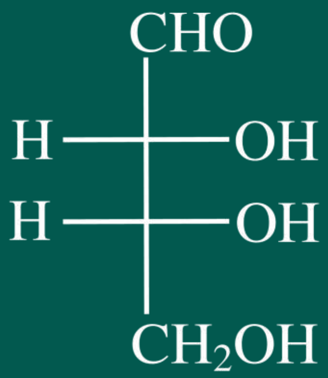

*
NCH₃
*
*
*
*
*
AcO
O
OAc


O
H
H
S
CH₃
(a)
R
C
NH
*
*
CH₃
*
COOH
N
O
(b)
H

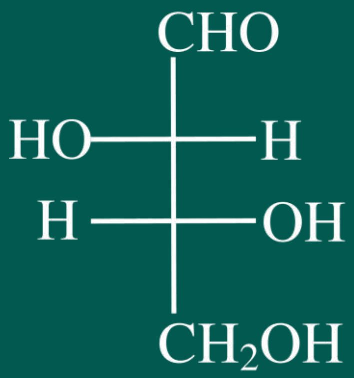
Configurational naming of stereoisomers :



Enantiomer

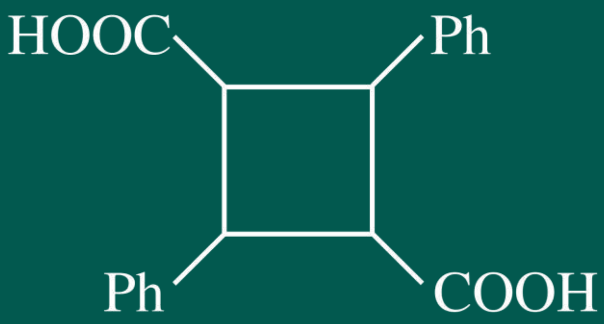


(Erythrose)

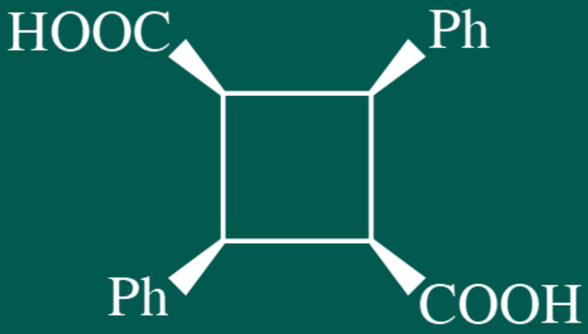


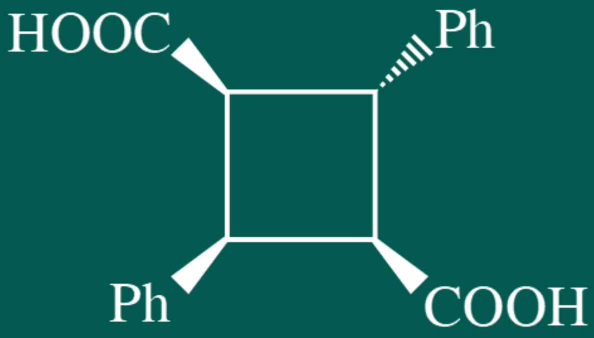
(Threose)

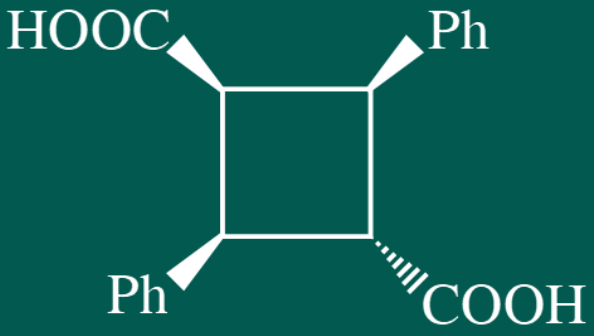
Question :

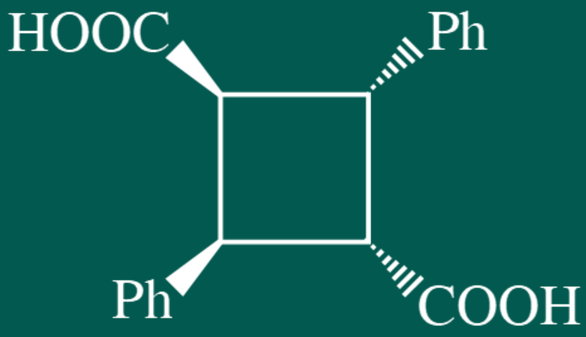


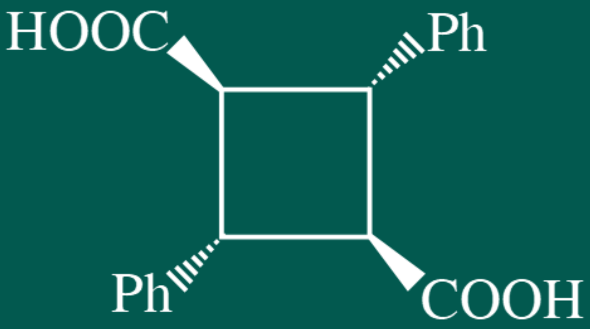
Sol.











Geometrical isomerism :

Such kind of isomerism arises due to different arrangement of atom or group present at restricted rotation system.

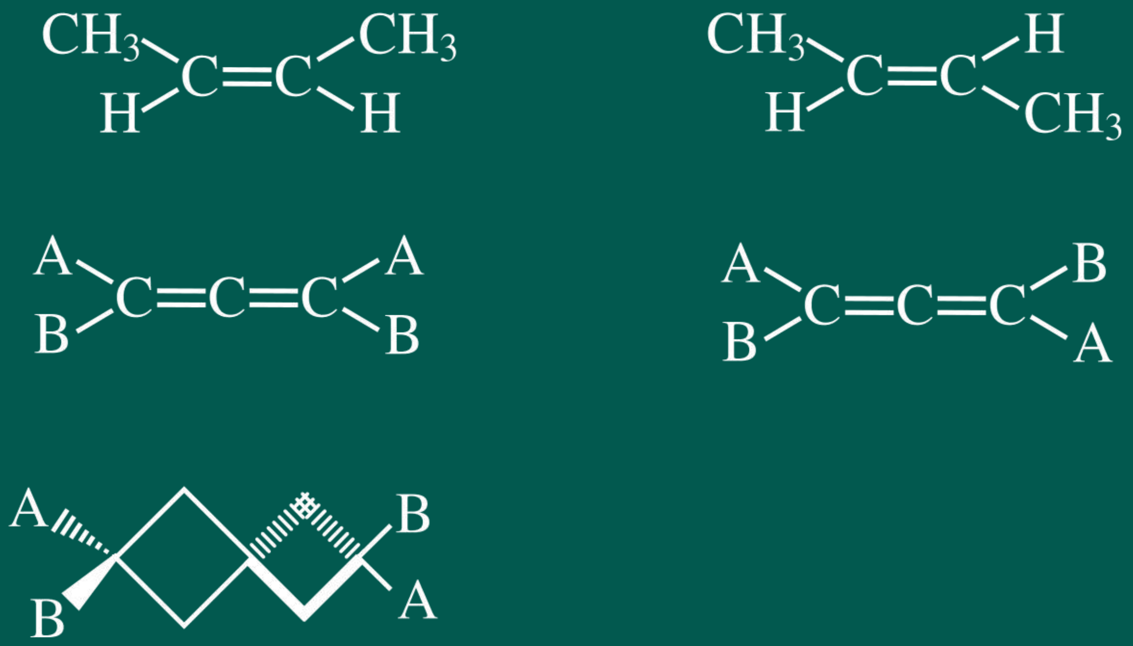
- Restricted Rotation System :

$>C=C<$, $>C=N<$, $-N=N-$, Ring

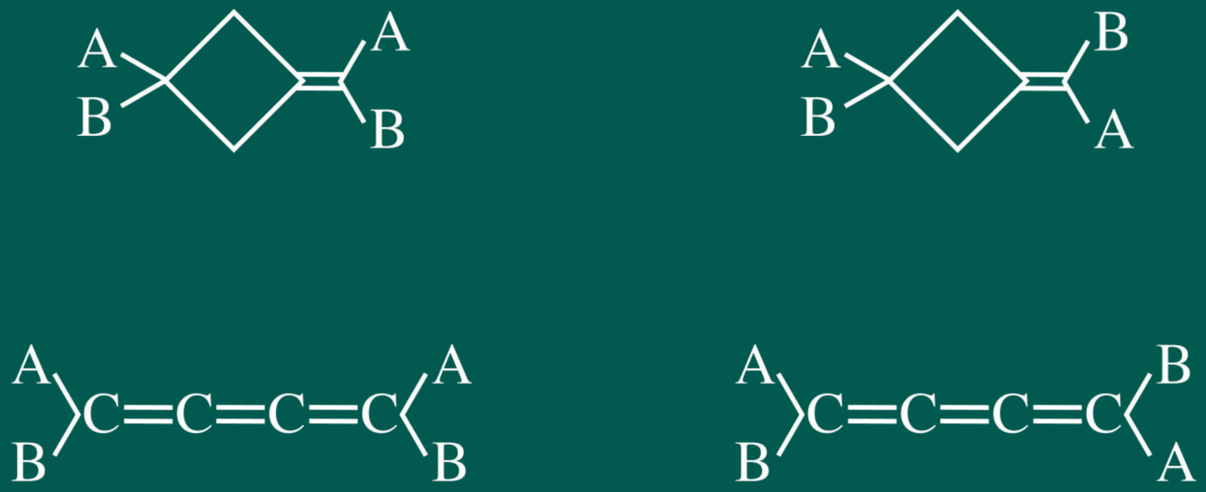
, $>C=C=C=C<$, Cycloalkylidine, Polyphenyl

- Terminal atom / group must be present in same plane
- Distance between terminal atom / group must be changed in both isomer

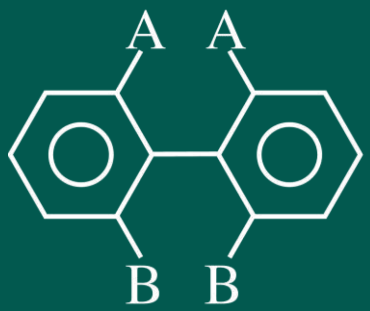
Eg.

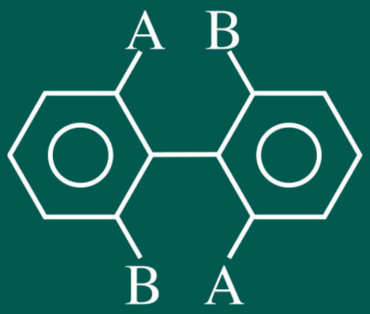


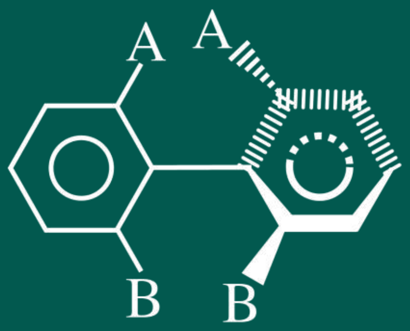
Eg.



Eg.





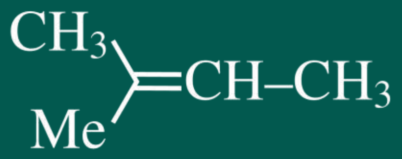


Find out which can show G.I.

Compounds	G.I.	cis/trans
		
$F{-}CH{=}CH{-}F$		
$F{-}CH{=}CH{-}Cl$		
$CH_2{=}CH{-}CH{=}CH_2$		
$CH_3{-}CH{=}CH{-}CH{=}CH_2$		

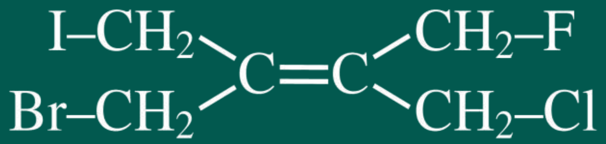
Find out which can show G.I.

$CH_3{-}CH{=}CH{-}CH{=}CH_3$



$\begin{matrix}CH_3\\ Me\end{matrix}\!\!>\!\!{=}CH{-}CH_3$

Find out which can show G.I.



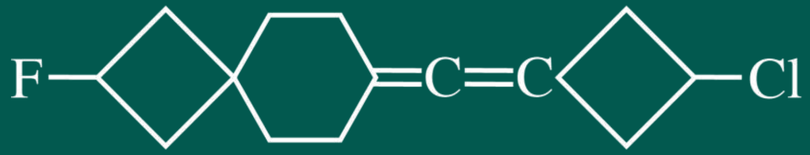
$$\begin{array}{r}\mathrm{I{-}CH_2}\\ \mathrm{Br{-}CH_2}\end{array}\!\!\!\!\!\!\begin{array}{c}\diagdown\\ \diagup\end{array}\!\!\mathrm{C{=}C}\!\!\begin{array}{c}\diagup\\ \diagdown\end{array}\!\!\!\!\!\!\begin{array}{l}\mathrm{CH_2{-}F}\\ \mathrm{CH_2{-}Cl}\end{array}$$

Find out which can show G.I.

$CH_3{-}CH{=}C{=}CH_2{-}CH_3$

$CH_3{-}CH{=}C{=}C{=}CH{-}CH_3$

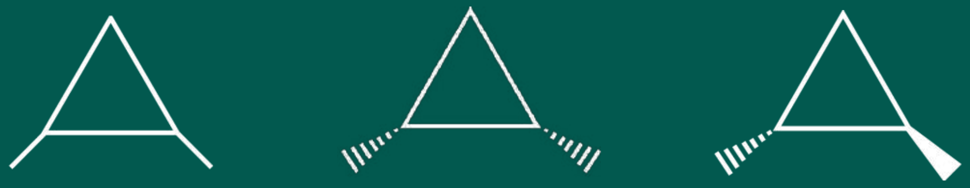
$F{-}CH{=}C{=}C{=}C{=}CH{-}F$



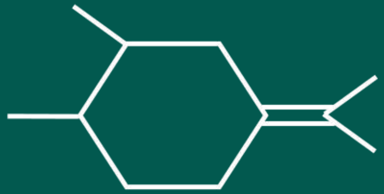
Find out which can show G.I.

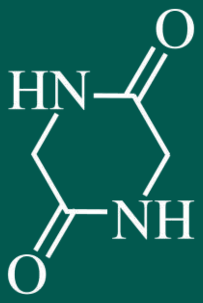
G.I. in Cycloalkane

A ≠ B   D ≠ E

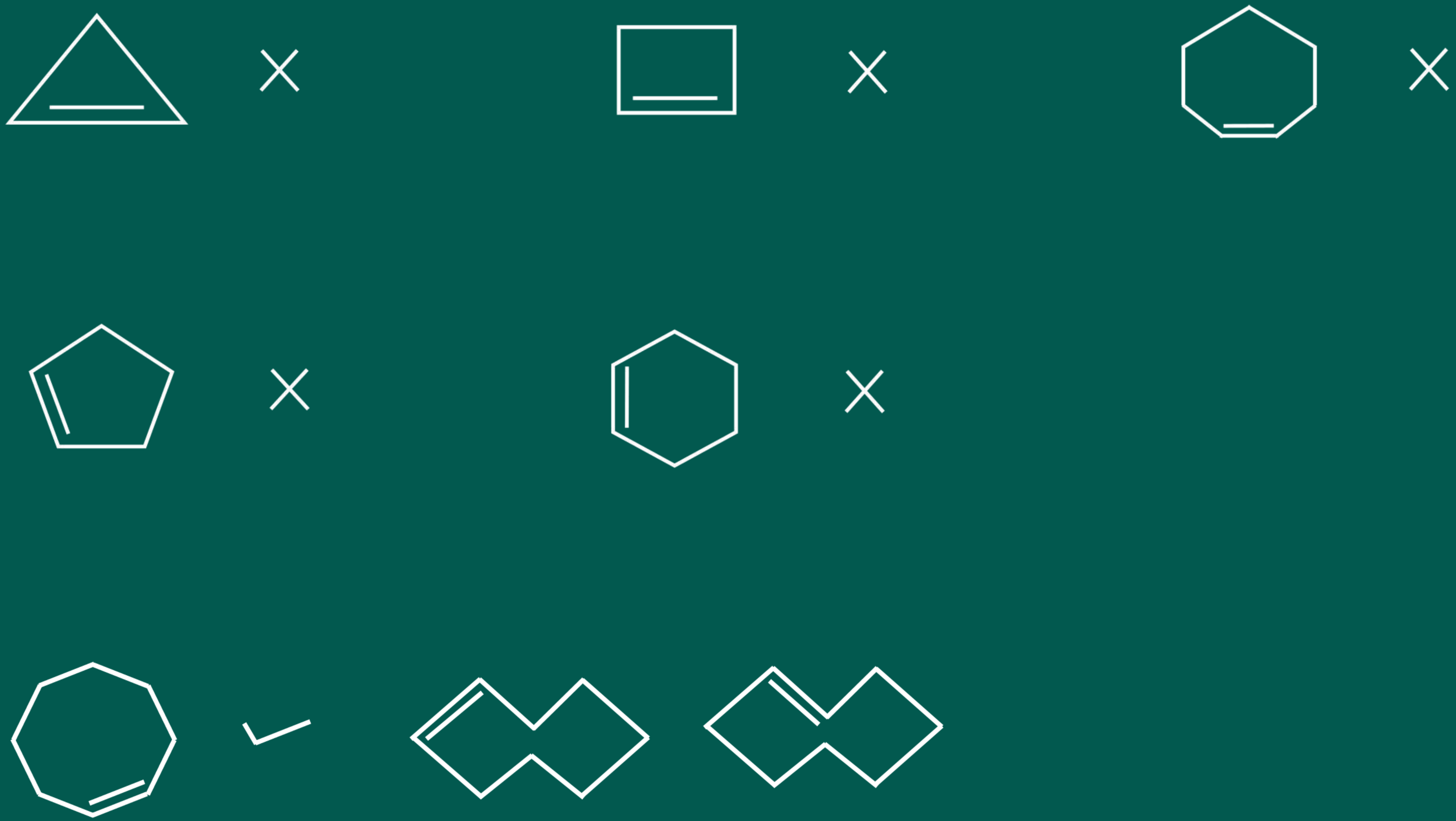


G.I. in Cycloalkane



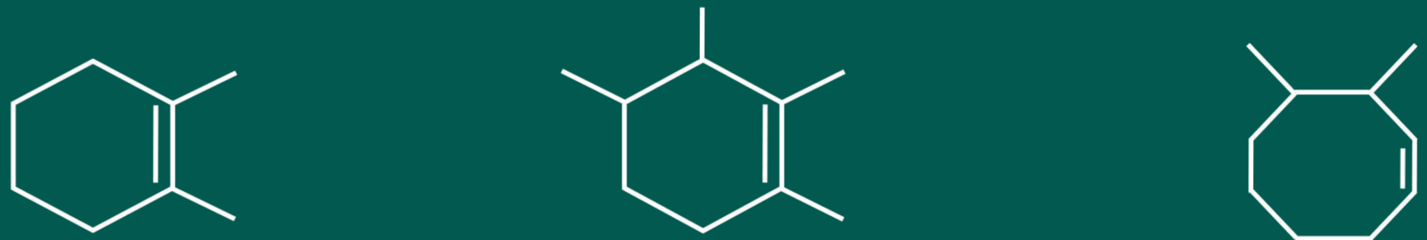


G.I. in Cycloalkene



Note:

Smallest ring which can show G.I. across double bond is cyclooctene



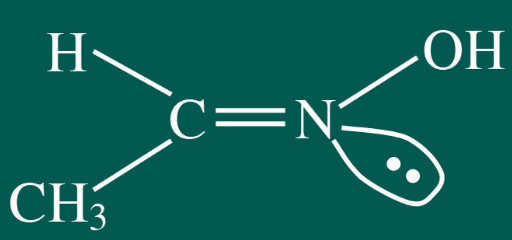
G.I. in $>C=N-$

Oxime $>=N-OH$

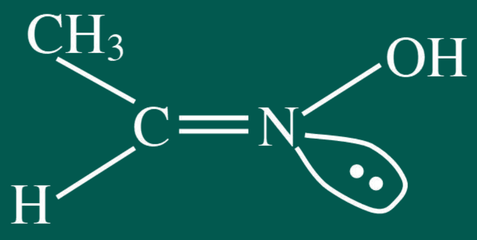
Oxime

$$CH_3-CH=O + NH_2-OH \longrightarrow CH_3-CH=N-OH$$

(Aldoxime)

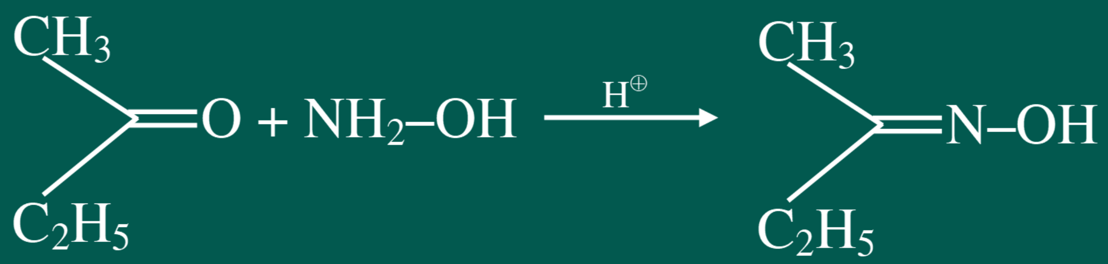


Syn

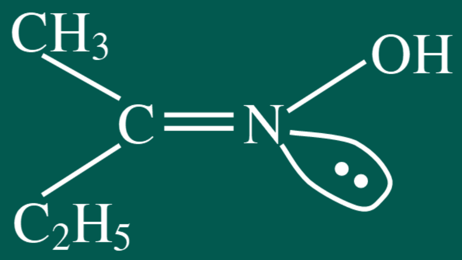


Anti

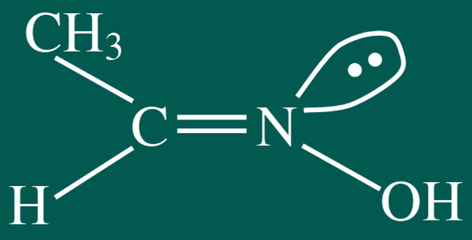
G.I. in $>C{=}N-$



(Ketoxime)



Syn – CH_3
Anti– C_2H_5



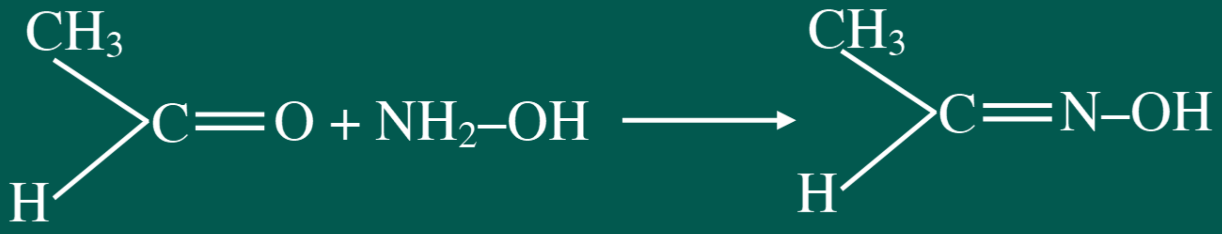
Syn – C_2H_5
Anti– CH_3

Question :

A mixture of smallest aldehyde and its next homologous is treated with excess of hydroxyl amine how many oxime will be formed?

Solution :

(1)

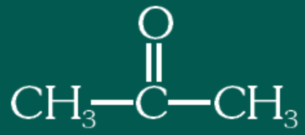


(2)

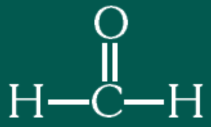
Ans. (3)

Question :

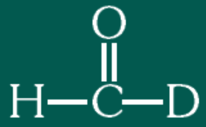
Which of the following compounds show geometrical isomerism after reaction with NH_2OH?

(a) 

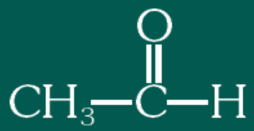
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(b) 

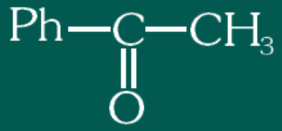
$H-\overset{\overset{O}{\|}}{C}-H$

(c) 

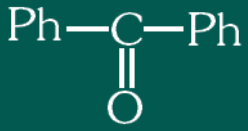
$H-\overset{\overset{O}{\|}}{C}-D$

(d) 

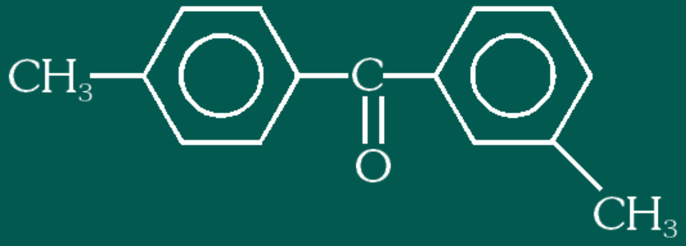
$CH_3-\overset{\overset{O}{\|}}{C}-H$

(e) 

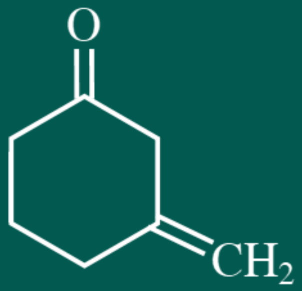
$Ph-\underset{\underset{O}{\|}}{C}-CH_3$

(f) 

$Ph-\underset{\underset{O}{\|}}{C}-Ph$

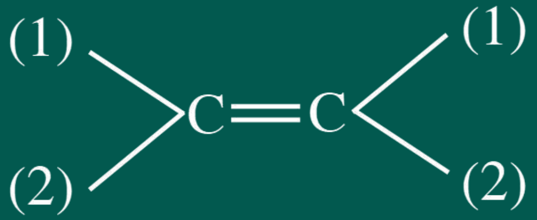
(g) 

(h) 

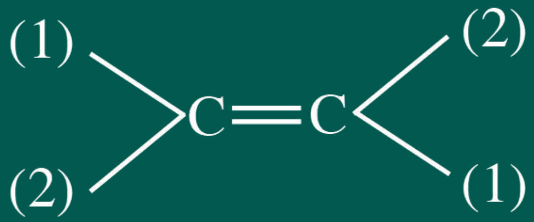
(i) 

Ans. (c, d, e, g, i)

E/Z Nomenclature



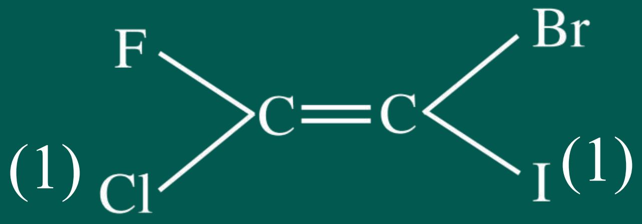
Z



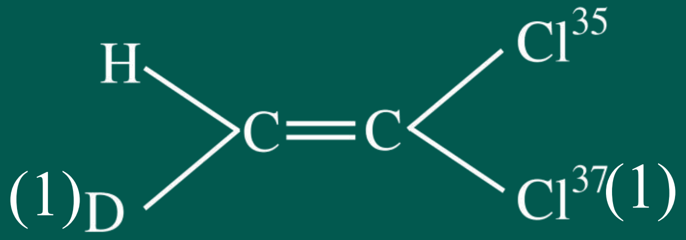
E

CIP rule (Cahn, Ingold & Prelog rule)

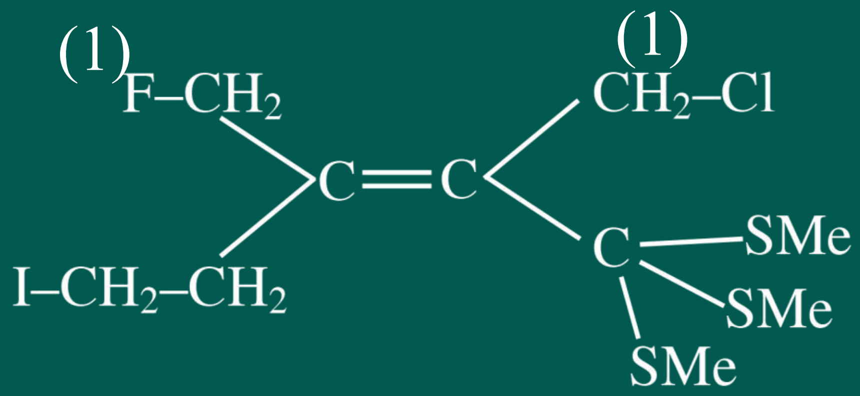
Rule – 1 :



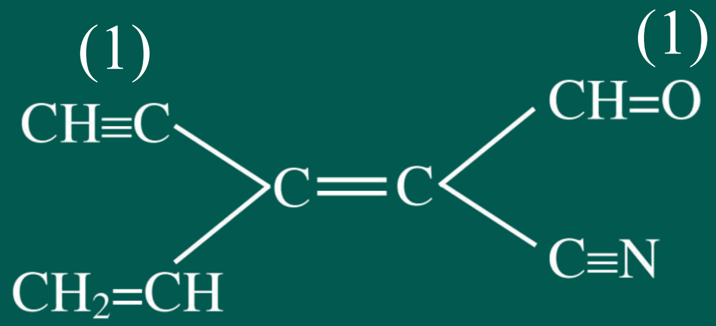
Rule – 2 :



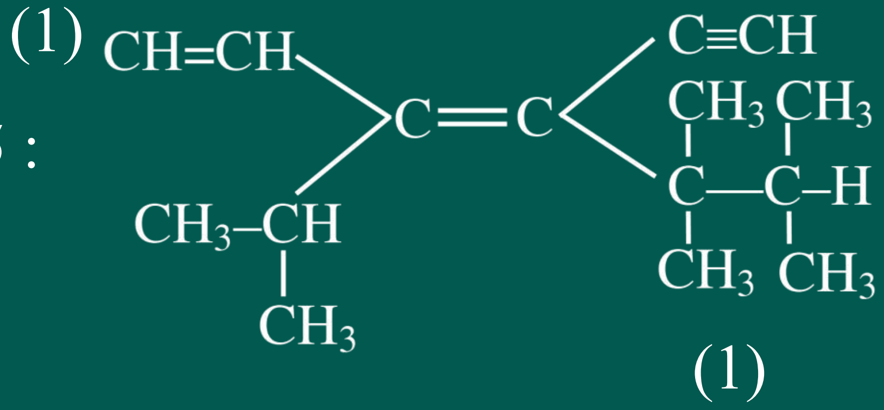
Rule – 3 :

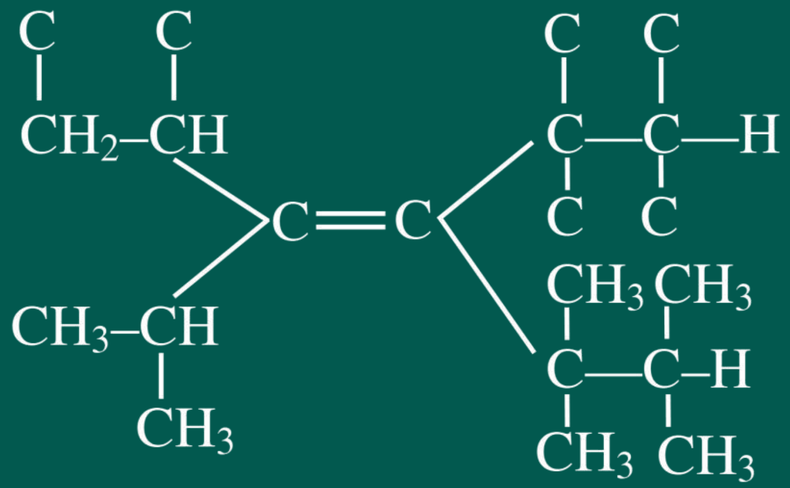


Rule – 4 :



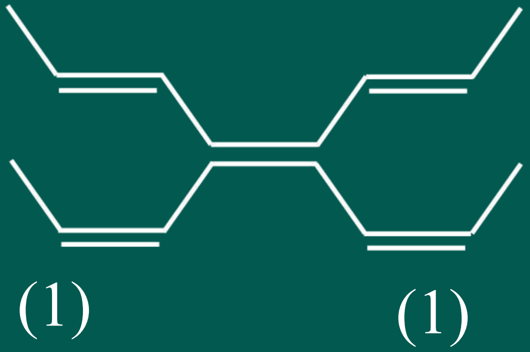
Rule – 5 :





Rule – 6 :

Cis > Trans
Z > E
R > S

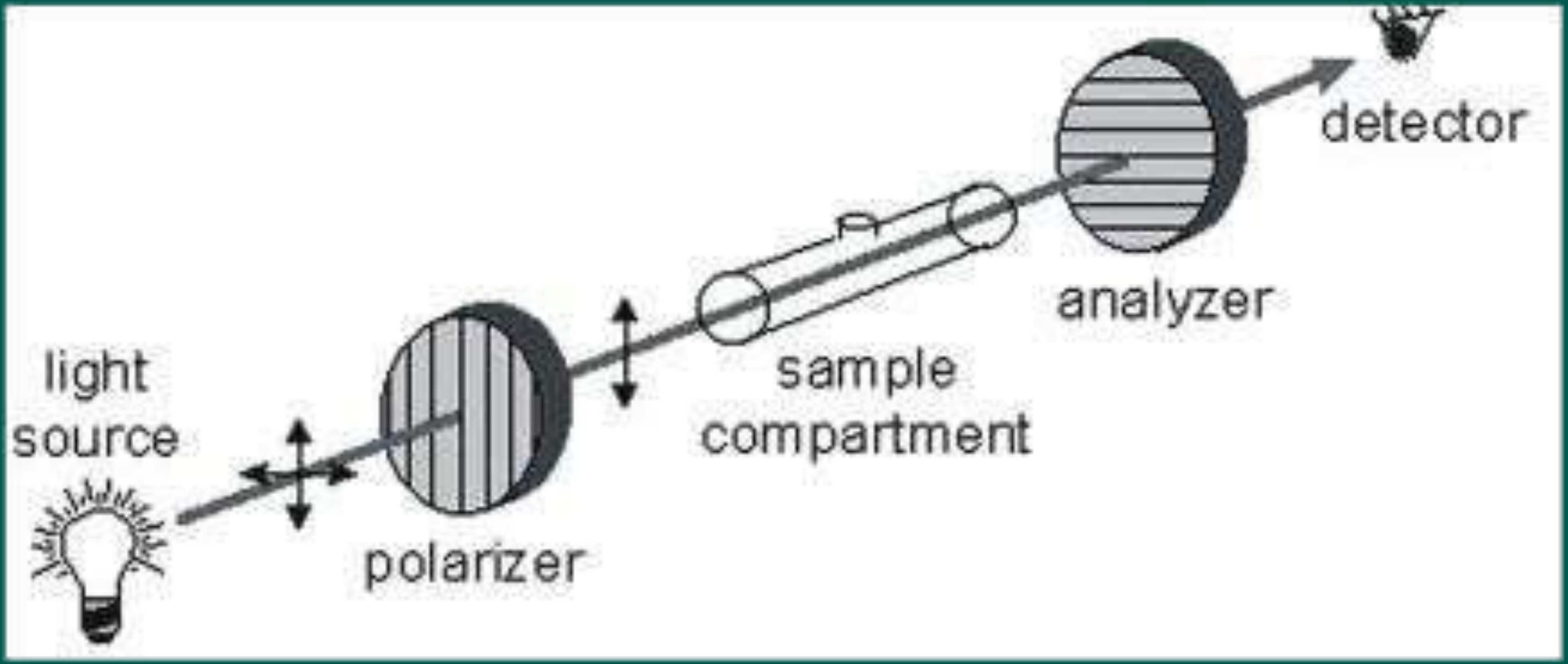


OPTICAL ISOMERS

Optical activity

Certain substances possess the property to rotate the plane of polarized light. Such substances are called optical active substances and this phenomenon is called optical activity or chiratily.

Light has vibrations occur in all planes at right angles to the line of propagation. In plane polarized light the vibrations take place only in one plane. Plane polarized light can be obtained by passing ordinary light through a Nicol prism (Polarizer).



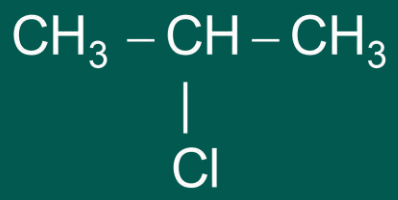
Condition for optical activity

The minimum condition for a compound to show optical activity is molecular dissymmetry i.e. absence of plane of symmetry, centre of symmetry and alternating axis of symmetry.

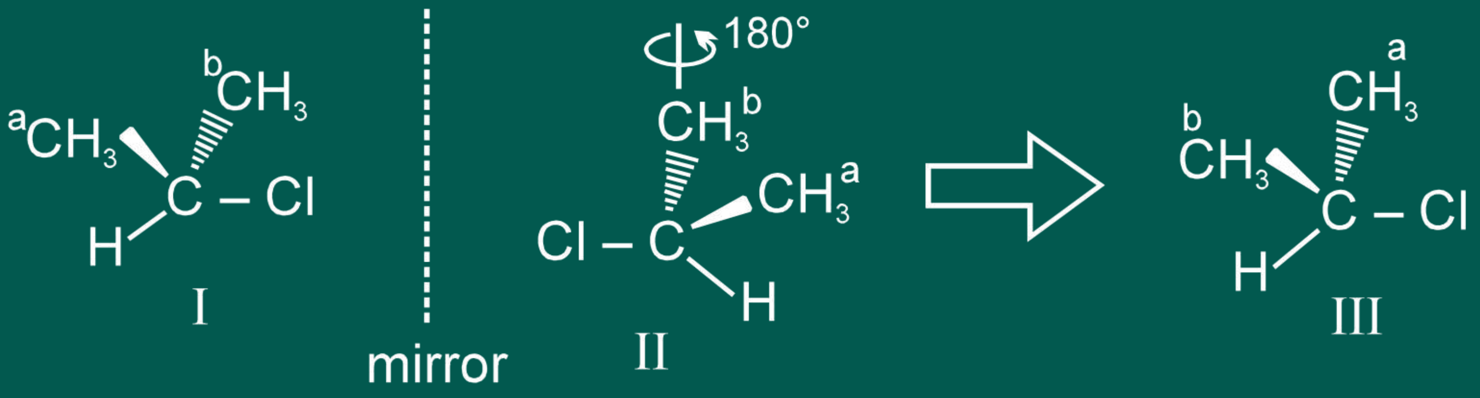
Chirality

A compound which is non-superimposable to its mirror image is called chiral while a compound which is superimposable to its mirror image is called achiral.

The necessary condition for chirality is not just the presence of asymmetric carbon atoms but the dissymmetry of the molecule as a whole.



$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$ (2-chloropropane) :

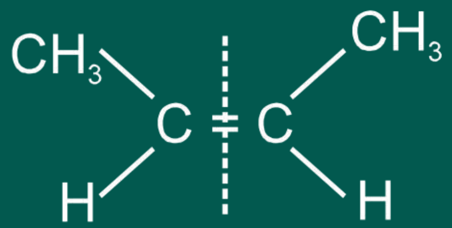


Element of symmetry

(I) Plane of symmetry (σ)

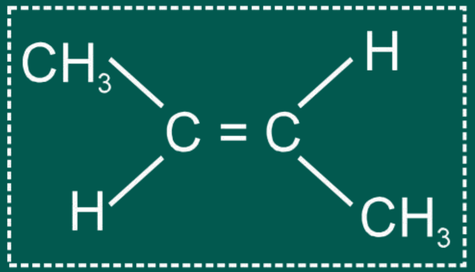
It is an imaginary plane which bisects the molecule in two equal halves in such a way that each half of the molecule is the mirror image of the other half.

(a)



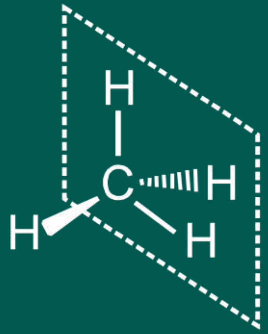
Plane of symmetry

(b)



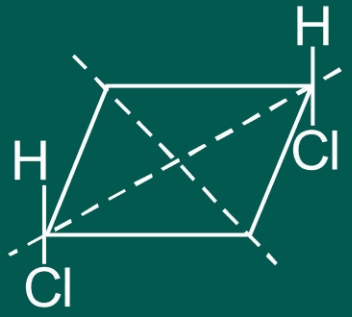
Plane of symmetry

(c)



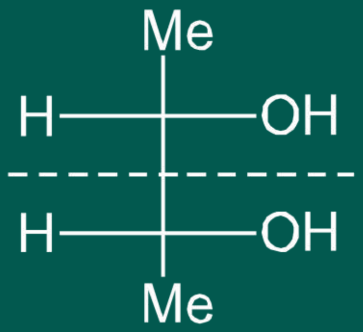
Plane of symmetry

(d)



Plane of symmetry

(e)

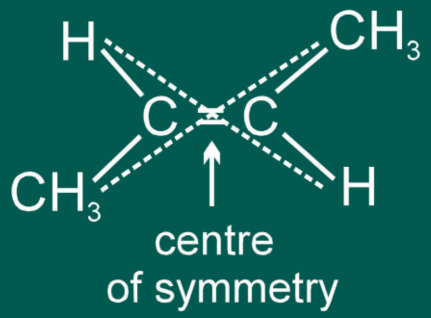


Plane of symmetry

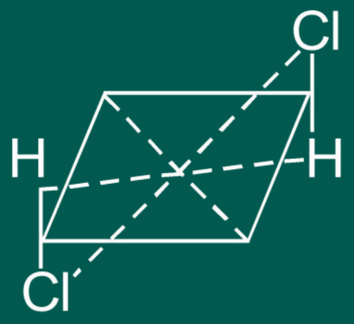
(II) Centre of symmetry (i)

A centre of symmetry is a point from which lines, when drawn on one side and produced an equal distance on the other side, will meet identical points in the molecule.

(a)

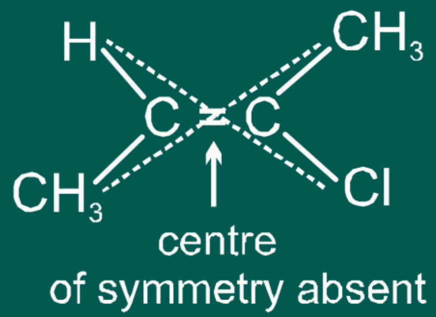


(b)



Centre of symmetry

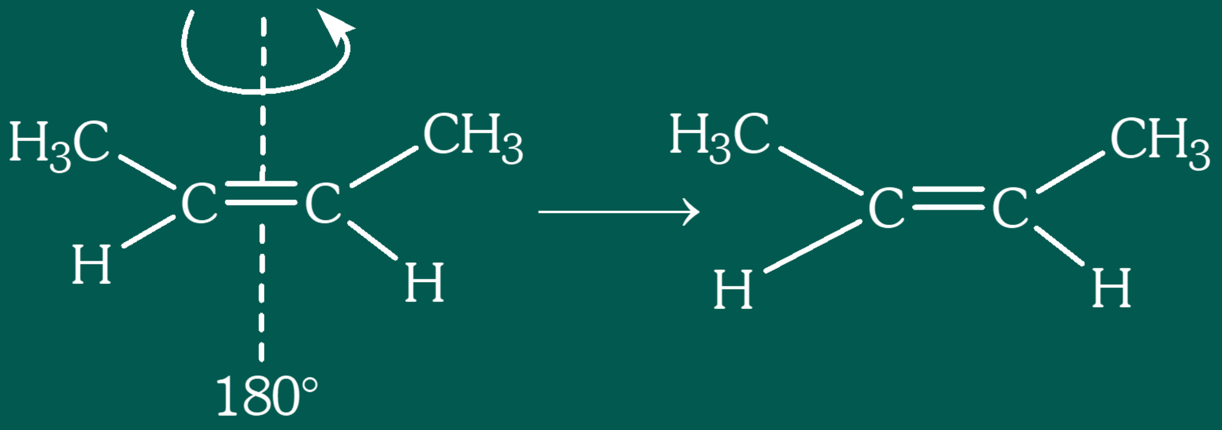
(c)



(III) Axis of symmetry (C_n)

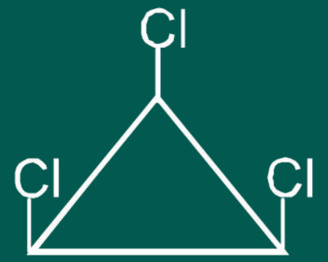
Axis of symmetry is an line about which the molecule can be rotated by 360º/n and thereby produce a molecule indistinguishable from the original molecule.

(a)



C_2 axis of symmetry

(b)

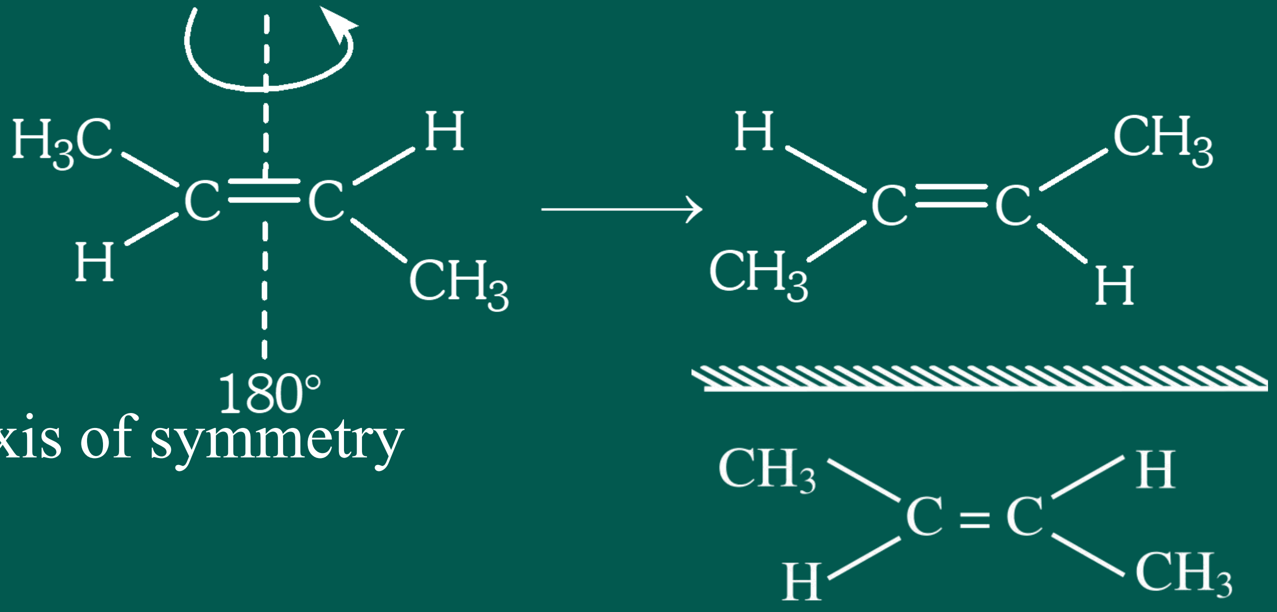


(IV) Alternating axis of symmetry (Sn)

A molecule possess an n-fold alternating axis of symmetry if it is rotated through an angle of 360º/n about this axis and then followed by reflection in plane perpendicular to the axis ; the molecule is indistinguishable from the original molecule.

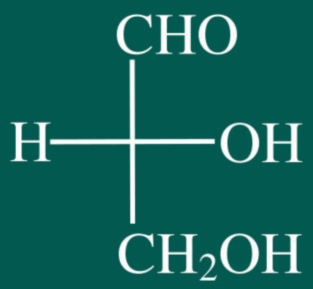
It is also called Improper axis of symmetry.

(a)

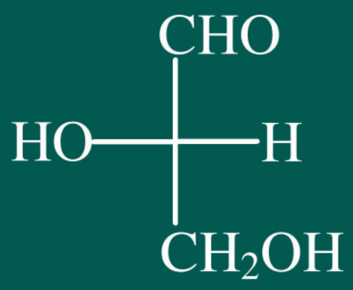


S_2 axis of symmetry

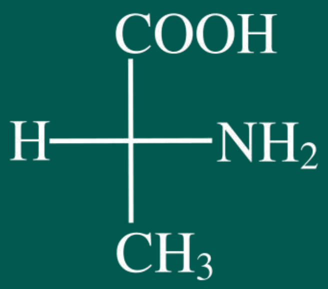
D/L : Configuration

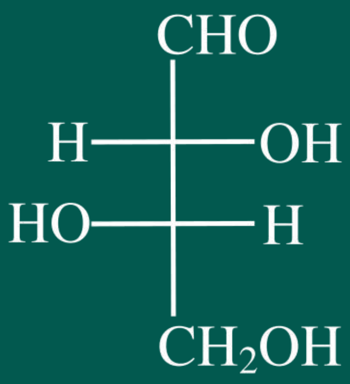


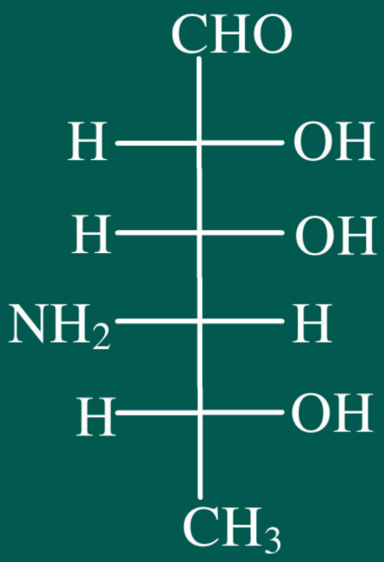
D-Glyceraldehyde

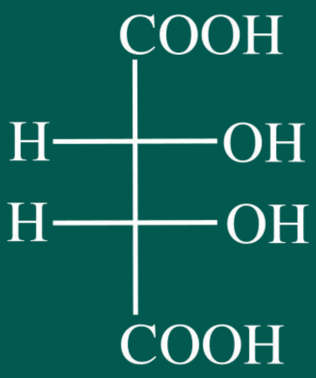


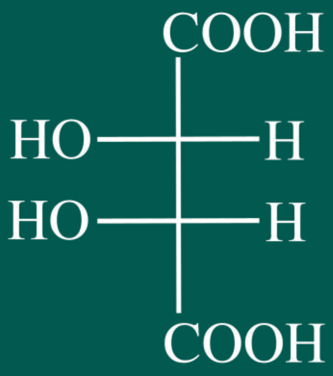
L-Glyceraldehyde

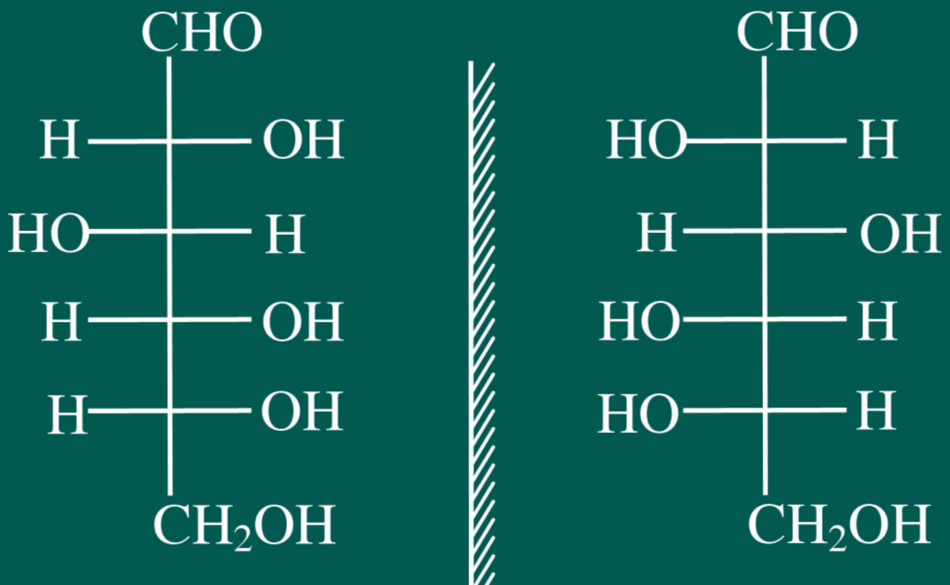








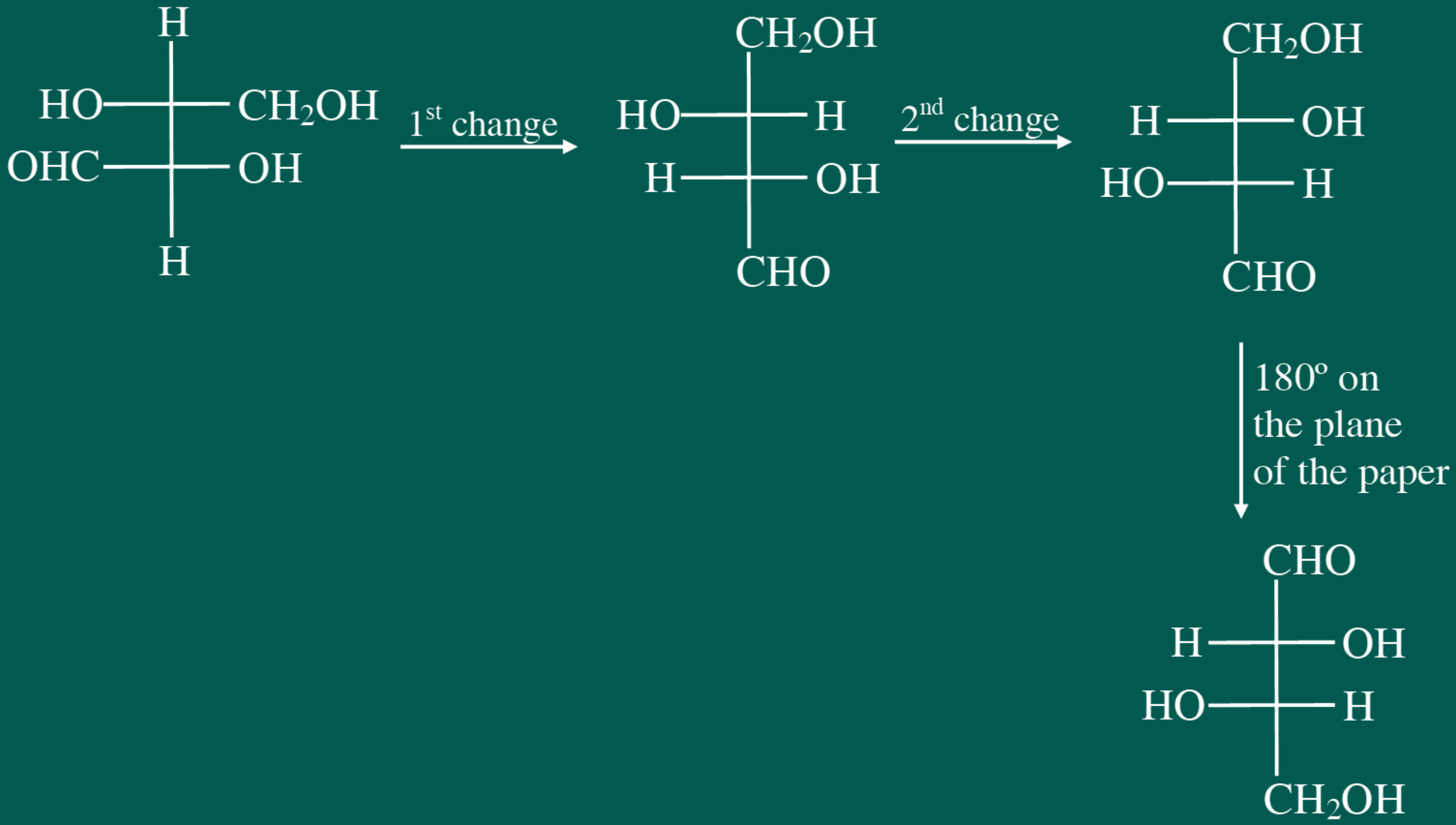




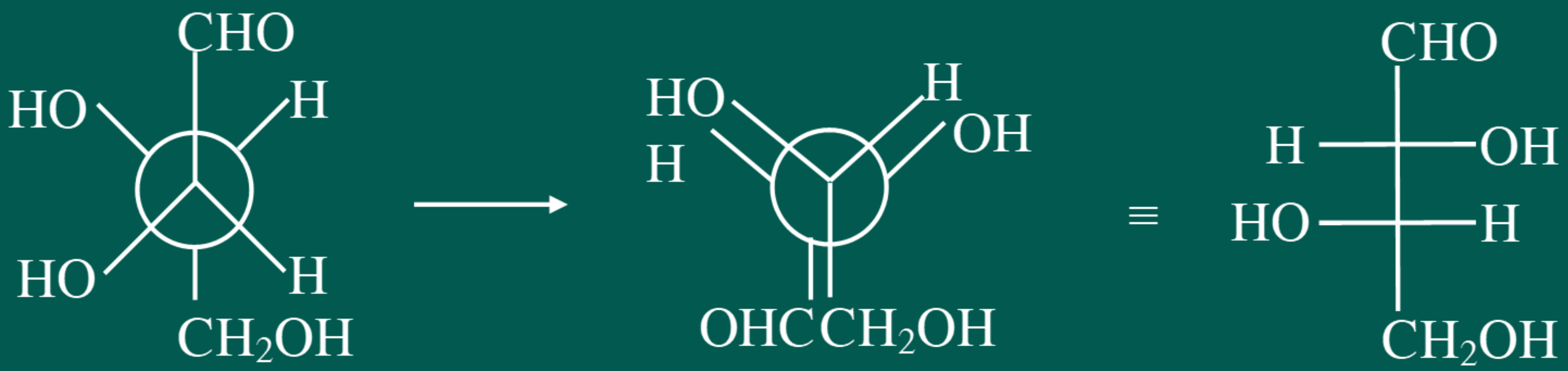
D-Glucose

L-Glucose

Q.

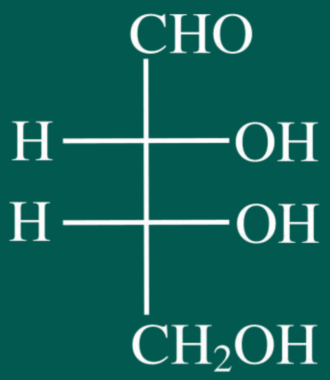

H
HO
CH₂OH
OHC
OH
H
1st change
CH₂OH
HO
H
H
OH
CHO
2nd change
CH₂OH
H
OH
HO
H
CHO
180° on the plane of the paper
CHO
H
OH
HO
H
CH₂OH

Q.

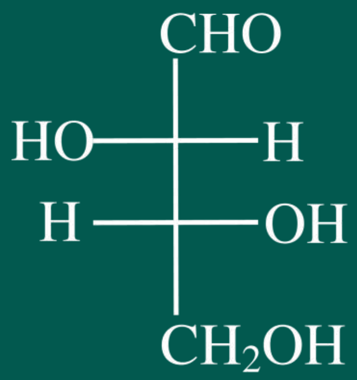


L-Configuration

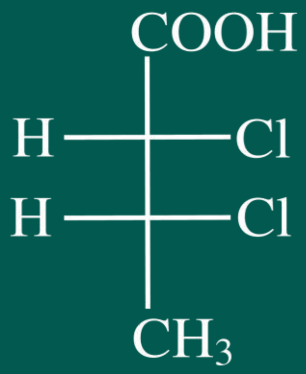
Erythro & Threo

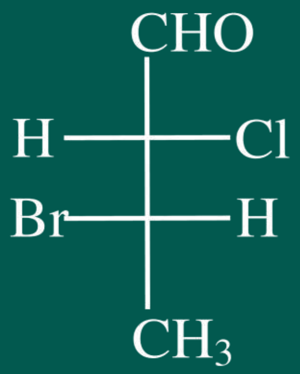


(Erythrose)



(Threose)

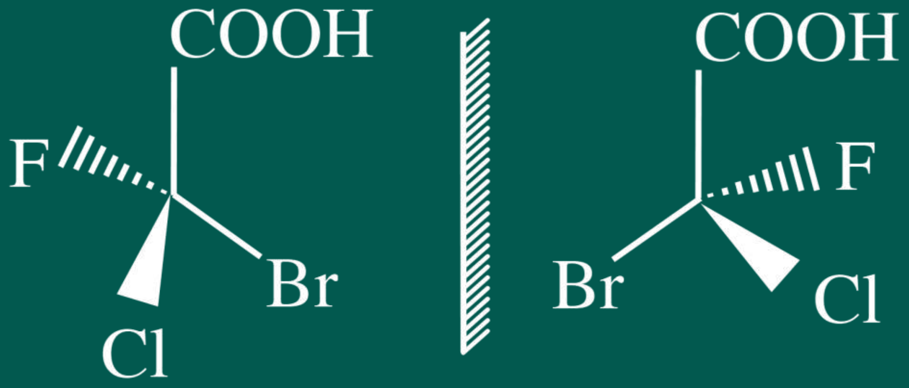


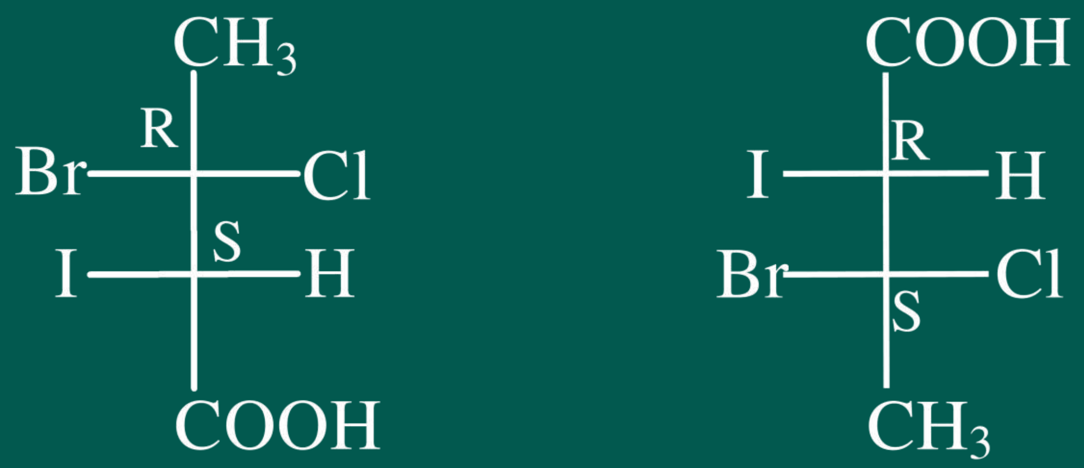


Enantiomers

Compound which are non-superimposable (NO POS, NO COS, NO Improper axis of symmetry) mirror images of each other are known as enantiomer.

Example :



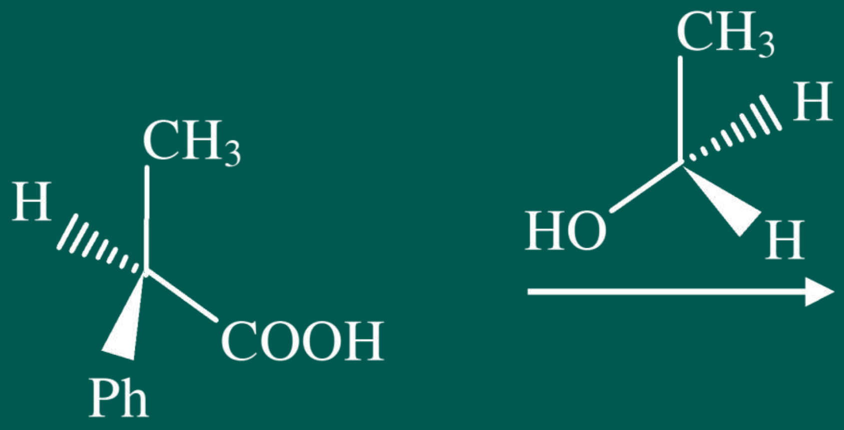


Enantiomer

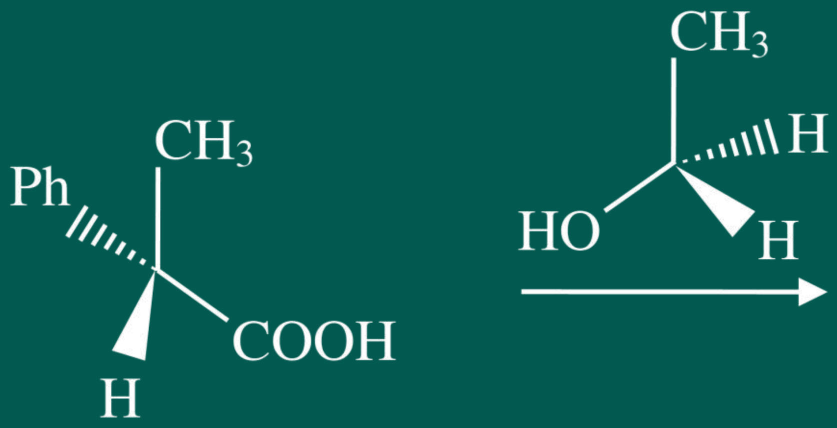
Note :

1. Physical properties like B.P., M.P. solubility, dissociation constant refractive index for enantiomers is same.
2. Enantiomeric mixture can't be separated by fractional distillation method.
3. Enantiomer reacts with same rate whenever treated with optically inactive species.

(a)



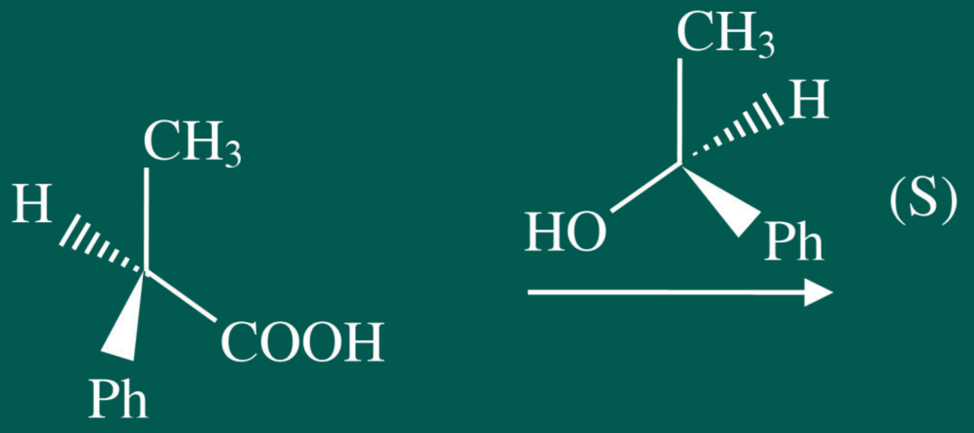
(b)



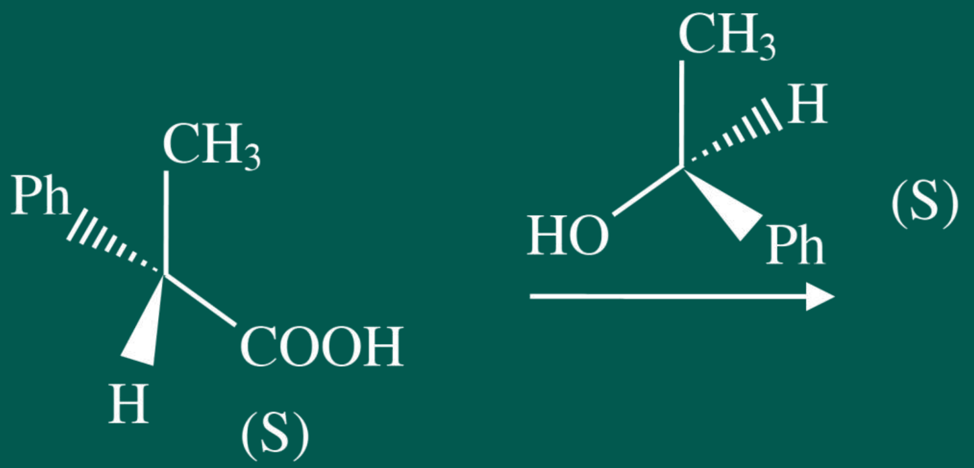
$$\boxed{r_a = r_b}$$

4. Enantiomer reacts with different rate whenever treated with optically active species.

(a')



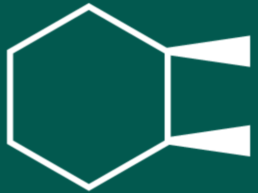
(b')

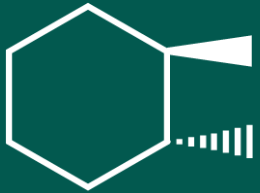


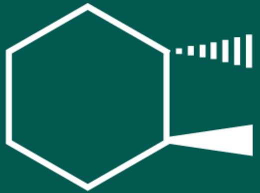
Diastereomer

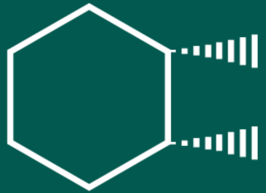
- Compound which are stereo isomer of each other either geometrical isomer on optical isomer.
- Non-mirror image of each other.
- Geometrical isomer are diastereomer.
- Physical properties of diastereomer is different.
- Diastereomeric mixture can be separated by using fractional distillation.

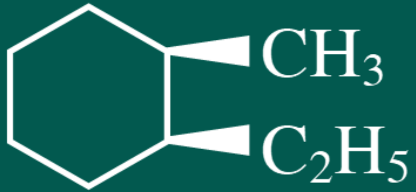
Examples :

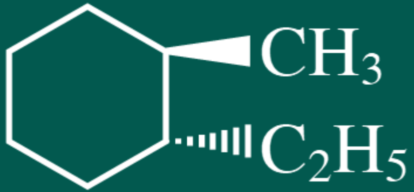


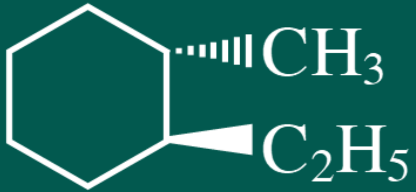


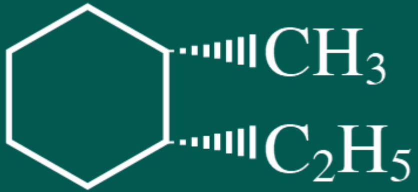


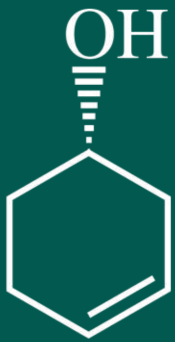




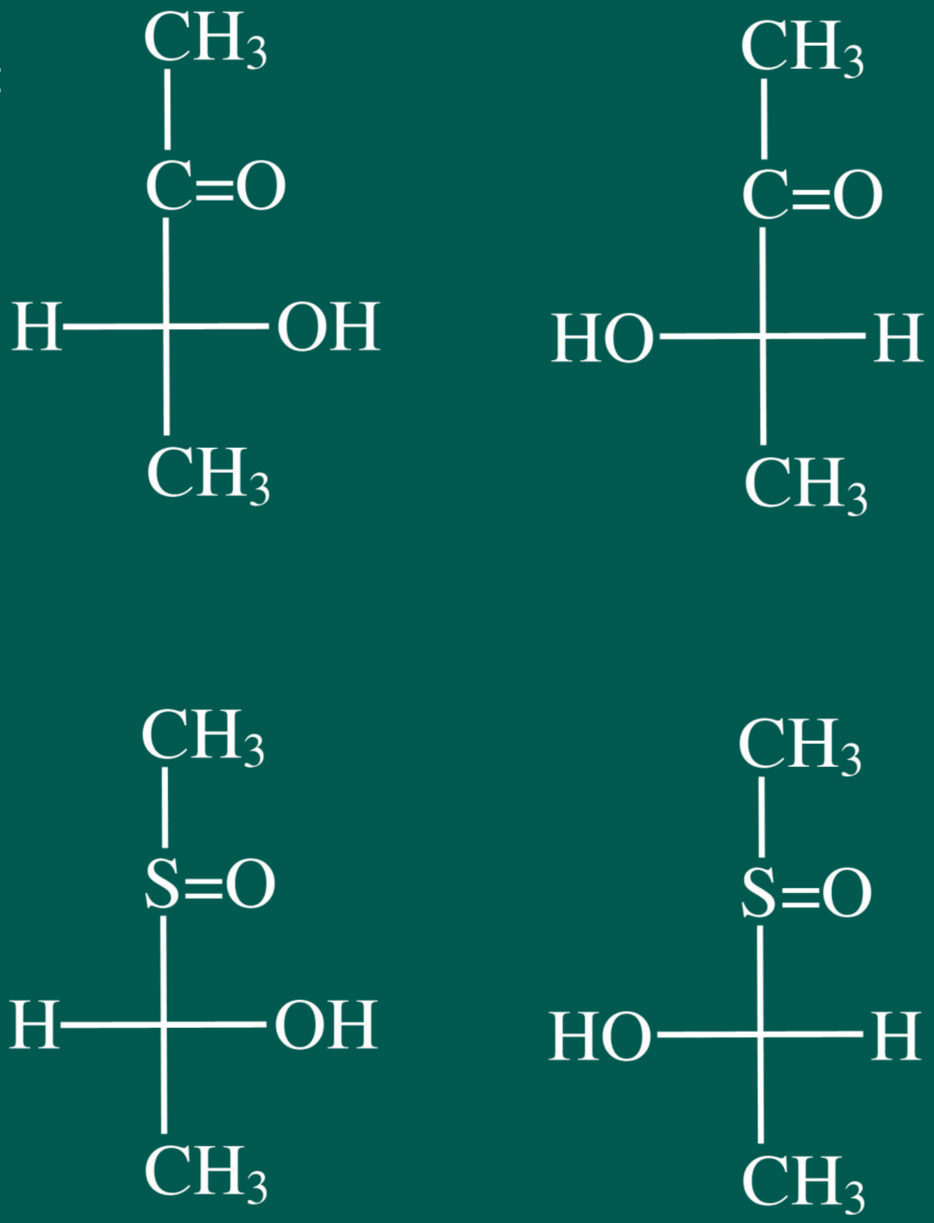




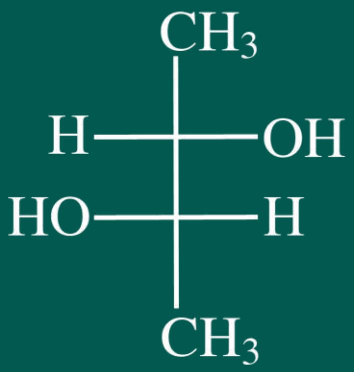


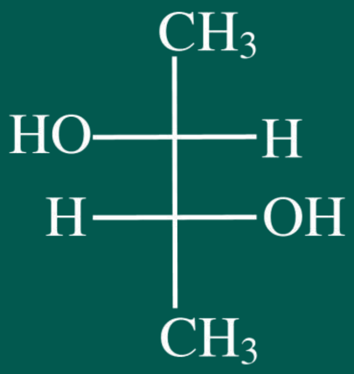


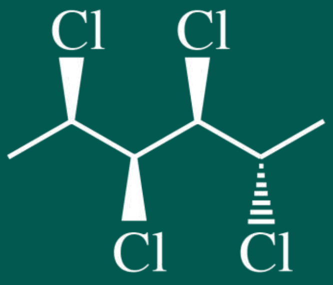
Examples :

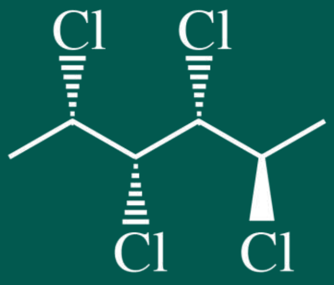


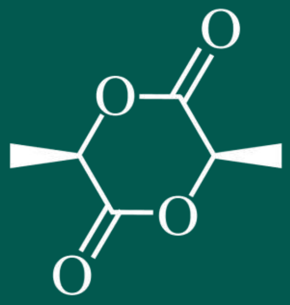
Examples :

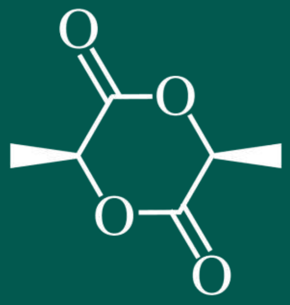




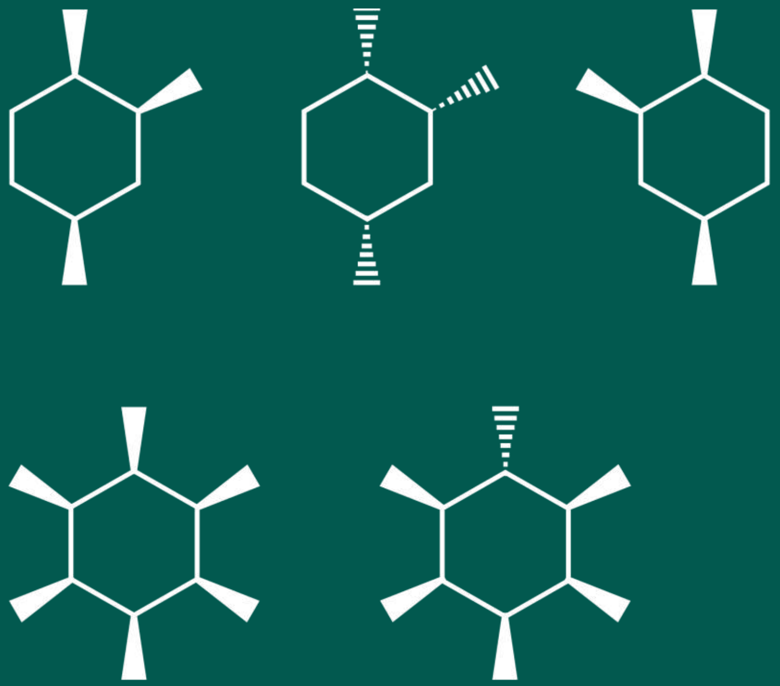


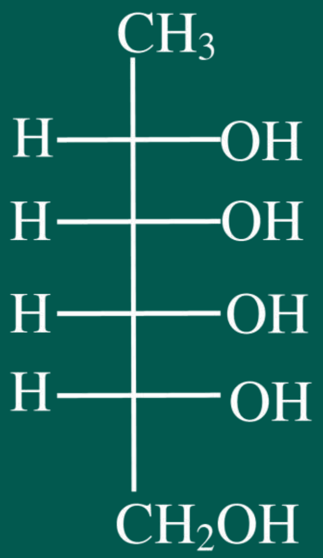


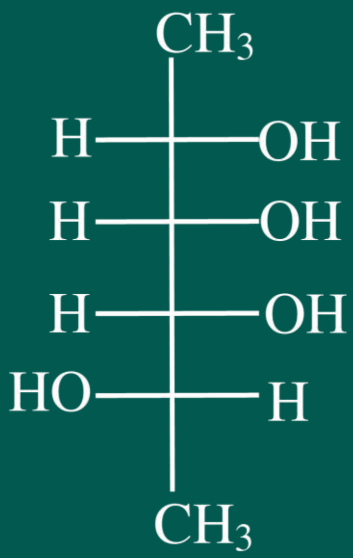




Examples :

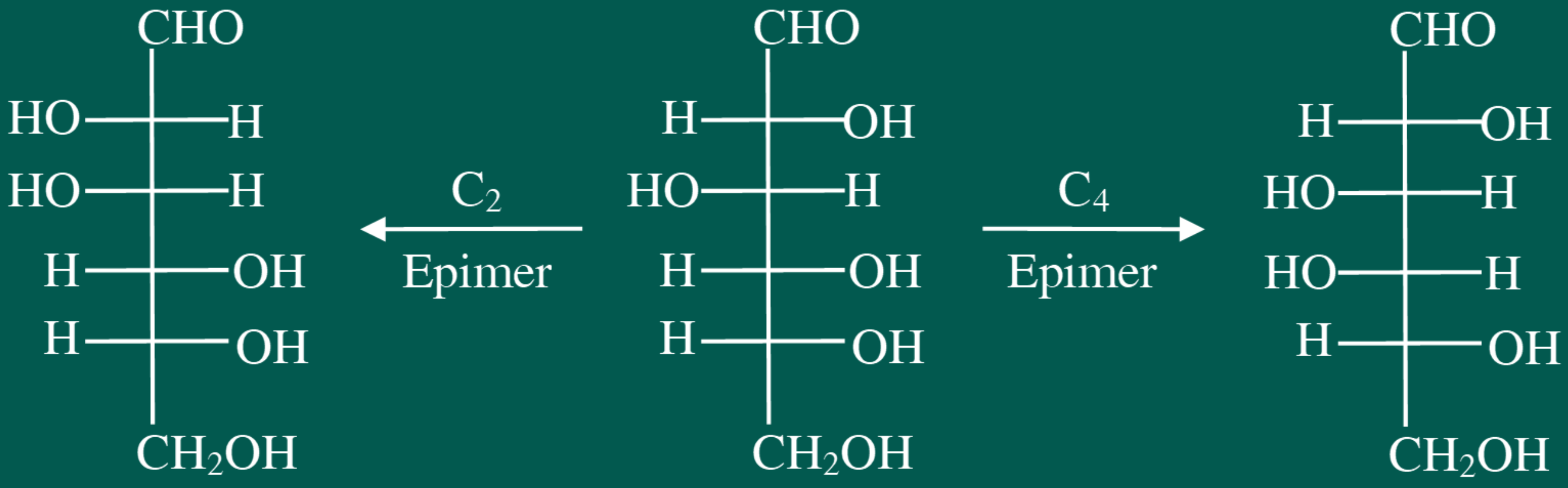






Epimer :

Diastereomer having difference only at single site (chiral centre) are known as epimer.



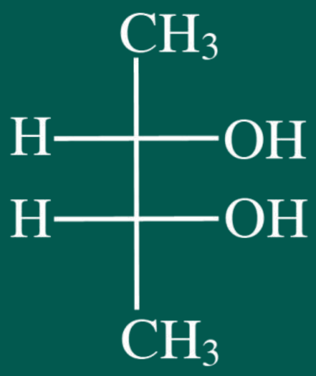
(I) D-Mannose

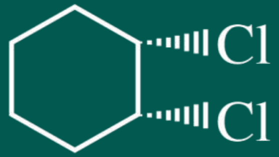
(II) D-Glucose

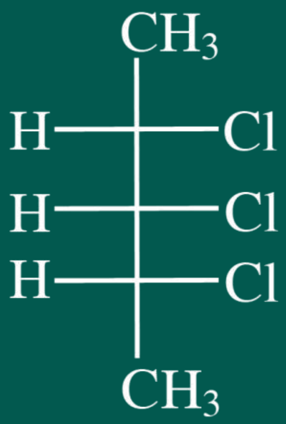
(III) D-Galactose

Meso Compound

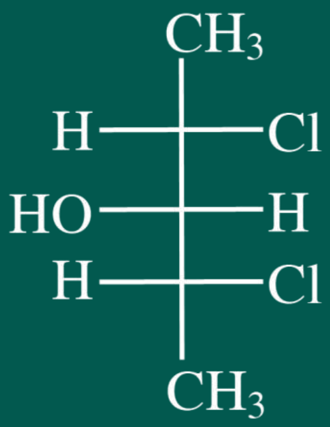
Examples :

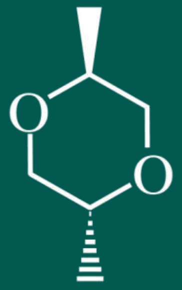


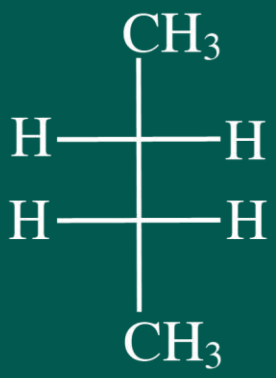


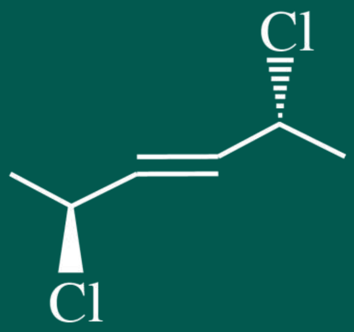


Examples :









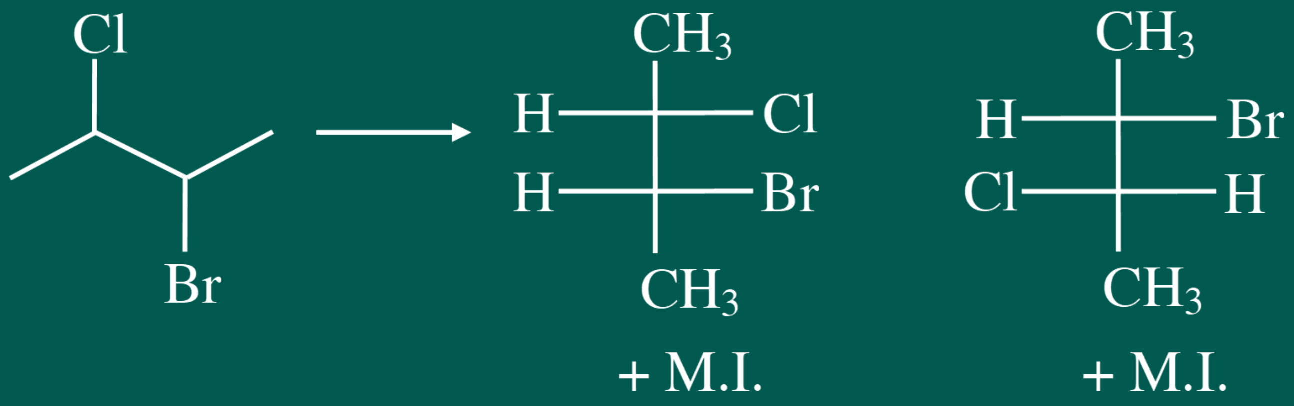
Note :

Meso compound are optically inactive due to internal compensation of angle of rotation.

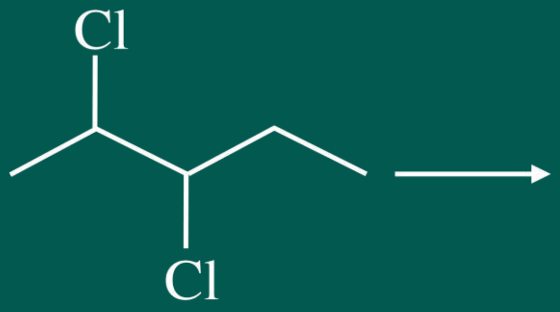
Calculation of Stereoisomer

1.

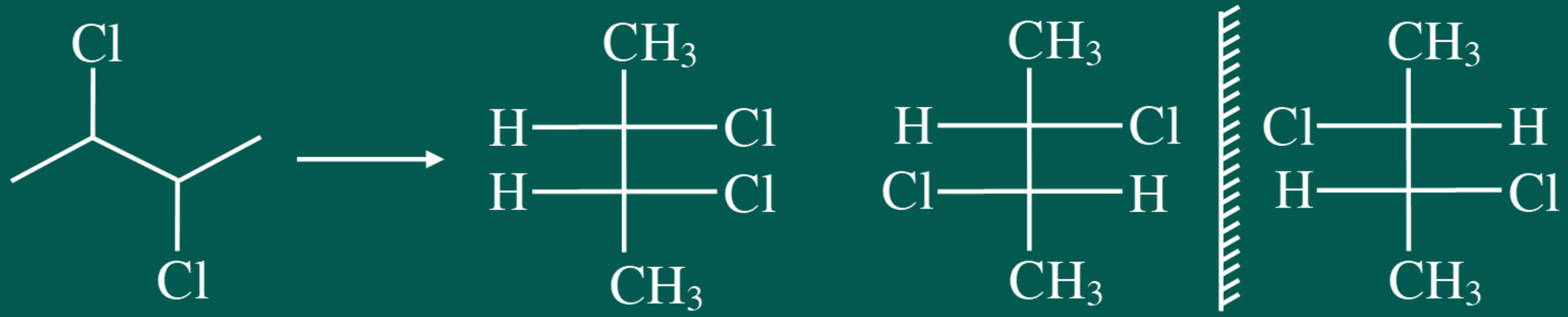
2.



3.



4.



Meso

5.

6.

$$CH_3-\overset{\overset{Cl}{|}}{CH}-CH=CH-\overset{\overset{Cl}{|}}{CH}-CH_3$$

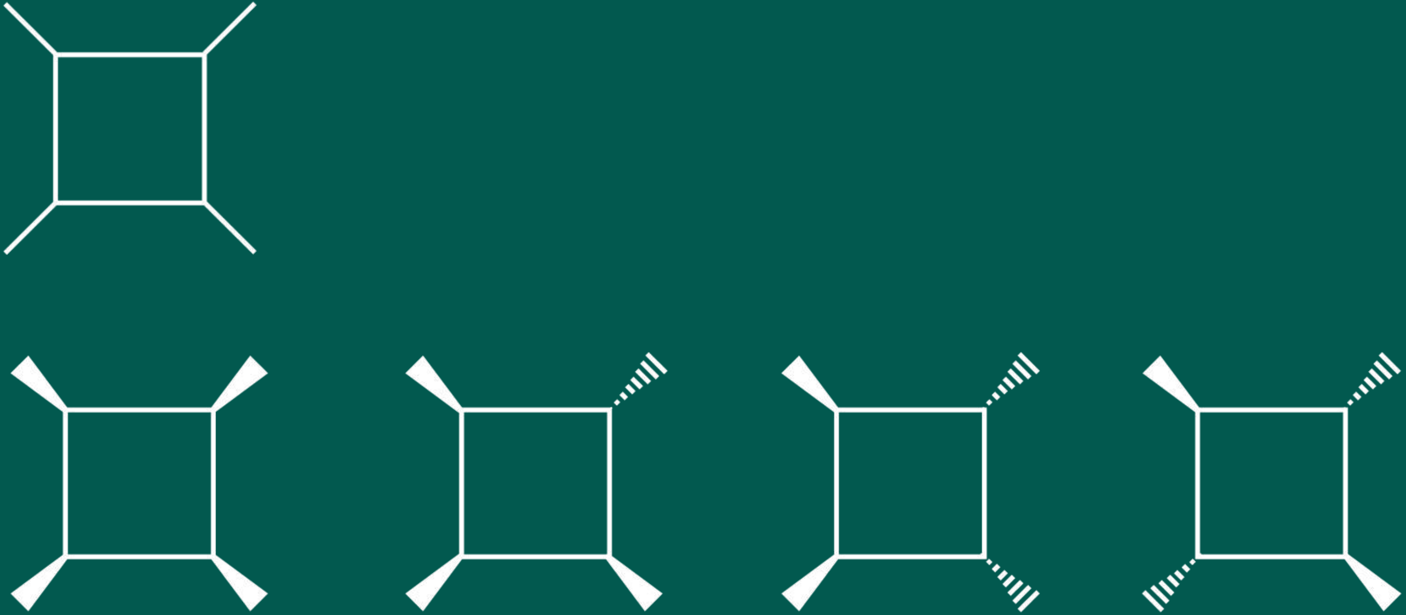
7.

$$CH_3{-}CH{=}CH{-}\overset{\overset{\displaystyle Cl}{|}}{CH}{-}CH{=}CH{-}CH_3$$

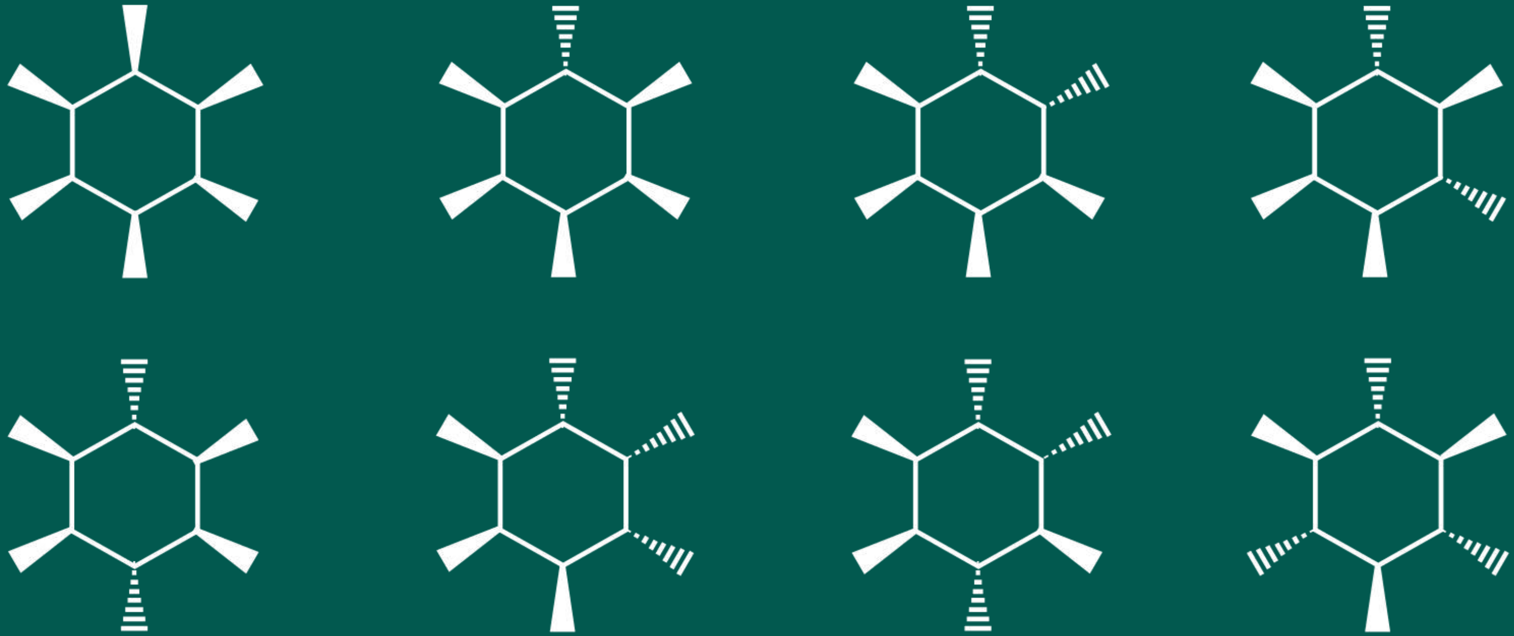
8.

10.

11.

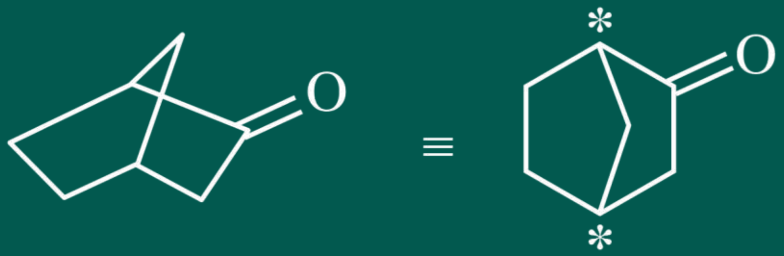


14.

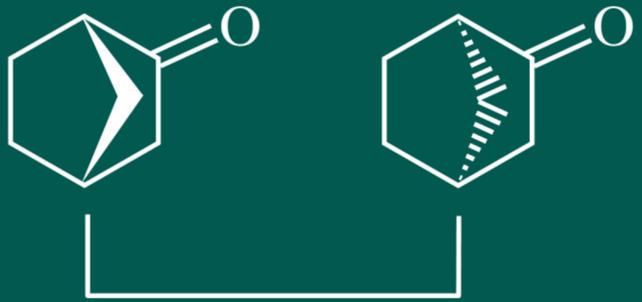


16.

17.



C.C=2

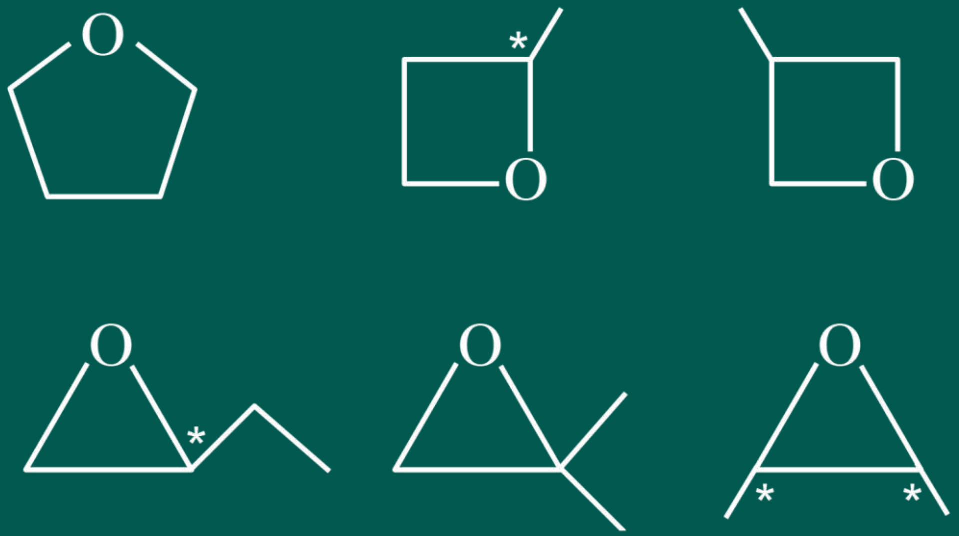


Enantiomer

Question :

Total number of isomers considering both structural and stereoisomers, of cyclic ethers with the molecular formula C_4H_8O is- **[IIT-JEE 2019]**

Solution :



Ans. **10**

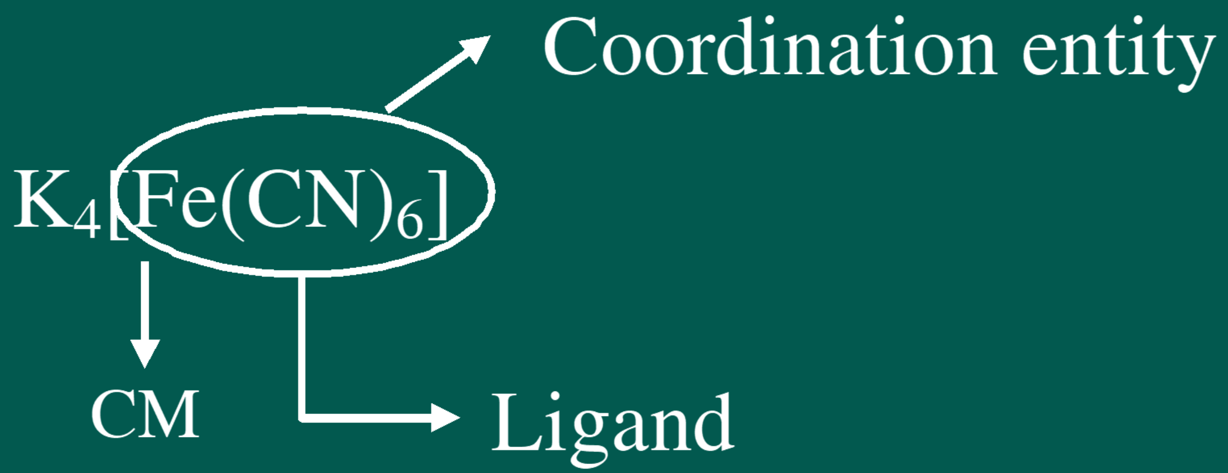
COORDINATION COMPOUNDS

Frequently Asked Concepts in JEE Main & JEE Advanced :

- IUPAC Nomenclature
- Hybridisation, spin state & magnetic behaviour of Coordination compounds
- Colour of Coordination compounds (d-d transition)
- Isomerism in Coordination compounds

Coordination compound :

Potassium ferrocyanide



Coordination entity

$K_4[Fe(CN)_6]$

CM

Ligand

CM acts as Lewis acid and it is usually d-block metal cation.

IUPAC nomenclature of coordination compounds

- Name of cation followed by name of anion
- **Name of coordination entity :**

Number of ligand in prefix (di, tri etc.)

Name of ligands in alphabetical order name of CM (oxidation number of CM in Roman)

Example :

Complex Compounds	**IUPAC Name**
(i) $[Co\ (NH_3)_6\ ]\ Cl_3$	Hexamminecobalt(III) chloride
(Cationic complex)	
(ii) $K_4[Fe(CN)_6\ ]$	Potassium hexacyanoferrate(II)
(Anionic complex)	

(iii) $[Pt(NH_3)_2Cl_4]$	Diamminetetrachloridoplatinum(IV)
(iv) $[Co(NO_2)_6]^{3-}$	Hexanitrito-N-cobaltate(III) ion
(v) $[Fe(en)_3]Cl_3$	Tris(ethylenediamine)iron(III) chloride
(vi) $[Ni(Gly)_2]$	Bis(glycinato)nickel(II)

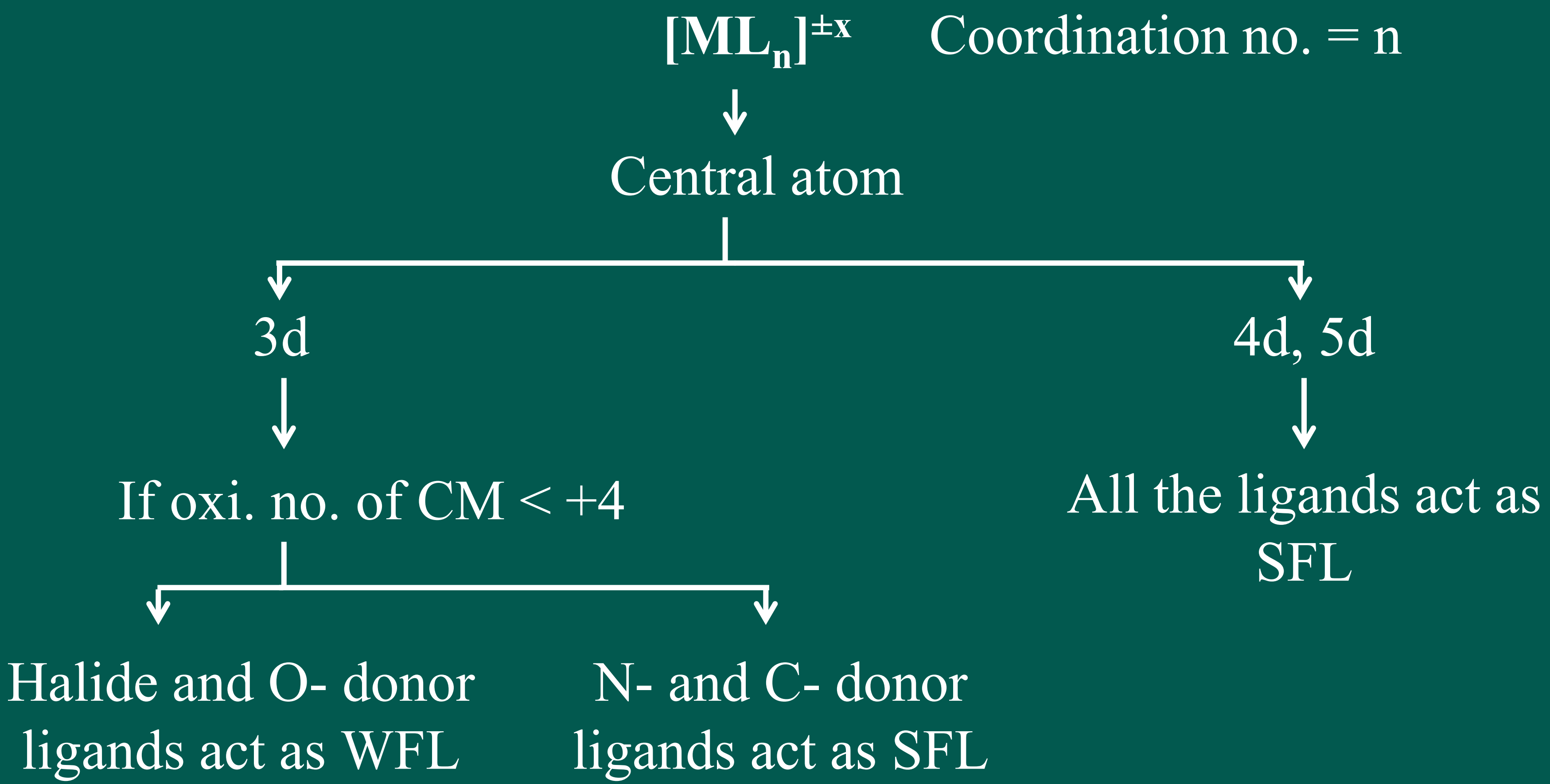
Steps to predict hybridisation, spin state & magnetic behaviour of given coordination compound

- In general, ligands can be arranged in a series in the orders of increasing field strength as given below :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O$
$< NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

*Halide donors < O donors < N donors < C donors

Such a series is termed as **spectrochemical** series.



$[ML_n]^{\pm x}$ Coordination no. = n

Central atom

3d

If oxi. no. of CM < +4

Halide and O- donor ligands act as WFL

N- and C- donor ligands act as SFL

4d, 5d

All the ligands act as SFL

If oxi. no. of CM ≥ +4
All the ligands act as SFL

$[ML_6]^{\pm x}$ Coordination no. = 6

Calculate oxidation no. of CM

↓

Write electronic configuration of CM in given oxi. no. (d^x)

↓

- d^0, d^1, d^2, d^3 → No extra pairing of electrons occur → d^2sp^3 (inner orbital complex)
- d^8, d^9, d^{10} → No extra pairing of electrons occur → sp^3d^2 (outer orbital complex)

- d^4, d^5, d^6, d^7
  - With WFL → No extra pairing of electrons occur
    → sp^3d^2 (outer orbital & high spin complex)
  - With SFL → Extra pairing of electrons occur
    → d^2sp^3 (inner orbital & low spin complex)

$[ML_4]^{\pm x}$ Coordination no. = 4

d^6, d^7, d^8 with SFL

↓

Square planar complex

dsp^2

Inner orbital & low spin complex

- d^{10} with any ligand

  ↓

  Tetrahedral complex

  sp^3

  Outer orbital complex

- $3d^5$ to $3d^9$ with WFL

  ↓

  Tetrahedral complex

  sp^3

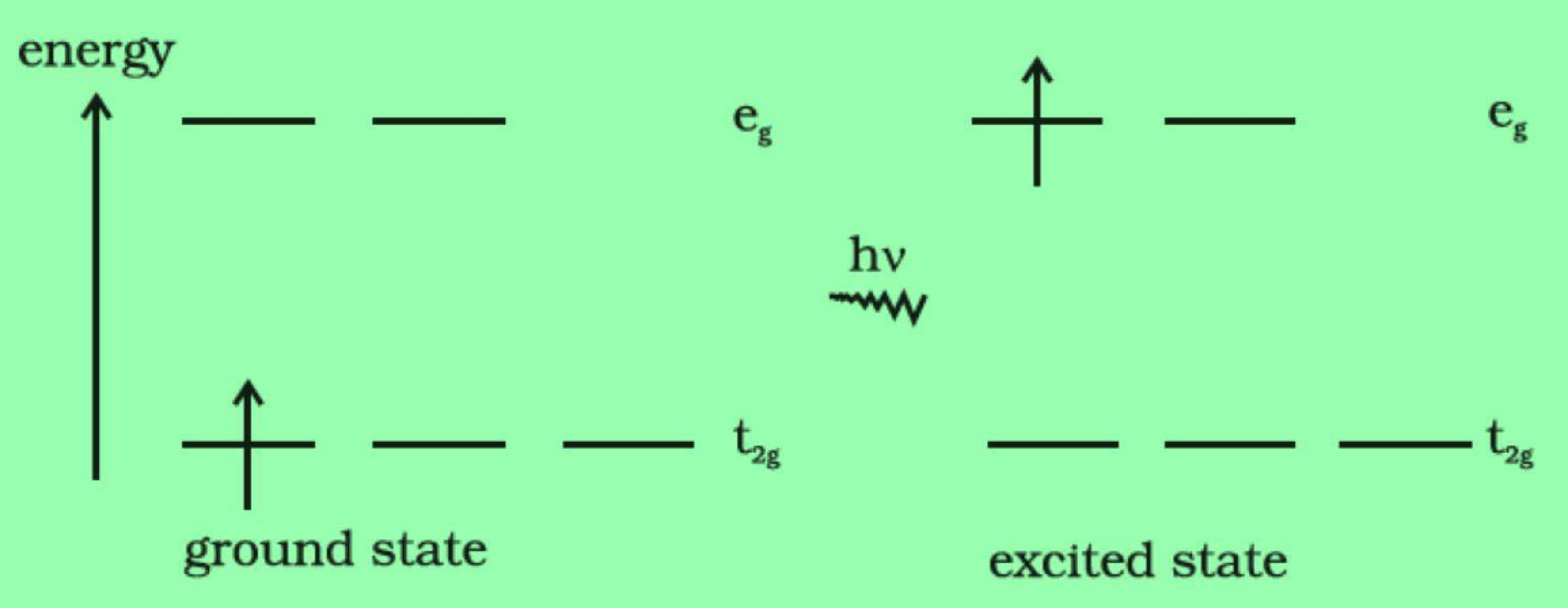
  Outer orbital complex

Example :

Complex	**Oxi.no.**	**d^x**	**SFL/WFL**	**Hybridisation**	**Magnetic behaviour**
$[CoF_6]^{3-}$	+3	$3d^6$	WFL	sp^3d^2	Paramagnetic
$[Mn(CN)_6]^{4-}$	+2	$3d^5$	SFL	d^2sp^3	Paramagnetic
$[Mn(H_2O)_6]^{2+}$	+2	$3d^5$	WFL	sp^3d^2	Paramagnetic
$[NiCl_4]^{2-}$	+2	$3d^8$	WFL	sp^3	Paramagnetic
$[Ni(CN)_4]^{2-}$	+2	$3d^8$	SFL	dsp^2	Diamagnetic
$[PtCl_4]^{2-}$	+2	$5d^8$	SFL	dsp^2	Diamagnetic
$[Zn(CN)_4]^{2-}$	+2	$3d^{10}$	SFL	sp^3	Diamagnetic
$[NiF_6]^{2-}$	+4	$3d^6$	SFL	d^2sp^3	Diamagnetic

Colour in coordination compounds :

- According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. d (t_{2g}) → d (e_g) transition



Q. Simplified absorption spectra of three complexes ((i), (ii) and (iii)) of M^{n+} ion are provided below; their λ_{max} values are marked as A, B and C respectively. The correct match between the complexes and their λ_{max} values is:

[JEE(Main) 2020 Online (Sept.)]

(i) $[M(NCS)_6]^{(-6+n)}$

(ii) $[MF_6]^{(-6+n)}$

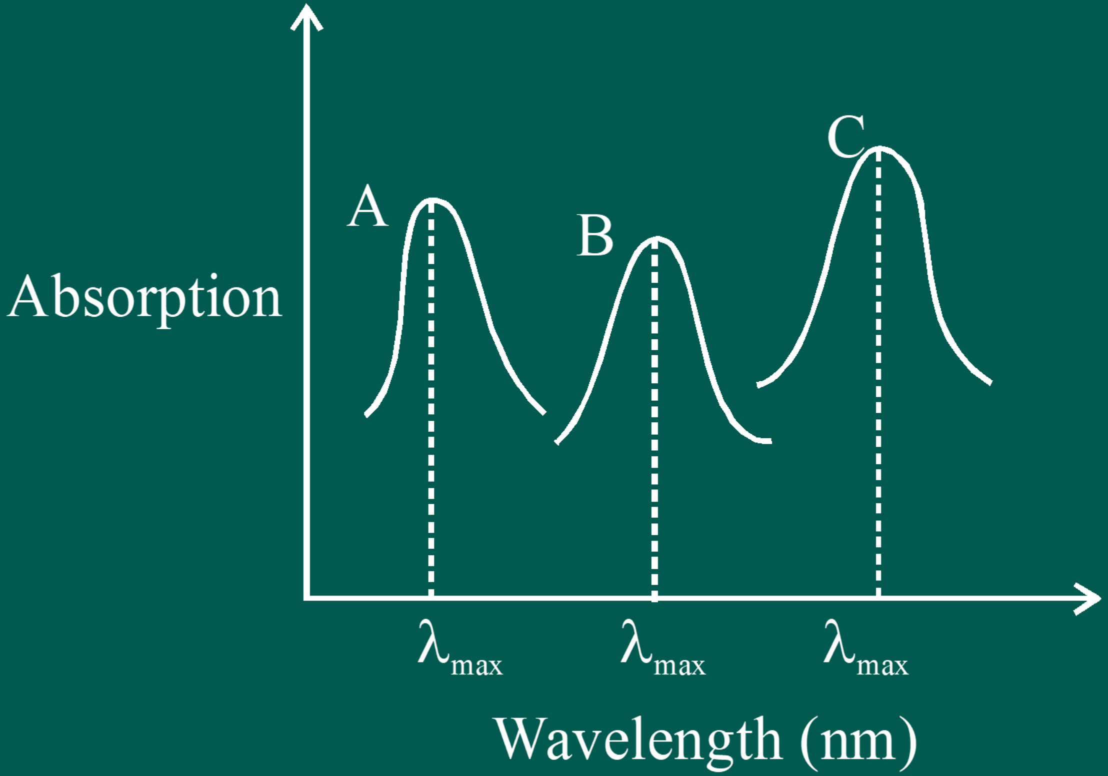
(iii) $[M(NH_3)_6]^{n+}$

(1) A-(ii), B-(i), C-(iii)

(2) A-(iii), B-(i), C-(ii)

(3) A-(ii), B-(iii), C-(i)

(4) A-(i), B-(ii), C-(iii)



Sol. Strength of ligand $F^- < NCS^- < NH_3$

$$\underset{\text{(ii)}}{[MF_6]^{(-6+n)}} \quad \underset{\text{(i)}}{[M(NCS)_6]^{(-6+n)}} \quad \underset{\text{(iii)}}{[M(NH_3)_6]^{n+}}$$

$$\xrightarrow{\hspace{20em}} \Delta_O \uparrow$$

$$\xrightarrow{\hspace{20em}} \lambda_{max} \downarrow$$

As given in graph : A < B < C (λ_{max})

∴ Correct matching is A-(iii), B-(i), C-(ii)

Ans. (2)

- Complex $Ti(H_2O)_6^{3+}$ absorbs yellow green colour & appeared violet

🟩 🟪

Note : No d-d transition in absence of ligands

$$CuSO_4.5H_2O \text{ (blue)} \xrightarrow{\Delta} CuSO_4 \text{ (white)}$$

🟦 ⬜

$$[Ti(H_2O)_6]Cl_3 \text{ (violet)} \xrightarrow{\Delta} TiCl_3 \text{ (white)}$$

🟪 ⬜

ISOMERISM

Two types

- Structural isomerism → different bonding
- Stereoisomerism → identical bonding but different orientation of groups/atoms in space

(1) Structural isomerism :

(A) Ionisation isomerism :

$[Co(NH_3)_5SO_4]NO_3$ and $[Co(NH_3)_5NO_3]SO_4$

$[Co(NH_3)_4BrCl]Cl$ and $[Co(NH_3)_4Cl_2]Br$.

(B) Linkage isomerism :

Due to the presence of ambidentate ligands

For example :

$[Co(ONO)(NH_3)_5]Cl_2$ & $[Co(NO_2)(NH_3)_5]Cl_2$

$[Pt(NH_3)_2(NO_2)_2]$, $[Pt(NH_3)_2(ONO)_2]$ & $[Pt(NH_3)_2(NO_2)(ONO)]$

(C) Coordination isomerism :

Examples are :

(i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(ii) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

Stereoisomerism :

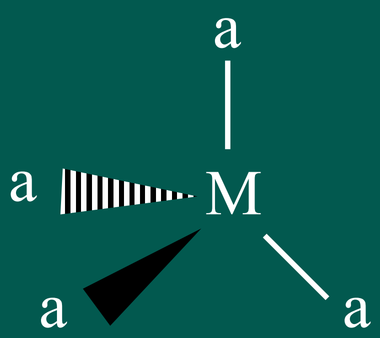
Two types
- Geometrical isomerism → Diastereoisomers
- Optical isomerism → Enantiomers

a, b, c, d, e, f → Symbols of monodentate ligands (Cl$^-$, CN$^-$, NH$_3$, H$_2$O etc.)

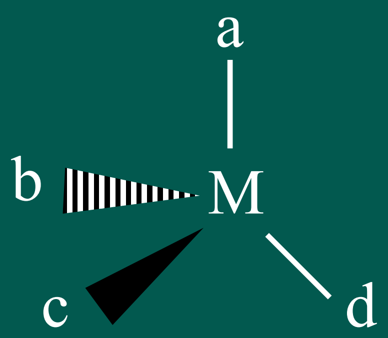
(AA), (BB) → Symbols of symmetrical didentate ligands (en, OX^{2-} etc.)

(A) Tetrahedral Complex (Coordination Number = Four) :

The tetrahedral compounds cannot show geometrical isomerism



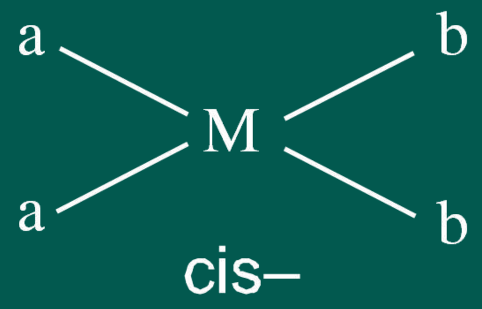
Optically inactive

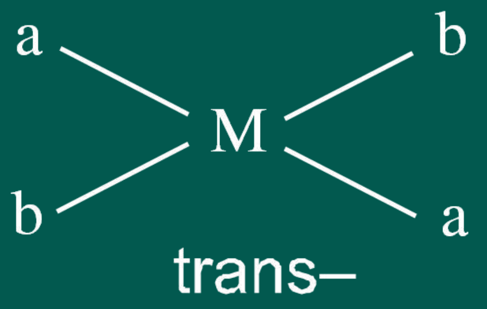


Optically active

(B) Square Planar Complex (Coordination Number = Four) :

In a square planar complex of formula $[Ma_2b_2]$



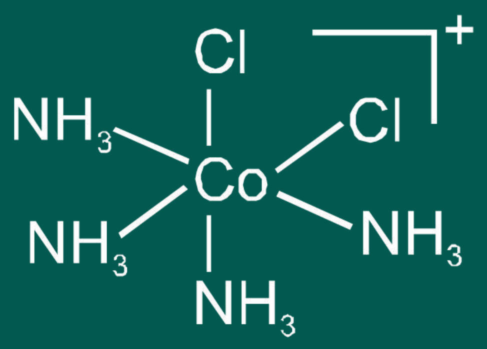


Example : $[Pt(NH_3)_2Cl_2]$, $[Pd(NH_3)_2ClBr]$

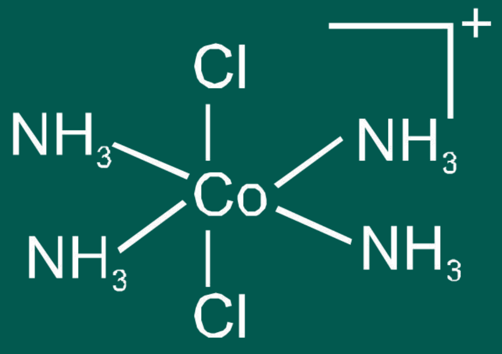
(C) Octahedral complex (Coordination Number = Six) :

(i) Ma_2b_4 – 2

Example : Geometrical isomers $[Co(NH_3)_4Cl_2]^+$



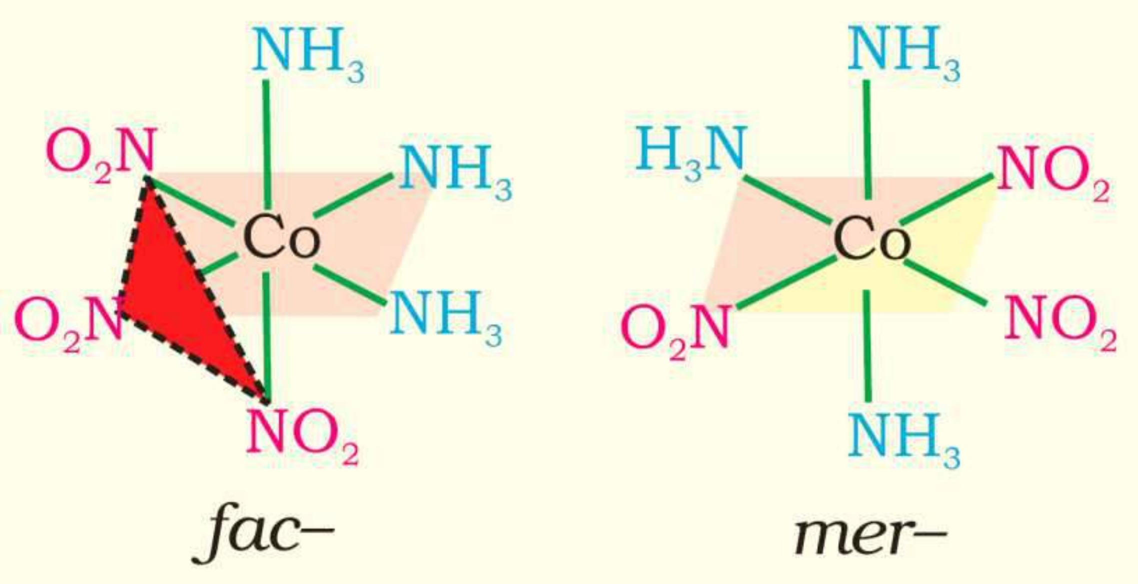
cis–



trans–

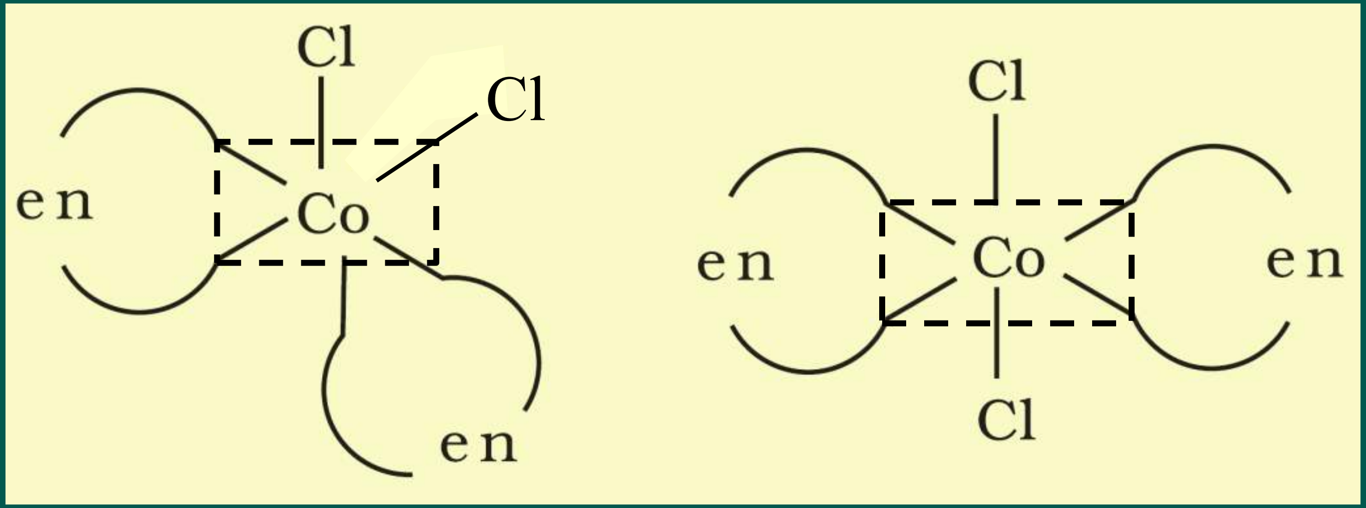
(ii) Ma_3b_3 – 2

Example : Geometrical isomers $[Co(NH_3)_3(NO_2)_3]$



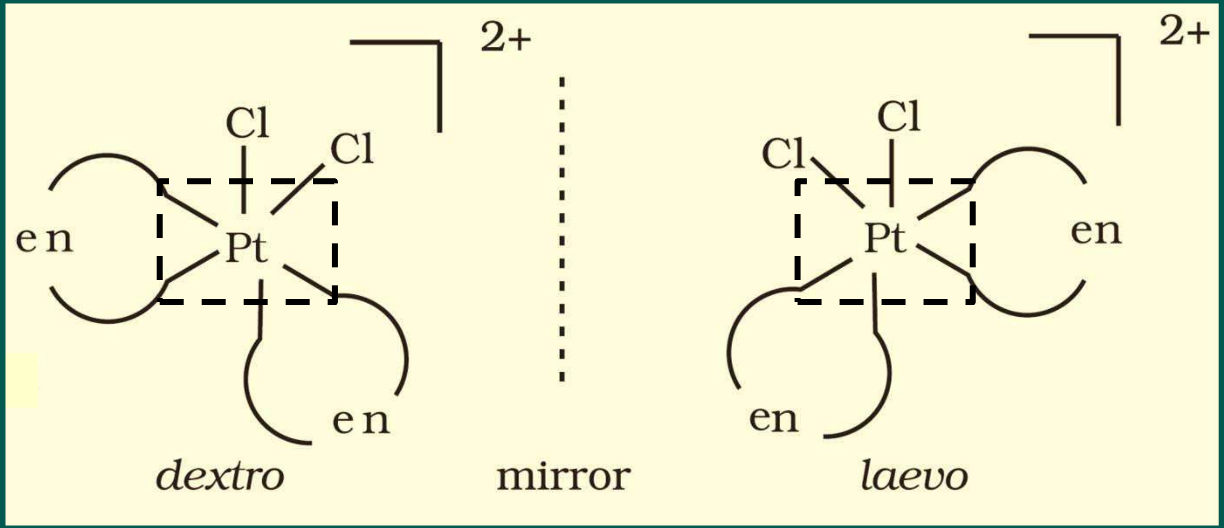
(iii) $M(AA)_2a_2$ – 2

Example : Geometrical isomers $[CoCl_2(en)_2]$

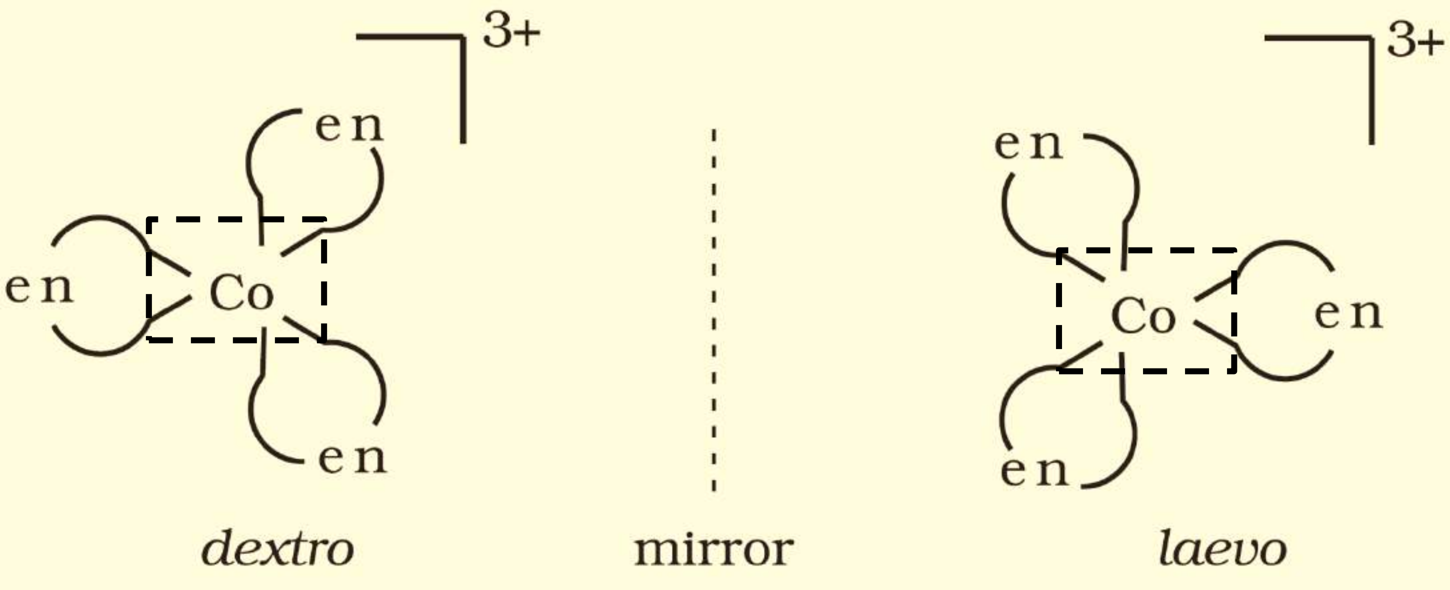


Cis- Trans-

Example : Optical isomers cis- $[PtCl_2(en)_2]^{2+}$



Example : Optical isomers of $[Co(en)_3]^{3+}$



dextro mirror *laevo*

Q. The stepwise formation of $[Cu(NH_3)_4]^{2+}$ is given below

$$Cu^{2+} + NH_3 \xrightleftharpoons{K_1} [Cu(NH_3)]^{2+}$$

$$[Cu(NH_3)]^{2+} + NH_3 \xrightleftharpoons{K_2} [Cu(NH_3)_2]^{2+}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \xrightleftharpoons{K_3} [Cu(NH_3)_3]^{2+}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \xrightleftharpoons{K_4} [Cu(NH_3)_4]^{2+}$$

The value of stability constants K_1, K_2, K_3 and K_4 are 10^4, 1.58×10^3, 5×10^2 and 10^2 respectively. The overall equilibrium constants for dissociation of $[Cu(NH_3)_4]^{2+}$ is $x \times 10^{-12}$. The value of x is ________.

(Rounded off to the nearest integer) **[JEE(Main) 2021 Online (Feb.)]**

Sol. $[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$

$$K = \frac{1}{K_1K_2K_3K_4} = \frac{1}{10^4 \times 1.58 \times 10^3 \times 5 \times 10^2 \times 10^2}$$

$$= 1.26 \times 10^{-12} = 1.26$$

Question :

The CORRECT statement on the isomerism associated with the following complex ions, **[JEE(Main) 2015, Online]**

(a) $[Ni(H_2O)_5NH_3]^{2+}$

(b) $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and

(c) $[Ni(H_2O)_3(NH_3)_3]^{2+}$ is :

(1) (a) and (b) show geometrical and optical isomerism

(2) (b) and (c) show geometrical and optical isomerism

(3) (a) and (b) show only geometrical Isomerism

(4) (b) and (c) show only geometrical Isomerism

Ans. **(4)**

Question :

Which one of the following complexes shows optical isomerism ?

(en = ethylenediamine) **[JEE(Main) 2016, 4/120]**

(1) cis$[Co(en)_2Cl_2]Cl$

(2) trans$[Co(en)_2Cl_2]Cl$

(3) $[Co(NH_3)_4Cl_2]Cl$

(4) $[Co(NH_3)_3Cl_3]$

Ans. **(1)**

Question :

Identify the CORRECT trend given below : **[JEE(Main) 2016, Online]**

(Atomic No.= Ti : 22, Cr : 24 and Mo : 42)

(1) Δ_O of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_O of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$

(2) Δ_O of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_O of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$

(3) Δ_O of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_O of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$

(4) Δ_O of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_O of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$

Ans. (2)

Question :

The correct order of spin-only magnetic moments among the following is :

(Atomic number : Mn = 25, Co = 27, Ni= 28, Zn = 30)

[JEE(Main) 2018, Online]

(1) $[ZnCl_4]^{2-} > [NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

(2) $[CoCl_4]^{2-} > [MnCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$

(3) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$

(4) $[NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-} > [ZnCl_4]^{2-}$

Ans. (3)

CHEMICAL BONDING

Types of Bonding

1. **Ionic bond**

   Examples : NaCl, MgO etc.

Properties :

- Good conductors of electricity in molten state and in aqueous solution but not in solid state.
- Generally soluble in polar solvents like water.

2. Covalent bond

Examples : H_2, CH_4, HCl etc.

Properties :

- Species containing covalent bonds are generally soluble in organic solvents.

COVALENT BOND

How to choose central atom while drawing a structure

- Least in number
- Capable of forming maximum number of bonds

Note : H & F can never behave as central atoms.

Examples :

CH_4

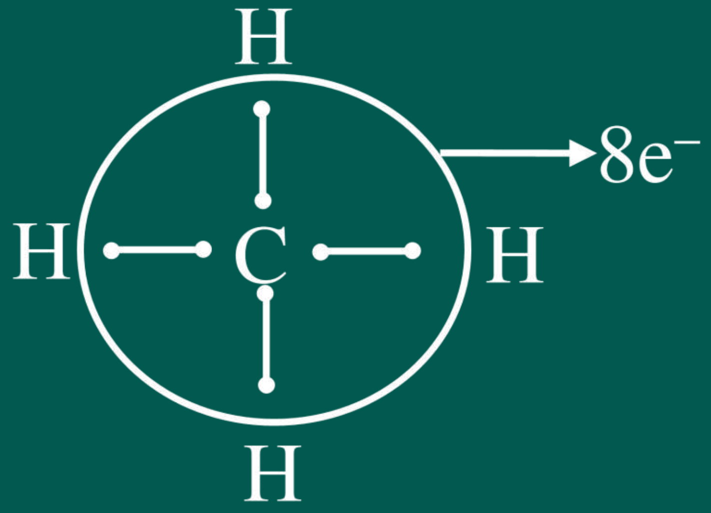
$C \Rightarrow 2s^2\ 2p^2 \Rightarrow$ 2 unpaired e^-

(G.S.)

$C^* \Rightarrow 2s^1\ 2p^3 \Rightarrow$ 4 unpaired e^-

(E.S.)

⇒ Bonding takes place in excited state



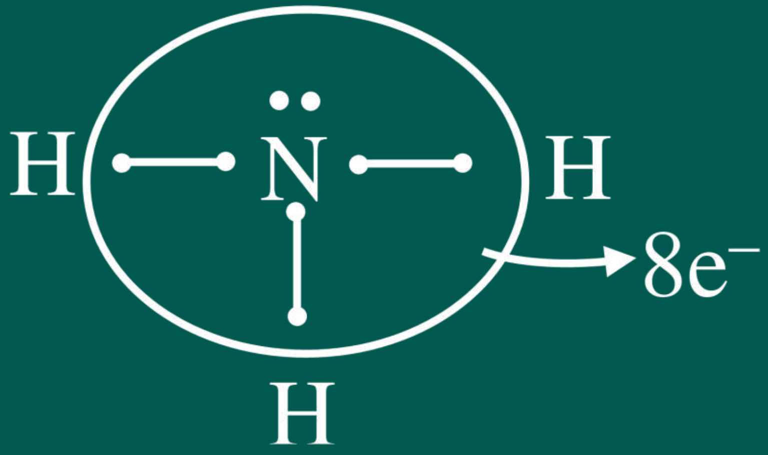
Examples :

NH_3

$N \Rightarrow 2s^2 2p^3 \Rightarrow 3$ unpaired e^-

(G.S.)

$\Rightarrow$ Bonding takes place in ground state.



Co-ordinate Bond (dative bond)

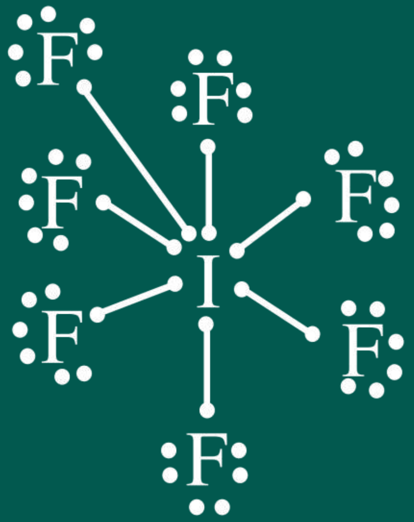
A special type of covalent bond in which shared e^- pair comes from one atom only.

Eg. O_3

Eg. CO

Eg. SO_2

$$\ddot{\underset{\cdot\cdot}{O}} = \ddot{S} = \ddot{\underset{\cdot\cdot}{O}}$$



Eg. IF_7 $I^* \Rightarrow$ $5s^1 5p^3 5d^3$

$\Rightarrow$ 7 unpaired e^-

Some more examples :

Eg. ICl_2^+

BrF_4^-

Note : $\underbrace{NCl_5,\ FCl_3,\ HFO_4,\ OF_4,\ F_3^-,\ BF_6^{3-}}_{\text{do not exist}}$

Since central atom is of 2nd period, so it does not have vacant d-orbitals. Hence octet expansion not possible.

Limitations of Octet Rule :

(1) Existence of species with incomplete octet of atoms & expanded octet of atoms.

Eg. BeF_2, $AlCl_3$

Eg. PCl_5, SF_6

(2) Existence of species containing odd e^-.

Eg. NO, NO_2, ClO_2

(3) Formation of compounds by noble gas atoms.

Eg. XeF_2, XeO_3, XeO_2F_2 etc.

(4) No idea about actual shape of molecule is obtained here.

Valence Bond Theory (VBT)

Important Points :

- Usually, 2 type of overlapping are observed :

  (1) Along inter-nuclear axis ⇒ σ-bond

  (2) Perpendicular to inter-nuclear axis ⇒ π-bond

Different Types of Overlapping

(1) s-s overlapping :

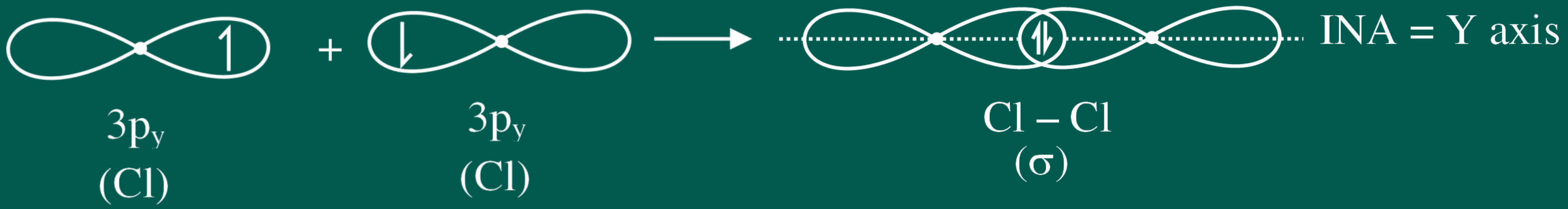
Eg. H_2

(2) s-p overlapping :

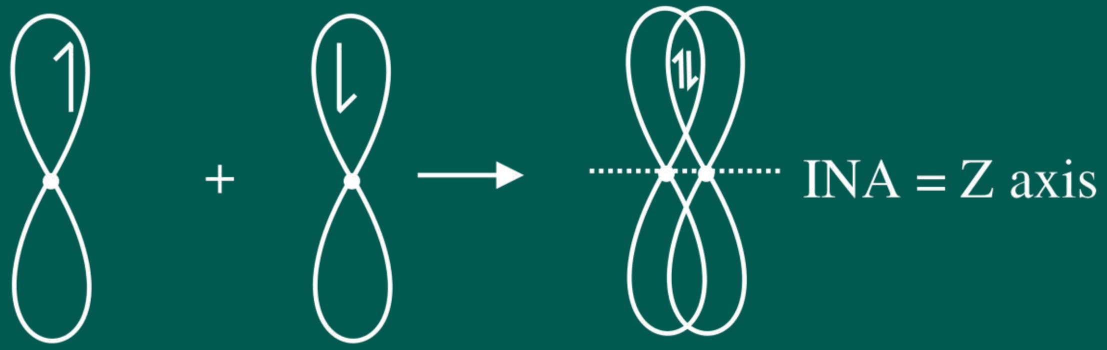
Eg. HF

(3) p-p overlapping (Head on) :

Eg. Cl_2



(4) p-p overlapping (sideways) :



$2p_x$ —— $2p_x$

or $2p_y$ —— $2p_y$

π-bond

General strength order : $\sigma > \pi$

- Greater internuclear repulsions
- Cannot exist individually

Eg. O_2 Eg. N_2

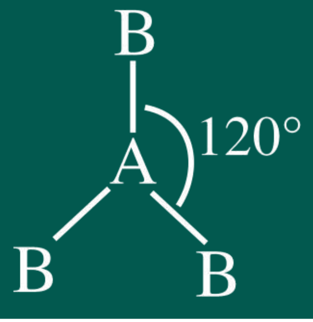
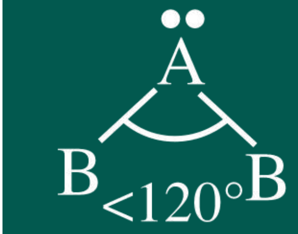
$$\mathrm{O}\overset{\sigma}{\underset{\pi}{=}}\mathrm{O} \qquad \mathrm{N}\overset{\sigma}{\underset{\pi}{\overset{\pi}{\equiv}}}\mathrm{N}$$

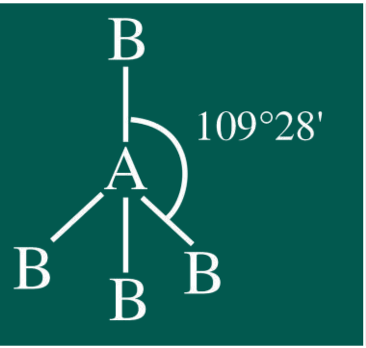
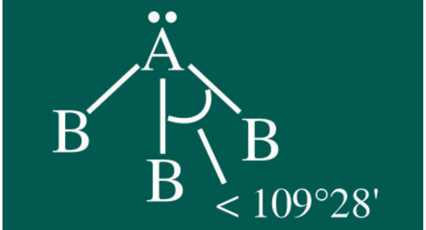
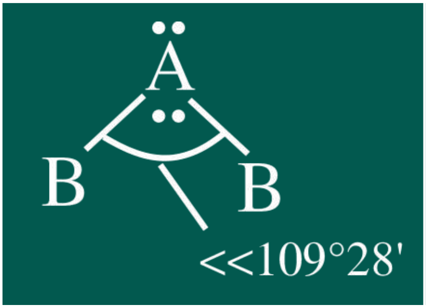
Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

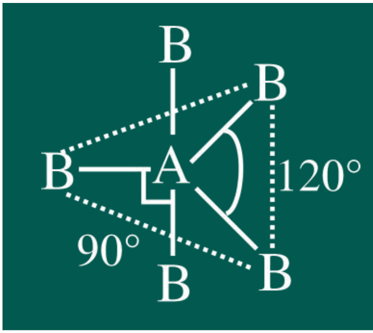
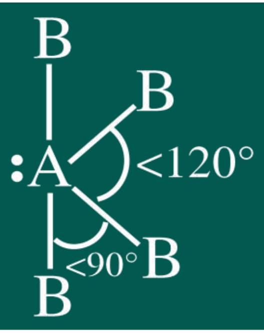
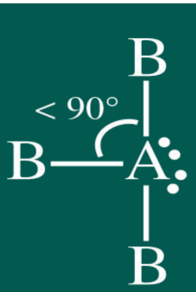
- Order of repulsion of e^- pairs :
  lp – lp > lp – bp > bp – bp

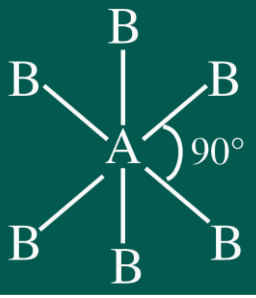
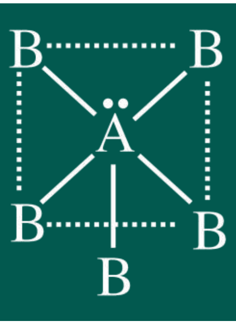
Various Possible Arrangements

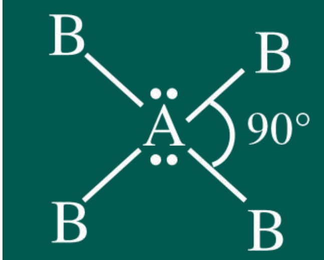
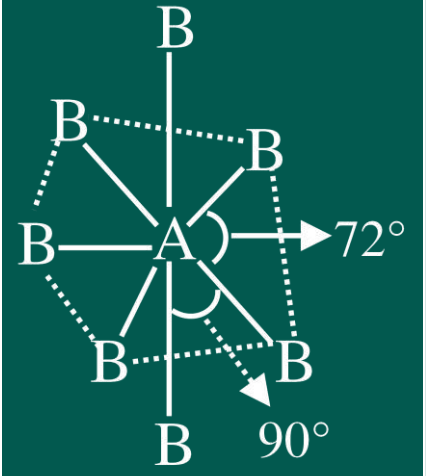
- Geometry : Arrangement of electron pairs (both ℓp & bp involved)
- Shape : Arrangement of atoms /bp (not ℓp)

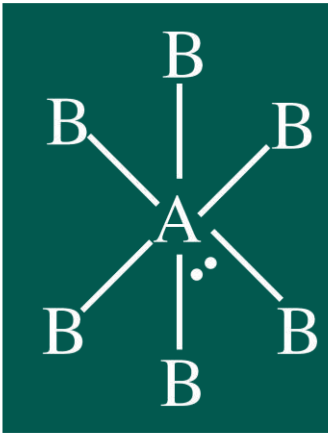
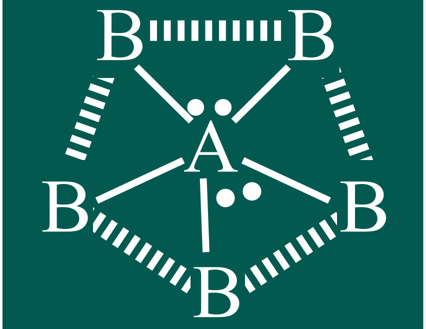
Formula Type	**Examples**	**Arrangement**	**Geometry/Shape**
AB_2	BeF_2, H–C≡N, CO_2, N_2O, N_3^-, NO_2^+		Geometry/shape : Linear
AB_3	BX_3, CO_3^{2-}, NO_3^-, SO_3		Geometry/shape : Trigonal planar
AB_2L	O_3, SO_2, NO_2^-, NOCl		Shape : Bent /V-shape/Angular

Formula Type	**Examples**	**Arrangement**	**Geometry/Shape**
AB_4	CH_4, BF_4^-, NH_4^+, PO_4^{3-}, SO_4^{2-}, ClO_4^-		Geometry/shape : Tetrahedral
AB_3L	NH_3, PX_3, XeO_3, ClO_3^-		Shape : Pyramidal
AB_2L_2	H_2O, NH_2^-, ClO_2^-		Shape : Bent /V-shape/Angular

Formula Type	**Examples**	**Arrangement**	**Geometry/Shape**
AB_5	$PCl_5(g)$, XeO_3F_2		Geometry/shape : Trigonal Bipyramidal (TBP)
AB_4L	SF_4, XeO_2F_2, $IO_2F_2^-$		Shape : See-saw/K-shape
AB_3L_2	ClF_3, XeF_3^+		Shape : T-shape

Formula Type	**Examples**	**Arrangement**	**Geometry/Shape**
AB_2L_3	I_3^-, ICl_2^-, XeF_2		Shape : Linear
AB_6	SF_6		Geometry/Shape : Octahedral
AB_5L	BrF_5, $XeOF_4$, XeF_5^+		Shape : Square pyramidal

Formula Type	**Examples**	**Arrangement**	**Geometry/Shape**
AB_4L_2	XeF_4, ICl_4^-, BrF_4^-		Shape : Square planar
AB_7	IF_7		Geometry/Shape : Pentagonal bipyramidal

Formula Type	**Examples**	**Arrangement**	**Geometry/Shape**
AB_6L	XeF_6		Shape : Distorted Octahedral or Capped Octahedral
AB_5L_2	XeF_5^-		Shape : Pentagonal planar

Hybridisation

- Steric No. of central atom = No. of atoms attached with central atom + No. of lone pairs on central atom

SN = 2 ⇒ sp hybridisation

SN = 3 ⇒ sp^2 hybridisation

SN = 4 ⇒ sp^3 hybridisation

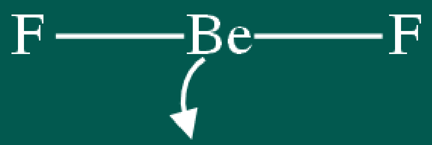
SN = 5 ⇒ sp^3d hybridisation

SN = 6 ⇒ sp^3d^2 hybridisation

SN = 7 ⇒ sp^3d^3 hybridisation

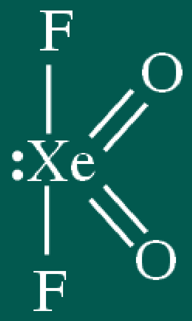
Examples

BeF_2



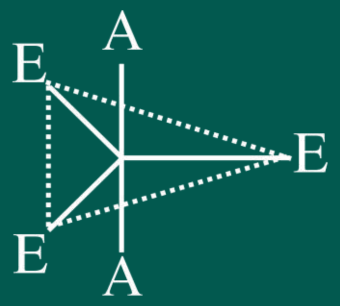
SN = 2 + 0 = 2 ⇒ sp hybridised

XeO_2F_2



SN of Xe = 4 + 1 = 5 ⇒ sp^3d hybridised

sp^{3}d Hybridisation



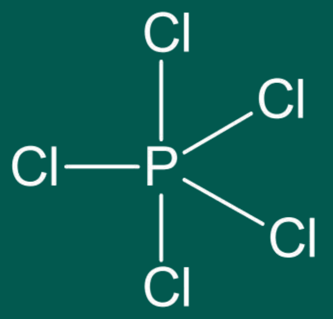
Geometry : TBP

- Axial bonds (A) are slightly longer & weaker than Equatorial bonds (E).

VSEPR → More EN atom prefers Axial position

VSEPR → Lone pair & multiple bonds prefer Equatorial position

Eg. $PCl_5(g)$



Shape / Geometry = TBP ; $A_{BL} > E_{BL}$

$PCl_5(s) \Rightarrow$ Ionic Solid ; composed of :

$\underset{\underset{sp^3}{\searrow}}{PCl_4^+}$ (Tetrahedral) & $\underset{\underset{sp^3d^2}{\searrow}}{PCl_6^-}$ (Octahedral)

sp^3d^2 Hybridisation

Geometry : Octahedral

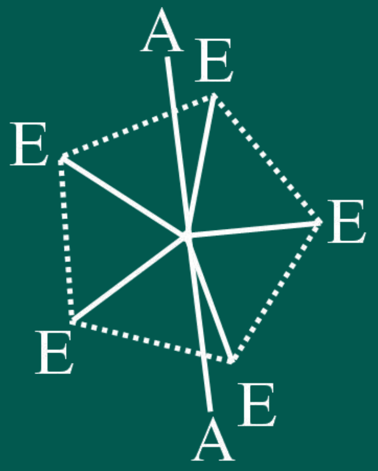
VSEPR ⇒ 2 ℓp / 1 ℓp + 1 db / 2 db prefer arrangement at 180°.

Eg. SF_6 ⇒ Geometry / Shape : Octahedral

⇒ All 6 BLs are identical

Note : $SiCl_6^{2-}$ does not exist.

sp^3d^3 Hybridisation



Geometry : Pentagonal Bipyramidal (PBP)

Bond Length Comparison

→ Depends on following factors :

(1) Size of atom ↑ $\Rightarrow$ BL ↑ (see along group)

Eg. H–F < H–Cl < H–Br < H–I

(2) ΔEN ↑ $\Rightarrow$ BL↓ (see along period)

Eg. C–C > C–N > C–O > C–F

(3) Bond order or No. of bonds ↑ $\Rightarrow$ BL ↓

Eg. $C \equiv C < C = C < C - C$

Note : In general, BE or Bond strength $\propto \frac{1}{BL}$

Bond Angle Comparison

- Depends on the following factors sequentially

(1) Hybridisation of Central Atom :

Eg.	sp	>	sp^2	>	sp^3
	(180°)		(120°)		(109°28')

(2) No. of l.p.'s on central atom ↑ $\Rightarrow$ BA↓

Eg.	CH_4	>	NH_3	>	H_2O
n_{lp}	0		1		2

(3) EN of central atom ↑ $\Rightarrow$ BA ↑

Eg. NH_3 > PH_3 > AsH_3 > SbH_3

∵ EN of N_{max} ≈93° ≈92° ≈91°

(4) Size of attached atom ↑ $\Rightarrow$ BA ↑

Eg. $PF_3 < PCl_3 < PBr_3 < PI_3$

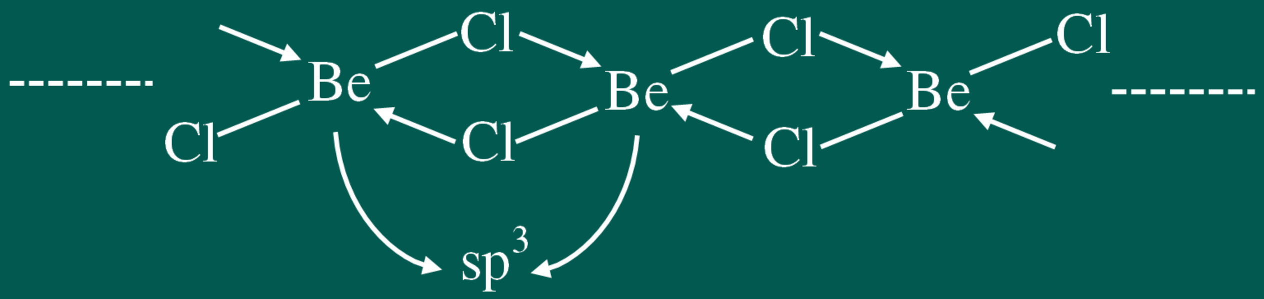
Eg. $BF_3 = BCl_3 = BBr_3 = BI_3 = AlCl_3$ (All have BA = 120°)

(No l.p. on central atom as well as identical attached atoms
$\Rightarrow$ angle adjustments not possible)

Multicentred Species

1. Compounds of Be, B & Al :

$BeCl_2(s)$

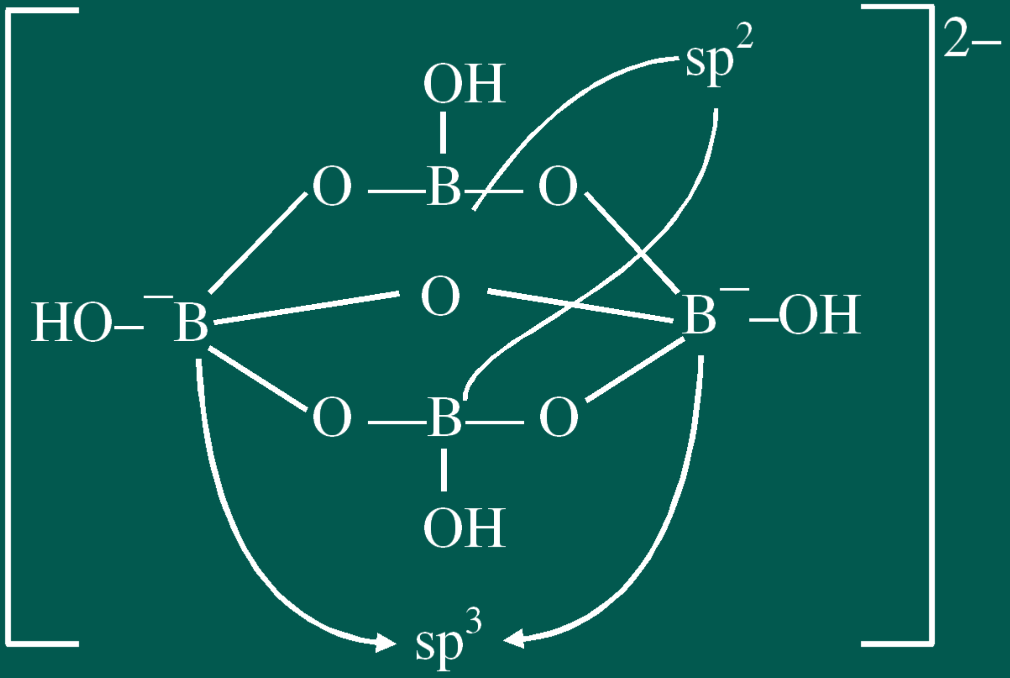


Linear polymeric structure

Eg. Borax $Na_2[B_4O_5(OH)_4].8H_2O$

- Total 5B–O–B linkages are present.

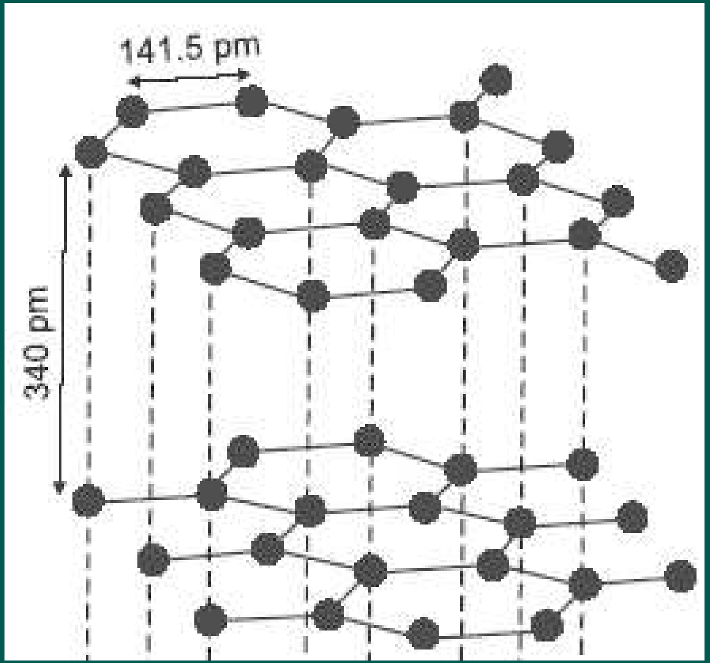
Anion of Borax :



2. Species of Carbon & Silicon

Allotropes of Carbon :

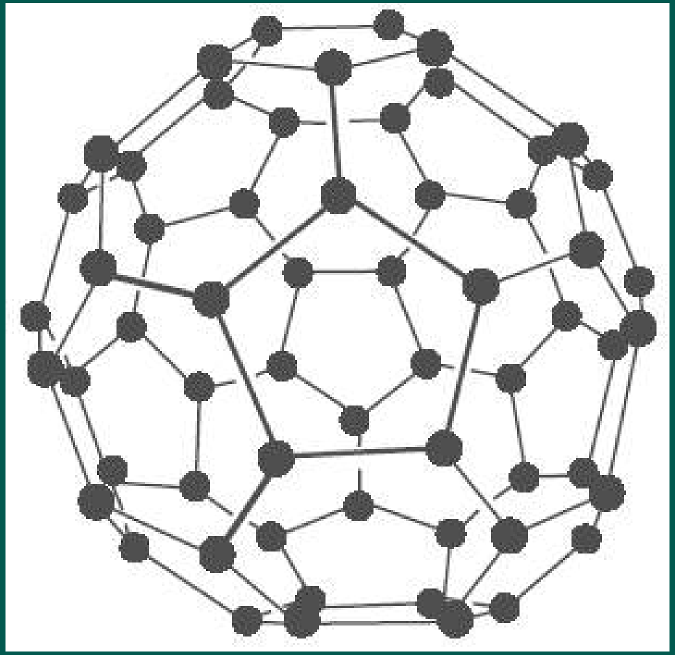
1. Graphite :



- sp^2 hybridisation & $1e^-$ left on each C is involved in π bond formation. So, graphite is diamagnetic.
- Only one type of C–C BL is observed (intermediate between C–C & C = C).
- Good conductor of electricity along layer.
- Thermodynamically, most stable allotrope of carbon

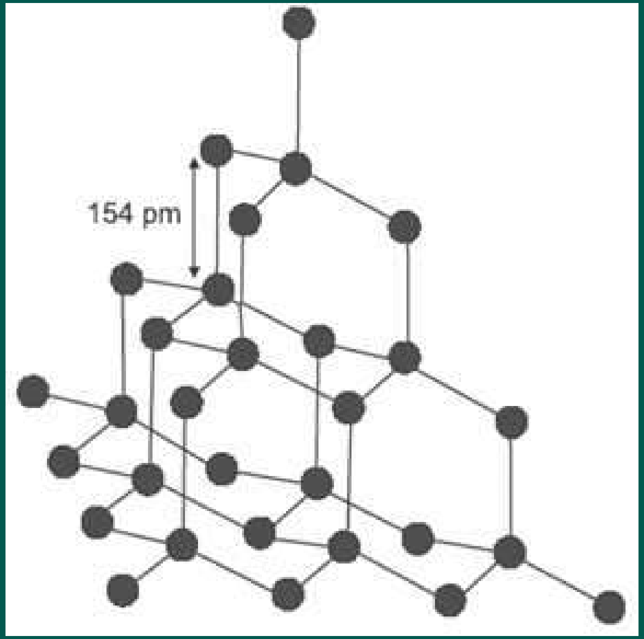
2. Fullerenes :

C_{60} (Buckminster Fullerene)



- sp^2 hybridised forming a football-like structure consisting of 20 hexagonal rings & 12 pentagonal rings.
- 2 different types of C-C BLs are observed.
- Six-membered rings are fused to both six and five membered rings.
- Five-membered rings are fused to only six membered rings.

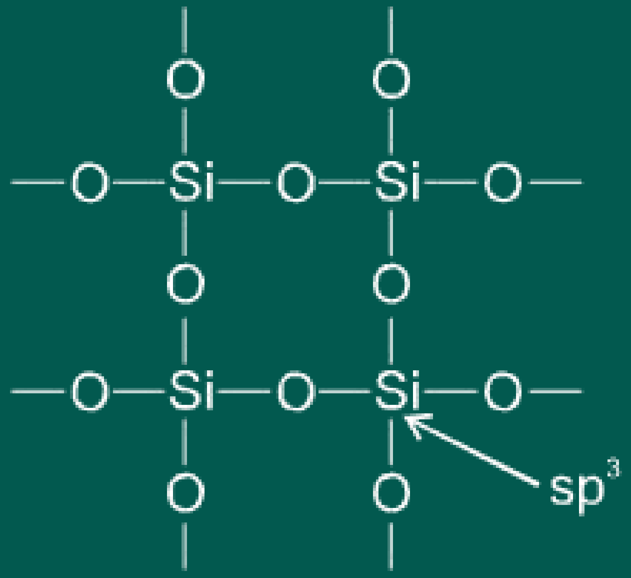
3. Diamond :



- 3D network like structure ; sp^3 hybridised.
- Hardest natural substance known.
- Only one type of BL (C–C = 1.54 Å) is observed.
- Very high melting point & boiling point ; no delocalisation of e^-, so bad conductor of electricity.

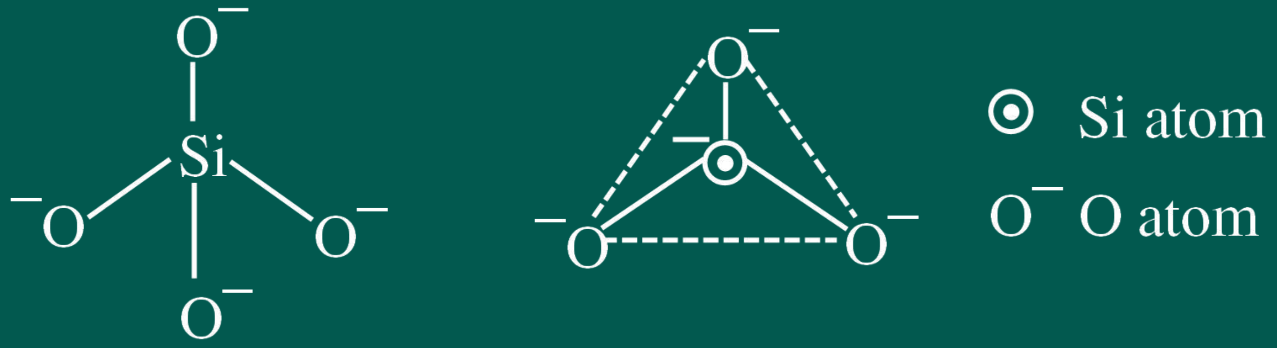
Eg. SiO_2 (Silica)

- 3D network like structure

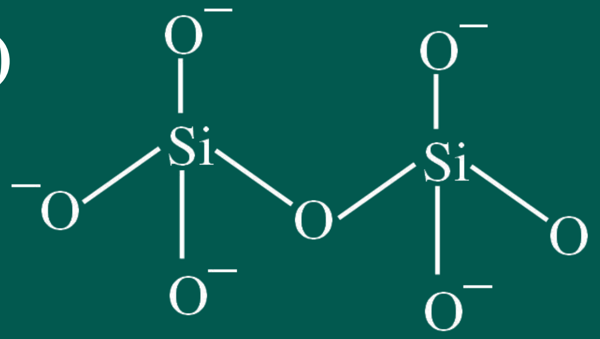


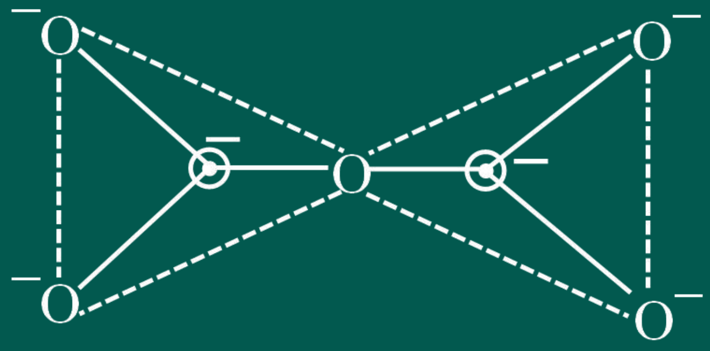
Eg. Silicates

(1) Orthosilicates (SiO_4^{4-})



(2) Pyrosilicates ($Si_2O_7^{6-}$)



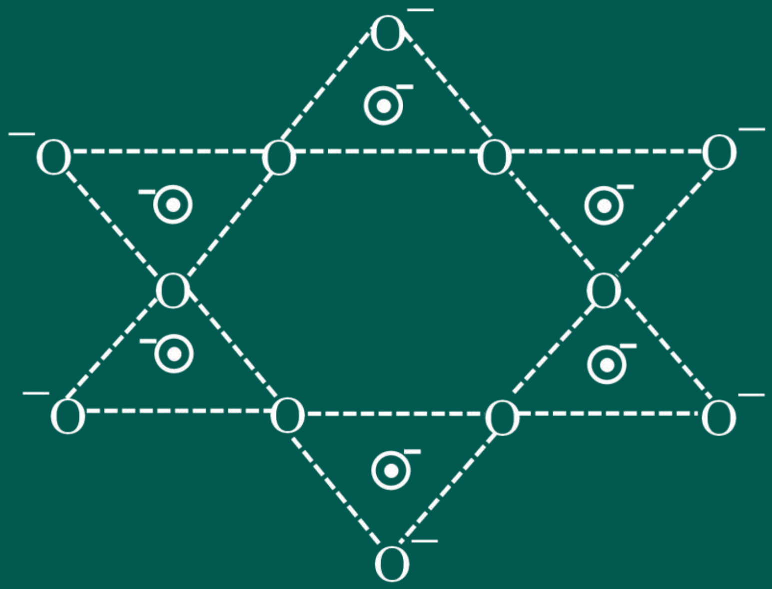


(3) Cyclic silicates ($(SiO_3^{2-})_n$)

- 2 O-atoms per basic tetrahedral unit are shared.

n = 6

($Si_6O_{18}^{12-}$)



Eg. Beryl mineral, $Be_3Al_2Si_6O_{18}$

(4) Sheet silicates or 2D silicates $(Si_2O_5^{2-})_n$

- 3 O-atoms per basic tetrahedral unit are shared.

3. Compounds of Nitrogen and Phosphorus

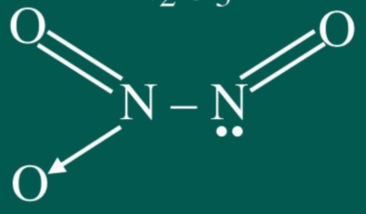
Eg.

N_2O

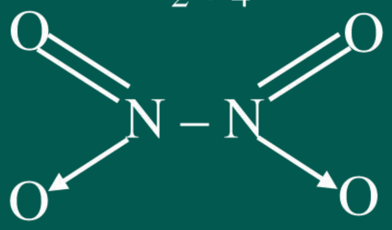
$N \equiv N \rightarrow O$

(sp)

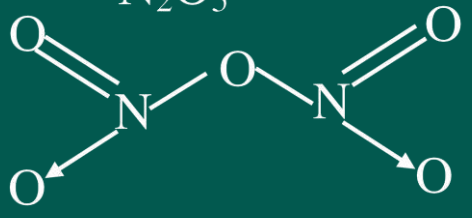
N_2O_3



N_2O_4



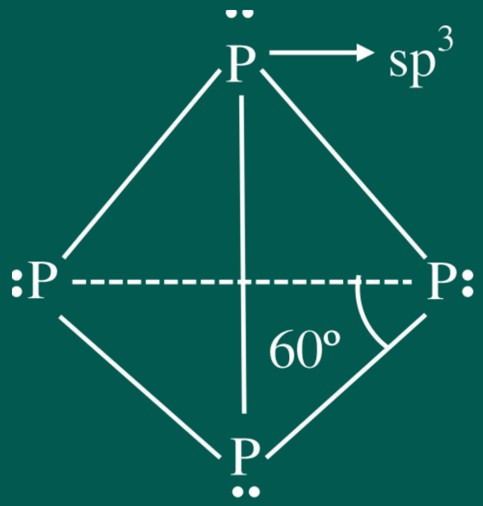
N_2O_5



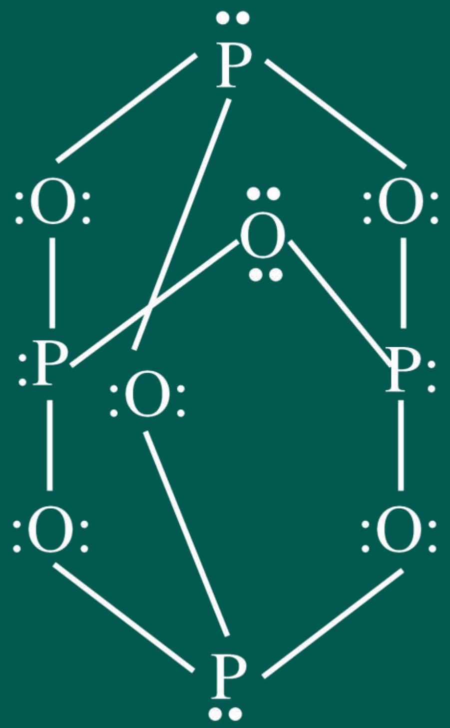
All N-atoms are sp^2 hybridisation

P_4 (white)

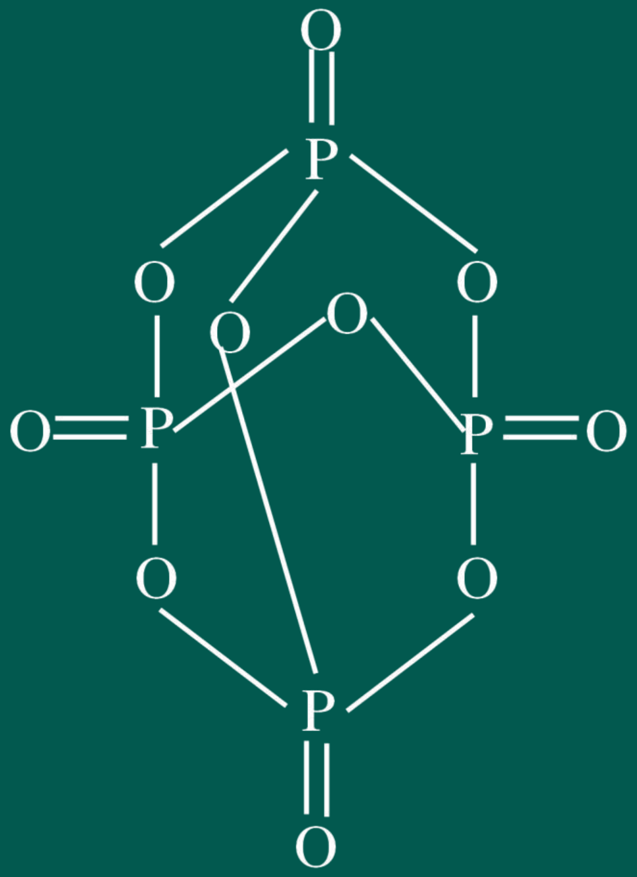
- 6 P–P Bonds ; 4 trigons (triangles)
- Highly strained molecule



P_4O_6



P_4O_{10}

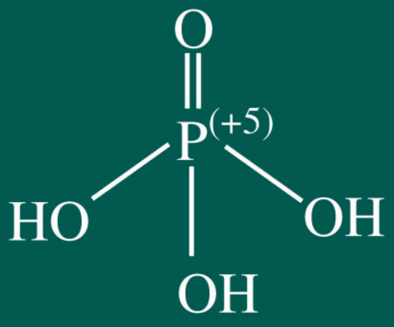


6 P–O–P linkages

Structures & Names of Oxyacids

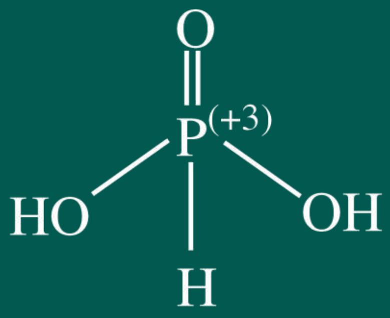
(1) Phosphorus

H_3PO_4



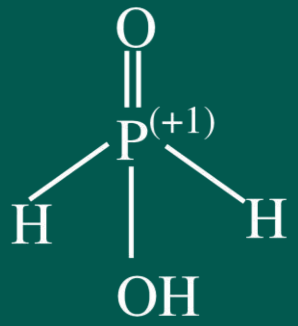
Ortho Phosphoric acid

H_3PO_3



Phosphorous acid
(Phosphonic acid)
(Dibasic)

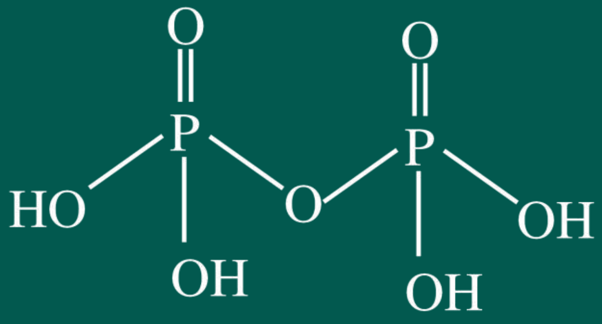
H_3PO_2



Hypophosphorous acid
(Phosphinic acid)
(Monobasic)

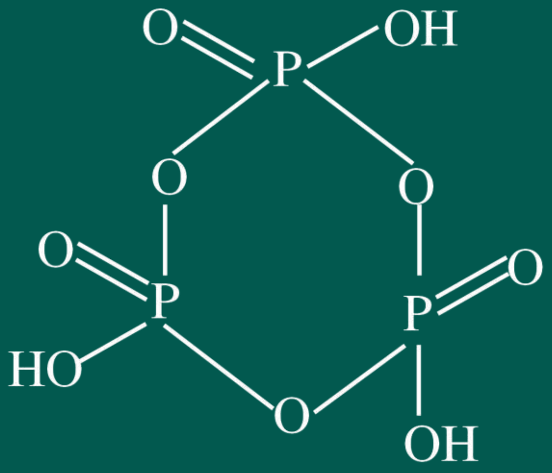
$H_4P_2O_7$

$(2H_3PO_4–H_2O)$



Pyrophosphoric acid

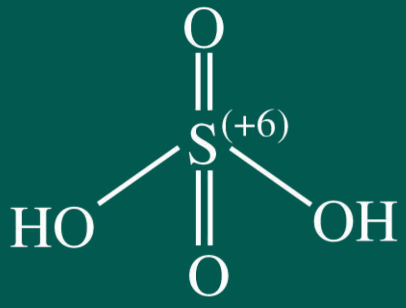
$(HPO_3)_3$



Trimetaphosphoric acid
3P–O–P linkage; 3dπ-pπ
bonds.

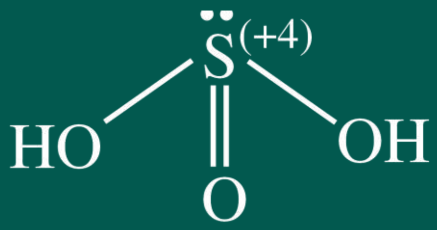
(2) Sulphur

H_2SO_4



Sulphuric acid

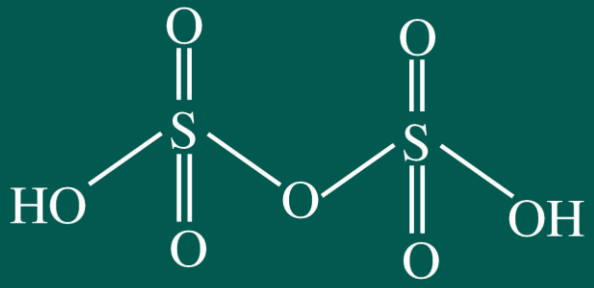
H_2SO_3



Sulphurous acid

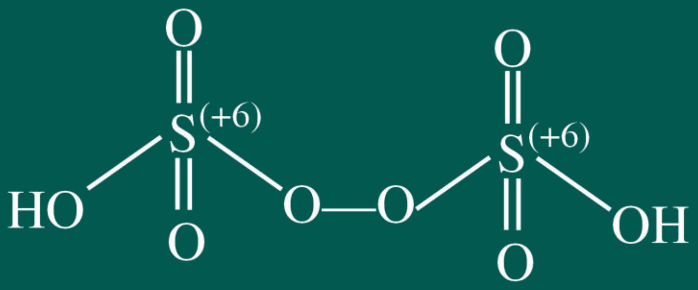
$H_2S_2O_7$

$(2H_2SO_4{-}H_2O)$



Pyrosulphuric acid

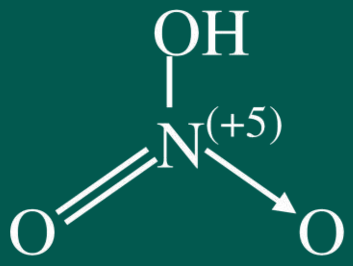
$H_2S_2O_8$



Peroxydisulphuric acid
(Marshall's acid)

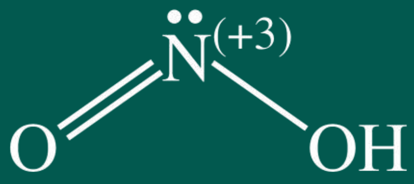
(3) Nitrogen :

HNO_3



Nitric acid

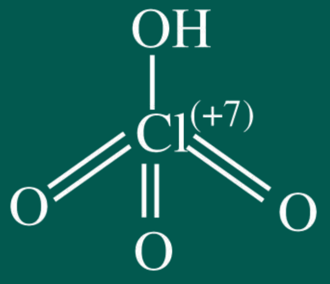
HNO_2



Nitrous acid

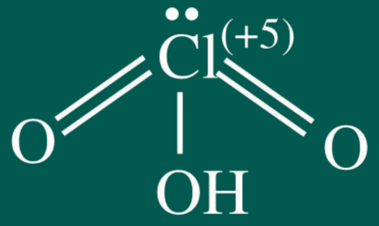
(4) Chlorine, Bromine and Iodine

$HClO_4$



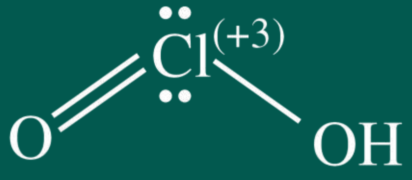
Perchloric acid

$HClO_3$



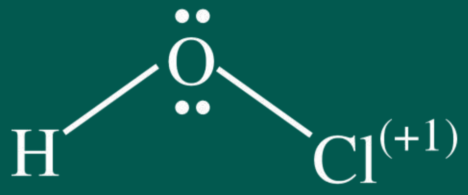
Chloric acid

$HClO_2$



Chlorous acid

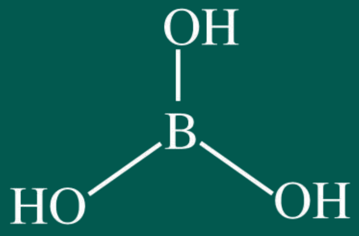
HOCl



Hypochlorous acid

(6) Boron

H_3BO_3



Orthoboric acid

Back Bonding

(1) pπ-pπ back bonding :

Eg. BF_3 (I) & BF_4^- (II) (B – F BL comparison)

$\therefore$ B –F BL : (I) (Partial double bond character) < (II)

Eg. $BF_3 < BCl_3 < BBr_3 < BI_3$ (Lewis acid strength
$\Rightarrow$ Lone pair accepting tendency)

B.B. 2p-2p 2p-5p

In BF_3, comparable energy orbitals are involved

$\therefore$ better BB $\Rightarrow$ Lesser electron deficiency

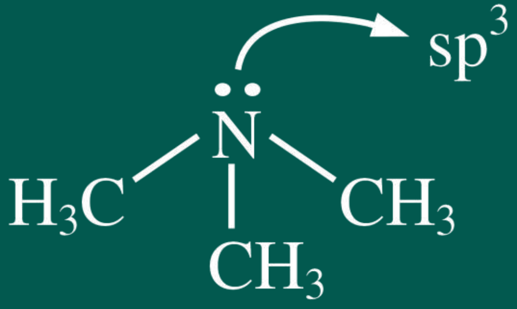
$\Rightarrow$ l.p. accepting tendency from an external atom $\downarrow$

$\Rightarrow$ Lewis acid strength $\downarrow$

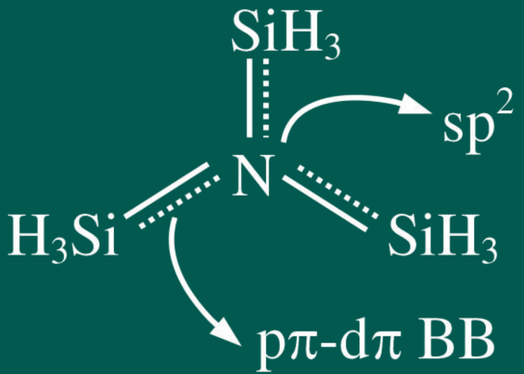
(2) pπ-dπ back bonding :

Eg. $(CH_3)_3N$ & $(SiH_3)_3N$

Trimethyl amine — Trisilyl amine



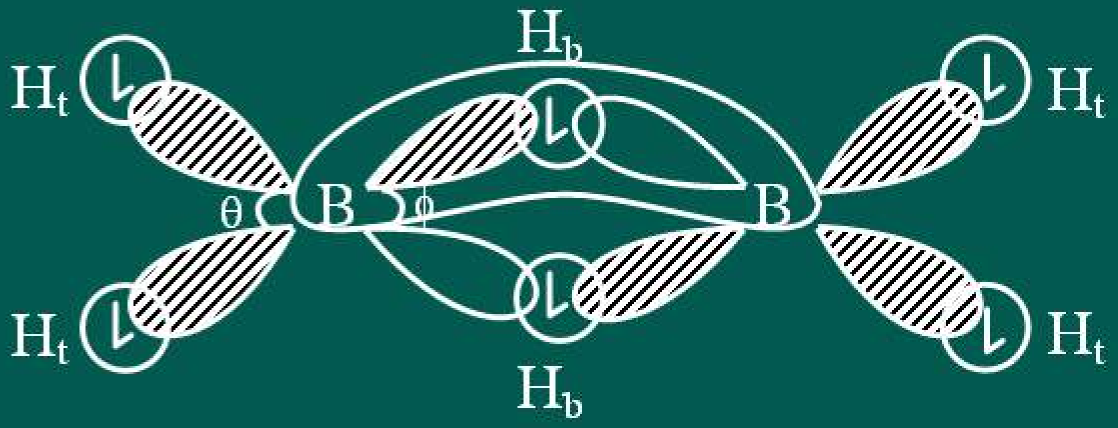
(Pyramidal)



(Planar about N-atom)

Electron Deficient Bonding (3 centre 2 e⁻ bonding) Banana Bonding

Eg. B_2H_6 (Diborane)
sp^3



- 4 2c-2e⁻ bonds ; 2 3c-2e⁻ bonds
- Bridged B.L. > Terminal B.L.
- Angle : θ > ϕ

H_t = Terminal H-atoms, H_b = Bridged H-atoms

Dipole Moment (μ_{net})

$$\boxed{|\vec{\mu}| = \delta \times d}$$

Direction : from less EN atom towards more EN atom.

Important Points :

1. Molecules having symmetrical shape as well as identical attached atoms have zero μ_{net} & molecule is **non-polar**.
   Eg. BeF_2, CO_2, BCl_3 , CCl_4 , PCl_5 , SF_6 , XeF_4 , IF_7 , XeF_2 etc.

2. Molecules having unsymmetrical shape or different attached atoms have non-zero μ_{net} & molecule is **polar**.
   Eg. SO_2, NH_3, H_2O, SF_4, ClF_3, BrF_5 etc.

Intermolecular forces (van der Waal forces)

1. **Ion-Dipole Attraction :**
2. **Dipole-dipole attraction :** (Interaction energy $\propto \frac{1}{r^3}$)

Note : In case of ion-ion interaction, (Interaction energy $\propto \frac{1}{r}$)

3. **Ion-induced dipole attraction :**
4. **Dipole-induced dipole attraction :**
5. **Instantaneous Dipole-induced dipole attraction or Dispersion forces or London forces :** (Interaction energy $\propto \frac{1}{r^6}$)

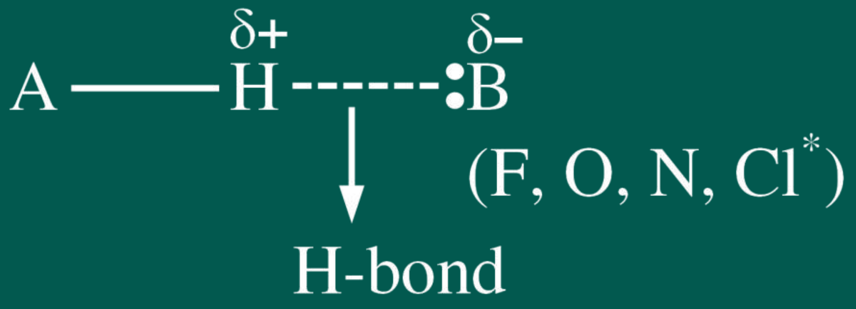
General order of strength : (1) > (2) > (3) > (4) > (5)

Note :

- If type of force of attraction is same, then strength $\propto$ molecular mass
- Strength of van der Waal forces $\propto$ boiling point

Eg. Boiling point : Xe > Kr > Ar > Ne > He

Hydrogen Bonding (A dipole-dipole attraction)



$$A - \overset{\delta+}{H} \text{------} :\overset{\delta-}{B}$$

Types of H-bonding

(1) Intermolecular H-bonding : Between 2 atoms belonging to different molecules.

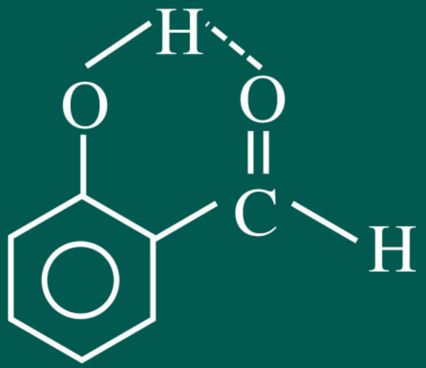
Eg.

$$\text{-----}\underset{\underset{H}{|}}{O}-H\text{------}\underset{\underset{H}{|}}{O}-H\text{-----}$$

$H_2O(l)$

(2) Intramolecular H-bonding : Between 2 atoms belonging to same molecule.

Eg. Salicyaldehyde



Properties getting affected by intermolecular H-bonding

- Boiling point ↑
- Viscosity of substance ↑

Boiling point :

Eg. $D_2O > H_2O$

(∵ D is less EN than H, so D_2O will have stronger H-bonding than H_2O)

Eg. HF > HI > HBr > HCl

↓

∵ H-bonding

⟶ mol. mass ↓ ⇒ strength of van der Waal forces ↓

∴ boiling point ↓

Note : $CuSO_4.5H_2O$ (blue vitriol) has four H_2O molecules directly attached with Cu^{2+} ions and remaining one H_2O molecule is attached through H-bonding.

- $D_2O(s)$ sinks in $H_2O(\ell)$

$\because$ D_2O has stronger H-bonding, so compact structure. So, its density is high.

Molecular Orbital Theory (MOT)

Electron Filling Order in MO's

(for homonuclear diatomic species with total $e^- \leq 20$)

(1) Total $e^- \leq 14$

$$\text{Order :}\quad \sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \underbrace{\pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z}}_{\substack{\text{expected to be because of}\\ \text{mixing of s \& p orbitals}}} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_y}$$

(2) Total $e^- > 14$

$$\text{Order :}\quad \sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \underbrace{\sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y}}_{\text{same as expected}} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$$

Bond Order, Type & Number of Bonds, Bond Length & Bond Strength

- $$\text{B.O.} = \frac{\text{Total no. of } e^- \text{ in BMO's} - \text{Total no. of } e^- \text{ in ABMO's}}{2}$$

  $$= \text{No. of bonds}$$

  $\text{BO} = 0 \Rightarrow$ species does not exist.

- $\text{BL} \propto \dfrac{1}{\text{B.O.}}$; Bond strength & Stability $\propto$ B.O.

Some examples based on MOT

- N_2 or C_2^{2-} $\left(\text{Total } e^{-} = 12 + 2 = 14\right)$

MO config. : $\sigma_{1s}^{2}\sigma_{1s}^{*2}\,\sigma_{2s}^{2}\sigma_{2s}^{*2}\,\pi_{2p_x}^{2} = \pi_{2p_y}^{2}\,\sigma_{2p_z}^{2}$

$$\text{B.O.} = \frac{10-4}{2} = 3 \Rightarrow 3\text{ bonds }\left(1\sigma + 2\pi\right)\text{ \& Diamagnetic}$$

- $O_2 \left(\text{Total } e^- = 8 + 8 = 16\right)$

  MO config. : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2}\ \sigma_{2p_z}^2 \pi_{2p_x}^2 = \pi_{2p_y}^2 \pi^{*1}{}_{2p_x} = \pi^{*1}{}_{2p_y}$

  $\text{B.O.} = \dfrac{10-6}{2} = 2 \Rightarrow$ 2 bonds $(1\sigma + 1\pi$ bonds$)$ & paramagnetic $\left(2 \text{ unpaired } e^-\right)$

Note : He_2, Be_2 & Ne_2 do not exist because they have B.O. = 0.

Note : Total e^- = Odd $\Rightarrow$ Paramagnetic

Total e^- = Even $\Rightarrow$ Diamagnetic or Paramagnetic (check from MOT)

Acidic & Basic Strength of Oxides, Oxyacids, Hydroxides & Hydra-acids

1. **For oxides, oxy-acids & hydroxides :**

$L \rightarrow R \Rightarrow EN \uparrow \Rightarrow$ Acidic strength of oxides & oxyacids ↑
Basic strength of oxides & hydroxides ↓

$T \rightarrow B \Rightarrow EN \downarrow \Rightarrow$ Basic strength of oxides & hydroxides ↑
Acidic strength of oxides & oxyacids ↓

- If same element with different ON is involved, then
  as $ON \uparrow \Rightarrow EN \uparrow \Rightarrow$ Acidic strength ↑ & Basic strength ↓

2. For Hydra-acids

- T → B $\Rightarrow$ Stability of anion formed $\uparrow$ $\Rightarrow$ Acidic strength $\uparrow$

Eg. $HF < HCl < HBr < HI$

Nature of Oxides :

1. Neutral oxides : Those oxides which neither react with an acid nor with a base.

Eg. CO, NO, N_2O, H_2O

2. Amphoteric oxides : Those oxides which react with both acids & bases.

Eg. BeO, V_2O_5, Cr_2O_3, ZnO, Al_2O_3, Ga_2O_3, SnO, SnO_2, PbO, PbO_2, As_2O_3, Sb_2O_3 etc.

METALLURGY

INTRODUCTION

Order of abundance of metals in earth crust :

O > Si > Al > Fe > Ca > Na > Mg > K

The minerals from which metal can be economically and conveniently extracted are called **ores**.
All ores are minerals but all minerals are not ores.

Important ores :

Oxide ores :

(i) Bauxite → $Al_2O_3.2H_2O$ (Major ore of Al)

(ii) Haematite → Fe_2O_3

(iii) Cassiterite or tin stone → SnO_2 (Black Tin = 60 – 70% SnO_2)

Carbonate ores :

(i) Lime stone → $CaCO_3$

(ii) Dolomite → $CaCO_3.MgCO_3$

(iii) Siderite → $FeCO_3$

(iv) Malachite → $CuCO_3.Cu(OH)_2$

(v) Azurite → $2CuCO_3.Cu(OH)_2$

(vi) Calamine → $ZnCO_3$

(vii) Cerussite → $PbCO_3$

Sulphate ore :

Epsom salt → $MgSO_4.7H_2O$

Sulphurised ore :

(i) Iron pyrites → FeS_2

(ii) Copper glance → Cu_2S

(iii) Copper pyrite or chalcopyrite → $CuFeS_2$ **or** $Cu_2S.Fe_2S_3$

(iv) Zinc Blende → ZnS

(v) Galena → PbS

(vi) Cinnabar → HgS

Halide ores :

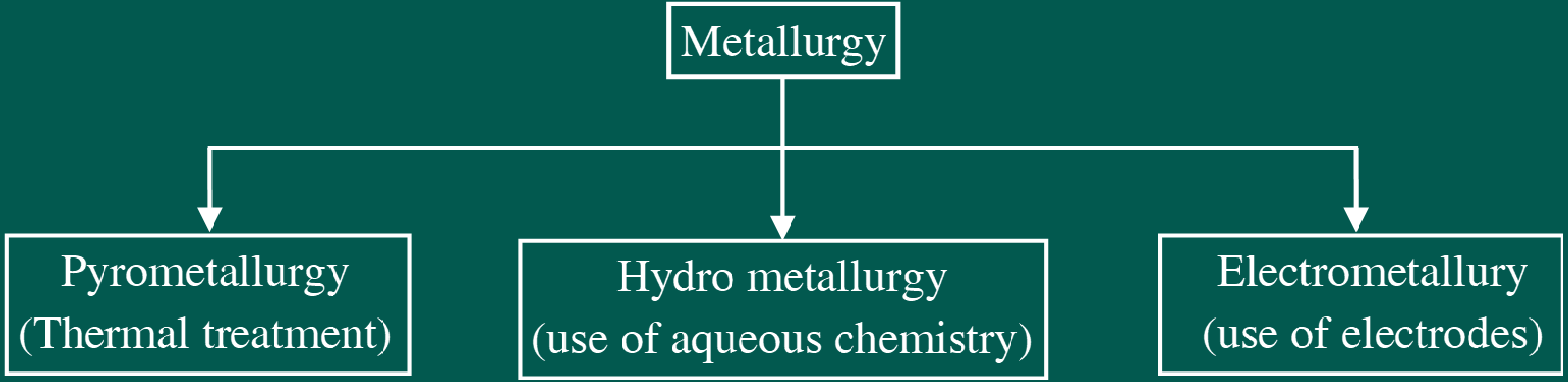
(i) Cryolite → Na_3AlF_6

(ii) Sylvine → KCl

(iii) Carnallite → $KCl.MgCl.6H_2O$

(iv) Fluorspar → CaF_2

(v) Horn silver → AgCl



Metallurgy

- Pyrometallurgy
  (Thermal treatment)
- Hydro metallurgy
  (use of aqueous chemistry)
- Electrometallury
  (use of electrodes)

Steps involved in Metallurgy (Pyrometallurgy)

The isolation and extraction of metals from their ores involve the following major steps:

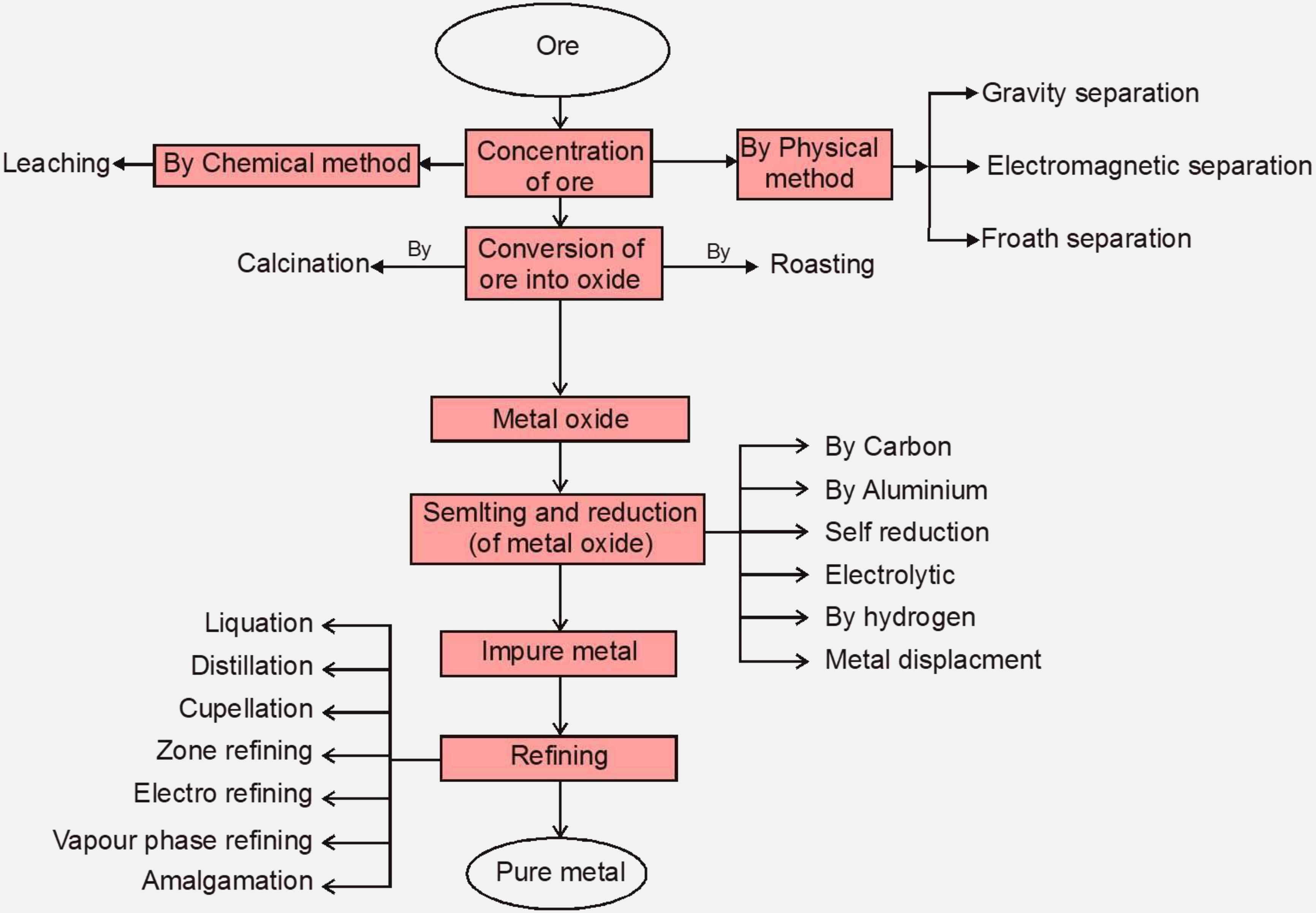
Step-1 Crushing of the ore.

Step-2 Dressing or concentration of the ore.

Step-3 Conversion of concentrated ore into metal oxide

Step-4 Reduction of metal oxide into impure metal

Step-5 Purification or refining of the metal.



Ore

Leaching

By Chemical method

Concentration of ore

By Physical method

Gravity separation

Electromagnetic separation

Froath separation

Calcination

By

Conversion of ore into oxide

By

Roasting

Metal oxide

Semlting and reduction (of metal oxide)

- By Carbon
- By Aluminium
- Self reduction
- Electrolytic
- By hydrogen
- Metal displacment

Impure metal

Refining

- Liquation
- Distillation
- Cupellation
- Zone refining
- Electro refining
- Vapour phase refining
- Amalgamation

Pure metal

STEP-2 CONCENTRATION OF ORE

The removal of unwanted useless impurities (gangue) from the ore is called dressing **or** concentration or benefaction of ore. There are two types of methods.

(A) Physical Methods :

(a) **<u>Hydraulic washing or Gravity separation or Levigation method :</u>**

It is based on the difference in the densities of the gangue and ore particles.

This method is used for concentration of oxide ores, halide ores & carbonate ores.

(b) Electromagnetic separation :

It is based on differences in magnetic properties of the ore components.

Examples :

Haematite (Fe_2O_3) ore & Chromite ore($FeO.Cr_2O_3$) are separated from non–magnetic silicious impurities

Cassiterite ore (SnO_2) is separated from magnetic Wolframite ($FeWO_4 + MnWO_4$).

(c) Froth floatation process :

- This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper pyrites $Cu_2S.Fe_2S_3$ or $CuFeS_2$ (ore of copper) ; zinc blende, ZnS (ore of zinc) etc.,
- It is based on the fact that gangue and ore particles have difference in wettability with water and pine oil.
- The gangue particles are preferentially wetted by water while the ore particles are wetted by oil.

Important Chemicals Used in This Process are :

(i) **Frothers :** Oils like pine oil, camphor oil. These are added in small quantity.

(ii) **Collectors :** Potassium or sodium ethyl xanthate.

These get attached with the particles of the sulphide ore and thus make them water-repellant.

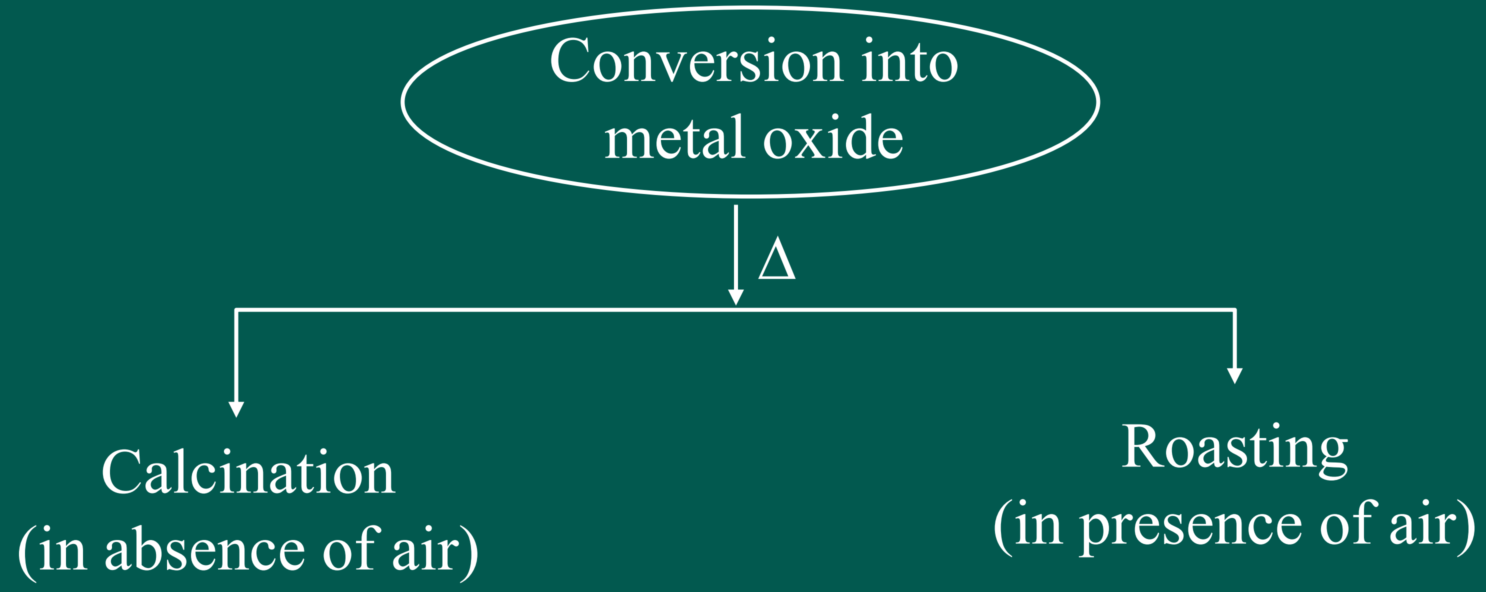
(B) Chemical Method :

Leaching : It is used if the ore is soluble in some suitable solvent, e.g, acids, bases and suitable chemical reagents.

e.g. Al ore, Ag ore, Au ore, low grade copper ore.

Step-3 Conversion of concentrated ore into metal oxide

There are two methods :



Conversion into
metal oxide

Δ

Calcination
(in absence of air)

Roasting
(in presence of air)

Calcination in used for carbonate ore, oxide ore, hydrated oxide ore, halide ore. Roasting in used for sulphide ore

Calcination :

It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air.

$FeCO_3 \xrightarrow{\Delta} FeO + CO_2$;

(siderite)

$PbCO_3 \xrightarrow{\Delta} PbO + CO_2$

(cerrussite)

$2Fe_2O_3.3H_2O \xrightarrow{\Delta} 2Fe_2O_3(s) + 3H_2O(g)$

(limonite)

Roasting :

It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2 ;$$

$$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4 ; \quad \text{(At low temperature)}$$

$$2ZnS + 2O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

SMELTING

Slag formation :

$$\text{Flux} \quad + \quad \text{non-fusible impurties} \xrightarrow{\Delta} \text{slag (molten layer)}$$

Type of Flux

Basic Flux

Ex. Metal oxides

CaO, MgO

It removes acidic impurity

Acidic Flux

Ex. Non-metal oxides

SiO_2, B_2O_3, P_2O_5

It removes basic impurity

$$\underset{\text{Basic flux}}{CaO} + \underset{\text{Acidic impurity}}{SiO_2} \xrightarrow{\Delta} \underset{\text{slag}}{CaSiO_3}$$

$$\underset{\text{Acidic flux}}{SiO_2} + \underset{\text{Basic impurity}}{FeO} \xrightarrow{\Delta} \underset{\text{slag}}{FeSiO_3}$$

Step-4 Reduction of metal oxide into impure metal

There are following methods

(i) Chemical reduction method : Reducing agents are C, Al, Mg, Electricity .

(a) Reduction with carbon :

$PbO + C \longrightarrow Pb + CO$ (extraction of lead)

$2Fe_2O_3 + 3C \longrightarrow 4Fe$ (spongy iron) $+ 3CO_2$

$ZnO + C \xrightarrow{1200^{\circ}C} Zn + CO$ (Balgian process)

(b) Reduction with CO : In some cases CO produced in the furnace itself is used as a reducing agent.

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$$

$$Fe_3O_4 + 4CO \xrightarrow{\Delta} 3Fe + CO_2$$

Reduction by other metals :

Oxides of Cr and Mn are reduced by Aluminium. The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe \text{ (molten) ; } \Delta H = -3230 \text{ kJ}$$

(The reaction is used for thermite welding)

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

Self-reduction method :

This method is used for sulphides of Cu, Pb & Hg.

Examples :

(i)
$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$$
$$2HgO + \underset{\text{(remaining)}}{HgS} \longrightarrow 2Hg + SO_2$$

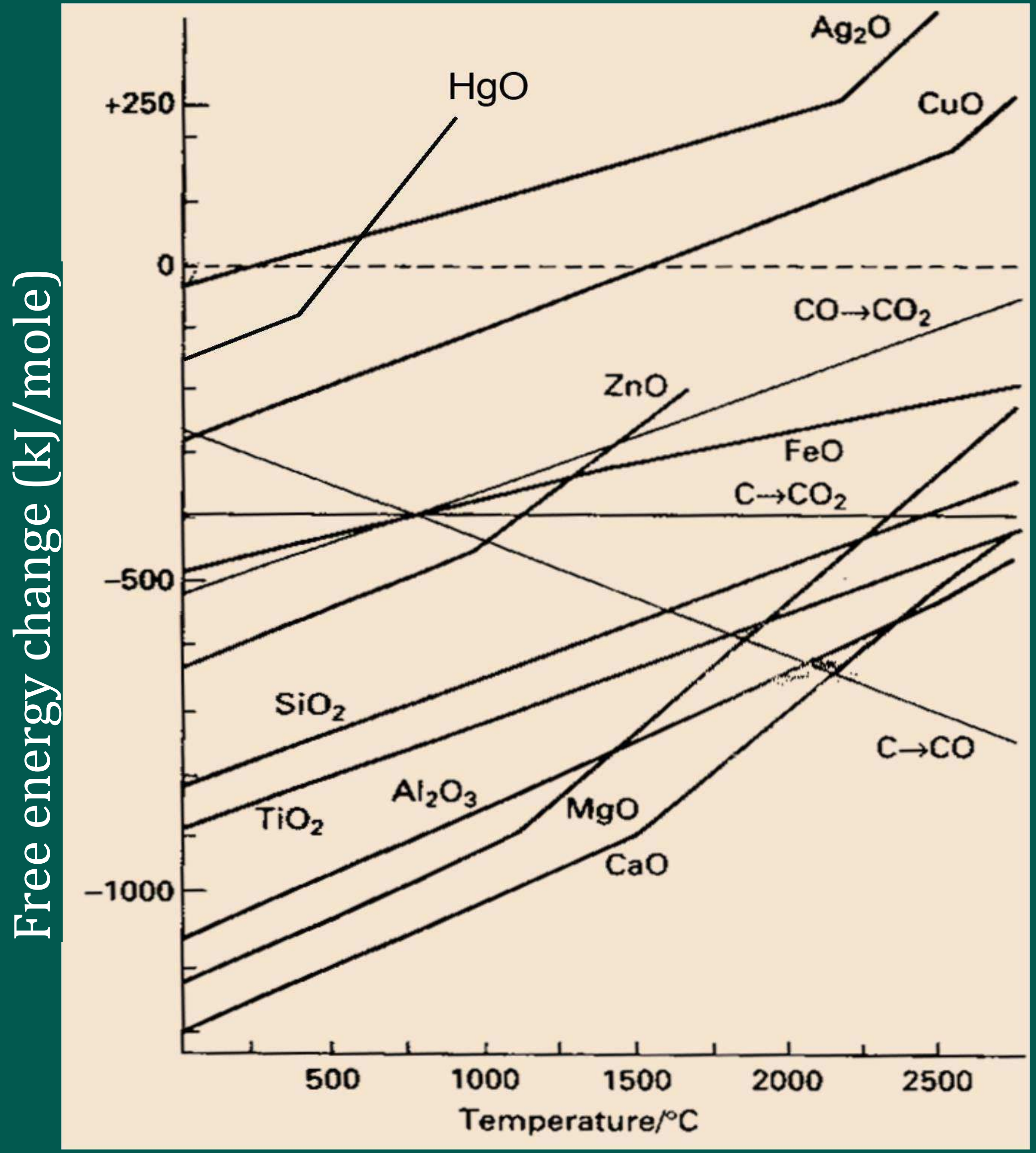
(ii)
$$Cu_2S + 3O_2 \longrightarrow 3Cu_2O + 2SO_2$$
$$2Cu_2O + \underset{\text{(remaining)}}{Cu_2S} \longrightarrow 6Cu + SO_2$$

(iii)
$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2PbO + \underset{\text{(remaining)}}{PbS} \longrightarrow 3Pb + SO_2$$

Electrolytic reduction :

It presents the most powerful method of reduction and gives a very pure product.It is used for Al_2O_3 (bauxite ore)

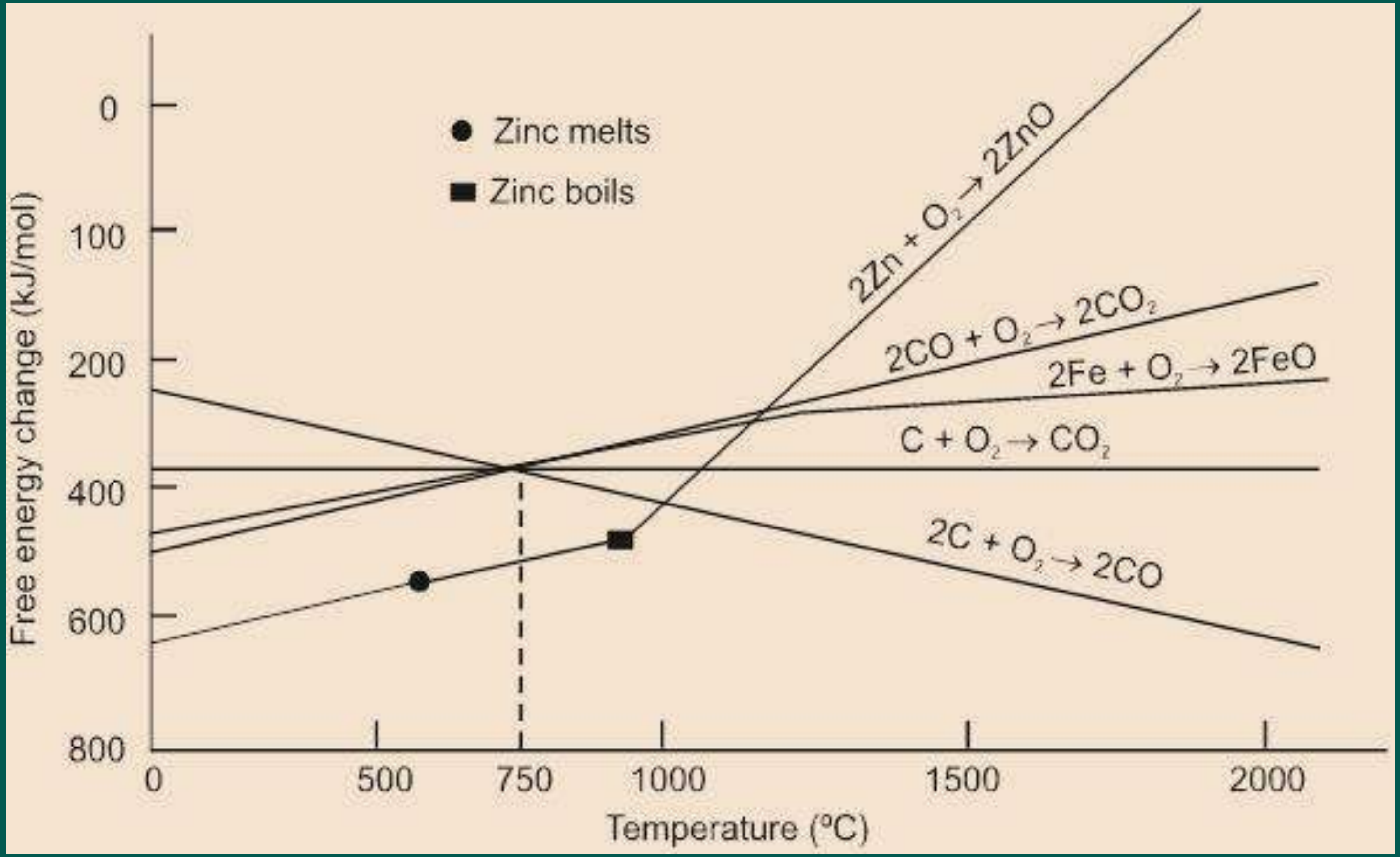
THERMODYNAMICS OF EXTRACTION : ELLINGHAM DIAGRAM OF A METAL



ΔG is the free energy of formation per mole of O_2 consumed.

- This graph is shown in figure and is called an Ellingham diagram for oxides.
- In principle, when the plot of one metal lies below that of another, the first metal is capable of reducing the oxide of the second.
- A vertical line drawn on the Ellingham plot of the metal oxides at any T gives the sequence of the stabilities of metal oxides.
- If the two lines intersect, the free energy change for the reduction will be zero at that temperature and equilibrium results

Carbon or carbon monoxide as reducing agent:



A temperature of 710ºC, CO is a more effective reducing agent than carbon, but above this temperature the reverse is true.

Purification or Refining of metals : There are following methods.

(A) Physical methods :

(a) Liquation process : This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not infusible.This process is used for the purification of Sn and Zn

(b) Fractional distillation process :

This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.

(c) Zone refining method (Fractional crystallisation method) :

This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.

(d) Chromatographic methods :

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

(B) Chemical methods :

(a) Oxidative refining:

The method is used when the impurities have a greater affinity for oxygen than metal.

This method is used for Pb, Ag, Cu, Fe, etc.

- Bessemerisation (Purification of iron)
- Cupellation (removal of lead)

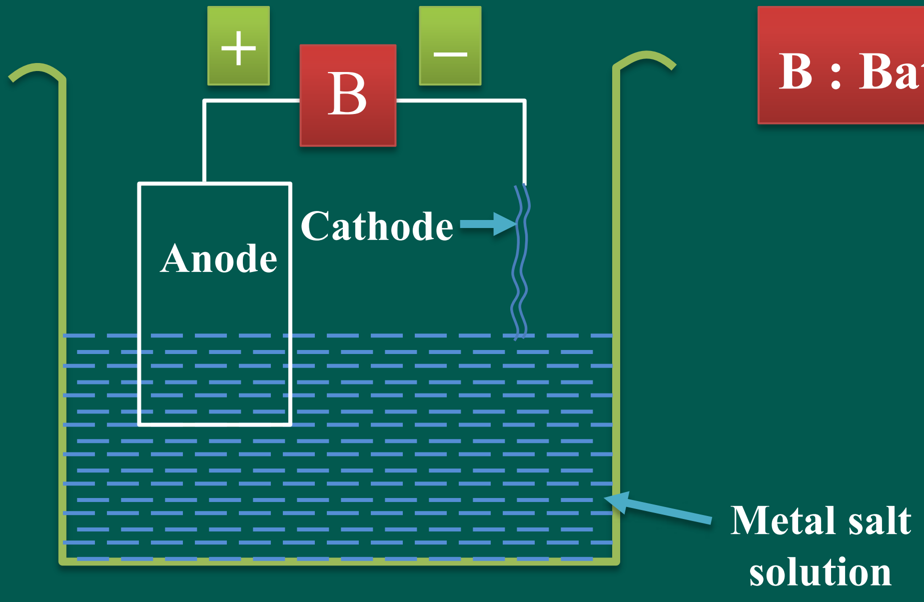
(b) Poling process :

This process is used for the purification of copper and tin.

$$\text{Green wood} \longrightarrow \text{Hydrocarbons} \longrightarrow CH_4$$

$$4CuO + CH_4 \longrightarrow 4Cu\ (\text{pure metal}) + CO_2 + 2H_2O$$

(c) Electrolytic refining :



B : Battery

Anode : Impure metal block

Cathode : Pure metal strip

Electrolytic : Aqueous solution of metal salt

At Anode (oxidation)

$$\mathbf{M\ (solid) \longrightarrow M^{n+}_{(aq.)} + ne}$$

At Cathode (Reduction)

$$\mathbf{M^{n+}_{(aq.)} + ne \longrightarrow M\ (solid)}$$

In this method metal is transfer from anode rod and cathode rod wia electrolytic solution. There is no change in the concentration of electrolytic solution.

This is the most common method.

(d) Vapor phase refining :

(i) Extraction of Nickel (Mond's process) :

$$Ni(s) + 4\ CO(s) \xrightarrow{50^{\circ}C} [Ni(CO4)]\ (g)$$

$$[Ni\ (CO)4](g) \xrightarrow{200^{\circ}C} Ni + 4CO(g)$$

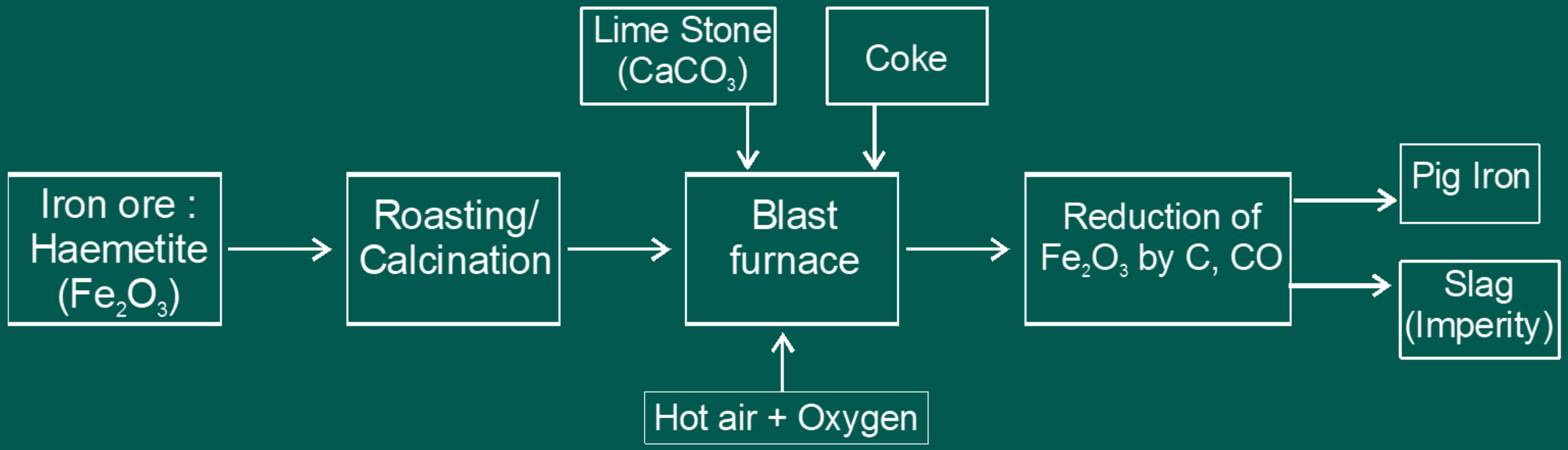
(ii) Van Arkel–De Boer process :

Small amounts of very pure metals (Ti, Zr, or Bi) can be produced by this method. This process is based on the fact that iodides are the least stable of the halides.

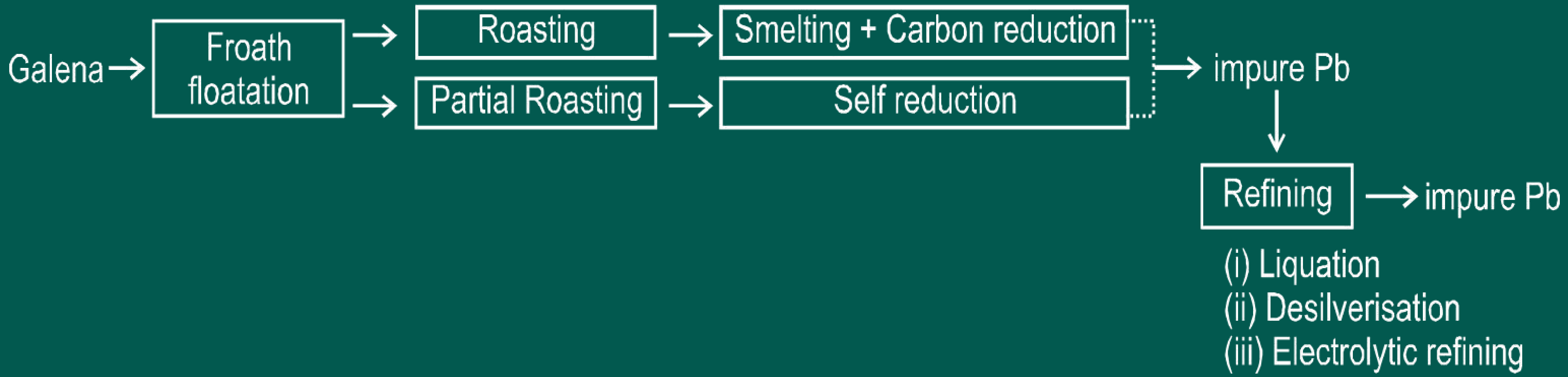
Metallurgy of Some Important Metals

Extraction of iron (Fe)

Ore: Haematite



Extraction of lead :
Ore: PbS (Lead sulphide)



EXTRACTION OF ALUMINIUM :

(a) Purification of bauxite :

(i) Bayer's Method : (used for red bauxite containing Fe_2O_3 and silicates as impurities)

$$Al_2O_3.2H_2O + 2NaOH \xrightarrow[8\text{ atm}]{190°C} 2NaAlO_2(\text{soluble}) + 3H_2O$$

$$NaAlO_2 + 2H_2O \xrightarrow{H^+} NaOH + Al(OH)_3 \downarrow$$

$$2Al(OH)_3 \xrightarrow{1473\text{ K }\Delta} Al_2O_3 + 3H_2O$$

(ii) Hall's Method

(used for red bauxite containing Fe_2O_3 and silicates as impurities)

$$Al_2O_3.2H_2O + Na_2CO_3 \xrightarrow{\text{Fuse}} 2NaAlO_2(\text{soluble}) + CO_2 + 2H_2O$$

(iii) Serpeck's Method

(used for white bauxite containing silica as impurities)

$$Al_2O_3.2H_2O + 3C + N_2 \xrightarrow[\text{Electric furnace}]{1800°C} 2AlN + 3CO + 2H_2O$$

$$2AlN + 3H_2O \longrightarrow Al(OH)_3 \downarrow + NH_3$$

(b) Electrolytic reduction (Hall-Heroult process) :

The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used.

The electrolytic reactions are :

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

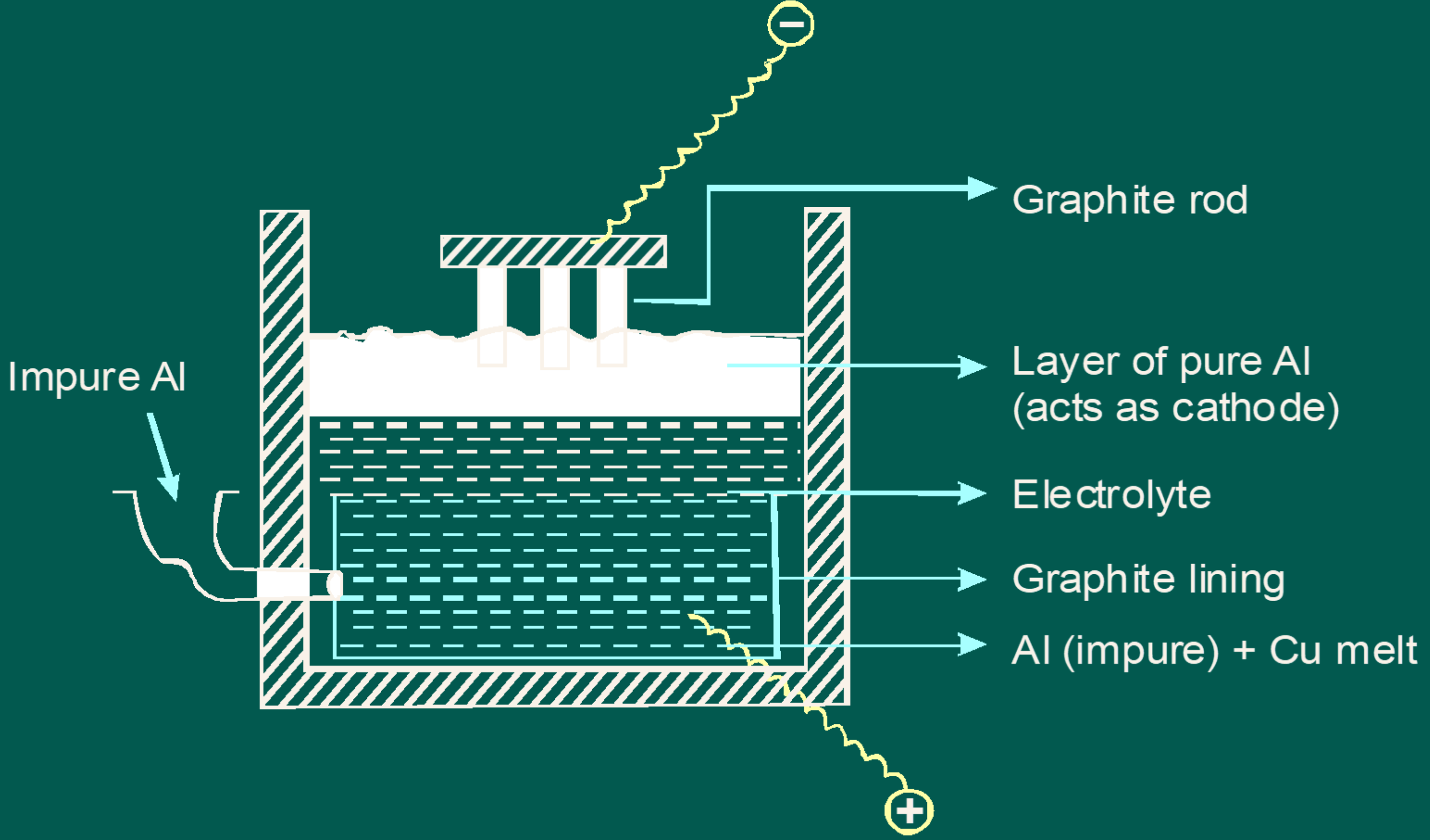
Anode : $C(s) + O^{2-}$ (melt) $\longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}$ (melt) $\longrightarrow CO_2(g) + 4e^-$

Overall

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

(c) Electro-refining of impure Al (Hoop's process) :



At Anode (oxidation)

$$\text{Al (solid)} \longrightarrow \text{Al}^{3+}_{(aq.)} + 3e$$

At Cathode (Reduction)

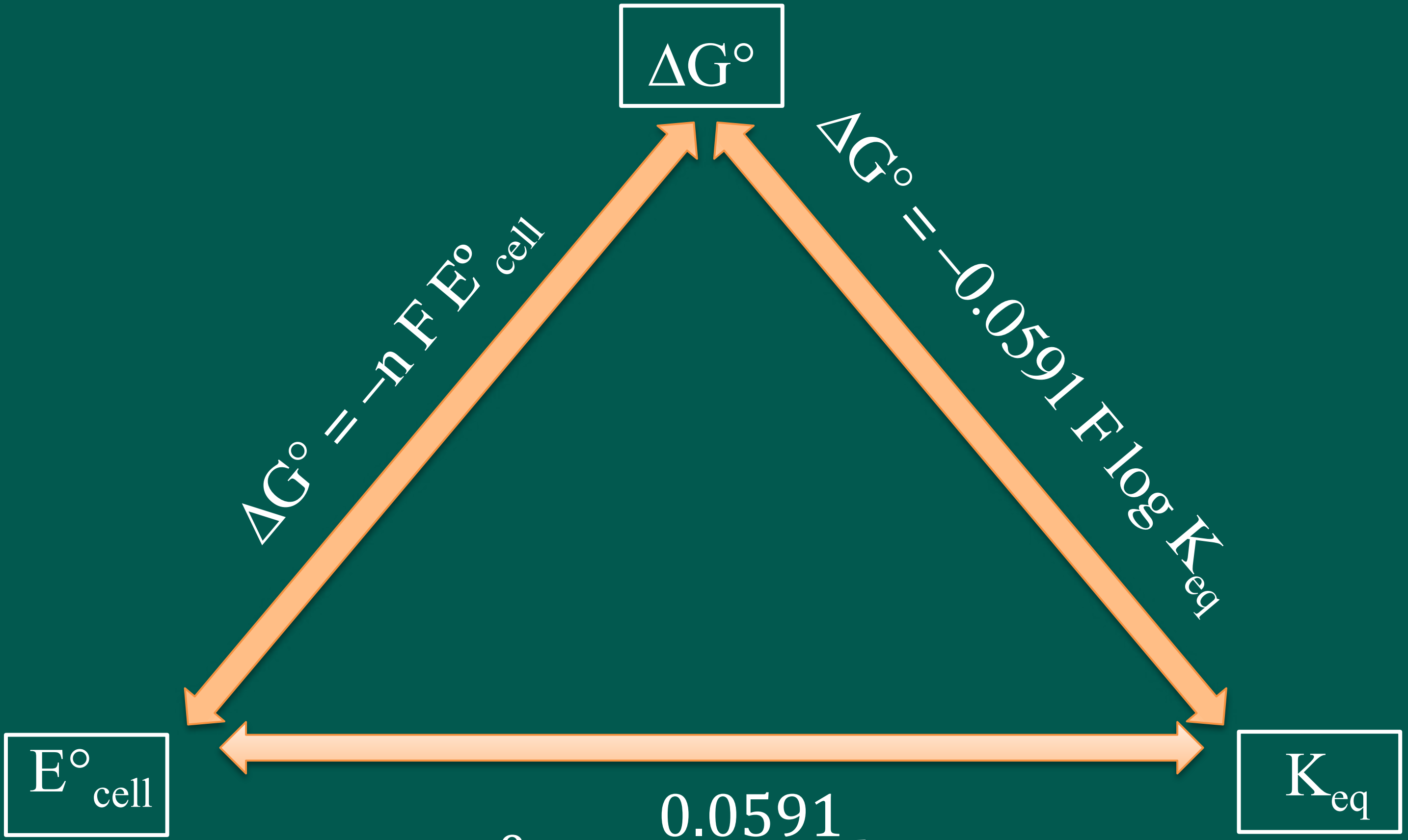
$$\text{Al}^{3+}_{(aq.)} + 3e \longrightarrow \text{Al (solid)}$$

ELECTROCHEMISTRY

Frequently Asked Concepts in JEE Main & JEE Advanced :

- Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.
- Electrochemical series
- Nernst Equation & Concentration cell
- Conductivity and molar conductivity
- Kohlrausch’s Law

Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.



ΔG°

$\Delta G^\circ = -n\,F\,E^\circ_{cell}$

$\Delta G^\circ = -0.0591\,F\log K_{eq}$

E°_{cell}

K_{eq}

$$E^o_{cell} = \frac{0.0591}{n}\log K_{eq.}$$

Example :

Given that $E^\circ_{Cu^{2+}/Cu^+} = 0.153$ V and $E^\circ_{Cu^+/Cu} = 0.521$ V.

Then calculate $E^\circ_{Cu^{2+}/Cu}$.

Solution :

$$\begin{tikzcd} Cu^{2+} \arrow[r, "\Delta G^\circ_1"] \arrow[rr, bend right, "\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2"'] & Cu^{+} \arrow[r, "\Delta G^\circ_2"] & Cu \end{tikzcd}$$

$$\Delta G^\circ_1 + \Delta G^\circ_2 = \Delta G^\circ_3$$

$$-FE^\circ_1 - FE^\circ_2 = -2FE^\circ_3$$

$$E^\circ_3 = \frac{E^\circ_1 + E^\circ_2}{2}$$

$$= (0.521 + 0.153)/2$$

$$= 0.337 \text{ V}$$

Q. Given $E^\circ_{MnO_4^- | Mn^{2+}} = +1.51\ V$ $\quad E^\circ_{MnO_2/Mn^{+2}} = +\ 1.23\ V$

Calculate $E^\circ_{MnO_4^-/MnO_2}$ (All in acidic medium)

Sol.

$$\begin{tikzcd}
MnO_4^- \arrow[r, "\Delta G^\circ_3"] \arrow[rr, bend right, "\Delta G^\circ_1"'] & MnO_2 \arrow[r, "\Delta G^\circ_2"] & Mn^{2+}
\end{tikzcd}$$

$$\Delta G^\circ_3 + \Delta G^\circ_2 = \Delta G^\circ_1$$

$$\Delta G^\circ_3 = \Delta G^\circ_1 - \Delta G^\circ_2$$

$$-3FE^\circ_3 = -\ 5FE^\circ_1 + 2FE^\circ_2$$

$$E^\circ_3 = \frac{5 \times 1.15 - 2 \times 1.23}{3}$$

$$= 1.096V$$

Electrochemical series: Standard aqueous electrode potentials at 298 K

Reaction (oxidised form + ne$^-$	**→ Reduced form)**	**E°/V**
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$2H^+ + 2e^-$	$\rightarrow H_2(g)$	0.00
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	–0.44
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	–1.66
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

Application of electrochemical series :

(i) Calculation of E^o_{cell} of Galvanic cell

Anode || Cathode

E^o_{cell} = SRP of cathode – SRP of anode

For a working cell in a standard conditions

$\because \Delta G^o_{reac.} < 0$

$\therefore E^o_{cell} > 0$

SRP of cathode > SRP of anode

(ii) Calculation of equilibrium constant of redox reaction

$$E^{\circ}_{(\text{cell})} = \frac{0.059}{n}\log K_{eq}$$

Example :

Calculate the equilibrium constant of the reaction:

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

$$E^{\circ}_{Cu^{2+}/Cu} = 0.34\,,\ E^{\circ}_{Ag^{+}/Ag} = 0.8$$

Solution :

$$E^{\circ}_{(\text{cell})} = \text{SRP of cathode} - \text{SRP of anode} = 0.46\text{V}$$

$$E^{\circ}_{(\text{cell})} = \frac{0.059}{2} \log K_C = 0.46 \text{ V}$$

$$K_C = 3.92 \times 10^{15}$$

(iii) Feasibility of redox reaction

For the feasibility of redox reaction, E°_{cell} of corresponding galvanic cell should be positive

Ex. $F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$

$Cl_2 + 2F^- \longrightarrow$ No reactions

Since SRP of F_2 is greater than SRP of Cl_2

Ex. $E°_{MnO_4^- | Mn^{2+} | H^+} = +1.5V$

$E°_{Cr_2O_7^{2-} | Cr^{3+} | H^+} = 1.3V$

$E°_{Cl_2 | Cl^-} = 1.4V$

Therefore Cl^- can be oxidised by $KMnO_4$ in acidic medium

but not by $K_2Cr_2O_7$

Nernst Equation

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

$$= E^\circ - \frac{0.0591}{n}\log Q \qquad \text{(at 298K)}$$

Nernst Equation is applicable for electrode potential

as well as for cell potential

Q. For the galvanic cell, **[JEE-Mains (online) Aug. 2021]**

$Zn(s) + Cu^{2+}\ (0.02\ M) \longrightarrow Zn^{2+}\ (0.04\ M) + Cu(s)$,

$E_{cell} =$ ________ $\times 10^{-2}$ V. (Nearest integer)

[Use : $E°_{Cu/Cu^{2+}} = -0.34$ V, $E°_{Zn/Zn^{2+}} = +0.76$ V,

$\frac{2.303\ RT}{F} = 0.059$ V]

Sol. $Zn(s) + Cu^{2+}\ (0.02\ M) \longrightarrow Zn^{2+}\ (0.04\ M) + Cu(s)$

$$E^{o}_{Cell} = 0.34 - (-0.76) = 1.1\ V$$

$$E_{Cell} = -\ E^{o}_{Cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.1 - \frac{0.059}{2} \log\left(\frac{0.04}{0.02}\right) = 1.09\ V$$

Ans. **(109)**

DIFFERENT TYPES OF ELECTRODES

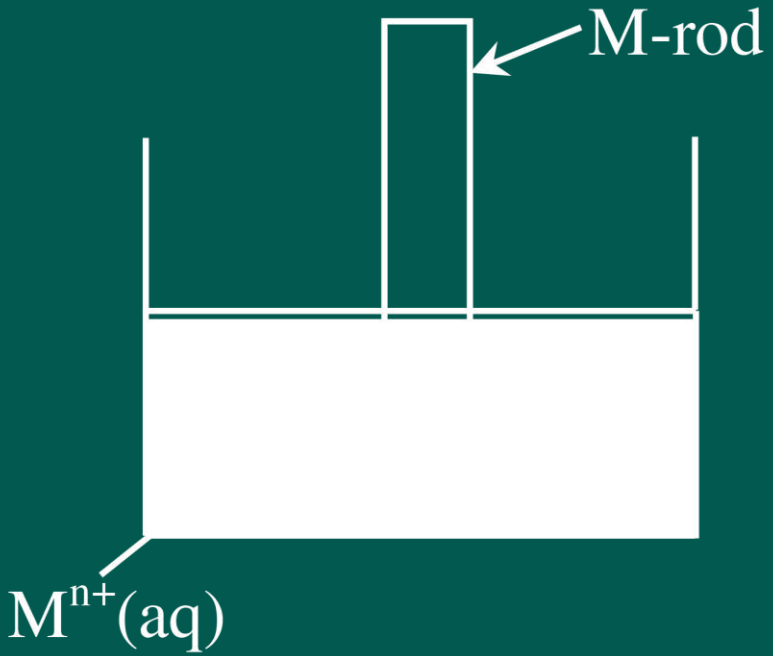
Metal - Metal ion electrode :

Metal rod is present in aqueous solution of same metal ion

Ex. - $M^{+n} | M$

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

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$



Gas - ion Electrode :

Cathode : $H^+(c) \mid H_2\,(P\text{ atm}) \mid Pt$

Cathodic reaction : $H^+\,(aq) + e^- \longrightarrow \frac{1}{2}H_2\,(P\text{ atm})$

$$E = E^o - 0.0591\log\frac{P_{H_2}^{\frac{1}{2}}}{[H^+]} = -0.0591\text{ pH}$$

$$\left[\because\ E^o_{H^+/H_2} = 0\ \&\ P_{H_2} = 1bar\right]$$

CONCENTRATION CELL

Cell consist of two electrodes which are chemically identical but have different concentration or partial pressure of gas.

$$\mathrm{Zn(s)} \mid \mathrm{ZnSO_4}\ (C_1) \parallel \mathrm{ZnSO_4}\ (C_2) \mid \mathrm{Zn(s)}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\mathrm{Zn^{2+}|Zn}} - E^{\circ}_{\mathrm{Zn^{2+}|Zn}} = 0$$

$\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}}\ (C_1) + 2e^-$ (Anodic process)

$\mathrm{Zn^{2+}}(C_2) + 2e^- \rightarrow \mathrm{Zn\ (s)}$ (Cathodic process)

$\mathrm{Zn^{2+}}(C_2) \rightarrow \mathrm{Zn^{2+}}\ (C_1)$ (Overall process)

$$E = \frac{2.303\ RT}{2F} \log \left[\frac{C_2}{C_1}\right]$$

Enqronms` mdhsx ne rt bg bdkkqd` bshnm+$B_1 = B_0$

Electrolytic conductivity

$$\kappa = \frac{1}{R}\left(\frac{\ell}{A}\right) = \frac{1}{R} \text{ (cell constant)}$$

where $\kappa = \frac{1}{\rho}$ = specific conductance or conductivity (Ω^{-1} cm^{-1})

Molar conductance (λ_m or Λ_m) :

$$\Lambda_m = \frac{\kappa}{c}$$

[SI unit : $S\ m^2\ mol^{-1}$]

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

[$S\ cm^2\ mol^{-1}$]

$1\ S\ m^2\ mol^{-1} = 10^4\ S\ cm^2\ mol^{-1}$

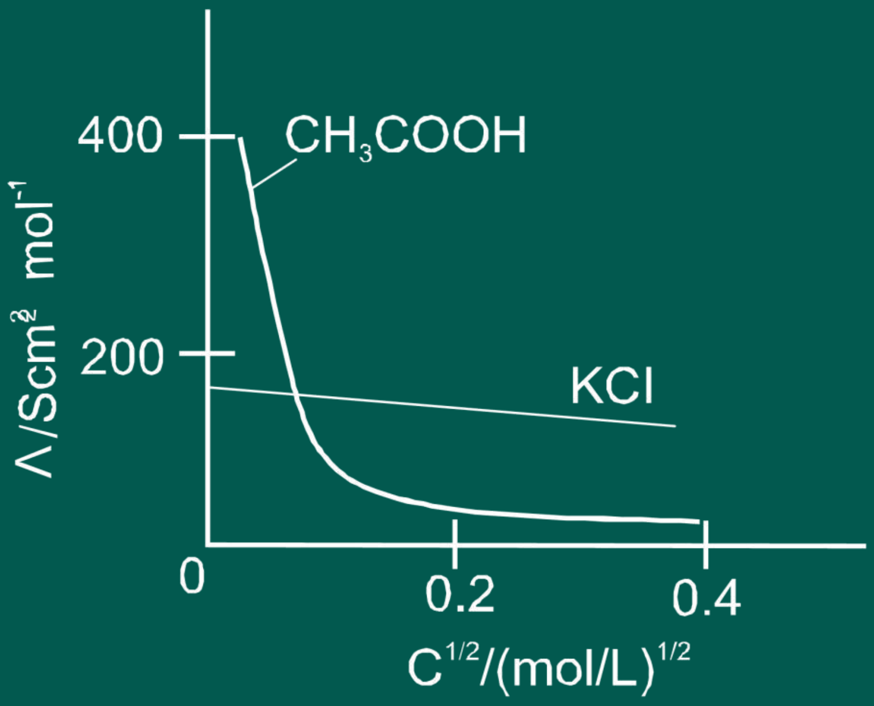
Effect of dilution on the molar conductivity & conductivity of electrolytes

- For strong electrolytes. Λ increases slowly with dilution and can be represented by the equation

$$\Lambda = \Lambda^\circ - A\, C^{1/2}$$

(Debye-Huckel equation)

- For weak electrolyte Λ increases rapidly with dilution due to increase in number of ions



Kohlrausch’s law of independent migration of ions.

“Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.’’

$$\Lambda^{\circ}_{m}\ (\mathrm{NaCl}) = \lambda^{\circ}_{\mathrm{Na}^{+}} + \lambda^{\circ}_{\mathrm{Cl}^{-}}$$

$$\Lambda^{\circ}_{m}\ (\mathrm{MgCl_2}) = \lambda^{\circ}_{\mathrm{Mg}^{2+}} + 2\lambda^{\circ}_{\mathrm{Cl}^{-}}$$

i.e., for $A_{\nu+} B_{\nu-}$ $\Lambda^{\circ}_{m} = \nu_{+}\Lambda^{\circ}_{m}(+) + \nu_{-}\Lambda^{\circ}_{m}(-)$

Applications of Kohlrausch's Law :

(i) Calculate Λ° for any electrolyte from the Λ ° of three different electrolytes

Q. Λ°_m for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S $cm^2\,mol^{-1}$ respectively. Calculate Λ° for HAc.

Sol.

$$\Lambda^\circ_{m(HAc)} = \lambda^\circ_{H^+} + \lambda^\circ_{Ac^-}$$

$$= \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{Ac^-} + \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+}$$

$$= \Lambda^\circ_{m(HCl)} + \Lambda^\circ_{m(NaAc)} - \Lambda^\circ_{m(NaCl)}$$

$= (425.9 + 91.0 - 126.4)\ \text{S cm}^2\ \text{mol}^{-1} = 390.5\ \text{S cm}^2\ \text{mol}^{-1}$.

(ii) Degree of dissociation :

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}}$$

Dissociation constant of weak electrolyte :

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{C\left(\frac{\Lambda_m}{\Lambda_m^{\circ}}\right)^2}{1-\frac{\Lambda_m}{\Lambda_m^{\circ}}} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ}(\Lambda_m^{\circ}-\Lambda_m)}$$

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

Sol. $$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{4.95 \times 10^{-5}\,S\ cm^{-1}}{0.001028\ mol\,L^{-1}} \times \frac{1000 cm^3}{L} = 48.15\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{48.15}{390.5} = 0.1233$$

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

(iii) Solubility(s) and solubility product of any sparingly soluble salt.

Sparingly soluble salt = Very small solubility

Solubility = molarity $\cong$ $s \to 0$

So, solution can be considered to be of zero conc. or infinite dilution.

$$\Lambda_m^\circ \simeq \Lambda_m = \frac{\kappa \times 1000}{s}$$

$$s = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

Ex. The specific conductance of a saturated solution of AgCl at 25°C after subtracting the specific conductance of conductivity of water is 2.28×10^{-6} mho cm^{-1}. $(\Lambda^{\infty}_{AgCl} = 138.3 \text{ mho cm}^2 \text{mol}^{-1})$ Find the solubility product of AgCl at 25°C.

Sol. $\kappa_{AgCI} = 2.28 \times 10^{-6} \text{ S cm}^{-1}$, $\quad 138.3 = \dfrac{1000 \times 2.28 \times 10^{-6}}{S}$

$S = 1.65 \times 10^{-5}$

and $\quad K_{sp} = (S)^2 = 2.72 \times 10^{-10} \text{ M}^2$.

Ans. 2.72×10^{-10} (mole/litre)^2.

Ex. Given that : $E^{o}_{O_2/H_2O} = +1.23V$, $E^{o}_{S_2O_8^{2-}/SO_4^{2-}} = +2.05V$

$E^{o}_{Br_2/Br^-} = +1.09V$ $E^{o}_{Au^{3+}/Au} = +1.4V$

The strongest oxidizing agent is –

[JEE-MAINS (ONLINE) APRIL. 2019]

(1) O_2 (2) Br_2 (3) $S_2O_8^{2-}$ (4) Au^{3+}

Sol. For strongest oxidising agent, standard reduction potential should be highest.

Correct option : (3)

Ex. If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction at 300 K is approximately.

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ **[JEE-Mains Jan. 2019]**

$(R = 8\ JK^{-1}\ mol^{-1},\ F = 96000\ C\ mol^{-1})$

(1) e^{160} (2) e^{320} (3) e^{-160} (4) e^{-80}

Sol. $\Delta G° = - RT\ lnk = - nFE°_{cell}$

$$\ln K = \frac{n \times F \times E^{o}}{R \times T} = \frac{2 \times 96000 \times 2}{8 \times 300} = 160$$

$K = e^{160}$

Ans. **(1)**

Ex. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are – 0.76, – 0.23 and –0.44 V respectively. The reaction

$X + Y^{2+} \rightarrow X^{2+} + Y$ will be spontaneous, when :

[JEE-Main 2012, 4/120]

(1) X = Ni, Y = Fe
(2) X = Ni, Y = Zn
(3) X= Fe, Y = Zn
(4) X= Zn, Y = Ni

Sol. $X + Y^{2+} \longrightarrow X^{2+} + Y$

For reaction to be spontaneous E° must be positive.

$$E^\circ_{Ni^{2+}/Ni} - E^\circ_{Zn/Zn^{+2}} = (-0.23) - (-0.76) = +0.53 \text{ (positive)}$$

Ans. (4)

Ex. Given : $E^{\circ}_{Cr^{3+}/Cr} = -0.74\ V$; $E^{\circ}_{MnO_4^-/Mn^{2+}} = 1.51\ V$

$E^{\circ}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V$; $E^{\circ}_{Cl/Cl^-} = 1.36\ V$

Based on the data given above, strongest oxidising agent will be :

[JEE(Main) 2013, 4/120]

(1) Cl (2) Cr^{3+} (3) Mn^{2+} (4) MnO^{4-}

Sol. Higher the SRP, better is oxidising agent

Hence MnO_4^- is strongest oxidising agent

Ans. (4)

Ex. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is :

[JEE(Main) 2014, 4/120]

(1) 5×10^{-4} (2) 5×10^{-3}

(3) 5×10^{3} (4) 5×10^{2}

Sol. $\kappa = 1.4\ \text{S m}^{-1}$ $R = 50\ \Omega$ Molarity = 0.2

$$\kappa = \frac{1}{R} \times \frac{\ell}{A}$$

$$\frac{\ell}{A} \Rightarrow = 1.4 \times 50\ \text{m}^{-1}.$$

Now, new solution has Molarity = 0.5, $R = 280\ \Omega$

$$\Rightarrow \kappa = \frac{1}{R} \times \frac{\ell}{A} = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4}\ \text{S m}^{-1}$$

$$\Rightarrow \Lambda_M = \frac{\kappa}{M \text{ in mol m}^{-3}} = \frac{\frac{1}{4}}{1000 \times 0.5} = \frac{1}{2000} = 5 \times 10^{-4}$$

Ans. (1)

Ex. The equation that is incorrect is :

(1) $\left(\Lambda_m^\circ\right)_{NaBr} - \left(\Lambda_m^\circ\right)_{NaI} = \left(\Lambda_m^\circ\right)_{KBr} - \left(\Lambda_m^\circ\right)_{NaBr}$

(2) $\left(\Lambda_m^\circ\right)_{H_2O} = \left(\Lambda_m^\circ\right)_{HCl} + \left(\Lambda_m^\circ\right)_{NaOH} - \left(\Lambda_m^\circ\right)_{NaCl}$

(3) $\left(\Lambda_m^\circ\right)_{KCl} - \left(\Lambda_m^\circ\right)_{NaCl} = \left(\Lambda_m^\circ\right)_{KBr} - \left(\Lambda_m^\circ\right)_{NaBr}$

(4) $\left(\Lambda_m^\circ\right)_{NaBr} - \left(\Lambda_m^\circ\right)_{NaCl} = \left(\Lambda_m^\circ\right)_{KBr} - \left(\Lambda_m^\circ\right)_{KCl}$

[JEE-MAINS (ONLINE) JAN. 2020]

Sol. According to Kohlrausch's law correct expression is

$$\left(\Lambda_m^\circ\right)_{NaBr}-\left(\Lambda_m^\circ\right)_{NaI}=\left(\Lambda_m^\circ\right)_{KBr}-\left(\Lambda_m^\circ\right)_{KI}$$

Option (1) is incorrect.

The other statements are correct.

IONIC EQUILIBRIUM

Properties of Water :

Water acts as an acid as well as base according to Arrhenius & Bronsted - Lowry theory, but according to Lewis concept it is a base, not an acid.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$K_w = [H^+]\,[OH^-] = 10^{-14}$ at 25°C $\quad\quad \therefore\ pK_w = 14$

Dissociation of water is endothermic, so as T ↑ +

K_w ↑, ZG*\ ↑, ZNG$^-$\ ↑, pH ↓, p0H ↓

pH calculation :

(1) Mixture of SA & SB

Q. Calculate the pH of the resulting solution formed by mixing 20 mL of 0.2 M $Ba(OH)_2$ & 30 mL of 0.1 M HCl at 25°C.

Sol. Millimoles of $OH^- = 20 \times 0.2 \times 2 = 8$.

Millimoles of $H^+ = 30 \times 0.1 \times 1 = 3$

$\therefore$ Millimoles of OH^- left $= 8 - 3 = 5$

$$\therefore \quad [OH^-] = \frac{5}{50} = \frac{1}{10} \text{ M.}$$

$\therefore$ pOH = log 10 = 1. $\therefore$ pH = 13.

Ans. 13

(2) pH of Salt of WASB (Eg. CH_3COONa)
&
Salt of SAWB (Eg. NH_4Cl)

Types of salt	**Expression for pH**
(i) Salt of weak acid and strong base	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$
(ii) Salt of strong acid and weak base	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$

Q. The pH values order of 0.1 M solution of each of the following is :
HCOONa (I), HCOOH (II), CH_3COONH_4(III), NaOH (IV), HCl (V)

Sol.
HCOONa (I) - Salt of WASB
HCOOH (II) - Weak acid
CH_3COONH_4(III) - Salt of WAWB
NaOH (IV) - Strong base
HCl (V) - Strong acid

Order of pH :

(V) < (II) < (III) < (I) < (IV)

Buffer Solutions

Buffer solutions are those solutions which resist the change in pH upon addition of small amount of acid or base.

There are various types of buffers :

(i) Acidic buffer : Buffer of a weak acid and its salt with a strong base.

Eg. CH_3COOH & CH_3COONa

(ii) Basic buffer : Buffer of a weak base and its salt with a strong acid.

Eg. NH_4OH & NH_4Cl

pH of Buffer Solution

$$\text{Acidic buffer, pH} = \text{p}K_a + \log \frac{[\text{Anion of Salt}]}{[\text{Acid}]}$$

$$\text{Basic buffer, pOH} = \text{p}K_b + \log \frac{[\text{Cation of Salt}]}{[\text{Base}]}$$

Q. An acidic buffer is obtained on mixing :

(1) 100 mL of 0.1 M CH_3COOH and 200 mL of 0.1 M NaOH

(2) 100 mL of 0.1 M CH_3COOH and 100 mL of 0.1 M NaOH

(3) 100 mL of 0.1 M HCl and 200 mL of 0.1 M CH_3COONa

(4) 100 mL of 0.1 M HCl and 200 mL of 0.1 M NaCl

Solution

	CH_3COOH	+	$NaOH$	$\rightarrow$	CH_3COONa	+	H_2O
(1) i	$100 \times 0.1 = 10$ mm		$200 \times 0.1 = 20$ mm				
f	0		10 mm		10 mm		

$$\therefore [OH^-] = \frac{10}{300} M$$

	CH_3COOH	+	$NaOH$	$\rightarrow$	CH_3COONa	+	H_2O
(2) i	$100 \times 0.1 = 10$ mm		$100 \times 0.1 = 10$ mm				
f	0		0		10 mm		

$$\therefore [CH_3COONa] = \frac{10}{200} = c \Rightarrow pH = \frac{1}{2}(pK_w + pK_a + \log c)$$

$$\begin{array}{lccccccc}
(3) & CH_3COONa & + & HCl & \rightarrow & CH_3COOH & + & NaCl \\
i & 200 \times 0.1 = 20\ mm & & 100 \times 0.1 = 10\ mm & & & & \\
f & 10\ mm & & 0 & & 10\ mm & &
\end{array}$$

$\therefore$ mixture of weak acid & its conjugate base $\Rightarrow$ acidic buffer

$$\Rightarrow pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log \frac{10/300}{10/300} = pK_a$$

(4) 100 mL of 0.1 M HCl and 200 mL of 0.1 M NaCl

$\Rightarrow$ No reaction

$$\therefore [H^+] = \frac{10}{300} M$$

Q. 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is :
[pK_b of $NH_4OH = 4.7$]

(1) 9.4 (2) 5.0 (3) 9.0 (4) 5.2

Sol. 20 ml, 0.1 M $H_2SO_4 \Rightarrow n_{H^+} = 4$

30 ml, 0.2 M $NH_4OH \Rightarrow n_{NH_4OH} = 6$

$$\begin{array}{lccccc} & NH_4OH & + \; H^+ & \rightleftharpoons & NH_4^{\oplus} & + \; H_2O \\ mm_i & 6 & 4 & & 0 & \\ mm_f & 2 & 0 & & 4 & \end{array}$$

Solution is basic buffer. So, $pOH = pK_b + \log \dfrac{NH_4^+}{NH_4OH}$

$= 4.7 + \log 2$

$= 4.7 + 0.3 = 5$

So, $pH = 14 - 5 = 9$ Ans. (3)

Solubility Product (K_{sp})

Solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of ions given by the dissociation of electrolyte at a given temperature when the solution is saturated.

	$A_xB_y(s)$	$\rightleftharpoons$	$xA^{+y}(aq)$	$+$	$yB^{-x}(aq)$
C_{eq}	Let solubility be S mol/L		xS		yS

$$K_{sp} = [A^{+y}]^x\,[B^{-x}]^y = (xS)^x\,(yS)^y = x^x.\,y^y.\,S^{x+y}$$

Eg. For AB type salt, $K_{sp} = S^2$

For AB_2 type salt, $K_{sp} = 4S^3$

Q. The K_{sp} for the following dissociation is 1.6×10^{-5}

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

Which of the following choices is correct for a mixture of 300 mL 0.134 M $Pb(NO_3)_2$ and 100 mL 0.4 M NaCl ?

(1) $Q < K_{sp}$

(2) $Q > K_{sp}$

(3) $Q = K_{sp}$

(4) Not enough data provided

Sol. New concentration after mixing :

$$[Pb(NO_3)_2] = \frac{300 \times 0.134}{400}$$

$$[NaCl] = \frac{100 \times 0.4}{400}$$

$$Q = [Pb^{2+}]\,[Cl^-]^2$$

$$= \frac{300 \times 0.134}{400} \times \left(\frac{100 \times 0.4}{400}\right)^2$$

$= 1.05 \times 10^{-3}$. So, $Q > K_{sp}$

$\Rightarrow$ Precipitation will occur.

Ans. (2)

Q. The solubility product of PbI_2 is 8.0×10^{-9}. The solubility of lead iodide in 0.1 molar solution of lead nitrate is $x \times 10^{-6}$ mol/L. The value of x is __________. $\left[\text{Given} : \sqrt{2} = 1.41\right]$

(Rounded off to the nearest integer)

Concept : Solubility in presence of common ions

Solution

$$\begin{array}{lllll} & Pb(NO_3)_2 & \rightarrow & Pb^{2+} + & 2NO_3^- \\ C_f & & & 0.1 & 2 \times 0.1 \end{array}$$

$$\begin{array}{llllll} & PbI_2 & \rightleftharpoons & Pb^{2+} & + & 2I^- \\ C_f & \text{Let solubility be s mol/L} & & s + 0.1 & & 2s \end{array}$$

$$K_{sp}(PbI_2) = (s + 0.1)(2s)^2$$

$$8 \times 10^{-9} = 0.1 \times 4s^2$$

$$\therefore\ s = 1.414 \times 10^{-4} = 141.4 \times 10^{-6} \text{ mol/L} \Rightarrow x = 141$$

Key Point to Remember

The solubility of salts of weak acids like cyanides, phosphates etc. increases at lower pH. This is because at lower pH, the concentration of the anion decreases due to its protonation, making the solubility equilibrium shift forward.

Solubility of such a salt MX in a solution (having [H^+]) is given by :

$$S = \left[\frac{K_{sp}([H^+] + K_a)}{K_a} \right]^{1/2}$$

THERMODYNAMICS
&
THERMOCHEMISTRY

Frequently Asked Concepts in JEE Main & JEE Advanced :

In First law of thermodynamics

- Calculation of work (w)
- Calculation of work (w) by graph
- Calculation of ΔU
- Calculation of ΔH

Calculation of work (w)

$$w = -\int_{V_1}^{V_2} P_{ext}\,dv$$

In reversible process

$(P_{gas} \approx P_{ext})$

$w = -\int_{V_1}^{V_2} P\,dv$

In irreversible process

$(P_{ext} = \text{constant})$

$w = -P_{ext}(V_2 - V_1)$

- Reversible isothermal process for an ideal gas

$$w = -nRT\ell n\left(\frac{V_2}{V_1}\right)$$

$$= -nRT\ell n\left(\frac{P_1}{P_2}\right)$$

- Polytropic process for an ideal gas

$PV^x = \text{constant}$

$$w = \frac{P_2V_2 - P_1V_1}{(x-1)}$$

Irreversible isothermal process for an ideal gas

$$w = -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

Question :

At 25°C, 50 g of iron reacts with HCl to form $FeCl_2$. The evolved hydrogen gas expands against a constant pressure of 1 bar. The work done by the gas during this expansion is _______ J. (Round off to the Nearest Integer)
[Given : R = 8.314 J mol^{-1} K^{-1}. Assume, hydrogen is an ideal gas]
[Atomic mass off Fe is 55.85 u] **[JEE(Main) 2021 Online March 4/120]**

Solution :

$Fe + 2HCl \longrightarrow FeCl_2 + H_2$

$W = -P_{ext}(V_2 - V_1)$

$V_1 << V_2$ (So V_1 can be neglected in comparison to V_2)

$$= -nRT$$

$$= -\frac{50}{55.85} \times 8.314 \times 298$$

$$= -2218.05 \text{ J}$$

Ans. 2218

Calculation of work (w) by P v/s V graph

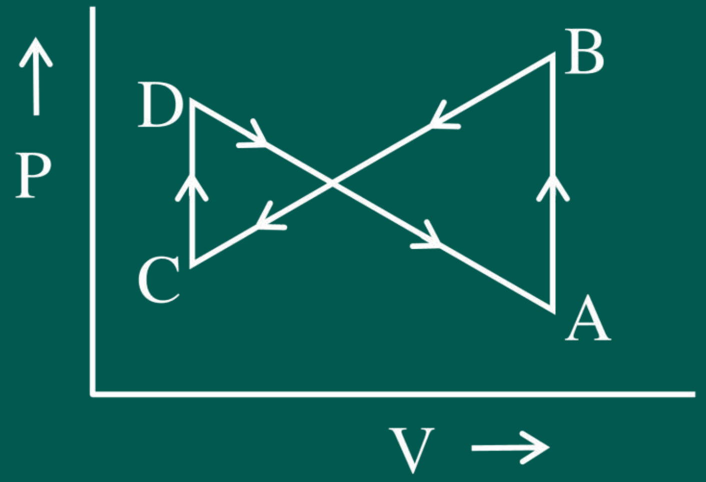
$|w|$ = Area under the curve on P-V diagram

$|w_{\text{cycle}}|$ = Area of cycle

$$\left\{ \begin{array}{l} \text{If cycle is anticlockwise put '+' sign} \\ \text{If cycle is clockwise put '–' sign} \end{array} \right\}$$

Question :

Net work done during the following cyclic process ABCDA is :



(1) Zero

(2) Positive

(3) Negative

(4) Can’t be predicted

Calculation of ΔU

For ideal gas during any process & for other substances during isochoric process

$dU = nC_{V,\,m}\,dT$

$\Delta U = nC_{V,\,m}\,\Delta T$ (If $C_{V,\,m}$ is a constant)

For ideal gas, if T is constant,

U is constant, $\Delta U = 0$

First law of Thermodynamics

$\Delta U = q + w$

- At constant volume

$$w = 0$$
$$\Delta U = q_V$$

Q. Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero) **[JEE(Main) 2019 Online April. 4/120]**

(1) Cyclic process : $q = -w$

(2) Isothermal process : $q = -w$

(3) Adiabatic process : $\Delta U = -w$

(4) Isochoric process : $\Delta U = q$

Ans. (3)

Enthalpy (H)

$H = U + PV$

- **Calculation of ΔH**

$\Delta H = \Delta U + \Delta(PV)$

- For ideal gas during any process & for other substances during isobaric process

$dH = nC_{P,\,m}\, dT$

$\Delta H = nC_{P,\,m}\, \Delta T$ (If $C_{P,\,m}$ is a constant)

For ideal gas, if T is constant,

H is constant, $\Delta H = 0$

Frequently Asked Concepts in JEE Main & JEE Advanced :

In Second law of thermodynamics

- Calculation of ΔS_{system}
- Calculation of $\Delta S_{surrounding}$
- Calculation of ΔG by ΔH & ΔS
- Prediction of spontaneity

Second law of Thermodynamics :

Entropy of the universe is constantly increasing.

$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ for a spontaneous process.

Where **(S)** = entropy is the measure of randomness or disorder.

It is a state function and extensive property.

It can be determined exactly.

- $S_{\text{solid}} < S_{\text{liq.}} < S_{\text{gas}}$

Question :

For which of the following processes, ΔS is negative ?

[JEE(Main) 2018 Online (16-04-18), 4/120]

(1) C(diamond) $\rightarrow$ C(graphite)

(2) $N_2(g, 1\text{ atm}) \rightarrow N_2(g, 5\text{ atm})$

(3) $N_2(g, 273\text{ K}) \rightarrow N_2(g, 300\text{ K})$

(4) $H_2(g) \rightarrow 2H(g)$

Sol.

Entropy (graphite > diamond)

$N_2(g, 1\text{ atm}) \rightarrow N_2(g, 5\text{ atm})$ as pressure increases $\Rightarrow$ Volume decreases

$\Rightarrow$ Entropy decreases

Mathematically

$$dS = \frac{dq_{rev}}{T} \quad \text{or} \quad \Delta S = \int \frac{dq_{rev}}{T}$$

$$dS \propto dq_{rev}\ , \quad dS \propto \frac{1}{T}$$

At Higher T - entropy is already high. Therefore, heat addition will not introduce much change in the entropy.

Calculation of ΔS_{system}

$$\Delta S_{irrev} = \Delta S_{rev,\ system} = \int_A^B \frac{dq_{rev}}{T} \text{ rev path.}$$

- For ideal gas

$$\Delta S_{system} = nC_V \ell n\frac{T_2}{T_1} + nR\ell n\,\frac{V_2}{V_1}$$

$$= nC_P \ell n\frac{T_2}{T_1} + nR\ell n\,\frac{P_1}{P_2}$$

- **For solid or liquid system**

$$\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{\text{msdT}}{T} = \text{ms}\ell\text{n}\,\frac{T_2}{T_1}$$

- **For phase transition**

Reversible phase transition occur at constant pressure and temperature

$$\Delta S_{\text{fus.}} = \frac{\Delta H_{\text{fus}}}{T_{\text{M.Pt.}}} \qquad \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{B.Pt.}}}$$

Calculation of $\Delta S_{\text{surrounding}}$

$$\boxed{\Delta S_{\text{surr.}} = -\frac{q_{\text{process}}}{T_{\text{surr.}}}}$$

In reversible process

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{system}}$$

In irreversible process

$$\Delta S_{\text{surr.}} = -\frac{q_{\text{irr.}}}{T_{\text{surr.}}}$$

Gibb’s free energy (G) :

A system parameter to predict the spontaneity of chemical reaction was introduced by Gibb’s so that entropy calculation for the surrounding need not be carried out.

$$G = H - TS$$

$$\boxed{(\Delta G_{\text{system}})_{T,\,P} = -\,T\Delta S_{\text{universe}}}$$

New criteria of spontaneity :

(i) If ΔG_{system} is (–ve) < 0 ⇒ process is spontaneous

(ii) If ΔG_{system} is > 0 ⇒ process is non-spontaneous

(iii) If $\Delta G_{\text{system}} = 0$ ⇒ system is at equilibrium

Question :

A process has $\Delta H = 200\ \text{Jmol}^{-1}$ and $\Delta S = 40\ \text{JK}^{-1}\text{mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous : **[JEE(Main) 2019 Online Jan. 4/120]**

(1) 5 K
(2) 4 K
(3) 20 K
(4) 12 K

Sol. for spontaneous process, $\Delta G < 0$

$\Rightarrow \Delta H - T\Delta S < 0$

$\Rightarrow 200 - T \times 40 < 0$

$\Rightarrow T > 5K$

ΔG^{o} = standard free energy change :

(At standard condition : P = 1 bar and T = any fixed temp.)

When the reactants under standard conditions gets converted into products which is also under standard condition, then the free energy change is known as ΔG^{o} (it is a constant) for 1 mole at 1 bar.

At standard conditions :

$$\Delta G^{\circ} = \Delta H^{o} - T\Delta S^{o}$$

$$= \text{constant for a given reaction at constant temp.}$$

- ΔG_f^0 (elements in their standard states) = 0
- $\Delta G^o_{\text{reaction}} = \sum \Delta G^0_{\text{f,product}} - \sum \Delta G^0_{\text{f,reactant}}$

- **For a reaction in progress**

  $\Delta G = \Delta G^o + RT\ \ell n\ Q$

  Q is thermodynamic reaction quotient.

  $\Delta G > 0$ backward is feasible,

  $\Delta G < 0$ forward is feasible
- At equilibrium $\Delta G = 0$ $\quad \therefore\ Q = K$ (thermodynamic equilibrium const.)

  $\therefore \quad \Delta G^o = -RT\ \ell n\ K$

Question :

$\Delta_f G°$ at 500 K for substance ‘S’ in liquid state and gaseous state are +100.7 kcal mol^{-1} and +103 kcal mol^{-1}, respectively. Vapour pressure of liquid ‘S’ at 500 K is approximately equal to : (R = 2 cal K^{-1} mol^{-1})

[JEE(Main) 2018 Online (15-04-18), 4/120]

(1) 0.1 atm (2) 1 atm (3) 10 (4) 100 atm

Sol. $S(\ell) \rightleftharpoons S(v)$

$\Delta G° = \Delta G°_f S(v) - \Delta G°_f S(l) = 103 - 100.7 = 2.3\text{Kcal/mole}$

$\Delta G° = -RT \times 2.3\log(K_P)$

$\Rightarrow 2.3 \times 1000 = -2 \times 500 \times 2.3 \log(K_P) \Rightarrow K_P = .1$

at equilibrium $K_P = P_{S(v)}|_{eq} = V.P = 0.1\text{atm}$

Frequently Asked Concepts in JEE Main & JEE Advanced :

In Thermochemistry

- Relation between ΔH and ΔU for a reaction
- Standard enthalpy of formation (ΔH_f^o)
- Standard enthalpy of combustion (ΔH_c^o)
- Bond energy
- Standard enthalpy of neutralisation

Relation between ΔH and ΔU for a reaction :

$$\Delta_r H = \Delta_r U + (\Delta v_g)RT$$

where $\Delta v_g = \Sigma$ stoichiometric coeff. of gaseous products

$- \ \Sigma$ stoichiometric coeff. of gaseous products

Eg. $2A(g) + B(\ell) \longrightarrow 3C(g)$

$\Delta v_g = 1$

Question :

For a reaction, $A(g) \rightarrow A(l)$; $\Delta H = -3RT$. The correct statement for the reaction is :

[JEE(Main) 2017 Online (08-04-17), 4/120]

(1) $\Delta H = \Delta U \neq O$

(2) $|\Delta H| > |\Delta U|$

(3) $|\Delta H| < |\Delta U|$

(4) $\Delta H = |\Delta U| = O$

Sol. $(\Delta n)_{(g)} = -1$

$\Delta H = \Delta U + (\Delta n)_{(g)}RT$

$\Rightarrow -3RT = \Delta U - RT$

$\Rightarrow \Delta U = -2RT$

Kirchoff's equation (Variation of ΔH^o with temperature)

$$\Delta H_2^\circ = \Delta H_1^\circ + \int \Delta C_P.dT$$

$$\frac{\Delta H_2^o - \Delta H_1^o}{T_2 - T_1} = (\Delta C_P)_r$$ (If C_P is constant)

Standard enthalpy of formation (ΔH_f^o)

- "The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value". The specified temperature is usually taken as 25°C.

A few examples are

ΔH_f° (O_2 , g) = 0

ΔH_f° (C, graphite) = 0

ΔH_f° (C, diamond) $\neq 0$

ΔH_f° (Br_2, liquid) = 0

ΔH_f° (S, rhombic) = 0

ΔH_f° (S, monoclinic) $\neq 0$

ΔH_f° (P, white) = 0

ΔH_f° (P, black) $\neq 0$

- "The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation".

Enthalpy of formation of HBr(g) :

$$\frac{1}{2}H_2\,(g) + \frac{1}{2}Br_2\,(\ell) \rightarrow HBr(g)$$

$$\Delta H_f^\circ(HBr,\ g) = H_m^0\,(HBr,\ g) - \frac{1}{2}\,H_m^0\,(H_2,\ g)\ -\ \frac{1}{2}\,H_m^0\,(Br_2,\ell)$$

Question :

Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. **[JEE(Advanced) 2019]**

(A) $\frac{3}{2}O_2(g) \rightarrow O_3(g)$

(B) $\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$

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

(D) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

Sol.

Enthalpy of formation is defined as enthalpy change for formation of 1 mole of substance from its elements, present in their natural most stable form.

Ans. **(A, B)**

Standard Enthalpy of Combustion (ΔH_C^o) :

- It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.

$$CH_4\,(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O\,(\ell) \qquad \Delta H^\circ = -\,890\ \text{kJ mol}^{-1}$$

Bond Enthalpies :

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state.

$H_2(g) \rightarrow 2H(g) \qquad \Delta H° = B.E_{H-H}$

$H-Cl(g) \rightarrow H(g) + Cl(g) \qquad \Delta H° = B.E_{H-Cl}$

Determination of standard enthalpy of a reaction (ΔH_r^o)

(i) Standard enthalpy of formation (ΔH_f^o)

$$\Delta H_r^\circ = \Sigma\, \nu_B\, \Delta H_f^\circ{}_{,\text{products}} - \Sigma\, \nu_B\, \Delta H_f^\circ{}_{,\text{reactants}}$$

ν_B is the stoichiometric coefficient

Determination of standard enthalpy of a reaction (ΔH_r^o)

(ii) Standard Enthalpy of Combustion (ΔH_C^o)

$$\Delta H_r^\circ = \Sigma\, \nu_B\, \Delta H_C^\circ,_{\text{reactants}} - \Sigma\, \nu_B\, \Delta H_C^\circ,_{\text{products}}$$

ν_B is the stoichiometric coefficient

Question :

The standard heat of formation ($\Delta_f H^0_{298}$) of ethane in (kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are –1560, –393.5 and –286 kJ/mol, respectively is ________. **[JEE(Main) 2020 Online Jan. 4/100]**

Sol. $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$

$\Delta H = 2\Delta H_C C(s) + 3\Delta H_C(H_2) - \Delta H_C(C_2H_6)$

$= (-286) + 3(-393.5) - (-1560)$

$= -1925$ kJ/mol

Determination of standard enthalpy of a reaction (ΔH_r^o)

(iii) Bond energy

$$\Delta H_r^o = \begin{pmatrix}\text{Enthalpy required to break reactants} \\ \text{into gasesous atoms}\end{pmatrix} - \begin{pmatrix}\text{Enthalpy released to form products} \\ \text{from the gasesous atoms}\end{pmatrix}$$

Question :

For the reaction

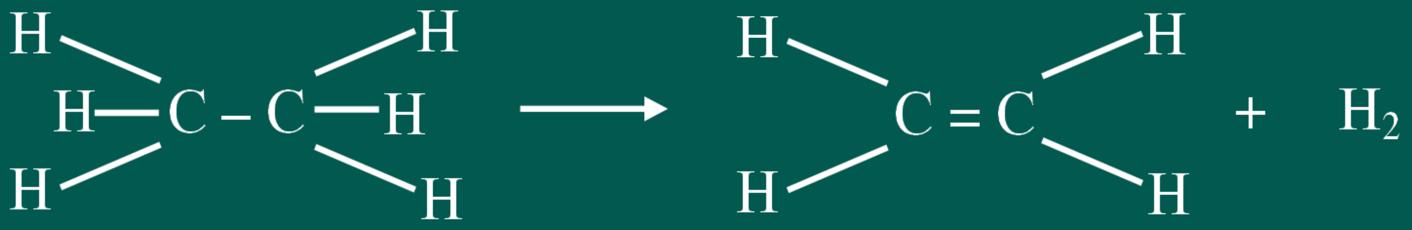
$C_2H_6 \rightarrow C_2H_4 + H_2$

the reaction enthalpy $\Delta_r H$ = ______ kJ mol^{-1}.

(Round off to the Nearest Integer).

[Given: Bond enthalpies in kJ mol^{-1} : C–C : 347, C=C : 611; C–H : 414, H–H : 436]

Sol.



$$\Delta_r H = [E_{C-C} + 6E_{C-H}] - [E_{C=C} + 4\,E_{C-H} + E_{H-H}]$$

$$= E_{C-C} + 2E_{C-H} - E_{C=C} - E_{H-H}$$

$$= 347 + 2(414) - 611 - 436$$

$$= 128 \text{ KJ/mol}$$

Standard Enthalpy of Neutralization :

- The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) \qquad \Delta H = -57.1\ \text{kJ/mole} = -13.7\ \text{kcal/mol}$$

Remember :

- For **Strong Acid + Strong Base**, heat of neutralisation is always equal to –13.7 kcal/mole or –57.1 kJ/mole.
- For any other combination of **acid and base** this heat is less than –13.7 kcal/mole or –57.1 kJ/mole.

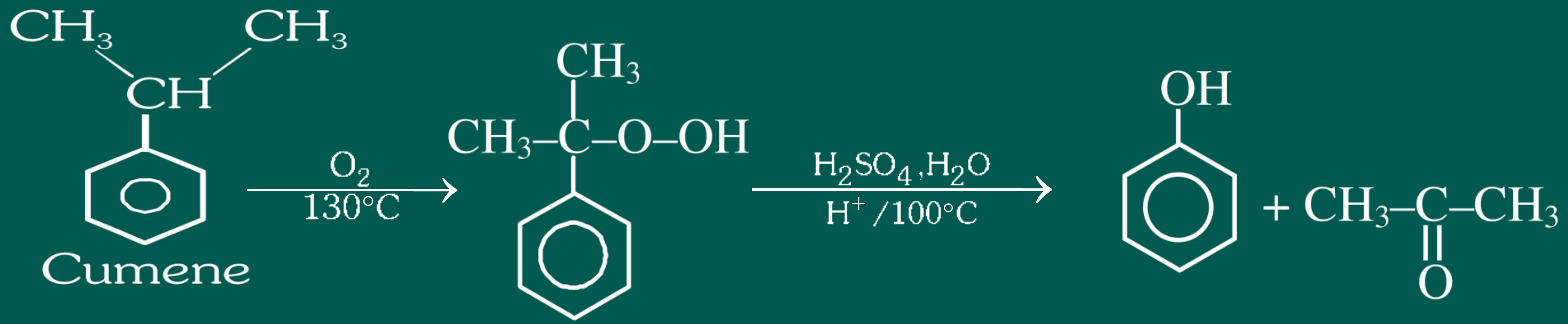
AROMATIC COMPOUNDS

PHENOL

Method of Preparation

(I) From cumene (Isopropyl benzene) :

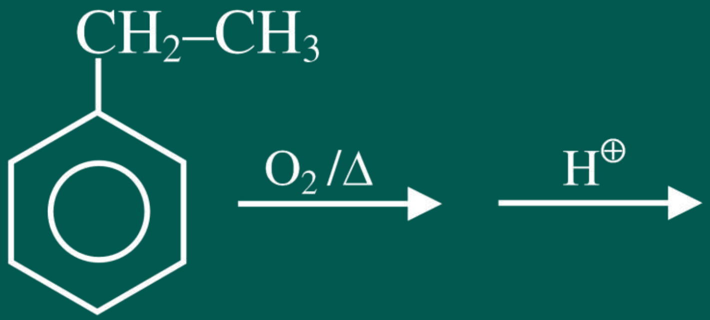
Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.



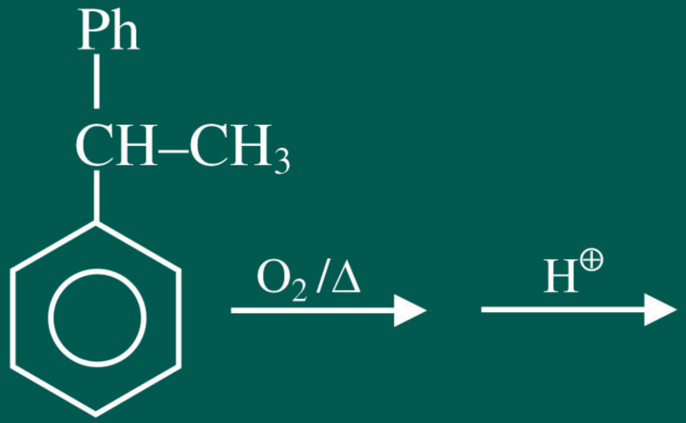
Note : Migration order is as follows :

$$\boxed{-H > -Ph - R}$$

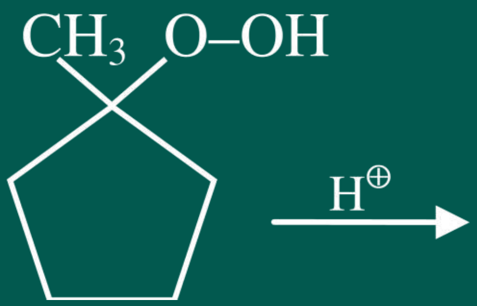
Q.1



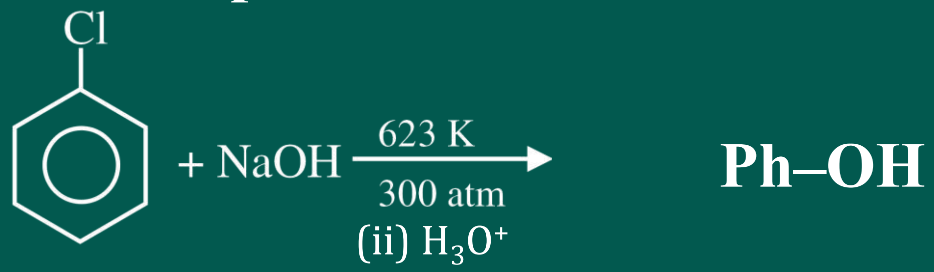
Q.2



Q.3



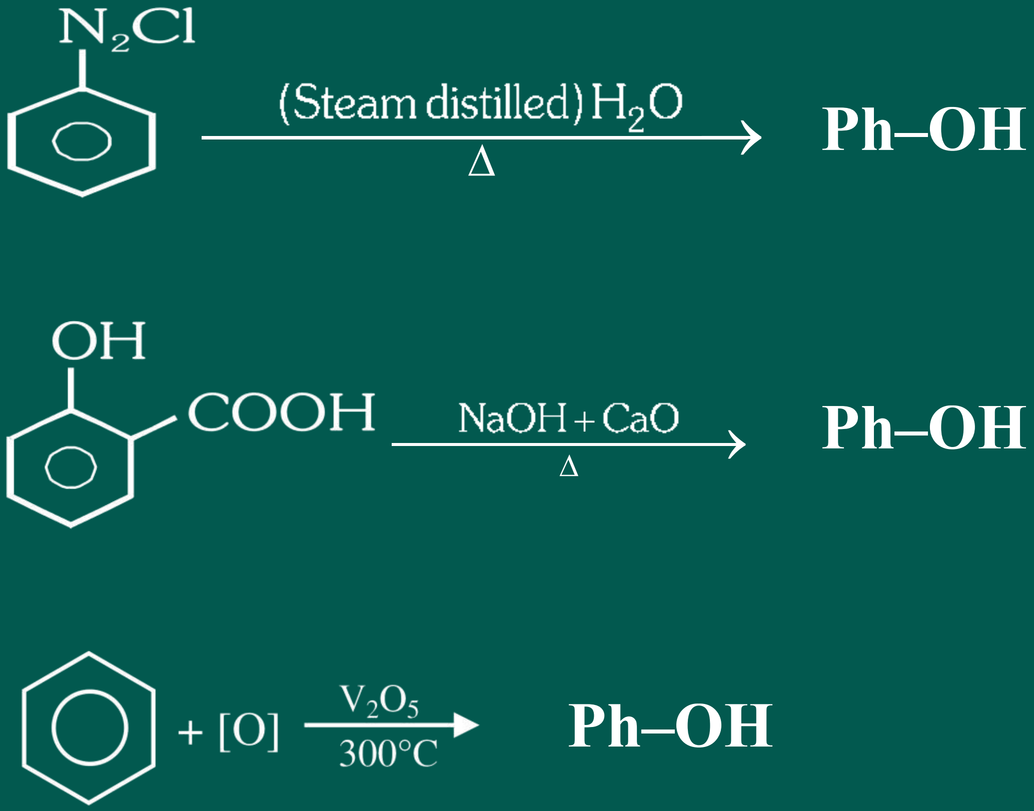
(II) Other Preparation of Phenol other



$$C_6H_5Cl + NaOH \xrightarrow[\text{300 atm} \\ \text{(ii) } H_3O^+]{\text{623 K}} \textbf{Ph–OH}$$

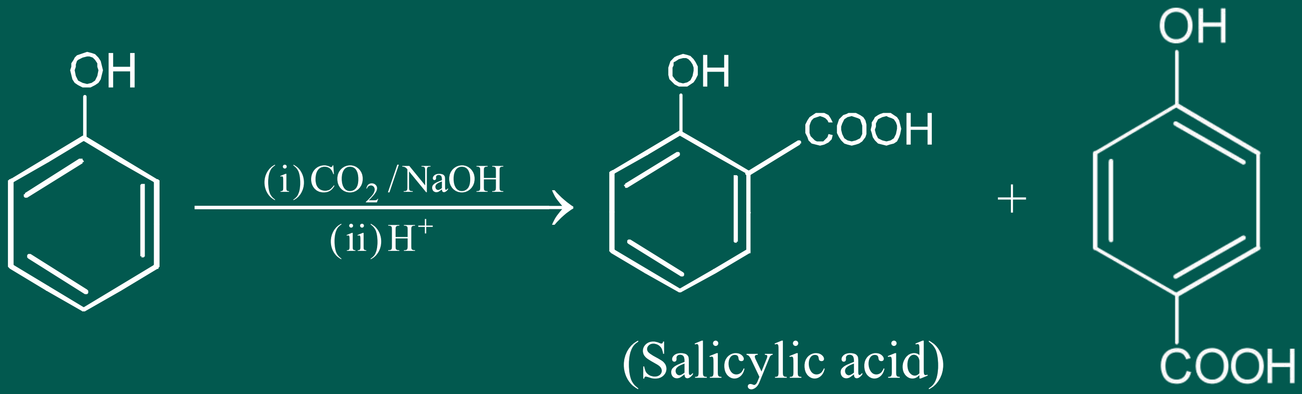
$$C_6H_5SO_3Na \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) NaOH}} \textbf{Ph–OH}$$

$$C_6H_5MgBr \xrightarrow{O_2} 2Ph-O-MgBr \xrightarrow{NH_4Cl} \textbf{Ph–OH}$$


N2Cl
(Steam distilled) H2O
Δ
Ph–OH
OH
COOH
NaOH + CaO
Δ
Ph–OH
+ [O]
V2O5
300°C
Ph–OH

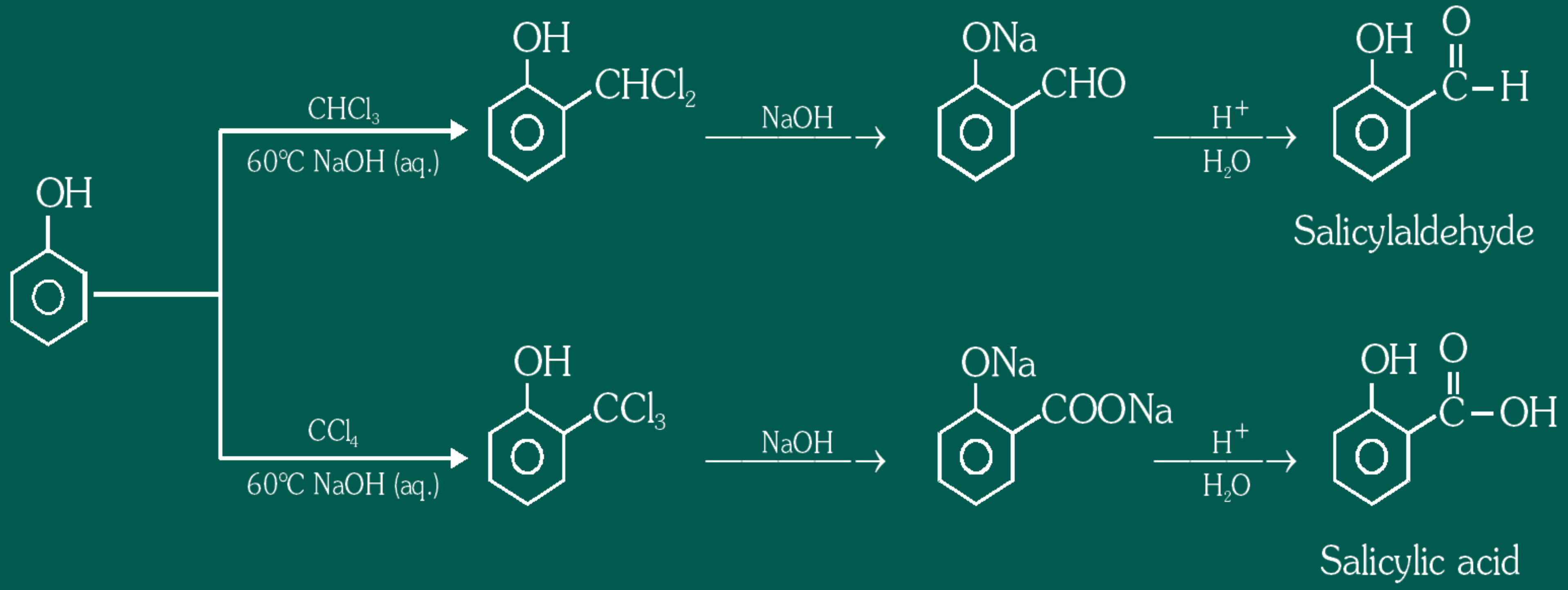
Chemical Reaction of Phenol :

(I) Kolbe Schmidt Reaction :

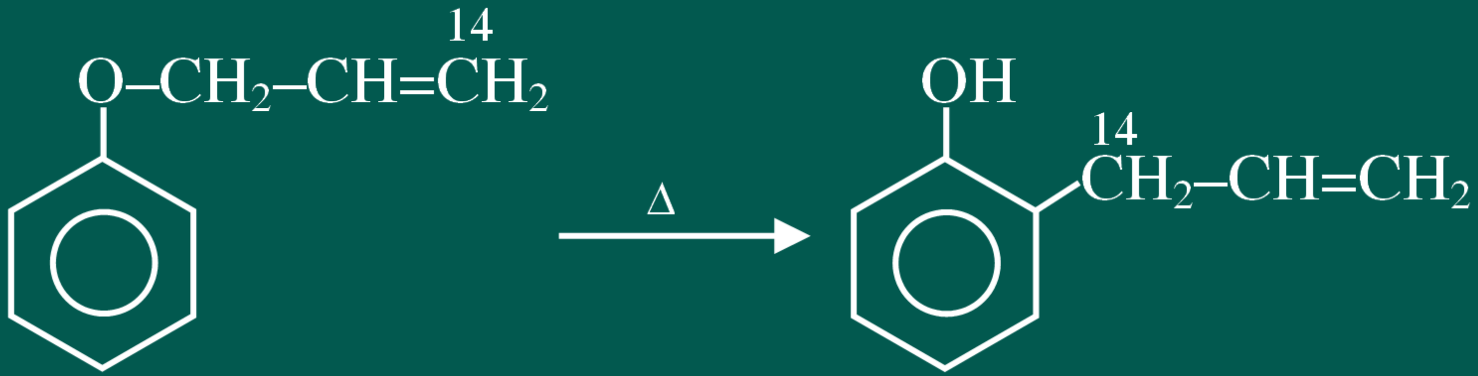


(Salicylic acid)

(II) Reimer – Tiemann Reaction :

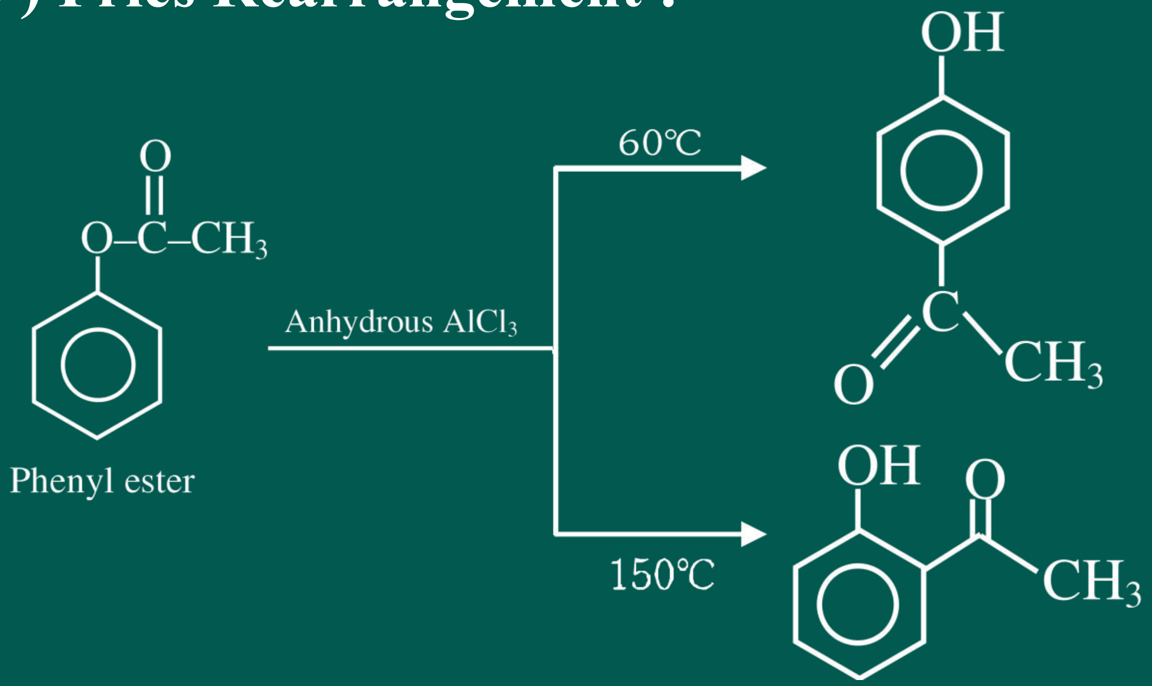


(III) Claisen Rearrangement :



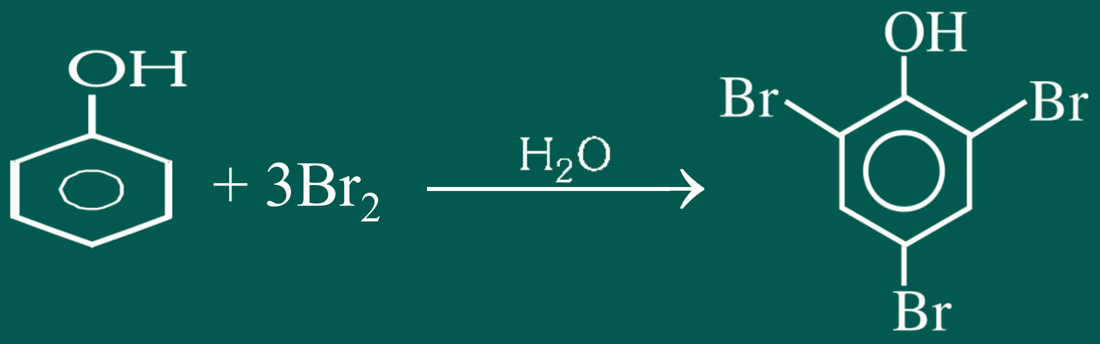
Allyl phenyl ether

(IV) Fries Rearrangement :

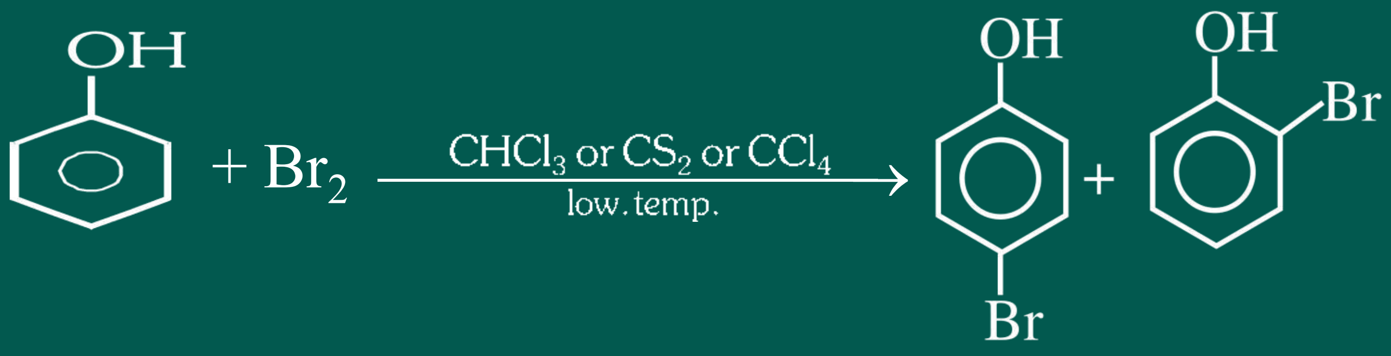


(V) Reaction with aqueous Br_2 or HOBr / $H^{\oplus}$

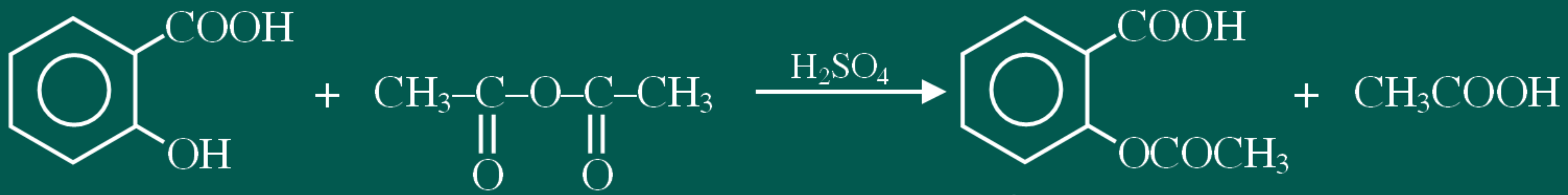
(a)



(b)



(VI) Use of salicyclic acid :

(i) 

Aspirin

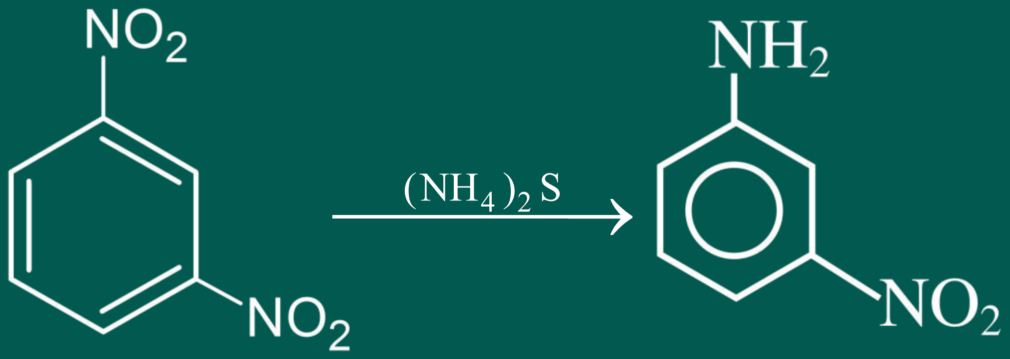
Reduction of nitrobenzene :

(1) Acidic medium :

(2) Selective Reduction :

In the polynitro compound only one $-NO_2$ group reduce into $-NH_2$ group in presence of sulphide or bisulphide.

Reagent : S^{-2} / $\overset{\ominus}{S}H$ / Na_2S / K_2S / NH_4SH / KSH / $SnCl_2$ + HCl / $(NH_4)_2S$

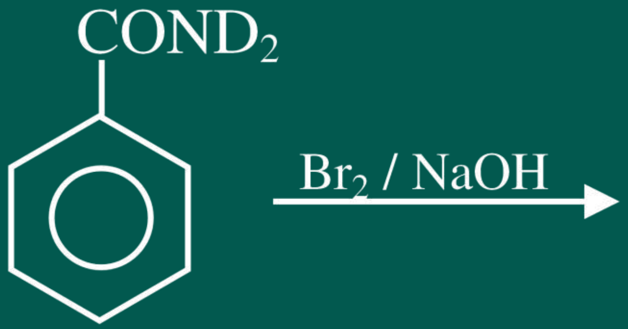


General methods of preparation of Aniline

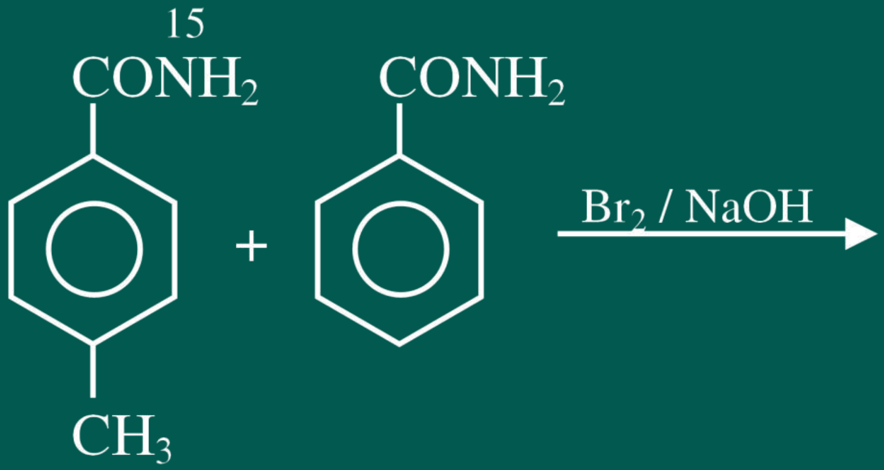
(1) **From benzamide** (Hofmann's bromamide reaction)**:**
Aniline is formed when benzamide is treated with Br_2 and KOH.

$$C_6H_5CONH_2 + Br_2 + 4KOH \rightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

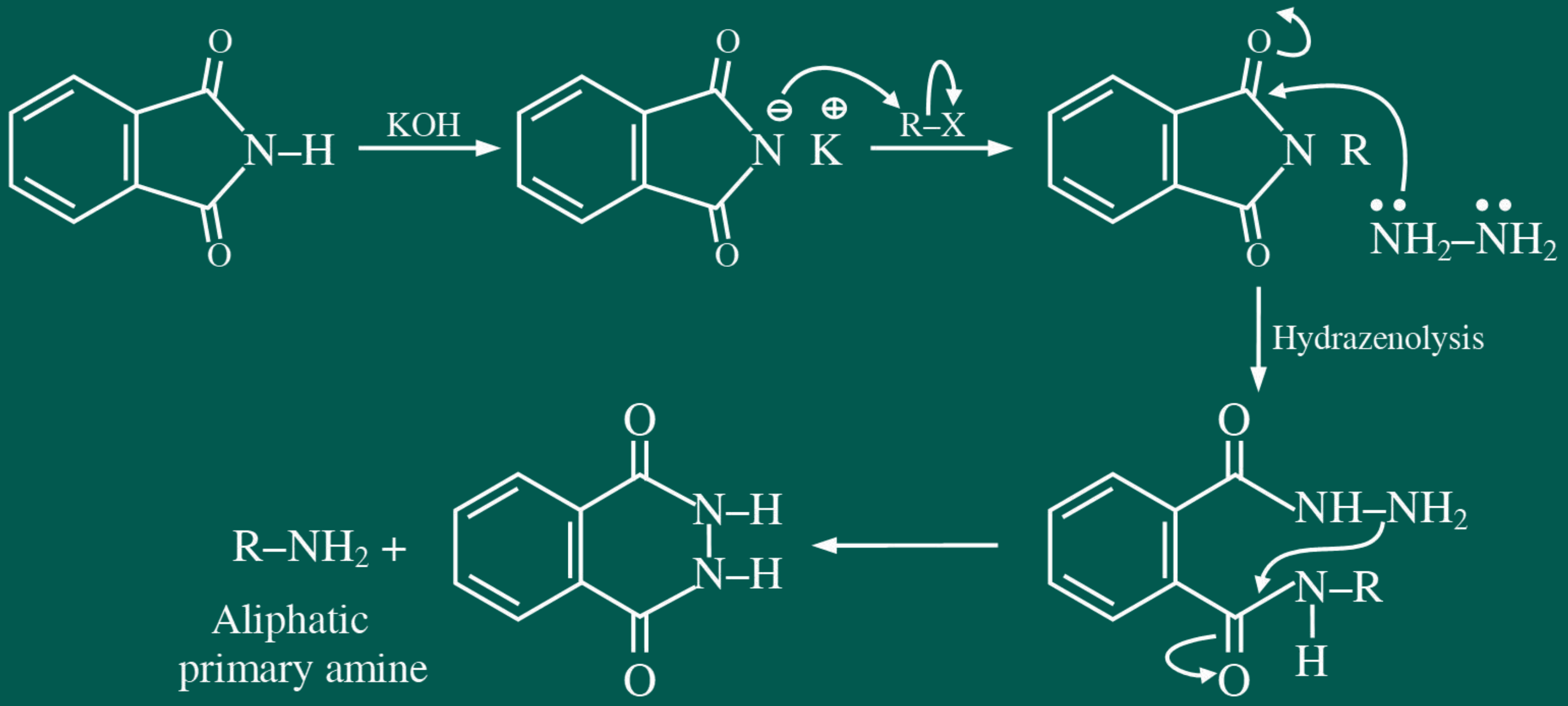
Q.1



Q.2

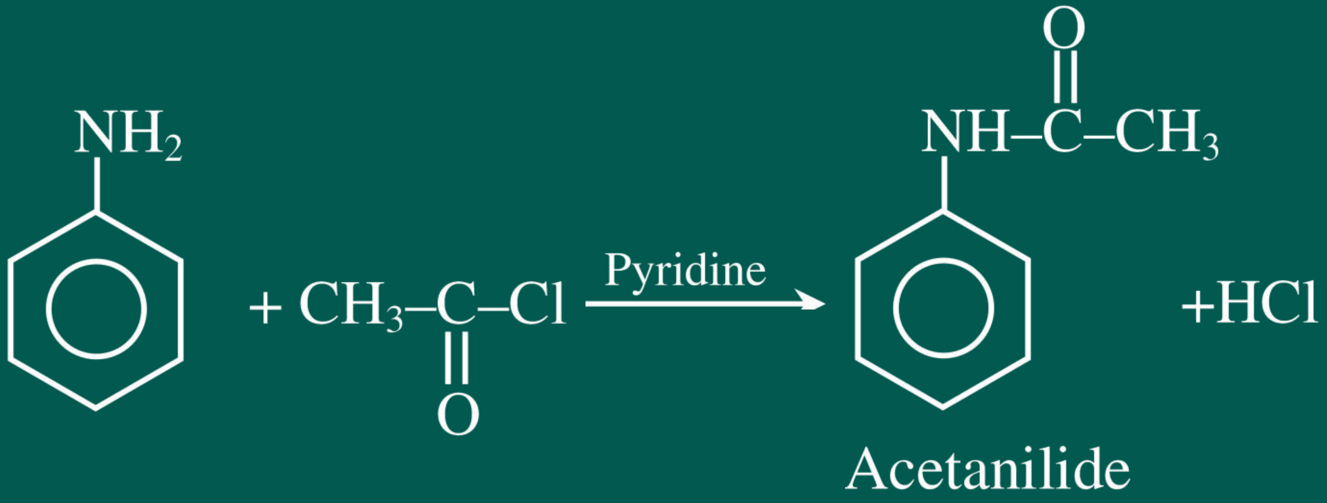


(2) Gabriel phthalimide synthesis :



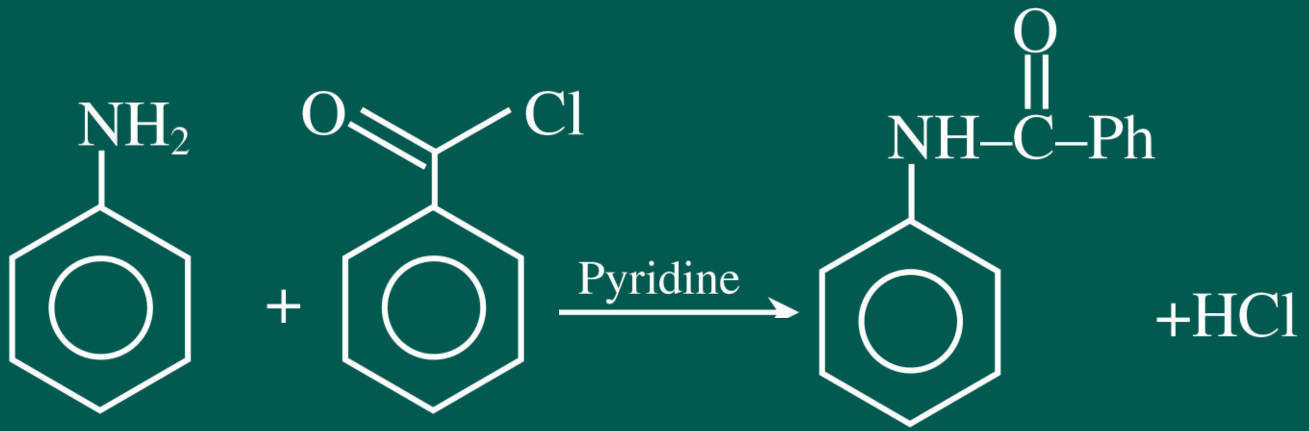
Chemical Properties

(1) Acylation :



Acetanilide

(2) Benzoylation (Schotten Baumann reaction) :



(III) Carbylamine reaction :

When aniline is heated with $CHCl_3$ and KOH it gives isocyanide having unpleasent smell which can be easily detected.

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

Note :

(i) Intermediate species is dichloro carbene [: CCl_2].

(ii) This is a test of aniline and other primary amines and is known as **isocyanide test.**

(IV) Hofmann's mustard oil reaction :

$$C_6H_5NH_2 + S{=}C{=}S \xrightarrow{HgCl_2} \underset{\text{Phenyl isothiocyanate}}{C_6H_5NCS} + HgS + 2HCl$$

Benzene diazonium salt

Preparation :

$$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow[-H_2O]{0^\circ-5^\circ C} C_6H_5N_2Cl$$

$$R\text{–}NH_2 + NaNO_2 + HCl \longrightarrow R\text{–}OH + N_2 + NaCl$$

Chemical reactions of benzene diazonium salt :

$$\left.\begin{array}{ll}
\text{(i)} & C_6H_5N_2Cl \xrightarrow{\text{CuCl/HCl}} C_6H_5Cl + N_2 + HCl \\[2ex]
\text{(ii)} & C_6H_5N_2Cl \xrightarrow{\text{CuBr/HBr}} C_6H_5Cl + N_2 + HCl \\[2ex]
\text{(iii)} & C_6H_5N_2Cl \xrightarrow{\text{CuCN/HCN}} C_6H_5CN + N_2 + HCl
\end{array}\right\} \begin{array}{l}\text{Sandmeyer}\\ \text{reactions}\end{array}$$

(iv) $C_6H_5N_2Cl \xrightarrow{Cu+HCl} C_6H_5Cl + N_2$ Gattermann reactions

(v) $C_6H_5N_2Cl \xrightarrow{KI(aq.)} C_6H_5I + N_2 + KCl$

(vi) $C_6H_5N_2Cl \xrightarrow[\Delta]{H_2O} C_6H_5OH$

(vii) $C_6H_5N_2Cl \xrightarrow{C_2H_5OH} C_6H_6$ (Benzene) + CH_3CHO

(viii) $C_6H_5N_2Cl \xrightarrow{H_3PO_2} C_6H_6$ (Benzene) + H_3PO_3

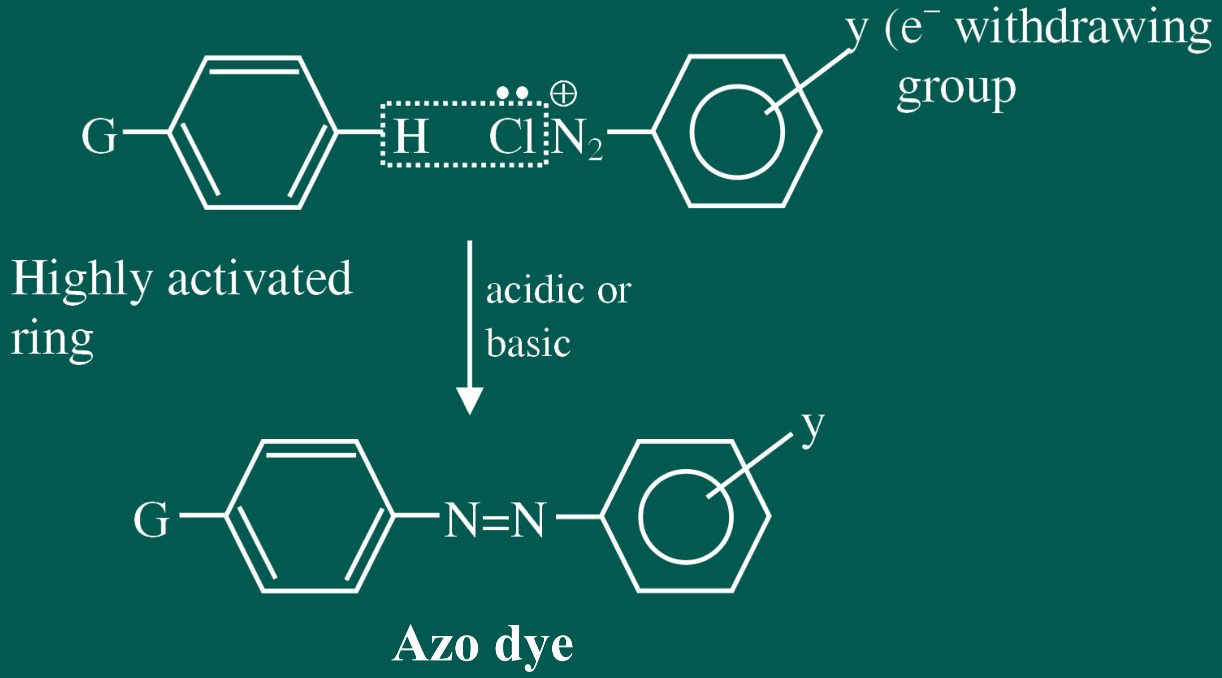
(ix) $C_6H_5N_2Cl \xrightarrow{HCOOH} C_6H_6$ (Benzene) + CO_2 + H_2O

(x) Balz-Schiemann reaction :

$$\begin{tikzcd}
C_6H_5NH_2 + NaNO_2 + HBF_4 \arrow[r] & C_6H_5N_2^{\oplus}\,BF_4^{\ominus} \arrow[d, "\Delta"] \\
& C_6H_5F + BF_3 + N_2
\end{tikzcd}$$

Coupling reactions of benzene diazonium salt :

Ph $N_2^{\oplus}$ is weak electrophile, any e^- withdrawing group increase rate of coupling reaction.



$G =$ (1) $-\bar{N}H$

(2) $-\bar{O}$

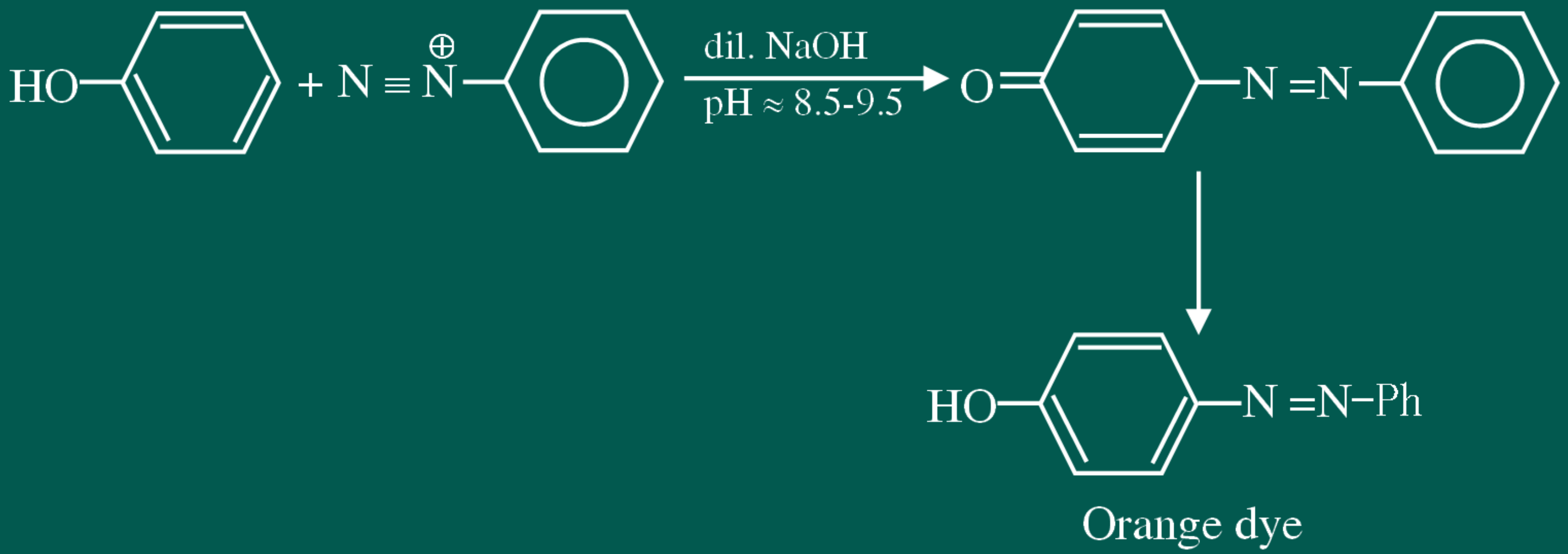
(3) $-NH_2$

(4) $-NHR$

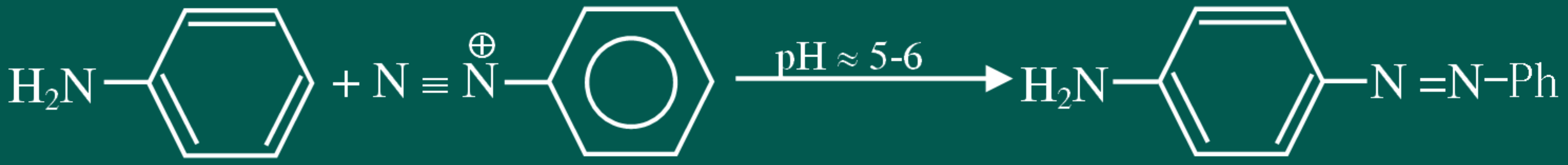
(5) $-NR_2$

(6) $-OH$

Coupling Reaction of phenol :



Coupling Reaction of aniline :



Yellow dye

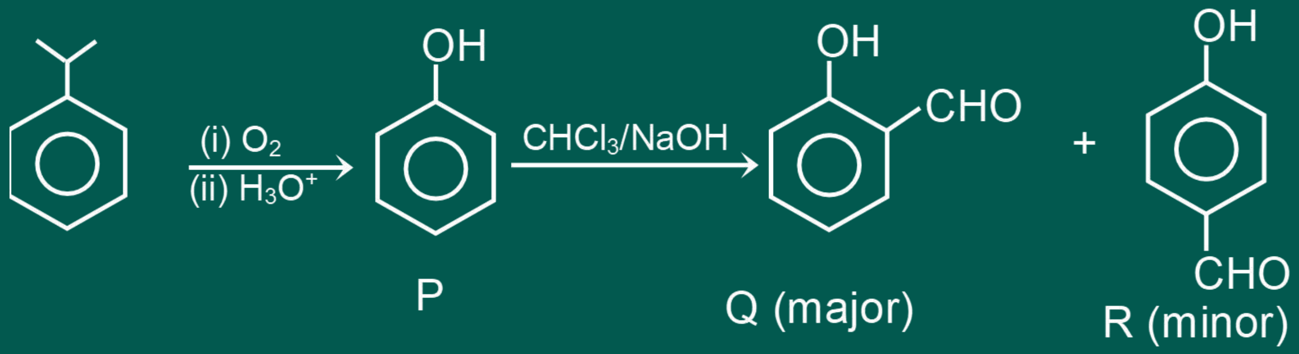
Q. 1 The correct statements(s) about the following reaction sequence is(are)

$$\text{Cumene}(C_9H_{12}) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2} \mathbf{P} \xrightarrow{CHCl_3/NaOH} \mathbf{Q}\ \text{(major)} + \mathbf{R}\ \text{(minor)}$$

$$\mathbf{Q} \xrightarrow[PhCH_2Br]{NaOH} \mathbf{S}$$

(A) R is steam volatile.
(B) Q gives dark violet coloration with 1% aqueous $FeCl_3$ solution.
(C) S gives yellow precipitate with 2,4-dinitrophenylhydrazine.
(D) S gives dark violet coloration with 1% aqueous $FeCl_3$ solution.

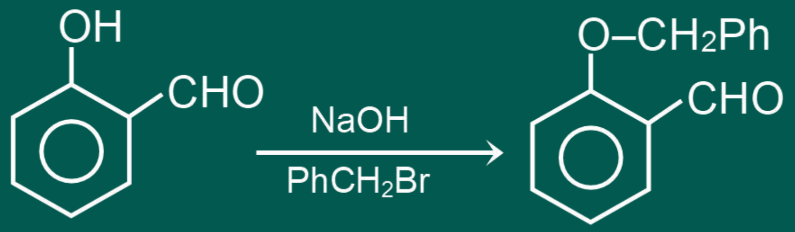
Sol.



P

Q (major)

R (minor)



S

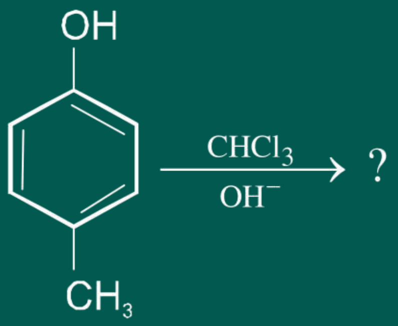
Q is steam volatile not R.

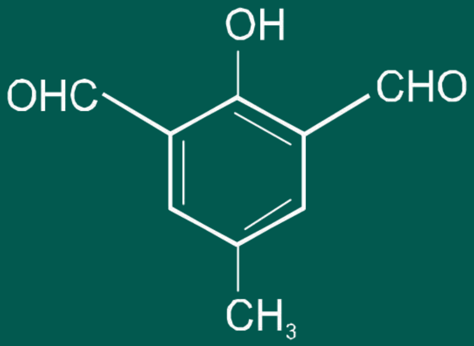
Q & R show positive test with 1% aqueous $FeCl_3$ Solution.

Q, R, S show positive 2,4-dinitrophenyl hydrazine.

Ans. (B, C)

Q. 2 In the following reaction, the product(s) formed is(are)

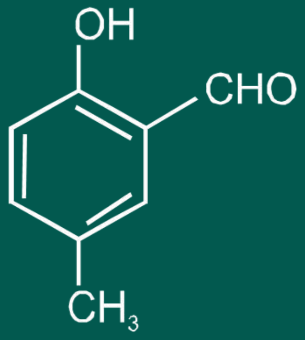




P

Q

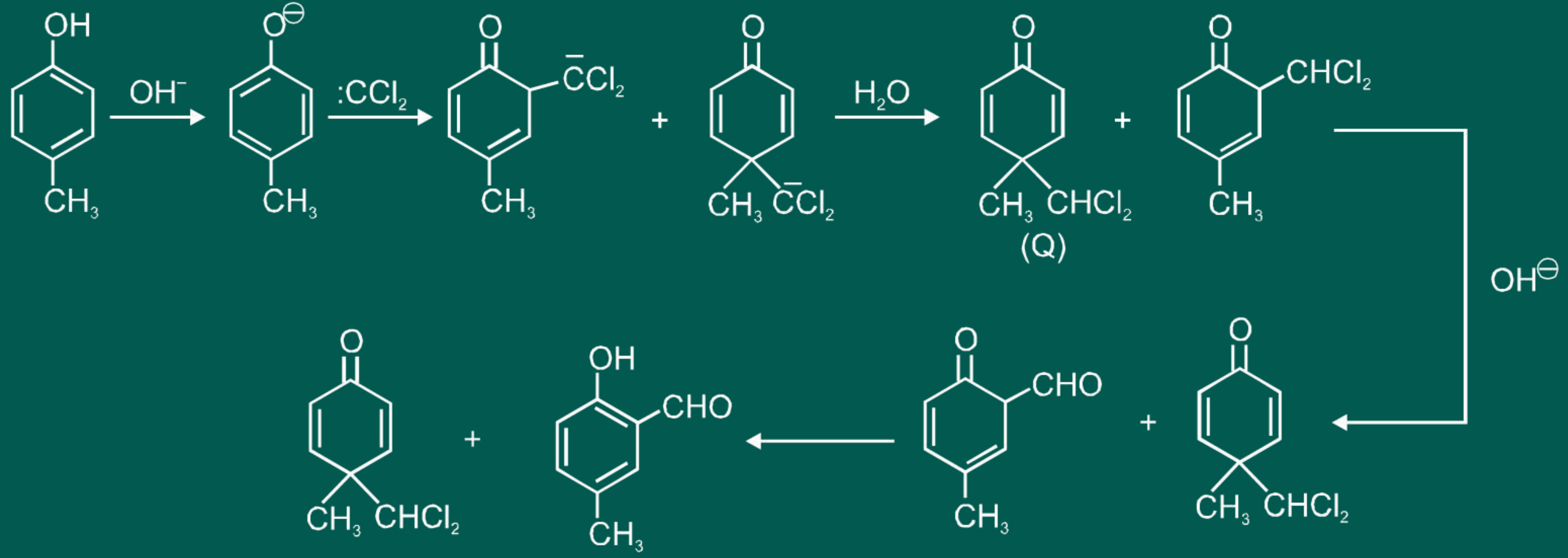
R



S

(A) P (major) (B) Q (minor) (C) R (minor) (D) S (major)

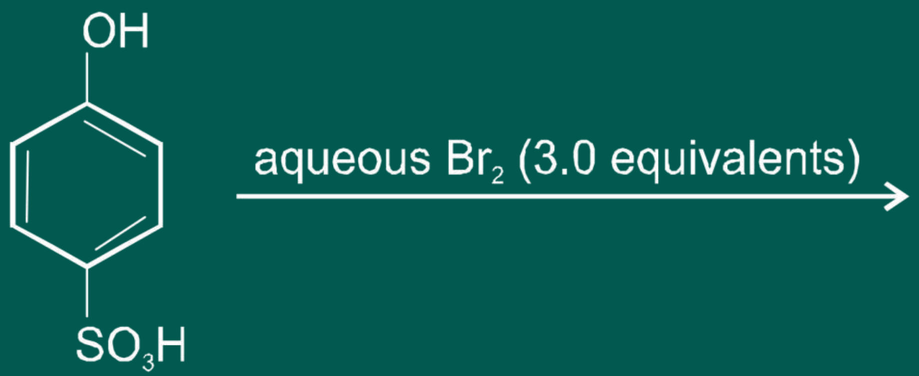
Sol.

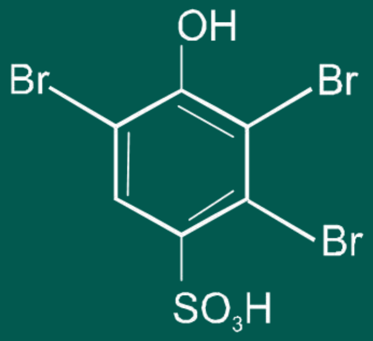


OH
CH$_3$
OH$^-$
O$^\ominus$
:CCl$_2$
$\bar{C}$Cl$_2$
+
H$_2$O
CH$_3$ CHCl$_2$
(Q)
CHCl$_2$
OH$^\ominus$
CHO

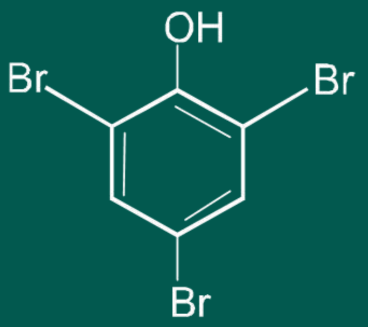
Ans. **(B,D)**

Q.3 The major product(s) of the following reaction is (are)

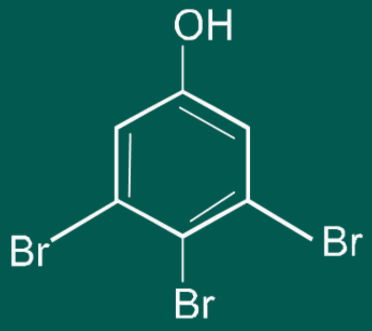




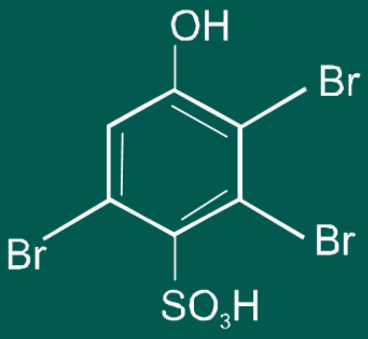
P



Q



R



S

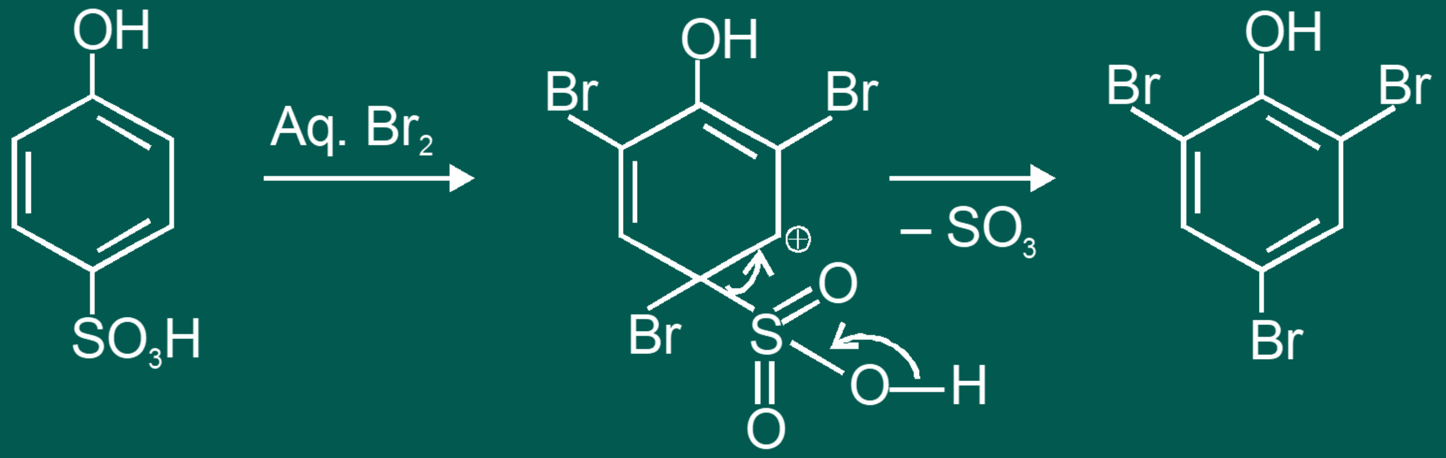
(A) P

(B) Q

(C) R

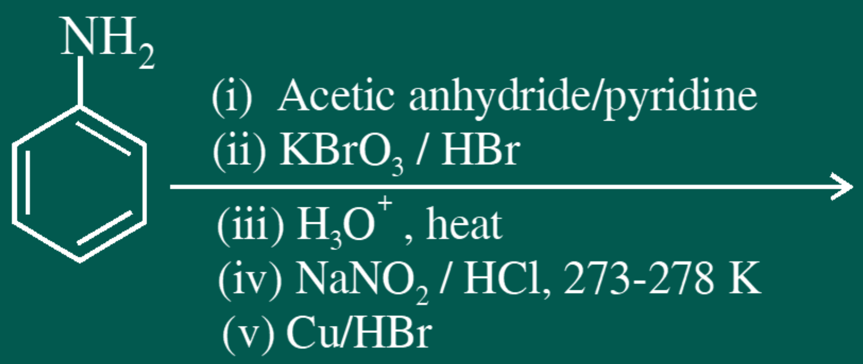
(D) S

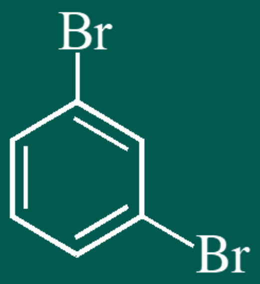
Sol.



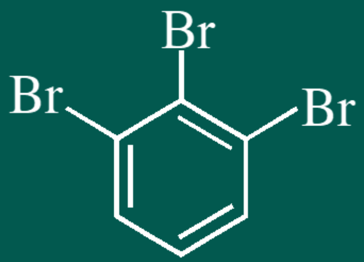
Ans. (B)

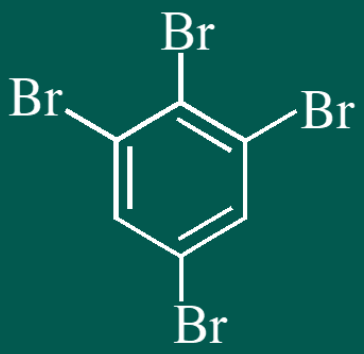
Q.4 The product(s) of the following reaction sequence is(are)



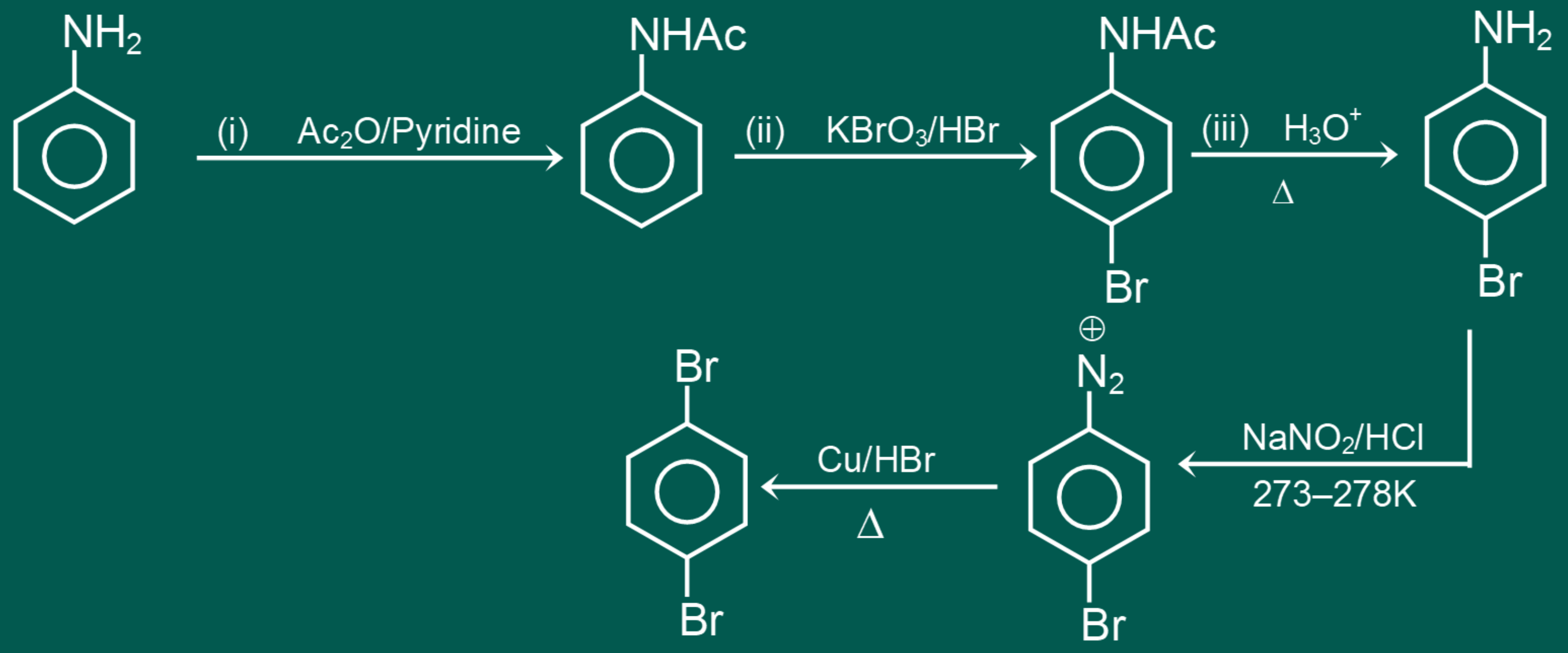
(A)


(B)


(C)


(D)


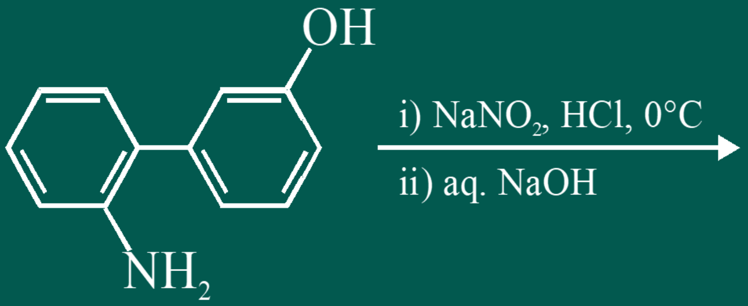
Sol.

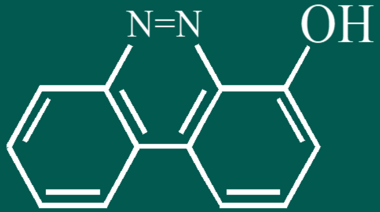


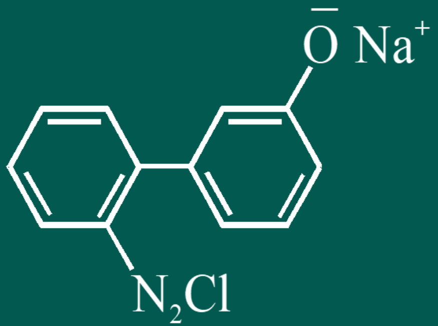
NH2
(i) Ac2O/Pyridine
NHAc
(ii) KBrO3/HBr
NHAc
Br
(iii) H3O+
Δ
NH2
Br
NaNO2/HCl
273–278K
⊕
N2
Br
Cu/HBr
Δ
Br
Br

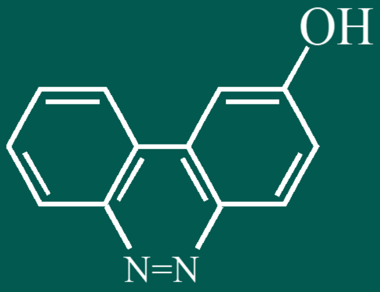
Ans. (B)

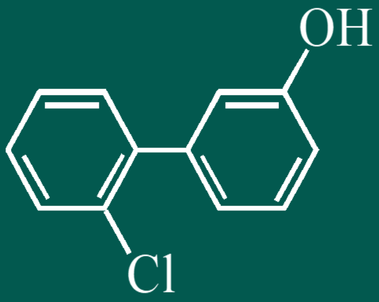
Q.5 The major product of the following reaction is :



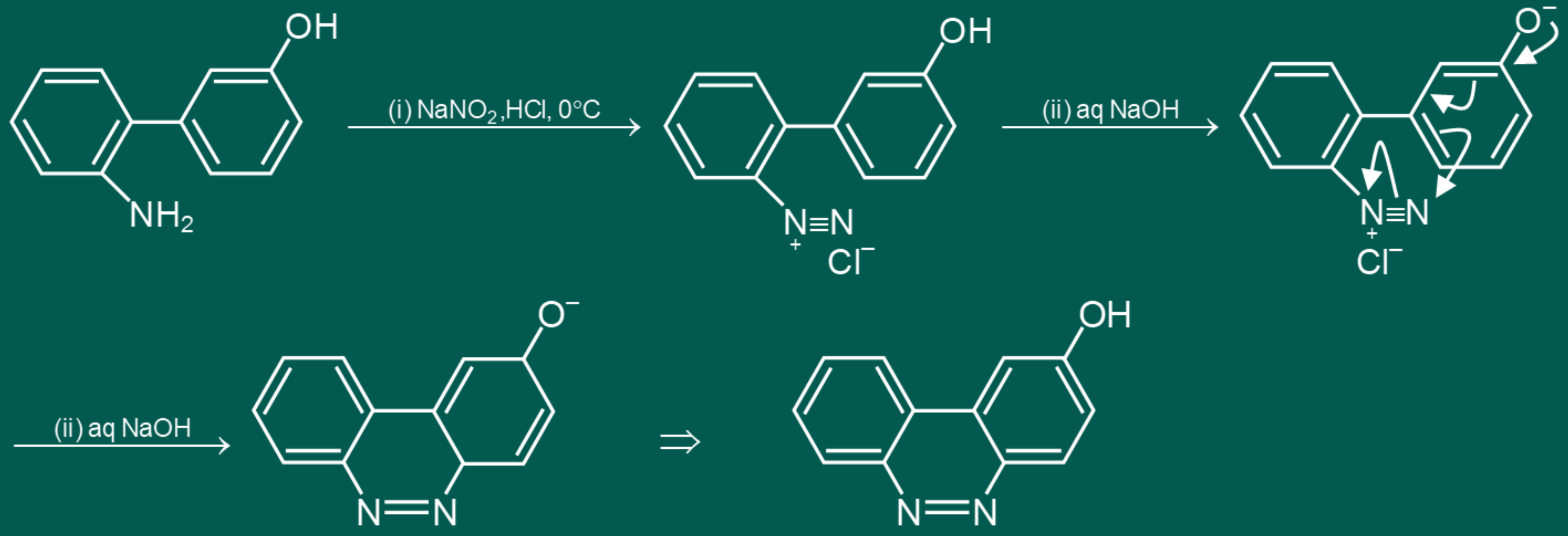
(A)


(B)


(C)


(D)


Sol.


OH
NH2
(i) NaNO2,HCl, 0°C
OH
N≡N
+
Cl⁻
(ii) aq NaOH
O⁻
N≡N
+
Cl⁻
(ii) aq NaOH
O⁻
N=N
⇒
OH
N=N

Ans. (C)

CARBONYL COMPOUNDS

ALDOL REACTIONS & ALDOL CONDENSATION

Reagent : Dilute base

($NaOH$, KOH, $Ba(OH)_2$, $Ca(OH)_2$, K_2CO_3, Na_2CO_3)

Requirement : α-Hydrogen

Aldol : β-Hydroxy carbonyl compound

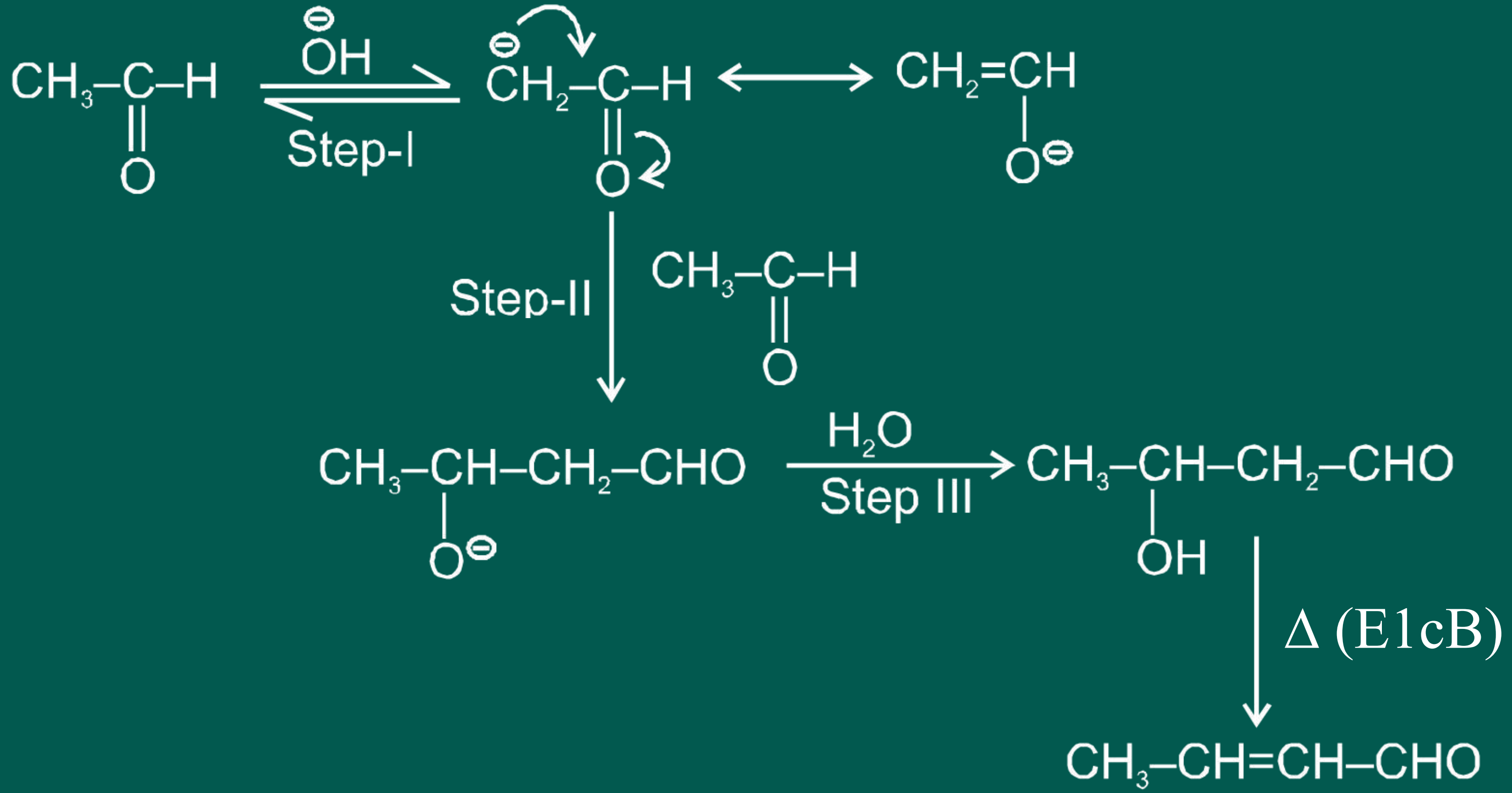
Aldol condensation : α, β-unsaturated carbonyl compound

Hint : New carbon-carbon bond form in product

Ex.1 $2CH_3{-}CHO \underset{}{\xrightleftharpoons{\text{dil.NaOH}}}$

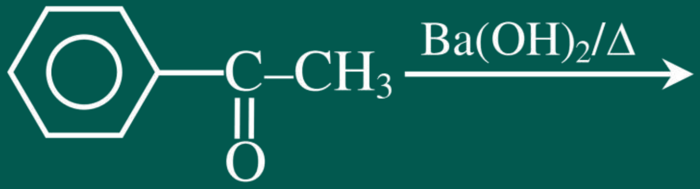
Ethanal

Mechanism :


CH3–C–H
O
⊖OH
Step-I
⊖CH2–C–H
O
CH2=CH
O⊖
Step-II
CH3–C–H
O
CH3–CH–CH2–CHO
O⊖
H2O
Step III
CH3–CH–CH2–CHO
OH
Δ (E1cB)
CH3–CH=CH–CHO

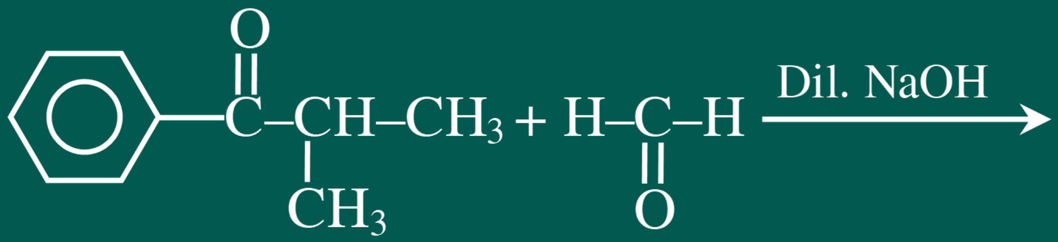
Ex.2

Ex.3

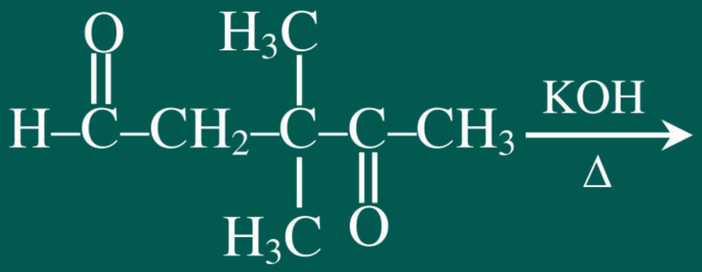


Ex.4

Ex.5



Ex.6



$$H-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{H_3C}{|}}{\underset{\underset{H_3C}{|}}{C}}-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{KOH}$$

Ex.7

$$\xrightarrow[\text{(ii) Zn, H}_2\text{O}]{\text{(i) O}_3}$$

(iii) dil. NaOH, Δ

Ex.8

Ex.9

Ex.10

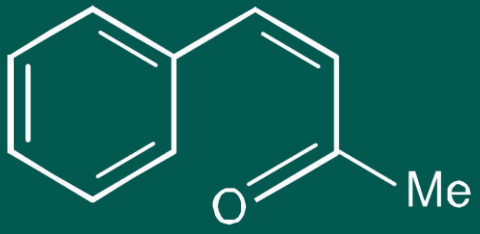
Comprehension (1-3) :

A carbonyl compound **P**, which gives positive iodoform test. R undergoes intramolecular aldol reaction to give predominantly **S**.

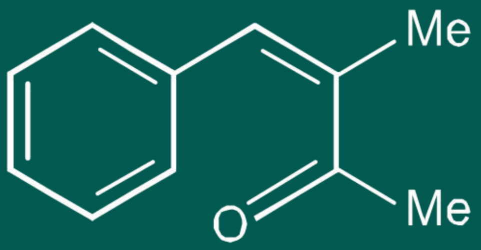
$$\mathbf{P} \xrightarrow[\substack{2.\ H^+,\ H_2O \\ 3.\ H_2SO_4,\ \Delta}]{1.\ \text{MeMgBr}} \mathbf{Q}\ (\text{olefin}) \xrightarrow[2.\ Zn,\ H_2O]{1.\ O_3} \mathbf{R} \xrightarrow[2.\ \Delta]{1.\ OH^-} \mathbf{S}$$

1. The structure of the carbonyl compound **P** is :

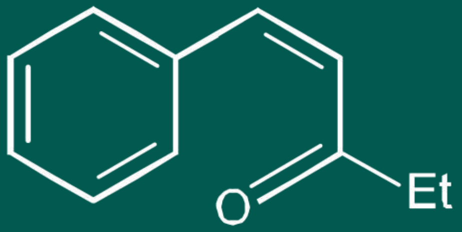
(A)



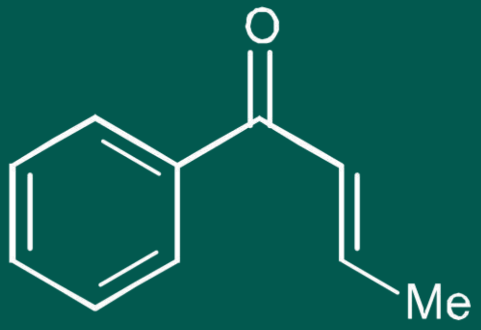
(B)



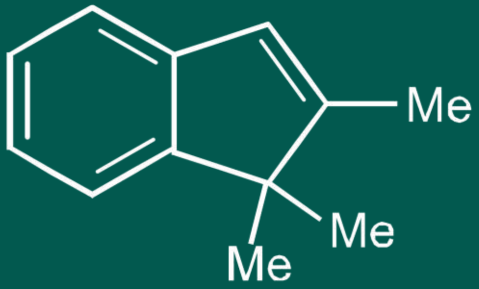
(C)

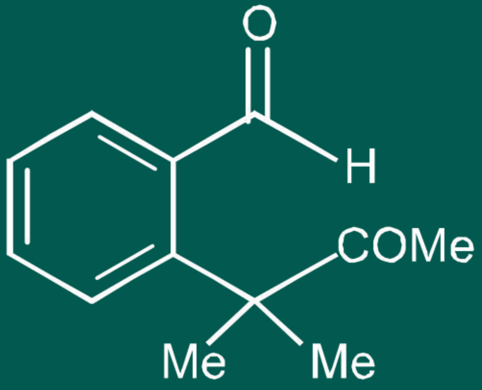


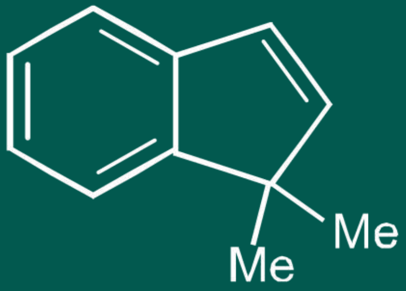
(D)

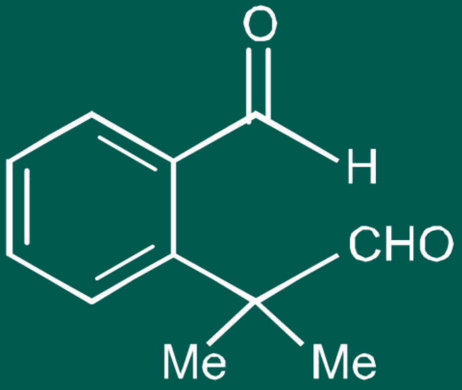


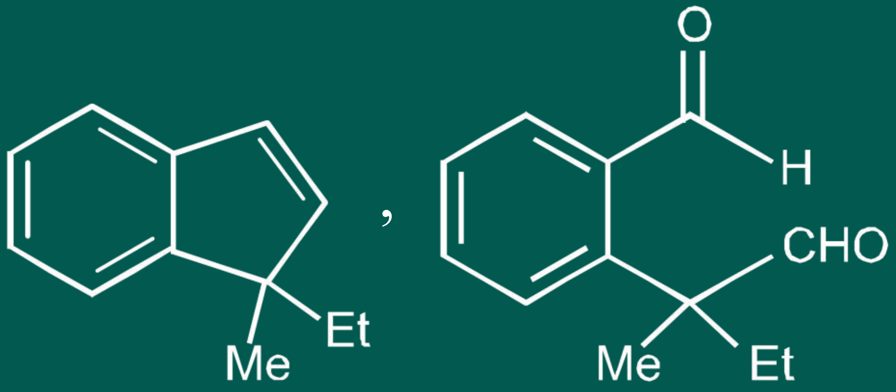
2. The structures of the products **Q** and **R**, respectively, are :

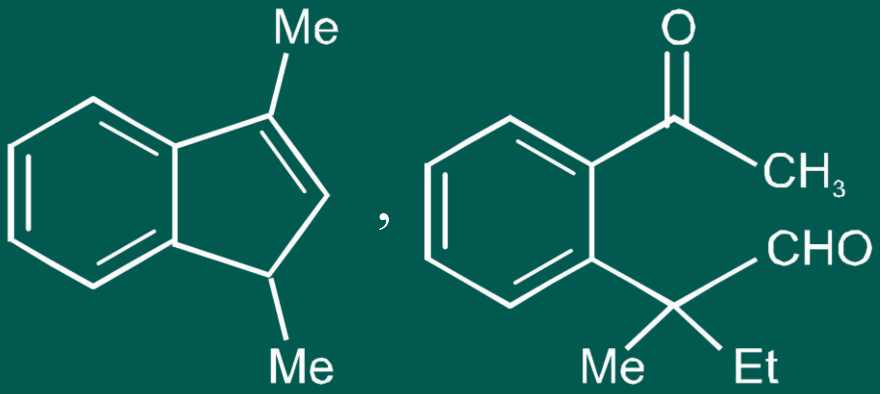
(A) 

, 

(B) 

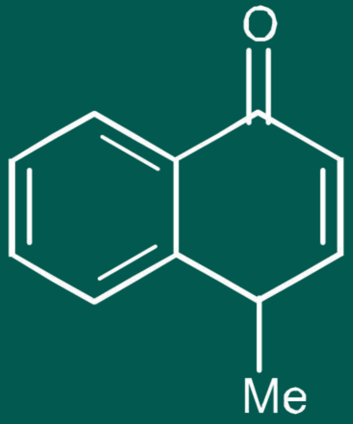
, 

(C) 

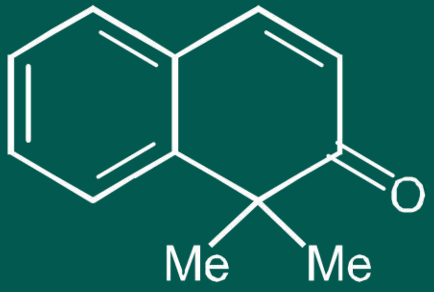
(D) 

3. The structure of the product **S** is :

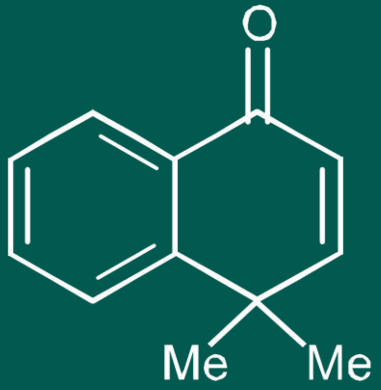
(A)



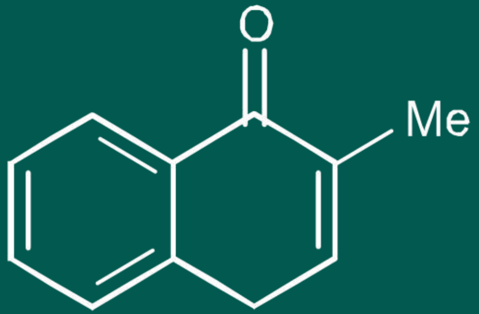
(B)



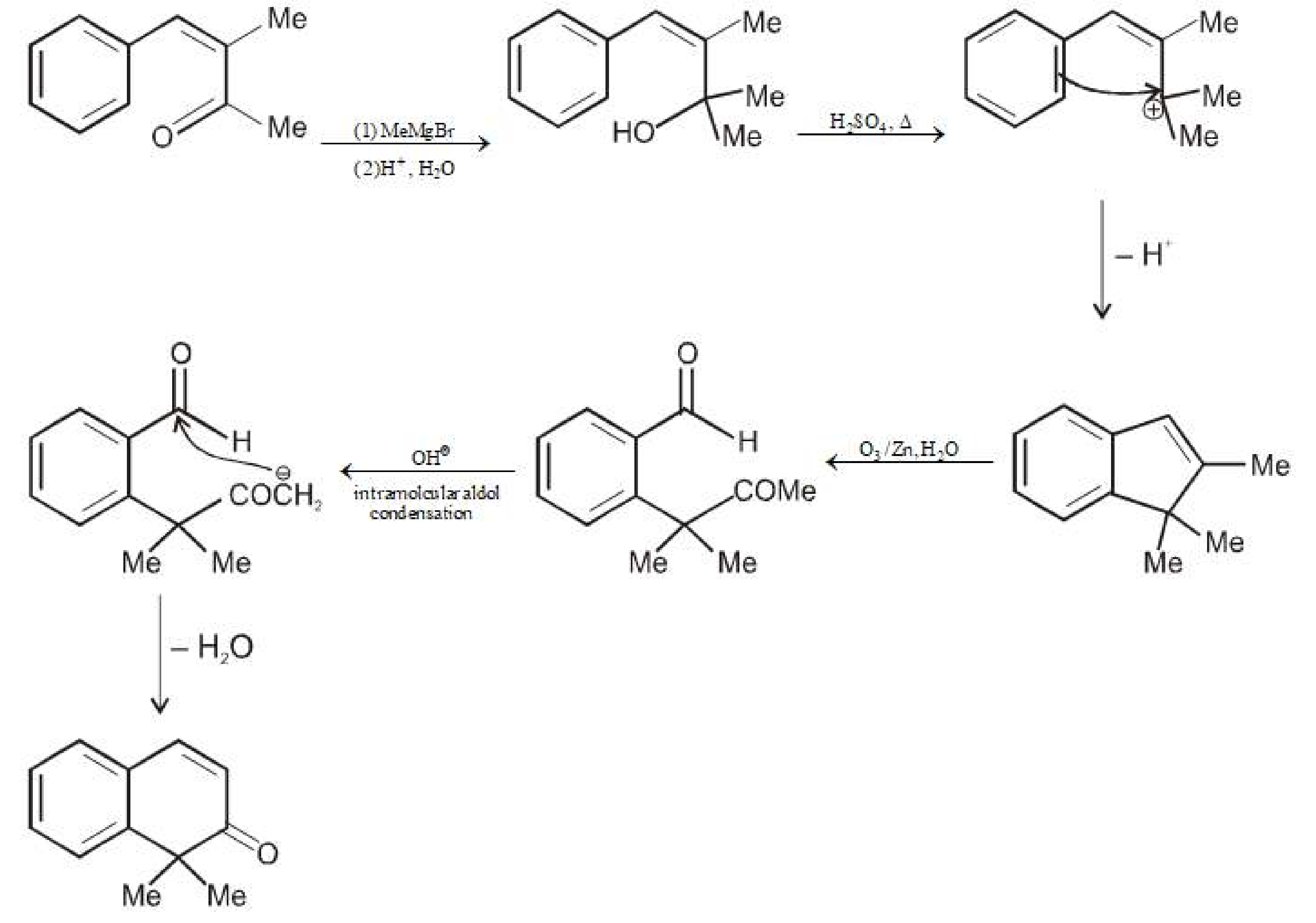
(C)



(D)



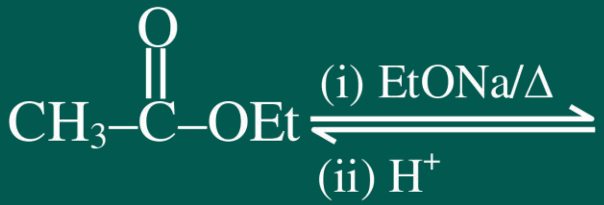
Sol.


Me
O
Me
(1) MeMgBr
(2)H$^+$, H$_2$O
Me
Me
HO
Me
H$_2$SO$_4$, Δ
Me
Me
Me
– H$^+$
Me
Me
Me
O$_3$/Zn,H$_2$O
O
H
COMe
Me
Me
OH$^⊖$
intramolecular aldol condensation
O
H
COCH$_2^⊖$
Me
Me
– H$_2$O
O
Me
Me

Claisen Ester Condensation :

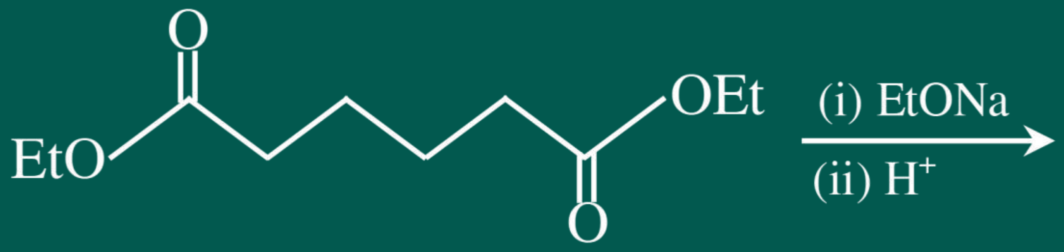
Product : β-keto ester

Ex. 11



$$CH_3-\overset{\overset{O}{\parallel}}{C}-OEt \xrightleftharpoons[\text{(ii) } H^+]{\text{(i) } EtONa/\Delta}$$

Ex. 12

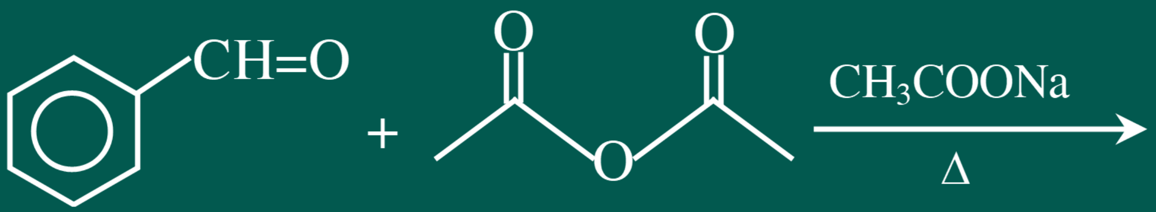


Ex. 13

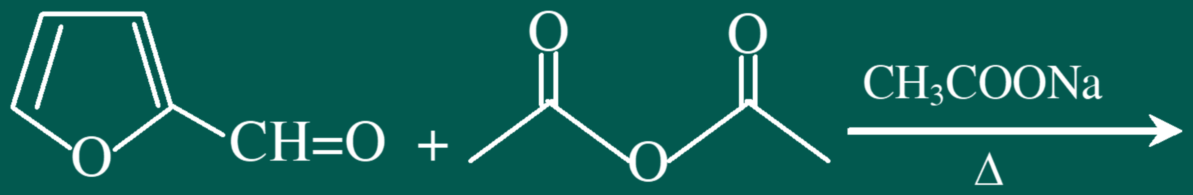
Perkin Reaction :

Aromatic aldehyde + Anhydride ⟶ Product
(with α-H)

Ex. 14



Ex. 15



Furfural

Comprehension (1-2) :

In the following reactions sequence, the compound J is an intermediate.

$$\mathrm{I} \xrightarrow[\mathrm{CH_3COONa}]{\mathrm{(CH_3CO)_2O}} \mathrm{J} \xrightarrow[\substack{\text{(ii) } \mathrm{SOCl_2} \\ \text{(ii) anhyd.} \mathrm{AlCl_3}}]{\text{(i) } \mathrm{H_2, Pd/C}} \mathrm{K}$$

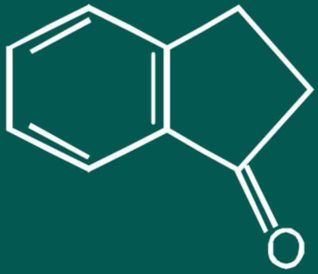
J ($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and positive Baeyer's test

1. The compound K is

(A)

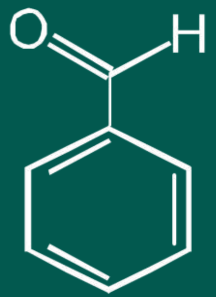
(B)

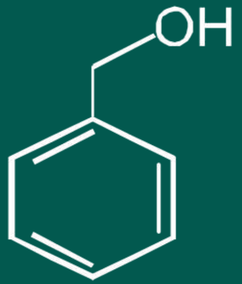
(C)

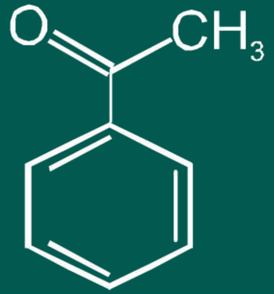


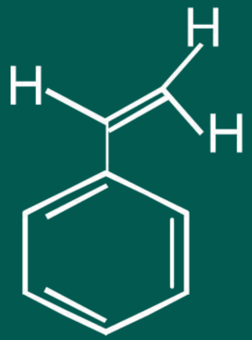
(D)

2. The compound I is

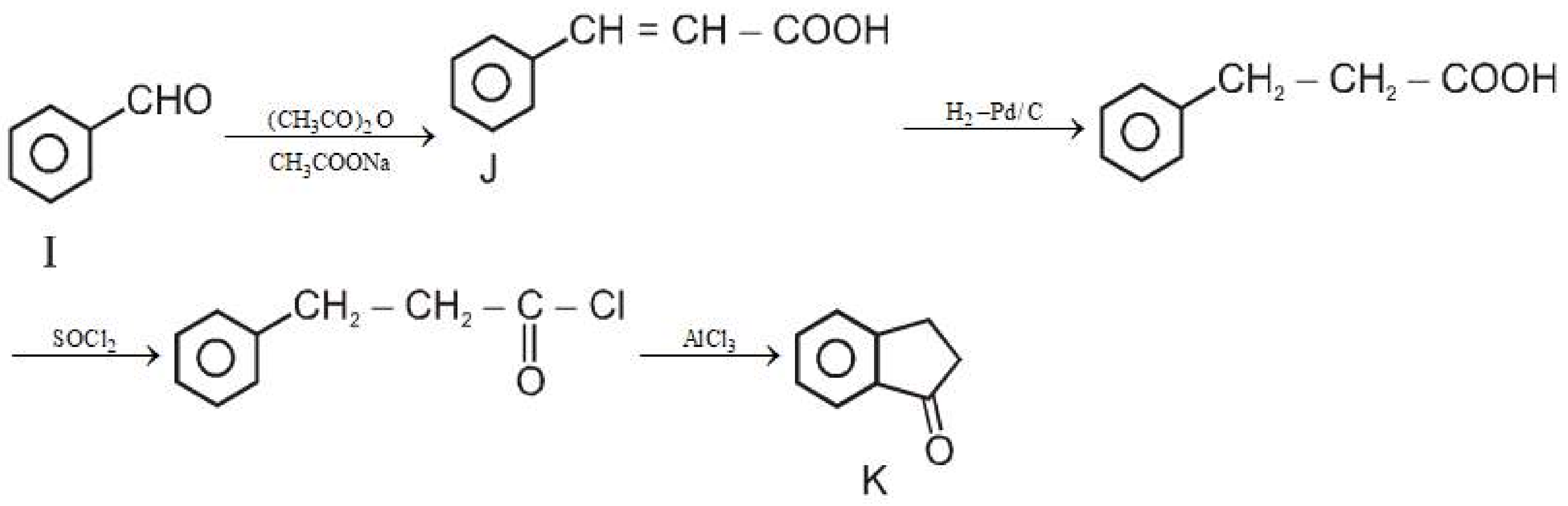
(A) 

(B) 

(C) 

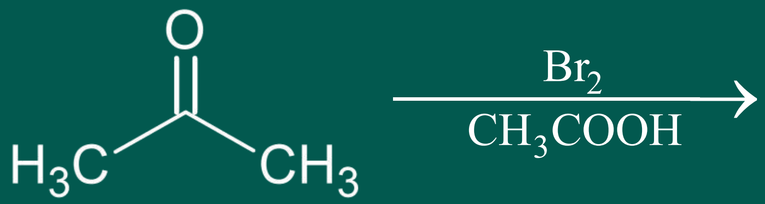
(D) 

Sol.


CHO
I
(CH3CO)2O
CH3COONa
CH = CH – COOH
J
H2–Pd/C
CH2 – CH2 – COOH
SOCl2
CH2 – CH2 – C – Cl
O
AlCl3
O
K

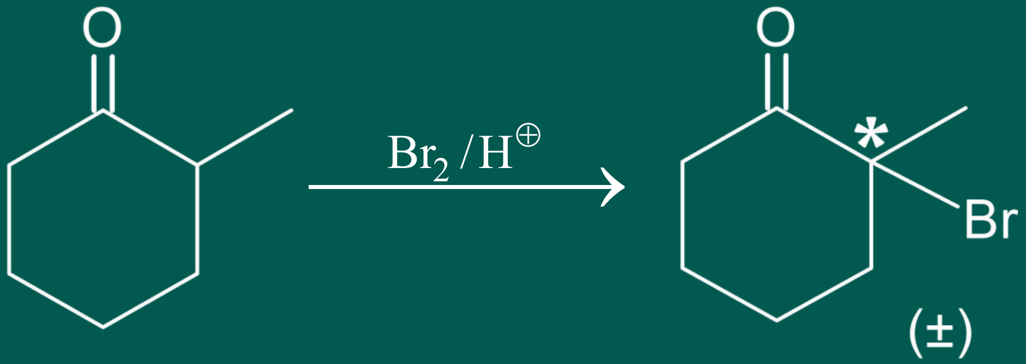
α-Halogenation

(i) In acidic medium :

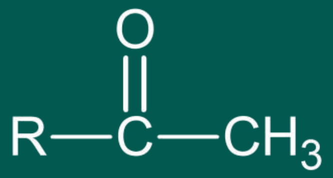


α-monohalogenation in acidic medium

Ex. 17



(ii) α-Halogenation in basic medium : (Haloform reaction)

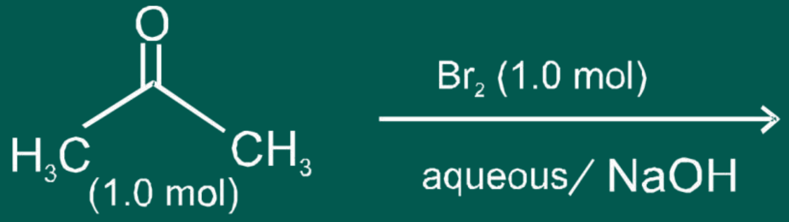


$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[KOH/X_2]{NaOH/X_2\ \text{or}} CHX_3 + R\text{–}COONa$$

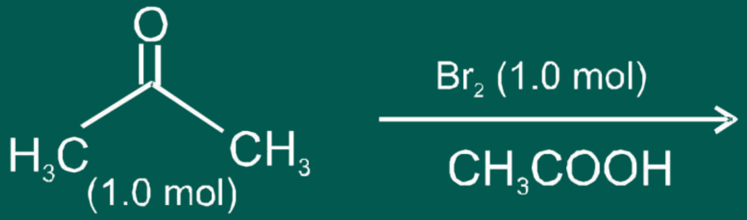
Condition :

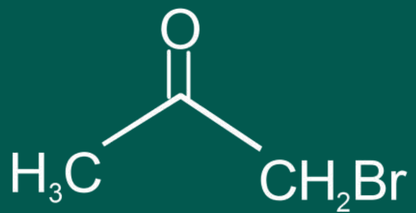
1. After completion of the reactions (**I** and **II**), the organic compound(s) in the reaction mixtures is (are)

Reaction **I** :

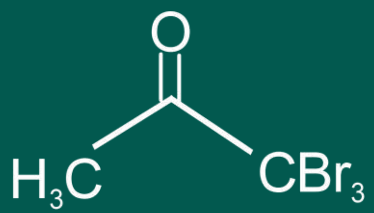


Reaction **II** :

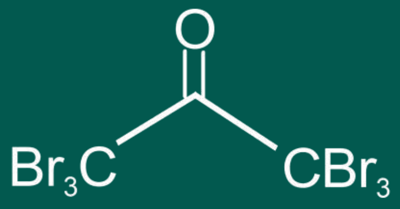




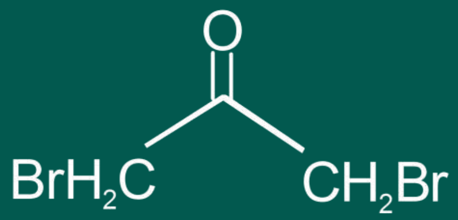
P



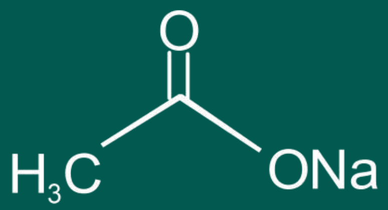
Q



R



S



T

$CHBr_3$

U

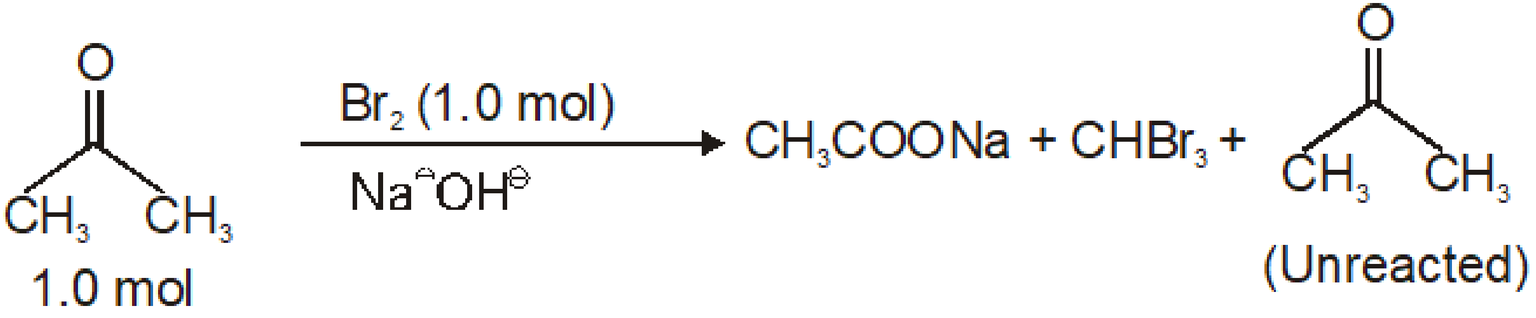
(A) Reaction **I** : **P** and Reaction **II** : **P**

(B) Reaction **I** : **U**, acetone and Reaction **II** : **Q**, acetone

(C) Reaction **I** : **T**, **U**, acetone and Reaction **II** : **P**

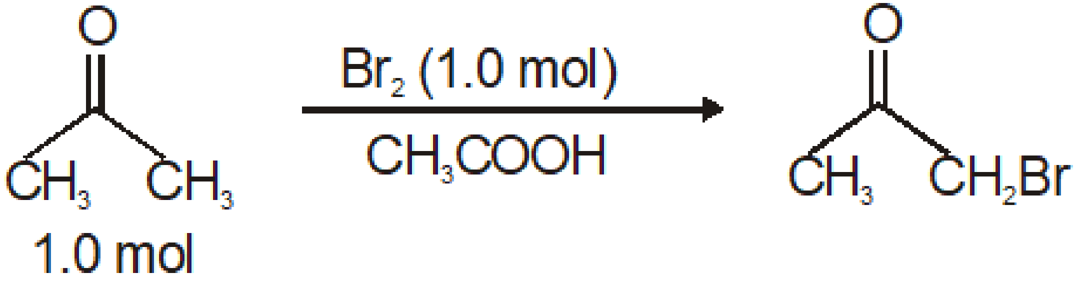
(D) Reaction **I** : **R**, acetone and Reaction **II** : **S**, acetone

Sol. Reaction I :



(In basic medium complete haloform reaction takes place since the rate of reaction increases with each α-halogenation)

Reaction II :



(In acidic medium monohalogenation takes place with 1-mol of halogen)

Cannizzaro reaction :

Given by carbonyl compounds without α-hydrogen

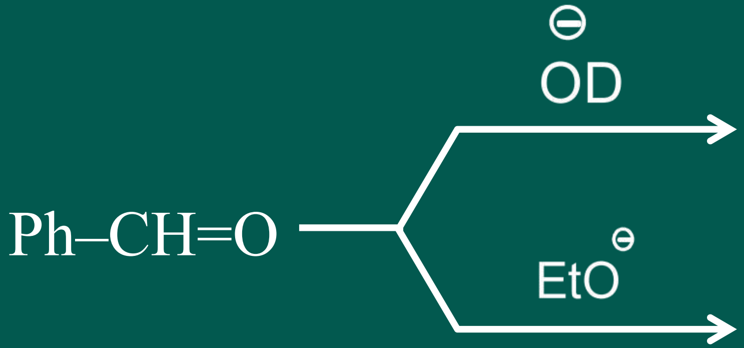
e.g. HCOOH, PhCHO, $(CH_3)_3CHO$ etc.

Reagents : conc. base

Product : Disproportionation (when only one reactant) /redox reaction (2 different reactants)

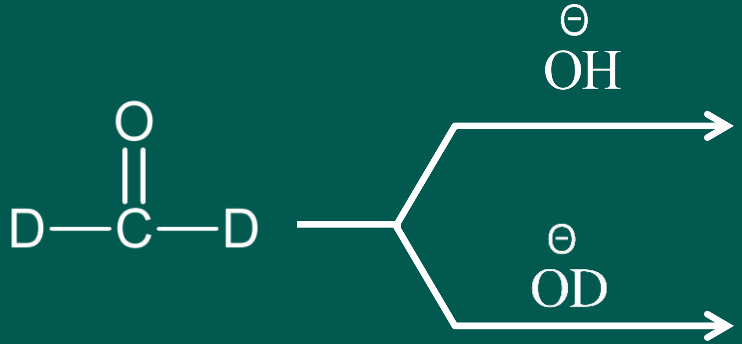
$$Ph{-}CH{=}O \xrightarrow{50\%KOH} Ph{-}CH_2{-}OH + Ph{-}COO^{\ominus}K^{\oplus}$$

Ex. 18

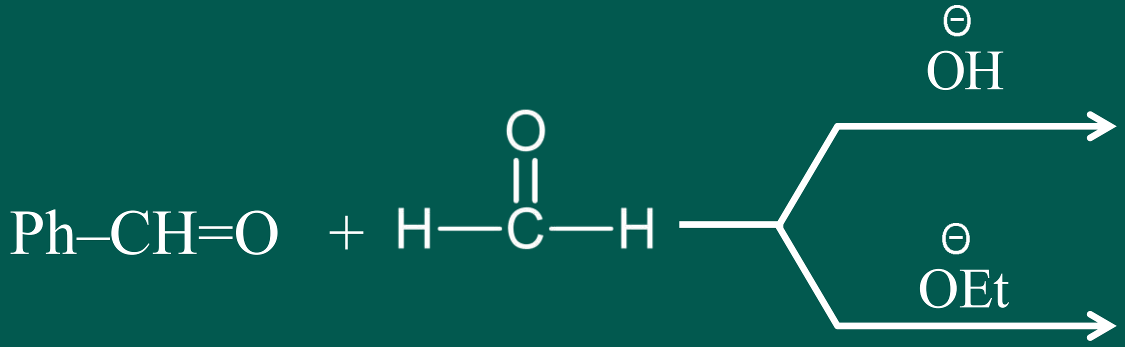


Ph–CH=O

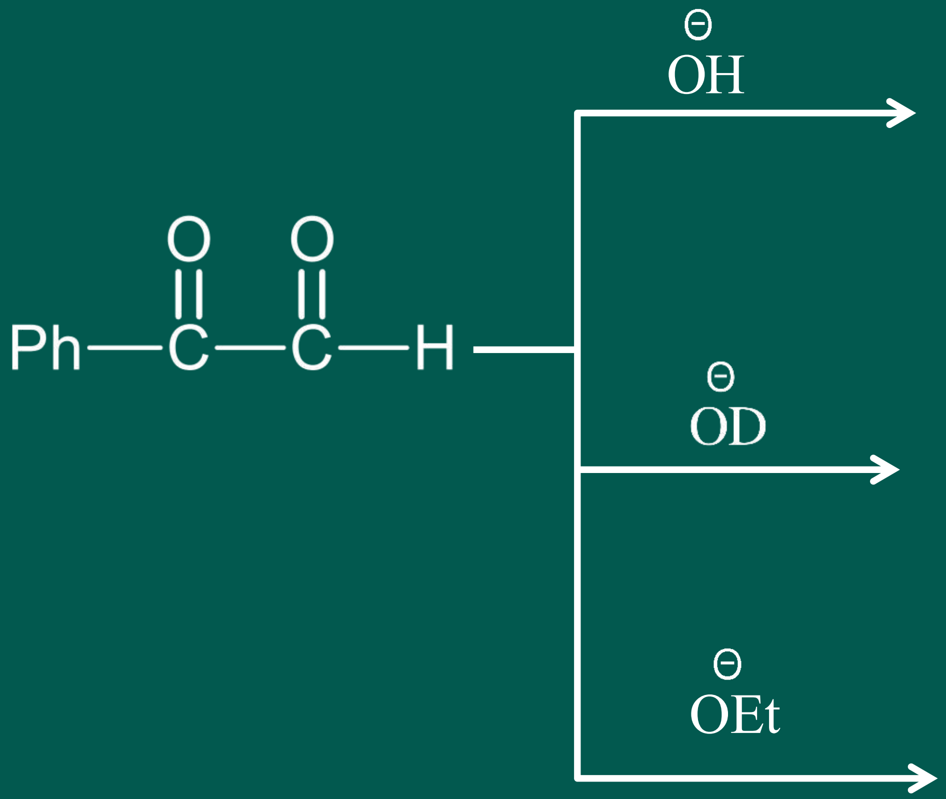
Ex. 19


D—C(=O)—D
$\overset{\ominus}{O}H$
$\overset{\ominus}{O}D$

Ex. 20


Ph–CH=O + H—C(=O)—H
$\overset{\ominus}{O}H$
$\overset{\ominus}{O}Et$

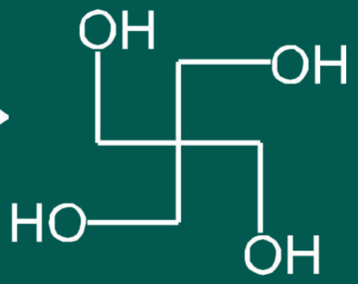
Ex. 21



$$Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

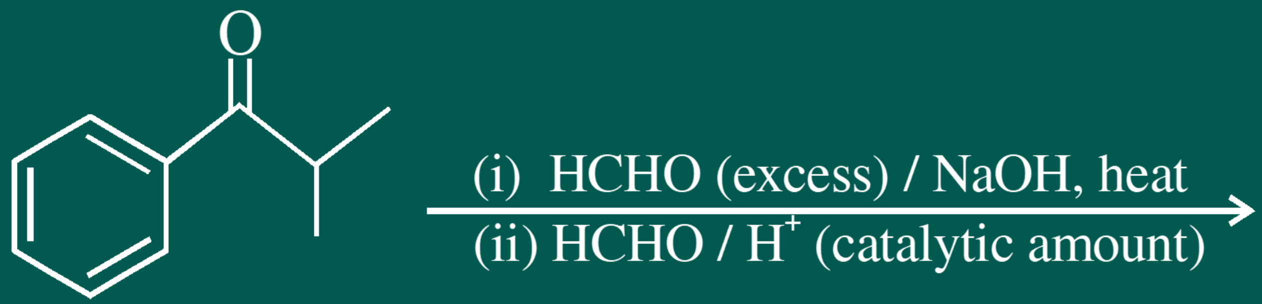
1. The number of aldol reaction (s) that occurs in the given transformation is :

$$CH_3CHO + 4HCHO \xrightarrow{\text{conc. aq. NaOH}}$$

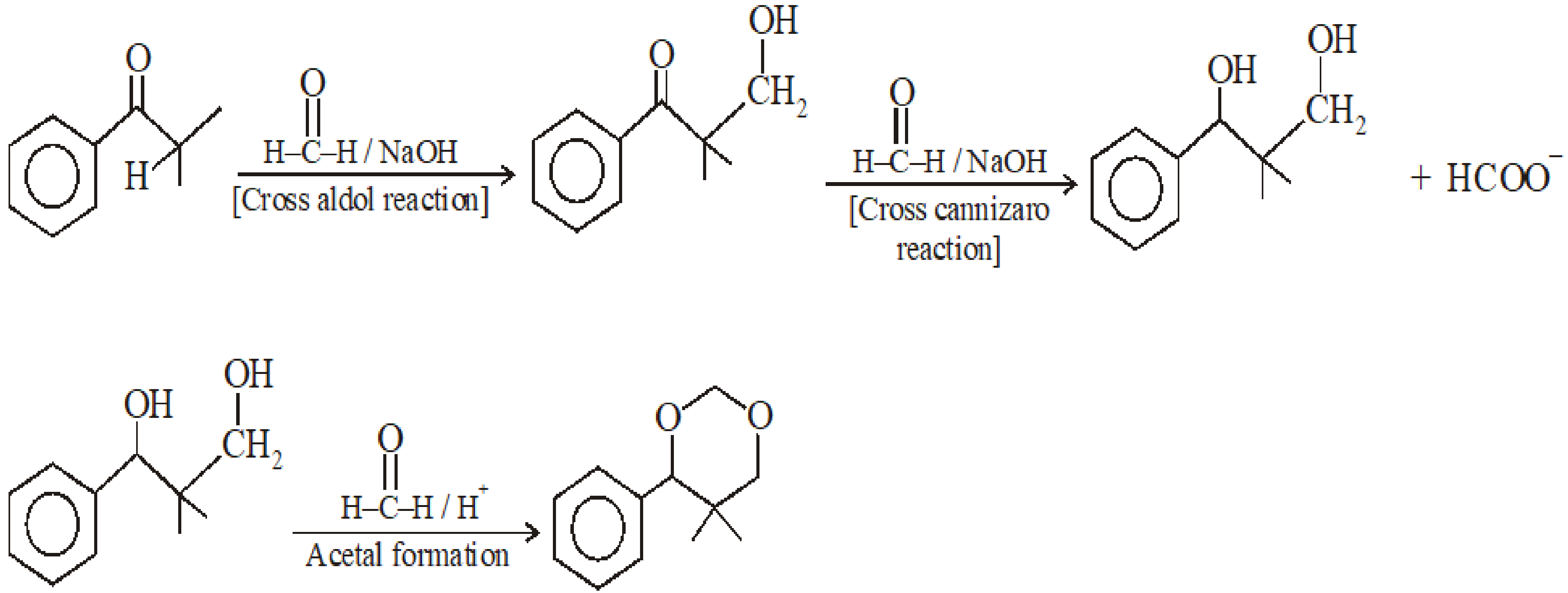


(A) 1
(B) 2
(C) 3
(D) 4

2. The major product of the following reaction sequence is :



Sol.


H–C–H / NaOH
[Cross aldol reaction]
H–C–H / NaOH
[Cross cannizaro reaction]
+ HCOO⁻
H–C–H / H⁺
Acetal formation

SOLUTIONS
&
COLLIGATIVE PROPERTIES

Frequently Asked Concepts in JEE Main & JEE Advanced :

Solutions

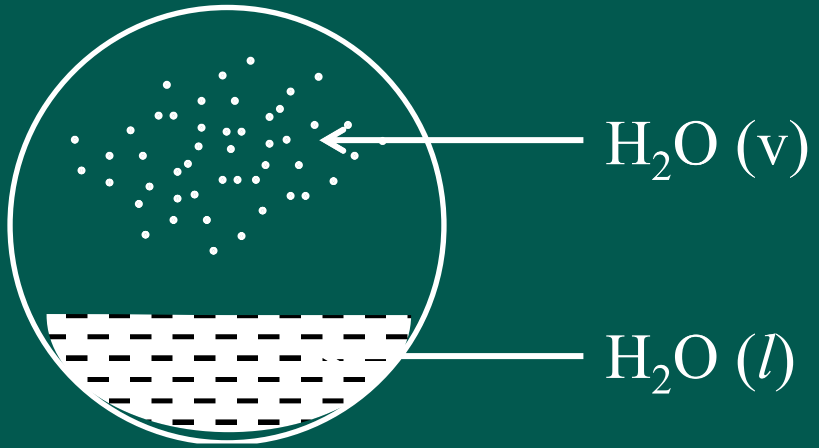
- Vapour pressure
- Completely miscible liquid : Raoult's law
- Ideal & non-ideal solution

Colligative properties

- Osmosis & osmotic pressure
- R.L.V.P
- Elevation in B.P. and depression in F.P.

Vapour pressure :

Pressure applied by vapours when they are in equilibrium with corresponding liquid



$$H_2O(\ell) \rightleftharpoons H_2O\ (v)$$

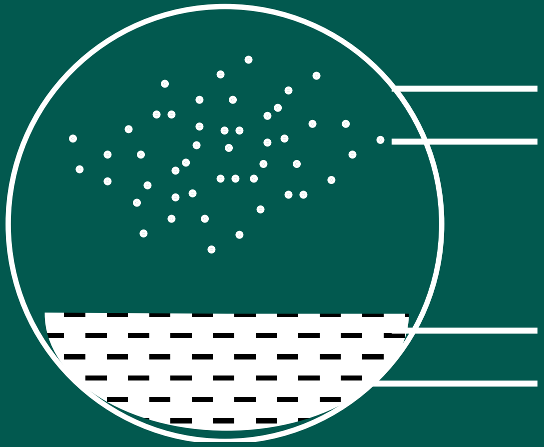
At equilibrium $K_P = P_{H_2O/Eq.} = V.P$

Note :

- Vapour pressure is a function of only temperature.

  For given liquid
- As T ↑ V.P. ↑
- As intermolecular forces ↑, V.P. ↓

Completely miscible liquids



$A : y_A$

$B : y_B$

mole fraction in vapour phase

$A : X_A$

$B : X_B$

mole fraction in solution phase

P_A: V.P of A

P_B: V.P of B

Total V.P $(P_T) = P_A + P_B$

$P_A° =$ V.P of pure A

$P_B° =$ V.P of pure B

Raoult's law :

V.P of any component in a mixture is directly proportional to its mole fraction is solution phase

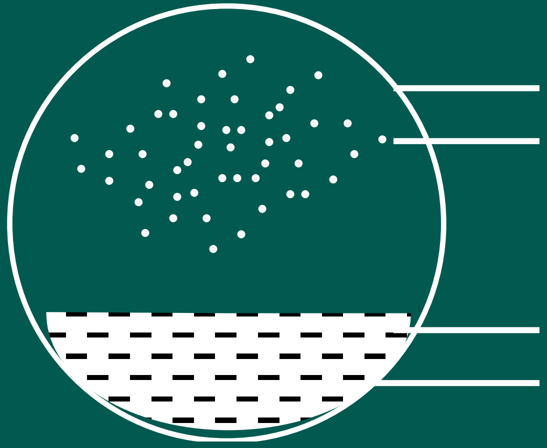
$\boxed{P_A = P_A^{\circ} x_A}$ $\boxed{P_B = P_B^{\circ} x_B}$

$$\boxed{P_T = P_A^{\circ} x_A + P_A^{\circ} x_B} \quad \ldots \text{(i)}$$

$$\boxed{P_A^{\circ} x_A = P_T y_A} \quad \ldots \text{(ii)}$$

Raoult's law Daltons law

$$\boxed{\frac{1}{P_T} = \frac{y_A}{P_A^{\circ}} + \frac{y_B}{P_B^{\circ}}} \quad \ldots \text{(iii)}$$



$A : y_A$
$B : y_B$
mole fraction in vapour phase

$A : X_A$
$B : X_B$
mole fraction in solution phase

Example :

Determine vapour pressure and composition of vapour phase of a solution having equimolar mixture of Volatile liquids A and B ($P_A^\circ = 200$, $P_B^\circ = 600$)

Solution :

$$P_T = P_A^o x_A + P_B^o \mathbf{x_B}$$

$$= 200\left(\frac{1}{2}\right) + 600\left(\frac{1}{2}\right)$$

$$\Rightarrow \quad P_T = 400$$

$$\therefore \quad y_A = \frac{P_A^o x_A}{P_T} = \frac{200\left(\frac{1}{2}\right)}{400} = \frac{1}{4}$$

$$y_A = \frac{3}{4}$$

Example :

Two liquids A and B form an ideal solution. At the specified temperature, the vapour pressure of pure A is 200 mm Hg while that of pure B is 100 mm Hg. If the vapour over the mixture consists of 50 mole percent A in the liquid, determine vapour pressure and composition of solution phase.

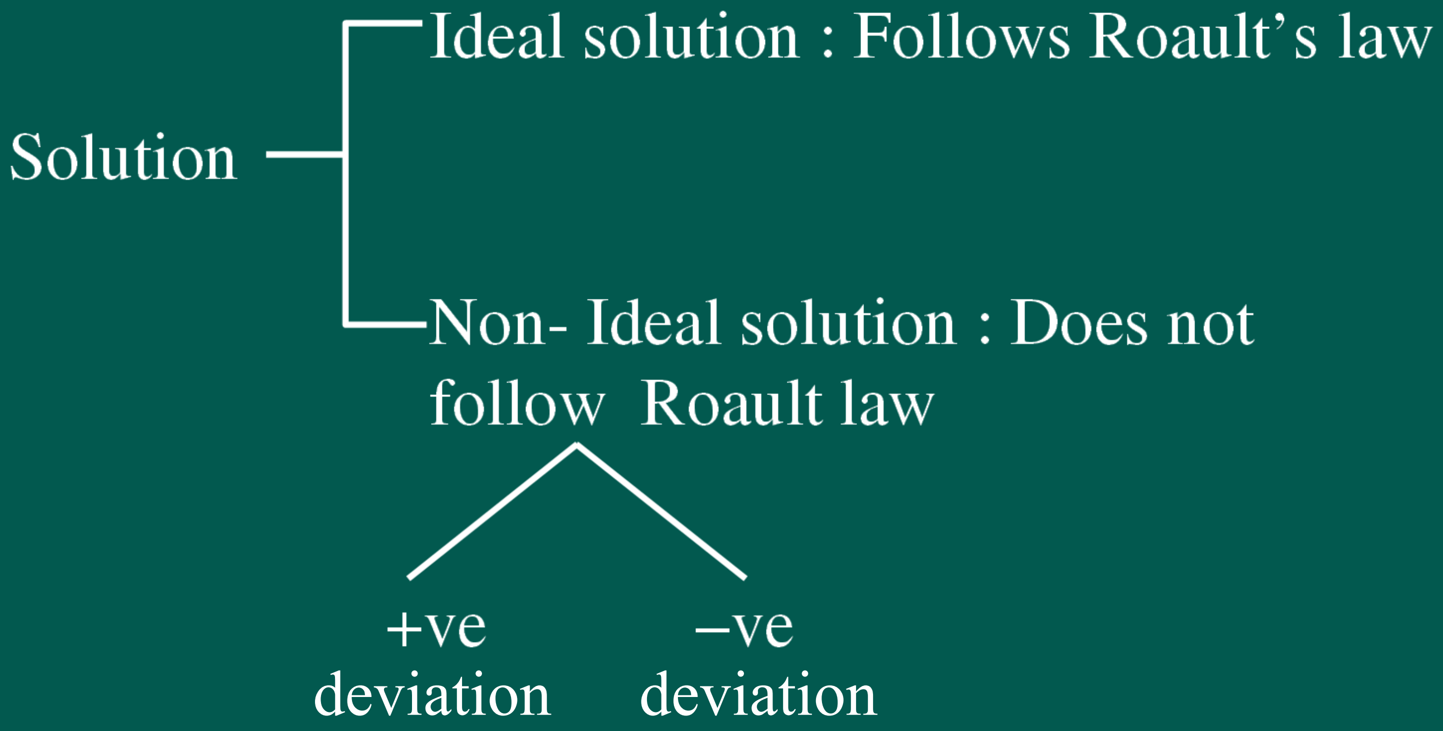
Solution :

$$\frac{1}{P_T} = \frac{y_A}{P_A^o} + \frac{y_B}{P_B^o} = \frac{0.5}{200} + \frac{0.5}{100}$$

$$\Rightarrow \qquad P_T = \frac{400}{3}$$

$$\therefore \qquad x_A = \frac{P_T y_A}{P_A^o} = \frac{\left(\frac{400}{3}\right)\times\left(\frac{1}{2}\right)}{200} = \frac{1}{3}$$

$$x_B = \frac{2}{3}$$



Solution

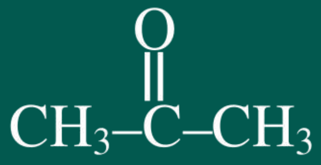
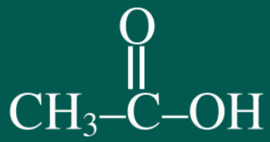
Ideal solution : Follows Roault's law

Non- Ideal solution : Does not follow Roault law

+ve deviation

–ve deviation

Ideal solution	**+ve deviation**	**–ve deviation**
$P_T = P^\circ_A x_A + P^\circ_B x_B$	$P_T > P^\circ_A x_A + P^\circ_B x_B$	$P_T < P^\circ_A x_A + P^\circ_B x_B$
A---A ≡ B---B ≡ A---A	A---B < A╥╥╥A @╥╥╥@	A---B > A╥╥╥A @╥╥╥@
$\Delta G_{mix} = -ve$	$\Delta G_{mix} = -ve$	$\Delta G_{mix} = -ve$
$\Delta S_{mix} = +ve$	$\Delta S_{mix} = +ve$	$\Delta S_{mix} = +ve$
$\Delta H_{mix} = 0$	$\Delta H_{mix} = +ve$	$\Delta H_{mix} = -ve$
$\Delta V_{mix} = 0$	$\Delta V_{mix} = +ve$	$\Delta V_{mix} = -ve$

Ideal solution	+ve deviation	–ve deviation
	polar + nonpolar	$CHCl_3$ +  $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
Hexane + Heptane	$CCl_4 + CHCl_3$	$Ph-NH_2$ + Ph-OH
	CS_2 +  $CH_3-\overset{\overset{O}{\|}}{C}-OH$	$H_2O + HNO_3$
	H_2O + R-OH	$H_2O + CH_3COOH$

Colligative properties

Properties that depend only on amount of solute particles & not on their nature

(1) Osmotic pressure

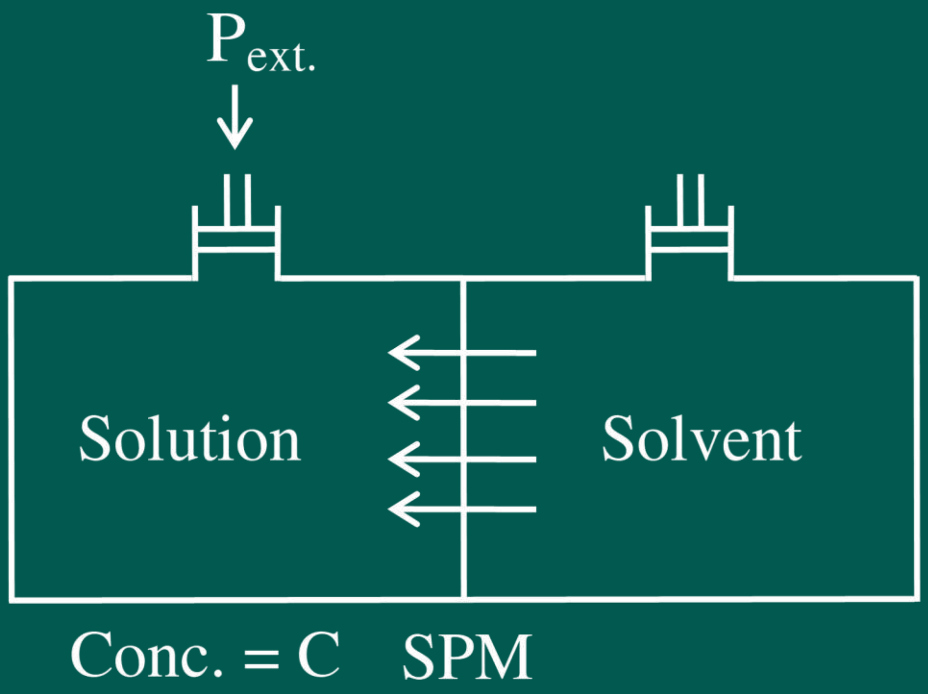
(2) R.L.V.P

(3) Elevation in B.P

(4) Depression in F.P

Osmosis :

The spontaneous flow of solvent particles from solvent side to solution side or from solution of low concentration side to solution of high concentration side through a semipermeable membrane (SPM) is known as osmosis.



Osmotic pressure (π) :

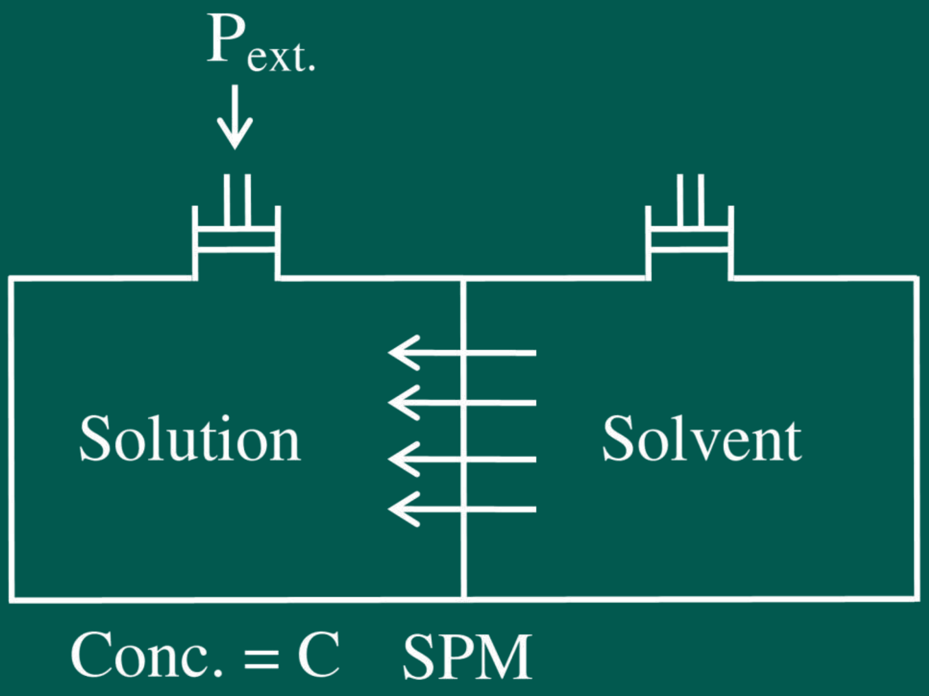
$$\boxed{\pi = \Sigma(iC)RT}$$

C = molarity of solute

R = Gas constant

T = Temperature

i = Vont-Hoff factor



Example :

Calculate the osmotic pressure of a solution containing 18 gm glucose, 6 gm urea and 5.85 gm NaCl per litre at 27°C.

Solution :

For Glucose, $C = \frac{18}{180} = 0.1, i = 1$

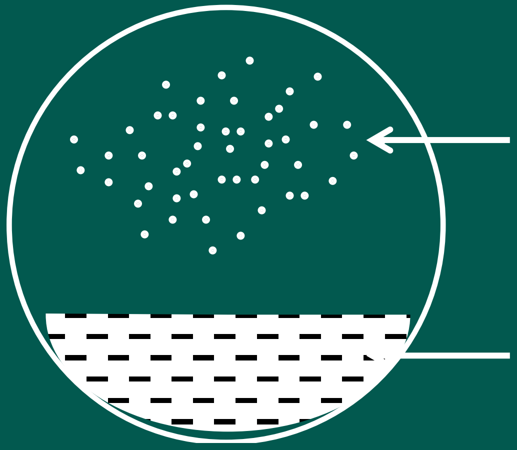
For Urea, $C = \frac{6}{60} = 0.1, i = 1$

For NaCl, $C = \frac{5.85}{58.5} = 0.1, i = 2$

$\therefore \quad \Sigma iC = 0.1 + 0.1 + 0.2 = 0.4$

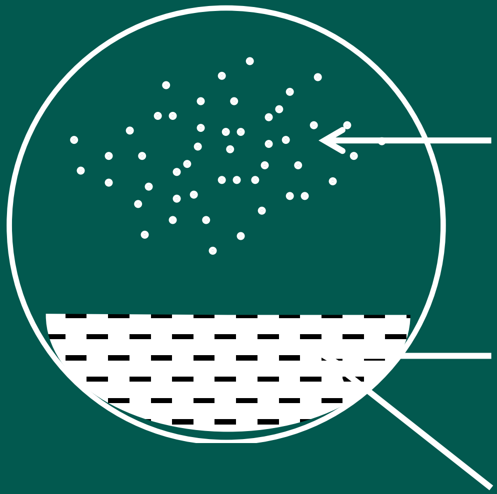
$\pi = \Sigma(iC)RT = 0.4RT = 0.4\left(\frac{1}{12}\right) \times 300 = 10 \text{ atm}$

Relative lowering in vapour pressure (RLVP) :



$P_{H_2O(v)} = P^\circ$

$H_2O\ (l)$

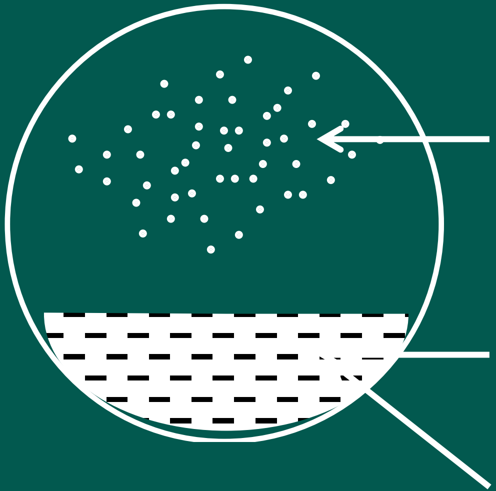


$P_{H_2O(v)} = P_s$

$H_2O\ (l)$: N-mol

A(s): n-mol

Non-volatile solute



$P_{H_2O(v)} = P_s$

H_2O (l): N-mol

A(s): n-mol

$$P_S = P^\circ X_{H_2O}$$

Lowering in V.P. $= P^\circ - P_S$

$$\text{RLVP} = \frac{P^\circ - P_S}{P^\circ} = \frac{P^\circ - P^\circ X_{H_2O}}{P^\circ}$$

$$\text{RVLP} = 1 - X_{H_2O}$$

$$\text{RVLP} = X_A$$

Relative lowering in vapour pressure (RLVP) :

$$\boxed{\mathrm{RLVP} = \frac{P^0 - P_s}{P^0} = x_{\mathrm{Solute}} = \frac{i\,n}{i\,n + N}}$$

$$\boxed{\frac{P^\circ - P_s}{P_s} = i \times \frac{n}{N} = i \times m \times \frac{M}{1000}}$$

m = Molality

M = Molar mass of solvent

Example :

10 g of a solute is dissolved in 80 g of acetone. Vapour pressure of this solution = 271 mm of Hg. If vapour pressure of pure acetone is 283 mm of Hg, calculate molar mass of solute.

Sol. $$\frac{P°-P_s}{P_s} = \frac{n}{N} = \frac{w}{m} \times \frac{M}{W}$$

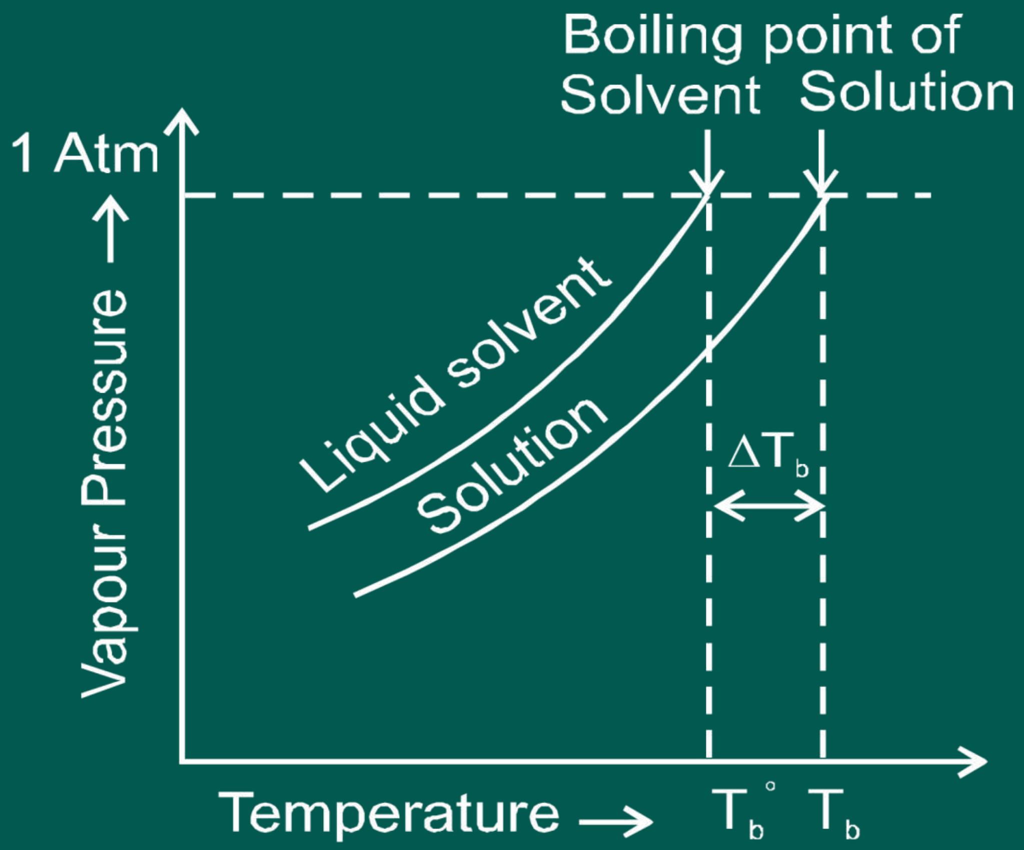
$$\Rightarrow \frac{283-271}{271} = \frac{10}{m} \times \frac{58}{80}$$

$$\Rightarrow m = 163 \quad g/mol.$$

Elevation in Boiling point (ΔT_b)

$$\boxed{\Delta T_b = i \times K_b \times \text{molality}}$$

K_b is dependent on property of solvent and known as ebullioscopic constant of solvent or molal depression constant.



Example :

A solution containing 0.5 g of naphthalene in 50 g CCl_4 yield a boiling point elevation of 0.4 K, while a solution of 0.6 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.65 K. Find the molar mass of the unknown solute.

Solution :

$\Delta T_b = K_b \times$ molality

$$0.4 = K_b \times \frac{0.5/128}{50} \times 1000 \qquad \text{.... (i)}$$

$$0.65 = K_b \times \frac{0.6/m}{50} \times 1000 \qquad \text{.... (ii) for unknown solution}$$

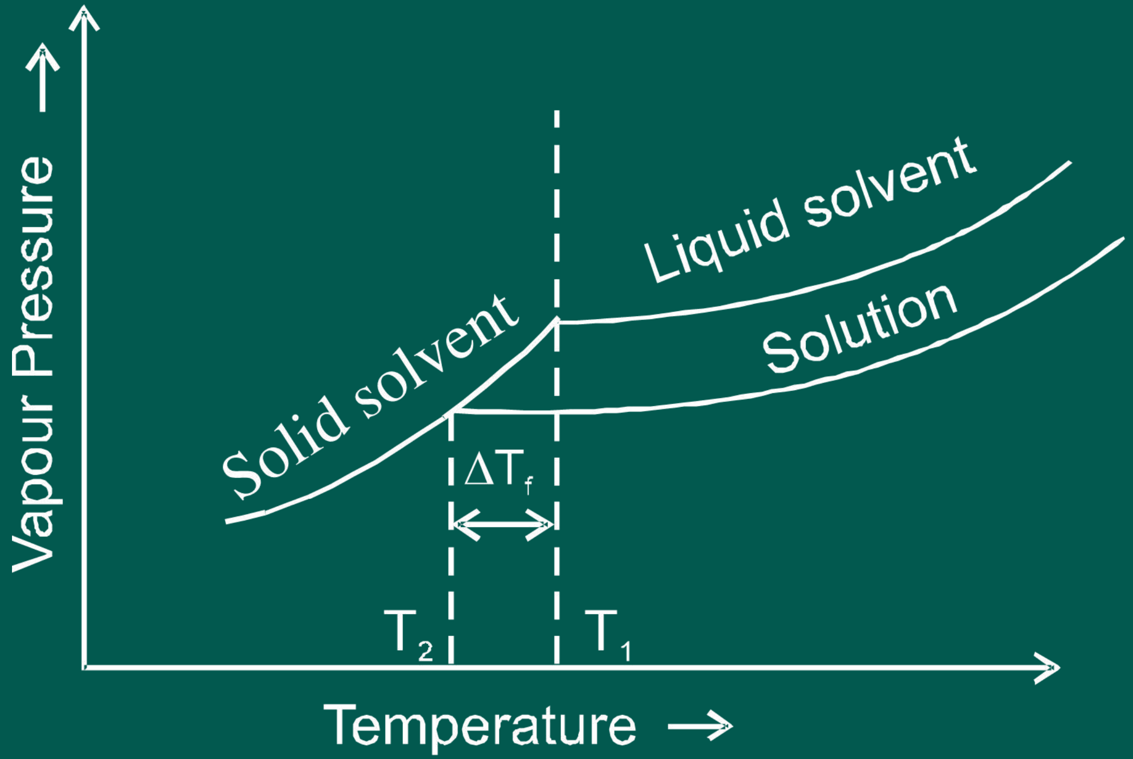
Dividing eq. (i) by (ii), we get

m = 94.5 Ans.

Depression In Freezing Point (ΔT_f) :

$$\boxed{\Delta T_f = i \times K_f \times \text{molality}}$$

K_f is dependent on property of solvent and known as cryoscopic constant of solvent or molal elevation constant.



Example :

What should be the freezing point of aqueous solution containing 6 gm of CH_3COOH in 1000 gm of water in °C? ($K_f = 1.86$ kgKmol^{-1}, $\alpha_{CH_3COOH} = 0.2$)

Solution :

$$m = \frac{6/60}{1000} \times 1000 = 1 \text{ m}$$

$$i = 1 + \alpha = 1.2$$

$$\Delta T_f = iK_f \times m = (1.2)(1.86)(1) = 2.23$$

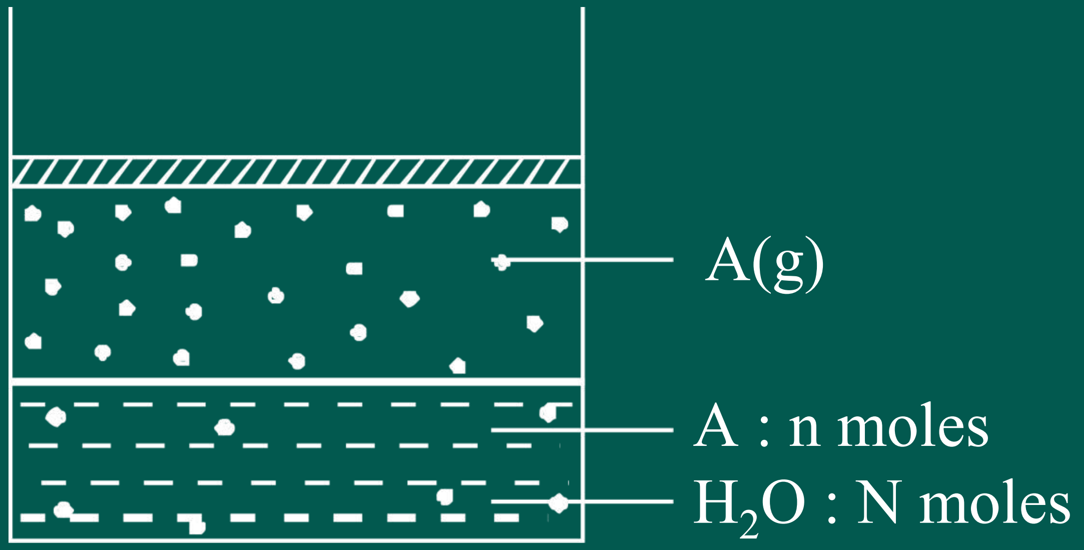
$$\therefore\ T_f = 0 - 2.23 = -2.23\ °C$$

Solubility of gases in solution :

Henry' Law :

The solubility of a gas in solution is directly proportional to its partial pressure

$$\boxed{P_A = K_H X = K_H \frac{n}{N}}$$



K_H = Henry's Law Constant
P_A = Partial pressure of gas
X = Mole fraction of gas in solution

Note :

- Henry's Law Constant depends on nature of gas and liquid as well as temperature.
- Greater K_H means low solubility.
- K_H increases with increases in temperature.

Example :

The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water of 298 K and 5 atm pressure is :

Solution :

$$P_{N_2} = K_H \times x_{N_2}$$

$$4 = 10^5 \times \frac{n}{10}$$

$$n = 4 \times 10^{-4}$$

CHEMICAL KINETICS

Frequently Asked Concepts in JEE Main & JEE Advanced :

Chemical Kinetics

- Rate & Rate law
- First order reactions
- Experimental determination of order
- Monitoring of progress of reaction
- Temperature dependence of rate constant
- Mechanism of reaction

Rate of chemical reaction :

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec}} = \text{mol lit}^{-1}\ \text{time}^{-1} = \text{mol dm}^{-3}\ \text{time}^{-1}$$

For a reaction $R \longrightarrow P$

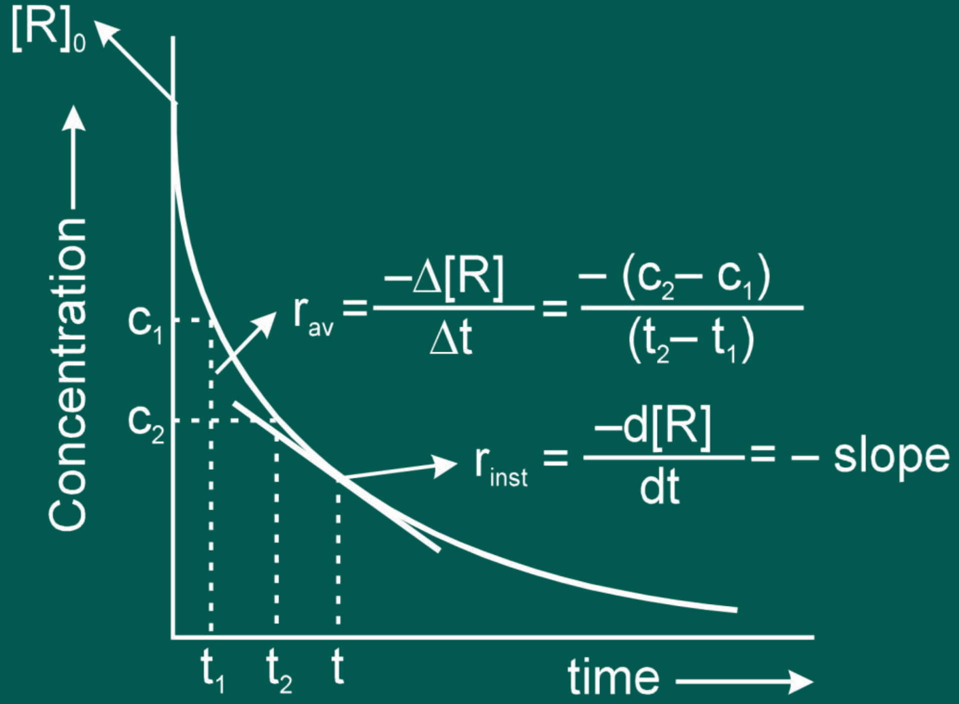
$$\textbf{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

$$= \frac{\Delta c}{\Delta t} = -\frac{\Delta [R]}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

Instantaneous rate : rate of reaction at a particular instant.

$$R_{\text{instantaneous}} = \lim_{t\to 0}\left[\frac{\Delta c}{\Delta t}\right] = \frac{dc}{dt} = -\frac{d\,[R]}{dt} = \frac{d\,[P]}{dt}$$

Instantaneous rate can be determined by drawing a tangent at time t on curve drawn for concentration versus time.



For the reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$

Rate of disappearance of $N_2 = -\frac{d[N_2]}{dt}$

Rate of disappearance of $H_2 = -\frac{d[H_2]}{dt}$

Rate of disappearance of $NH_3 = \frac{d[NH_3]}{dt}$

Rate of reaction $= -\frac{d[N_2]}{dt} = -\frac{1\,d[H_2]}{3\,dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

Note :

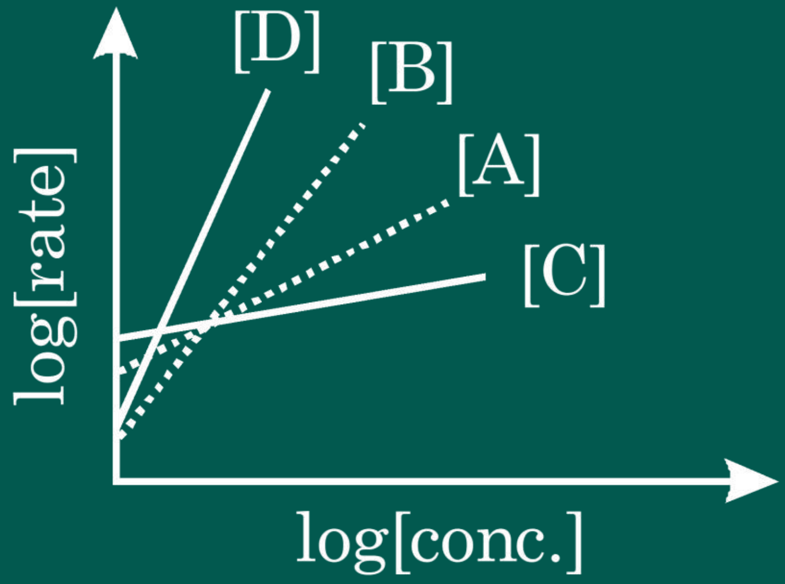
Rate of reaction value is dependent on the stoichiometric coefficients used in the reaction while rate of disappearance / appearance of any species will be fixed value under given conditions.

Question :

Consider the following reactions :

$A \rightarrow P1$; $B \rightarrow P2$; $C \rightarrow P3$; $D \rightarrow P4$

The order of the above reactions are a, b, c, and d, respectively. The following graph is obtained when log [rate] vs. log[conc] are plotted:



Among the following , the correct sequence for the order of the reactions is:

(1) a > b > c > d

(2) c > a > b > d

(3) d > b > a > c

(4) d > a > b > c

Solution :

General rate law : rate = $k(\text{conc.})^{\text{Order}}$

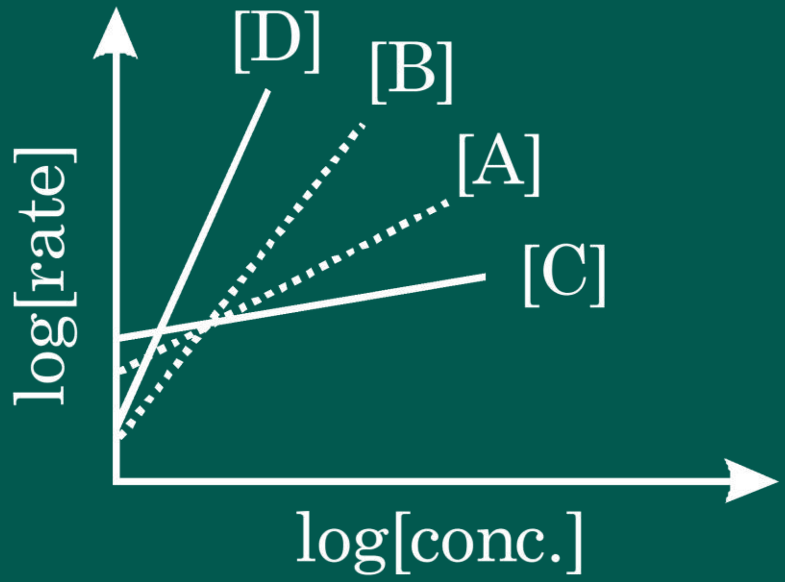
$\therefore$ log [rate] = log K + order × log(conc.)

So, greater the slope of log [rate] vs log [conc.] graph, greater is order of reaction.

Order of slope of graphs = [D] > [B] > [A] > [C]

$\therefore$ Order of corresponding orders of reactions

= d > b > a > c.



Rate law

$$\textbf{Rate} \propto \textbf{(conc.)}^{\textbf{order}}$$

$$\textbf{Rate} = \textbf{k (conc.)}^{\textbf{order}}$$

Where k = Rate constant

= specific reaction rate (rate of reaction when concentration is unity)

- unit of k = $(\text{conc})^{1-\text{order}}\ \text{time}^{-1}$

k depend on temperature only and not on concentration.

Order of reaction :

$$m_1A + m_2B \longrightarrow \text{products.}$$

$$R \propto [A]^p\,[B]^q$$

$$R = k\,[A]^p\,[B]^q$$

where p may or may not be equal to m_1 and similarly q may or may not be equal to m_2.

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and $(p + q)$ is **overall order of the reaction.**

INTEGRATED RATE LAWS

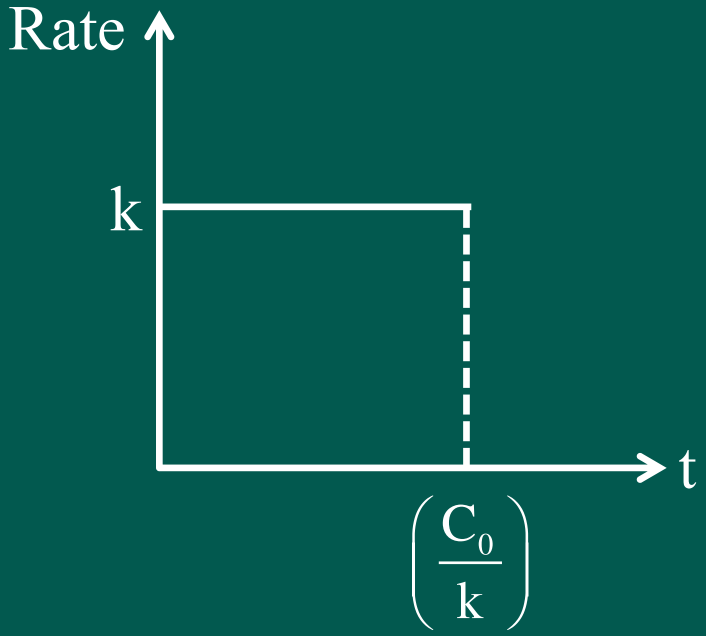
(a) Zero order reactions :

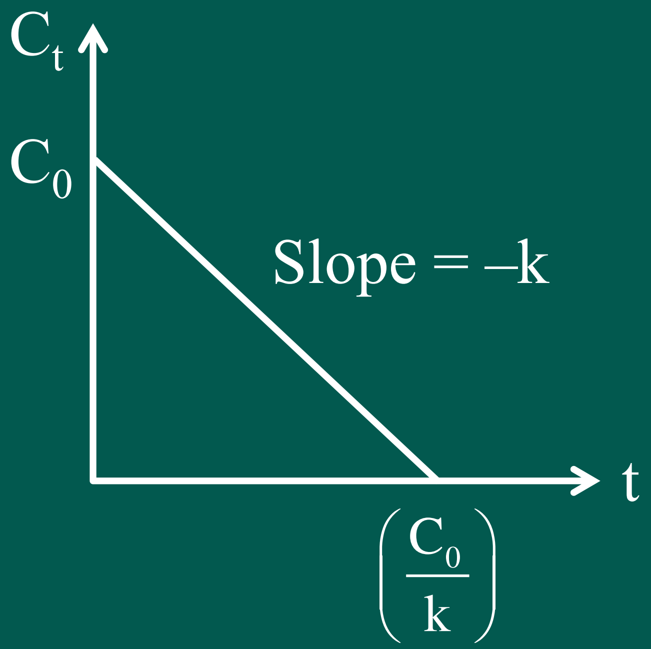
Rate $= k = \frac{C_0 - C_t}{'t'}$ or $kt = C_0 - C_t$ or $C_t = C_0 - kt$

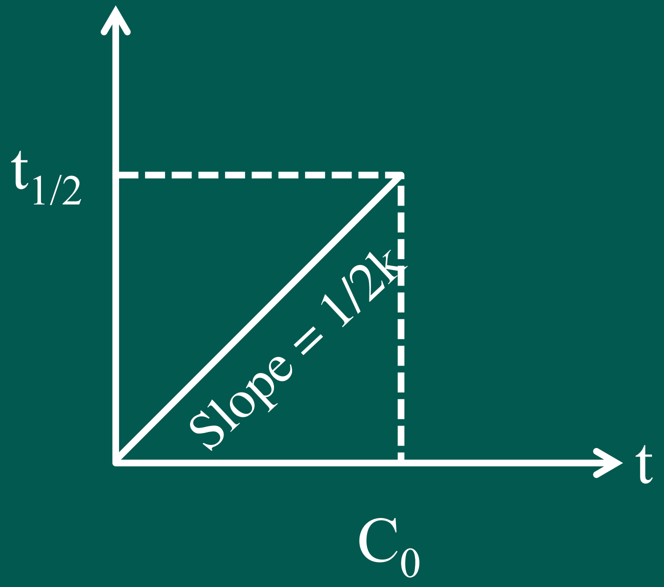
- Unit of k is same as that of Rate = mol lit^{-1} sec^{-1}.
- Time for completion $= \frac{C_0}{k}$
- Half life time ($t_{1/2}$) (at $t_{1/2}$, $C_t = \frac{C_0}{2}$)

$\Rightarrow$ $t_{1/2} = \frac{C_0}{2k}$

Graphical Representation :







(b) First Order Reactions :

$$\boxed{k = \frac{2.303}{t}\log\frac{C_0}{C_t}} \quad \boxed{C_t = C_0\ e^{-kt}} \quad \boxed{k = \frac{2.303}{(t_2 - t_1)}\log\frac{C_1}{C_2}}$$

- Half life time ($t_{1/2}$)

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

- Amount left after n half lives $= \frac{C_o}{2^n}$

Question :

A reaction has a half-life of 1 min. The time required for 99.9% completion of the reaction is _______ min. (Round off to the Nearest integer)

[Use: ln 2 = 0.69, ln 10 = 2.3]

Solution :

$$k = \frac{1}{t}\ln\left(\frac{C_0}{C_t}\right)$$

$$\frac{\ln 2}{1} = \frac{1}{t}\ln\left(\frac{100}{0.1}\right) \quad \therefore \ t = \frac{\ln 1000}{\ln 2} = \frac{3 \times 2.3}{0.69} = 10$$

Question :

A and B decompose via first order kinetics with half-lives 54.0 min and 18.0 min respectively. Starting from an equimolar non reactive mixture of A and B, the time taken for the concentration of A to become 16 times that of B is ______ min. (Round off to the Nearest Integer).

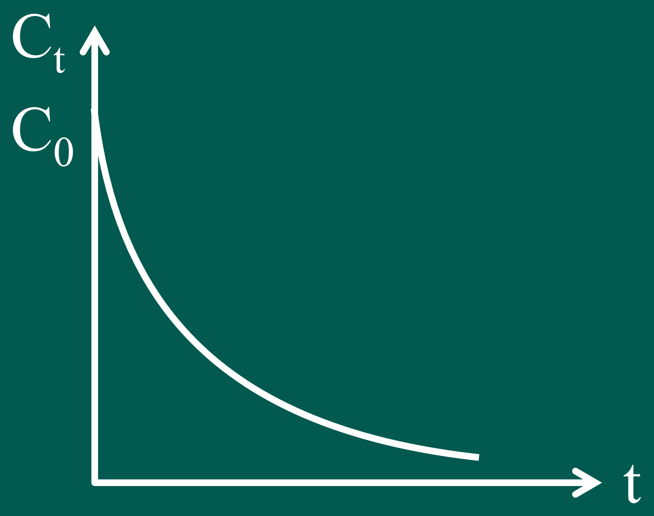
Solution :

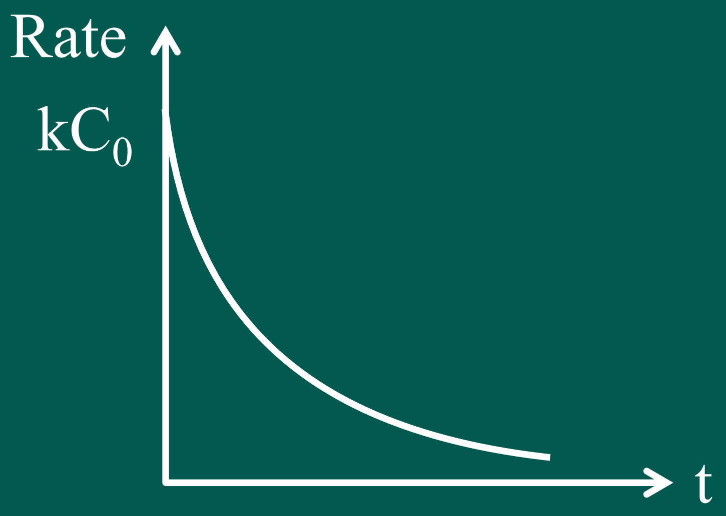
Let after n half lives of A conc. of A becomes 16 times that of B

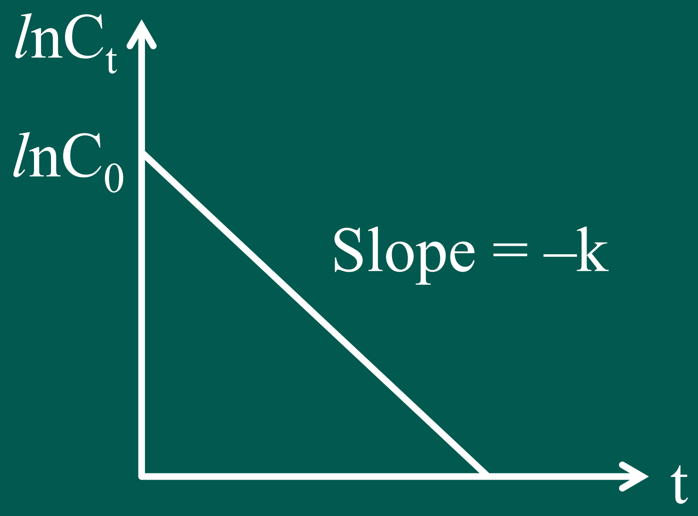
$$\frac{a}{2^n} = 16\frac{a}{2^{3n}}$$

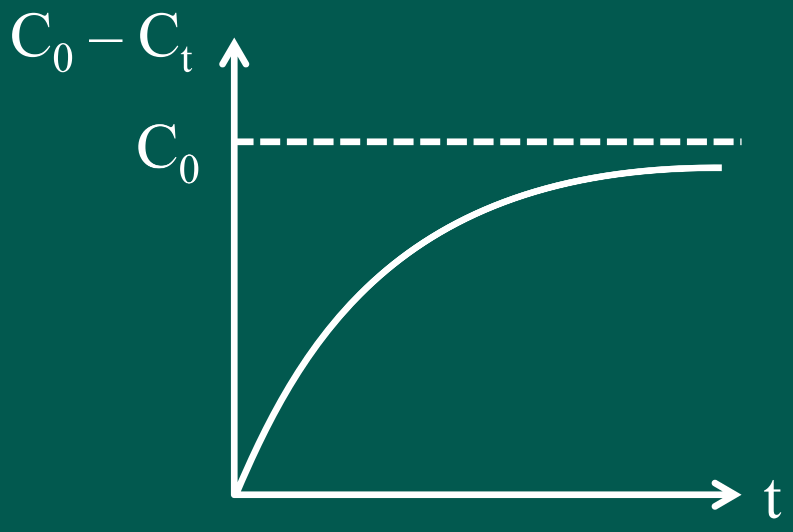
So, $n = 2$ and time $= 54 \times 2 = 108$ min.

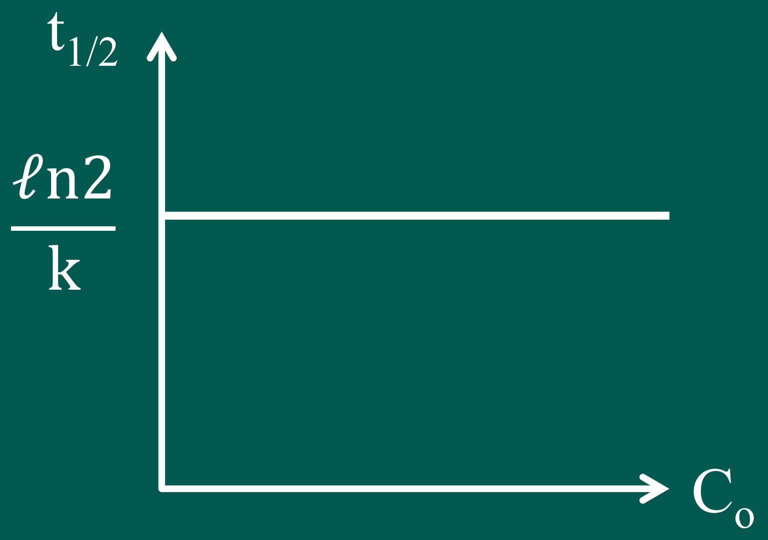
GRAPHICAL REPRESENTATION







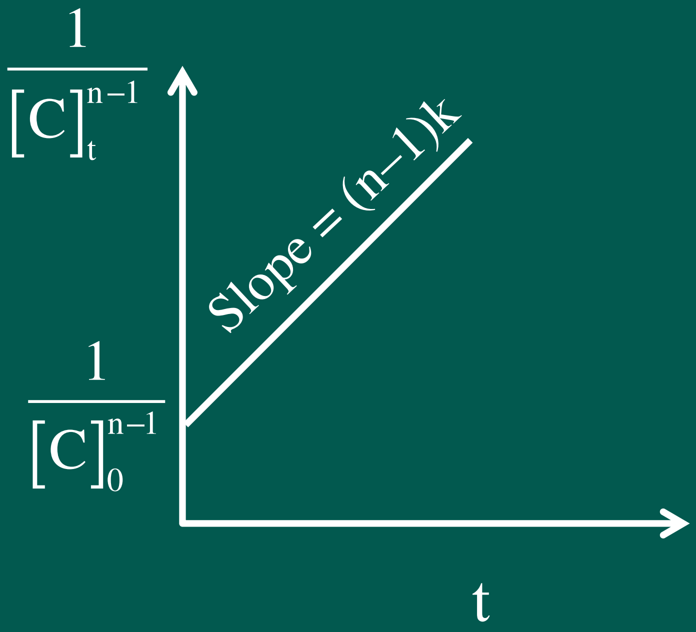




(c) n^{th} Order Reactions :

$$\frac{1}{[C]_t^{n-1}} - \frac{1}{[C]_0^{n-1}} = (n-1)kt$$

$$t_{1/2} \propto C_0^{1-n}$$



Experimental determination of order

Integrated rate law method

Question :

$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(s)$

This reaction was studied at –10°C and the following data was obtained

run	$[NO]_0$	$[Cl_2]_0$	r_0
1	0.10	0.10	0.18
2	0.10	0.20	0.35
3	0.20	0.20	1.40

$[NO]_0$ and $[Cl_2]_0$ are the initial concentrations and r_0 is the initial reaction rate.

The overall order of the reaction is _______. (Round off to the Nearest Integer).

Solution :

Let Rate = $K[NO]^{\alpha}[Cl_2]^{\beta}$

$$\frac{0.18}{0.35} = \frac{K[NO]^{\alpha}[Cl_2]^{\beta}}{K[NO]^{\alpha}[Cl_2]^{\beta}}$$

$$\frac{0.18}{0.35} = \frac{[0.1]^{\alpha}[0.1]^{\beta}}{[0.1]^{\alpha}[0.2]^{\beta}}$$

$\beta = 1$

$$\frac{0.35}{1.4} = \frac{K[0.1]^{\alpha}[0.2]^{\beta}}{K[0.1]^{\alpha}[0.2]^{\beta}}$$

$\alpha = 2$

Rate = $K[NO]^{1}[Cl_2]^{2}$

Overall order = 3

Methods to monitor the progress of the reaction :

By Pressure measurement :

Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature.

Question :

N_2O_5 decomposes to NO_2 and O_2 and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mmHg to 87.5 mmHg. The pressure of the gaseous mixture after 100 minute at constant temperature will be:

Sol.	$2N_2O_5 \longrightarrow$	$4NO_2$	$+$	O_2
Initial pressure (t = 0)	50 mm	0		0
Pressure at t = 50 min	$50 - 2x$	$4x$		x

$$50 + 3x = 87.5$$

$$3x = 37.5$$

$$x = 12.5$$

$\therefore t_{1/2} = 50$ min.

Pressure at t = 100 min	$\frac{50}{4}$ $= 12.5$	$2 \times \frac{3}{4} \times 50$ $= 75$	$\frac{1}{2} \times \frac{3}{4} \times 50$ $= 18.75$

P_{total} (at t = 100 min) = 106.25 mm

Temperature Dependence of the Rate of a Reaction

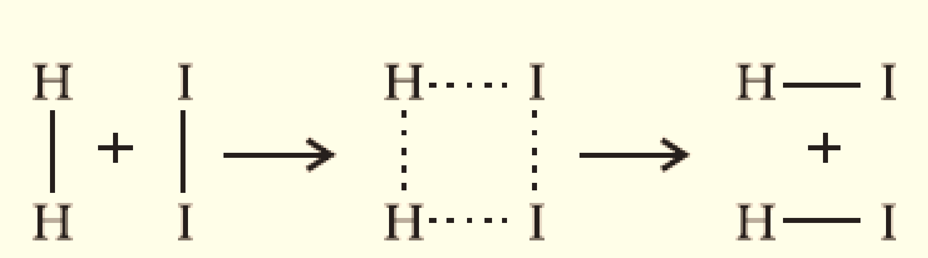
Arrhenius equation :

$$\boxed{k = Ae^{-Ea/RT}}$$

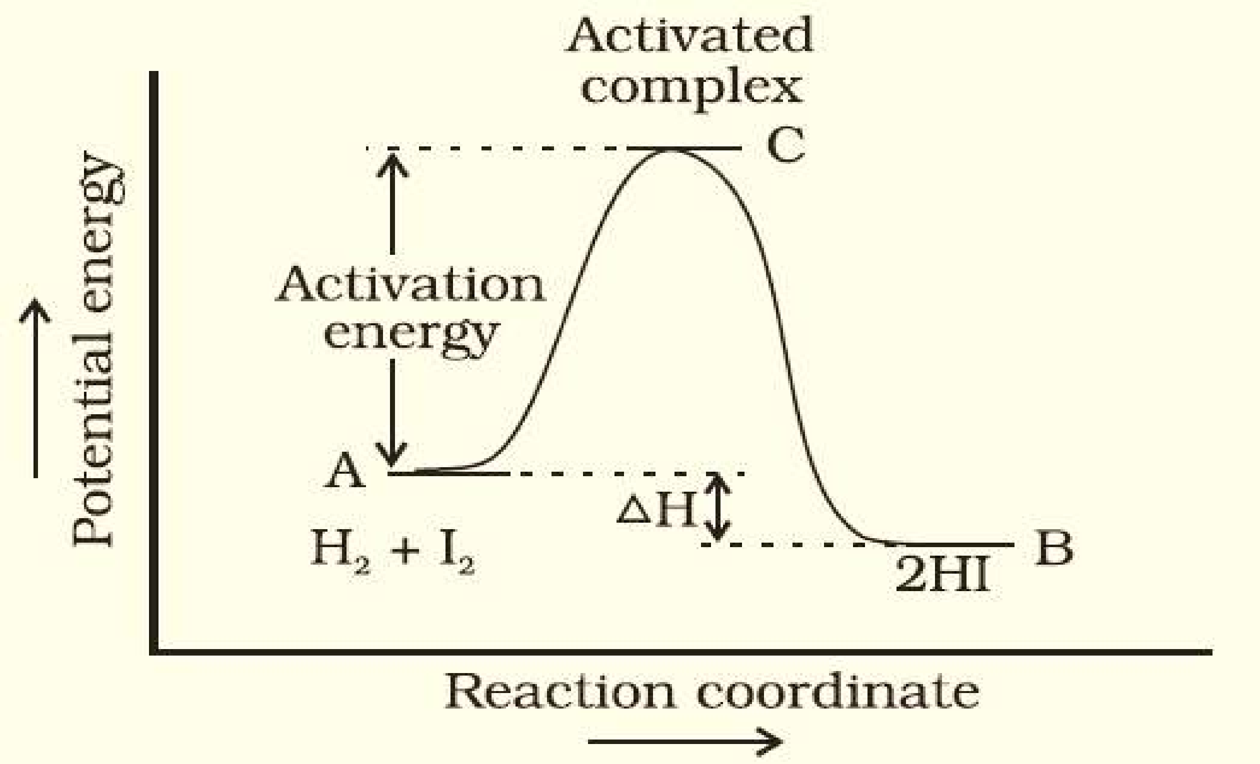
where

- A is the Arrhenius factor or frequency factor or pre-exponential factor.
- R is gas constant
- Ea is activation energy measured in joules/mole ($Jmol^{-1}$).

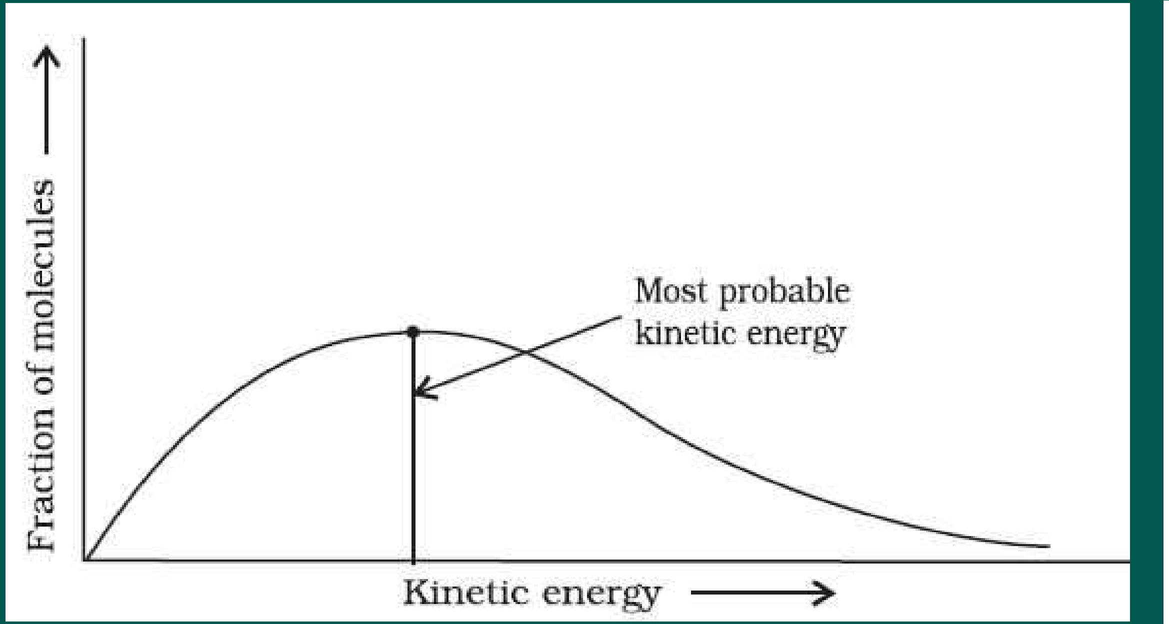
$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

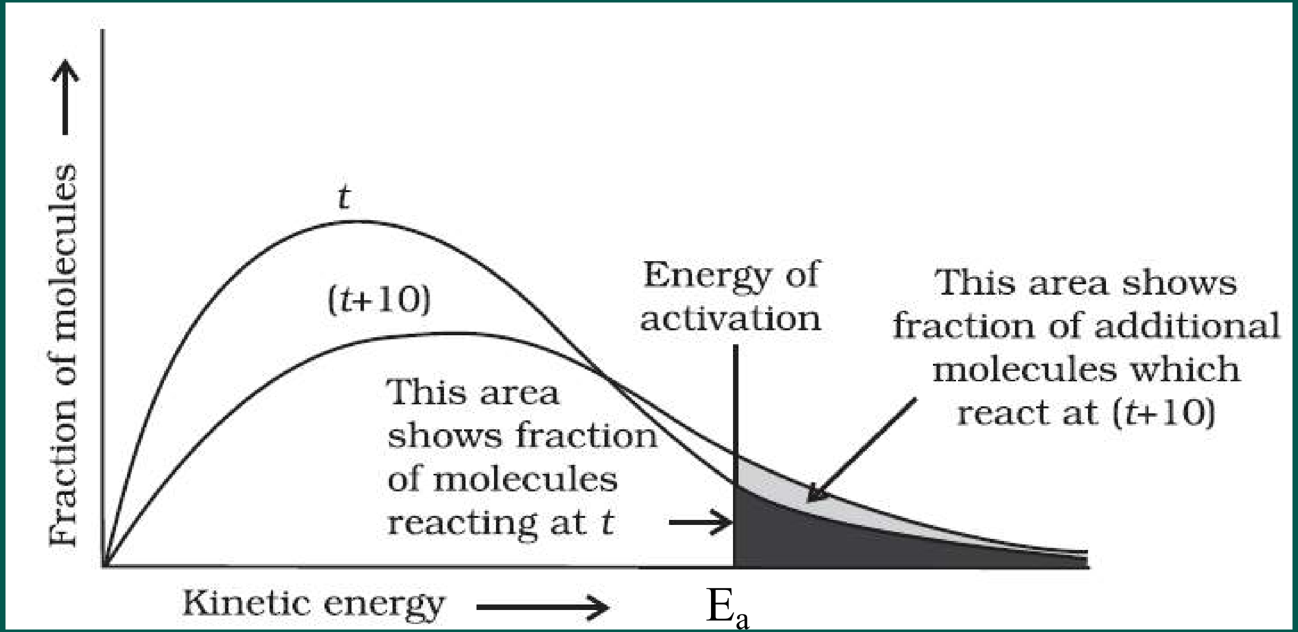


Transition state



The energy required to form this transition state, called **activated complex** (C), is known as **activation energy** (E_a).



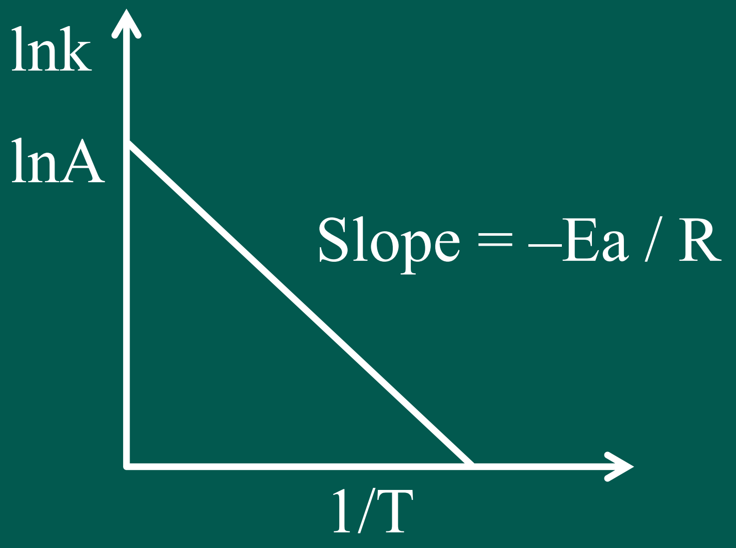


Distribution curve showing energies among gaseous molecules

Distribution curve showing temperature dependence of rate of a reaction

Fraction of molecules crossing energy barrier = $e^{-Ea/RT}$

$$\ln k = \frac{E_a}{RT} + \ln A$$



$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Question :

A reactant (A) forms two products :

$A \xrightarrow{k_1} B$, Activation Energy Ea_1

$A \xrightarrow{k_2} C$, Activation Energy Ea_2

If $Ea_2 = 2\ Ea_1$, then k_1 and k_2 are related as :

(1) $k_2 = k_1 e^{Ea_1/RT}$ (2) $k_2 = k_1 e^{Ea_2/RT}$

(3) $k_1 = Ak_2 e^{Ea_1/RT}$ (4) $k_1 = 2k_2 e^{Ea_2/RT}$

Sol.

$$k_1 = A_1 e^{-Ea_1/RT}$$

$$k_2 = A_2 e^{-Ea_2/RT}$$

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} e^{(E_{a_2} - E_{a_1})/RT}$$

$$k_1 = k_2 A \times e^{E_{a_1}/RT}$$

Molecularity of a reaction

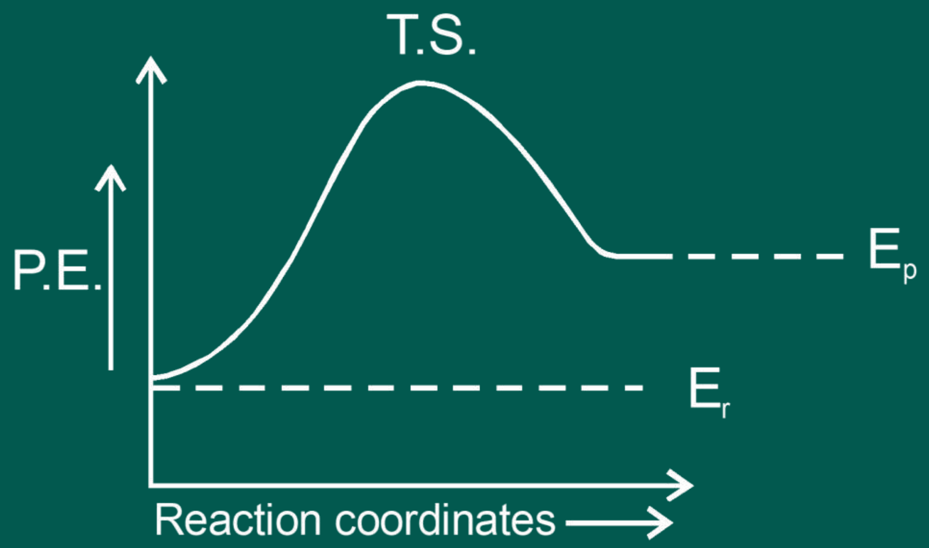
The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

- The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

Mechanism of reaction :

Elementary reaction :

- These reaction take place in single step without formation of any intermediate

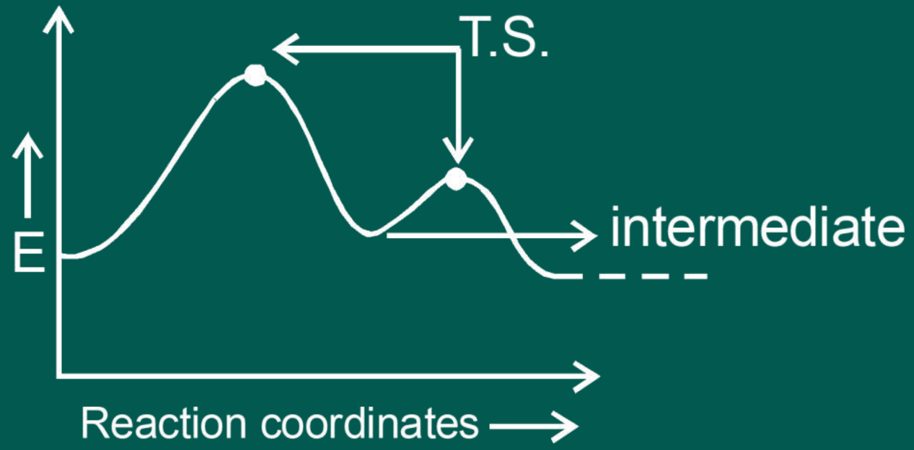


- For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity

Complex reaction :

- Reaction which proceed in more than two steps. or having some mechanism.

(sequence of elementary reaction in which any complex reaction proceeds)



- Order of complex reaction can be zero, fraction, whole no, even negative w.r.t. some species.
- Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using Rate determine step (R.D.S) if given.
- Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.

Question :

For an elementary chemical reaction,

$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is :

(1) $2k_1[A_2]-k_{-1}[A]^2$ (2) $k_1[A_2]-k_{-1}[A]^2$

(3) $2k_1[A_2]-2k_{-1}[A]^2$ (4) $k_1[A_2]+k_{-1}[A]^2$

Solution : $r_f = k_1[A_2] = \frac{1}{2}\frac{d[A]}{dt}$ R.O.A. of A = $2k_1[A_2]$

$r_b = k_{-1}[A]^2 = -\frac{1}{2}\frac{d[A]}{dt}$ R.O.D. of A = $2k_{-1}[A]^2$

$$\frac{d[A]}{dt} = 2k_1[A_2] - 2k_{-1}[A]^2$$

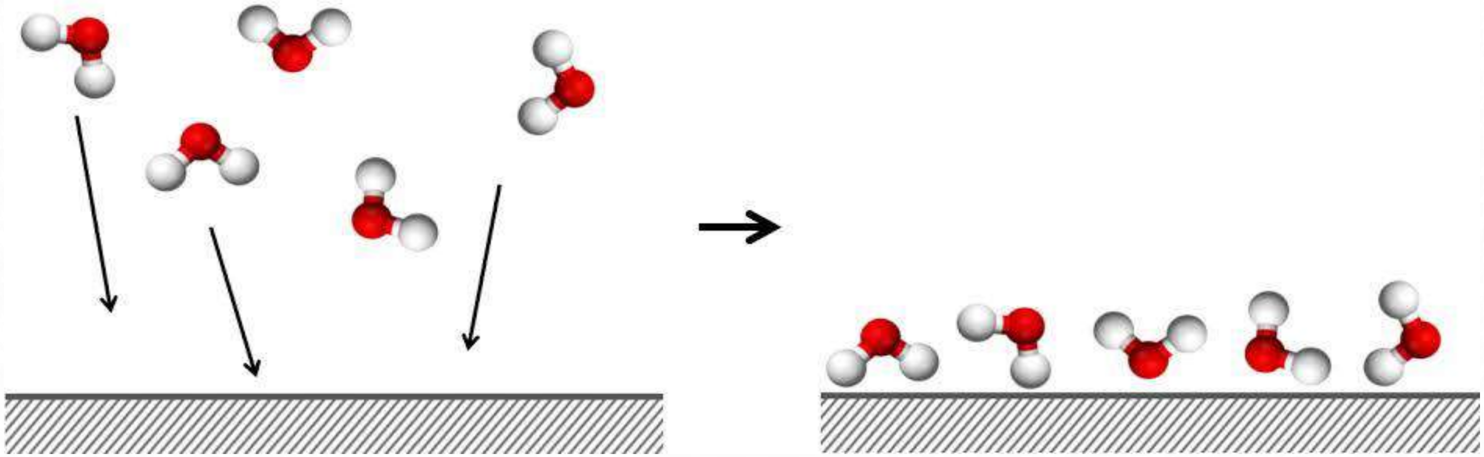
SURFACE CHEMISTRY

- Study of phenomena occurring
  …….at the surface or interface:

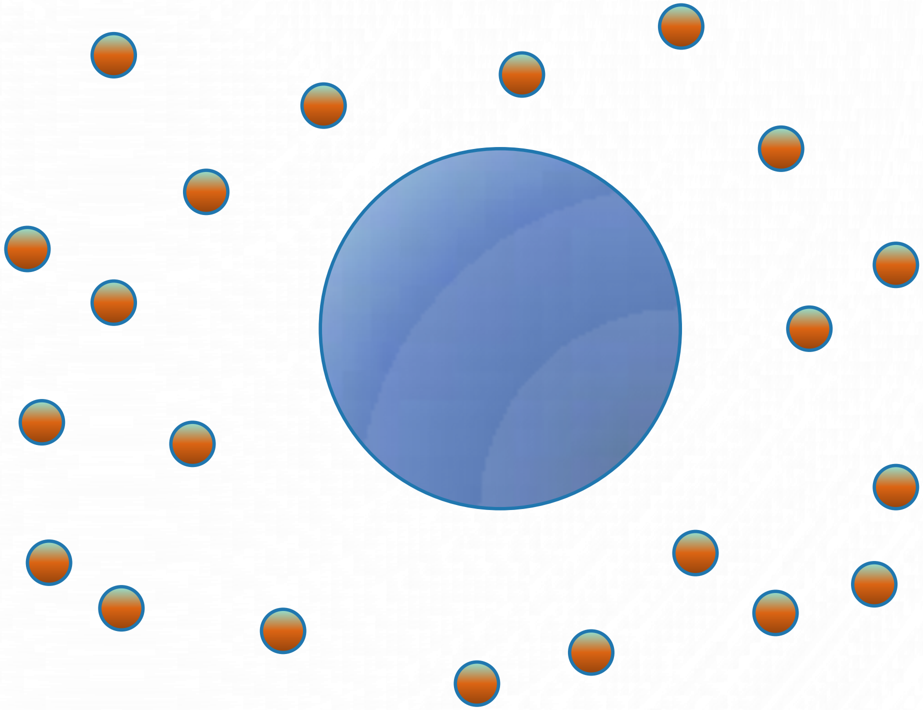
Adsorption, Colloids & Heterogeneous catalysis …

Adsorption

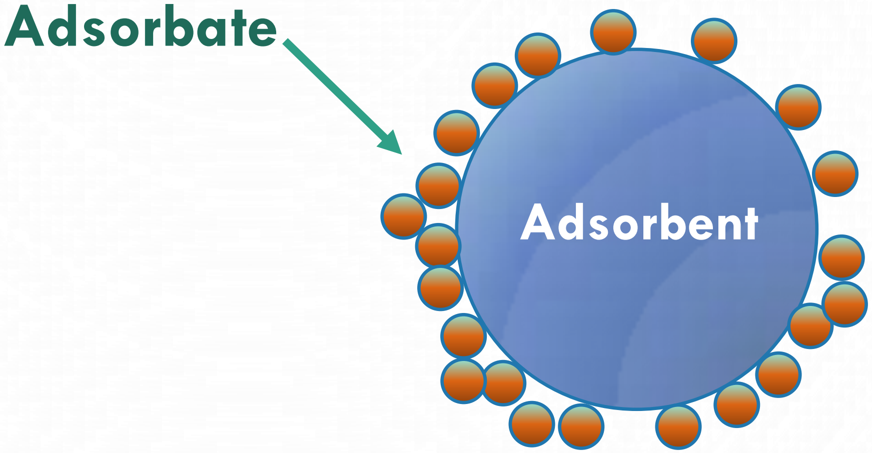
Accumulation of a substance on the surface of another substance



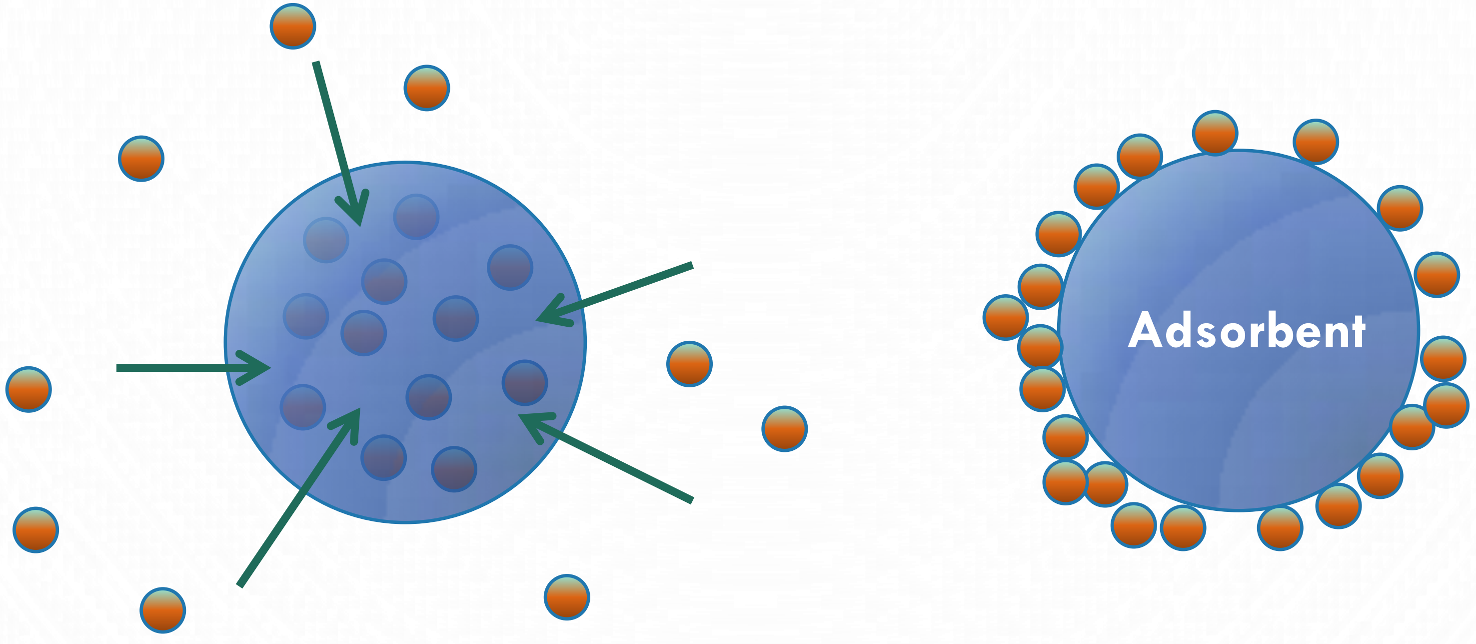
Adsorbent and adsorbate :



Adsorbent and adsorbate :



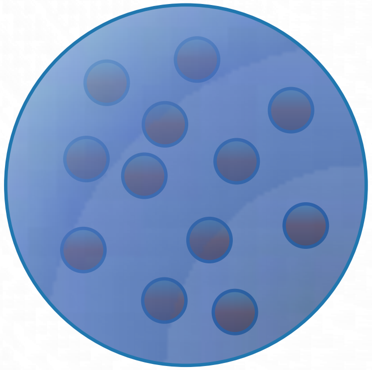
Difference between Absorption and Adsorption

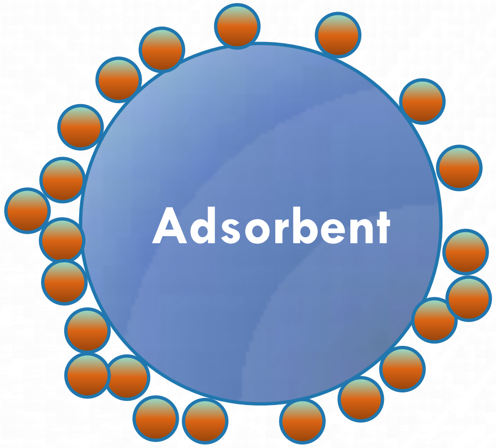


Absorption

Absorption

Absorption	Adsorption
It is a bulk phenomenon.	It is a surface phenomenon.
Concentration is the same throughout the material.	The conce^{n} on the surface of the adsorbent > in the bulk.





Types of adsorption :

(i) Physical adsorption (Physisorption) :

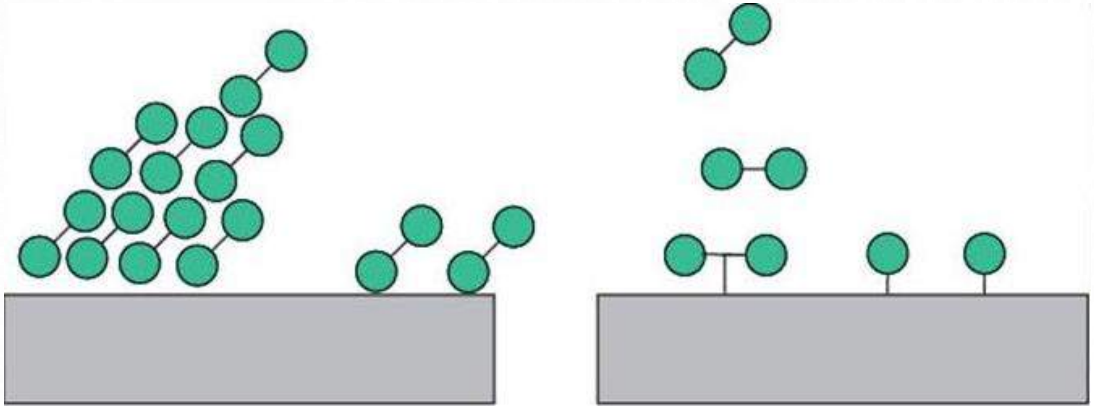
van der Waals adsorption

(ii)Chemical adsorption (Chemisorption) :

Activated adsorption

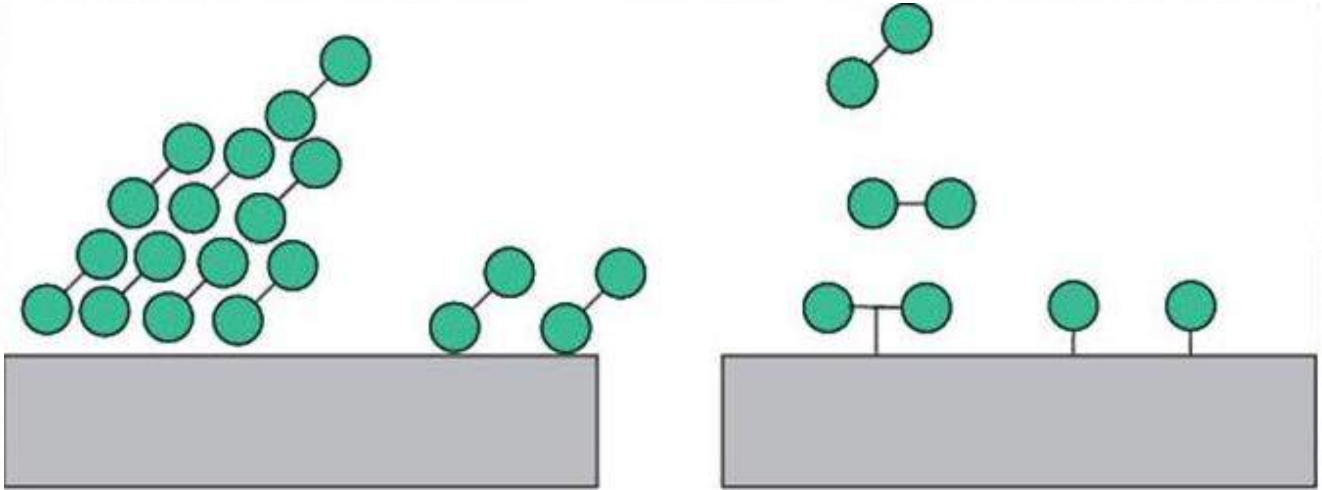
Differences between Physical and Chemical Adsorption

Property	Physical Adsorption	Chemical Adsorption
Nature of adsorption	Weak WVF	Strong Chemical bond
$\Delta H_{\textbf{adsorption}}$	- (20 to 40)kj/mol	- (80 to 240)kj/mol
Reversibility	Reversible / rapid	Irreversible / slow
Specificity	Less specific	Highly specific
Layers of adsorbate	Multi-layered	Mono-layered
Energy of activation	Very low	Significantly high



Thermodynamics of adsorption

- $\Delta H_{adsorption}$ is always negative.
- ΔS is always negative.
- $\Delta G = \Delta H - T\Delta S$



Adsorption of gases on solids :

factors:

The nature of the adsorbate gas

Easily liquefiable gases	Permanent gases
such as HCl, NH_3, Cl_2	such as H_2, N_2 , O_2.

Nature of adsorbent:

Activated charcoal/metal oxides (silica gel and Al_2O_3) and clay etc. → **Adsorb easily liquefiable gases more**

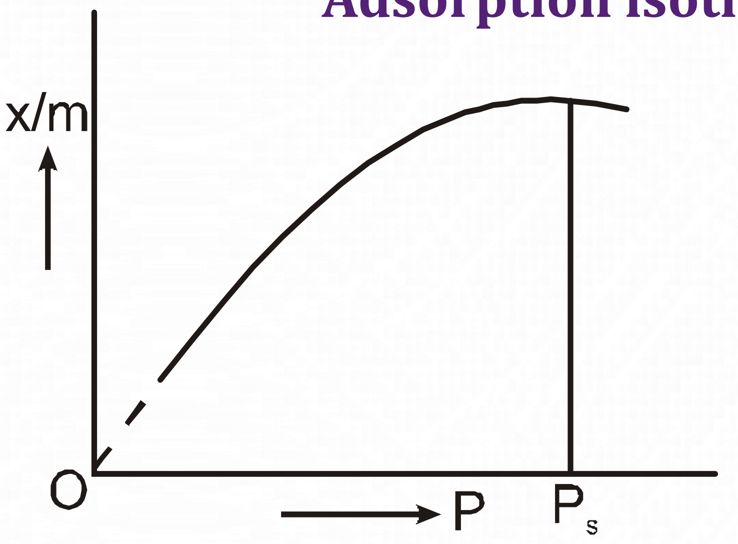
Finely divided transition metals Ni and Co etc. → **Adsorb Permanent gases more (H_2, N_2 and O_2)**

Effect of pressure

Freundlich Adsorption isotherm

$$\frac{x}{m} = k\,p^{1/n}$$

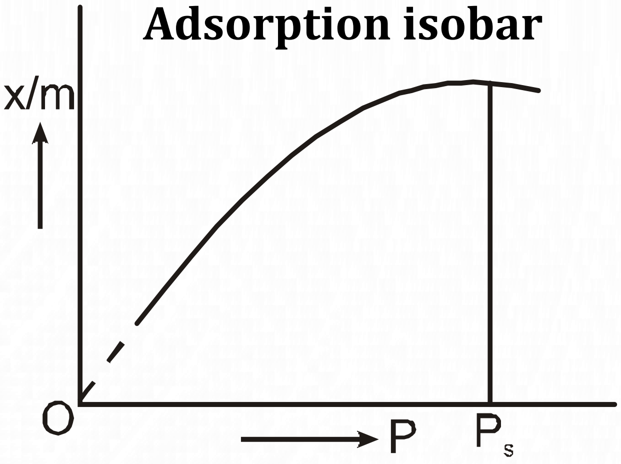
Adsorption isotherm



Effect of pressure

Freundlich Adsorption isotherm

$$\frac{x}{m} = k\,p^{1/n}$$

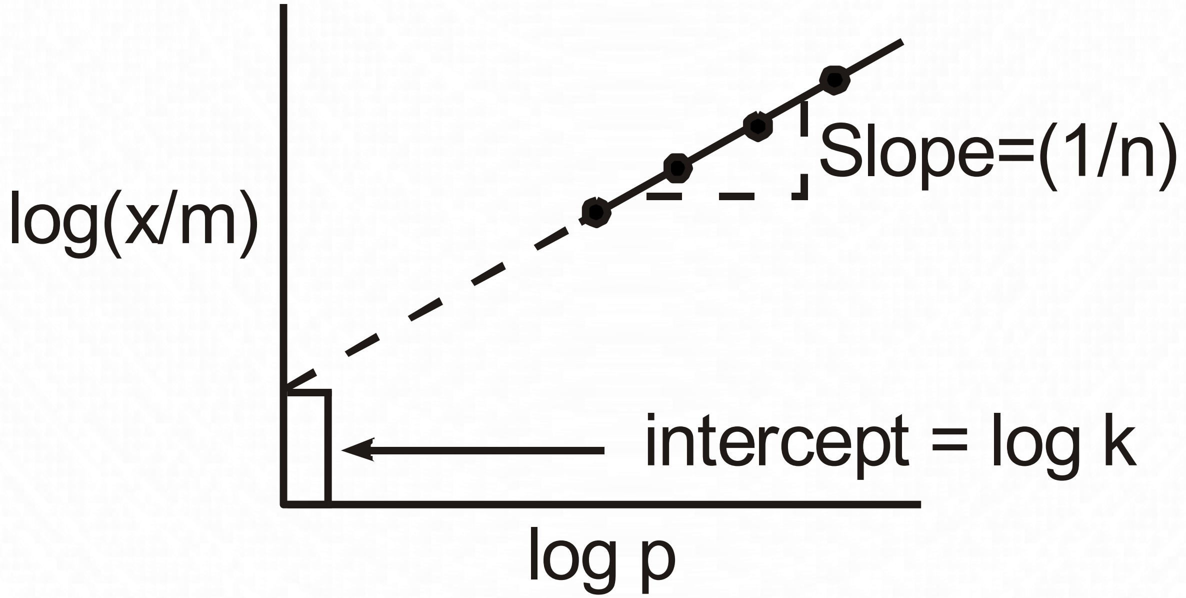


- x = mass of gas adsorbed,
- m = Mass of adsorbent,
- x/m = specific adsorption or mass of gas adsorbed per gram of the adsorbate
- K and n are adsorption constants, which depends upon the nature of adsorbate and adsorbent.

Calculation of constants k and n

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

$\log (x/m) = \log k + (1/n) \log P$



Q. When a graph is plotted between log x/m and log p, it is straight line with an angle 45° and intercept 0.3010 on y-axis. If initial pressure is 0.3 atm, what will be the amount of gas adsorbed per gram of adsorbent :

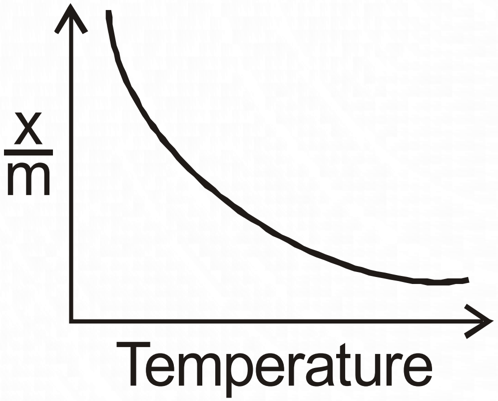
Sol. $\log \frac{x}{m} = \log k + \frac{1}{n} \log P$

$\frac{1}{n} = \tan 45°$ $\quad$ $n = 1$

$\log k = 0.3010$ $\quad$ $k = 2$

$\frac{x}{m} = 2 \times (0.3)1$ $\quad$ $x = 0.6$

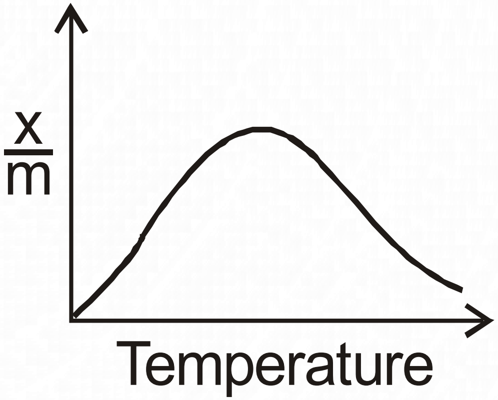
Effect of temperature :



Physical adsorption

Physisorption

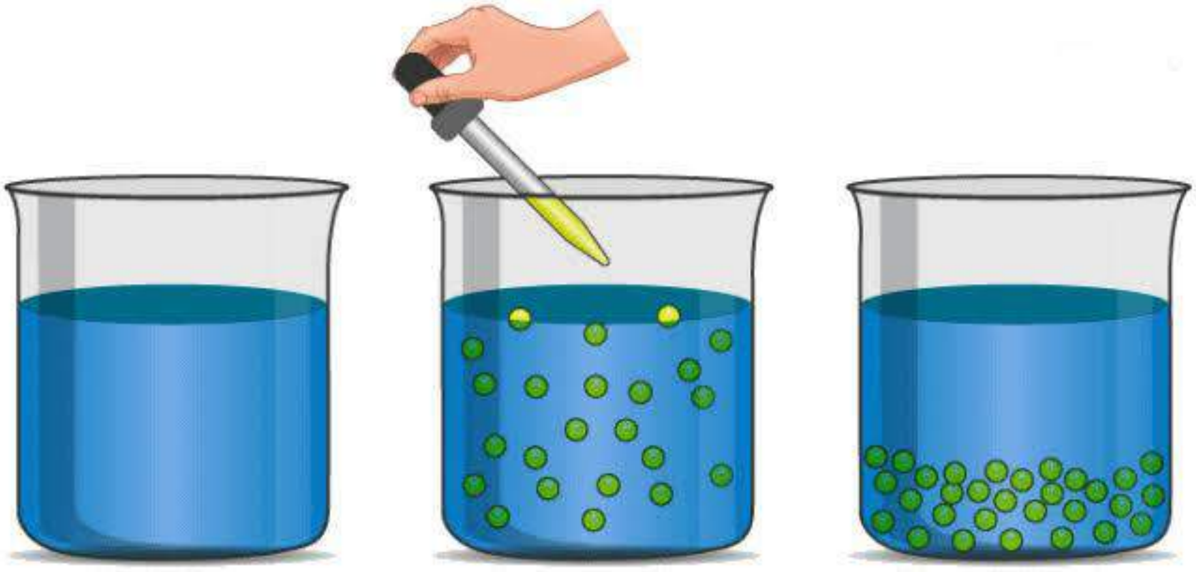
van der Waals adsorption



Chemical adsorption –

Chemisorption

“Activated adsorption”



	True Solution	Colloid Solution	suspension
Particle size	< 1nm	1 to 1000 nm	> 1000 nm

Classification of colloids :

1. On the basis of physical state of D.P. and D.M.

D P	D M	Type of colloid	Examples
Solid	Solid	Solid Sol	Gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Liquid Aerosol	Fog, mist, cloud,
Gas	Solid	Solid Sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream
Gas	Gas	--×--	--×--

Classification of colloids :

2. On the basis of interaction of D.P. for D.M.

(i) Lyophilic colloids:

- liquid loving sols
- intrinsic colloid.

D.P have a great affinity (or love) for the D.M.

(ii) Lyophobic colloids:

- solvent hating colloid
- extrinsic colloid.

No affinity between particles of the D.P. and the D.M

Property	Lyophilic colloids	Lyophobic colloids
interaction of D.P. for D.M	great affinity (or love)	no affinity
Ease of preparation	easily formed by direct mixing	formed only by special methods
Ease of preparation	(reversible nature)	(Irreversible nature)
Stability	very stable	unstable / require stabilizers
Viscosity	> D.M.	≈ DM
Surface tension	< D.M.	≈ DM
Example	Mostly organic nature; Starch and Gelatin, glue, proteins, egg albumin, rubber, etc.	The sol of metals like Ag and Au, hydroxides like Al $(OH)_3$, $Fe(OH)_3$, metal sulphides like As_2S_3 etc.

Classification of colloids :

3. On the basis of nature of colloidal particle:

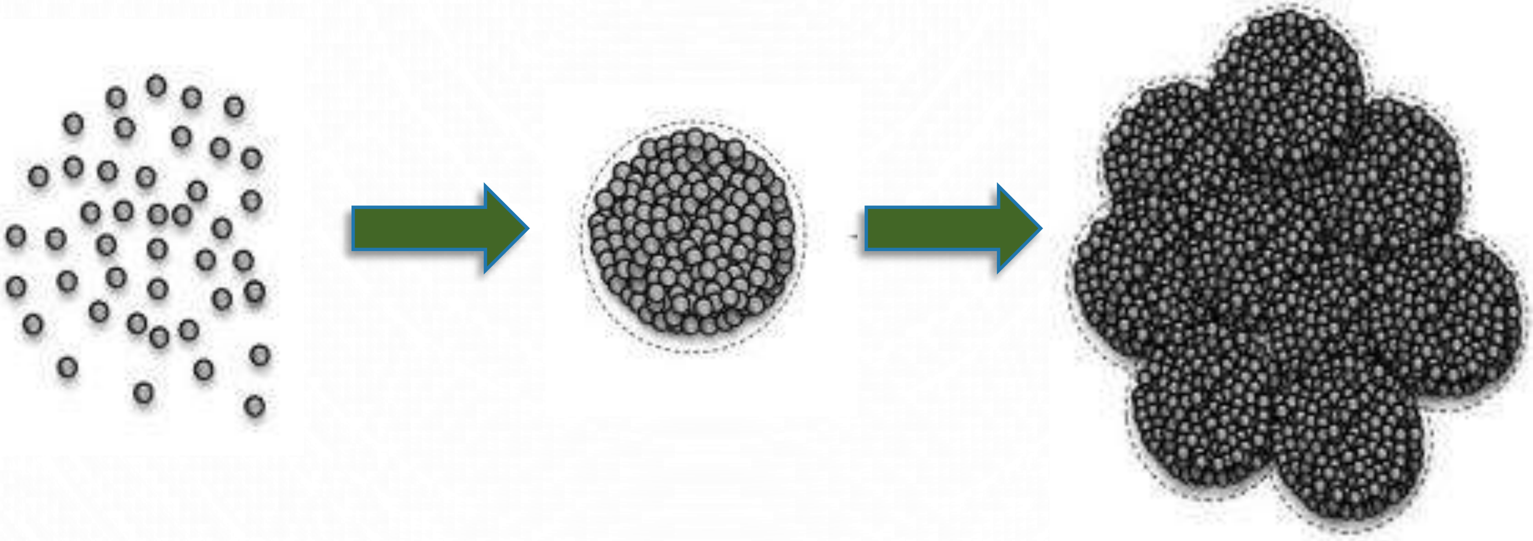
Multimolecular,

Macromolecular,

Associated colloids

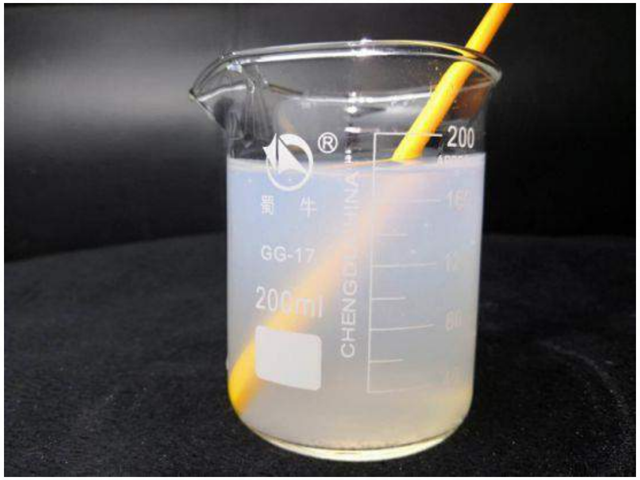
- **Multimolecular :**

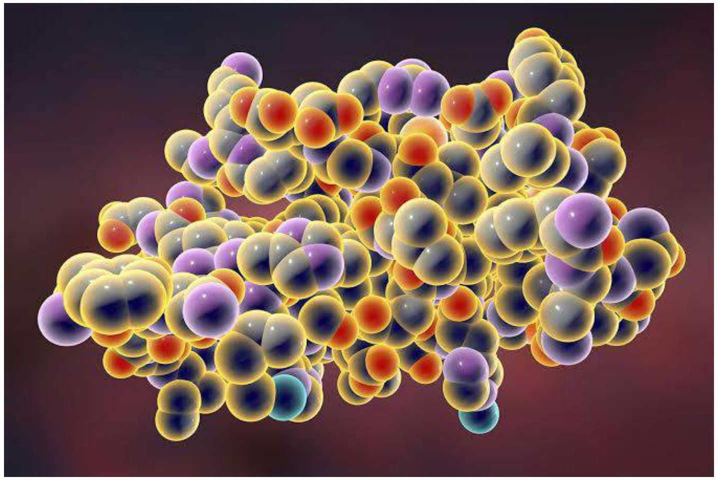
  In these colloids, the particles are held together by van der Waals forces.



Macromolecular colloids

- The colloidal particles ⇒ are **sufficiently big in size** (macro) to be of colloidal dimensions.
- **Naturally occurring** polymers macromolecules are starch, cellulose, proteins, enzymes, gelatin, etc.





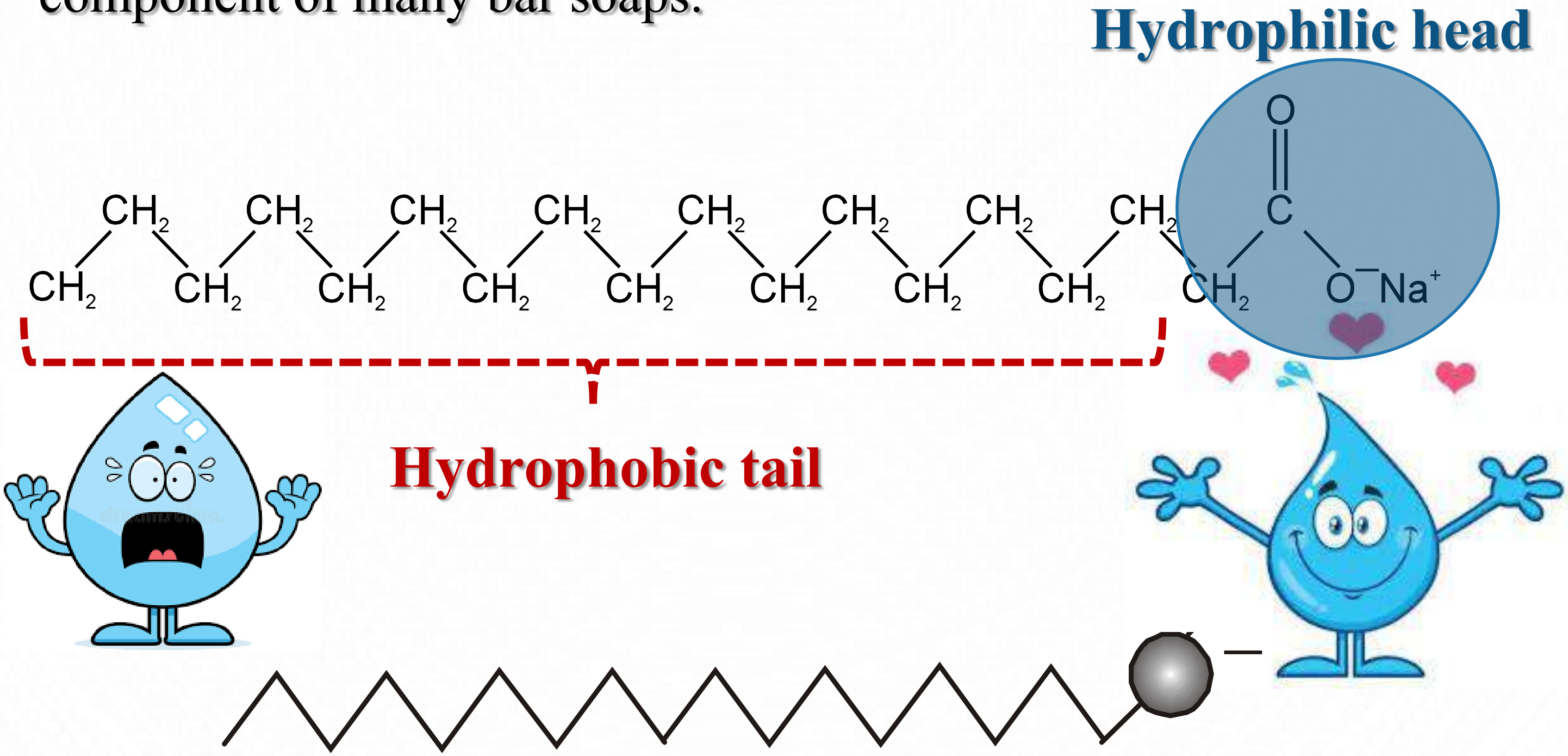
Associated colloids (Micelles):

- behave as normal electrolytes **at low concentration**
- behave as colloidal particles **at higher concentration**.
- Ex. Soap/ Detergent

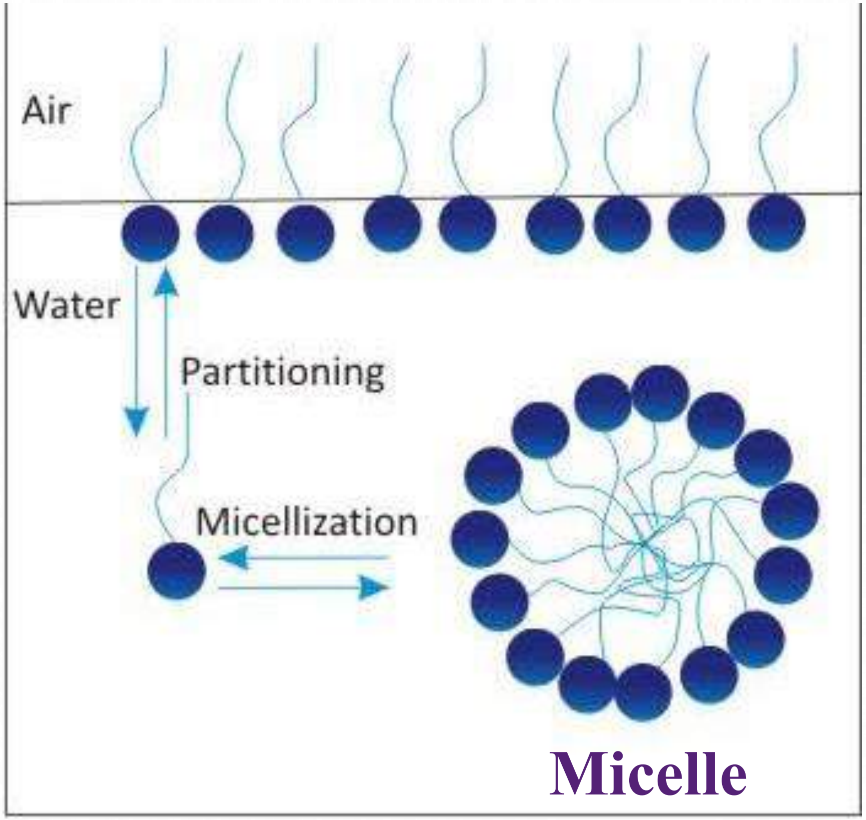
Mechanism of micelle formation:

$$CH_3(CH_2)_{16}COO^- \, Na^+ \longrightarrow CH_3(CH_2)_{16}COO^- \; + \; Na^+$$

sodium stearate a major
component of many bar soaps.



Mechanism of micelle formation:



Mechanism of micelle formation:

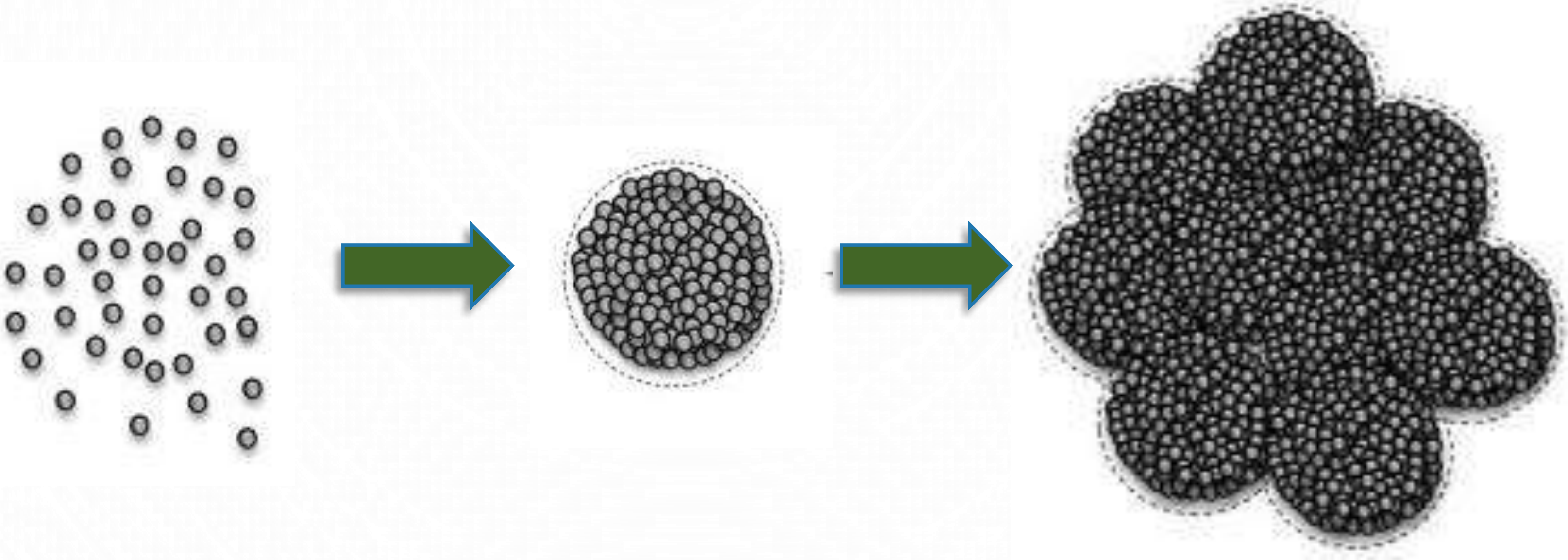
- The formation of micelles takes place only at particular temp, that temperature is called **Kraft temperature (${T}_k$).**
- The formation of micelles takes place only above a certain minimum conc. called **Critical micelle conc. (C.M.C.)**

Note:

The longer the hydrocarbon change less will be C.M.C.

Preparation of lyophobic colloidal sols :

[A] Condensation methods :



(a) Chemical methods.

(a) Chemical methods.

(i) Double decomposition :

$$As_2O_3 \quad + \quad 3H_2S \longrightarrow As_2S_3(sol) \; + \; 3H_2O$$

(in hot water)

saturated
solution in H_2O

(ii) Oxidation :

- $SO_2 + 2H_2S \longrightarrow 3S(sol) + 2H_2O$

(iii) Reduction :

$$2\ AuCl_3 + 3\ HCHO + 3H_2O \longrightarrow 2Au(sol) + 3HCOOH + 6HCl$$

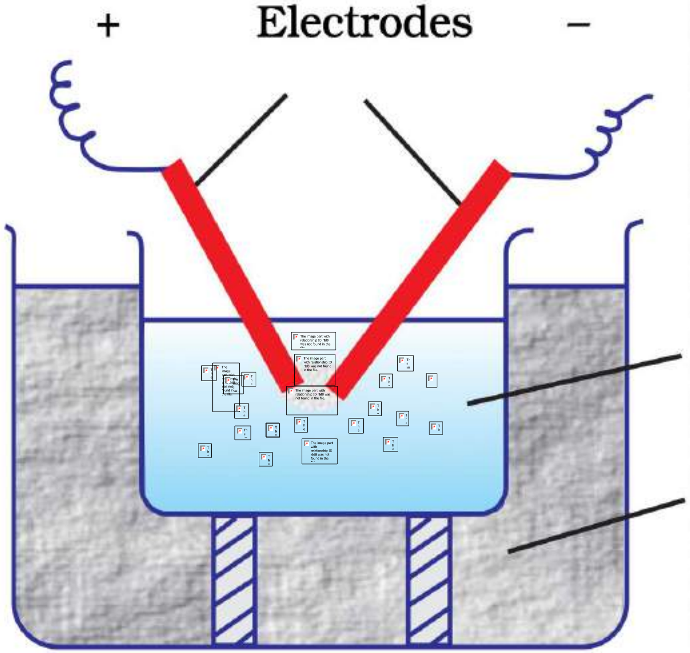
(iv) Hydrolysis

- $FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3\ (sol) + 3HCl$

[B] Dispersion Methods

(b) Electrical disintegration or Bredig's Arc method :

- Sols of less reactive metals Au, Ag, Pt, Pb, Cu etc., are prepared by this method.
- The intense heat produced vaporises the metal, which then condenses to form particles of colloidal size
- This process involves dispersion as well as condensation.



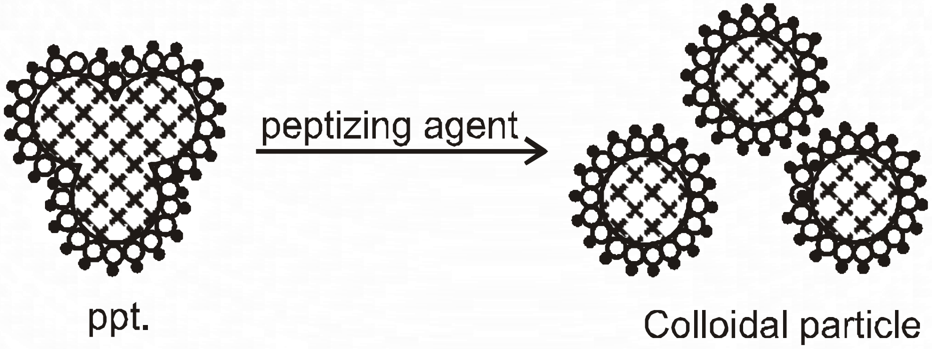
[B] Dispersion Methods

(d) Peptization:

- Freshly prepared precipitate ⇒ colloidal sol.
- The electrolyte used for this ⇒ peptizing agent
- precipitate adsorbs one of the common ion of the peptizing agent and become charged ⇒ which causes the precipitate break up into smaller (colloidal) particles.

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^- \;;$$

$$Fe(OH)_3 + Fe^{3+} \longrightarrow Fe(OH)_3 \mid Fe^{3+}$$



Important properties of colloidal sols :

Filterability :

- Colloidal particles pass through an ordinary filter paper.
- Do not pass through ultrafilters

Important properties of colloidal sols :

Colligative Properties :

As size of of colloidal particles ↑

⇒ molecular masses ↑

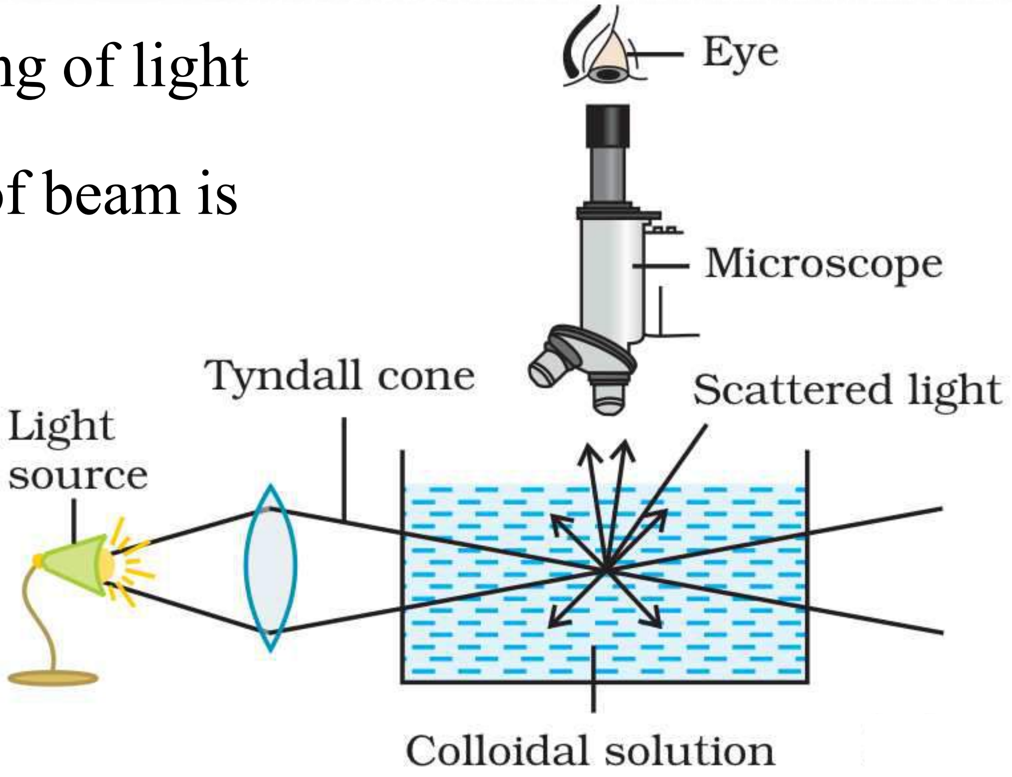
⇒ concentration ↓ ; $\left[\ C = \dfrac{W}{M \times V}\ \right]$

⇒ values of the colligative properties ↓

Important properties of colloidal sols :

Optical Properties-Tyndall effect :

- When beam of light is passed through a colloidal sol
  - The path of the beam gets illuminated.
  - It is due to scattering of light
- The illuminated path of beam is called Tyndall cone.



Optical Properties-Tyndall effect :

- **The intensity of tyndall effect**

  $\propto$ Δ(Refractive Index) of the D.P and D.M.

  - In lyophobic sols ⇒ Tyndall effect is quite well
  - In lyophilic sols ⇒ Tyndall effect is very weak.

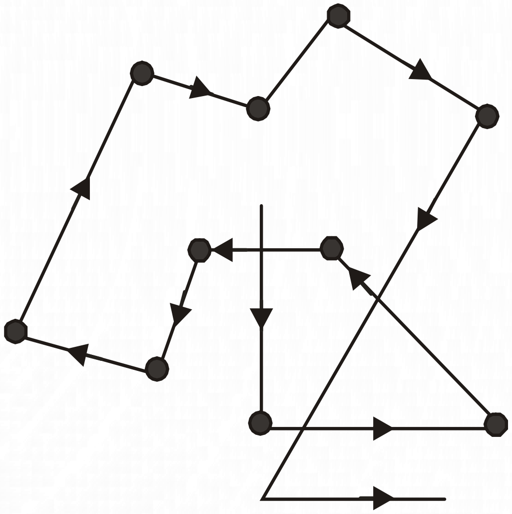
- For Tyndall effect ⇒ The diameter of the colloidal particles is not much smaller than the wavelength of the light used.

Colour of colloids:

- The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles.
- The wavelength of light further depends on the size and nature of the particles.
- Colour of gold sol changes with size of particles
  - **Red** < **Purple** < **Golden** .

Mechanical Properties :

Brownian movement:

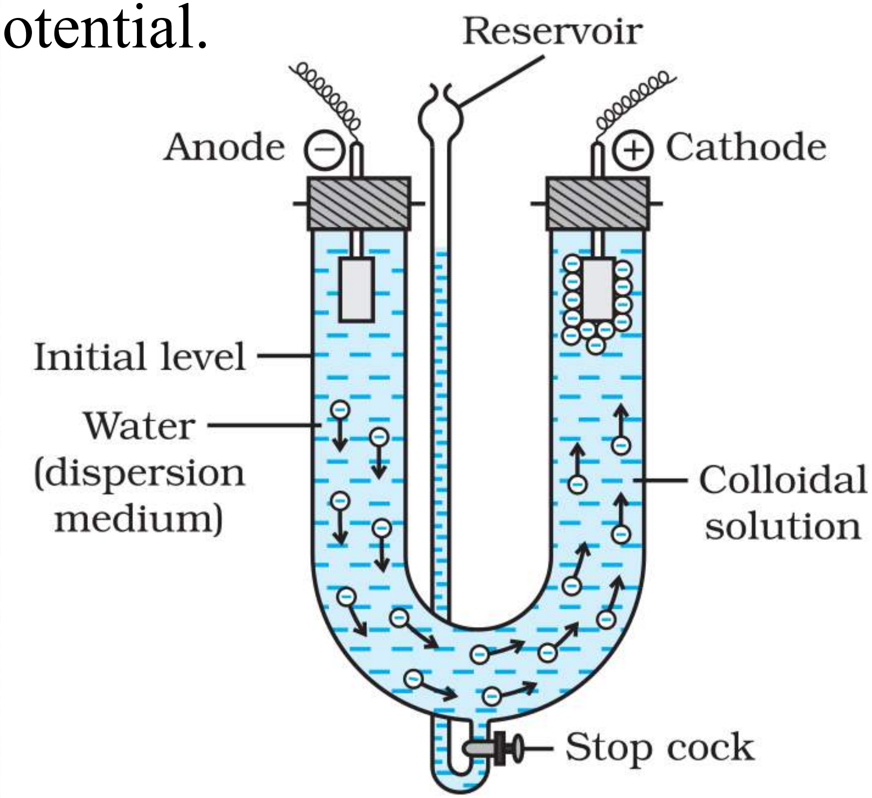


- ➢ Continuous zig-zag motion of colloidal particles
- ➢ It is due to the impact of the molecules of the dispersion medium with the colloidal particles.
- ➢ **Stability of colloidal sols $\propto$ Brownian movement**

Electrical Properties:

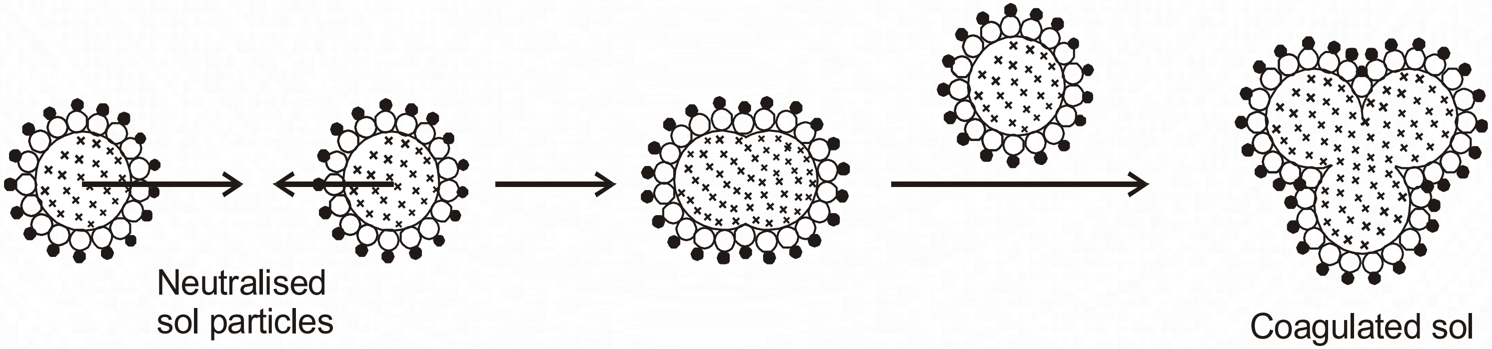
Electrophoresis:

The movement of colloidal particles under on applied electric potential.



Coagulation/Flocculation :

- **This process of aggregation of colloidal particles into an insoluble precipitate**
- The stability of the lyophobic colloids is due to presence of charge on colloidal particles.
- If, somehow, the charge is removed, the particles form aggregates and settle down under the force of gravity.



- **Hardy-Schulze Rule:**

- Oppositely charged ion is effective for coagulation.
- Coagulating power increases greatly with valency of coagulating ion
  - In case of positive charged sol,

    $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$
  - In case of negative charged sol,

    $Al^{3+} > Ba^{2+} > Na^+$.

Q. Which one of the following electrolytes is most effective for the coagulation of $Fe(OH)_3$ sol and why ?

$NaCl$, Na_2SO_4, Na_3PO_4.

Ans. Na_3PO_4 i.e. (PO_4^{-3}) is most effective.

Q. Which of the following 0.0005 M solution would be most effective in coagulating As_2S_3 colloidal solution.

KCl, $MgCl_2$, $AlCl_3$ or Na_3PO_4? Explain.

Ans. Al^{3+} would be most effective.

Coagulation/Flocculation :

Coagulation value or Flocculation value :

- It is the minimum concentration of electrolyte **in millimoles** required to cause coagulation of **one litre** of colloidal sol.
- It is express in terms of **millimoles /litre.**

$$\text{Coagulation value} = \frac{\text{millimoles of electrolyte}}{\text{volume of sol in litre}}$$

$$\text{Coagulating power} \propto \frac{1}{\text{coagulation value}}$$

Protective colloidal sols :

- lyophilic colloid function as protective colloid for lyophobic colloids
- This is due to formation of a protective layer by lyophilic sols outside lyophobic sols.
- **Eg :** Gelatin, Sodium caseinate, Egg albumin, Gum arabic, Potato starch etc.,

Gold Number :

- It is the minimum amount of the protective colloid in **milligrams** which when added to 10 ml of a standard gold sol is just sufficient to prevent a colour change from red to blue on the addition of 1 ml of 10% sodium chloride solution.
- It may be noted that smaller of the gold number, greater will be protecting power of the protective colloid.

$$\boxed{\text{Gold Number} = \frac{\text{weight of lyophilic sol in mg} \times 10}{\text{volume of gold sol in mL}}}$$

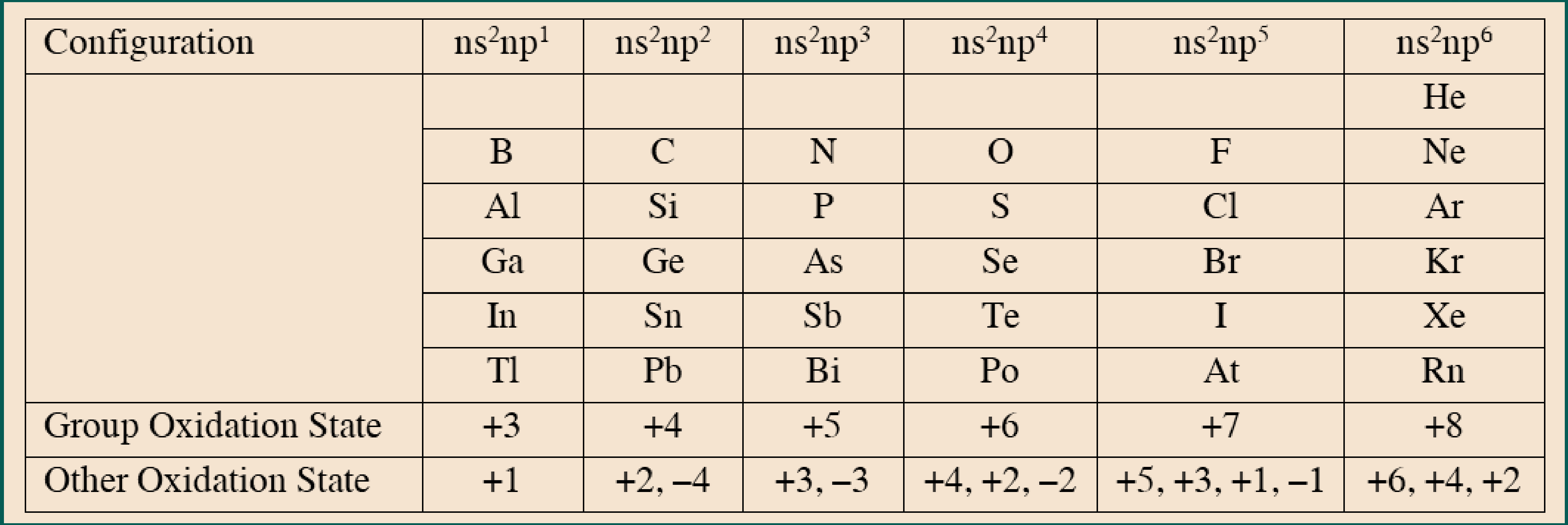
$$\boxed{\text{Protecting power} \propto \frac{1}{\text{gold number}}}$$

BLOCK CHEMISTRY

p-block
(13-14 Group)

INTRODUCTION

The p–block contains metals, metalloids as well as non–metals.



Configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
						He
	B	C	N	O	F	Ne
	Al	Si	P	S	Cl	Ar
	Ga	Ge	As	Se	Br	Kr
	In	Sn	Sb	Te	I	Xe
	Tl	Pb	Bi	Po	At	Rn
Group Oxidation State	+3	+4	+5	+6	+7	+8
Other Oxidation State	+1	+2, –4	+3, –3	+4, +2, –2	+5, +3, +1, –1	+6, +4, +2

General valence shell electronic configuration $ns^2\ np^{1-6}$ except Helium ($1s^2$)

The first member of each group from 13–17 of the p–block elements differ in many respects from the other members of their respective groups because of following :

(i) small size,
(ii) high electronegativity and
(iii) absence of d–orbitals.

Group 13 element : THE BORON FAMILY

Property	**B**	**Al**	**Ga**	**In**	**Tl**
Character	Metalloid	Metallic	Metallic	Metallic	Metallic
Atomic Number	5	13	31	49	81
Atomic Mass/g mol^{-1}	10.81	26.98	69.72	114.82	204.38
Electronic configuration *General electronic configuration*=$(ns^2\ np^1)$	[He] $2s^2$ $2p^1$	[Ne] $3s^2$ $3p^1$	[Ar] $3d^{10}$ $4s^2 4p^1$	[Kr] $4d^{10}$ $5s^2$ $5p^1$	[Xe] $4f^{14}$ $5d^{10}$ $6s^2 6p^1$
Covalent Radius / pm	85	143	135	167	170
(B < Ga < Al < In < Tl)	*In Ga, poor shielding of 10 d-electrons*				
Ionic Radius X^- / pm *(B < Al < Ga < In < Tl)*	27	53.5	62	80	88.5

Ionization enthalpy (kJ mol^{-1}) *(B > Al < Ga > In < Tl)*	Δ_iH_1	I	801	577	579	558	589
	Δ_iH_2	II	2427	1816	1979	1820	1971
	Δ_iH_3	III	3659	2744	2962	2704	2877
			Poor shielding of d-orbital and f-orbital in Ga & Tl respectively				
Electronegativity *(B > Al < Ga < In < Tl)*			2.0	1.5	1.6	1.7	1.8
			Marginal increase after Al				
Melting point / K			2453	933	303	430	576
Boiling point / K *(B > Al > Ga > In > Tl)*			3923	2740	2676	2353	1730
Density/g cm^{-3} (at 293 K) *(B < Al < Ga < In < Tl)*			2.35	2.70	5.90	7.31	11.85
Oxidation State			+3	+3	+3, +1	+3, +1	+3, +1
			+1 oxidation state arises due to inert pair effect.				
			Stability of Oxidation state: +1: Ga < In < Tl +3 : Al > Ga > In > Tl				

Gallium with low melting point (303 K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.

Borax ($Na_2B_4O_7.10H_2O$) :

Preparation :

It is found in nature but can also be prepared by the following methods.

(i) From Colemanite.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

(ii) From orthoboric acid.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2 \uparrow$$

Properties

(1) Action of heat :

When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O \uparrow$$

$$Na_2B_4O_7 \xrightarrow{740^0C} \underbrace{2NaBO_2 + B_2O_3}_{\text{(borax bead)}}$$

(2) Aqueous solution of borax is a useful primary standard for titrating against acids.

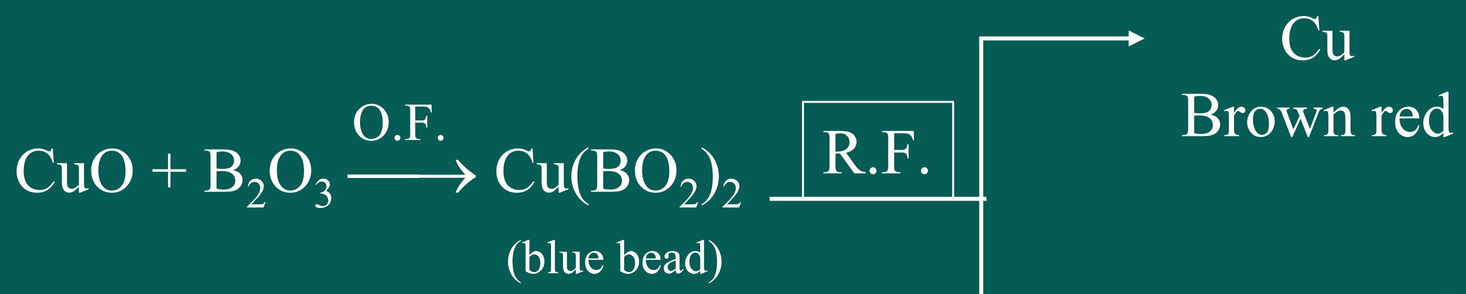
$$[B_4O_5(OH)_4]^{2-} + 5H_2O \rightleftharpoons \underbrace{\underset{\text{(weak acid)}}{2B(OH)_3} \quad + \quad \underset{\text{(salt)}}{2[B(OH)_4]^-}}_{\textbf{Acidic Buffer}}$$

- Borax is also used as a buffer since its aqueous solution contain equal amounts of weak acid and its salt.

(3) Borax-bead test :

Borax reacts with certain metal salts such as, Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

$$Na_2B_4O_7\cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740^{\circ}C} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}}$$



$$CuO + B_2O_3 \xrightarrow{O.F.} \underset{\text{(blue bead)}}{Cu(BO_2)_2} \xrightarrow{\boxed{R.F.}} \begin{cases} \underset{\text{Brown red}}{Cu} \\ \underset{\text{Colourless}}{CuBO_2} \end{cases}$$

$$CoO + B_2O_3 \xrightarrow{O.F.} \underset{\text{(blue bead)}}{Co(BO_2)_2} \xrightarrow{\boxed{R.F.}} \text{No change}$$

O.F. : Oxidising flame
R.F. : Reducing flame

Boric acid (H_3BO_3) :

Preparation :

It is precipitated by treating a concentrated solution of borax with sulphuric acid.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3 \downarrow$$

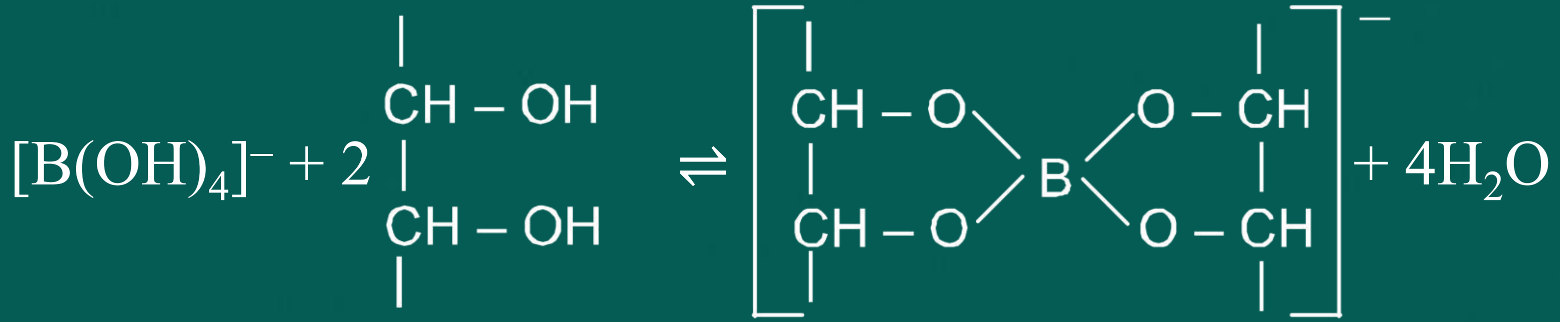
Properties:

(i) It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting OH^- from water molecules:

$$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq).$$

- It, therefore act as a Lewis acid and not as a proton donor like most acids.

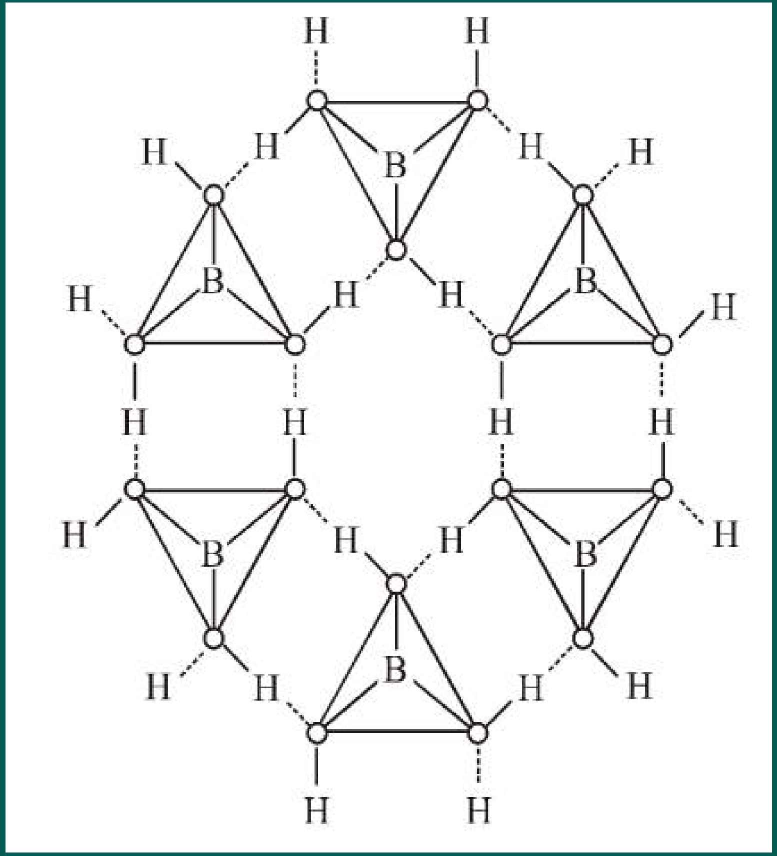
In presence of water soluble polyhydroxy compound having cis-1,2-diol, boric acid act as strong acid



(2) Heating effect

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100^\circ C} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{160^\circ C} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow{\text{red hot}} \underset{\text{Boric Anhydride}}{B_2O_3}$$

(3) In the solid state, the $B(OH)_3$ units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. Amorphous solid.



(4) Test for Borate radical :

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

COMPOUNDS

Diborane (B_2H_6) :

Preparation of Diborane (B_2H_6) :

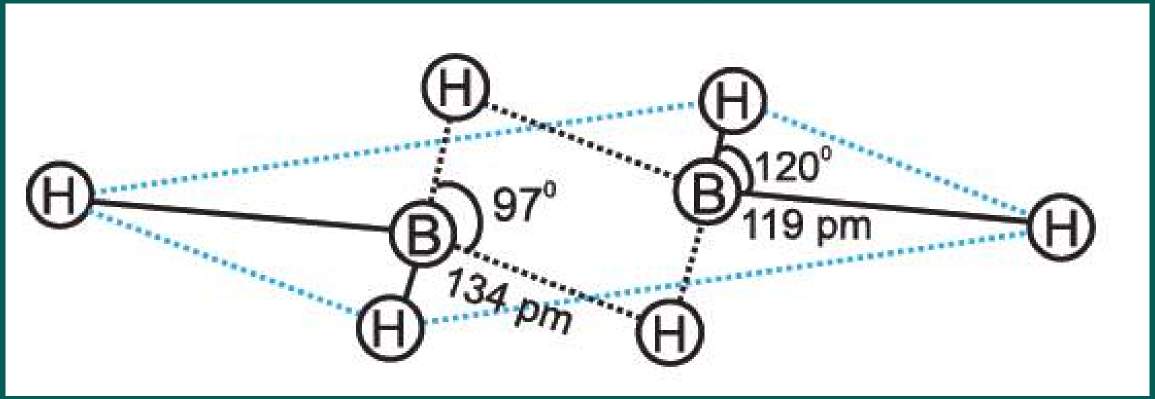
(i) Lab Method :

$$2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$$

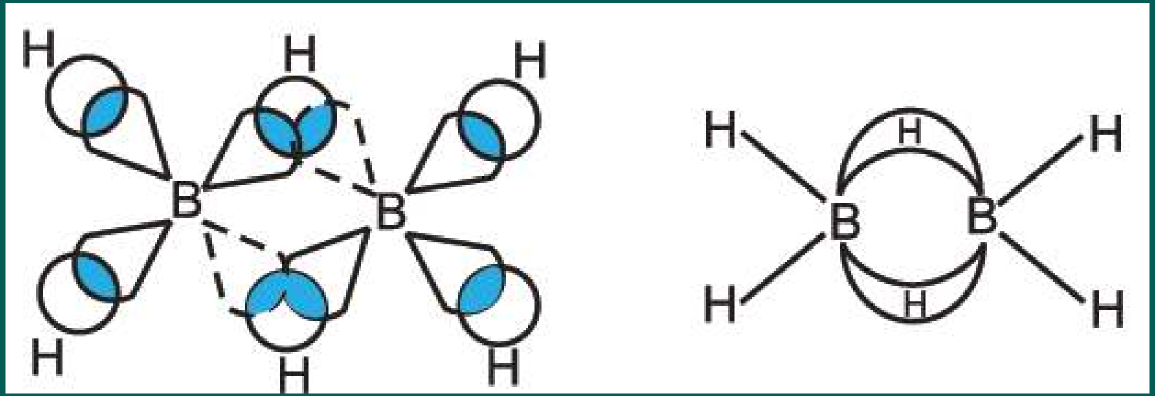
(ii) Industrial Method :

$$8BF_3 + NaH \xrightarrow{\text{ether}} B_2H_6 + 6LiBF_4$$

The structure of diborane, B_2H_6



Boron is sp^3 hybridised
Non-planar structure
electron deficient species
(It have two banana bonds)



(v) The electron deficient 3c-2e BHB bridges are sites of nucleophilic attack.

- Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.

  $B_2H_6 + 2NH_3 \longrightarrow [H_2B\,(NH_3)_2]^+ + [BH_4]^-$

- Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.

  $2(CH_3)_3N + B_2H_6 \quad 2H_3B \leftarrow N(CH_3)_3$

  $B_2H_6 + 2Me_3P \longrightarrow 2Me_3P \rightarrow BH_3$

- $B_2H_6 + 2CO \xrightarrow{200°C,\ 20\ atm} 2BH_3 \leftarrow CO$ (borane carbonyl)

- The reaction with ammonia depends on conditions.

$$B_2H_6 + NH_3 \xrightarrow[\text{low temperature}]{\text{Excess } NH_3} B_2H_6.2NH_3 \text{ or } [H_2B(NH_3)_2]^+ [BH_4]^-$$

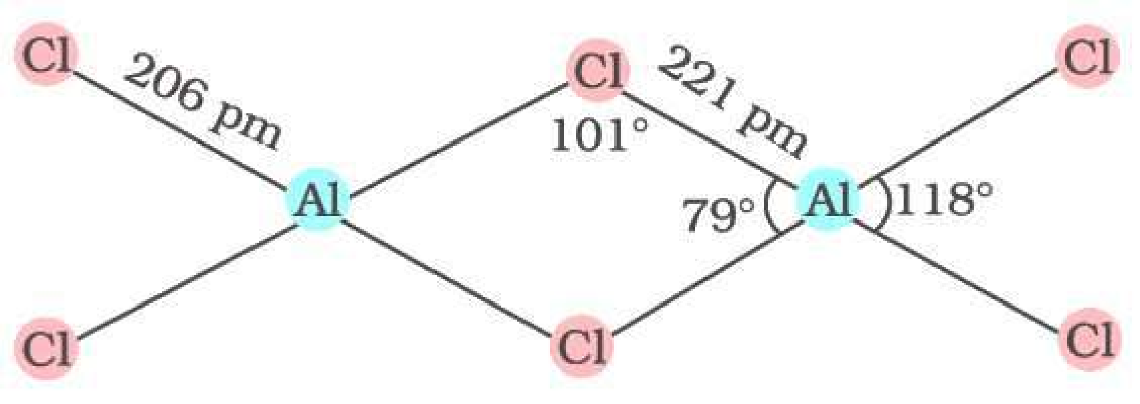
(ionic compound).

$$\xrightarrow[\text{higher temperature } (> 200^\circ C)]{\text{Excess } NH_3} (BN)_x \text{ boron nitride} + H_2$$

$$\xrightarrow[\text{higher temperature } (200^\circ C)]{\text{Ratio } 2NH_3 : 1B_2H_6} B_3N_3H_6 \text{ borazine} + H_2$$

ALUMINIUM

Aluminium Chloride ($AlCl_3.6H_2O$) :



Alums : Double salt having following formula:

$MM'(SO_4)_2 . 12H_2O$ or $M_2SO_4 . M'_2(SO_4)_3 . 24H_2O$

M = Monovalent metal ion (NH_4^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+)

M' = Trivalent metal ion (Al^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Co^{3+}, Ga^{3+} etc.)

Alums contain the ions $[M(H_2O)_6]^+$, $[M'(H_2O)_6]^{3+}$ and SO_4^{2-} in the ratio 1 : 1 : 2.

Some important alums are :

(i) Potash alum $KAl(SO_4)_3.12H_2O$ or $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$

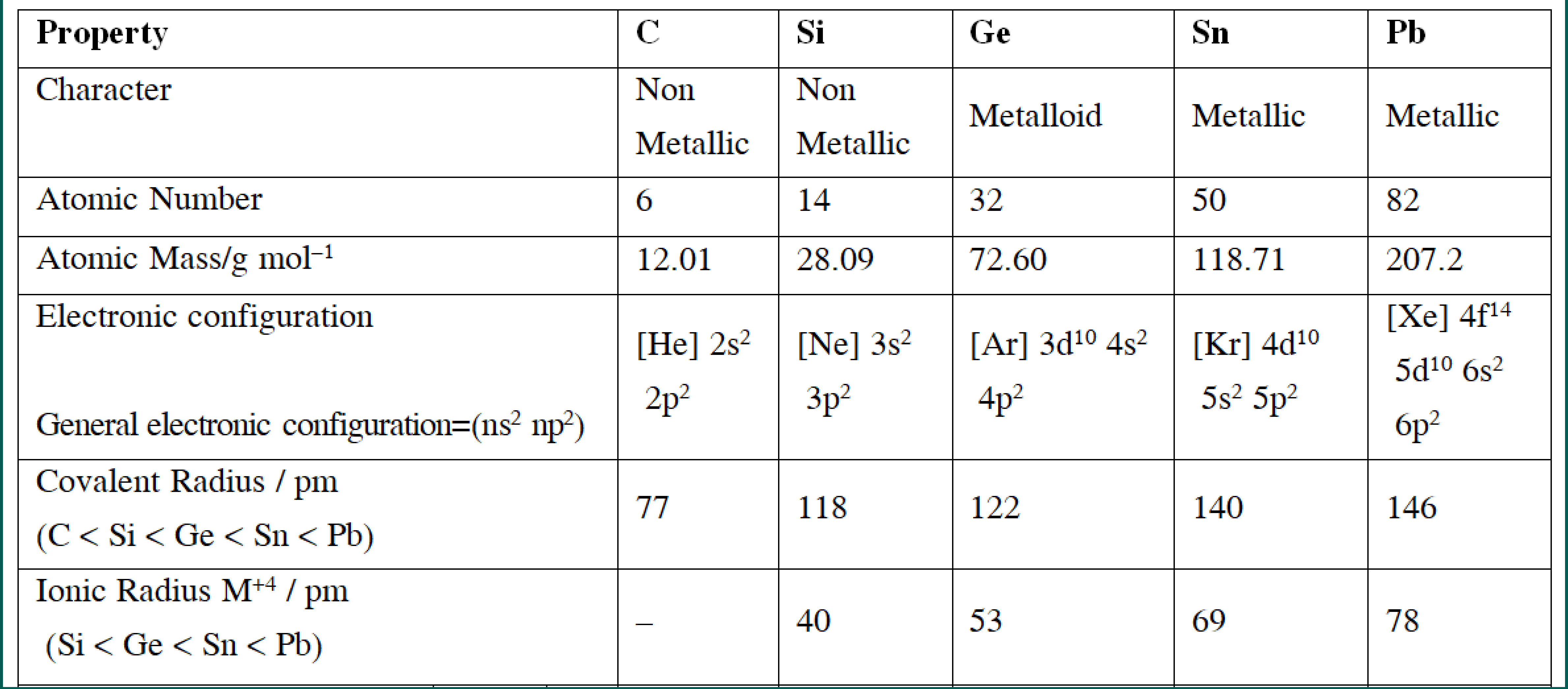
(ii) Chrome alum $KCr(SO_4)_3.12H_2O$ or $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$

(iii) Ferric alum $KFe(SO_4)_3.12H_2O$ or $K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$

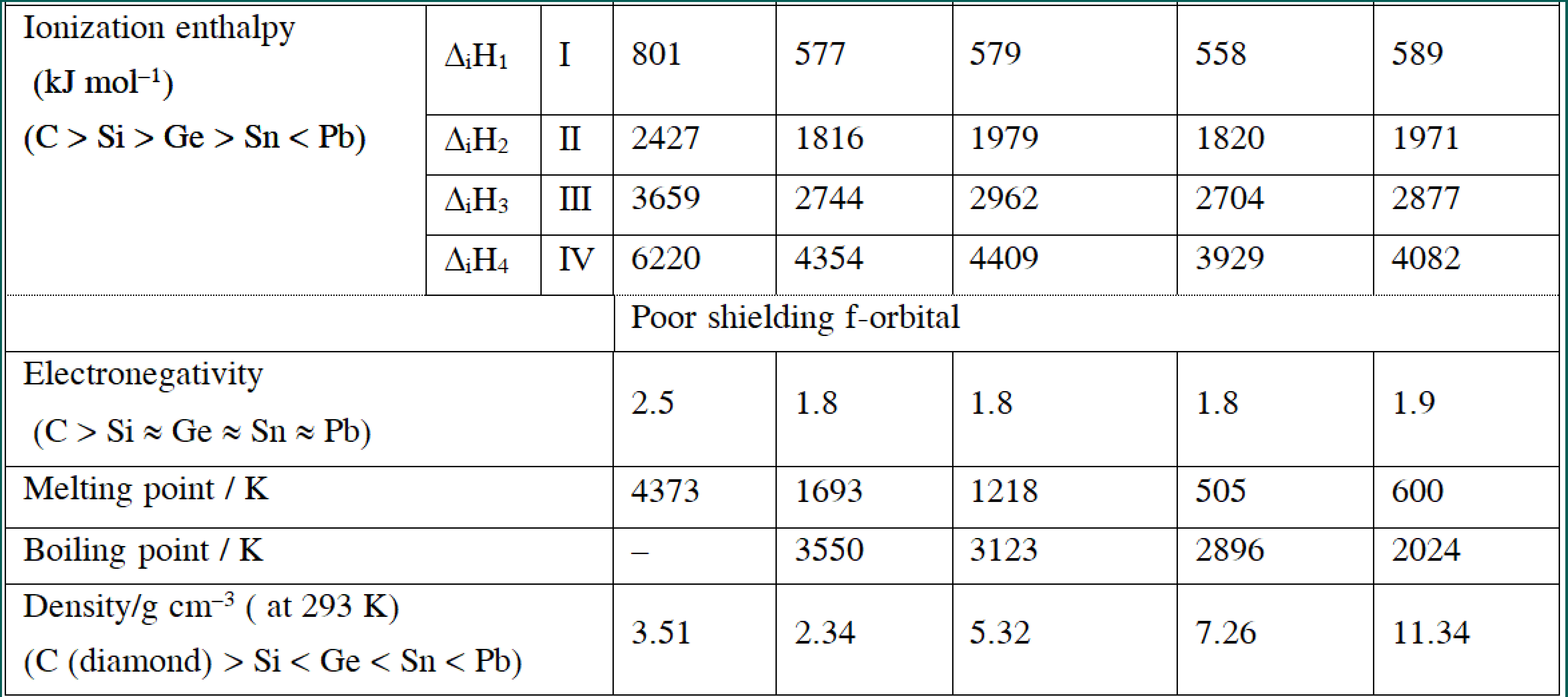
(iv) Ammonium alum $NH_4Al(SO_4)_3.12H_2O$ or $(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$

Aqueous solution of alum is acidic in nature.

GROUP 14 ELEMENTS: THE CARBON FAMILY

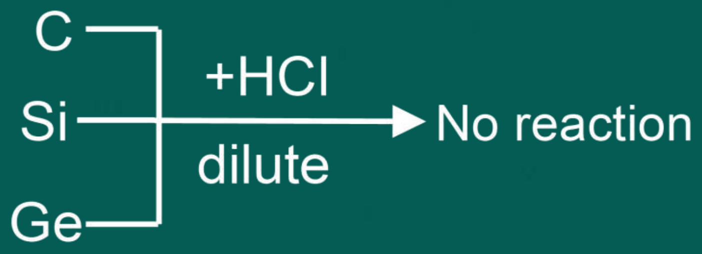


Property	**C**	**Si**	**Ge**	**Sn**	**Pb**
Character	Non Metallic	Non Metallic	Metalloid	Metallic	Metallic
Atomic Number	6	14	32	50	82
Atomic Mass/g mol^{-1}	12.01	28.09	72.60	118.71	207.2
Electronic configuration General electronic configuration=(ns^2 np^2)	[He] $2s^2$ $2p^2$	[Ne] $3s^2$ $3p^2$	[Ar] $3d^{10}$ $4s^2$ $4p^2$	[Kr] $4d^{10}$ $5s^2$ $5p^2$	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$
Covalent Radius / pm (C < Si < Ge < Sn < Pb)	77	118	122	140	146
Ionic Radius M^{+4} / pm (Si < Ge < Sn < Pb)	–	40	53	69	78



Ionization enthalpy (kJ mol^{-1}) (C > Si > Ge > Sn < Pb)	Δ_iH_1	I	801	577	579	558	589
	Δ_iH_2	II	2427	1816	1979	1820	1971
	Δ_iH_3	III	3659	2744	2962	2704	2877
	Δ_iH_4	IV	6220	4354	4409	3929	4082
			Poor shielding f-orbital				
Electronegativity (C > Si ≈ Ge ≈ Sn ≈ Pb)			2.5	1.8	1.8	1.8	1.9
Melting point / K			4373	1693	1218	505	600
Boiling point / K			–	3550	3123	2896	2024
Density/g cm^{-3} (at 293 K) (C (diamond) > Si < Ge < Sn < Pb)			3.51	2.34	5.32	7.26	11.34

Reactivity with Acids :



C

Si

Ge

$\xrightarrow[\text{dilute}]{+\text{HCl}}$ No reaction

Sn dissolves in HCl (dil. & conc) but Pb in only dil.HCl.

SILICON

Preparation

SiO_2 (excess) + 2C $\longrightarrow$ Si (pure) + 2CO

Si (pure) + $2Cl_2 \longrightarrow SiCl_4$

$SiCl_4$ + 2Mg $\longrightarrow$ Si (highly pure) + $MgCl_2$

Silicones :

- Silicones are synthetic organosilicon compounds having repeated R_2SiO units held by Si–O–Si linkages.
- These compounds have the general formula $(R_2SiO)_n$ where R = alkyl or aryl group.
- The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation.

$RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$

$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$

$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$

$RSiCl_3 \longrightarrow$ Crosslink / 3-D

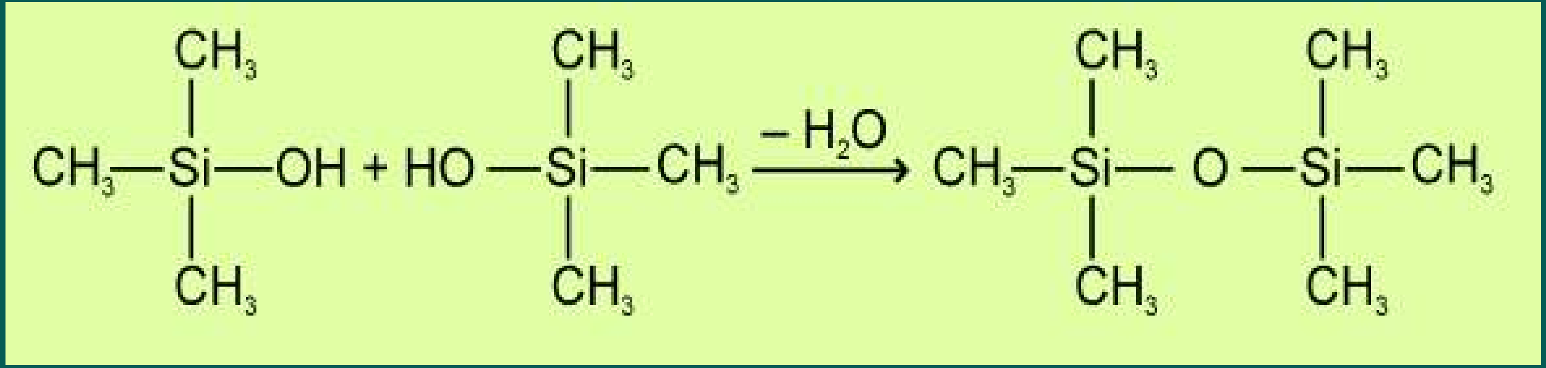
$R_2SiCl_2 \longrightarrow$ Linear chain

$R_3SiCl \longrightarrow$ Dimer

Silicones can be prepared from the following types of compounds only.

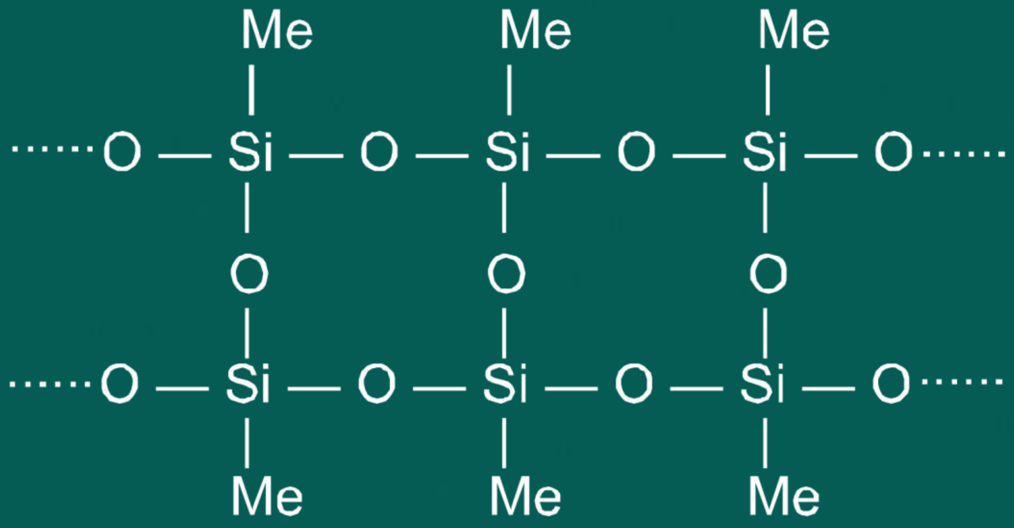
(i) R_3SiCl (ii) R_2SiCl_2 (iii) $RSiCl_3$

Silicones from the hydrolysis of $(CH_3)_3$ SiCl



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH + HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3 \xrightarrow{-H_2O} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3$$

When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three places as



CARBIDES : Carbides are of three types according to the type of bonding

(i) Salt like carbides (ionic carbides)

(ii) Covalent carbides (giant molecular carbides)

(iii) Interstitial carbides.

(I) Salt like carbides (ionic carbides) :

(a) These are formed by strong electropositive elements of groups 1, 2 and 13

(i) Methanides (Methides) – Methanides are the carbides which give methane on hydrolysis. They contain C^{4-} ions.

Ex. Be_2C , Al_4C_3

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + H_2O \longrightarrow Al(OH)_2 + CH_4 \uparrow$$

(ii) Acetylides – These are the carbides which yield acetylene on hydrolysis. They contain the C_2^{2-} ion .

e.g. : CaC_2, Al_2C_6

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

(iii) Allylides – These carbides give methylacetylene or allylene ($CH_3{-}C{\equiv}CH$) on hydrolysis. They contain C_3^{4-} ions.

e.g. : Mg_2C_3

$$Mg_2C_3 + H_2O \longrightarrow Mg(OH)_2 + C_3H_4\uparrow$$

(II) **Covalent carbides (giant molecular carbides)**

(a) Covalent carbides are the compounds of carbon with elements having similar electronegativity.

e.g. : B_4C and SiC

(III) **Interstitial carbides.**

Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retains their close packed lattice and carbons are incorporated in their interstitial spaces.

GROUP 15 ELEMENTS: THE NITROGEN FAMILY

GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

Nitrogen and phosphorus are **non-metals**, arsenic and antimony **metalloids** and bismuth is a **typical metal**.

DINITROGEN (N_2)

Prepartion :

(1) Lab Method

$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + H_2O\ (\ell) + NaCl(aq)$ (NCERT)

(2) Thermal decomposition

(i) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 \uparrow + 4H_2O + Cr_2O_3$ (NCERT)

(ii) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$ (NCERT)

In this method we get pure nitrogen gas

INDUSTRIAL METHODS OF PREPARATION

(i) From liquified air by fractional distillation : The boiling point of N_2 is –196°C and that of oxygen is –183°C and hence they can be separated by distillation using fractional column.

(ii) From producer gas from furnaces : Producer gas is a mixture of CO and N_2. When the mixture of CO and N_2 is passed over heated CuO, the CO gas is oxidized to CO_2 which is absorbed in alkalies & N_2 remains which is collected in gas cylinders.

Properties :

(i) Dinitrogen is a colourless, odourless, tasteless and non-toxic gas. It is neither combustible nor a supporter of combustion.

(ii) Dinitrogen is rather inert at room temperature because of the high bond enthalpy of $N \equiv N$ bond. Reactivity, however, increases rapidly with rise in temperature.

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Uses of Dinitrogen

1. For providing an inert atmosphere during many industrial processes where presence of air or O_2 is to be avoided.
2. For manufacture of NH_3 by the Haber's process.
3. Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.
4. For manufacture of HNO_3
5. For manufacture of calcium cynamide (nitrolim).

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	–
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) Distance/pm	101.7	141.9	151.9	170.7	–
HEH angle (°)	107.8	93.6	91.8	91.3	–
$\Delta_f H^\ominus$/kJ mol^{-1}	–46.1	13.4	66.4	145.1	278
$\Delta_{diss}H^\ominus$(E–H)/kJ mol^{-1}	389	322	297	255	–

AMMONIA (NH_3)

Prepartion :

(i) On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or calcium hydroxide.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2 \qquad \text{(NCERT)}$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4 \quad \text{(NCERT)}$$

(ii) **Haber's process :** (Industrial method)

$$N_2 + 3H_2 \xrightarrow[\text{Iron oxide}+K_2O\,\&\,Al_2O_3]{500^0C,\ 200\ atm.} 2NH_3 \qquad \text{(NCERT)}$$

Chemical properties :

(i) NH_3 as weak base :

As a weak base, it precipitates the hydroxides of many metals from their salt solutions.

$$2\ FeCl_3\ (aq) + 3NH_4OH\ (aq) \longrightarrow Fe_2O_3\ .\ xH_2O\ (s) + 3NH_4Cl\ (aq)$$

(NCERT)

(ii) Complex formation by NH_3 :

Cu^{2+} (aq) + 4 NH_3(aq) $\rightleftharpoons$ $[Cu(NH_3)_4]^{2+}$(aq) (NCERT)

(blue) (deep blue)

Ag^+ (aq) + Cl– (aq) $\longrightarrow$ AgCl (s) (NCERT)

(colourless) (white ppt)

AgCl + 2NH_3 (aq) $\longrightarrow$ $[Ag(NH_3)_2$ Cl(aq) (NCERT)

(white ppt) (colourless)

(iii) Thermal decompostion of ammonium salts :

$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$; $(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$

If the anion is more oxidising

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$; $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

OXY ACIDS OF NITROGEN :

NITRIC ACID (HNO_3) :

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ (NCERT)

On a large scale it is prepared mainly by **Ostwald's process**.

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

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

$3NO_2(g) + H_2O\ (\ell) \longrightarrow 2HNO_3\ (aq) + NO(g)$ (NCERT)

(A) Metals placed above H in electrochemical series (ECS)

	Element	**Nature of HNO_3**	**Changes to**	**Reactions**
1	Mg, Mn	cold and dilute (1-2%)	$M(NO_3)_2$	$M + 2HNO_3 \rightarrow M(NO_3)_2 + H_2$
2	Zn, Fe	(a) dilute	N_2O	$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$ (NCERT)
		(b) concentrated	NO_2	$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$ (NCERT)
3	Sn	(a) dilute	NH_4NO_3	$4Sn+10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$
		(b) concentrated	NO_2	$Sn + 4HNO_3 \rightarrow \underbrace{H_2SnO_3}_{\text{meta stannic acid}} + 4NO_2 + H_2O$
4	Pb	(a) dilute	NO	$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$
		(b) concentrated	NO_2	$Pb + 4HNO_3 \rightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$

(B) Metals below H in ECS				
5	Cu,Ag,Hg	(a) dilute	NO	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$. (NCERT) Hg forms $Hg_2(NO_3)_2$
		(b) concentrated	NO_2	$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ (NCERT)
(C) Metalloids				
	Sb, As	concentrated	NO_2	$Sb + 5HNO_3 \rightarrow \underset{\text{antimonic acid}}{H_3SbO_4} + 5NO_2 + H_2O$

ALLOTROPIC FORMS OF PHOSPHORUS :

White or yellow phosphorus (P_4), Red phosphorus and black phosphorus :

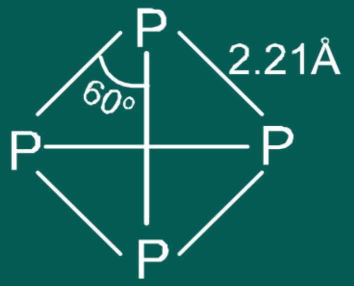
PREPARATION

(i) $2Ca_3(PO_4)_2$ (from bone-ash) + $10C + 6SiO_2 \quad 6CaSiO_3 + 10CO + P_4(s)$

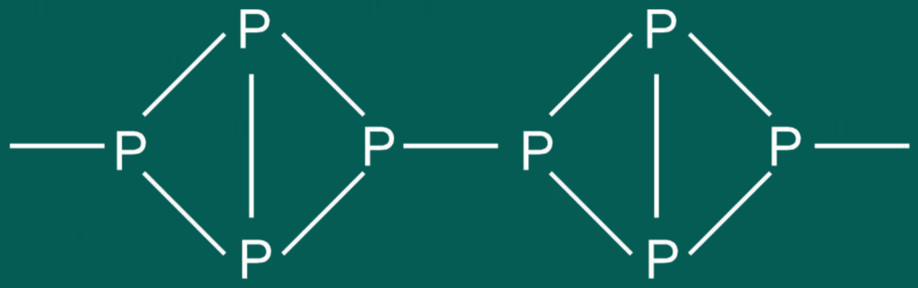
(electric furnace method)

(white phosphorus)

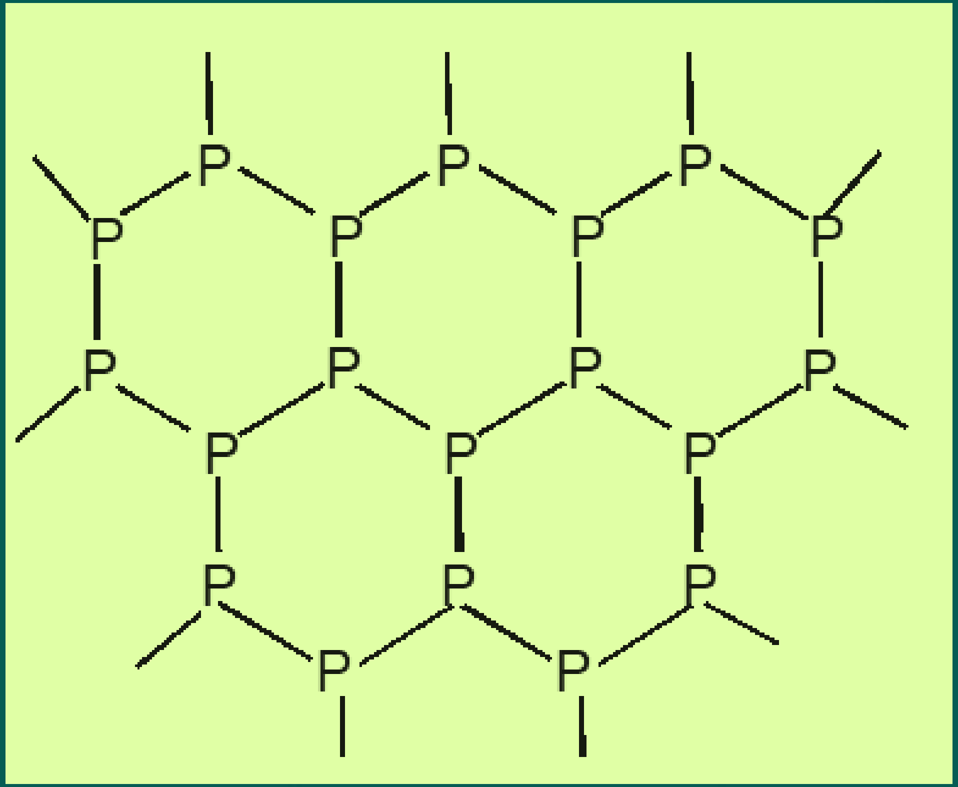
(ii) When white phosphorus is heated in the atmosphere of CO_2 or coal gas at 573 K red phosphorus is produced.



White-P



Red-P



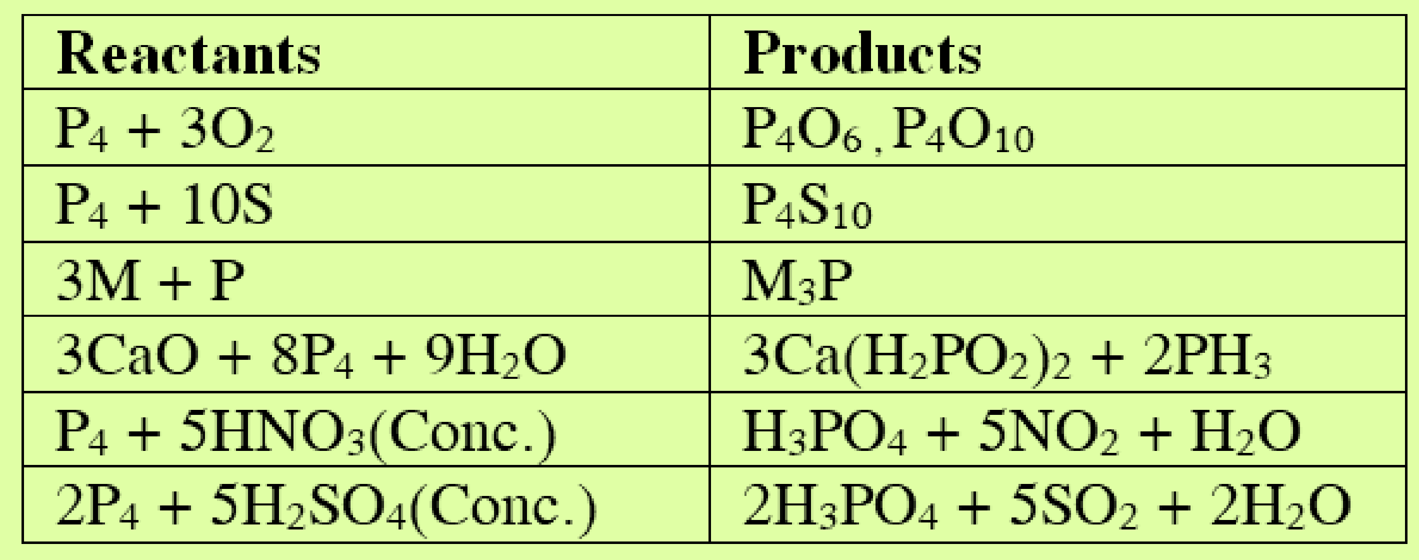
Black-P

CHEMICAL PROPERTIES OF PHOSPHORUS

Reactivity order :
white > red > black

Black phosphorus being almost inert i.e. most stable.

Reactions of white phosphorus



Reactants	**Products**
$P_4 + 3O_2$	P_4O_6 , P_4O_{10}
$P_4 + 10S$	P_4S_{10}
$3M + P$	M_3P
$3CaO + 8P_4 + 9H_2O$	$3Ca(H_2PO_2)_2 + 2PH_3$
$P_4 + 5HNO_3$(Conc.)	$H_3PO_4 + 5NO_2 + H_2O$
$2P_4 + 5H_2SO_4$(Conc.)	$2H_3PO_4 + 5SO_2 + 2H_2O$

PHOSPHORUS

Compounds of Phosphorus :

Phosphine :

$Ca_3P_2 + 6H_2O \longrightarrow 3\,Ca(OH)_2 + 2PH_3$ (NCERT)

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$ (NCERT)

$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ (NCERT)

(sodium hypophosphite)

Phosphorus Trichloride :

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$ (NCERT)

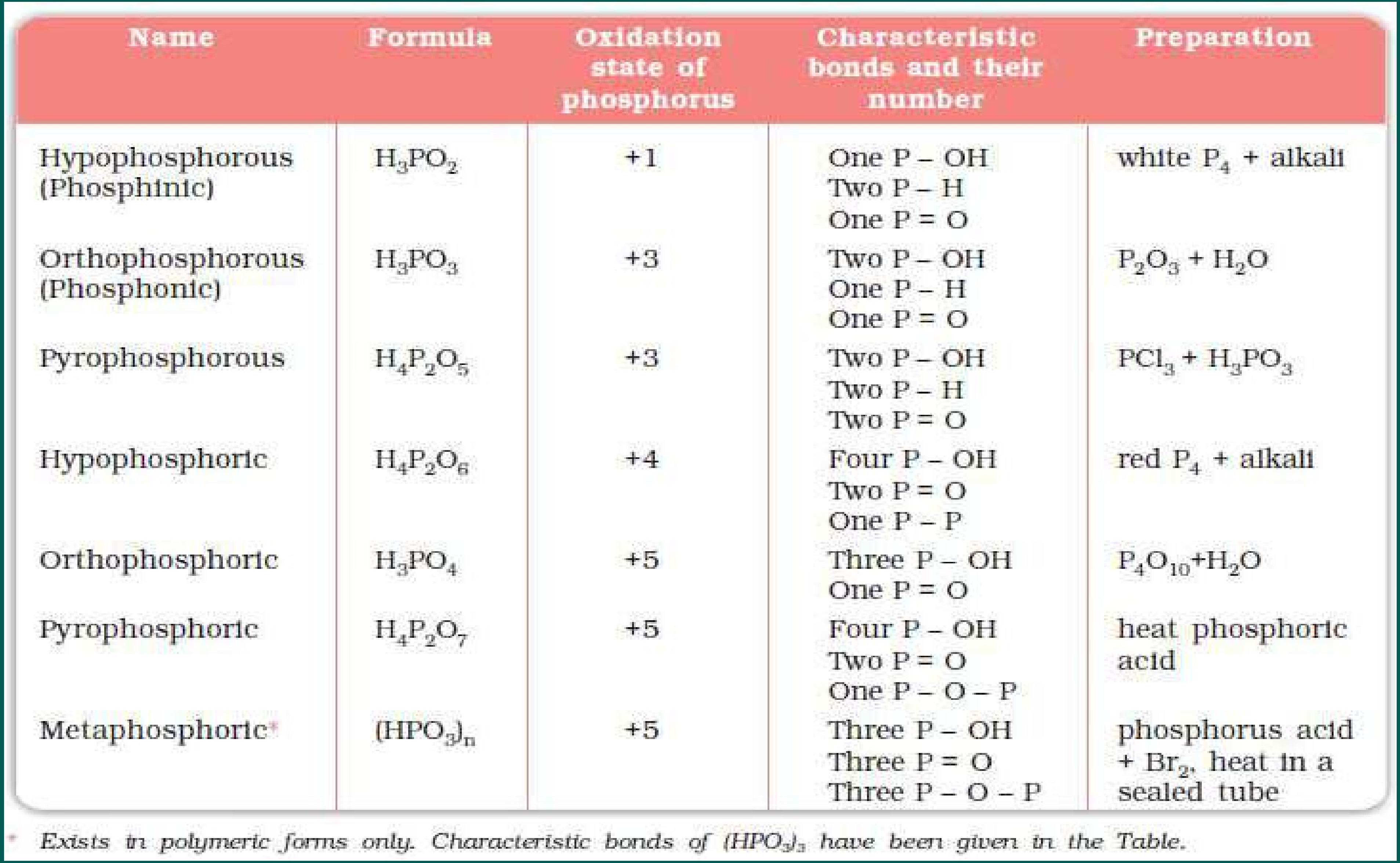
$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2\,S_2Cl_2$ (NCERT)

Phosphorus pentachloride :

$P_4 + 10Cl_2 \longrightarrow 4PCl_5$ (NCERT)

$P_4 + 10\,SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$ (NCERT)

Oxy acids of Phosphours :



Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	$P_4O_{10}+H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2, heat in a sealed tube

* *Exists in polymeric forms only. Characteristic bonds of $(HPO_3)_3$ have been given in the Table.*

GROUP 16 ELEMENTS : THE OXYGEN FAMILY

DIOXYGEN (O_2) : Lab methods of preparation are following :

(i) $2\ KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$ (NCERT)

(ii) $2\ HgO \xrightarrow{450^0C} 2Hg + O_2$ (NCERT)

Allotropy : All element exhibit allotropy for e.g.
Oxygen – O_2 and O_3
Liquid O_2 - pale blue
Solid O_2 - blue

Sulphur -
The main allotropic forms are
(i) Rhombic sulphur (a sulphur)
(ii) Monoclinic (b sulphur)
(iii) Plastic sulphur (d sulphur)

OXIDES :

(i) Acidic oxides : CO_2, SO_2 , SO_3 etc.

(ii) Basic oxides : Na_2O, CaO, CuO etc.

(iii) Neutral Oxides : CO, N_2O, NO etc.

(iv) Amphoteric Oxides : ZnO, Al_2O_3, BeO etc.

(v) Mixed Oxides : Pb_3O_4 ($2PbO + PbO_2$) ;

Fe_3O_4 ($FeO + Fe_2O_3$) ;

Mn_3O_4 ($2MnO + MnO_2$)

OZONE (O_3)

PREPARATION :

Formation of ozone from oxygen is an endothermic process so, it is prepared by passing silent electric discharge through pure and dry oxygen.

$$O_2 \xrightarrow{\text{energy}} O + O$$

$$O_2 + O \longrightarrow O_3\ ;\ \Delta H = 2845\ \text{kJ mol}^{-1}$$

$$3O_2 \rightleftharpoons 2O_3\ \Delta H^\circ = +\ 142\ \text{kJ mol}^{-1}$$

Mixture obtained contains 5-10% ozone by volume and this mixture is called ozonised oxygen.

PHYSICAL PROPERTIES

(i) Pale blue gas which forms a blue liquid on cooling and on solidification forms violet black crystals. The colour is due to intense absorption of red light.

(ii) It also absorbs strongly in the UV region. Thus it protects the people on the earth from the harmful UV radiation from the sun.

(iii) It has sharp smell often associated with sparking electrical equipment. It is toxic and is slightly soluble in water but more in turpentine oil, glacial acetic acid or CCl_4. O_3 molecule is diamagnetic but O_3^- is paramagnetic.

CHEMICAL PROPERTIES

(i) Oxidising agent : Ozone is a strong oxidising agent in acidic medium.

$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$; SRP = + 2.07 v (in acidic medium)

$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$; SRP = + 1.24 v (in alkaline medium)

Ex.

(a) It oxidises I^- to I_2 (from neutral solution of KI)

(b) $KI + 3O_3 \longrightarrow KIO_3 + 3O_2$; $KI + 4O_3 \longrightarrow KIO_4 + 4O_2$

Note : Similarly S^{2-} to SO_4^{2-} (but not H_2S), NO_2^- to NO_3^- , SO_3^{2-} to SO_4^{2-}, AsO_3^{3-} to AsO_4^{3-} , Sn^{2+} to Sn^{4+} (acidic medium).

Reaction with dry I_2 : $2\ I_2 + 9[O_3] \longrightarrow I_4O_9 + 9O_2$

I_4O_9 yellow solid has the composition $I^{+3}\ (IO_3^-)_3$. Formation of this compound is a direct evidence in favour of basic nature of I_2 (i.e. its tendency to form cations).

Reaction with moist iodine :

$5O_3 + I_2 + H_2O \longrightarrow 2HIO_3 + 5O_2$

Reaction with H_2O_2 :

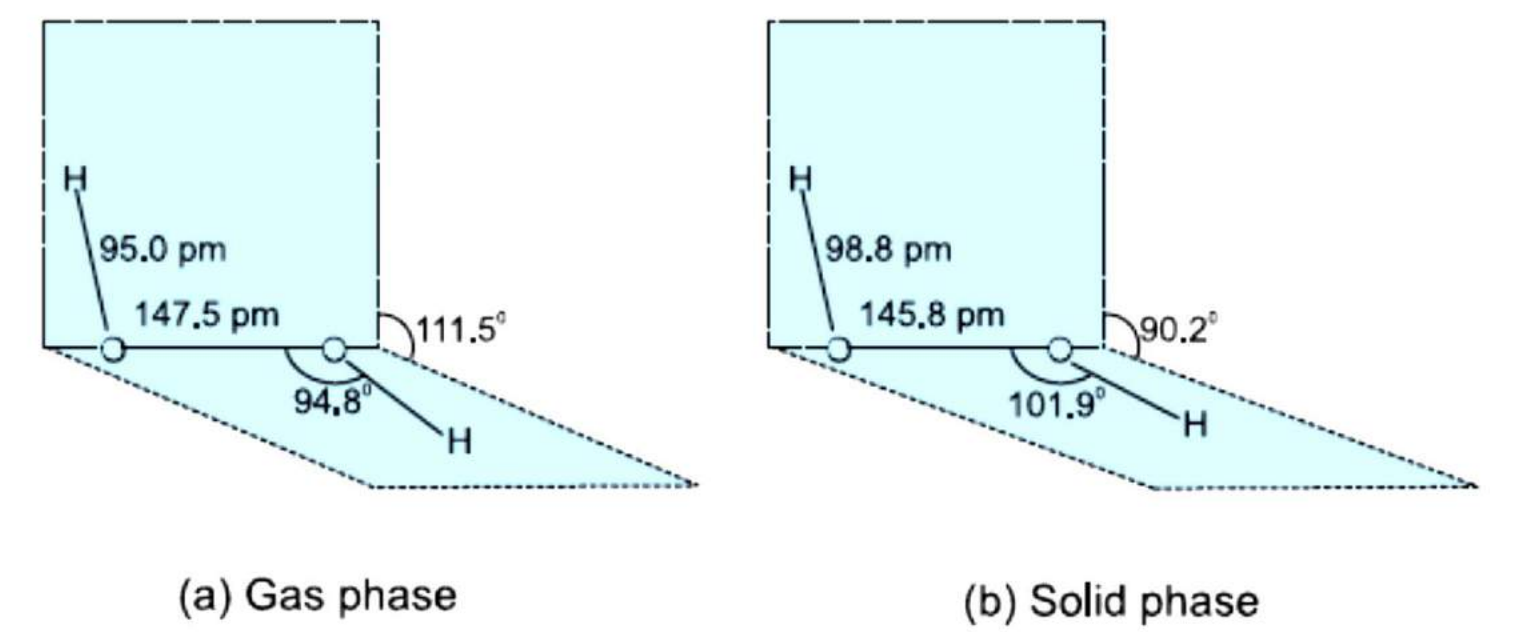
$O_3 + H_2O_2 \longrightarrow 2O_2 + H_2O$

(ii) Bleaching Action : O_3 also bleaches coloured substances through oxidation.

(iii) Tailing of mercury : $2\ Hg + O_3 \longrightarrow Hg_2O + O_2$

HYDROGEN PEROXIDE (H_2O_2) :

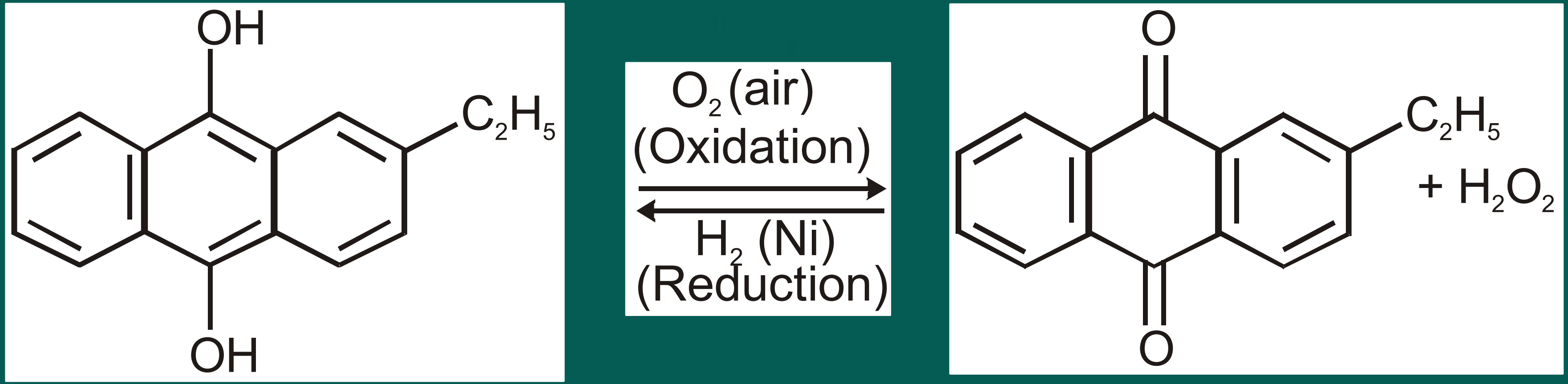
STRUCTURE



(a) Gas phase (b) Solid phase

PREPARATION :

$BaO_2 . 8H_2O + H_2SO_4 \text{ (cold)} \longrightarrow BaSO_4\downarrow \text{ (white)} + H_2O_2 + 8H_2O$ (NCERT)



2- Ethyl anthraquinol

2-Ethylanthraquinone

Chemical Properties :

Oxidising Agent :

On the basis of the potentials, we can say that H_2O_2 is strong oxidising agent in acidic medium but kinetically it is found that reactions are faster in basic medium.

In acidic medium : $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ (NCERT)

In alkaline medium : $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$ (NCERT)

Reducing Agent : It acts as a reducing agent towards powerful oxidising agen

In acidic medium :

$2MnO^{4-} + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$ (NCERT)

In alkaline medium :

$I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$ (NCERT)

SULPHUR (S)

Allotropic Forms Of Sulphur :

(i) Rhombic sulphur (α- sulphur) :

This allotrope is yellow in colour. Rhombic sulphur Crystals are formed on evaporating the solution of roll sulphur in CS_2.

(ii) Monoclinic sulphur (β - sulphur) :

This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling till crust is formed.

It is stable above 369 K and transforms into α - sulphur below it .

(iii) **Plastic Sulphur :** It is formed when molten sulphur (μ) is poured into cold water. It consists of chain like molecule and has rubber like properties when formed.

COMPOUNDS OF SULPHUR :

HYDROGEN SULPHIDE (H_2S) :

(i) $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$

It is prepared in kipp's apparatus

Chemical Properties :

Reducing Agent :

Acts as a strong reducing agent as it decomposes evolving hydrogen.

$H_2S + X_2 \longrightarrow 2HX + S$;

$H_2O_2 + H_2S \longrightarrow H_2O + S + O_2$

Acidic Nature :

Its aqueous solution acts as a weak dibasic acid according to following reaction. Therefore, It forms two series of salts as given below

$NaOH + H_2S \longrightarrow NaHS + H_2O$; $NaOH + H_2S \longrightarrow Na_2S + 2H_2O$

SULPHUR DIOXIDE

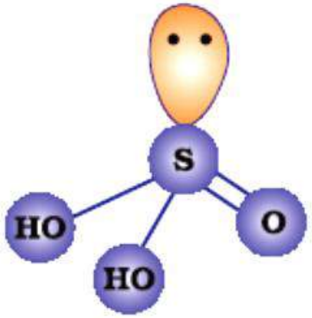
PREPARATION

$S(s) + O_2(g) \rightarrow SO_2\ (g)$ (NCERT)

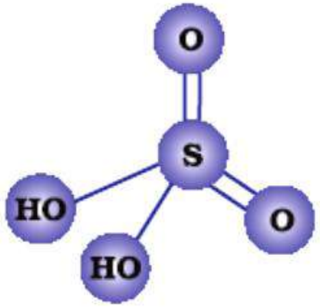
$SO_3^{2-}(aq) + 2H^+\ (aq) \rightarrow H_2O(l) + SO_2\ (g)$ (NCERT)

$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$ (NCERT)

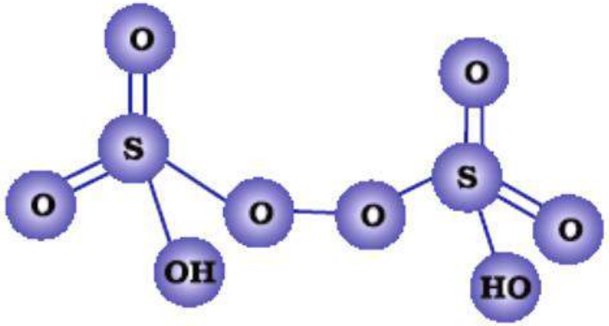
OXYACID OF SULPHUR



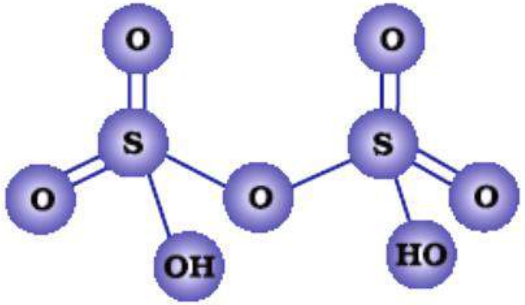
Sulphurous acid
(H_2SO_3)



Sulphuric acid
(H_2SO_4)



Peroxodisulphuric acid
($H_2S_2O_8$)



Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

SULPHURIC ACID (H_2SO_4) :

Manufacture :

Contact process :

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7} \qquad \text{(NCERT)}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Chemical Properties :

(i) Concentrated sulphuric acid is a strong dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O \quad (\text{NCERT})$$

$$H_2C_2O_4 \xrightarrow{H_2SO_4} CO + CO_2$$

(ii) Hot concentrated sulphuric acid is moderately strong oxidising agent.

$$Cu + 2H_2SO_4\ (\text{concentrated}) \longrightarrow CuSO_4 + 2H_2O \qquad (\text{NCERT})$$

$$3S + 2H_2SO_4\ (\text{concentrated}) \longrightarrow 3SO_2 + 2H_2O \qquad (\text{NCERT})$$

$$C + 2H_2SO_4\ (\text{concentrated}) \longrightarrow CO_2 + 2SO_2 + 2H_2O\ (\text{NCERT})$$

HALOGEN FAMILY

Group 17 Elements (F, Cl, Br, I, At)

- These are collectively known as the halogens (Greek halo means 'salt' and genes means 'born' i.e., salt producers).
- Astatine is a radioactive element.

Chemical reactivity :

(i) All the halogens are highly reactive.

(ii) Reactivity order of halogens : $F_2 > Cl_2 > Br_2 > I_2$

(iii) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens.

$F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X = Cl, Br or I) [NCERT]

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ (X = Br or I) [NCERT]

$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$ [NCERT]

CHLORINE (Cl_2)

PREPARATION

(i) By heating manganese dioxide with concentrated hydrochloric acid.

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$ [NCERT]

However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$
[NCERT]

Manufacture of chlorine

(i) **Deacon's process :**

By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$ [NCERT]

(ii) Electrolytic process :

Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as a by–product in many chemical industries.

PROPERTIES

(i) It is a greenish–yellow gas with pungent and suffocating odour.

(ii) Chlorine reacts with a number of metals and non-metals to form chlorides.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$; $P_4 + 6Cl_2 \rightarrow 4PCl_3$

$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$; $2Fe + 3Cl_2 \rightarrow 2FeCl_3$

(iii) With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$$\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \rightarrow 6NH_4Cl + N_2$$ [NCERT]

$$NH_3 + \underset{\text{(excess)}}{3Cl_2} \rightarrow NCl_3 + 3HCl$$ [NCERT]

(iv) **Oxidising & bleaching properties :** Chlorine dissolves in water giving HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

$2\ FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2\ HCl$ [NCERT]

$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2\ HCl$ [NCERT]

$SO_2 + 2\ H_2O + Cl_2 \longrightarrow H_2SO_4 + 2\ HCl$ [NCERT]

$I_2 + 6\ H_2O + 5\ Cl_2 \longrightarrow 2\ HIO_3 + 10\ HCl$ [NCERT]

- It is a powerful bleaching agent ; bleaching action is due to oxidation.

$Cl_2 + H_2O \longrightarrow 2\ HCl + O$ [NCERT]

Coloured substance + O → Colourless substance

(Bleaching effect of chlorine is permanent.)

(v) Reaction with NaOH :

(a) $2\ NaOH\ (\text{cold \& dil.}) + Cl_2 \longrightarrow NaCl + NaClO + H_2O$

(b) $6\ NaOH\ (\text{hot \& conc.}) + 3\ Cl_2 \longrightarrow 5\ NaCl + NaClO_3 + 3\ H_2O$

These reactions are also given by Br_2 and I_2.

OXOACIDS OF HALOGENS

(i) Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid.

(ii) The other halogens form several oxoacids.

OXOACIDS OF HALOGENS

Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluorous acid)	**$HOCl$** (Hypochlorous acid)	**$HOBr$** (Hypobromous acid)	**HOI** (Hypoiodous acid)
Halic (III) acid (Halous acid)	—	**$HOClO$** (Chlorous acid)	—	—
Halic (V) acid (Halic acid)	—	**$HOClO_2$** (Chloric acid)	**$HOBrO_2$** (Bromic acid)	**$HOIO_2$** (Iodic acid)
Halic (VII) acid (Perhalic acid)	—	**$HOClO_3$** (Perchloric acid)	**$HOBrO_3$** (Perbromic acid)	**$HOIO_3$** (Periodic acid)

GROUP 18 ELEMENTS

(THE NOBLE GASES / ZERO GROUP FAMILY)

- Group 18 consists of six elements: helium, neon, argon, krypton , xenon and radon .
- All these are gases and chemically unreactive.
- They form very few compounds . Because of this they are termed noble gases.

COMPOUNDS OF XENON

(i) Xenon fluorides

Preparation :

$$Xe + F_2 \longrightarrow 2 : 1 \text{ mixture} \xrightarrow{400°C,\ 1\ atm} XeF_2 \quad \text{(NCERT)}$$

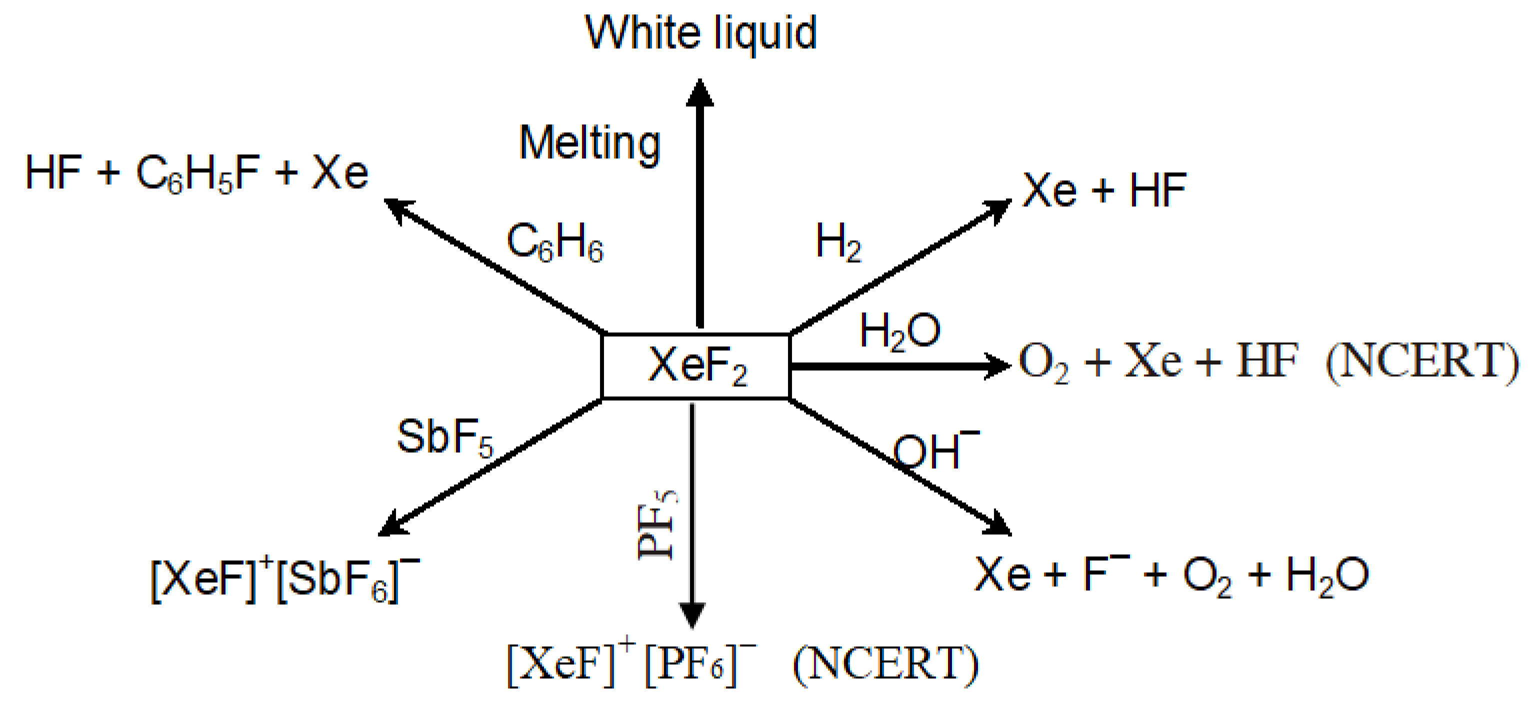
$$Xe + F_2 \longrightarrow 1 : 5 \text{ mixture} \xrightarrow{600°C,\ 7\ atm} XeF_4 \quad \text{(NCERT)}$$

$$Xe + F_2 \longrightarrow 1 : 20 \text{ mixture} \xrightarrow{200°C,\ 70\ atm} XeF_6 \quad \text{(NCERT)}$$

Note : $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$ (NCERT)

Chemical properties :

1. **XeF_2 :**



$XeF_2 \xrightarrow{\text{Melting}} \text{White liquid}$

$XeF_2 \xrightarrow{C_6H_6} HF + C_6H_5F + Xe$

$XeF_2 \xrightarrow{H_2} Xe + HF$

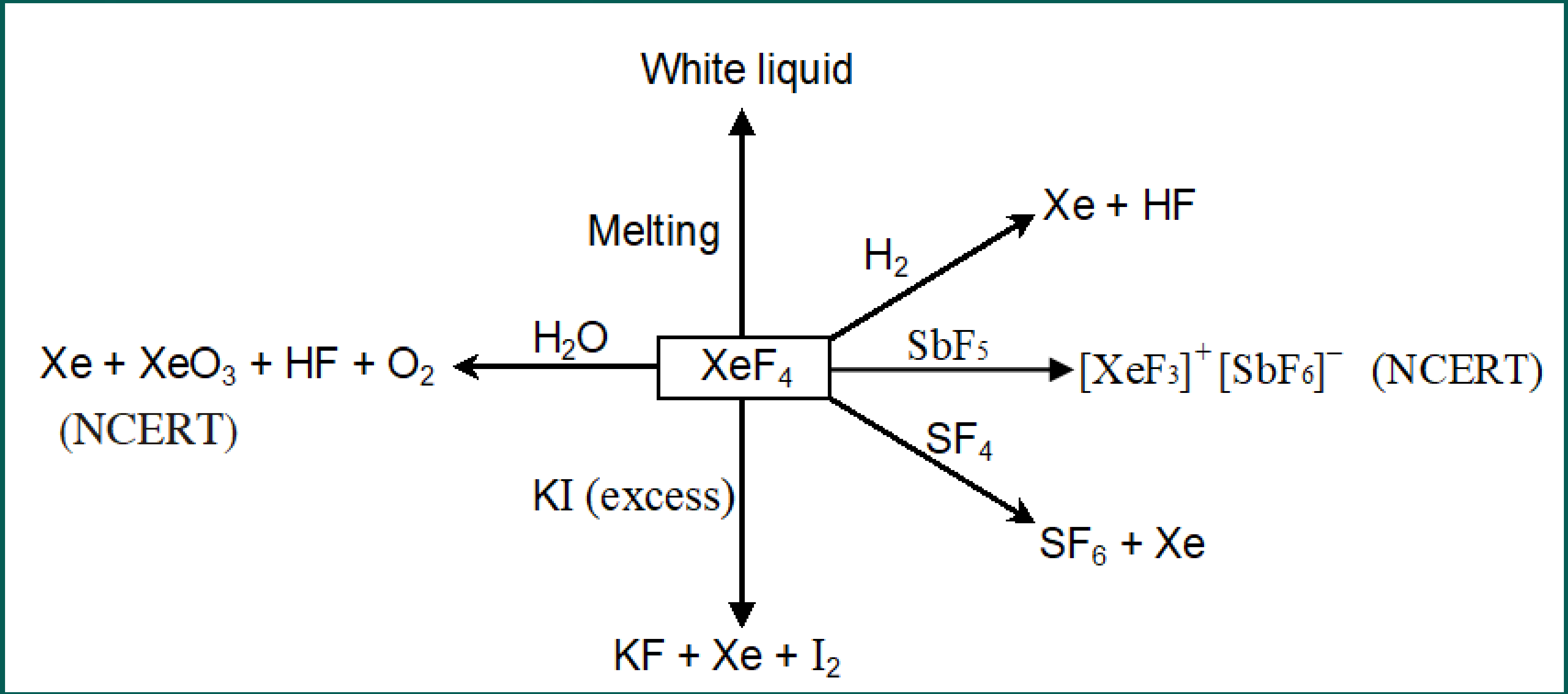
$XeF_2 \xrightarrow{H_2O} O_2 + Xe + HF$ (NCERT)

$XeF_2 \xrightarrow{OH^-} Xe + F^- + O_2 + H_2O$

$XeF_2 \xrightarrow{PF_5} [XeF]^+[PF_6]^-$ (NCERT)

$XeF_2 \xrightarrow{SbF_5} [XeF]^+[SbF_6]^-$

2. XeF_4 :



White liquid

Melting

H_2

Xe + HF

H_2O

Xe + XeO_3 + HF + O_2

(NCERT)

XeF_4

SbF_5

$[XeF_3]^+[SbF_6]^-$ (NCERT)

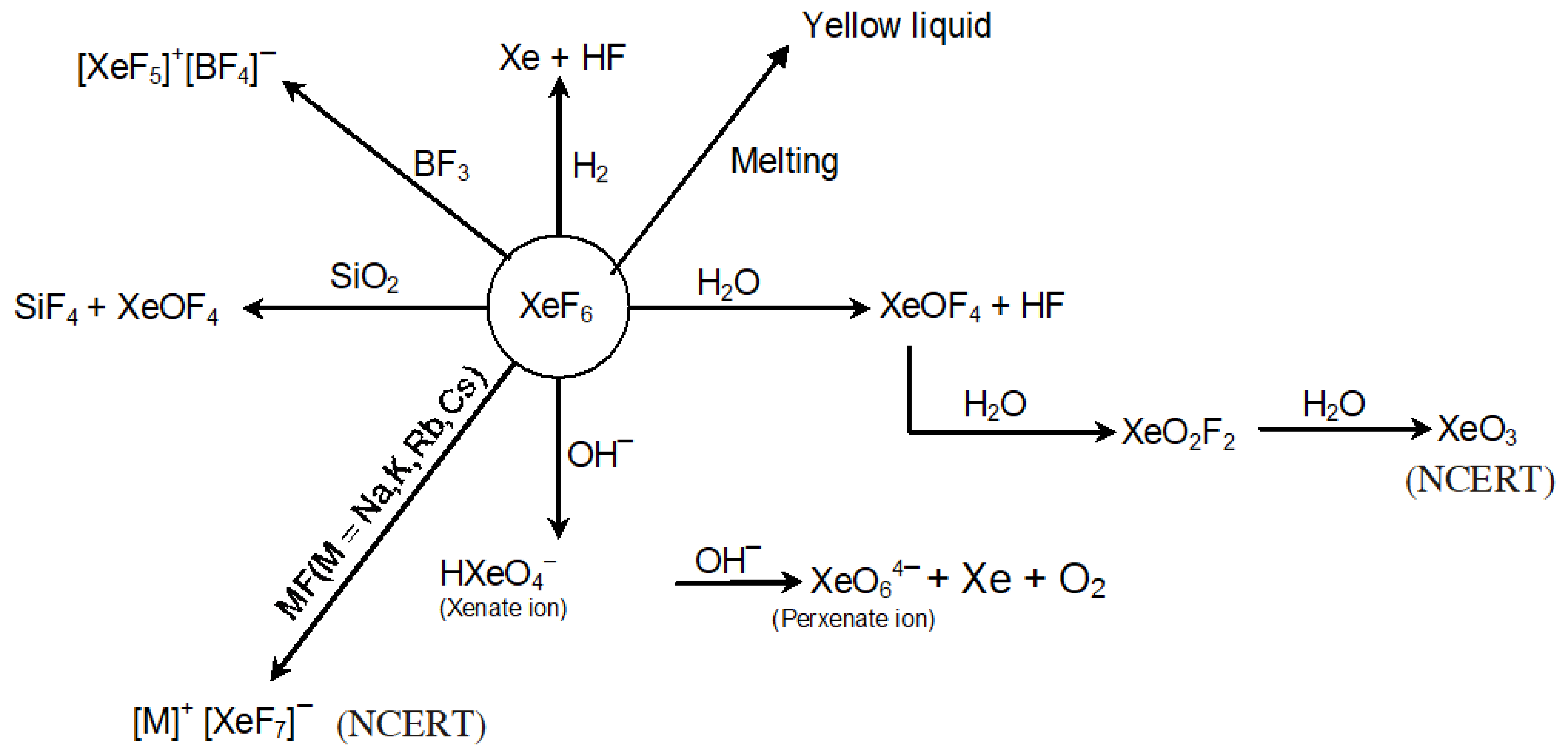
SF_4

SF_6 + Xe

KI (excess)

KF + Xe + I_2

3. XeF_6 :


XeF_6
BF_3
$[XeF_5]^+[BF_4]^-$
H_2
$Xe + HF$
Melting
Yellow liquid
SiO_2
$SiF_4 + XeOF_4$
H_2O
$XeOF_4 + HF$
H_2O
XeO_2F_2
H_2O
XeO_3
(NCERT)
OH^-
$HXeO_4^-$
(Xenate ion)
OH^-
$XeO_6^{4-} + Xe + O_2$
(Perxenate ion)
MF(M = Na,K,Rb,Cs)
$[M]^+ [XeF_7]^-$
(NCERT)

(ii) Xenon–oxygen compounds :

$6\ XeF_4 + 12\ H_2O \longrightarrow 4\ Xe + 2\ XeO_3 + 24\ HF + 3\ O_2$

$XeF_6 + 3\ H_2O \longrightarrow XeO_3 + 6\ HF$

$XeF_6 + H_2O \longrightarrow XeOF_4 + 2\ HF$

$XeF_6 + 2\ H_2O \longrightarrow XeO_2F_2 + 4\ HF$

- XeO_3 is a colourless explosive solid and has a pyramidal molecular structure.
- $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.

D & F-BLOCK ELEMENTS

d-block Elements

Last electron enters in (n – 1)d subshell. d-block elements lie in middle of periodic table.

General Introduction :

Occurrence	Three of transition metals are very abundant in the earth’s crust.
	Fe → 4th most abundant elements in earth’s crust by weight. Ti → 5th most abundant elements in earth’s crust by weight. Mn → 12th most abundant elements in earth’s crust by weight.

First row	Element with even atomic no. are in general more abundant than their neighbours with odd atomic no. except for Mn (Z = 25) but still 12th most abundant element by weight.
2nd and 3rd row	Less abundant than 1st d- series elements. Tc → does not occur in nature. Last six members of 2nd and 3rd row occur less than 0.16 ppm in earth's crust.
Coinage metals	Cu, Ag and Au are called coinage metals.
Noble metals	Cu, Ag, Au, Hg and Pt.
No. of elements	Total d-block elements – (40) Total transition elements – (36). If 112 elements are included in periodic table. (Except Zn, Cd, Hg and Uub)

Groups	**IIIB to VIIB, VIII, IB, IIB or group 3 to 12 (IUPAC).**
Period	4 th to 7 th 4th period 3d- series (Sc - Zn) 5th period 4d- series (Y - Cd) 6th period 5d- series (La - Hg) 7th period 6d- series (Ac - Uub)

The electronic structure of 2nd and 3rd rows do not always follow the pattern of the first row, e.g. Group 10

Ni	$3d^8\ 4s^2$
Pd	$4d^{10}5s^0$
Pt	$5d^9\ 6s^1$

d-orbitals are complete at Cu, Pd, Ag, Au.

Ni ($3d^8\ 4s^2$) Cu($3d^{10}4s^1$) Zn($3d^{10}4s^2$)
Pd($4d^{10}5s^0$) Ag($4d^{10}5s^1$) Cd($4d^{10}5s^2$)

Transition elements :

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.
Zinc, Cadmium and Mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, they are some times not regarded as transition metals.
All transition elements are d-block elements but all d-block elements are not transition elements.

Oxidation-State :

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
+3	+2	+2	+1	**+2**	+1	**+2**	**+2**	+1	**+2**
	+3	+3	+2	+3	**+2**	**+3**	+3	**+2**	
	+4	+4	**+3**	+4	**+3**	+4	+4		
		+5	+4	+5	+4				
			+5	+6					
			+6	**+7**	+6				

Element (M)	$E^0_{M^{3+}/M^{2+}}$	$E^0_{M^{2+}/M}$	**Comments**
Ti	–0.37	–1.63	+3 Oxidation states is more stable
V	–0.26	–1.18	+3 Oxidation states is more stable
Cr	–0.41	–0.9	+3 Oxidation states is more stable
Mn	1.57	–1.18	+2 Oxidation states is more stable
Fe	0.77	–0.44	+2 Oxidation states is more stable

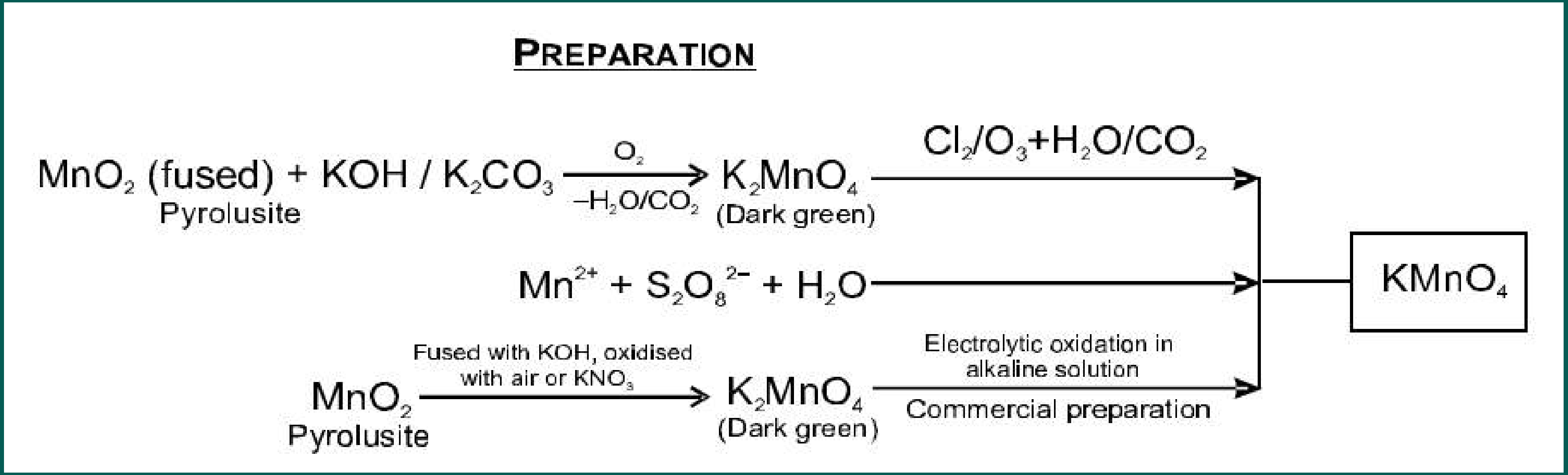
Element (M)	$E^0_{M^{3+}/M^{2+}}$	$E^0_{M^{2+}/M}$	**Comments**
Co	1.97	–0.28	+2 Oxidation states is more stable
Ni	–	–0.25	+3 Oxidation states does not exist for Ni
Cu	–	0.34	+3 Oxidation states does not exist for Cu. 0 Oxidation states is more stable
Zn	–	0.76	+3 Oxidation states does not exist for Zn

Colour of MnO_4^-

MnO_4^- is coloured inspite of d^0 configuration of Mn.

It is not due to d-d transition but it occurs due to charge transfer between Mn and O.

Potassium Permanganatic ($KMnO_4$)

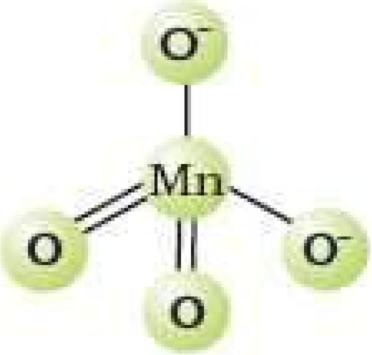


PREPARATION

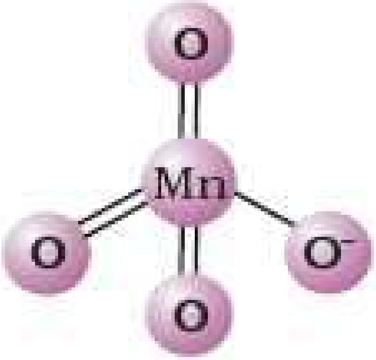
$$\underset{\text{Pyrolusite}}{MnO_2\ (\text{fused})} + KOH / K_2CO_3 \xrightarrow[-H_2O/CO_2]{O_2} \underset{\text{(Dark green)}}{K_2MnO_4} \xrightarrow{Cl_2/O_3+H_2O/CO_2} KMnO_4$$

$$Mn^{2+} + S_2O_8^{2-} + H_2O \longrightarrow KMnO_4$$

$$\underset{\text{Pyrolusite}}{MnO_2} \xrightarrow{\text{Fused with KOH, oxidised with air or } KNO_3} \underset{\text{(Dark green)}}{K_2MnO_4} \xrightarrow[\text{Commercial preparation}]{\text{Electrolytic oxidation in alkaline solution}} KMnO_4$$



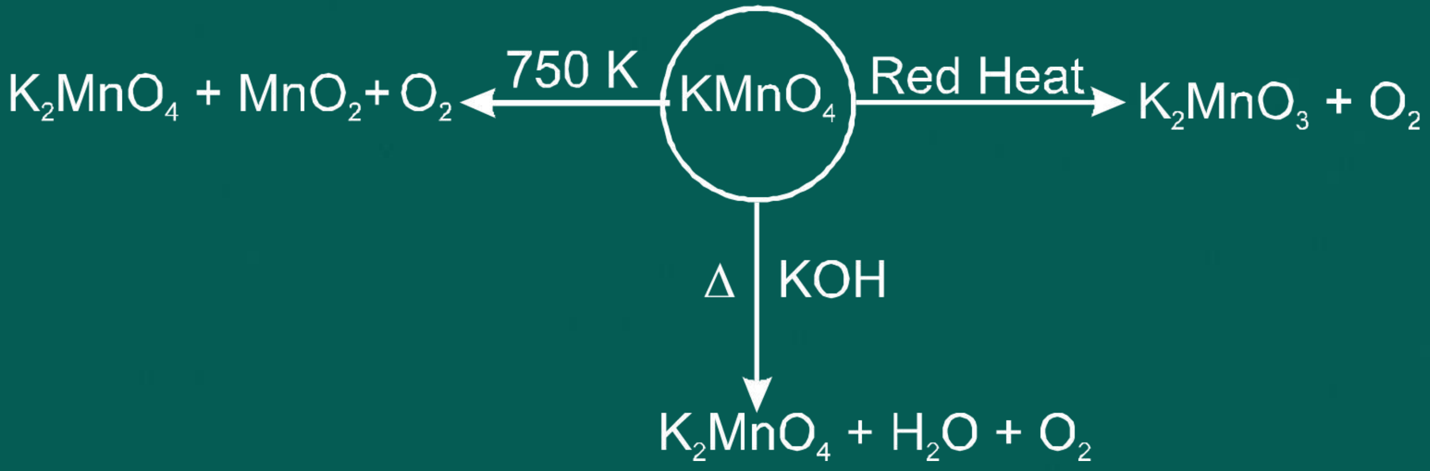
Tetrahedral manganate (green) ion



Tetrahedral permanganate (purple) ion

Chemical Properties

(i) Heating effect

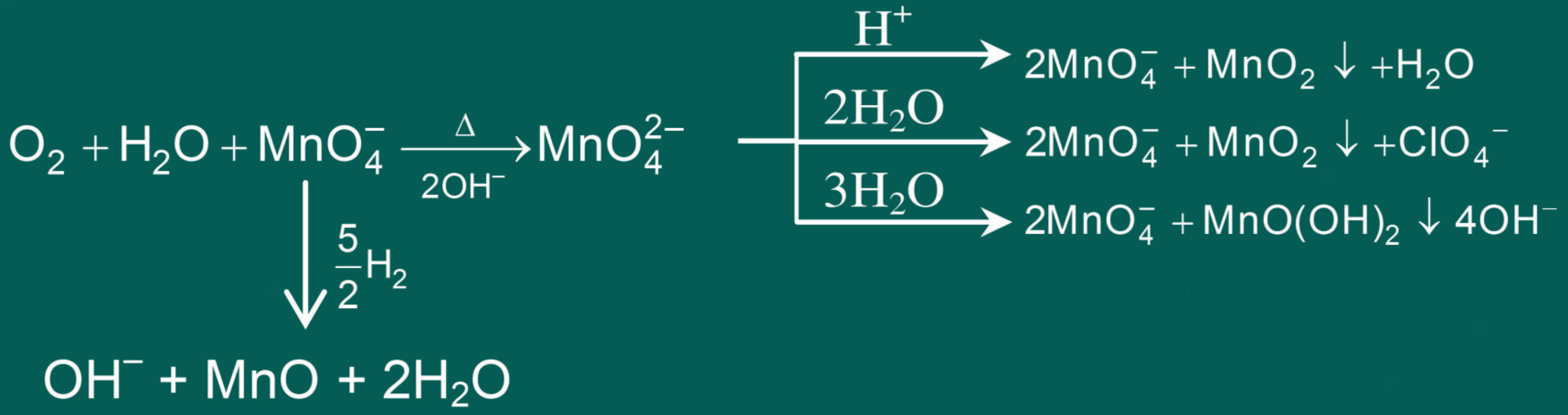


$$KMnO_4 \xrightarrow{750\ K} K_2MnO_4 + MnO_2 + O_2$$

$$KMnO_4 \xrightarrow{Red\ Heat} K_2MnO_3 + O_2$$

$$KMnO_4 \xrightarrow[\Delta]{KOH} K_2MnO_4 + H_2O + O_2$$

(ii) Reactions with MnO_4^{2-} in dil. alkaline, water and acidic solutions



$$O_2 + H_2O + MnO_4^- \xrightarrow[2OH^-]{\Delta} MnO_4^{2-}$$

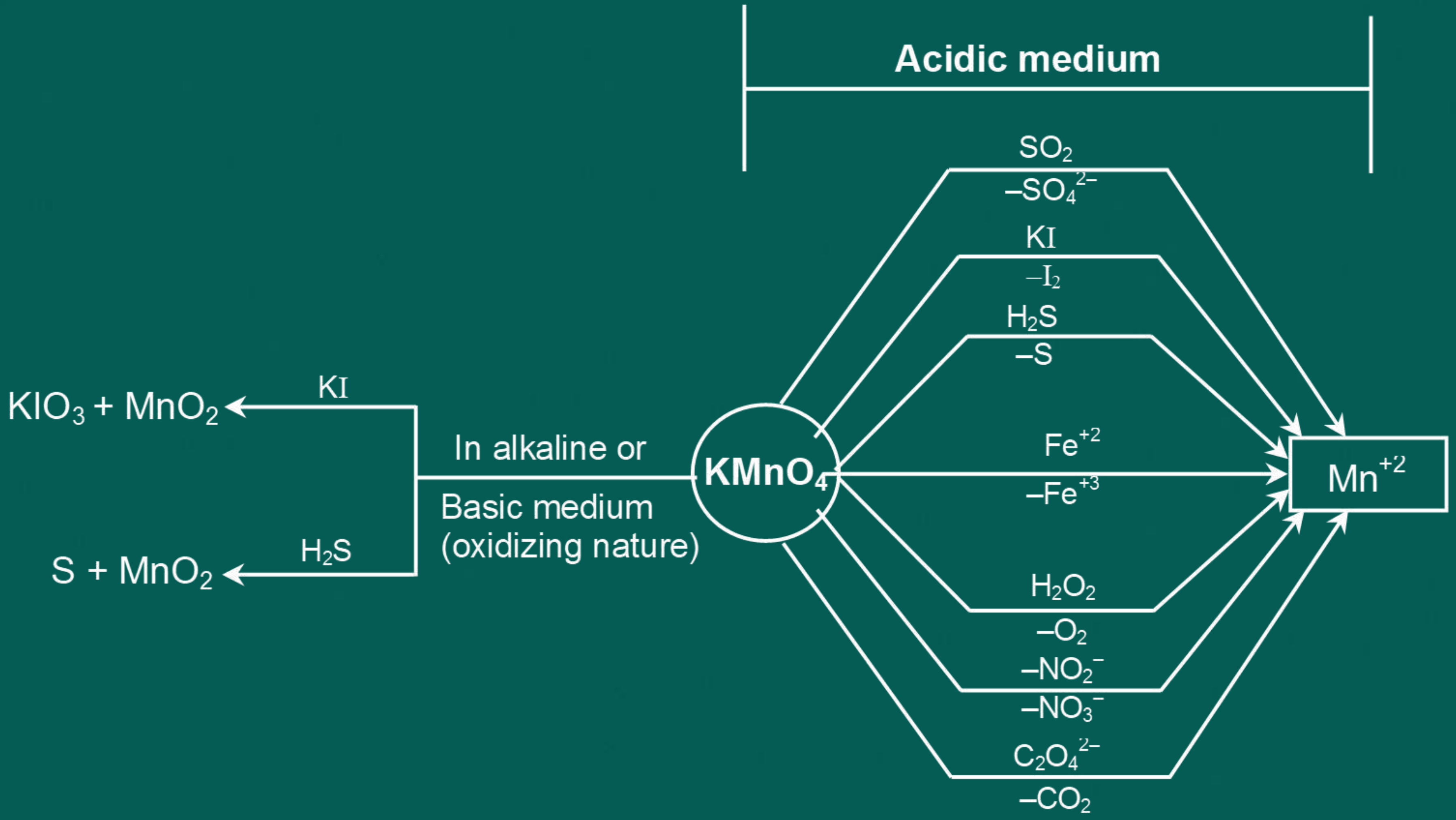
$$MnO_4^{2-} \xrightarrow{H^+} 2MnO_4^- + MnO_2\downarrow + H_2O$$

$$MnO_4^{2-} \xrightarrow{2H_2O} 2MnO_4^- + MnO_2\downarrow + ClO_4^-$$

$$MnO_4^{2-} \xrightarrow{3H_2O} 2MnO_4^- + MnO(OH)_2\downarrow 4OH^-$$

$$O_2 + H_2O + MnO_4^- \xrightarrow{\frac{5}{2}H_2} OH^- + MnO + 2H_2O$$

Reactions of $KMnO_4$



Acidic medium

SO_2
$-SO_4^{2-}$

KI
$-I_2$

H_2S
$-S$

Fe^{+2}
$-Fe^{+3}$

H_2O_2
$-O_2$

$-NO_2^-$
$-NO_3^-$

$C_2O_4^{2-}$
$-CO_2$

Mn^{+2}

$KMnO_4$

In alkaline or
Basic medium
(oxidizing nature)

KI
$KIO_3 + MnO_2$

H_2S
$S + MnO_2$

Potassium Dichromate ($K_2Cr_2O_7$)

Preparation

$$4FeO.Cr_2O_3 + 8Na_2CO_3 \xrightarrow[+7O_2]{\text{Roasting in air}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

(yellow)

$$\Big\downarrow 4H_2SO_4$$

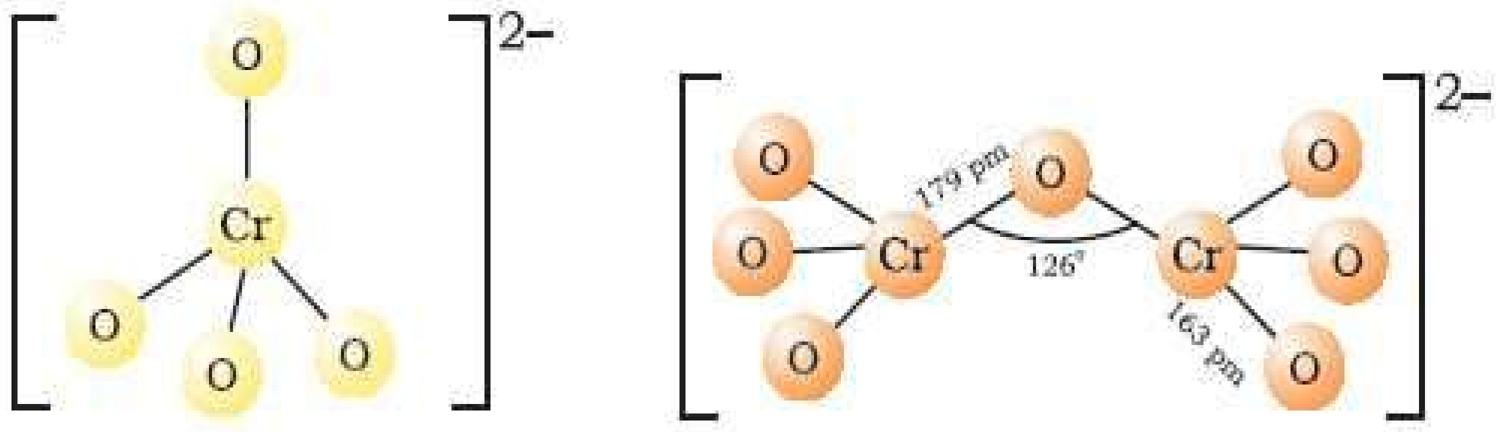
$$4Na_2CrO_7 + 4Na_2SO_4 + 4H_2O$$

(orange) (Crystalise)

$$\Big\downarrow 8\ KCl$$

$$\boxed{K_2Cr_2O_7} + 8NaCl$$

Structure of Chromate and Dichromate ion



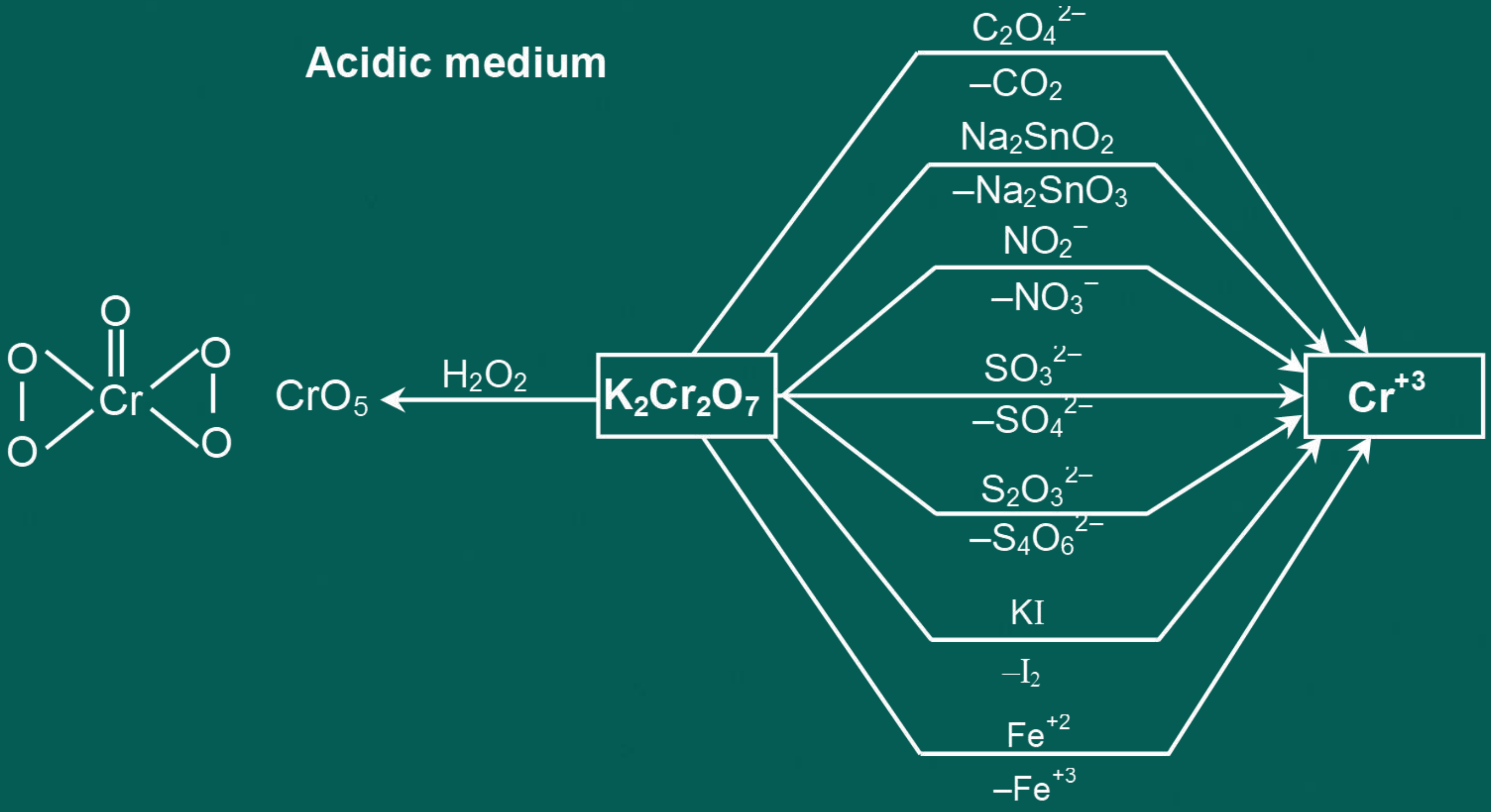
Chromate ion

Dichromate ion

Chemical Properties

Reactions of $K_2Cr_2O_7$

Acidic medium



CrO_5

H_2O_2

$K_2Cr_2O_7$

Cr^{+3}

$C_2O_4^{2-}$

$-CO_2$

Na_2SnO_2

$-Na_2SnO_3$

NO_2^-

$-NO_3^-$

SO_3^{2-}

$-SO_4^{2-}$

$S_2O_3^{2-}$

$-S_4O_6^{2-}$

KI

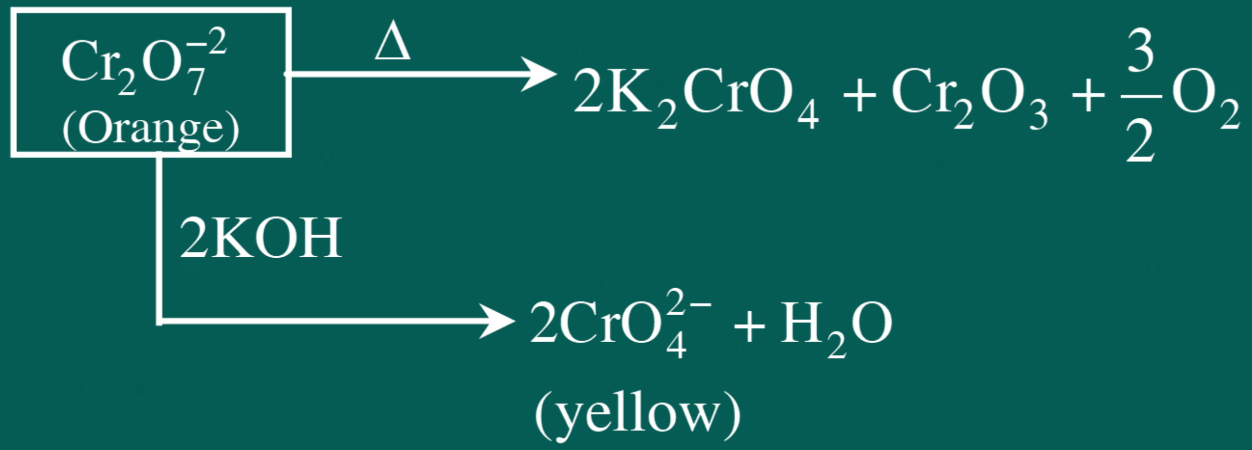
$-I_2$

Fe^{+2}

$-Fe^{+3}$

Effect of heating :

On heating strongly, it decomposes liberating oxygen.



$$\boxed{\begin{array}{c}Cr_2O_7^{-2}\\ \text{(Orange)}\end{array}} \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$$

$$\xrightarrow{2KOH} \underset{\text{(yellow)}}{2CrO_4^{2-}} + H_2O$$

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Chromyl chloride test

$$2Cl^- + \frac{1}{2}Cr_2O_7^{2-} + 3H^+ \longrightarrow \boxed{\begin{array}{c} CrO_2Cl_2 \\ \text{(deep red)} \end{array}}$$

$$\xrightarrow{4OH^-} \underset{\text{(yellow)}}{CrO_4^{2-}} + 2Cl^- + 2H_2O$$

$$\xrightarrow{Pb^{+2}} \underset{\text{(yellow)}}{PbCrO_4\downarrow}$$

Some important alloys

(a)	Bronze	Cu (75 - 90 %) +Sn (10 - 25 %)
(b)	Brass	Cu (60 - 80 %) +Zn (20 - 40 %)
(c)	Gun metal	(Cu + Zn + Sn) (87 : 3 : 10)
(d)	German Silver	Cu + Zn + Ni (2 : 1 : 1)
(e)	Bell metal	Cu (80 %) + Sn(20 %)
(f)	Nichrome	(Ni + Cr + Fe)
(g)	Alnico	(Al, Ni,Co)

Some important alloys

(h)	**Type Metal**	**Pb + Sn + Sb**
(i)	Alloys of steel	
	• Chromium steel	Cr (2 - 4 %)
	• Manganese steel	Mn (10 -18 %)
	• Stainless steel	Cr (12 - 14 %)& Ni (2 - 4 %)
(j)	24 Carat Gold	100 %Au
(k)	Artificial Gold	Cu (90 %) + Al (10%)
(l)	Solder	Pb + Sn

Some important alloys

(m)	**Constantan**	**Cu(60%) + Ni (40%)**
% of Carbon in different type of Iron		
	Name	% of C
(a)	Wrought Iron	0.1 to 0.25
(b)	Steel	0.25 to 2.0
(c)	Cast Iron/Pig Iron	2.6 to 4.3

(4) f - block :

(i) last electron enters in f-orbital

(ii) General valence shell electronic configuration

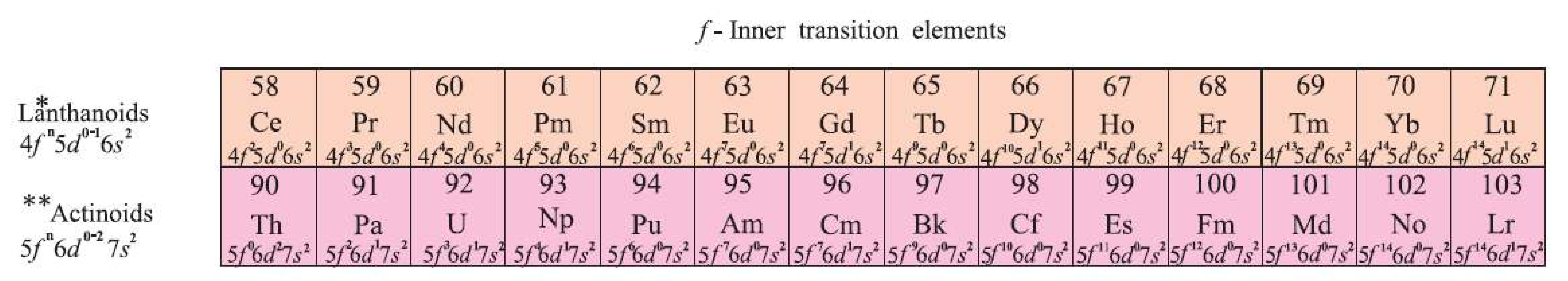
$(n - 2)\, f^{0-14}\ (n - 1)\, d^{0-2}\, ns^2$

(iii) There are two series 4f (Lanthanides) & 5f (Actinides) belong to 6th & 7th period respectively. Each series consist of 14 elements.

f-block Elements

Differentiating electrons enters in (n – 2)f subshell.
f-block elements lie on the Bottom portion of periodic table.

1. **General characters :**
   All the f-block elements are heavy metals. It shows high melting and boiling point. The most common oxidation state of these elements is +3.
2. **No. of elements :** Total number of f-block elements – (28)



f - Inner transition elements

*Lanthanoids $4f^n 5d^{0-1} 6s^2$	58 Ce $4f^2 5d^0 6s^2$	59 Pr $4f^3 5d^0 6s^2$	60 Nd $4f^4 5d^0 6s^2$	61 Pm $4f^5 5d^0 6s^2$	62 Sm $4f^6 5d^0 6s^2$	63 Eu $4f^7 5d^0 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 5d^0 6s^2$	66 Dy $4f^{10} 5d^1 6s^2$	67 Ho $4f^{11} 5d^0 6s^2$	68 Er $4f^{12} 5d^0 6s^2$	69 Tm $4f^{13} 5d^0 6s^2$	70 Yb $4f^{14} 5d^0 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
**Actinoids $5f^n 6d^{0-2} 7s^2$	90 Th $5f^0 6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 6d^0 7s^2$	95 Am $5f^7 6d^0 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 6d^0 7s^2$	98 Cf $5f^{10} 6d^0 7s^2$	99 Es $5f^{11} 6d^0 7s^2$	100 Fm $5f^{12} 6d^0 7s^2$	101 Md $5f^{13} 6d^0 7s^2$	102 No $5f^{14} 6d^0 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

3. **Group/period :** IIIB/3rd group is called longest group having 32 elements including 14 Lanthanides and 14 Actinides.

Period	**III B/ 3rd**	
	Sc	
	Y	
6th period	La	Lanthanides (14) $Ce_{58} - Lu_{71}$
7th period	Ac	Actinides (14) $Th_{90} - Lr_{103}$

4. **Electronic Configuration :**

Lanthanide series $4f^{1-14}\ 5d^{0 \text{ or } 1}\ 6s^2$

Actinide series $5f^{1-14}\ 6d^{0 \text{ or } 1}\ 7s^2$

5. **Inner transition elements :**

The elements in which all the three shells that is ultimate (n) penultimate (n– 1) and pre or antipenultimate (n – 2) shell are incomplete are called inner transition elements.Ce_{58} = [Xe] $6s^2$, $5d^1$, $4f^1$

6. **Lanthanides :**

- Lanthanides are found rarely on earth so these are called rare earth metals.
- The first element of this series is Cerium and not Lanthanum.
- Promethium ($_{61}Pm$) is the only lanthanide which is synthetic and radioactive in nature.

7. Actinides :

- All the actinides are radioactive elements.
- The first element of this series is Thorium and not Actinium.
- First three elements (Th, Pa, U) are found in nature while others are synthetic in nature.

Electronic Configurations and Radii of Lanthanum and Lanthanides

Atomic Number	Name	Symbol	Electronic configurations
57	Lanthanum	La	$5d^1 6s^2$
58	Cerium	Ce	**$4f^1 5d^1 6s^2$**
59	Praseodymium	Pr	$4f^3 6s^2$
60	Neodymium	Nd	$4f^4 6s^2$
61	Promethium	Pm	$4f^5 6s^2$
62	Samarium	Sm	$4f^6 6s^2$
63	Europium	Eu	$4f^7 6f^2$
64	Gadolinium	Gd	**$4f^7 5d^1 6s^2$**
65	Terbium	Tb	$4f^9 6s^2$

Atomic Number	**Name**	**Symbol**	**Electronic configurations**
66	Dysprosium	Dy	$4f^{10}6s^2$
67	Holmium	Ho	$4f^{11}6s^2$
68	Erbium	Er	$4f^{12}6s^2$
69	Thulium	Tm	$4f^{13}6s^2$
70	Ytterbium	Yb	$4f^{14}6s^2$
71	Lutetium	Lu	**$4f^{14}5d^{1}6s^2$**

The first ionisation enthalpies of the lanthanides are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium.

8. **Atomic and Ionic Sizes :**

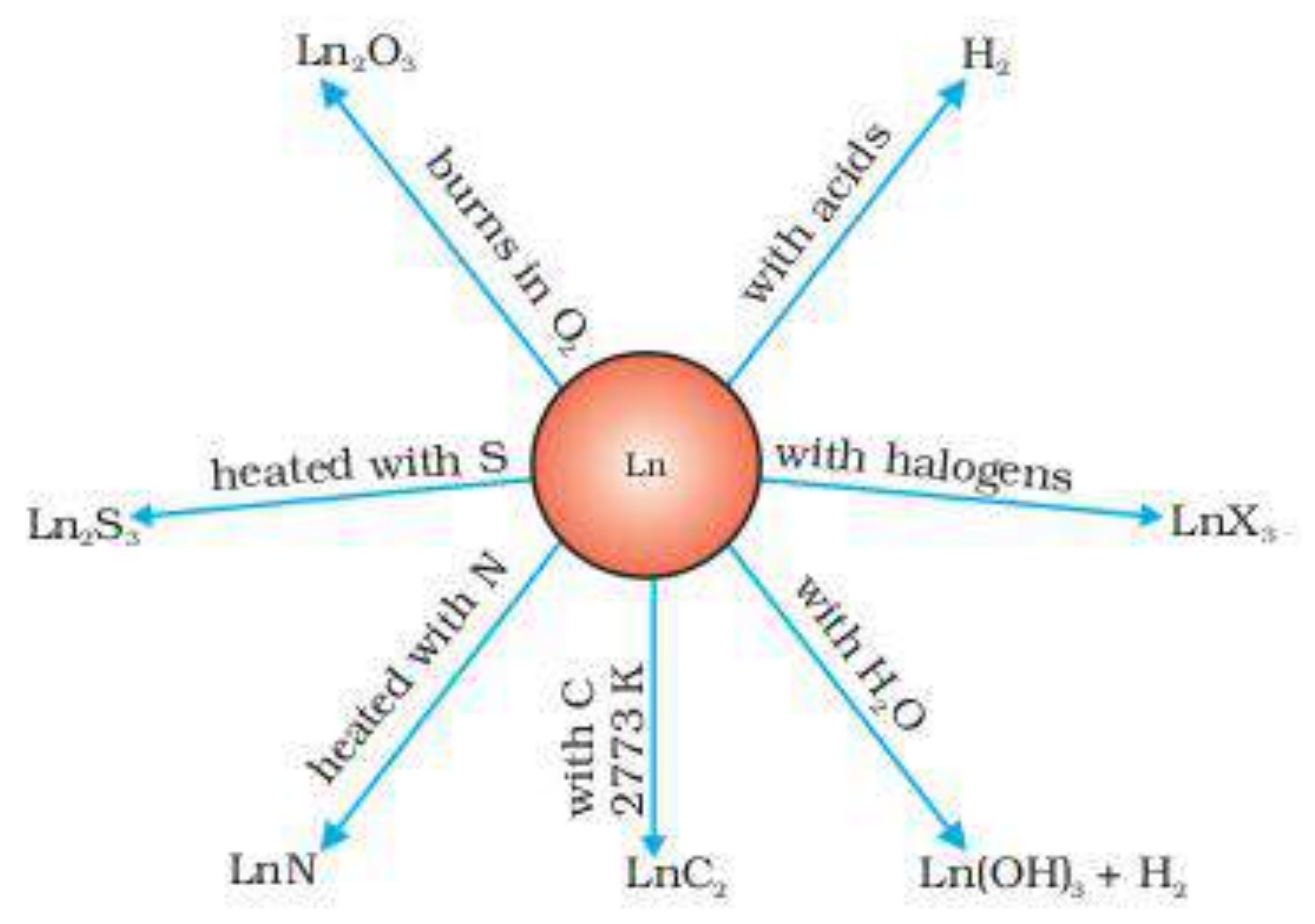
With increase in atomic number additional proton goes to the nucleusand corresponding electron goes to the 4f-subshell. Due to poor shielding of 4f and 5d orbitals, Z_{eff} increases hence size decreases.

This is known as lanthanide contraction.

9. **Oxidation States :**

In the lanthanides, La(III) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained.

Chemical properties :



The best single use of the lanthanides is for the production of alloy steels for plates and pipes. A well known alloy is mischmetall which consists of a lanthanide metal (~ 95%) and iron (~ 5%)

Electronic Configurations and Radii of Actinium and Actinoids

Atomic Number	Name	Symbol	Electronic configurations
89	Actinium	AC	$6d^17s^2$
90	Thorium	Th	$6d^27s^2$
91	Proctactiniium	Pa	$5f^26d^17s^2$
92	Uranium	U	$5f^36d^17s^2$
93	Neptunium	Np	$5f^46d^17s^2$
94	Plutonium	Pu	$5f^67s^2$
95	Americium	Am	$5f^77s^2$
96	Curium	Cm	$5f^76d^17s^2$
97	Berkelium	Bk	$5f^97s^2$

Atomic Number	**Name**	**Symbol**	**Electronic configurations**
98	Californium	Cf	$5f^{10}7s^2$
99	Einstenium	Es	$5f^{11}7s^2$
100	Fermium	Fm	$5f^{12}7s^2$
101	Mendelevium	Md	$5f^{13}7s^2$
102	Nobelium	No	$5f^{14}7s^2$
103	Lawrencium	Lr	$5f^{14}6s^{1}7s^2$

Oxidation States of Actinium and Actinides

Ac	Th	Pa	U	Np	Pu	Am	Cm	Cf	Es	Fm	Md	Lr
3		3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4				
		5	5	5	5	5						
			6	6	6	6						
				7	7							

The actinides show in general +3 oxidation state.

GENERAL ORGANIC CHEMISTRY
(GOC)

Conditions for resonance

(a) System must be planar. (b) System must be in conjugation

Following type of conjugation may be present in a molecule:

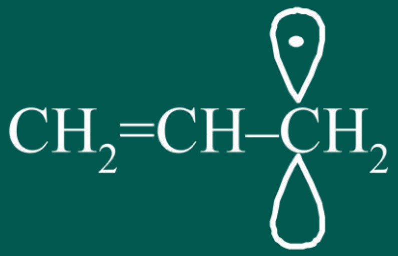
(I) $CH_2 = CH - CH = CH_2$

(II) $CH_2 = CH{-}\overset{\oplus}{C}H_2$

(III) $CH_2 = CH{-}\overset{\ominus}{C}H_2$

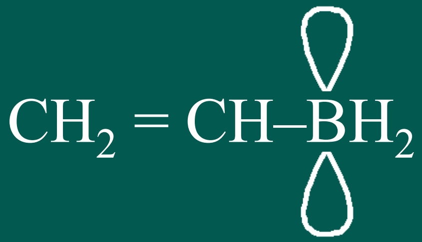
(IV) $CH_2 = CH{-}\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}H$

(V)



$CH_2{=}CH{-}CH_2$

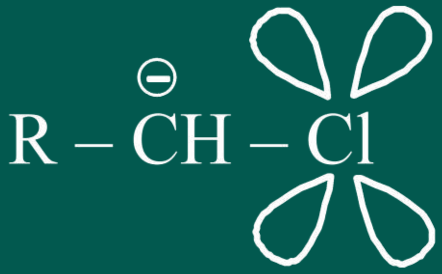
(VI)



$CH_2 = CH{-}BH_2$

(VII) $R{-}\overset{\oplus}{C}H - \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}H$

(VIII)



$R - \overset{\ominus}{C}H - Cl$

Rules for stability of resonating structures :

More stable resonating structure contribute more towards resonance hybrid.

(1) Maximum number of covalent bond (covalent maxima)

Neutral (non polar) > charged (polar)

(2) Charge : –ve charge on atom with more atomic number

(3)

⊕ve ⊖ve > ⊕ve ⊖ve

less charge separation

more charge separation

(4) Benzenoid > non benzenoid

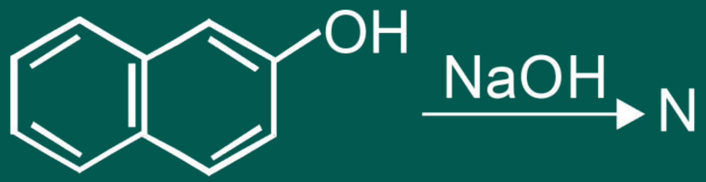
Q.1 The correct decreasing order of stability in the following resonating structures is :

$$\mathrm{H_2C{=}\overset{+}{N}{=}\overset{-}{N}} \qquad \mathrm{H_2\overset{+}{C}{-}N{=}\overset{-}{N}} \qquad \mathrm{H_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N} \qquad \mathrm{H_2\overset{-}{C}{-}N{=}\overset{+}{N}}$$

(I) (II) (III) (IV)

Ans. (I) > (III) > (II) > (IV)

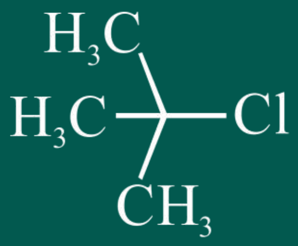
Q.2 The number of resonance structures for N is



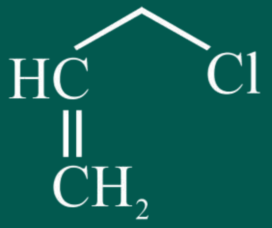
Ans. 9

Q.3 Among the following compounds, which one has the shortest C—Cl bond ?

(A) $H_3C–Cl$

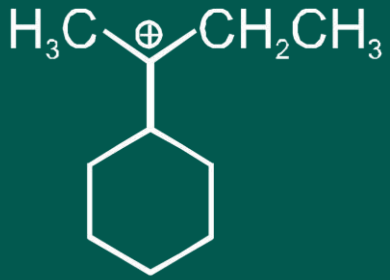
(B) 

(C) 

(D) 

Ans. (C)

Q.4 The total number of contributing structures showing hyperconjugation (involving C–H bonds) for the following carbocation is



Ans. 6

Q.5 The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to

(A) $\sigma \rightarrow \pi$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations.

(B) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations.

(C) $\sigma \rightarrow \pi$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations.

(D) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations.

Ans. (A)

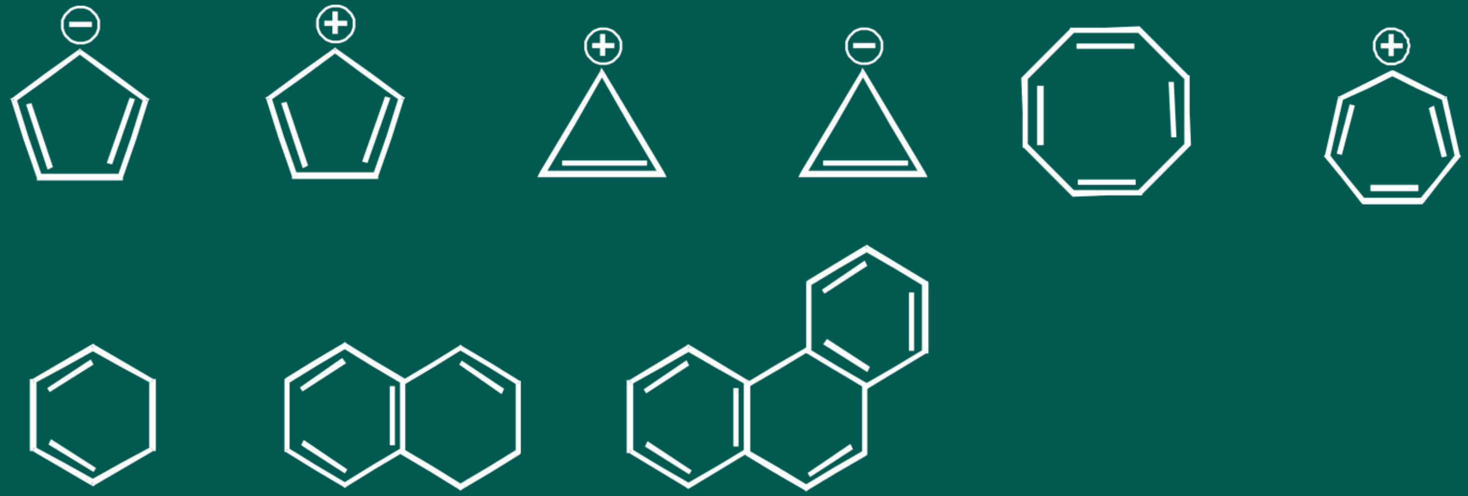
AROMATICITY

Conditions for Aromaticity	**Conditions for Anti-aromaticity**
Cyclic, planar, conjugated, $(4n + 2)\ \pi e^-$ [Huckel's Rule] $n = 0, 1, 2, 3, \ldots$ $2\pi e^-, 6\pi e^-, 10\pi e^-, 14\pi e^-, \ldots$	Cyclic, planar, conjugated, $4n\pi e^-$ [Huckel's Rule] $n = 1, 2, 3, \ldots$ $4\pi e^-, 8\pi e^-, 12\pi e^-, 16\pi e^-, \ldots$

Order of stability for prototype structure :

$$\boxed{\text{Aromatic} > \text{Non Aromatic} > \text{Anti Aromatic}}$$

Q.6 Among the following, the number of aromatic compound(s) is



Ans. 5 (1,3,6,8,9)

Q.7 Which compound(s) out of the following is/are not aromatic?

(a)


(b)


(c)


(d)


(A) only b

(B) b, c & d

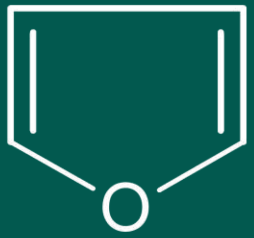
(C) c & d

(D) a & c

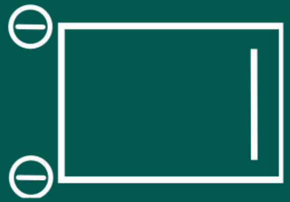
Q.8 Which one of the following compounds is non-aromatic ?

(A)

(B)



(C)



(D)

Factor affecting acidic strength

Acidic Strength (K_a) :

Acidic strength ↑, K_a ↑, pK_a ↓

$K_a \propto$ Stability of Conjugate Base (generally anion)

$\propto$ Size of donor atom (in same group)

$\propto$ E.N. of donor atom (in same period)

$\propto$ Delocalisation/aromaticity/$p\pi$-$d\pi$

$\propto$ –M and –I effects

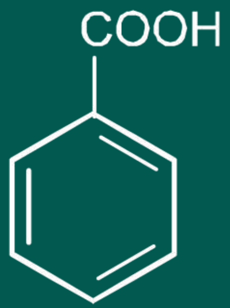
$$\propto \frac{1}{+M\,/\,+I \text{ effects}}$$

$\propto$ Ortho effect in benzoic acid

Q.9 The correct decreasing acidity order of the following is :


(I)


(II)


(III)


(IV)

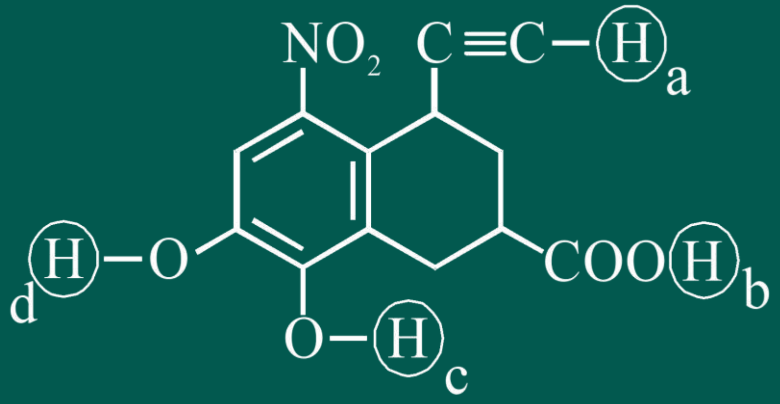
Ans. (III) > (IV) > (II) > (I)

Q.10 The compound that does NOT liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is :

(A) Benzoic acid
(B) Benzenesulphonic acid
(C) Salicylic acid
(D) Carbolic acid (Phenol)

Ans. (D)

Q.11 Arrange the following labelled hydrogens in decreasing order of acidity :

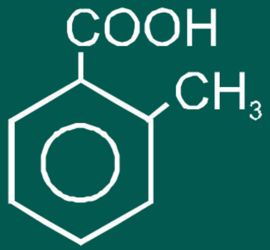


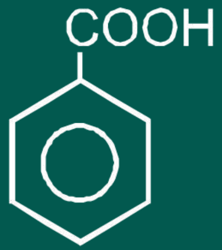
Ans. b > c > d > a

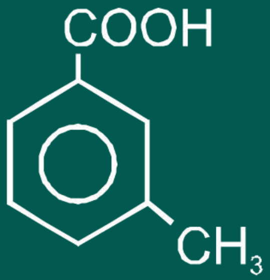
Ortho effect :

Generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself.

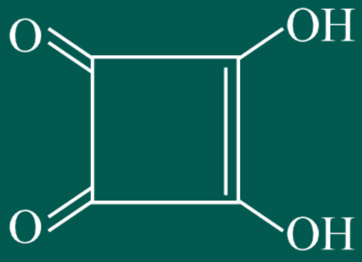
Ex.



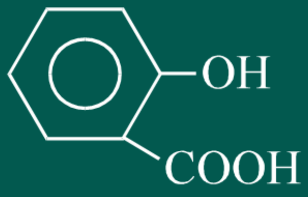




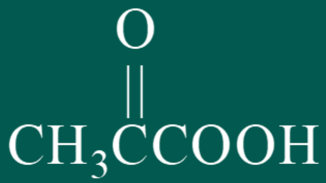
Q.12 Consider the following compound



I



II



$CH_3\overset{\overset{O}{\|}}{C}COOH$

III

Which of the above compounds reacts with $NaHCO_3$ giving CO_2

(A) I, II and III

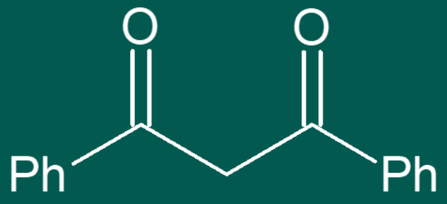
(B) I and III

(C) II and III

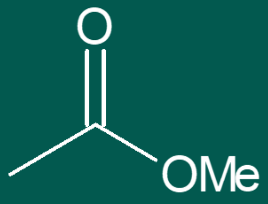
(D) I and II

Q.13 The increasing order of the acidity of the α-hydrogen of the following compounds is :

(A)



(B)



(C)

(D)

Ans. (D) < (C) < (A) < (B)

Basic Strength (K_b) :

Base : An e^- pair donor (generally to $H^\oplus$)
Basic strength ↑, K_b ↑, pK_b ↓, pK_a ↑

$$K_b \propto \text{Stability of Conjugate Acid}$$

$$\propto \frac{1}{\text{E.N. of donor atom(in same period)}}$$

$$\propto \frac{1}{\text{Size of donor atom (in same group)}}$$

$$\propto \frac{1}{\text{delocalisation/aromaticity/}p\pi-d\pi}$$

$$\propto +M/+I \text{ effects}$$

$$\propto \frac{1}{-M/-I \text{ effects}}$$

$$\propto \frac{1}{\text{ortho effect in aniline}}$$

Q.14 Which is least basic :

(A) $(CH_3CO)\ddot{N}HC_2H_5$

(B) $(C_2H_5)_3\ddot{N}$

(C) $(CH_3CO)_2\ddot{N}H$

(D) $(C_2H_5)_2\ddot{N}H$

Ans. (C)

Q.15 Decreasing order of K_b

(A) Phenyl methanamine or $ph{-}CH_2{-}NH_2$
(B) N,N-Dimethylaniline or $ph{-}N(Me)_2$
(C) N-Methyl aniline or $ph{-}NH{-}CH_3$
(D) Benzenamine or $ph{-}NH_2$

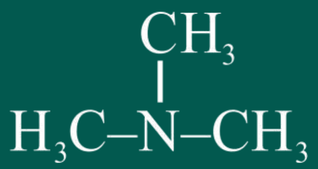
Ans. K_b order : $A > B > C > D$

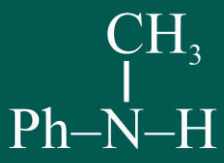
Q.16 Increasing K_b order is :

(A) $CH_3CH_2NH_2$

(B)

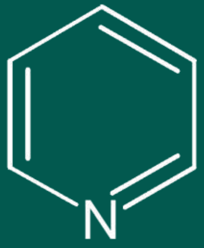
$CH_3CH_2\overset{CH_2CH_3}{\overset{|}{N}}H$

(C)

$H_3C-\overset{CH_3}{\overset{|}{N}}-CH_3$

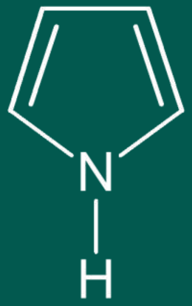
(D)

$Ph-\overset{CH_3}{\overset{|}{N}}-H$

Ans. (D) < (C) < (A) < (B)

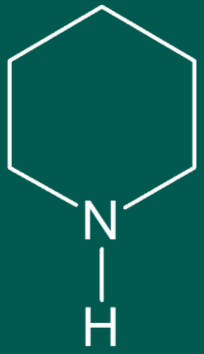
Q.17 Decreasing order of K_b :



I



II

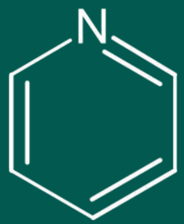


III

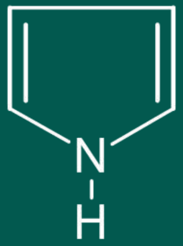
Ans. III > I > II

Q.18 Decreasing order of K_b is :


(I)


(II)


(III)

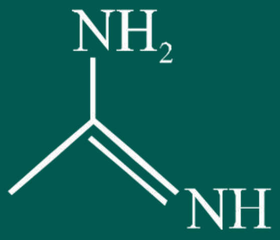

(IV)

Ans. (III) > (II) > (I) > (IV)

Q.19 Increasing order of K_b is :

(a)

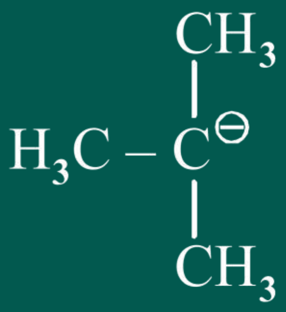

(b)


(c)


(d)


Ans. (b) < (a) < (d) < (c)

Q.20 Increasing order of K_b is :

(i) 

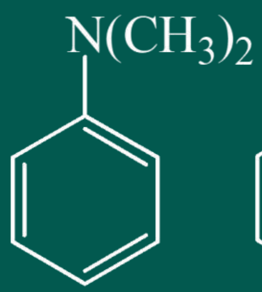
$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^{\ominus}}}}}$$

(ii) $H_2C=CH-\overset{\ominus}{C}H_2$ (iii) $HC\equiv\overset{\ominus}{C}$ (iv) $\overset{\ominus}{C}H_3$ (v) $\overset{\ominus}{C}N$

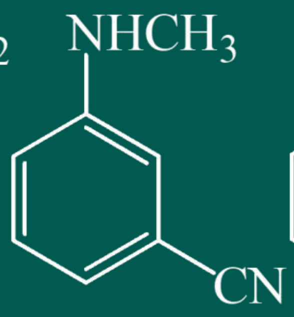
Ans. (v) < (iii) < (ii) < (iv) < (i)

Q.21 Increasing pK_b order is :

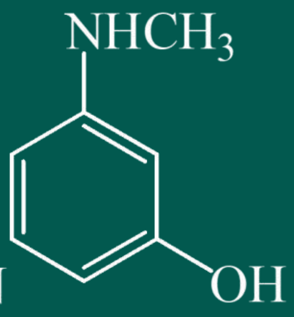
I



II



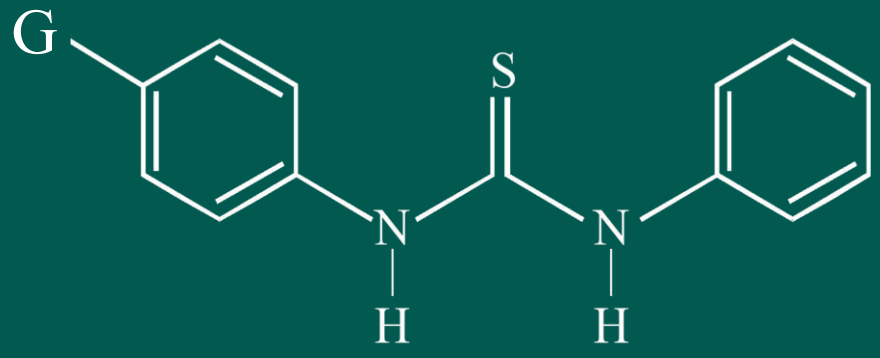
III



IV

Ans. I < II < IV < III

Q.22 Increasing order of the pK_b :



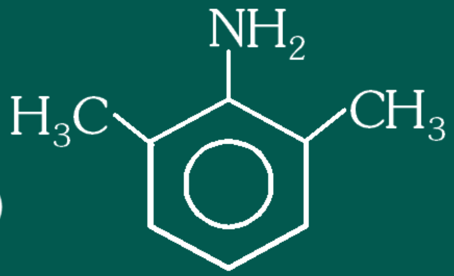
(A) G = –F (B) G = $-OCH_3$

(C) G = $-NO_2$ (D) G = $-CH_3$

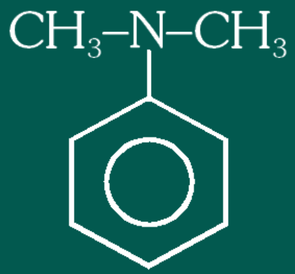
Ans. (B) < (D) < (A) < (C)

Q.23 Arrange the following in the decreasing order of basicity :

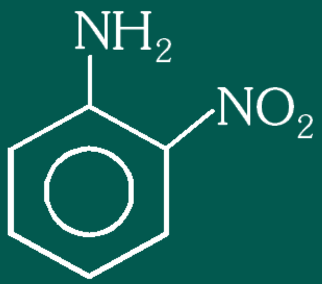
(I)



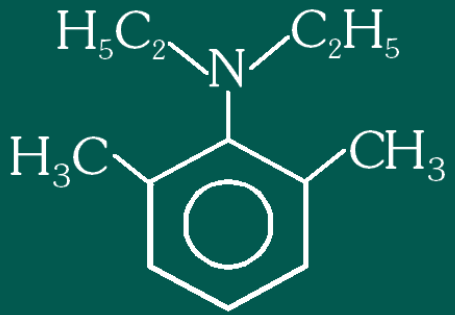
(II)



(III)

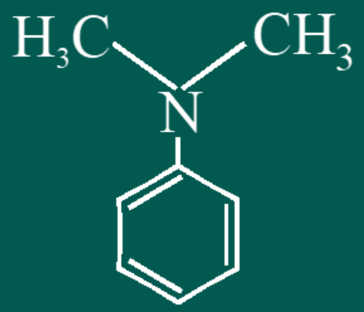


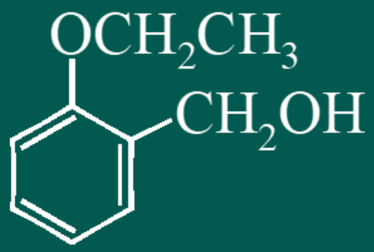
(IV)

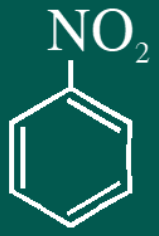


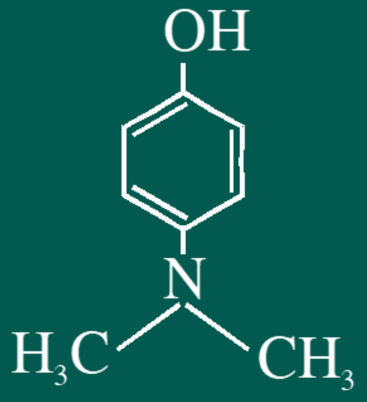
Ans. IV > II > I > III

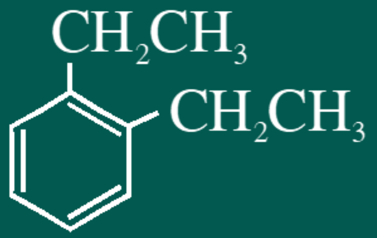
Q.24 Amongst the following, the total number of compounds soluble in aqueous NaOH is:

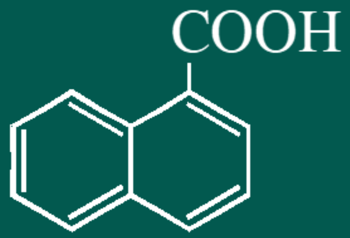










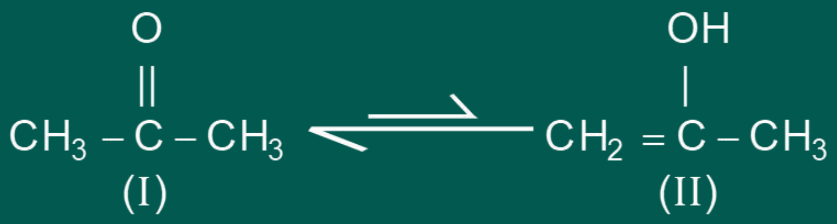


Ans. 4

TAUTOMERISM

Keto-enol tautomerisation

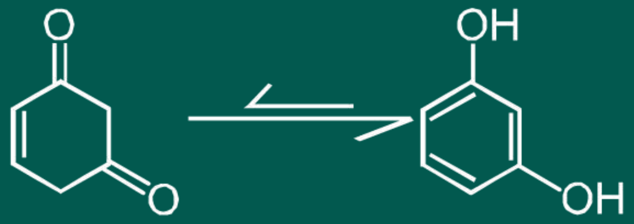
(i)



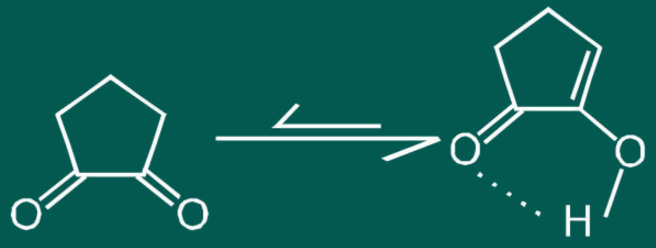
$$\underset{(I)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \rightleftharpoons \underset{(II)}{CH_2=\overset{\overset{OH}{|}}{C}-CH_3}$$

(ii)

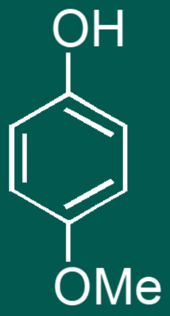
(iii)



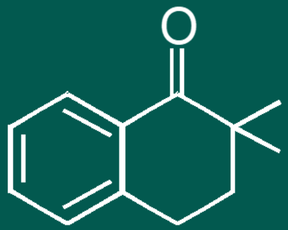
(iv)



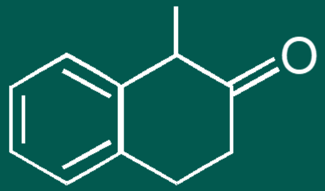
Q.25 The molecules that can exhibit tautomerism are



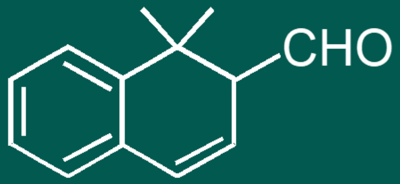
(I)



(II)



(III)

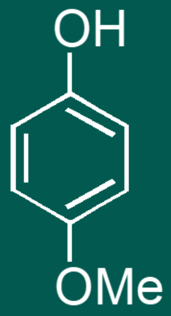


(IV)

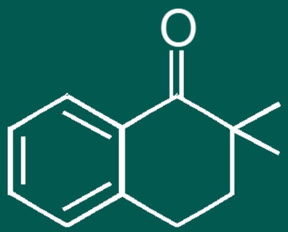
(A) I, IV (B) II, III (C) III, IV (D) I, II

Ans. (C)

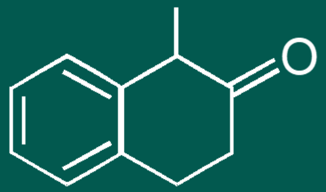
Q.26 The molecules that can exhibit tautomerism are



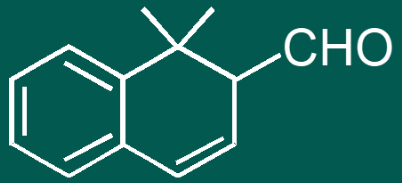
(I)



(II)



(III)

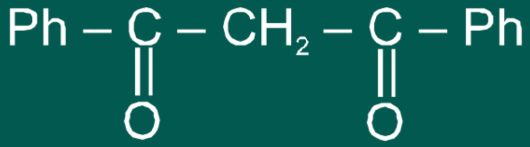
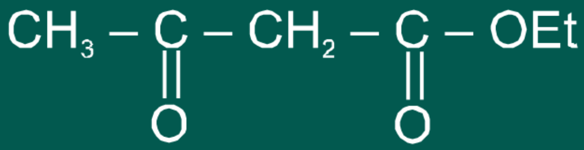
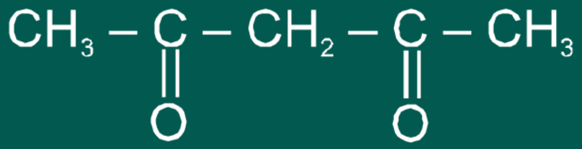


(IV)

(A) I, IV (B) II, III (C) III, IV (D) I, II

Ans. (C)

Q.27 Match the column :

Column-I (Keto)	**Column-II (% enol)**
(A) $CH_3-CH=O$	(x) 95 %
(B)  $Ph-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-Ph$	(y) 76 %
(C)  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt$	(z) 0.0001 %
(D)  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$	(w) 7.2 %

Ans. (A - z) ; (B - x) ; (C - w) ; (D - y)

HYDROCARBONS

ALKANES

Chemical reactions of alkanes: Characterstic reaction of alkanes are free radical substitution reaction.

Halogenation of alkanes

$$CH_4 + Cl_2 \xrightarrow{\text{UV Light or temp}} CH_3Cl + HCl$$

Free radical reaction take place in three steps

(i) Chain initiation → It is an endothermic step.

$$Cl—Cl \xrightarrow{\text{UV or temp.}} 2\dot{Cl}$$

(ii) Chain propagation step →

Step (a) $\dot{Cl} + CH_3\text{–}H \xrightarrow{\text{rds}} \dot{C}H_3 + HCl$

Step (b) $CH_3 + \cdot Cl\text{–}Cl \longrightarrow CH_3\text{–}Cl + \dot{Cl}$

(iii) Chain termination → It is always exothermic.

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$

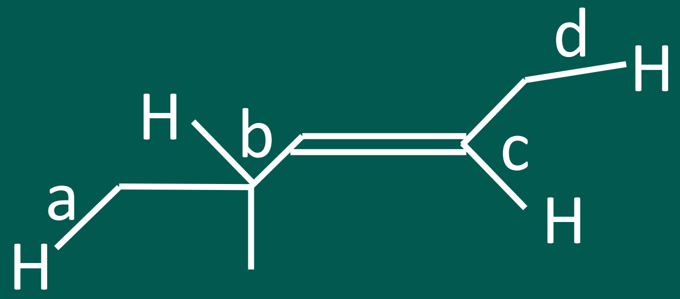
$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

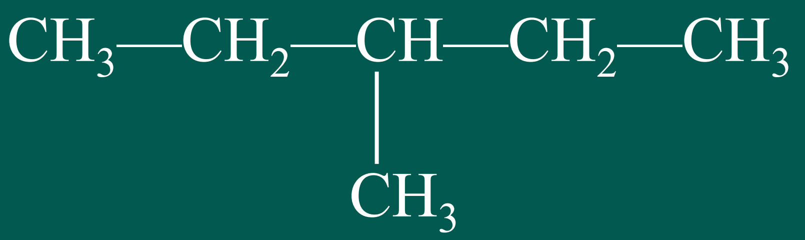
$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3 - Cl$$

Note :

Rate of halogenation $\propto$ stability of alkyl free radical

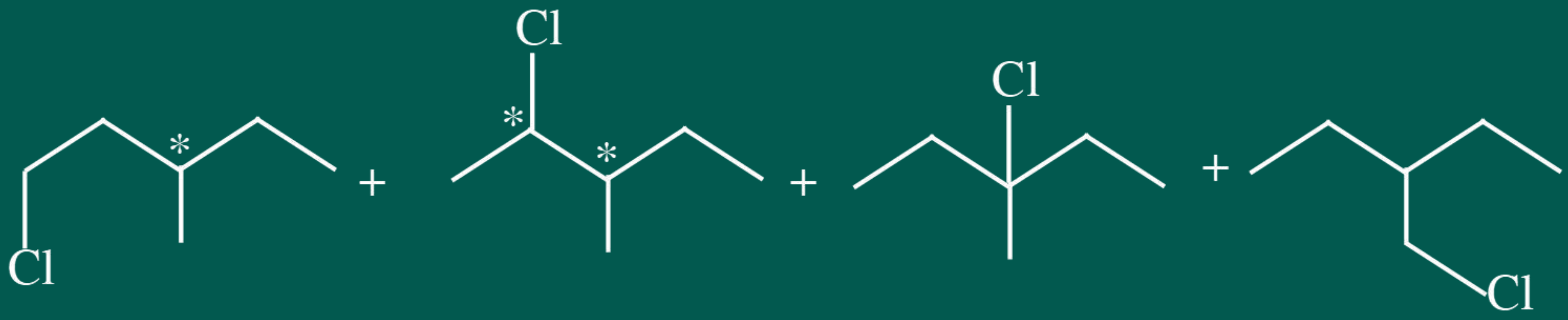
Q.1 Rate of reaction with Cl_2 / hν in following compound is



Q.2 

$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow{Cl_2/h\nu}$ Number of Monochloro Products

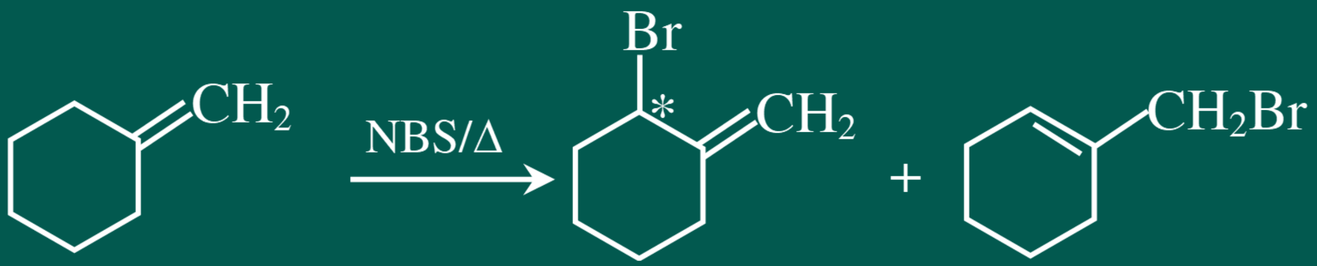
Sol.



Note-1 : NBS (N-Bromosuccinimide) will selectively brominate at allylic and benzylic hydrogen

Q.3 Methylenecyclohexane $\xrightarrow{\text{NBS}/\Delta}$ Total number of products :

Sol.



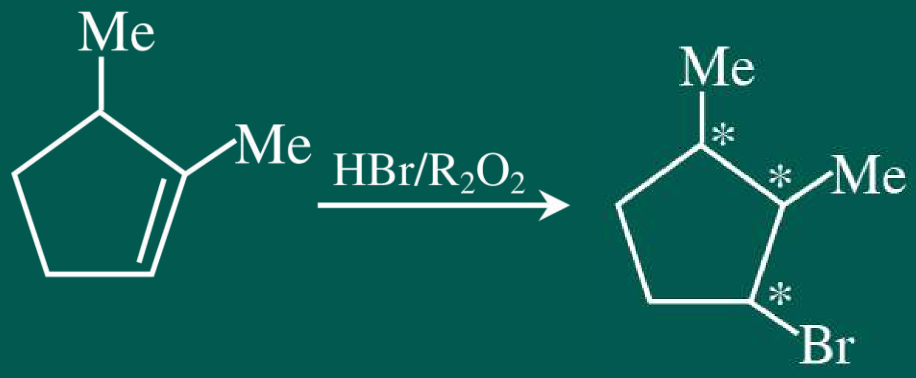
Note-2 : Free radical addition reactions (Kharash effect) :

Addition of only HBr in the presence of peroxide will be by AntiMarkovnikove's rule

Example : $CH_3CH{=}CH_2 \xrightarrow{HBr+R_2O_2}$

Q.4 How many products are formed when 1,5-dimethylcyclopentene react with HBr in presence of peroxide ?

Sol.



Chemical Reactions of Alkenes and Alkynes

- Characteristics reactions are electrophilic addition reactions.
- Intermediate carbocation will form in the RDS.
- So, Rate of reaction $\propto$ stability of intermediate carbocation.
- Hence + M, Reso, HC, + I groups increases rate of reaction.
- So, called **activators**
- –M & –I groups, called **deactivators**

Q.5 Rate of electrophilic addition reaction in following compound

$CH_3-O-CH=CH_2$ (I)

$CH_2=CH-CN$ (II)

$CH_2=CH_2$ (III)

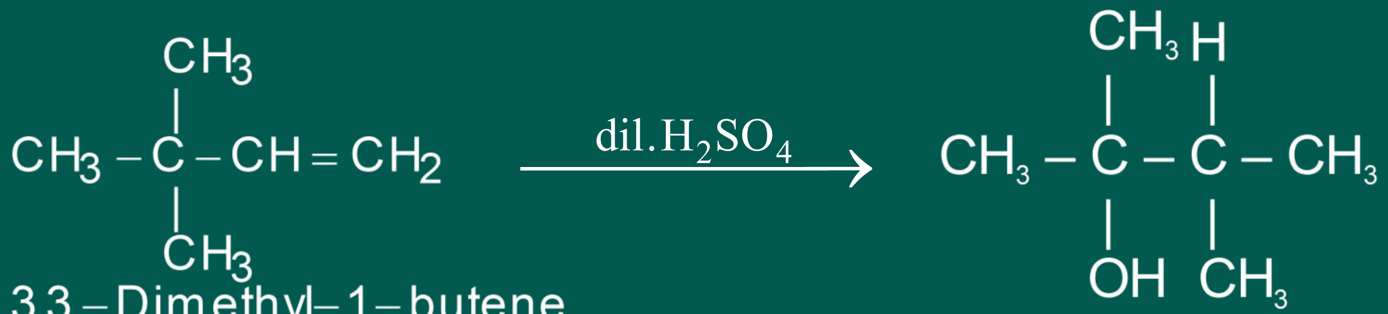
Reagents (A) Electrophile without lone pairs containing species

(A) (i) HX

(ii) dil. H_2SO_4

(iii) ROH/dry HCl

Example :



$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CH_3-C-CH=CH_2}\\ |\\ \mathrm{CH_3}\end{array} \xrightarrow{\text{dil.}H_2SO_4} \begin{array}{c}\mathrm{CH_3\ \ H}\\ |\qquad |\\ \mathrm{CH_3-C-C-CH_3}\\ |\qquad |\\ \mathrm{OH\ \ CH_3}\end{array}$$

3,3 – Dimethyl – 1 – butene

2, 3-Dimethyl-2-butanol
(major product)

Reagents (B) Electrophile having lone pair containing species :

(B) (i) $Cl_2/Br_2 + CCl_4$

(ii) $Cl_2/Br_2 + H_2O/C_2H_5OH$

(iii) IBr/BrCl

(iv) NOCl

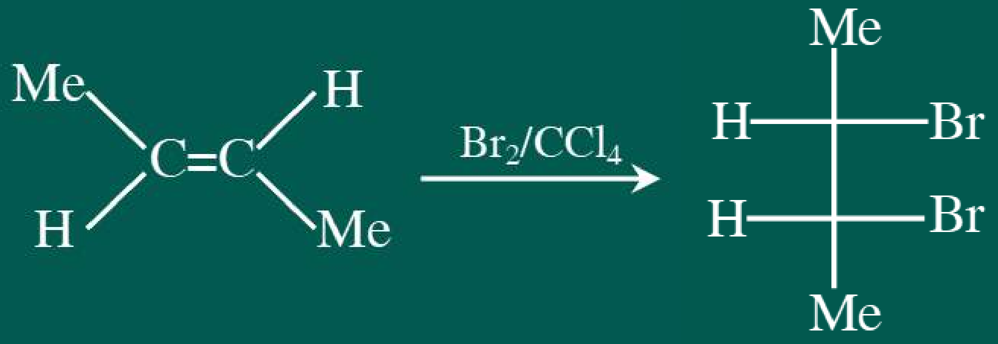
- Stereochemistry – anti addition

Examples :

Racemic trans-1,2-dichlorocyclohexane

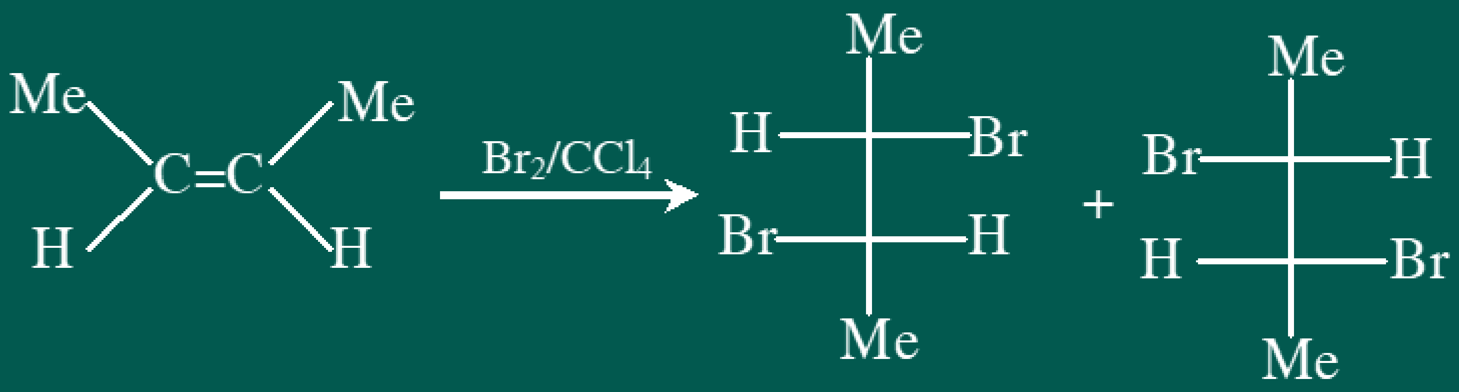
Q.6 What will happen when Br_2/CCl_4 react with
(a) trans But-2-ene. (b) cis But-2-ene

Sol. **(a)**



Meso

(b)



Racemic mixture

Reagents (C) : Hydration

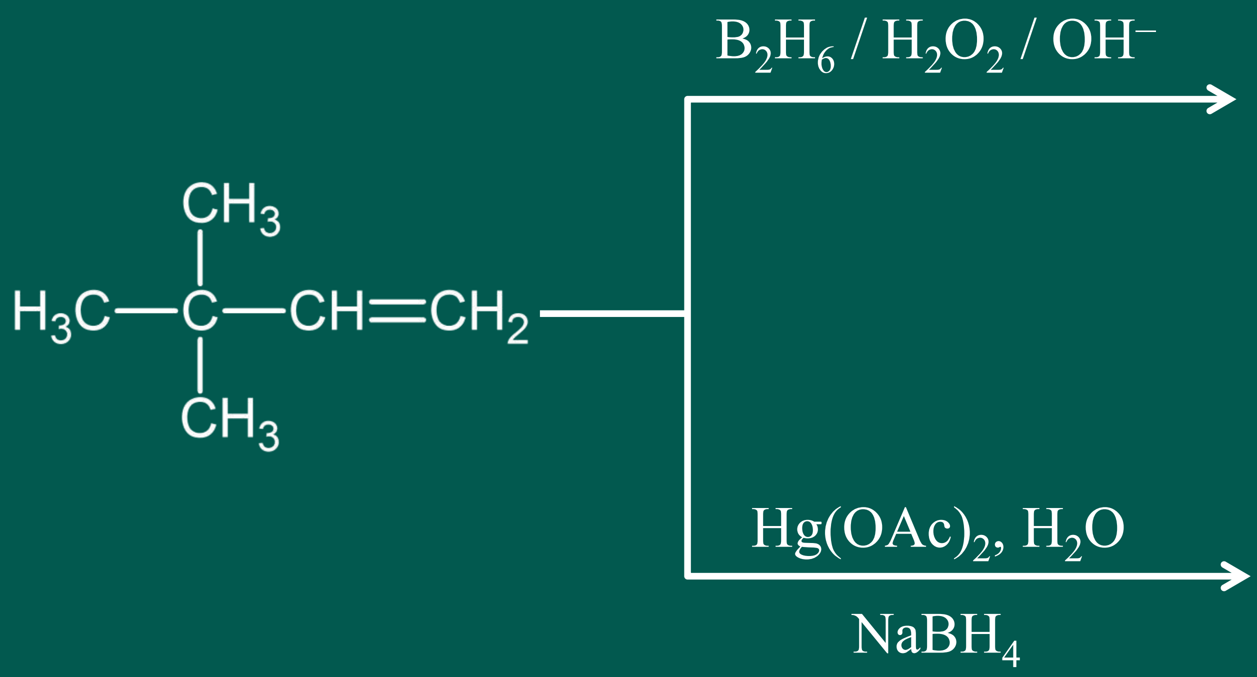
(C) (i) $Hg(AcO)_2 + H_2O + NaBH_4$

Note : It is overall addition of water molecule according to markovnikov's rule.

(ii) $B_2H_6 + H_2O_2 + OH^-$

Note : It is overall addition of water molecule according to anti-markovnikov's rule.

Example



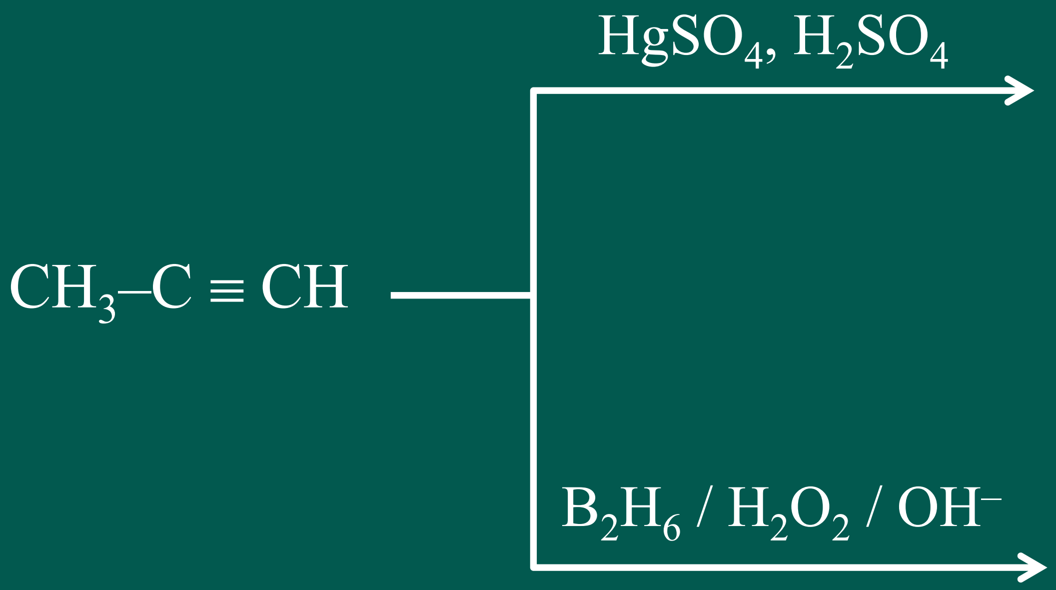
$$(CH_3)_3C{-}CH{=}CH_2$$

B_2H_6 / H_2O_2 / OH^-

$Hg(OAc)_2$, H_2O

$NaBH_4$

Q.7

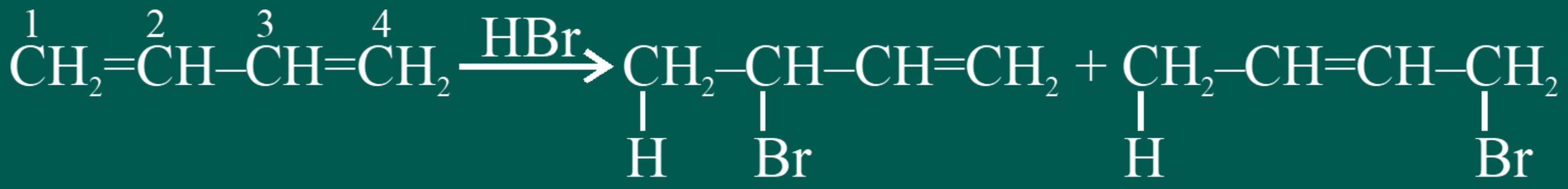


$CH_3-C\equiv CH$

$\xrightarrow{HgSO_4,\ H_2SO_4}$

$\xrightarrow{B_2H_6\ /\ H_2O_2\ /\ OH^-}$

Conjugated addition in dienes



$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2 \xrightarrow{HBr} \underset{H}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH=CH_2 + \underset{H}{\underset{|}{CH_2}}-CH=CH-\underset{Br}{\underset{|}{CH_2}}$$

(1, 2 Product)
Major at –80°C
KCP

(1, 4 Product)
Major at 40°C
TCP

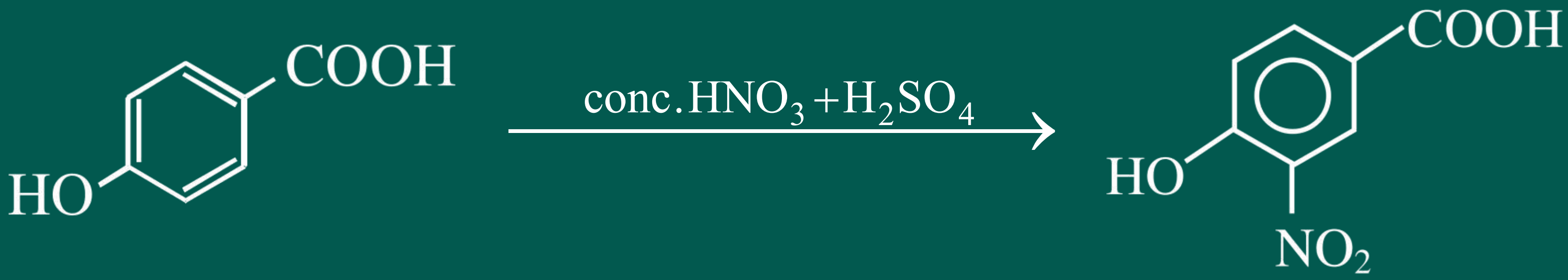
AROMATIC HYDROCARBON

Characteristic reaction of aromatic ring is electrophilic substitution reaction :

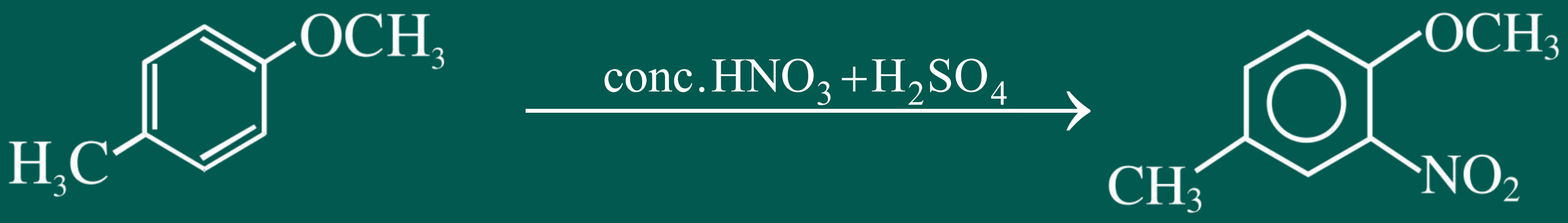
General reaction :

Q.8 Identify major product of following reaction :

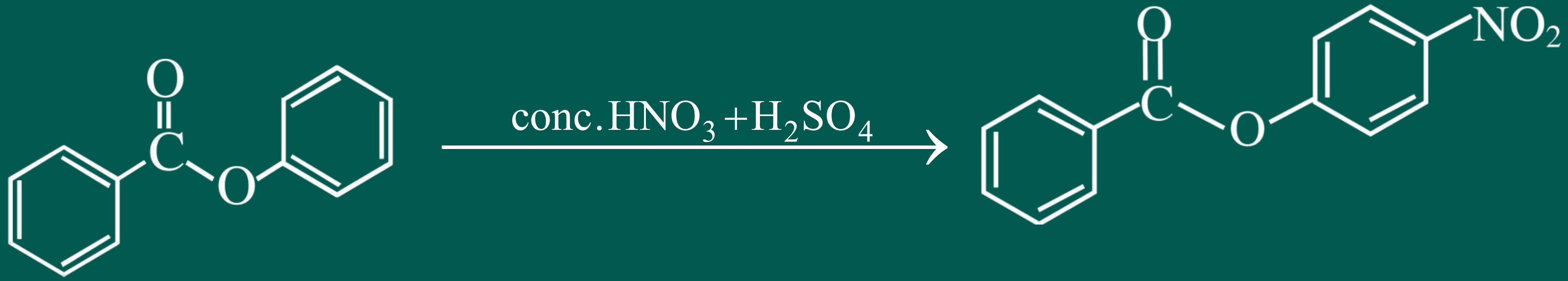
(i)



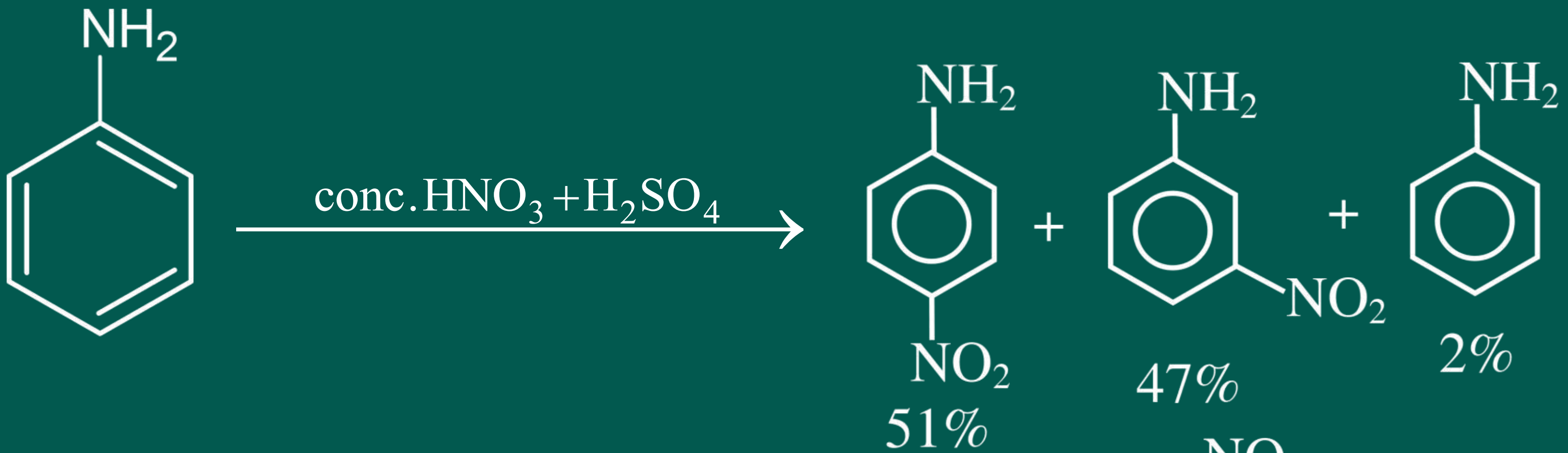
(ii)



(iii)

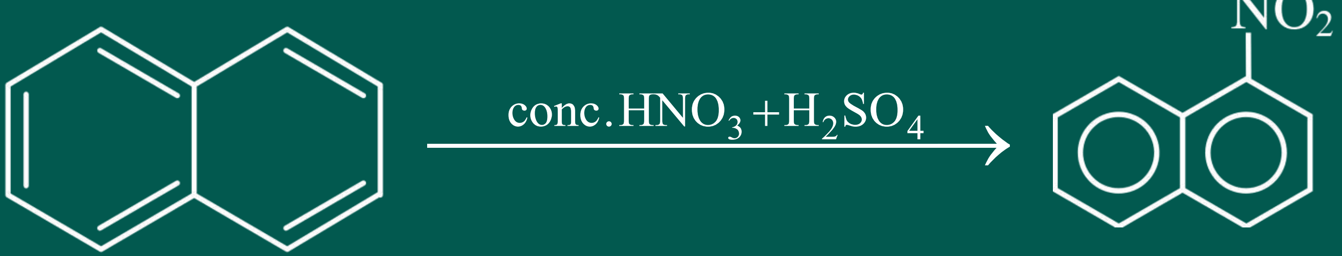


(iv)



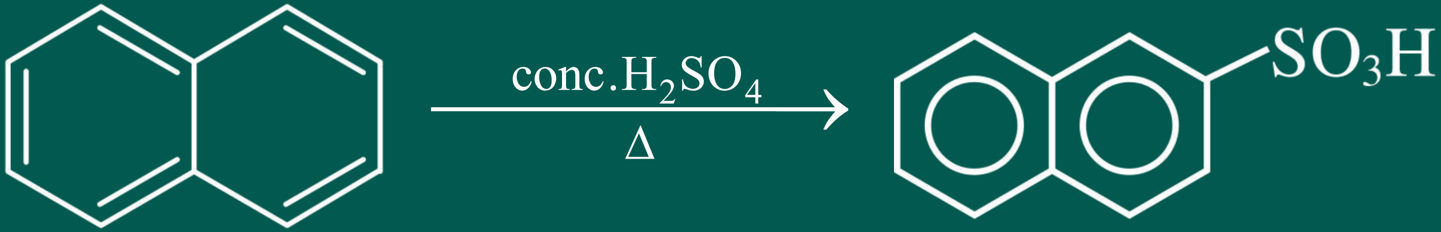
NH_2
conc.HNO_3 + H_2SO_4
NH_2
NO_2
51%
+
NH_2
NO_2
47%
+
NH_2
2%

(v)



conc.HNO_3 + H_2SO_4
NO_2

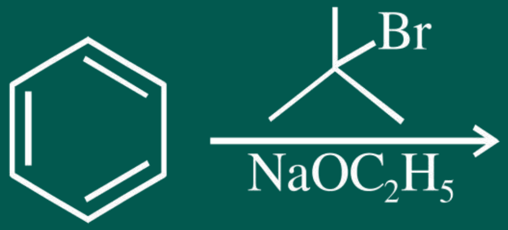
(vi)



conc.H_2SO_4
Δ
SO_3H

Q.9 Among the following reaction(s) which give(s) tert-butyl benzene as the major product is(are)

(A)

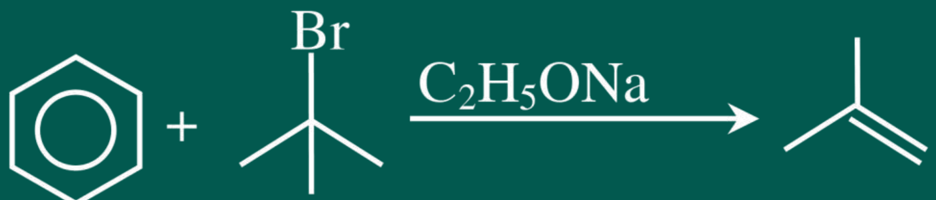


(B)

(C)

(D)

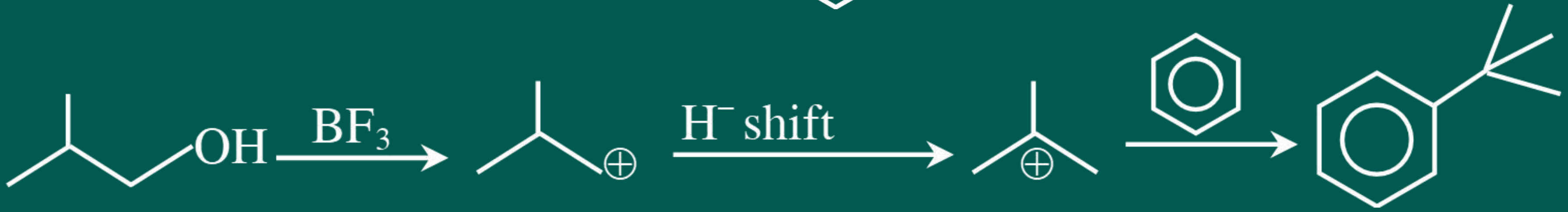
Sol. **(A)**



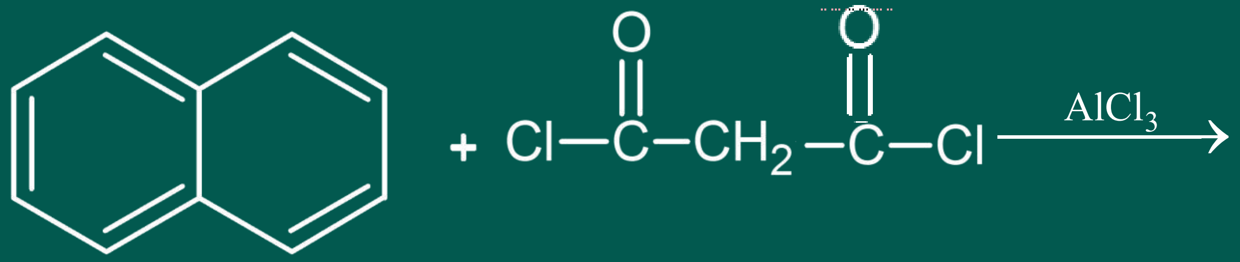
(B)

(C)

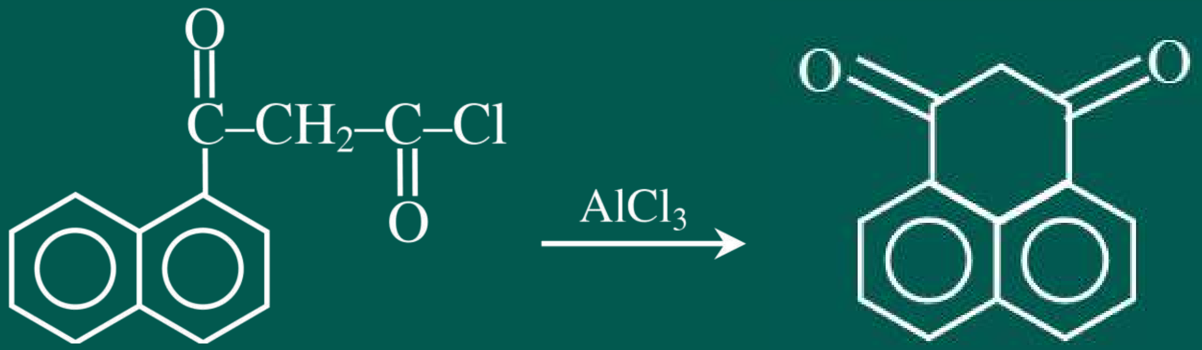
(D)



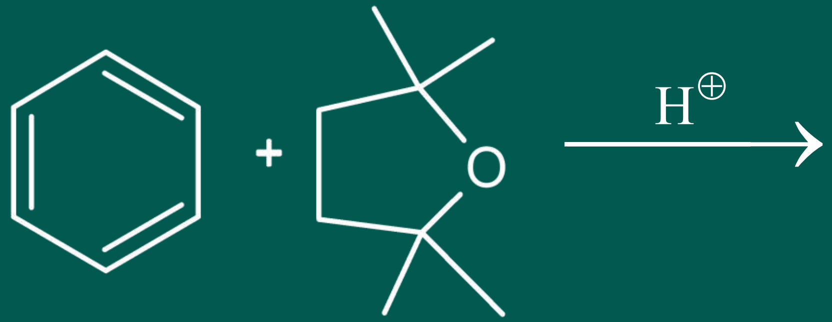
Q.10



Sol.

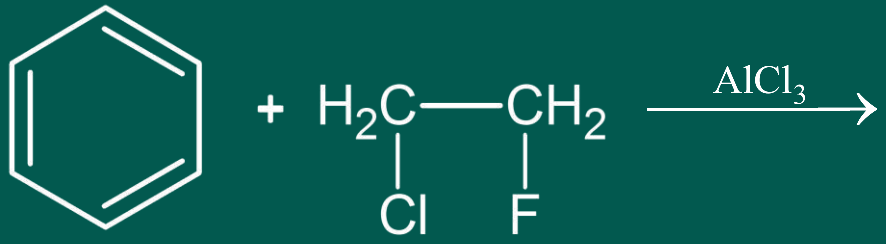


Q.11

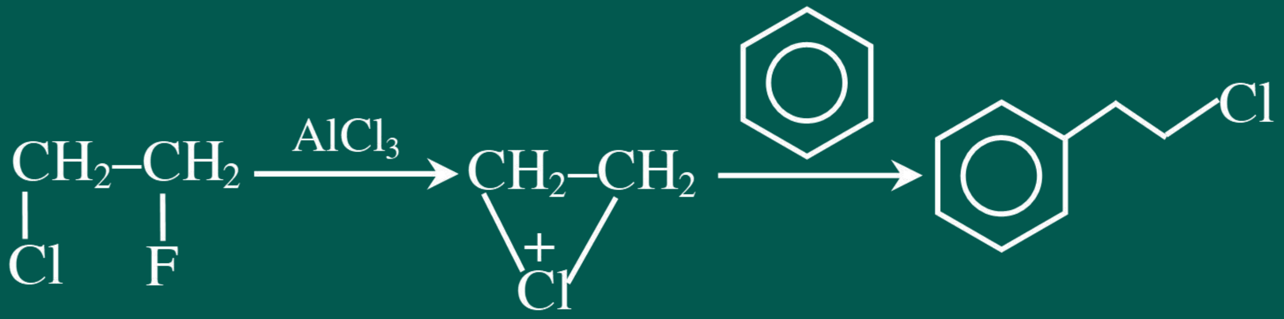


Sol.

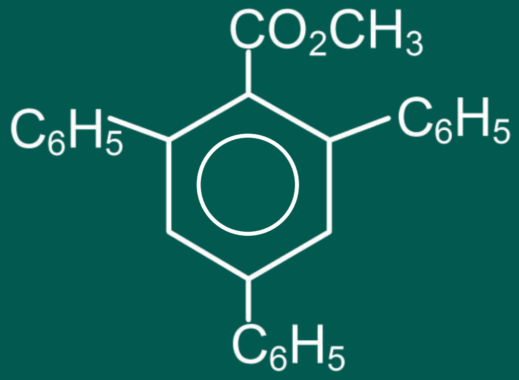
Q.12



Sol.



Q.13

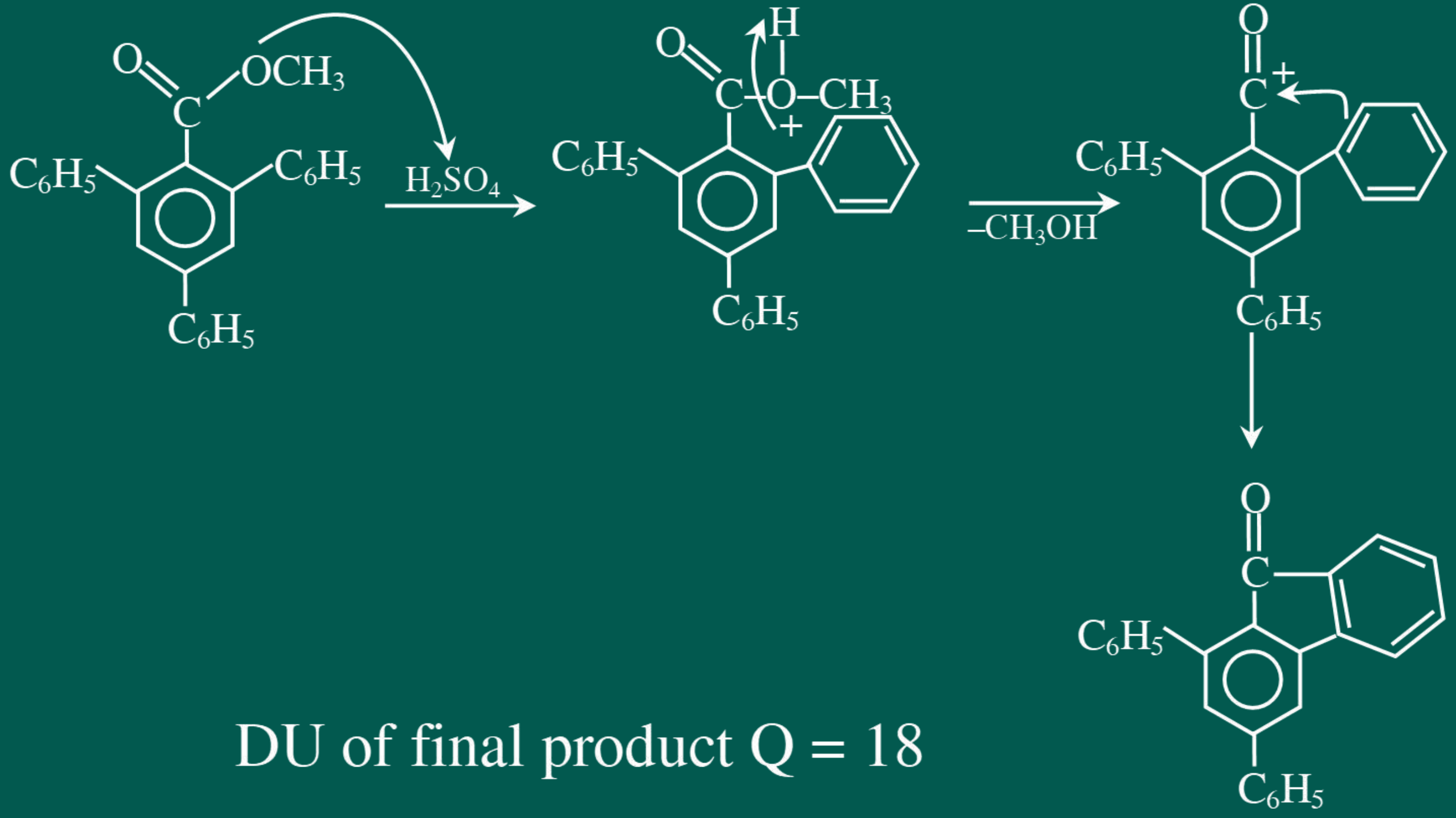


P

$\xrightarrow{\text{conc. } H_2SO_4}$ Q (A colored compound)

What is the degree of unsaturation of Q ?

Sol.



1,3-diphenylfluorenone

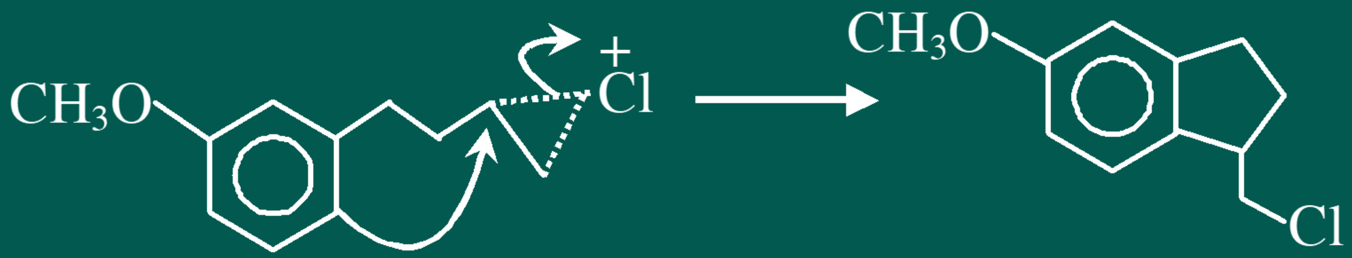
(Brilliant colour)

DU of final product Q = 18

Q.14 The major product of the following reaction is :-

$\xrightarrow[\text{(2) AlCl}_3\text{(anhyd.)}]{\text{(1) Cl}_2/\text{CCl}_4}$

Sol.



REACTION MECHANISM

1. (Haloalkanes & Haloarenes)

Reagents and solvents

(a) Strong nucleophile and strong base :

$RMgX$, $RC\equiv C^-$, NH_2^-, HO^-,

MeO^-, EtO^-, Alc.KOH

(b) Strong nucleophile but weak base :

RS^-, HS^-, PhS^-, CN^-,

I^-, Br^-, Cl^-, PPh_3

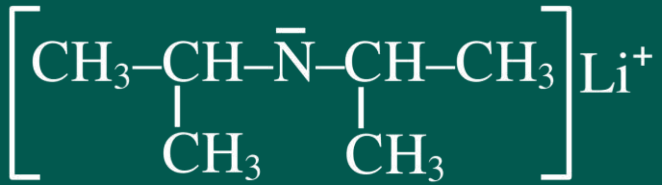
(c) Weak nucleophile and weak base :

H_2O, MeOH, EtOH, t-BuOH,

C_2H_5SH, HCOOH, CH_3COOH

(d) Weak nucleophile but strong base :

t-BuO^-, NEt_3, LDA



$$\left[CH_3-\underset{CH_3}{\underset{|}{CH}}-\bar{N}-\underset{CH_3}{\underset{|}{CH}}-CH_3\right]Li^+$$

Polar protic solvents (PPS) :

H_2O, ROH, RCOOH, NH_3, RNH_2

- PPS favours ionisation for S_N1 & E1 reactions.

Polar aprotic solvents (PAS) :

Acetone, ether, DMF, DMSO, DMA, CH_3CN

- PAS favours S_N2 reactions.

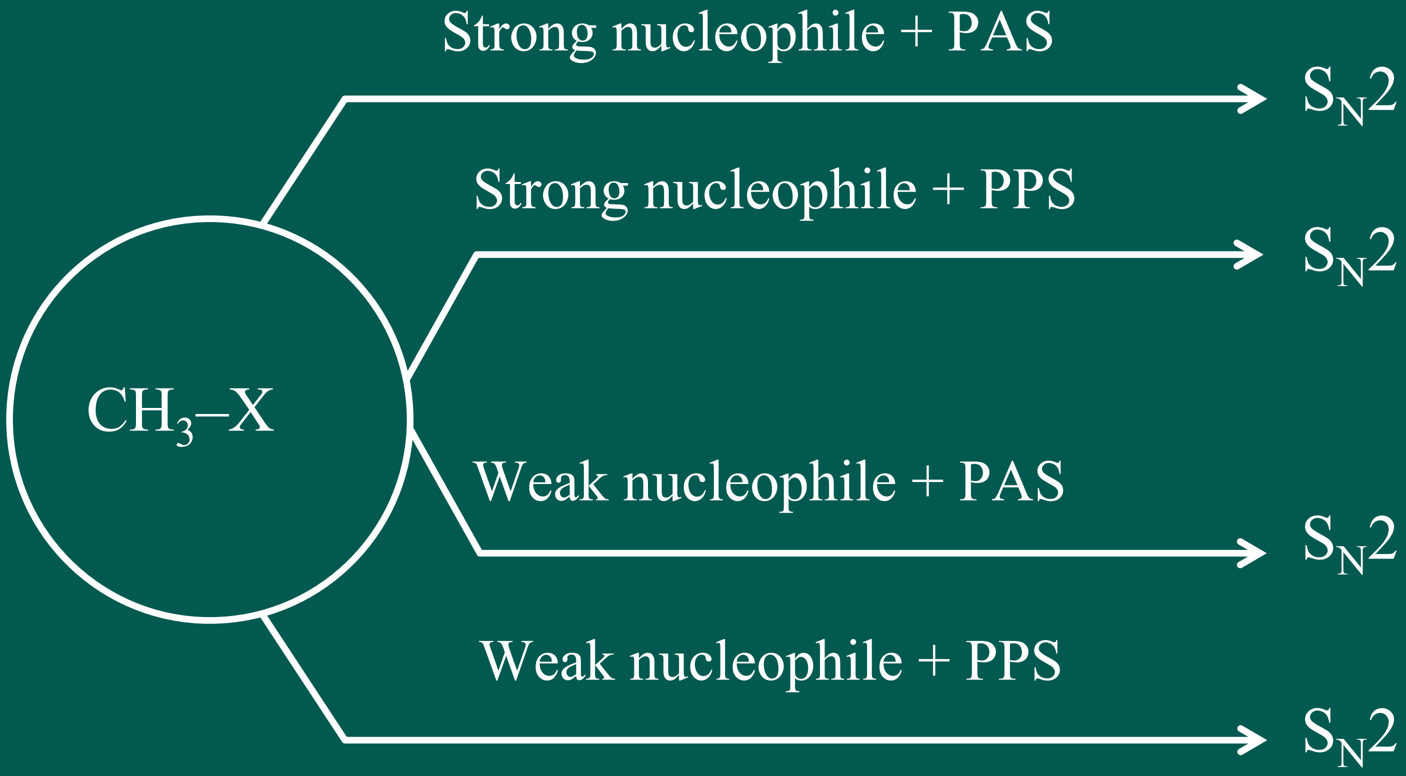
Nucleophilic substitutions of haloalkanes

	S_N1	S_N2
Promoting factors		
Nucleophile	Weak nucleophiles are OK	Strong nucleophile needed
Substrate (RX)	3° > 2°	CH_3X > 1° > 2°
Solvent	Good ionizing solvent needed	Wide variety of solvents
Leaving group	Good one required	Good one required
Other	$AgNO_3$ force ionization	
Characteristics		
Kinetics	First order, $k_r[RX]$	Second order, $k_r[RX][Nu:]$
Stereochemistry	Mixture of inversion & retention	Complete inversion
Rearrangements	Common	Impossible

Elimination reactions of haloalkanes

	E1	E2
Promoting factors		
Base	Weak bases work	Strong base required
Solvent	Good ionizing solvent	Wide variety of solvents
Substrate	3° > 2°	3° > 2° > 1°
Leaving group	Good one required	Good one required
Characteristics		
Kinetics	First order, $k_r[RX]$	Second order, $k_r[RX][B:^-]$
Orientation	Most substituted alkene	Most substituted alkene
Stereochemistry	No special geometry	Coplanar transition state required
Rearrangements	Common	Impossible

Favourable reactions of haloalkanes



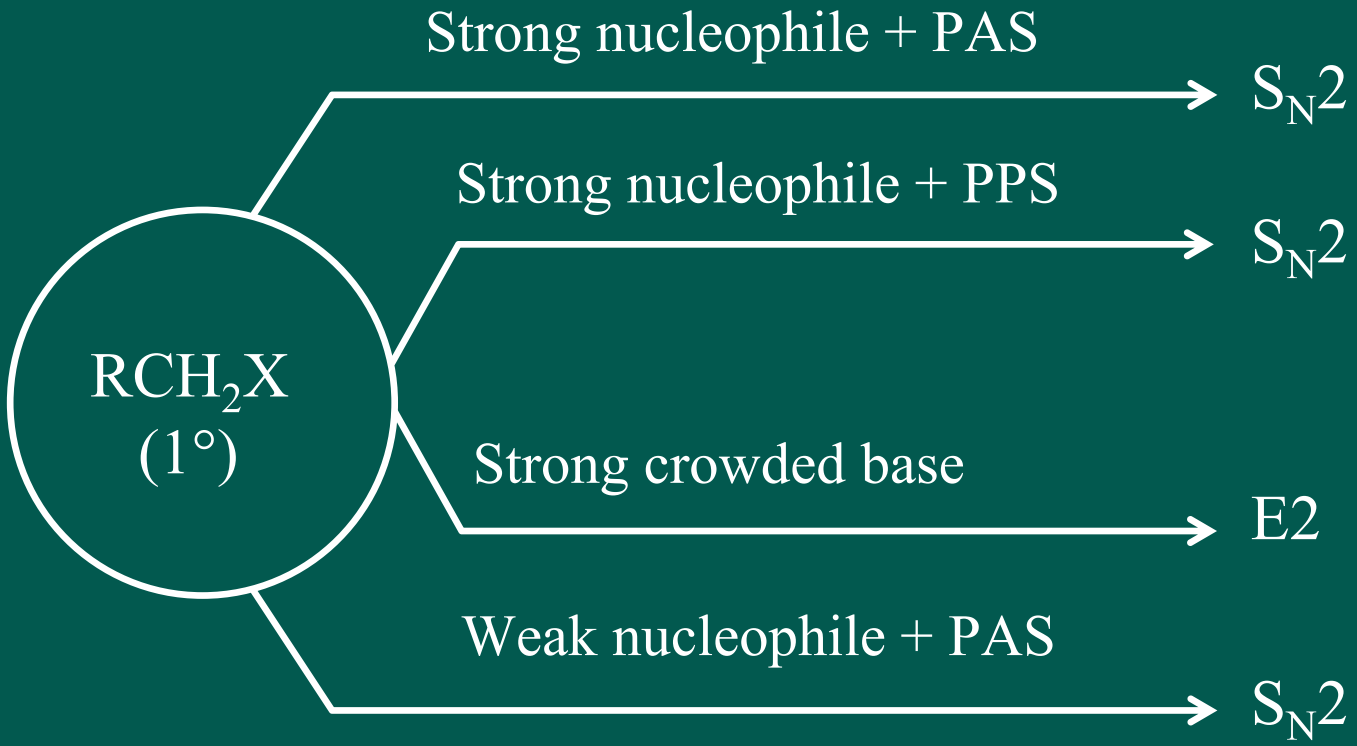
$CH_3–X$

Strong nucleophile + PAS → S_N2

Strong nucleophile + PPS → S_N2

Weak nucleophile + PAS → S_N2

Weak nucleophile + PPS → S_N2



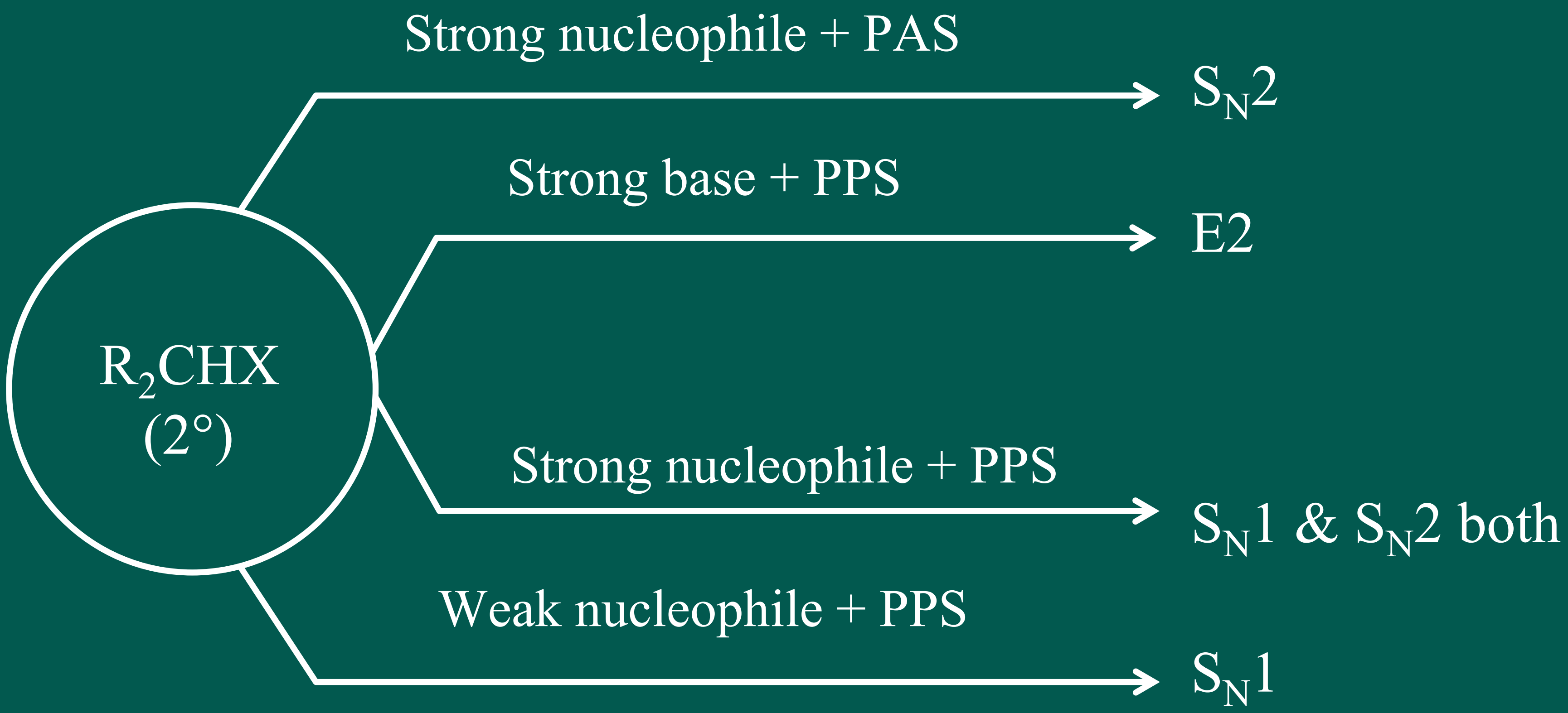
RCH$_2$X
(1°)

Strong nucleophile + PAS → S$_N$2

Strong nucleophile + PPS → S$_N$2

Strong crowded base → E2

Weak nucleophile + PAS → S$_N$2



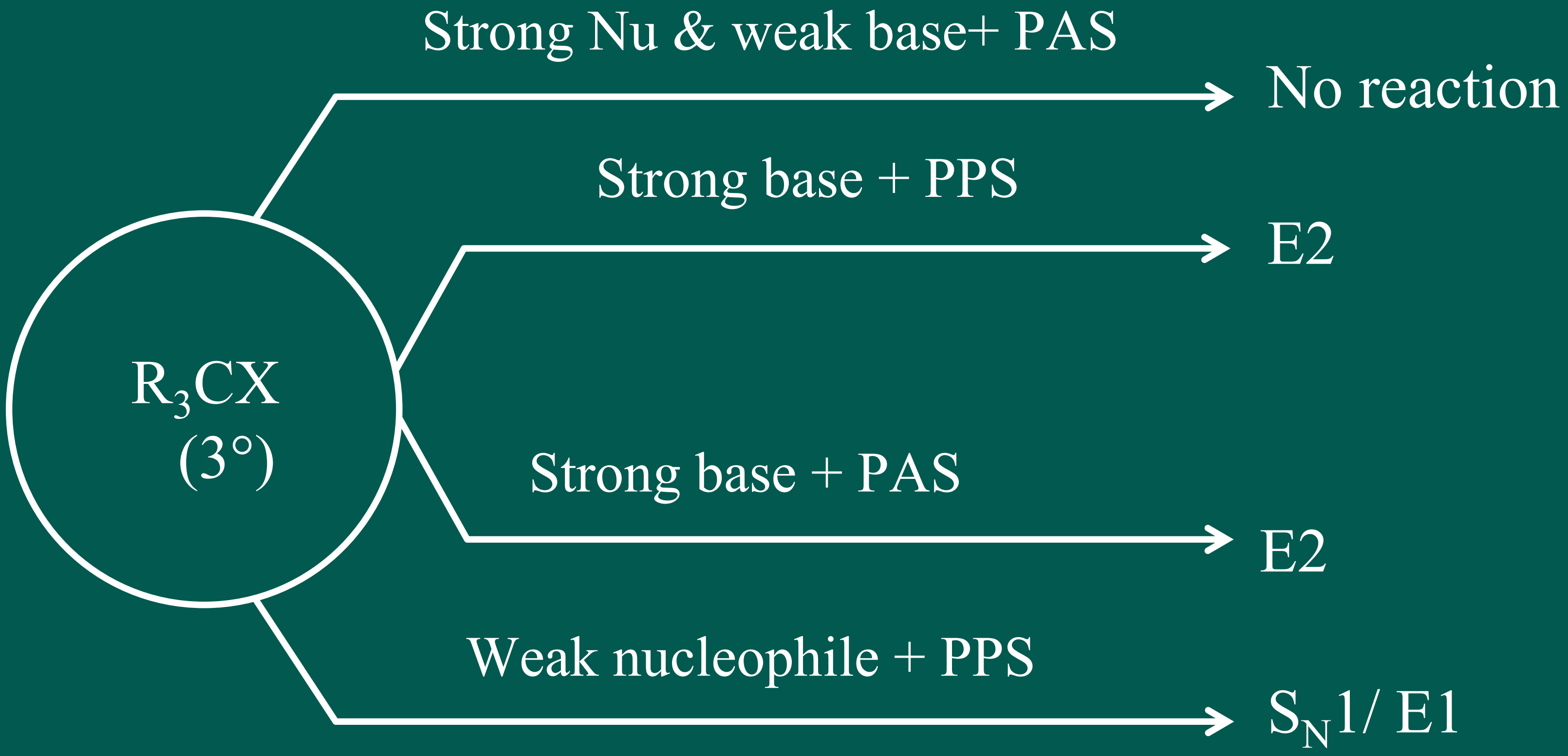
R_2CHX
(2°)

Strong nucleophile + PAS → S_N2

Strong base + PPS → E2

Strong nucleophile + PPS → S_N1 & S_N2 both

Weak nucleophile + PPS → S_N1



R_3CX

(3°)

Strong Nu & weak base+ PAS → No reaction

Strong base + PPS → E2

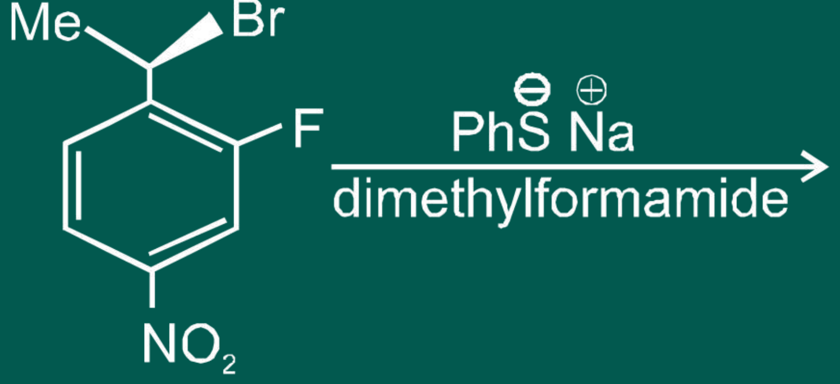
Strong base + PAS → E2

Weak nucleophile + PPS → S_N1/ E1

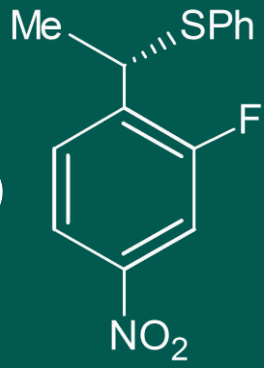
Reactivity : Haloalkane (R–X) > Haloarene (Ar–X)

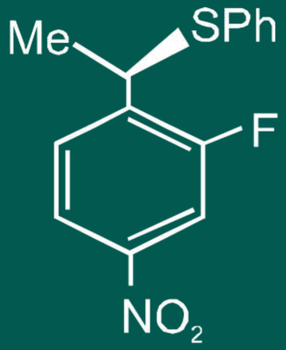
Haloarenes show aromatic nucleophilic substitution reaction (ArS_N2)

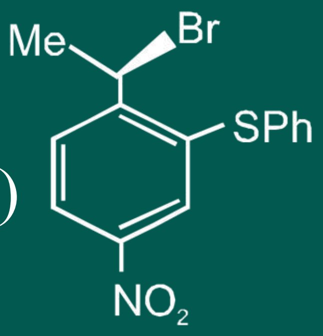
Q.1

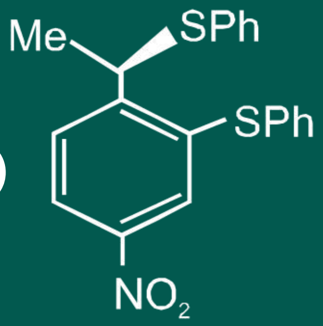


Major product

(A)


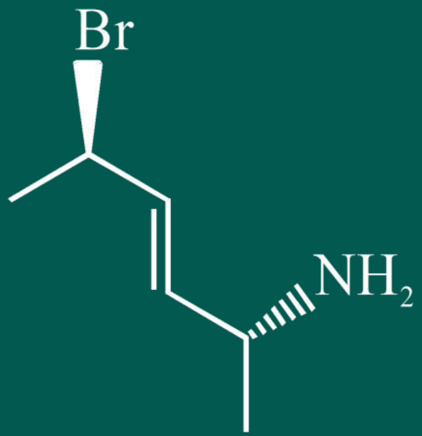
(B)


(C)


(D)


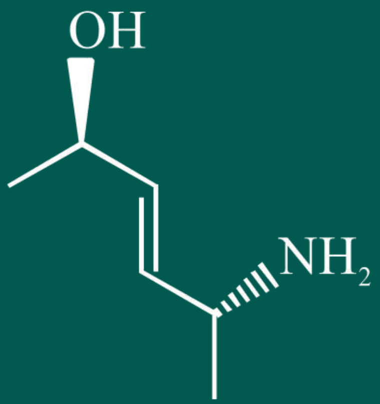
Ans. (A)

Q.2

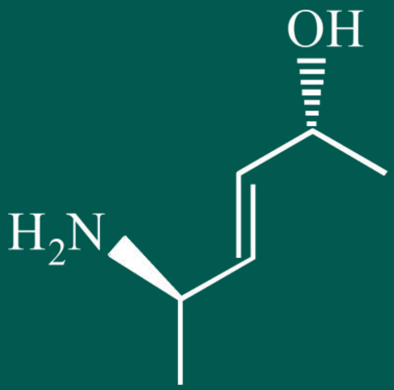


$\xrightarrow[S_N2]{KOH}$ Major product is :

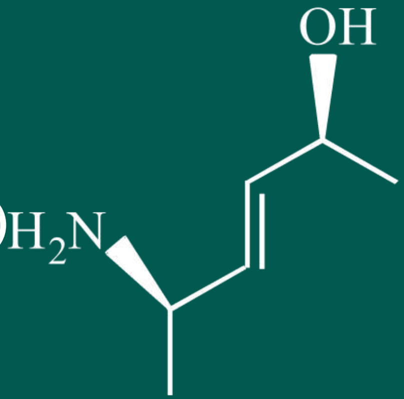
(A)



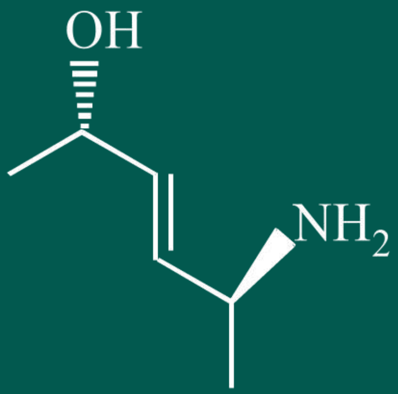
(B)



(C)



(D)



Ans. (C)

Q.3 R-Br (Y) + Alkyne(Z) $\xrightarrow{NaNH_2}$ 2–nbsxmd ($CH_3CH_2C{\equiv}CCH_2CH_2CH_2CH_3$)

(A) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

(B) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C{\equiv}CH$

(C) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C{\equiv}CH$

(D) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

Sol.

$$CH_3{-}CH_2{-}C \equiv C{-}H \xrightarrow{NaNH_2} CH_3{-}CH_2{-}C \equiv C^{\ominus}$$

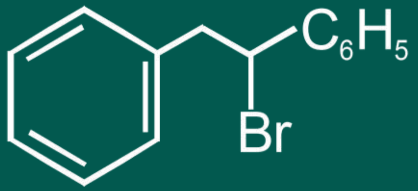
$$\xrightarrow{CH_3-CH_2-CH_2-CH_2-Br} CH_3CH_2C{\equiv}CCH_2CH_2CH_2CH_3$$

3–octyne

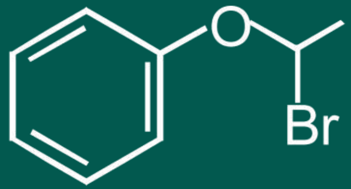
Ans. (D)

Q.4 Which of the following, upon treatment with tert-BuONa followed by addition of bromin water, fails to decolourize the colour of bromine?

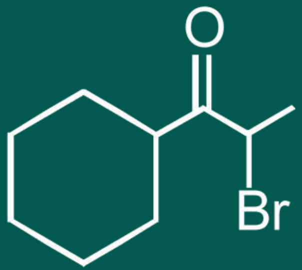
(A)



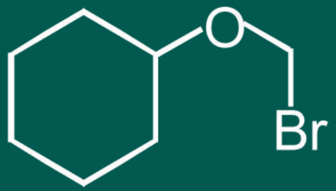
(B)



(C)



(D)



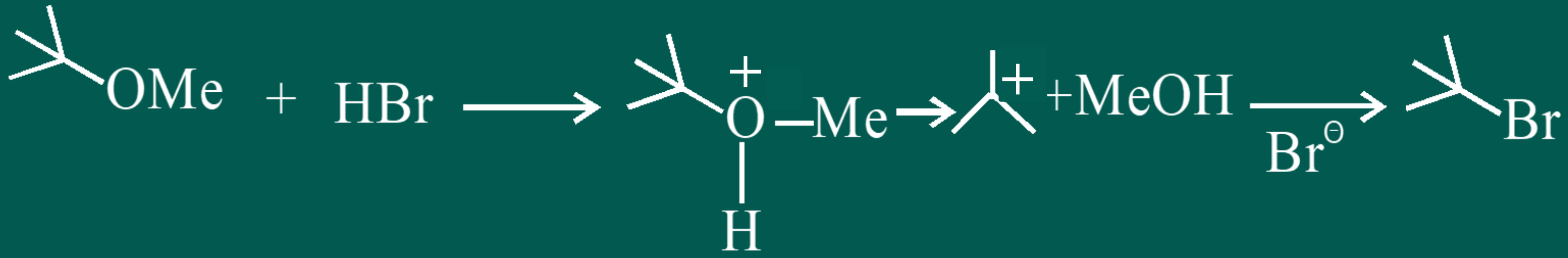
Q.5 LIST-I contains reactions and LIST-II contains major products.

LIST-I	**LIST-II**
(P) 	(1) 
(Q) 	(2) 
(R) 	(3) 
(S) 	(4) 
	(5) 

Sol. P.

(Elimination product)

Q.



R.

S.

Ans. P → 1,4; Q → 2; R → 4; S → 3

Finkelstein reaction

It is S_N2 reaction that involve exchange of one halogen atom

for another.

It is driven by differential solubility of halide salts.

$$\text{R–Br} + \text{NaI} \xrightarrow{\text{Acetone}} \text{R–I} + \text{NaBr}$$

NaBr & NaCl are insoluble in acetone but NaI is soluble.

Swarts reaction

Swarts reaction can be used for the complete replacement of Cl or Br with F.

It is quite important in the production of freons.

$$R\text{–}Br + AgF \xrightarrow{H_2O} R\text{–}F + AgBr$$

Reagents : AgF, CoF_2, SbF_3, Hg_2F_2

Wurtz reaction

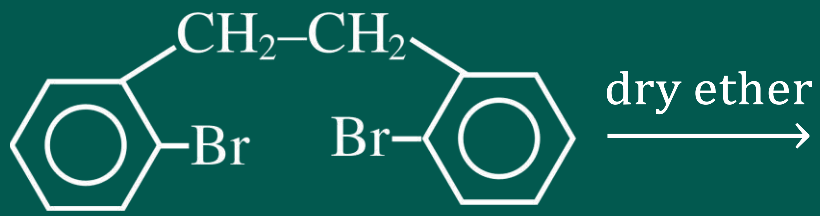
It is coupling reaction where two **alkyl** halides are reacted with sodium metal in dry ether to form a higher alkane.

$$2\text{R–Br} + 2\text{Na} \xrightarrow{\text{dry ether}} \text{R–R} + 2\text{NaBr}$$

Fittig reaction

It is coupling reaction where two **aryl** halides are reacted with sodium metal in dry ether to form a biphenyl derivative.

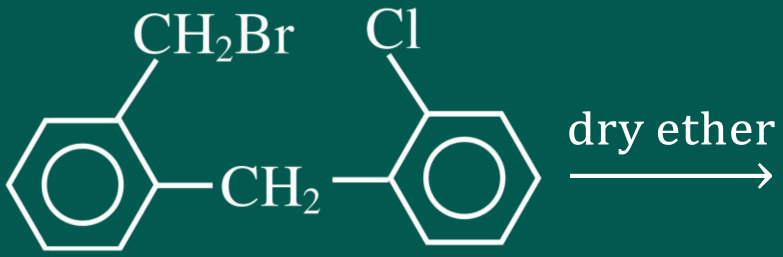
$$2\text{Ar–Br} + 2\text{Na} \xrightarrow{\text{dry ether}} \text{Ar–Ar} + 2\text{NaBr}$$



Wurtz-Fittig reaction

It is coupling reaction between **alkyl** halide and **aryl** halide in presence of sodium metal & dry ether to form an alkyl benzene derivative.

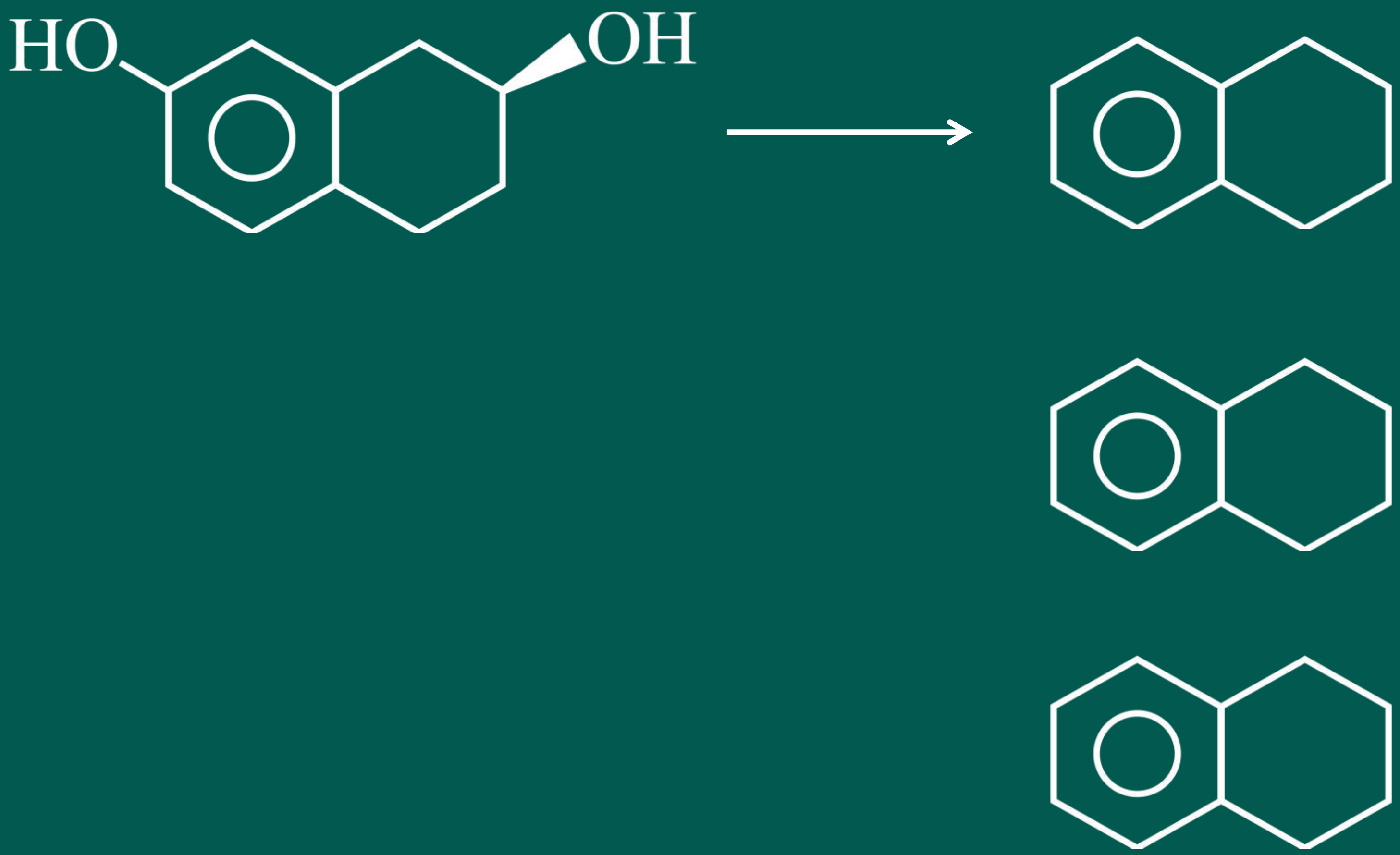
$$R{-}Br + 2Na + Br{-}Ar \xrightarrow{\text{dry ether}} R{-}Ar + 2NaBr$$



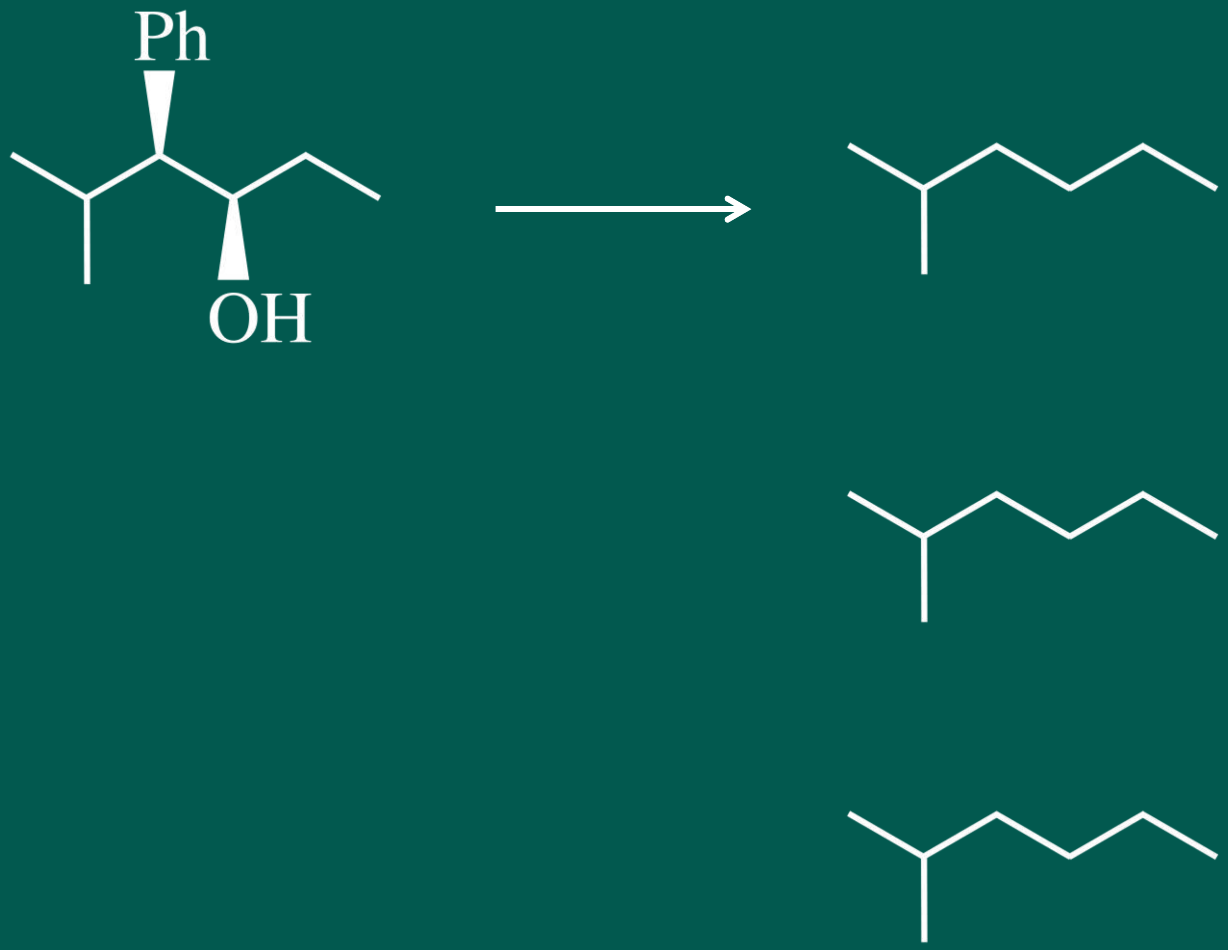
2. (Alcohols)

Mechanism		**Reagents**
S_N2	⟶	PCl_5 PX_3 (X = Cl, Br) $P + X_2$ (X = Cl, Br, I) $SOCl_2$ + Pyridine
S_N1	⟶	Conc. HX (HI > HBr > HCl) Lucas reagent (anhydrous $ZnCl_2$ + conc. HCl)
S_Ni	⟶	$SOCl_2$ in ether
E-1	⟶	conc. H_2SO_4, conc. H_3PO_4, H^+/ heat
Direct dehydration	⟶	Al_2O_3, P_2O_5, WO_3, $POCl_3$/heat

Q.6



Q.7

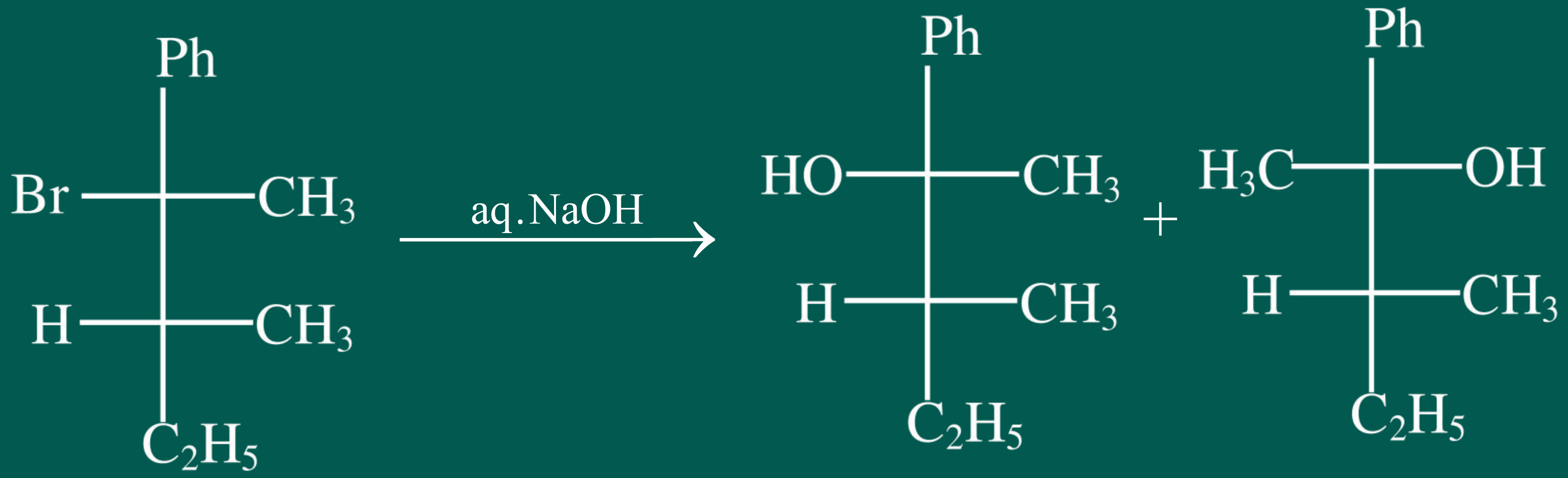


Stereochemistry of organic reactions

Case-1 (Reactant is chiral and product is chiral)

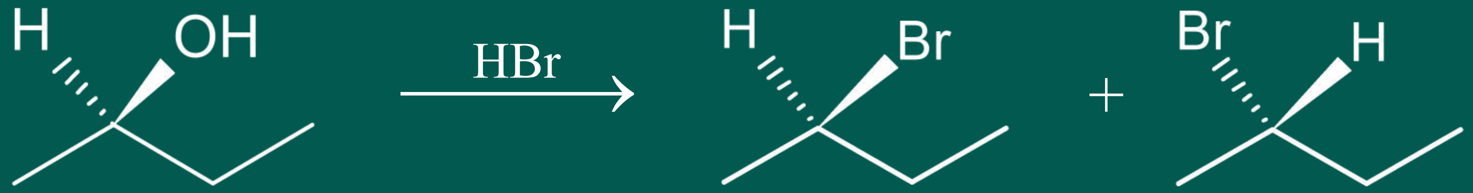
(i)

(ii)

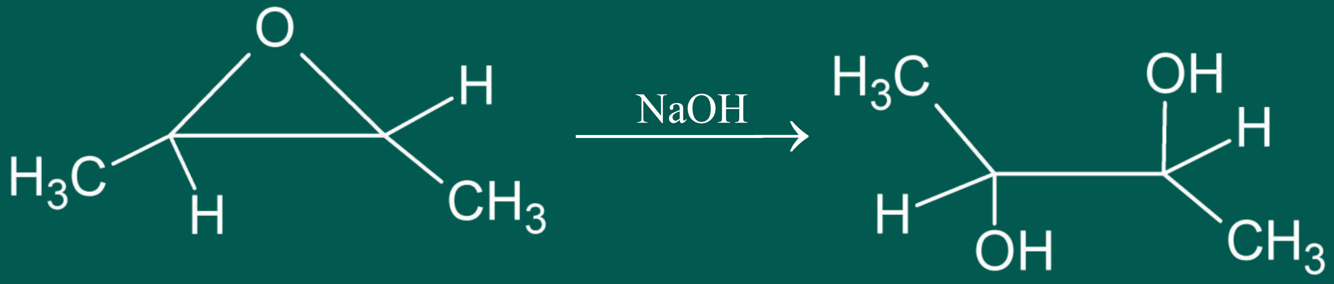

Ph
Br
CH3
H
CH3
C2H5
aq.NaOH
Ph
HO
CH3
H
CH3
C2H5
+
Ph
H3C
OH
H
CH3
C2H5

Case-2 (Reactant is chiral and product is achiral)

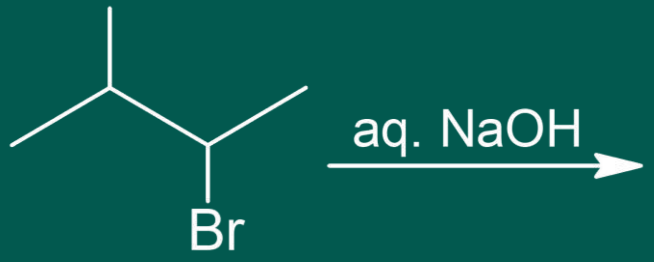
(i)



(ii)



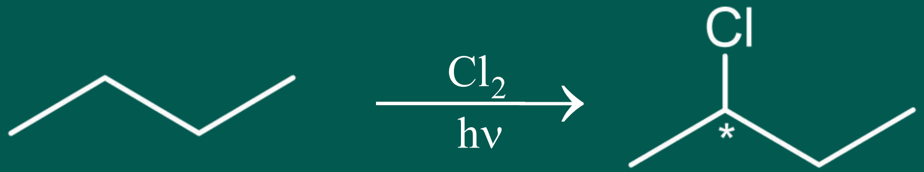
(iii)



Case-3 (Reactant is achiral and product is racemic mixture)

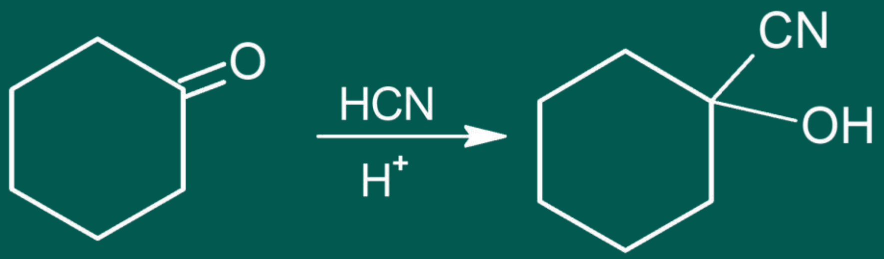
(i) $CH_2{=}CH{-}CH_2{-}CH_3 + HCl \longrightarrow CH_3{-}CH(Cl){-}CH_2{-}CH_3$

(ii)

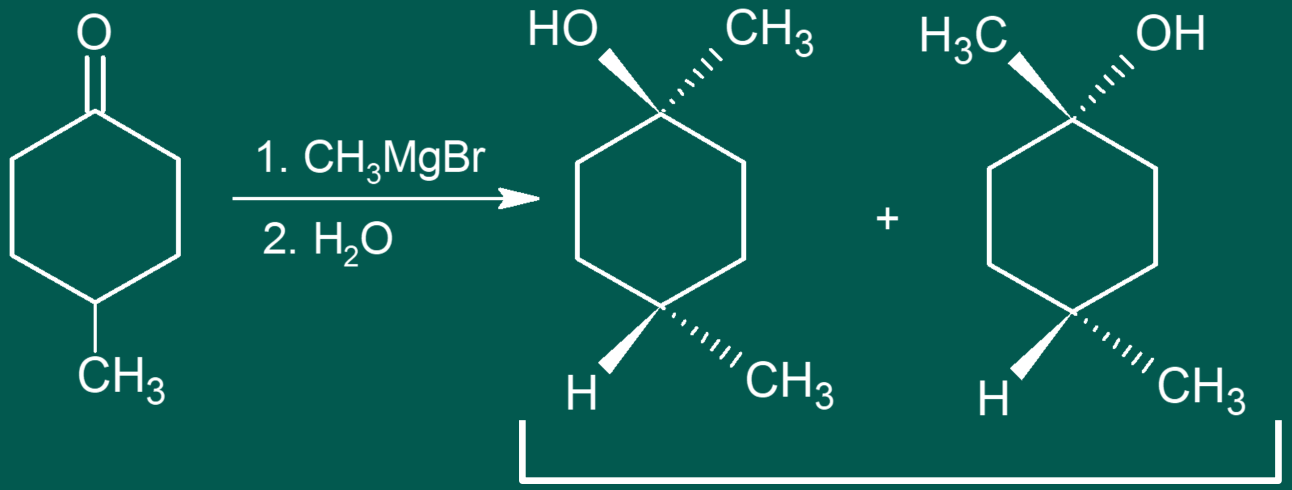


Case-4 (Reactant is achiral and product is achiral)

(i)

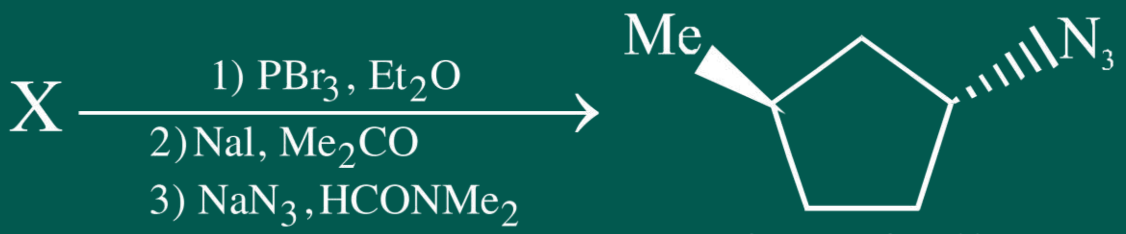


(ii)



Geometrical isomers

Q.8



enantiomerically pure

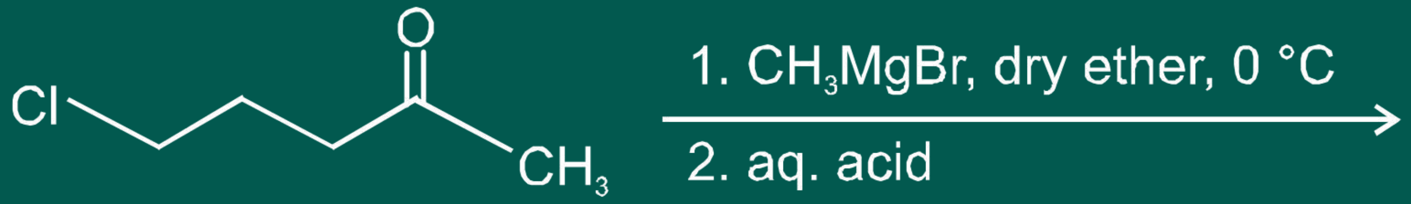
(A)

(B)

(C)

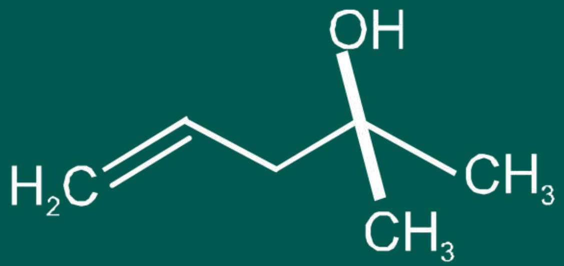
(D)

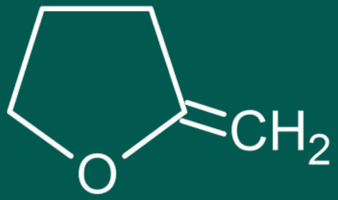
Q.9 The major product in the following reaction is :

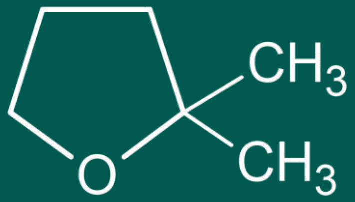


1. CH_3MgBr, dry ether, 0 °C
2. aq. acid

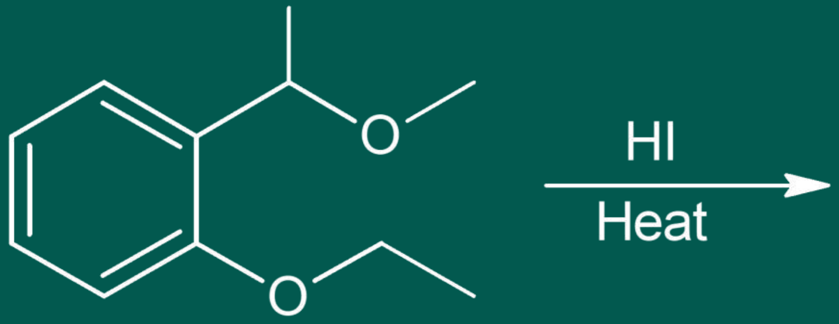
(A)

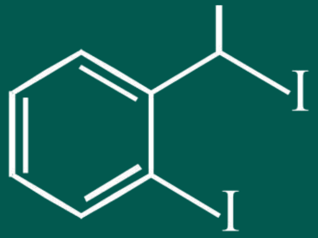

(B)


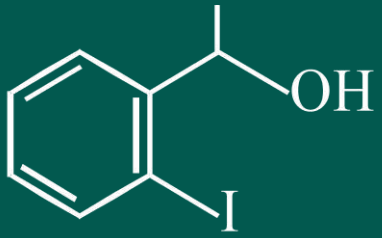
(C)


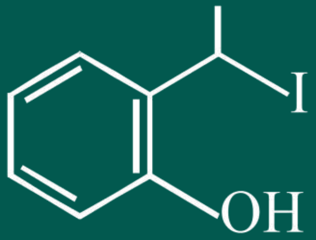
(D)


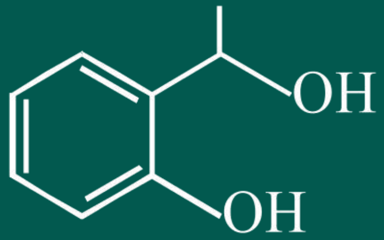
Q.10 The major product formed in the following reaction is :



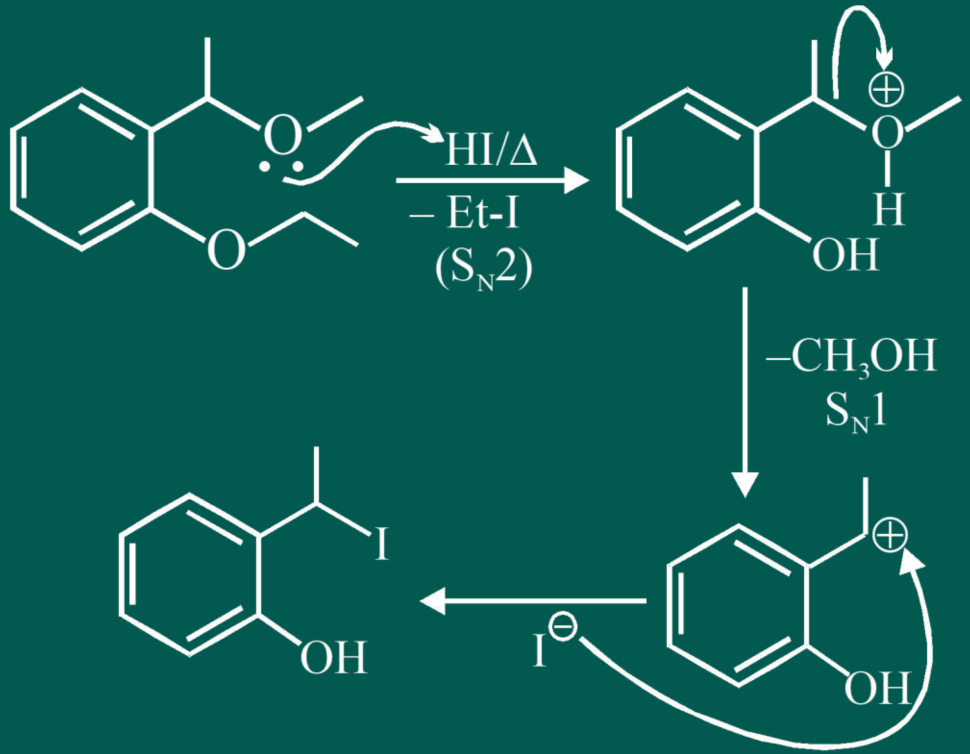
(A)


(B)


(C)


(D)


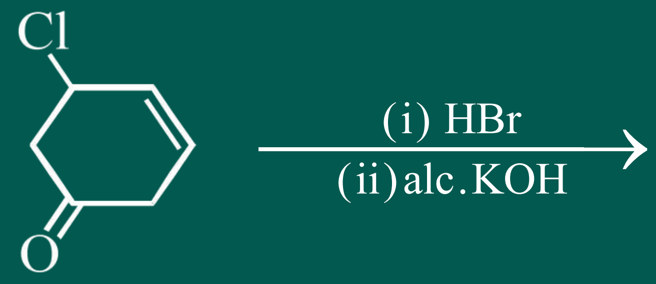
Sol.

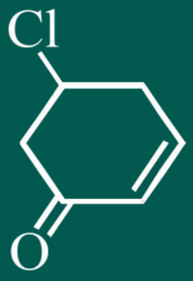


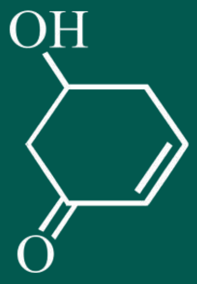
It is nucleophilic substitution reaction.

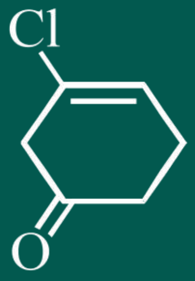
Ans. (C)

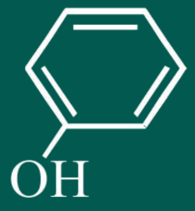
Q.11 The major poduct of the following reaction is :



(A) 

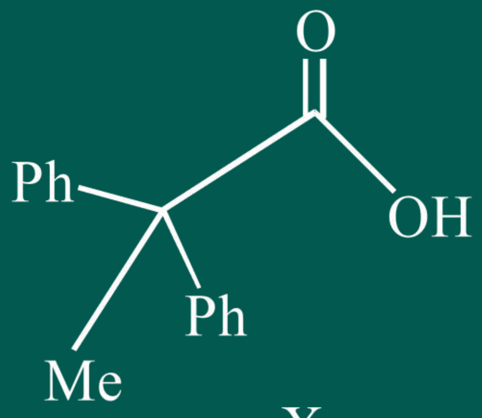
(B) 

(C) 

(D) 

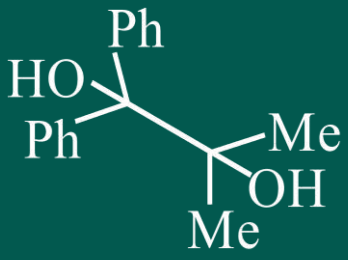
Ans. (D)

Q.12 The desired product X can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II. (given, order of migratory aptitude: aryl > alkyl > hydrogen)



X

LIST-I

(A).


+ H_2SO_4

LIST-II

1. I_2, NaOH

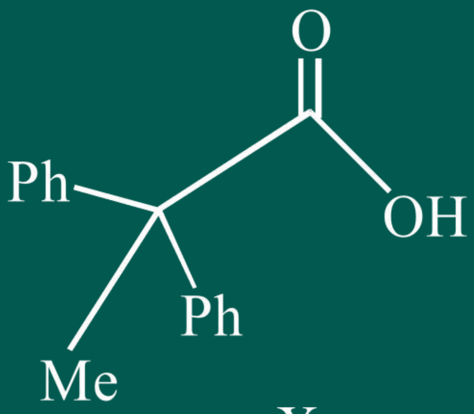
2. $[Ag(NH_3)_2]OH$

3. Fehling solution

4. HCHO, NaOH

5. NaOBr

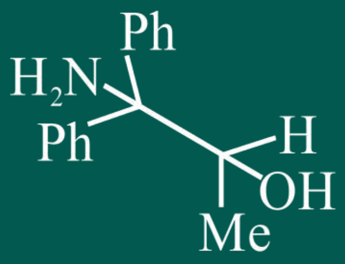
Product (X)



X

LIST-I

(B).

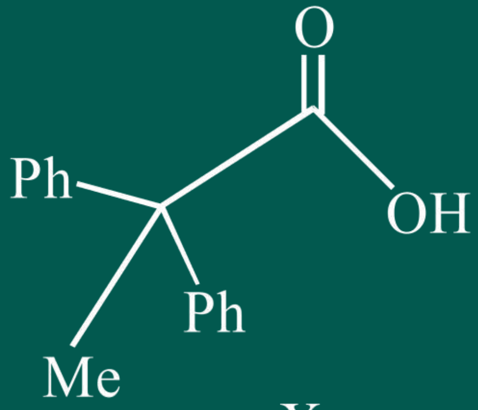


$+ HNO_2$

LIST-II

1. I_2, NaOH
2. $[Ag(NH_3)_2]OH$
3. Fehling solution
4. HCHO, NaOH
5. NaOBr

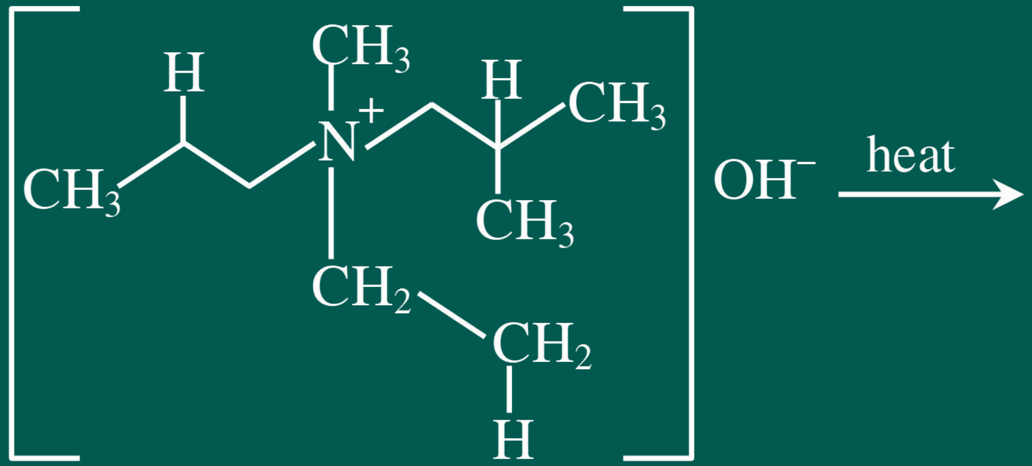
Product (X)



X

Hofmann elimination of quaternary ammonium salt

In this reaction Hofmann alkene is form on heating quaternay ammonium salt in basic medium.

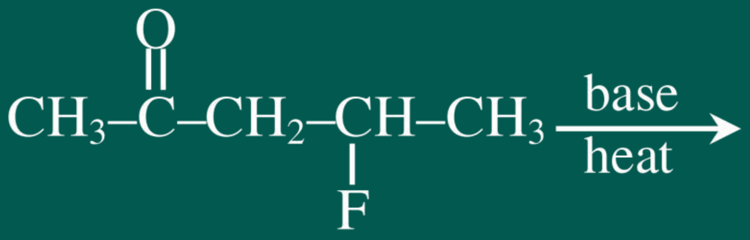


E1cB mechanism

Conditions :

(i) β-H must be sufficiently acidic
(ii) Poor leaving groups
(iii) heat in basic medium

E1cB reaction proceeds through carbanion intermediate.

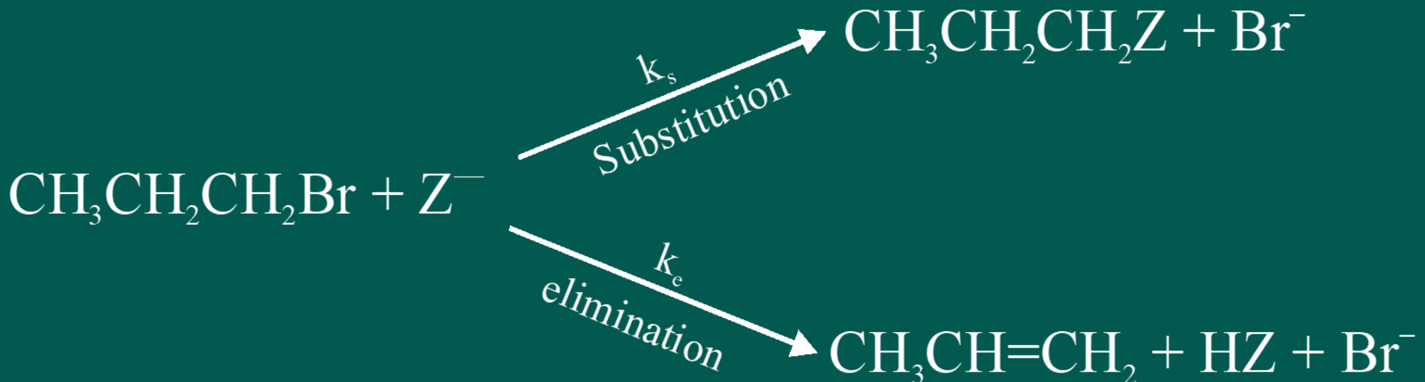


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\underset{\underset{\displaystyle F}{|}}{CH}-CH_3 \xrightarrow[\text{heat}]{\text{base}}$$

Structural variations of the S_N1 and S_N2 reactions

Type of electrophilic carbon atom	S_N1 reaction	S_N2 reaction
methyl (CH_3–X)	no	very good
primary alkyl (RCH_2–X)	no	good
secondary alkyl (R_2CH–X)	yes	yes
tertiary alkyl (R_3C–X)	very good	no
allylic (CH_2=CH–CH_2–X)	yes	good
benzylic ($ArCH_2$–X)	yes	good
α-carbonyl (RCO.CH_2–X)	no	excellent
α-alkoxy (RO.CH_2–X)	excellent	good
α-amino (R_2N.CH_2–X)	excellent	good

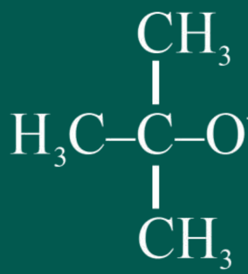
Q.13 For the following reactions :



$$CH_3CH_2CH_2Br + Z^- \xrightarrow[\text{Substitution}]{k_s} CH_3CH_2CH_2Z + Br^-$$

$$CH_3CH_2CH_2Br + Z^- \xrightarrow[\text{elimination}]{k_e} CH_3CH{=}CH_2 + HZ + Br^-$$

where $Z^- = CH_3CH_2O^-$ (A) or



$H_3C{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}O^-$ (B),

k_s and k_e are respectively the rate constants for the substitution and elimination, and $\mu = \dfrac{k_s}{k_e}$, the correct options is -

(A) $\mu_B > \mu_A$ and $k_e(B) > k_e(A)$

(B) $\mu_B > \mu_A$ and $k_e(A) > k_e(B)$

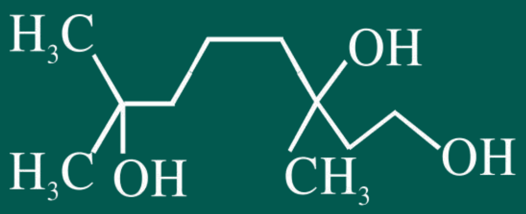
(C) $\mu_A > \mu_B$ and $k_e(B) > k_e(A)$

(D) $\mu_A > \mu_B$ and $k_e(A) > k_e(B)$

Ans. (C)

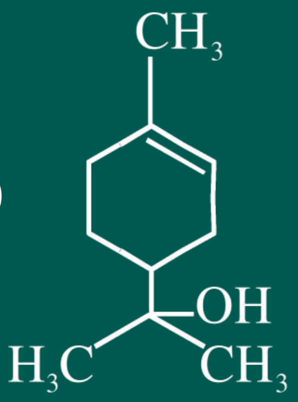
Q.14 The major product of the following reaction is :

(A)



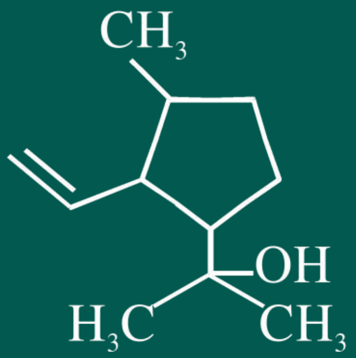
H3C
OH
H3C
OH
CH3
OH

(B)



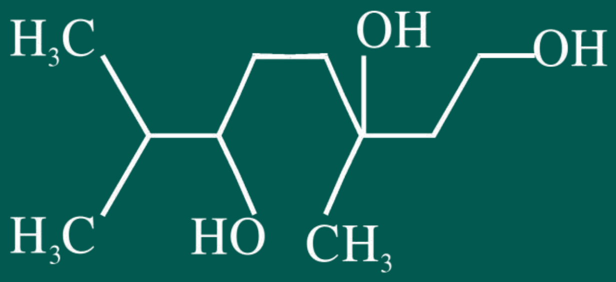
CH3
OH
H3C
CH3

(C)



CH3
OH
H3C
CH3

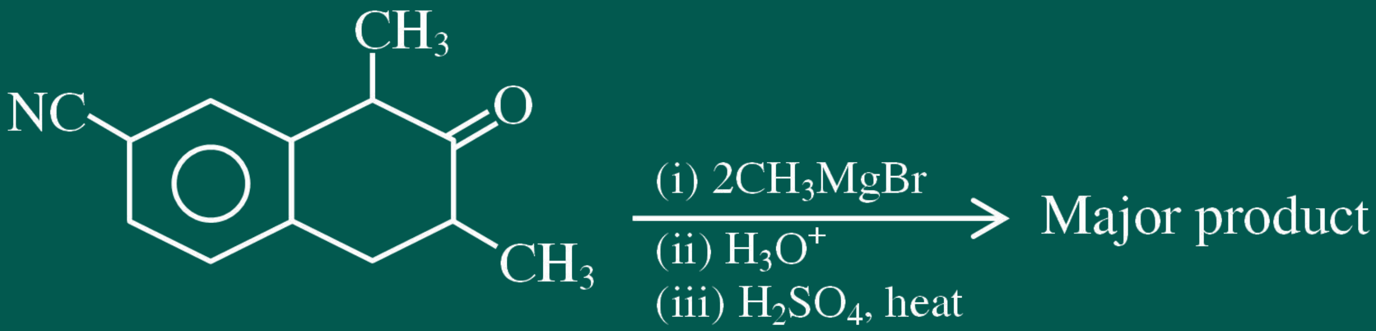
(D)



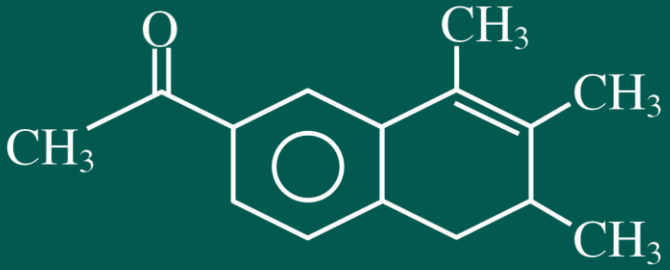
H3C
OH
OH
H3C
HO
CH3

Ans. (B)

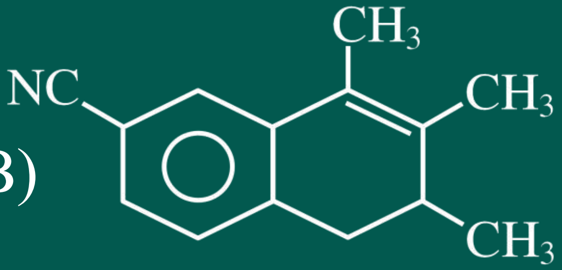
Q.15


NC
CH$_3$
O
CH$_3$
(i) 2CH$_3$MgBr
(ii) H$_3$O$^+$
(iii) H$_2$SO$_4$, heat
Major product

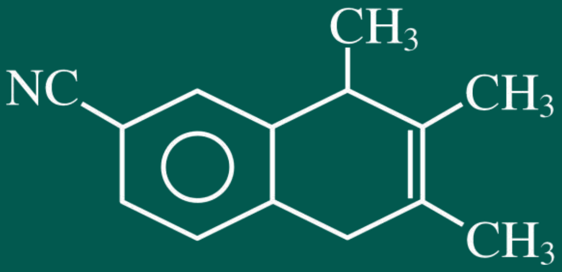
(A)


O
CH$_3$
CH$_3$
CH$_3$
CH$_3$

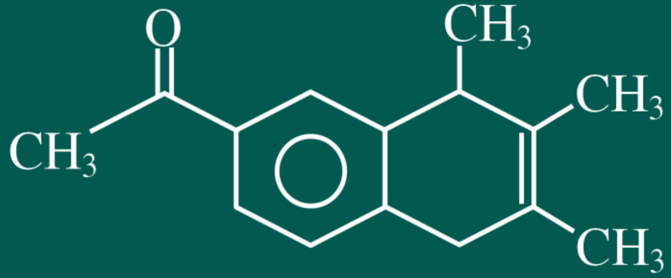
(B)


NC
CH$_3$
CH$_3$
CH$_3$

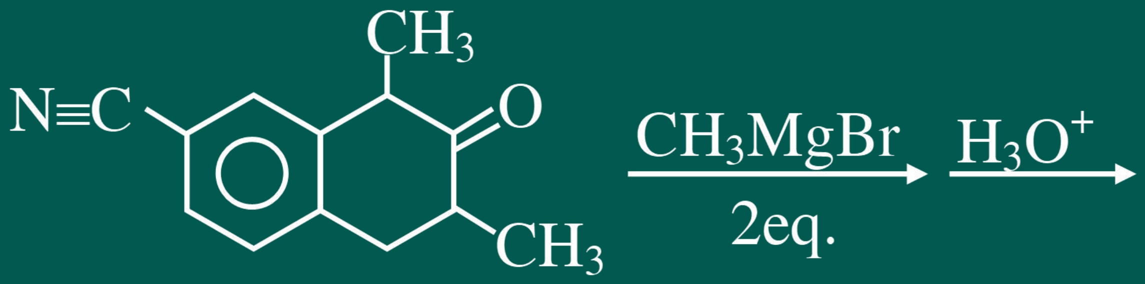
(C)

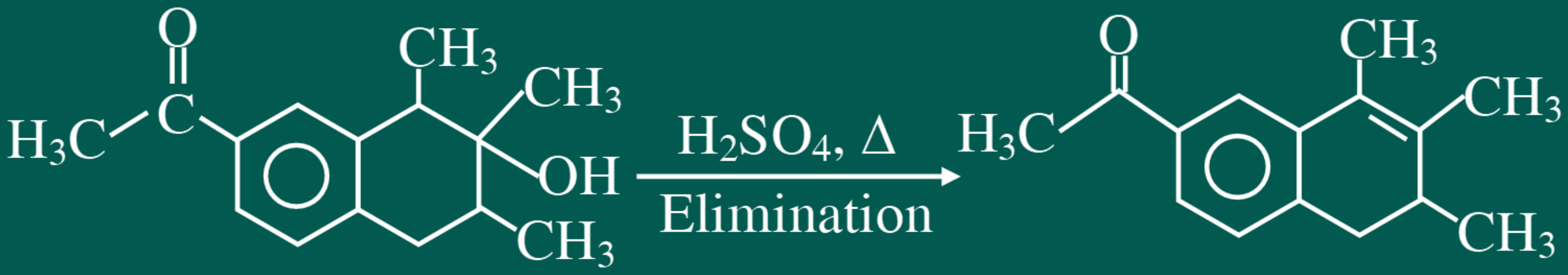

NC
CH$_3$
CH$_3$
CH$_3$

(D)


O
CH$_3$
CH$_3$
CH$_3$
CH$_3$

Sol.


N≡C
CH3
O
CH3
CH3MgBr
2eq.
H3O+


O
H3C
C
CH3
CH3
OH
CH3
H2SO4, Δ
Elimination
O
H3C
CH3
CH3
CH3

Ans. (A)

BEST WISHES

THANKS

Outstanding Performance in various Olympiads

KVPY (SA)
2020 RESULT

AIR 1

MAYANK MOTWANI
Classroom Student
(Stream - SA) Class XI

KANGAROO MATH
OLYMPIAD 2020

AWR 1

ASHISH RANJAN
Classroom Student
Perfect Score 120/120

NEST 2021 (NATIONAL ENTRANCE SCREENING TEST)

AIR 2

UAJJAN PAL

IOQJS PART II 2021

AYUSHMAN GUPTA

DESHANK PRATAP SINGH

IARCS
Indian Association for Research in Computing Science
Excellence in Computing. Provably.

Qualified for
INOI ▸
(Indian National Olympiad in Informatics) 2021

AYUSHMAN GUPTA

OMG BOOK OF RECORDS

Reliable Students Believe in
CREATING HISTORY

7th TIME CREATED A RECORD

5 WORLD & 2 NATIONAL RECORDS

by orally multiplying longest number of series given by Two individual people.

VANSHIKA SHARMA Roll No. 21770332

Reliable