Crash Course for NEET

CHEMISTRY

Study Package-2

Telegram @neetquestion



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Preface

Dear NEET Aspirant,

This book has been written specifically for the students who get themselves enrolled for the crash course for medical entrance exams. which is a limited days programme. It is meant for the quick brush-up of all the important topics. All the chapters have been written by the experienced faculties who have been preparing the students for qualifying various medical entrance exams. Each chapter covers all the important and must do topics and has been written in such a way that the student can grasp the contents easily.

After the theory portion in the study package, Try Yourself have been given to make the student practise the questions similar to those asked in entrance exams. The sequence of the questions has been kept same as the sequence of theory part so that a student can solve questions as per his/her coverage of theory part. The questions asked in previous AIPMT/NEET exam have also been included. This will help the students to assess the difficulty level in the setual medical entrance exams. We have also added two sample papers of 45 questions each covering the entire content of this study package.

As the days are limited, the students should never miss a single class and must cover the syllabus in tandem with the coverage in the classroom. Once the topic is finished, you must do all the questions of same topic given in the form of Try Yourself. If there is any doubt, you can get it clarified from the faculties.

Finally, you are advised to remain focused on your target and must work hard and complete all the necessary work sincerely in a planned manner. You must stay away from all distractions including the mobile phone. All other things can wait but time never waits for anyone. So gear up your preparations to realise your dream of joining the most prestigious and respected profession.

Wishing you a brighter career!

J. C. CHAUDHRY Managing Director

Analysis of NEET-2019

Subject-wise Report

Subject-wise Difficulty Level

S. No.	SUBJECT	EASY	MEDIUM	DIFFICULT	REMARKS
1	PHYSICS	18	25	2	Medium
2	CHEMISTRY	17	22	6	Medium
3	BOTANY	21	13	14	Easy
4	ZOOLOGY	9	25	8	Medium

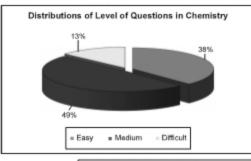
Topic-wise Credits & Difficulty Level

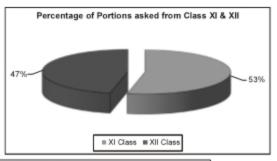
CHEMISTRY

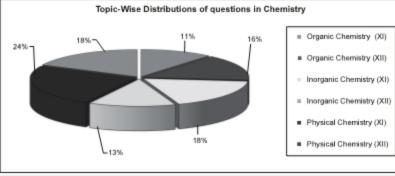
ANALYSIS OF CHEMISTRY PORTION OF NEET 2019

	ΧI	XII	ΧI	XII	XI	XII	
	Organic Chemistry	Organic Chemistry	Inorganic Chemistry	Inorganic Chemistry	Physical Chemistry	Physical Chemistry	Total
Easy	2	6	1	ş ^{il0} 2	4	2	17
Medium	2	1	6 e ^{io}	3	5	5	22
Difficult	1	0	(P)	1	2	1	6
Total	5	7	est 8	6	11	8	45

XI Class 24 XII Class 21







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Chapter 1

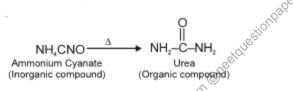
Organic Chemistry - Some Basic Principles and Techniques

Sub-topics

General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds, Electronic displacements in a covalent bond: inductive effect, electromeric effect, resonance effect and hyperconjugation. Homolytic and heterolytic fission of a covalent bond: free radicals, carbocations, carbanions; electrophiles and nucleophiles, types of organic reactions.

General Introduction

First organic compound synthesized was the urea from ammonium cyanate



This synthesis discarded vital force theory,

Methods of Purification

The common techniques used for purification are as follows:

- (i) Sublimation
- (ii) Crystallisation
- (iii) Distillation
- (iv) Differential extraction
- (v) Chromatography

Qualitative and Quantitative Analysis:

Detection of Elements

Element	Sodium Fusion Extract (S.E)	Confirmatory Test	Reactions
Nitrogen	Na + C + N → NaCN (S.E)	S.E + FeSO ₄ + Conc. H ₂ SO ₄ boil and cool, or SE + FeSO ₄ + FeCl ₃ + conc. HCl \rightarrow Prussian blue	 (i) FeSO₄ + 6NaCN → Na₄[Fe(CN)₆] + Na₂SO₄ (ii) 3Na₄[Fe(CN)₆] + 2Fe₂(SO₄)₃ → Fe₄[Fe(CN)₆]₃ + 6 Na₂SO₄ Prussian blue (Ferric ferrocyanide)

Element	Sodium Fusion Extract (S.E)	Confirmatory Test	Reactions
Sulphur	2Na + S $\xrightarrow{\Delta}$ Na₂S (S.E)	 (i) S.E + Sodium nitroprusside → Deep violet colour (ii) S.E + (CH₃COO)₂Pb → Black ppt. 	$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow$ Sodium thionitroprusside deep violet. $Na_4[Fe(CN)_5NOS]$ $Na_2S + (CH_3COO)_2Pb \rightarrow PbS$ $(black ppt)$ $+ 2CH_3COONa$
Halogens	$Na + X \xrightarrow{\Delta} NaX$ (S.E) $(X = CI, Br, I)$	S.E + AgNO₃ → AgX (X=Cl, Br, I) (i) White ppt soluble in NH₃(liq) Cl confirms (ii) Yellow ppt. partially soluble in NH₃(liq) Br confirms (iii) Pale yellow insoluble in NH₃(liq) I confirms	NaX + AgNO ₃ → AgX ppt
Nitrogen and Sulphur together	Na + C + N + S → NaCNS (S.E)	As in test for nitrogen instead of green or blue colour, blood red colouration confirms presence of N and S both	3NaCNS + FeCl₃ → Fe(CNS)₃ + 3NaCl blood red (Ferric thiocyanate)

Detection of C and H

Organic compound
$$\frac{\text{CuO}}{\text{strong heating}}$$
 $C + 2C@O \rightarrow 2Cu + CO$
 $2H + CuO \rightarrow Cu + H_2O$

CO2 turns lime water milky whereas H2O turns only anhydrous CuSO4 to blue.

Detection of Phosphorus

Organic compound + Na₂O₂ —Fuse → Na₃PO₄

$$Na_3PO_4 + 3HNO_3 \xrightarrow{\Delta} H_3PO_4 + 3NaNO_3$$

$${\rm H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4.12\ MoO_3 + 21\ NH_4NO_3 + 12\ H_2O_3 + 12\ MoO_3 + 21\ NH_4NO_3 + 12\ H_2O_3 + 12\ MoO_3 + 12\ NH_4NO_3 + 12\ NH_4$$

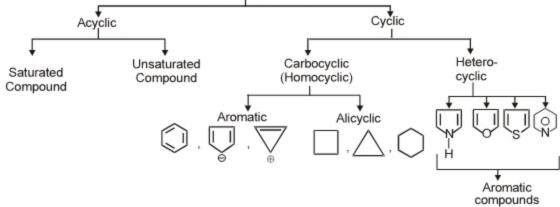
Quantitative Estimation of Elements in Organic Compounds

Element	Technique	Formula		
Carbon and Hydrogen	(Method) Liebig's Method	$C \rightarrow CO_2$ 12g 44g	% C = $\frac{12 \times \text{wt. of CO}_2 \times 10^{-3}}{44 \times weight of organic org$	
		2H → H₂O 2g 18g	% H = $\frac{2 \times \text{wt. of H}_2\text{O} \times 10}{18 \times \text{wt. of organic comp}}$	

Element	Technique	Formula
Nitrogen	(i) Duma's method (ii) Kjeldahl's method	(i) $2N \rightarrow N_2(g)$ $22.4 \text{ L at S.T.P. } \% \text{ N} = \frac{28 \times \text{V} \times 100}{22.4 \times \text{wt. of organic compound}}$ where V is the volume of N_2 gas in L as S.T.P.
		(ii) N \rightarrow NH ₃ = H ₂ SO ₄ % N = $\frac{1.4 \text{ N}_1\text{V}_1}{\text{wt. of organic compound}}$ where, N ₁ V ₁ is the m.eq. of H ₂ SO ₄ used or m.eq of NH ₃
Sulphur	Carius method	$S \rightarrow H_2SO_4 \rightarrow BaSO_4$ 32g $S = \frac{32 \times wt. \text{ of } BaSO_4}{233 \times wt. \text{ of org. comp.}} \times 100$
Halogens	Carius method	$CI \longrightarrow AgCI$ 35.5g 143.5g % $CI = \frac{35.5 \times \text{wt. of AgCI} \times 100}{143.5 \times \text{wt. of organic comp.}}$
		$\begin{array}{ccc} \text{Br} & \longrightarrow & \text{AgBr} \\ \text{80g} & \text{188g} & \text{\% Br} = & \frac{80 \times \text{wt. of AgBr} \times 100}{188 \times \text{wt. of organic comp.}} \end{array}$
		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
Oxygen		100 – (sum of % of all elements)
Phosphorus	Carius method	% P ² 62 × wt. of Mg₂P₂O ₇ formed × 100 wt. of organic comp.

Classification of Organic compounds organic compounds can be classified as per the chart given below.

Organic Compounds



Rules for IUPAC nomenclature of organic compounds

- 1. The longest carbon chain must be taken as the parent chain of the organic compound.
- 2. In case of unsaturation the carbon of the multiple bond must get the lower number.
- In case of different alkyl substituents in the compounds their names must be written in alphabetical order.
 We must remember the general preference order along different entities present in an organic compound must follow the order
 Functional group > unsaturation > substituent groups > (CI, Br, F, I, NO₂) > alkyl side chains (CH₃-, C₂H₅-)

- 4. Among alkyl groups choice must be made on the basis of alphabetical order.
- 5. Substituent groups are preferred as per alphabetical order also.
- Among unsaturation, if they are equally spaced then double bond is given preference over a triple bond, if unequal spacing then the firstly unsaturated carbon must receive lower number.

e.g.
$$CH_2 = CH - CH_2 - C \equiv CH$$
 Pent-1-en-4-yne
$$CH_3 - CH = CH - CH_2 - C \equiv CH$$
 Hex-4-en-1-yne

7. Among functional groups the preference must be as given below

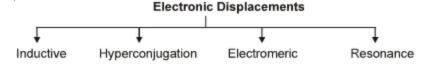
Functional Group	Prefix	Suffix
Carboxylic group	Carboxy	oic acid
2. Sulphonic group	Sulpho	sulphonic
3. Esters	Alkoxycarbonyl	oate
4. Acid Halides	Halocarbonyl (Carbalkoxy)	oyl halide
5. Amides	Carbamoyl	amide
6 Cyanide	Cyano	nitrile
7. Aldehydes	Aldo or Formyl or oxo	al
8. Ketones	Keto or oxo	one
9. Alcohols	Hydroxy	ol
10. Amines	Keto or oxo Hydroxy Amino	amine

8. Naming of polyfunctional group compound

We must understand that in an organic compound with polyfunctional groups a principal group must be chosen as per the above préférence order. The name of this group must be declared by using its suffix name so provided. All other functional groups except for the principal group must be declared by using their prefix name in alphabetical order.

5-amino-2-carbamoyl-3-hydroxyhex-3-enesulphonic acid.

Electronic Displacements in a Covalent Bond



1. Inductive Effect

The permanent displacement of electrons in a bond towards the more electronegative element is called inductive effect. The effect provides polarity to the molecule. The property of electron withdrawal shown by an atom or group is its (–I) effect and that of donation is called (+I) effect.

$$\mathsf{CH_3} - \overset{\delta\delta\delta\delta+++}{\mathsf{CH_2}} - \overset{\delta\delta+}{\mathsf{CH_2}} - \overset{\delta+}{\mathsf{CH_2}} - \overset{\delta-}{\mathsf{CH_2}}$$

Order of –I effect :
$$(CH_3)_3 \stackrel{+}{N} > -NO_2 > -CN > -COOH > -F > -CI > -Br > -I > -OH > -OR > C_cH_c - > -H$$

Order of +I effect : $(CH_3)_3C->(CH_3)_2CH->CH_3-CH_2->-CH_3>-H$

2. Electromeric Effect

The temporary shifting of π electrons towards the more electronegative element in the presence of a reagent is electromeric effect. If reagent is an electrophile then the effect is (+E) and if a nucleophile then (-E) effect.

3. Resonance Effect

The effect involves permanent delocalization of π electrons in a conjugated system. Intermediate structures formed are called resonating structures. The structure that collectively represents all resonating structures is believed to be the most stable and is called the resonance hybrid.

During resonance in a molecule all bond lengths happen to be the same if all the canonical forms are equivalent and lie in between those of a single and double bond.

Resonating structures must have the same position of nuclei and same number of unpaired electrons. The one having the more number of covalent bond, negative charge on electronegative and positive charge on electropositive element with less charge separation is found to be more stable than others.

The difference between energies of most stable resonating structure and the resonance hybrid is called the resonance energy of the molecule.

+M Effect
$$\longrightarrow$$

$$\begin{array}{c} \oplus \ddot{C} \\ \oplus \ddot{C} \\ \end{array}$$

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$$+ \begin{pmatrix} \oplus \ddot{C} \\ & \ddot$$

4. Hyperconjugation

It is an effect involving delocalization of σ electrons in a molecule. The effect is also called No-bond resonance or Baker-Nathan effect or anchimeric effect. For example,

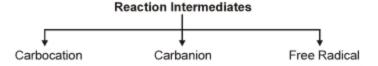
$$H = CH \xrightarrow{C} CH_{2} \leftrightarrow H = CH \xrightarrow{C} CH \xrightarrow{C}$$

Homolytic and Heterolytic Bond Fission and Reaction Intermediates

Heterolytic Cleavage: The bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments, which is more electronegative.

Homolytic Cleavage: One of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms.

Reaction Intermediates



1. Carbocation

The stability of different carbocations by resonance.

$$(C_8H_5)_3\overset{\oplus}{C} > (C_8H_5)_2\overset{\oplus}{CH} > C_8H_5\overset{\oplus}{CH}_2 > \overset{\oplus}{CH}_2 - CH = CH_2$$

The stability of different carbocation by inductive effect and hyperconjugation.

2. Carbanion

The stability of different carbanions by resonance

$$(C_4H_6)_3\overset{\ominus}{C} > (C_4H_6)_2\overset{\ominus}{C}H > C_4H_6 - \overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_2 - CH = CH_2$$

The stability of different carbanions by inductive effect.

3. Free Radicals

Stability of different free radicals by resonance

$$(C_{\varepsilon}H_{\varepsilon})_{3}\overset{\bullet}{C} > (C_{\varepsilon}H_{\varepsilon})_{2}\overset{\bullet}{C}H > \overset{\bullet}{C}H_{2} - CH = CH_{2} > C_{\varepsilon}H_{\varepsilon} - CH_{2}$$

Stability of different free radicals by hyperconjugation.

Electrophiles and Nucleophiles

Nucleus loving reagent is called nuleophile (Nu:) and electron seeking reagent is called electrophile (E[⊕])

Examples of nucleophiles : OH-, CN-, H,O:; R,N: etc.

Examples of electrophiles : $\overset{\bullet}{C}H_3$, $\overset{\bullet}{N}O_3$, CI^{\oplus} , BF_3 etc.

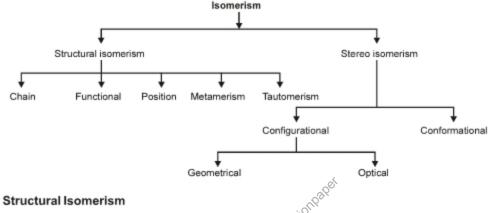
Types of Organic Reactions

Organic reactions can be classified into the following types:

- Substitution reactions
- (ii) Addition reactions
- (iii) Elimination reactions
- (iv) Rearrangement reactions

We will study details of these reactions in coming chapters.

Isomerism



Chain Isomerism: It is due to difference in the number of carbon atoms in the parent chain.

$$e.g.,\, \mathrm{CH_3-CH_2-CH_2-CH_3}\,,\,\, \mathrm{CH_3-CH-CH_3^{\circ,\circ}}$$

(ii) Functional Isomerism : It is due to difference in functional groups.

(iii) Position Isomerism: It is due to difference in the locant used for substituents, functional group, C = C bond or $C \equiv C$ bond.

$$e.g.,~\mathrm{CH_3-CH_2-CH_2-OH},~\mathrm{CH_3-CH-CH_3}\\\mathrm{OH}$$

(iv) Metamerism: It is due to attachment of different alkyl groups with the same polyvalent functional group.

$$e.g.,\,\mathsf{CH_3-CH_2-O-CH_2-CH_3},\qquad \mathsf{CH_3-O-CH_2-CH_2-CH_3}$$

Tautomerism: It is due to migration of proton. (v)

e.g.,
$$CH_3-C-H \rightleftharpoons CH_2 = C-H$$

$$CH_3-N \nearrow O \rightleftharpoons CH_2 = N \nearrow O$$



Try Yourself

SECTION - A

Objective Type Questions

Which of the following is an aromatic heterocyclic compound?









- IUPAC name of the given compound
 - (CH3)2N-CH2-CH(CI)-COOH is
 - (1) 2-chloro-3-(N, N-dimethyl amino) propanoic acid
 - (2) 2-chloro-4-N-methyl pentenoic acid
 - (3) 2-chloro-2-carboxy-N-ethyl amine
 - (4) All of these
- IUPAC name of CH-CH-CH-OH is
 - 1, 2-Epoxy-3-propanol
 - (2) 1, 2-Oxo-3-propanol
 - (3) 2, 3-Epoxy-1-propanol
 - (4) 2, 3 Epoxyallyl alcohol
- The IUPAC name of the compound NH2-CHO is
 - (1) 1-amino methanal
 - (2) Aminoformaldehyde
 - Aminocarboxaldehyde
 - (4) Methanamide
- In carbocations correct order of stability is

- (1) | > || > || > |V
- (2) II > I > III > IV
- (3) || > | > |V > ||
- (4) IV > III > II > I

The correct decreasing order of bond strength of C-CI in following compounds

> CH₂-CH₂-CI CH₂=CH-CI C_sH_s-CI

- (1) | | | > | > |
- (2) | | | > | > | |
- (3) | > || > ||
- (4) || > | > ||
- Which statement is false?
 - R–C≡O is more stable than R–C=O
 - (2) The addition across > C = O is an electrophilic @addition
 - + I group attached to carboxylic group weakens the acidity of carboxylic acid
 - (4) The oxygen atom in phenol has more dominating resonance effect than inductive
- Which of the following series contains atoms/ groups having only -R effect?
 - -COR, -OR, -COOR (2) -NO₂, -CN, -SO₃H

 - (3) -CI, -CHO, -NH₂ (4) -OH, -NR₂, -COOH
- Which of the following group will show maximum hyper conjugation effect when attached with unsaturated atom?
 - (1) CH₃-
- (2) CH₃-CH₂-
- (3) (CH₃)₂CH–
- (4) (CH₃)₃C-
- 10. The central carbon atom of a free radical is surrounded by
 - (1) 6 electrons
- (2) 7 electrons
- (3) 8 electrons
- (4) 5 electrons
- The following reaction

$$C_zH_sBr+KOH \rightarrow C_zH_sOH+KBr$$
 is

- (1) Nucleophilic substitution
- (2) Nucleophilic addition
- Electrophilic substitution
- (4) Free radical substitution

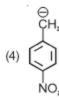
- 12. In which of the following resonance will be possible?
 - (1) CH2=CH-CH2-CHO
 - (2) CH₂=CH-CHO
 - (3) CH₂-CO-CH₂
 - (4) CH2=CH-CH2-CH2-CH=CH2
- 13. Polarization of electrons in acrolein may be written
 - (1) $CH_2=CH-CH=O$ (2) $CH_2=CH-CH=O$

 - (3) $\overset{\delta^+}{\text{CH}}_{3}=\text{CH-CH=O}$ (4) $\overset{\delta^+}{\text{CH}}_{3}=\overset{\delta^-}{\text{CH-CH=O}}$
- 14. Which among the given compounds is most stable?
 - (1) 1-butene
 - (2) 2, 3-dimethyl-2-butene
 - (3) Cis-2-butene
 - (4) Trans-2-butene
- 15. The reaction $(CH_s)_s$ C-Br \to $(CH_s)_s$ $\overset{\oplus}{C}$ + $\overset{\ominus}{B}$ r is an example of
 - Homolytic fisson
- (2) Heterolytic fisson
- (3) Cracking
- (4) Rearrangement
- Inductive effect involves
 - Displacement of σ electrons partially
 - (2) Displacement of σ and π electrons
 - Delocalization of π electrons
 - (4) Delocalization of σ and π electrons
- 17. Which of the following has +R effect?
 - (1) -CN
- (2) -CHO
- (3) -NH₂
- (4) -NO₂
- Hyperconjugation effect is also called
 - Baker-Nathan effect
 - (2) Anchimeric effect
 - (3) No-bond resonance
 - (4) All of these
- Most stable carbanion among the following is









- 20. Which of the following is most stable?
- –ён–сн,
- 21. Which of these species is electrophile?
 - (1) CCI.
- (2) BF₃
- (4) All of these
- 22. Stability of alkyl carbocations can be explained by
 - Inductive effect
 - (2) Hyperconjugation
 - (3) Both inductive and hyperconjugation
 - (4) Electromeric
- 23. The most stable free radical is







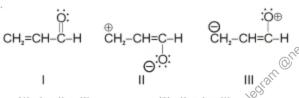
- The number of sigma and π bonds in but-1-en-3-yne
 - 5σ, 5π
- (2) 7σ , 3π
- (3) 6σ, 2π
- (4) 6σ, 3π
- Which of the following effects most appropriately describe the mechanistic step shown below?

- Hyperconjugation effect
- (2) Inductive effect
- (3) Electromeric effect
- (4) All of these
- Which of the following has all the carbon sp² hybridised?

 - (1) CH, = CH − CH, (2) CH, = CH − CH,
 - (3) CH, = CH CH,
- (4) All of these
- 27. How many sp hybridised C-atoms are present in NC-CH2-CH=C=CH-CN?
 - (1) 2
- (2) 3

- (3) 1
- (4) 4

- 28. Which of the following alkyl groups will show maximum +I effect?
 - (1) (CH₃)₃ C-
- (2) (CH₃)₂ CH-
- (3) CH₃-CH₂-
- (4) CH₃-
- 29. Which of the following will show maximum –I effect?
 - (1) -CHO
- (2) -NO₂
- (3) -F
- (4) -NH,
- 30. Which of the following species is a nucleophile?
 - (1) [⊕]NO,
- (2) : CX₂
- (3) :NH,
- (4) CH,
- 31. Which of the following is an isolated diene?
 - (1) Hexa-1, 5-diene
- (2) Propa-1, 2-diene
- (3) Buta-1, 3-diene
- (4) Penta-2, 3-diene
- Arrange the following resonating structures according to decreasing order of stability



- (1) | > || > ||
- (2) || > | > || /
- (3) | | | > | > | |
- (4) ||| > || > |
- 33. Which of the following is a secondary butyl group?
 - (1) CH₃-CH-CH₃-CH₃ CH₄
 - (3) CH₃-CH₂-CH-CH₃
 - (4) CH₃-C-CH₂-CH₃
- 34. Which one is a nucleophile?
 - (1) (CH₃), N
- (2) BF₃
- (3) NO.
- (4) CH -C=C

- When both N and S are present in an organic compound, the sodium extract with FeCl₃ gives
 - (1) Green colour
 - (2) Blue colour
 - (3) Yellow colour
 - (4) Red colour
- 0.12g of an organic compound gave 0.22g of Mg₂P₂O₇, by the usual analysis. The percentage of phosphorus in the compound is
 - (1) 15.23
- (2) 38.75
- (3) 51.20
- (4) 60.92
- 37. Beilstein's test is not given by
 - (1) Urea
 - (2) Thiourea

- (4) All of these
- The mixture of benzoic acid and napthalene can be separated by crystallization from
 - Hot water
 - (2) Cold water
 - (3) Benzene
 - (4) Ether
- During estimation in Duma's method 1.18 g of an organic compound gave 224 ml of N₂(g) at NTP. The precentage of N in the compound is
 - (1) 20.0
 - (2) 11.8
 - (3) 47.5
 - (4) 23.7
- Glycerol can be purified by
 - (1) Fractional distillation
 - (2) Vacuum distillation
 - (3) Steam distillation
 - (4) Simple distillation

SECTION - B

Previous Years Questions

Which nomenclature is **not** according to IUPAC system? [AIPMT 2012]

(1)	CH ₃ –CH–CH–CH ₂ CH ₃ , I I CH ₃ ⊚ 2–Methyl–3–phenylpentane
(2)	CH ₃ -C-CH ₂ -CH ₂ COOH, O 4-oxopentanoic acid
(3)	Br–CH ₂ –CH = CH ₂ , 1–Bromo–prop–2–ene
(4)	CH_3 I $CH_3-CH_2-CH-CH_2-CHCH_3$, I
	4-bioino-z,4-dimethylnexane

 Structure of the compound whose IUPAC name is 3-Ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is

[NEET 2013]

 The order of stability of the following tautomeric compounds is [NEET 2013]

$$CH_2 = C - CH_2 - C - CH_3 \Longrightarrow$$

- (1) ||| > || > |
- (2) || > | > |||
- (3) || > ||| > |
- (4) | > || > |||

The structure of isobutyl group in an organic compound is [NEET 2013]

 In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M H₂SO₄. The percentage of nitrogen in the soil is

[AIPMT 2014]

- (1) 37.33
- (2) 45.33
- (3) 35.33
- (4) 43.33

2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid? [Re-AIPMT-2015]

 The number of structural isomers possible from the molecular formula C₃H_qN is [Re-AIPMT-2015]

- (1) 2
- (2) 3
- (3) 4
- (4) 5

 Which of the following statements is not correct for a nucleophile? [Re-AIPMT-2015]

- Nucleophiles attack low e⁻ density sites
- (2) Nucleophiles are not electron seeking
- (3) Nucleophile is a Lewis acid
- (4) Ammonia is a nucleophile

Consider the following compounds

Hyperconjugation occurs in

[AIPMT-2015]

- (1) I and III
- (2) I only
- (3) II only
- (4) III only

Which of the following is the most correct electron displacement for a nucleophilic reaction to take place? [AIPMT-2015]

(1)
$$H_3C \rightarrow C = C - C - CI$$

(2)
$$H_3C \rightarrow C = C - C - C$$

(3)
$$H_3C \leftarrow C = C - C$$

(4)
$$H_3C \rightarrow C = C - C - CI$$

11. Given:

The enthalpy of hydrogenation of these compounds will be in the order as [AIPMT-2015]

- (1) || > | > ||
- (2) | > || > |||
- (3) | | | > | | > |
- (4) || > ||| > |

- 12. In Duma's method for estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is [AIPMT-2015]
 - (1) 15.76
- (2) 17.36
- (3) 18.20
- (4) 16.76

13. Given

Which of the given compounds can exhibit tautomerism? [AIPMT-2015]

- (1) I, II and III
- (2) I and II
- (3) I and III
- (4) II and III

14. For the following reactions :

(a)
$$CH_3CH_2CH_2Br + KOH \rightarrow$$

 $CH_3CH = CH_2 + KBr + H_2O$

(b)
$$H_3C \searrow CH_3 + KOH \longrightarrow H_3C \searrow CH_3 + KBr$$

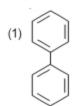
(c)
$$\longrightarrow$$
 + Br₂ \longrightarrow Br

Which of the following statements is correct?

[NEET-2016]

- (a) is substitution, (b) and (c) are addition reactions
- (2) (a) and (b) are elimination reactions and (c) is addition reaction
- (3) (a) is elimination, (b) is substitution and (c) is addition reaction
- (4) (a) is elimination, (b) and (c) are substitution reactions

- 15. The pair of electron in the given carbanion, $CH_3C \equiv C^{\Theta}$ is present in which of the following orbitals? [NEET-2016]
 - (1) sp
- (2) 2p
- (3) sp³
- (4) sp2
- 16. In which of the following molecules, all atoms are coplanar? [NEET (Phase-2) 2016]



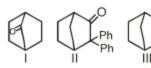
- (2)
- (3) CH₃ C=C CN
- (4)
- 17. In pyrrole



the electron density is maximum on

[NEET (Phase-2) 2016]

- (1) 2 and 3
- (2) 3 and 4
- (3) 2 and 4
- (4) 2 and 5
- 18. Which among the given molecules can exhibit tautomerism?



[NEET (Phase-2) 2016]

- (1) III only
- (2) Both I and III
- (3) Both I and II
- (4) Both II and III
- 19. The correct statement regarding electrophile is

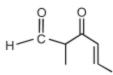
[NEET-2017]

- Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile
- (2) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile

- (3) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
- (4) Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile
- The most suitable method of separation of 1 : 1 mixture of ortho and para-nitrophenols is

[NEET-2017]

- (1) Sublimation
- (2) Chromatography
- (3) Crystallisation
- (4) Steam distillation
- The IUPAC name of the compound [NEET-2017]



is00

- (1) 3-keto-2-methylhex-4-enal
- (2) 5-formylhex-2-en-3-one
- (3) 5-methyl-4-oxohex-2-en-5-al
- (4) 3-keto-2-methylhex-5-enal
- 22. The number of sigma (σ) and pi (π) bonds in pent-2-en-4-yne is [NEET-2019]
 - 10σ bonds and 3π bonds
 - (2) 8σ bonds and 5π bonds
 - (3) 11σ bonds and 2π bonds
 - (4) 13σ bonds and no π bonds
- The most stable carbocation, among the following, is [NEET-2019 (Odisha)]
 - (1) CH₃ CH₂ CH₂
 - (2) (CH₃)₃ C − CH − CH₃
 - (3) CH₃ CH₂ CH CH₂ CH₃
 - (4) CH₃ CH₂ CH₃ CH₃ CH₃

Chapter 2

Hydrocarbons

Sub-topics

Alkanes- Nomenclature, isomerism, conformations (ethane only), physical properties, chemical reactions including free radical mechanism of halogenation, combustion and pyrolysis. Alkenes-Nomenclature, structure of double bond (ethene), geometrical isomerism, physical properties, methods of preparation: chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markovnikov's addition and peroxide effect), ozonolysis, oxidation, mechanism of electrophilic addition. Alkynes-Nomenclature, structure of triple bond (ethyne), physical properties, methods of preparation, chemical reactions: acidic character of alkynes, addition reaction of hydrogen, halogens, hydrogen halides and water. Aromatic hydrocarbons-Introduction, IUPAC nomenclature; Benzene; resonance, aromaticity; chemical properties: mechanism of electrophilic substitution- Nitration sulphonation, halogenation, Friedel Craft's alkylation and acylation; directive influence of functional group in mono-substituted benzene; carcinogenicity and toxicity.

ALKANES

Nomenclature and Isomerism:

$$\begin{aligned} \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_3 \;; \quad \text{Hexane} \\ \mathsf{CH}_3 - \mathsf{CH} - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_3 \;; \quad 2\text{-Methylpentane} \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \end{aligned}$$

$$\label{eq:CH3-CH3-CH3-CH3-CH3} \begin{array}{c} \operatorname{CH}_3-\operatorname{CH}_3-\operatorname{CH}_3-\operatorname{CH}_3; \end{array} \text{3-Methylpentane} \\ \operatorname{CH}_3 \end{array}$$

$$CH_3 - CH - CH - CH_3$$
; 2, 3-Dimethylbutane $CH_3 - CH_3 - CH_3$

$$\begin{array}{c} \operatorname{CH_3} \\ \mid \\ \operatorname{H_3C} - \operatorname{C} - \operatorname{CH_2} - \operatorname{CH_3}; \ \ 2, \ 2\text{-Dimethylbutane} \\ \mid \\ \operatorname{CH_3} \end{array}$$

All are isomers with molecular formula C6H14

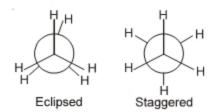
Conformations

The spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called conformations or conformers or rotamers.

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Conformations of ethane :

The two extreme conformers of ethane are



Staggered form is more stable than eclipsed

Physical Properties:

- In case of any hydrocarbon, as the number of C-atom increases the boiling point also increases.
- In case of isomeric alkanes, higher is the branching, lesser will be its boiling point. e.g. n-pentane > Isopentane > Neopentane. (order of boiling points)
- Melting points: The melting points of the alkanes depend upon the packing of the molecules in the 3. crystal structure. Melting points also increase with increase in number of carbon atoms but the increase in melting point, when we move from even C-numbered alkane to next odd C-numbered alkane is very less as compared to an increase in melting point, when we move from odd C-numbered alkane to next even C-numbered alkane.

Preparation of Alkane

(I) From Salts of Carboxylic acid

$$\text{(b)} \quad 2R - \underset{(aq)}{\mathsf{COOK}} \xrightarrow[\mathsf{electrolysis}]{\mathsf{Kolbe's}} \underset{(\mathsf{At} \; \mathsf{anode})}{\mathsf{R}} - R$$

(II) From Alkyl Halide

(a)
$$R - X + 2Na + X - R \xrightarrow{Dry} R - R$$
 (Wurtz reaction)

$$R-X+2Na+X-R' \xrightarrow{Dry} R-R, R-R', R'-R'$$
 (Wurtz reaction)

$$(b) \quad R - X \xrightarrow[Zn/HCl]{Pd/C} R - H$$

$$\xrightarrow[Zn/NaOH]{R-VH} Cu-Zn$$

$$\xrightarrow[Ni/H]{R-VH} R - H$$

(III) From Hydrogenation of Alkene/Alkyne

(a)
$$R-CH=CH_2 \xrightarrow{Ni/H_2} R-CH_2-CH_3$$

(b)
$$R-C \equiv CH \xrightarrow{Ni/H_2} R-CH_2-CH_3$$

(IV) From Reduction of Alcohol/Carbonyl Compound and Carboxylic acid

(a)
$$R - OH \xrightarrow{HI/P(Red)} R - H$$

(b)
$$R - CHO \xrightarrow{HI/P \text{ or } Zn-Hg \text{ Conc } HCl \text{ or} \atop NH_2-NH_2, KOH} \rightarrow R - CH_3$$

If Zn-Hg/conc. HCl is used then it is known as Clemmensen's reduction. If NH2 - NH2/KOH used, it is wolff Kishner reduction.

(c)
$$R - COOH \xrightarrow{HI/P(red)} R - CH_3$$

(V) From Hydrolysis of Grignard Reagent

$$R - Mg - X \xrightarrow{H_2O} R - H$$
 (Similar reaction with R-OH or NH₃ or RSH)

(VI) From Hydrolysis of Carbide

$$Be_2C \xrightarrow{H_2O} CH_4$$

$$AI_4C_3 \xrightarrow{H_2O} CH_4$$

$$R' - X + R_2CuLi \xrightarrow{Dry} R - R'$$
 (Corey House Synthesis) (' R_2CuLi' is Gillmann's reagent)

Chemical reactions of Alkane

Alkanes being saturated hydrocarbons show very little affinity towards other reagents.

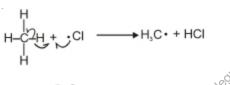
(I) Substitution Reaction

Substitution proceed via free radical mechanism

Mechanism: free radical substitution reaction

Chain Initiation

Chain Propagation



Chain Termination

Halogenation

$$CH_4 + CI_2 \xrightarrow{hv} CH_3 - CI$$

Nitration

$$CH_3 - CH_3 \xrightarrow{HNO_3(g)} CH_3 - CH_2 - NO_2 + CH_3 - NO_2$$

Sulphonation

$$C_6H_{13} - H \xrightarrow{H_2SO_4} C_6H_{13} - SO_3H$$

Only n-hexane and onwards can be sulphonated.

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(II) Oxidation

$$CH_{3} - \overset{H}{\overset{I}{C}} - CH_{3} \xrightarrow{Alk. \ KMnO_{4}} CH_{3} - \overset{OH}{\overset{I}{C}} - CH_{3} \ (Only \ tertiary \ alkanes \ give \ this \ reaction)}{CH_{3}}$$

$$R - CH_{3} \xrightarrow{(CH_{3}COO)_{2}Mn} R - COOH + H_{2}O$$

$$CH_{4} + O_{2} \xrightarrow{Cu \ tube} CH_{3} - OH$$

$$CH_{4} + O_{2} \xrightarrow{MO_{2}O_{3}} HCHO + H_{2}O$$

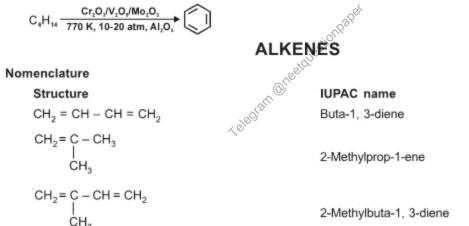
(III) Isomerisation

$$\begin{array}{c} \mathrm{CH_3} - \mathrm{CH_2} - \mathrm{CH_3} - \mathrm{CH_3} \xrightarrow{\quad \text{Anthy. AICl}_3/\mathrm{Conc.HCl} \quad} & \mathrm{CH_3} - \mathrm{CH} - \mathrm{CH_3} \\ & \downarrow & \\ & \mathrm{CH_3} \end{array}$$

(IV) Pyrolysis

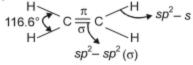
$$\mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_3 \xrightarrow{770 - 970 \mathsf{K} \atop \mathsf{Catalyst}} \mathsf{CH}_3 - \mathsf{CH} = \mathsf{CH}_2 + \mathsf{CH}_2 = \mathsf{CH}_2 + \mathsf{CH}_4 + \mathsf{H}_2$$

(V) Aromatisation



Structure of double bond

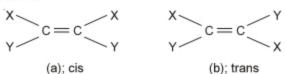
The strength of the double bond (bond energy, 681 kJ mol⁻¹) is greater than that of a carbon-carbon single bond in ethane (bond energy, 348 kJ mol⁻¹)



Structure of ethene

Geometrical isomerism

If the two atoms or groups attached to each doubly bonded carbon atoms are different, they can be represented in space as:



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(a) and (b) are geometrical isomers to each other having the same structure but different configuration

Preparation of alkene

(I) By dehydrohalogenation of Alkyl Halide (β-elimination)

$$\mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CI} \xrightarrow{\mathsf{Alcoholic}\,\mathsf{KOH}} \mathsf{CH}_2 = \mathsf{CH}_2$$

(II) By dehydration of Alcohol (β-elimination)

$$CH_3 - CH_2 - OH \xrightarrow{Conc. H_2SO_4} CH_2 = CH_2$$

(III) By dehalogenation of Dihalides

$$CH_2 - CI$$
 $CH_2 - CI$
 $CH_2 - CI$
 $CH_2 = CH_2$

(IV) By Partial Hydrogenation of Alkynes

$$R - C \equiv C - R \xrightarrow{H_2(Pd + BaSO_4)} \xrightarrow{R} C = C \xrightarrow{R} Cis - alkene$$

$$R - C \equiv C - R \xrightarrow{Na/liq. NH_3} \xrightarrow{R} C = C \xrightarrow{R} Trans-alkene$$

(V) Kolbe's Electrolytic Method

Physical properties of Alkenes

The first three members are gases, next fourteen are liquids and the higher ones are solids. They show a regular increase in boiling point with increase in size. Every -CH₂ group added increases boiling point by 20–30 K.

Chemical Properties: Alkenes undergo electrophilic addition reactions.

Mechanism:

Reaction:
$$CH_3-CH = CH_2 + HBr \longrightarrow H_3C-CH-CH$$
Br

Step-1: $H_3C-CH = CH_2 + H^9 \longrightarrow H_3C-CH-CH_3$

Markovnikov rule: During the electrophilic addition to alkene, the most stable product is formed via most stable carbocation.

e.g., (i)
$$H_3C-CH = C - CH_3 \xrightarrow{HBr} H_3C-CH_2 - C - CH_3$$

Br

$$CH_3 \xrightarrow{HBr} H_3C-CH_2 - C - CH_3$$

$$(ii) CH_3-C-CH = CH_2 \xrightarrow{HBr} H_3C-C-CH_2 - CH_3$$

$$H \xrightarrow{Br} (Major)$$
Chemical reactions of Alkene

$$\begin{array}{c} \text{NiH}_{5} \\ \text{525-575K} \\ \text{X,} \\ \text{In CS}_{1} \\ \text{HS} \\ \text{HIS + HBr > HCI} \\ \text{HOX} \\ \text{HO - CH}_{2} - \text{CH}_{2} \\ \text{CH}_{3} - \text{CH}_{2} - \text{X} \\ \text{HSO}_{1} \\ \text{ON - CH}_{2} - \text{CH}_{2} - \text{CI} \\ \text{Cold sik. KMnO}_{2} \\ \text{Bayers reagent} \\ \text{or OSO}_{2}, Na, SO, H_{2}O \\ \text{ON - CH}_{2} - \text{CH}_{2} - \text{OH} \\ \text{OSO}_{3}, Na, SO, H_{4}O \\ \text{Or Paracid, } \Delta \\ \text{(RCOOOH)} \\ \text{(I) O}_{4} \\ \text{(II) Zn/H_{2}O, CH_{2}CH_{2}} \\ \text{O}_{5} \Delta \\ \text{O}_{7} \text{CH}_{2} - \text{CH}_{2} \\ \text{O}_{7} \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} - \text{OH} \\ \text{(Anti addition of CH}_{2} - \text{OH} \\ \text{CH}_{2} - \text{OH} \\ \text{OH}_{2} - \text{CH}_{2} - \text{OH} \\ \text{OH}_{3} - \text{OH}_{2} - \text{OH} \\ \text{OH}_{3} - \text{CH}_{2} - \text{OH} \\ \text{ON GIVEN Pressure} \\ \text{ON OCCUPAL, IN CHARCH PROBLEM PROB$$

ALKYNES

Nomenclature

Structure

$$H_3C - CH - C \equiv CH$$

 CH_3

$$\begin{aligned} \text{HC} &\equiv \text{C} - \overset{\text{CH}_3}{\text{C}} \\ &\downarrow \\ &\text{CH}_3 \end{aligned}$$

$$CH_3 - C \equiv C - CH - CH_3$$

 CH_3

IUPAC name

3-Methylbut-1-yne

4-Methylpent-2-yne

Structure of Triple bond

The strength of $C \equiv C$ bond (bond energy, 823 kJ mol⁻¹) is more than those of $C \equiv C$ bond and C - C bond.

$$\begin{array}{c}
H - C = \frac{\pi}{\pi} C + H \\
sp - sp(\sigma) & sp - s(\sigma)
\end{array}$$

Both π -bonds are mutually perpendicular to each other. Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule.

Preparation of Alkyne

(I) Hydrolysis of Carbides

$$CaC_2 \xrightarrow{H_2O} CH = CH$$

 $Mg_2C_3 \xrightarrow{H_2O} CH_3 - C = CH$

(II) Dehydrohalogenation of Dihalide (β-elimination)

$$CH_2Br - CH_2Br \xrightarrow{Alc. KOH} CH \equiv CH$$

(III) Dehalogenation of Tetrahalide

$$CHBr_2 - CHBr_2 \xrightarrow{Zn} CH \equiv CH$$

(IV) From Alkyl Halide

$$R - C = CNa + X - R \rightarrow R - C = C - R$$

(V) Kolbe's Electrolytic Method

$$\begin{array}{c} H-C-COOK \\ II \\ H-C-COOK \end{array} (aq) \xrightarrow{Electrolysis} CH \equiv CH$$

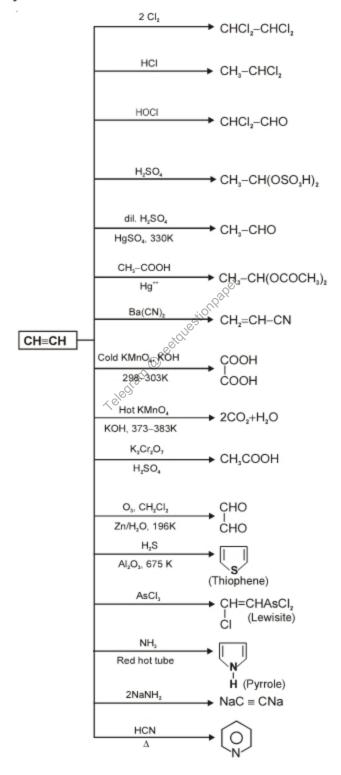
(VI)
$$2C + H_2 \xrightarrow{\text{Electric arc}} CH \equiv CH$$

NEET Hydrocarbons 21

Physical properties of Alkynes

First three members are gases, the next eight are liquids and the higher ones are solids. Except ethyne all alkynes are odourless. Alkynes are weakly polar in nature and soluble in organic solvents.

Chemical reactions of Alkynes



Aromatic Hydrocarbon

Benzene ring is highly unsaturated but in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids.

IUPAC Nomenclature

Aromaticity

Huckel's rule states that a planar, conjugated cyclic system containing (4n + 2)π e should be aromatic. Where n is an integer. Alternately, a compound is said to be aromatic if

- Ring is planar
- There is complete delocalisation of π -electrons which is only possible if it is a conjugated cyclic system (ii)
- Number of electrons used in delocalisation = (4n + 2) (lone pairs may be used) (n = 0, 1, 2,)



Antiaromatic compounds

A compound is said to be antiaromatic if

- Ring is planar (i)
- There is complete delocalisation of conjugated electrons
- Number of electrons used in delocalisation is $4n \pi e$, where n = 1, 2, 3, 4, 5...etc.

Among cyclic compounds aromatic compounds are the most stable and antiaromatic compounds are the least stable.

Preparation of Benzene

1.
$$3CH = CH$$
 Red hot Iron tube

2. NaOH

CI

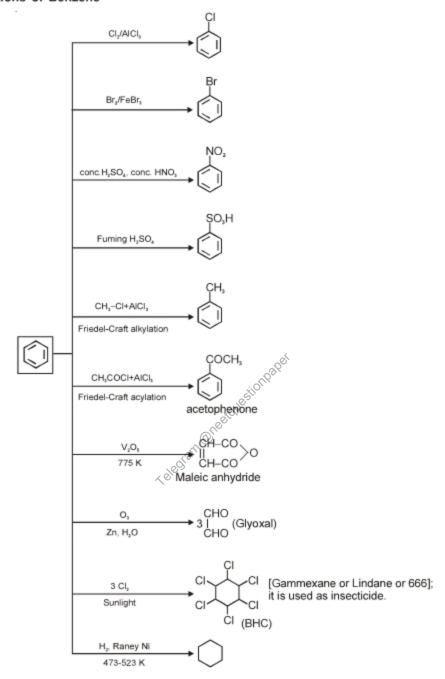
3. $\frac{NaOH}{CaO, \Delta}$

4. Ni - Al Alloy
NaOH

No H₃PO

No H₃

Chemical reactions of Benzene



Directive influence of a functional group in monosubstituted benzene

Ortho and para directing group: The group which directs the incoming group to ortho and para positions are called ortho and para directing groups.

$$e.g., - \operatorname{NH}_2, -\operatorname{NHR}, - \operatorname{OH}, -\operatorname{OCH}_3, -\operatorname{NHCOCH}_3, -\operatorname{CH}_3, -\operatorname{C}_2\operatorname{H}_5 \text{ etc.}$$

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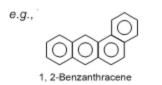
24 Hydrocarbons NEET

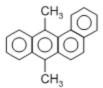
Meta directing group: The group which directs the incoming group to meta position are called meta directing groups.

$$e.g.,\,-\mathrm{NO}_2,\,-\mathrm{CN},\,-\mathrm{CHO},\,-\mathrm{COR},\,-\,\mathrm{COOH},\,-\mathrm{COOR},\,-\mathrm{SO}_3\mathrm{H}\,\,\mathrm{etc}.$$

Carcinogenicity and toxicity

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and possess cancer producing property.





9, 10-Dimethyl-1, 2-benzanthracene





Try Yourself

SECTION - A

Objective Type Questions

- 1. Methane can be obtained when
 - (1) Sodium acetate is heated with soda lime
 - (2) Iodomethane is reduced
 - (3) Aluminium carbide reacts with water
 - (4) All of these
- Halogenation of alkane takes place through the intermediate
 - (1) Carbocation
- (2) Carbanion
- (3) Free radical
- (4) Carbene
- 3. Which of the following reagent is used for converting butanoic acid to butane?
 - (1) HI/P
- (2) LiAlH_a
- (3) Both (1) & (2)
- (4) Zn Hg/HCl
- 4. In following reaction [A] will be

- Gillmann reagent
- (2) Jones reagent
- (3) Fenton reagent
- (4) Tollen's Reagent
- 5. Product [P] in the following reaction will be

$$\mathsf{CH_3} - (\mathsf{CH_2})_4 - \mathsf{CH_3} \xrightarrow{\quad \mathsf{Cr_2O_3} \quad } \mathsf{FR}_{2\mathsf{O_3}} = \mathsf{FR}_{2\mathsf{O_3}} + \mathsf{CH_3} = \mathsf{CH_3} - \mathsf{CH_3} = \mathsf{CH_3} - \mathsf{CH_3} = \mathsf{CH_3}$$

- (1) Benzene
- (2) Toluene
- (3) Napthalene
- (4) Anthracene
- 6. Which of the following has highest boiling point?
 - (1) Neopentane
- (2) n-pentane
- (3) n-hexane
- (4) Isobutane
- A reaction between methyl magnesium bromide and ethyl alcohol gives
 - (1) Methane
- (2) Ethane
- (3) Propane
- (4) Butane
- An alkyl halide reacts with sodium in dry ether the reaction is called
 - (1) Frankland's reaction (2) Sandmeyer's reaction
 - (3) Wurtz reaction
- (4) Kolbe's reaction

- If two different alkyl halides (1°) are taken in Wurtz reaction then number of alkanes that can be obtained would be
 - (1) 3

(2) 4

(3) 2

- (4) 1
- 10. Which of the following compounds is insoluble even in warmed concentrated H₂SO₄?
 - (1) Ethylene
- (2) Benzene
- (3) Methane
- (4) Aniline
- 11. Cis-2-butene on reaction with Br₂ + CCI₄ gives which of the following product?
 - (1) Racemic-2, 3-dibromo butane
 - (2) Meso-2, 3-dibromo butane
 - (3) But-2-yne
 - (4) 1,4-dibromobutane
- Arrange the following compounds according to decreasing order of stability
 - (I) CH₂=CH-CH₂-CH=CH₂
 - (II) CH2=CH-CH=CH2
 - (III) CH2=C=CH2
 - (1) || > | > ||
- (2) | > || > ||
- (3) | | | > | | > |
- (4) | | | > | > | |

Product of the reaction is

- (3) Mixture of (1) & (2) (4)
- (4) O CH

- Cold dilute alkaline KMnO₄ at room temperature reacts with R-CH=CH-R to give
 - (1) R-CHO
- (2) R-COOH
- (3) R-CH-CH-R
- (4) CO₂+H₂O
- During debromination of meso-2, 3-di bromo butane, the major product formed is
 - (1) n-butane
- (2) 1-butene
- (3) Cis-2-butene
- (4) Trans-2-butene
- A hydrocarbon of formula C₆H₁₀ absorbs only one molecule of H₂ upon catalytic hydrogenation, upon reductive ozonolysis the hydrocarbon yields

OHC-(CH2)4-CHO, the compound is

- (1) Cyclohexene
- (2) Cyclohexane
- (3) Benzene
- (4) Cyclobutane
- 17. Which of the following give cis diols?

- (3) Both (1) & (2)
- (4) CH₃CO₃H/H₃O+
- 18. An alkene may be converted into alcohol by
 - (1) B₂H₆ and H₂O₂/OH
 - (2) LiAlH
 - (3) NaBH,
 - (4) Hot and acidic KMnO₄
- The predominant product formed, when 3-methyl-2-pentene react with HOCI

- Position of double bond in an organic compound is determined by
 - (1) Ozonolysis
- (2) Addition of Cl₂
- (3) Hydrogenation
- (4) All of these
- Arrange the following hydrocarbons according to their decreasing order of C–C bond length

22. Product [P] in the following reaction is

(1)
$$(H_3 (OAc)_2, H_2O)$$
 $(III) Na BH_4$
(2) $(H_3 OH)$
 $(H_3 OH$

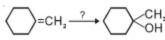
The product of following reaction is

- 24. Addition of bromine to 1, 3-butadiene gives
 - 1, 2 addition product only
 - 1, 4 addition product only
 - (3) 1, 2 and 1, 4 addition products but major is 1, 4 addition product in ionising solvent
 - (4) 1, 3 addition product

- The hydrocarbon obtain is
- (1) Ethene
- (2) Propene
- (3) Propane
- (4) Propyne
- Acetylene contains same degree of unsaturation as

25. On electrolysis of potassium succinate solution.

- Which reagent is used to bring about the following conversion?



- (1) KMnO₄/H₂O
- (2) H,O/H
- (3) OsO₄
- (4) CH₂-COOOH
- Which of the following is aromatic?





- 29. 1, 1, 2, 2 tetra bromo ethane on heating with Zn dust gives
 - (1) Ethyl bromide
- (2) Ethane
- (3) Ethene
- (4) Ethyne
- 30. In the following reaction [B] will be

$$CH \equiv CH \xrightarrow{2NaNH_2} [A] \xrightarrow{2CH_3-CI} [$$

- Butyne-2
- (2) Butyne-1
- (3) Butane
- (4) Ethane
- Structural formula for lewisite is
 - CHCI CH As CI,
- CH-CI CH As CI

- 32. $CH_3 C \equiv C CH_3 \xrightarrow{[X]}$

What is X?

- (1) H₂ + Pd/BaSO₄
- (2) Na + liq.NH₃
- (3) Ni₂B
- (4) H₂ + Pd
- 33. What is the end products of the following sequences of operations?

$$\text{CaC}_2 \xrightarrow{\text{H}_2\text{O}} [\text{A}] \xrightarrow{\text{dil } \text{H}_2\text{SO}_4} [\text{B}] \xrightarrow{\text{Ni/H}_2} [\text{C}]$$

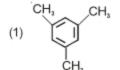
- (1) CH₃–OH
- (2) CH₃-CH₂-CHO
- (3) CH₃-CHO
- (4) C₂H_EOH

In the reaction

 $[X] + 2NH_4NO_3 + 2H_2O, [X]$ is

- (1) Ag₂C
- (2) Ag₂C₂
- (3) AgC
- (4) AgOH
- Which of the following alkynes gives oxalic acid on oxidation with Baeyer reagent?
 - (1) CH₃-C=CH
- (2) CH=CH
- (3) CH₃-CH₂-C≡CH
- (4) All of these
- Acetylene on heating with NH₂ gives
 - (1) CH2=CH-NH2
- (2) NH₂-CH=CH-NH₂
- (3) CH=C-NH₂
- (4) Pyrrole
- 37. Which of the following reactions will yield 2, 2-dibromopropane?
 - CH≡CH + 2HBr
- (2) CH₃ CH = CH₂+ HBr
- (3) CH₃-C≡CH + 2HBr
- (4) CH₃-CH=CHBr + HBr
- Oxidative ozonolysis of

- (1) CH,-CH-COOH+CH,-COOH
- (2) CH,-CH-CHO+CH,-CHO
- -ÇН−СНО+СН,-СООН
- (4) CH,-CH,-CH-COOH ĊН,
- Calcium carbide on reaction with water gives
 - Methane
- (2) Ethane
- (3) Ethene
- (4) Acetylene
- Which of the following does not give white precipitate with ammonical AgNO₃?
 - CH=CH
- (2) CH₂−C≡CH
- (3) CI–CH₂–C≡CH
- (4) CH₂-C≡C-CH₂
- 41. Product [P] will be







- Which of the following is a deactivating group for electrophilic substitution reaction in aromatic compound?
 - (1) -NHR
- (2) -OH
- (3) -OR
- (4) –COOH
- 43. Which of the following group is o and p directing towards electrophilic aromatic substitution reaction?
 - (1) -NO₂
- (2) -CH₃
- (3) –CI
- (4) Both (2) & (3)
- 44. When benzene is treated with V2O5 at 775 K product will be
 - (1) Aniline
- (2) Naphthalene
- (3) Phenol
- (4) Maleic anhydride
- Which of the following is aromatic?





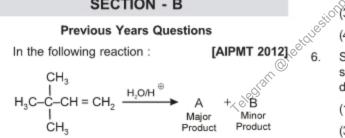




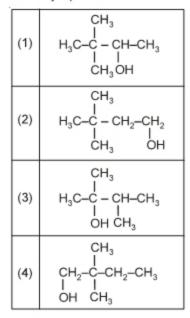
SECTION - B

Previous Years Questions

In the following reaction:



The major product is



2. Among the following compounds the one that is most reactive towards electrophilic nitration is

[AIPMT 2012]

- (1) Toluene
- (2) Benzene
- (3) Benzoic Acid
- (4) Nitrobenzene
- 3. Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne?

[AIPMT 2012]

- NaNH₂
- (2) HCI
- (4) Br₂
- Which of the following compounds will not undergo Friedal-Craft's reaction easily? [NEET 2013]
 - Xylene
- (2) Nitrobenzene
- (3) Toluene
- (4) Cumene
- CH₂ is aromatic because it The radical, has [NEET 2013]
 - 7 p-orbitals and 6 unpaired electrons
 - (2) 07 p-orbitals and 7 unpaired electrons
 - 6 p-orbitals and 7 unpaired electrons
 - (4) 6 p-orbitals and 1 unpaired electron
 - Some meta-directing substituents in aromatic substitution are given. Which one is most deactivating? [NEET 2013]
 - (1) —SO₃H
- (2) -COOH
- (3) —NO₂
- (4) -C = N
- In the reaction with HCI, an alkene reacts in 7. accordance with the Markovnikov's rule, to give a product 1-chloro-1-methylcyclohexane. The possible alkene is [Re-AIPMT-2015]

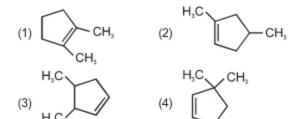




- (3) (1) and (2)
- A single compound of the structure

is obtainable from ozonolysis of which of the following cyclic compounds? [AIPMT-2015]

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- 9. The reaction of C₆H₅CH = CHCH₃ with HBr [AIPMT-2015] produces
 - CH = CHCH,
- The correct statement regarding the comparison of staggered and eclipsed conformations of ethane is

[NEET-2016]

- The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
- (2) The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain
- (3) The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain
- (4) The eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
- In the reaction

$$H-C \equiv CH - \frac{(1) \ NaNH_2/liq. \ NH_3}{(2) \ CH_3CH_2Br} \rightarrow X - \frac{(1) \ NaNH_2/liq. \ NH_3}{(2) \ CH_2CH_2Br} \rightarrow Y$$

X and Y are

[NEET-2016]

- X = 1-Butyne; Y = 2-Hexyne
- (2) X = 1-Butyne; Y = 3-Hexyne
- (3) X = 2-Butyne; Y = 3-Hexyne
- (4) X = 2-Butyne; Y = 2-Hexyne
- 12. Consider the nitration of benzene using mixed conc. H2SO4 and HNO3. If a large amount of KHSO4 is added to the mixture, the rate of nitration will be [NEET-2016]
 - Doubled
 - (2) Faster
 - (3) Slower
 - (4) Unchanged

13. Which of the following can be used as the halide component for Friedel Crafts reaction?

[NEET (Phase-2) 2016]

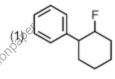
- Chlorobenzene
- (2) Bromobenzene
- (3) Chloroethene
- (4) Isopropyl chloride
- 14. Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction?

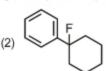
[NEET (Phase-2) 2016]

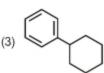
- In the given reaction

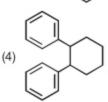
the product P is

[NEET (Phase-2) 2016]









The compound that will react most readily with gaseous bromine has the formula

[NEET (Phase-2) 2016]

- (1) C₃H₆
- (2) C₂H₂
- (3) C₄H₁₀
- (4) C₂H₄
- 17. Predict the correct intermediate and product in the following reaction

$$H_3C - C = CH \xrightarrow{H_2O, H_2SO_4} \text{ intermediate} \longrightarrow \text{product}$$

18. Which one is the correct order of acidity?

[NEET-2017]

(3)
$$CH = CH > CH_2 = CH_2 > CH_3 - C = CH > CH_3 - CH_3$$

(4)
$$CH_3 - CH_3 > CH_2 = CH_2 > CH_3 - C = CH > CH = CH$$

- With respect to the conformers of ethane, which of the following statements is true? [NEET-2017]
 - Bond angle remains same but bond length changes
 - (2) Bond angle changes but bond length remains same
 - (3) Both bond angle and bond length change
 - (4) Both bond angles and bond length remains same
- Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. (A) is [NEET-2018]
 - (1) CH = CH
- (2) CH₂ = CH₂
- (3) CH₄
- (4) CH₃ CH₃
- The compound C₇H₈ undergoes the following reactions:

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCe} C$$

The product 'C' is

[NEET-2018]

- (1) m-bromotoluene
- (2) o-bromotoluene
- (3) p-bromotoluene
- (4) 3-bromo-2,4,6-trichlorotoluene
- 22. Which of the following molecules represents the order of hybridisation sp², sp², sp, sp from left to right atoms? [NEET-2018]
 - (1) HC = C C = CH
 - (2) $CH_2 = CH C \equiv CH$
 - (3) CH₃ CH = CH CH₃
 - (4) CH2 = CH CH = CH2
- The most suitable reagent for the following conversion, is

$$H_3C-C\equiv C-CH_3 \longrightarrow H_{cis-2-butene} \xrightarrow{CH_3} H_{cis-2-butene}$$
[NEET-2019]

(1) Na/liquid NH₃

- (2) H2, Pd/C, quinoline
- (3) Zn/HCl
- (4) Hg²⁺/H⁺, H₂O
- Among the following, the reaction that proceeds through an electrophilic substitution, is

[NEET-2019]

(1)
$$N_2CI^- \xrightarrow{Cu_2Cl_2} CI + N_2$$

(2)
$$\longleftrightarrow$$
 + $Cl_2 \xrightarrow{AICl_3} \longleftrightarrow$ $CI + HCI$

(3)
$$\longrightarrow$$
 + $Cl_2 \xrightarrow{UV \text{ light}} Cl \longrightarrow Cl$

(4)
$$CH_2OH + HCI \xrightarrow{heat} CH_2CI + H_2O$$

25. An alkene "A" on reaction with O₃ and Zn-H₂O gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene "A" gives "B" as the major product. The structure of product "B" is

[NEET-2019]

$$\begin{array}{c} \mathsf{CH_3} \\ \mathsf{I} \\ \mathsf{(1)} \\ \mathsf{CI-CH_2-CH_2-CH} \\ \mathsf{I} \\ \mathsf{CH_3} \end{array}$$

26. In the following reaction,

 $H_3C-C \equiv CH \xrightarrow{\text{red hot iron tube}} A$, the number of sigma (σ) bonds present in the product A, is

[NEET-2019 (Odisha)]

- (1) 18
- (2) 21
- (3) 9
- (4) 24

Chapter 3

Haloalkanes and Haloarenes

Sub-topics

Haloalkanes: Nomenclature, nature of C –X bond, physical and chemical properties, mechanism of substitution reactions. Optical rotation. Haloarenes: Nature of C-X bond, substitution reactions (directive influence of halogen for monosubstituted compounds only). Uses and environment effects of – dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

HALOALKANES

Nomenclature

	O.,	
Compound	Common name tert-butylbromide Allyl bromide	IUPAC name
(CH ₃) ₃ CBr	tert-butylbromide	2-Bromo-2-methylpropane
CH ₂ =CHCH ₂ Br	Allyl bromide	3-Bromopropene
CH ₂ CI	Benzyl chloride	Chlorophenyl methane
H ₃ C-CHCl ₂	Ethylidene chloride	1, 1-Dichloroethane

Nature of C-X Bond

The carbon-halogen bond of alkyl halide is polarised. The carbon-halogen bond length increases from C-F to C-I.

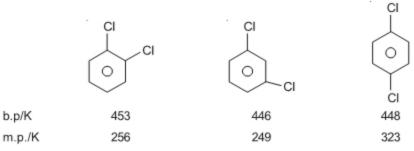
Bond	Bond length	C-X bond energy (kJ mol ⁻¹)	Dipole moment/debye
CH ₃ -F	139	452	1.847
CH ₃ -CI	178	351	1.860
CH ₃ -Br	193	293	1.830
CH ₃ -I	214	234	1.636

Physical Properties

The boiling points of isomeric haloalkanes decrease with increase in branching

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The boiling points of isomeric dihalobenzenes are nearly the same. However, the para-isomer has high melting point as compared to its ortho- and meta-isomers.



Preparation of Haloalkanes

(I) From Alcohol

- (a) $R OH \xrightarrow{Anhy.ZnCl_2} R CI$ [3° \rightarrow instant reaction, 2° \rightarrow take 2-5 minutes, 1° \rightarrow react on heating]
- (b) R-OH-PCI₅→R-CI
- (c) R OH SOCI₂ → R CI [Darzen reaction, best for 1° alcohols, best method for alkyl chloride]
- (d) $R OH \xrightarrow{PBr_3} R Br$

(II) From Alkene

(a)
$$CH_2 = CH_2 \xrightarrow{HX} CH_3 - CH_2 - X$$

(c)
$$CH_3 - CH = CH_2 \xrightarrow{Organic peroxide} CH_3 - CH_2 - CH_2 - Br$$
 [Kharasch effect]

(d)
$$CH_3-CH=CH-CH_3 \xrightarrow{Br_2} \xrightarrow{H-C-Br} \xrightarrow{H-C-Br} CH_3 \text{ (meso)}$$

$$CH_3-CH=CH-CH_3 \xrightarrow{Br_2} \xrightarrow{H-C-Br} \xrightarrow{H-$$

The addition of Br₂ is always anti addition.

(III) From Silver Salt

$$R - COOAg \xrightarrow{Br_2} R - Br + CO_2 + AgX$$
 (Hunsdiecker's reaction)

This reaction follows free radical mechanism and used for the preparation of alkyl bromides.

- For alkyl chloride yield is less
- RCOOAg
 ¹/_{bw}→RCOOR + AgI + CO₂ [Birnbaum Simonini reaction]

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(V) Swarts Reaction

$$R - CI \xrightarrow{Hg_2F_2} R - F$$

Optical rotation

When a compound rotates the plane polarized light, is said to be optically active.

The objects which are non-superimposable on their mirror images are called chiral and this property is known as **chirality**.

The sufficient and necessary condition for a compound to be optically active is chirality.

The carbon atom bearing all four different group is said to be asymmetric carbon. If a compound contains only one chiral carbon atom, it must be optically active.

The optically active compound which rotates the plane of polarized light towards right is known as **dextrorotatory** (d or +) and that rotates the plane polarized light left is known as **laevorotatory** (l or -)

Optically active compounds which are none superimposable mirror images to each other are called **enantiomers** e.g. (+) Lactic acid and (–) Lactic acid are enantiomers to each other.

Equimolar mixture of enantiomers is known as **racemic mixture** (± or dl). It is optically inactive due to external compensation.

Chemical Properties

The alkyl halides are extremely important reagants because they undergo a large variety of reactions that make them valuable in organic synthesis. This arises from the fact that the halide ion is a weak base and is readily displaced by stronger bases. The order of ease of displacement of the groups is not fixed; it depends on the nature of the R- group and on the conditions of the solvent. However it appears that, in general, the order is I > Br > CI > F.

The order of nucleophilicity (nucleophilic reactivity) is also dependent on the nature of the solvent and, in

general, follows the order: I > Br > CI > F

Mechanism of Nucleophilic Substitution Reactions Mechanism of S_N1 reaction

Reaction :
$$H_3C-C-Br \xrightarrow{\overset{\bullet}{\longrightarrow}} H_3C-C-OH$$

Step-1:
$$H_3C-C-Br \xrightarrow{Slow} H_3C-C\oplus + Br^{(-)}$$

$$H \xrightarrow{C_2H_5} H_3C-C\oplus + Br^{(-)}$$
Step-2: $H_3C-C^{(-)} \xrightarrow{fast} H_3C-C-OH$

Rate determining step involves formation of carbocation, which may rearrange to produce more stable product.

Mechanism of S_N2

Reaction

$$\begin{array}{c|c} CH, & \vdots \\ -Br & \vdots \\ H,C & CH, \\ H,C & CH, \\ -OH & H\\ \end{array}$$

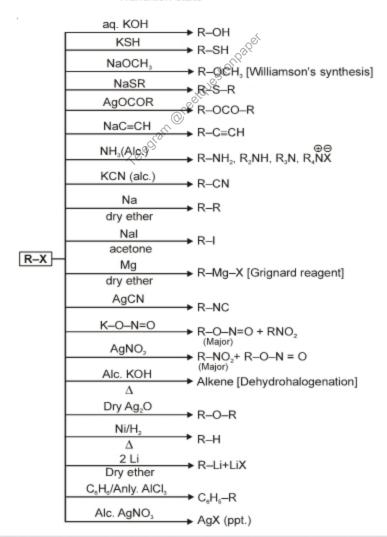
Mechanism

$$\begin{array}{c} CH_3 \\ \downarrow \\ H_3C \end{array} \xrightarrow{\vdots \overrightarrow{O}H} \begin{bmatrix} CH_3 \\ \downarrow \\ H_3C \end{array} \xrightarrow{Br} \begin{bmatrix} CH_3 \\ \downarrow \\ H_3C \end{array} \xrightarrow{H} \begin{bmatrix} CH_3 \\ \downarrow \\ H_3C \end{bmatrix} \xrightarrow{H} \begin{bmatrix} CH_3 \\ \downarrow \\ HO \end{bmatrix}$$

$$\begin{array}{c} CH_3 \\ \downarrow \\ HO \end{array} \xrightarrow{CH_3} \begin{bmatrix} CH_3 \\ \downarrow \\ CH_3 \end{bmatrix}$$

$$\begin{array}{c} CH_3 \\ \downarrow \\ HO \end{array} \xrightarrow{CH_3} \begin{bmatrix} CH_3 \\ \downarrow \\ CH_3 \end{bmatrix}$$

$$\begin{array}{c} CH_3 \\ \downarrow \\ CH_3 \end{array}$$

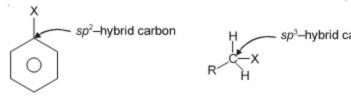


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HALOARENES

Nature of C-X bond

In case of haloarene, the carbon atom attached to halogen is sp^2 -hybridised, the sp^2 -hybridized carbon with greater s-character is more electronegative and can hold the electron-pair of C-X bond more tightly in comparison to the C-X bond in haloalkanes. Also C-X bond has partial double bond character due to resonance. Thus haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.



Preparation of Haloarenes

(I) From Benzene Diazonium Salt

(c)
$$C_6H_5N_2CI \xrightarrow{Cu/HCI} C_6H_6-CI$$

(d)
$$C_6H_6N_2\bar{C}I \xrightarrow{Cu/HBr} C_6H_6-Br$$
 [(c) & (d) are Gattermann reactions]

(e)
$$C_{\epsilon}H_{\epsilon}\overset{+}{N_{2}}\overset{-}{C}I \xrightarrow{\kappa_{I}} C_{\epsilon}H_{\epsilon}-I$$

(f)
$$C_{\epsilon}H_{s}\overset{+}{N_{2}CI} \xrightarrow{HBF_{4}} C_{\epsilon}H_{s}-F$$
 (Balz Schiemann Reaction)

(II) From Direct Halogenation of Benzene:

These reactions are electrophilic aromatic substitution reactions.

(a)
$$C_6H_6 \xrightarrow{CI_2/AICI_3} C_6H_5 - CI$$

(b)
$$C_6H_6 \xrightarrow{Br_2/FeBr_3} C_6H_5 - Br$$

(c)
$$C_6H_6 \xrightarrow{I_2/HIO_3} C_6H_5 -I$$

(III) Borodine Hunsdiecker Reaction:

Bromobenzene can be best prepared by this method

(a)
$$C_6H_5COOAg \frac{X_2}{X=CLBrA} C_6H_5 - X + AgX + CO_2$$

(b)
$$2C_6H_6 + 2HCI \xrightarrow{O_2} 2C_6H_5 - CI + 2H_2O$$
 (Raschig process)

Raschig process is used for industrial preparation of chlorobenzene.

36 Haloalkanes and Haloarenes NEET

Reactions of Holoarenes

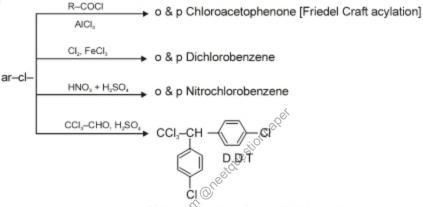
Nucleophilic substitution reaction

Haloarenes are resonance stabilized molecule hence substitution of halogen with other nucleophile is difficult and its takes place only under drastic conditions.

Presence of EWG such as -NO2, -CN at ortho and para positions increases the rate of substitution.

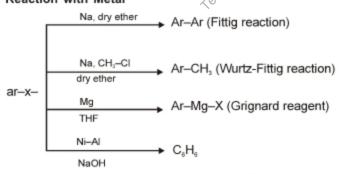
II. Electrophilic Aromatic Substitution Reaction

Halogens are ring deactivating but o, p-directing group hence substitution takes place at o and p positions



2, 2-Bis(p-chlorophenyl)-1, 1, 1-tricloroethane

III. Reaction with Metal



Uses and environmental effect of polyhalogen compounds.

- Dichloromethane (CH,Cl,) is widely used as a solvent, as a paint remover, as a propellent in aerosols.
- Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes
- Chloroform is used as a solvent for fats, alkaloids and other substances.
- The major use of chloroform is in the production of the freon refrigerant R-22.
- Chloroform exposure may cause damage to the lever and to the kidneys.
- Carbon tetrachloride (CCI₄) is used as fire extinguisher.
- CCI, depletes the ozone layer.
- Freon 12 (CCl₂F₂) is the one of the most common freons in industrial use.



Try Yourself

SECTION - A

Objective Type Questions

- 1. Ethylidene bromide is
 - (1) CH₃-CH₂-Br
- (2) Br-CH2-CH2-Br
- (3) CH₃-CHBr₂
- (4) CH₂=CBr₂
- 2. Hybrid state of C attached to X in vinyl halide is
 - (1) sp^3
- (2) sp
- (3) sp
- (4) May be sp3 or sp2
- 3. $CH_3-CH-CH = CH_2 + HBr \xrightarrow{H_2O_2} A$ CH_3 CH_3

What is A?

- 4. Which reagent cannot be used to prepare an alkyl halide from an alcohol?
 - (1) HCl + ZnCl₂
 - (2) PCI₅
 - (3) SOCI₂ + pyridine
 - (4) NaCl
- 5. Which of the following compound can be prepared by electrophilic substitution reaction?

(2) CH₃-CH₂-CH₂CI

6. The major product [P] obtained in the reaction is





- 7. The compound with the highest boiling point is
 - (1) CH₄
- (2) CH₃-CI
- (3) CH₃-F
- (4) CH₃-OH
- 8. Which of the following is correct decreasing order of C-halogen bond length?
 - (1) CH₃-I > CH₃-Br > CH₃-Cl > CH₃-F
 - (2) CH₃-F > CH₃-Br > CH₃-I > CH₃-CI
 - (3) CH₃-CI > CH₃-Br > CH₃-I > CH₃-F
 - (4) CH₃-I > CH₃-CI > CH₃-Br > CH₃-F
- The reaction

$$CH_3-CH=CH-CH_2-X$$
 Y $CH_3-CH-CH=CH_2$ is

an example of

- (1) S_N1 reaction
- (2) S_N2 reaction
- (3) E2 reaction
- (4) E1 reaction

- In polar protic solvent, (CH₃)₂CH–CI reacts with aq. KOH mainly through
 - (1) $S_N 1$
- (2) S_N2
- (3) Both S_N1 & S_N2
- (4) E1
- Most reactive compound towards aq. KOH





- 12. Which of the following compounds will be most easily attacked by an electrophile?
 - (1) CI C
- (2)
- (3) OH
- (4) CH
- Identify [Z] in the following series of reaction

$$CH_3-CH_2-Br \xrightarrow{Alcoholic} [X] \xrightarrow{Br_2} [Y] \xrightarrow{KCN} [Z]$$

- (1) CH₃-CH₂-CN
- (2) CH,-CN
- (3) Br-CH2-CH2-CN
- (4) Br-CH=CH-CN
- Ethyl chloride on heating with silver cyanide forms a compound [X]. The functional isomer of [X] is
 - (1) CH₃-CH₂-NC
- (2) CH₃-CH₂-CN
- (3) CH₃-NH-CH₃
- (4) CH₃-CH₂-NH₂
- Reaction of t-butyl bromide with sodium methoxide produces
 - Isobutane
 - (2) Isobutylene
 - (3) Sodium tert. butoxide
 - (4) Tert butyl methyl ether
- Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations

- X=dil.aq.NaOH, 60°C Y=HBr/acetic acid, 20°C
- (2) X=conc. alcoholic NaOH, 80°C Y=HBr/acetic acid, 20°C
- (3) X=dil.aq.NaOH, 20°C Y=Br₂/CHCl₃, 0°C
- (4) X=conc. alcoholic NaOH, 80°C Y=Br₂/CHCl₃, 0°C
- 17. Which of the following has highest M.P.?
 - (1) o-dichlorobenzene
- (2) m-dichlorobenzene
- (3) p-dichlorobenzene
- (4) All have same M.P.
- 18. Which of the following will be the least reactive towards nucleophilic substitution reaction?
 - (1) CH,(
- (2)
- (3) CH,
- (4) CH₃-CH₂-Cl
- 19 Product [P] in the following reaction is

- (1) CH
- (2)
- (3)
- (4)
- 20. The final product [B] in the following reaction is

- (1)
- (2)
- (3)
- (4)
- Chlorobenzene and benzylchloride can be distinguished by
 - (1) KMnO₄
- (2) Neutral FeCl₂
- (3) aq. KOH + AgNO₃
- (4) Br₂-water

22. The product [P] in the following reaction is

- (1) CH₃-CH₂-OH
- (2) CH₃-CHO
- (3) CH₃-C-C
- CH₂-CH (4) OH OH
- The final product formed upon the hydrolysis of CHCl₃ by aqueous KOH is
 - (1) HCOOH
- (2) HCOOK
- (3) CH₃-OH
- (4) None of these
- 24. The product A and B in the following reaction

- (1) CCI₂F₂ + 2HCI
- (2) CHCl₃ + HCl
- (3) CH2Cl2 + HCl
- (4) None of these
- Least reactive towards Nucleophilic Substitution reaction is



- (2) CH₂=CH-C
- (3) CH₂=CH-CH₂-CI
- (4) CH₂-CH₂-C

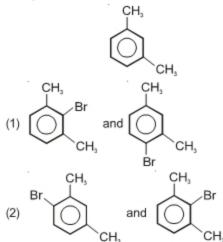
SECTION - B

Previous Years Questions

1. In the replacement reaction

The reaction will be most favourable if M happens to be [AIPMT 2012]

- (1) Na
- (2) K
- (3) Rb
- (4) Li
- What products are formed when the following compound is treated with Br₂ in the presence of FeBr₃? [AIPMT 2014]



- (3) Br CH₃ and CH₃ CH₃

 (4) CH₃ and CH₃

 (4) CH₃ CH₃

 (5) CH₃

 (6) CH₃

 (7) CH₃

 (8) CH₃

 (9) CH₃

 (10) CH₃

 (11) CH₃

 (12) CH₃

 (13) CH₃

 (14) CH₃

 (15) CH₃

 (16) CH₃

 (17) CH₃

 (18) CH₃

 (18
- Two possible stereo-structures of CH₃CHOH.COOH, which are optically active, are called

[Re-AIPMT-2015]

- (1) Enantiomers
- (2) Mesomers
- (3) Diastereomers
- (4) Atropisomers
- In an S_N1 reaction on chiral centres, there is

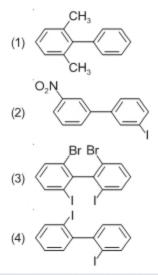
[Re-AIPMT-2015]

- (1) 100% retention
- (2) 100% inversion
- (3) 100% racemization
- (4) Inversion more than retention leading to partial racemization
- In which of the following compounds, the C Cl bond ionisation shall give most stable carbonium ion?

 [AIPMT-2015]

(1)
$$H_3C$$
 H_3C H_3

 Which of the following biphenyl is optically active? [NEET-2016]

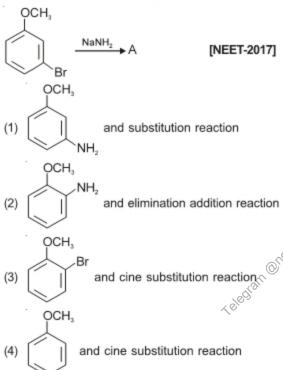


7. Consider the reaction

> CH₂CH₂CH₂Br + NaCN → CH₃CH₂CH₂CN + NaBr This reaction will be the fastest in

> > [NEET (Phase-2) 2016]

- (1) Ethanol
- (2) Methanol
- N, N'-dimethylformamide (DMF)
- (4) Water
- Identify A and predict the type of reaction



The compound C7H8 undergoes the following 9. reactions: [NEET-2018]

$$C_7H_8 {\overset{3Cl_2/\Delta}{\longrightarrow}} A {\overset{Br_2/Fe}{\longrightarrow}} B {\overset{Zn/HCl}{\longrightarrow}} C$$

The product 'C' is

- (1) m-bromotoluene
- o-bromotoluene
- (3) p-bromotoluene
- (4) 3-bromo-2,4,6-trichlorotoluene

10. Among the following, the reaction that proceeds through an electrophilic substitution, is

[NEET-2019]

(3)
$$+ Cl_2 \xrightarrow{\text{UV light}} Cl \xrightarrow{\text{Cl}} Cl$$

(4)
$$CH_2OH + HCI \xrightarrow{heat}$$
 $CH_2CI + H_2O$

- on chlorination with Cl₂ in presence of diffused sunlight is [NEET-2019 (Odial-10)]

 - 2, 2-dimethylbutane
 - (3) Neopentane
 - (4) n-pentane
 - The hydrolysis reaction that takes place at the slowest rate, among the following is

[NEET-2019 (Odisha)]

(1)
$$\sim$$
 CH₂CI $\xrightarrow{\text{aq. NaOH}} \sim$ CH₂OH

- (3) H₃C − CH₂ − CI sq. NaCH → H₃C − CH₂ −OH
- (4) H₂C=CH-CH₂CI aq. NaOH H₂C=CH-CH₂OH

Chapter 4

Alcohols, Phenols and Ethers

Sub-topics

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only); identification of primary, secondary and tertiary alcohols; mechanism of dehydration, uses with special reference to methanol and ethanol. Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols. Ethers: Nomenclature, methods of preparation, physical and chemical properties and its uses.

ALCOHOLS

Nomenclature

Compound	Common name	IUPAC name
CH ₃ - CH - CH ₂ - CH ₃	sec-butyl alcohol	Butan-2-ol
OH CH ₃ - CH - CH ₂ - OH CH ₃ CH ₃	sec-butyl alcohol	2-Methylpropan-1-ol
H ₃ C – C – OH	tert-butyl alcohol	2-Methylpropan-2-ol
CH ₃ HO – CH ₂ – CH – CH ₂ – OH I OH	Glycerol	Propane-1,2,3-triol

Methods of Preparation

From hydrolysis of alkyl halide

$$R-X + aq. KOH \rightarrow R-OH$$

2. From reduction of carbonyl compounds

From reduction of acid, esters, acid halide and anhydride

R-COOH
$$\xrightarrow{\text{(i)} \text{ LiAlH}_4}$$
 R-CH₂-OH

R-COOR' $\xrightarrow{\text{(i)} \text{ LiAlH}_4}$ R-CH₂-OH + R'OH

R-COCI $\xrightarrow{\text{(i)} \text{ LiAlH}_4}$ R-CH₂-OH

O

O

R-COCI $\xrightarrow{\text{(i)} \text{ LiAlH}_4}$ R-CH₂-OH

O

R-COCI $\xrightarrow{\text{(i)} \text{ LiAlH}_4}$ R-CH₂-OH

From reaction of Grignard reagent with carbonyl compound

$$R-MgX + HCHO \xrightarrow{H_2O/H} R-CH_2OH$$

$$O \qquad OH$$

$$R-Mg-X + CH_3-C-CH_3 \xrightarrow{H_2O/H} CH_3-C-CH_3 (3° alcohols)$$

5. From hydration of alkene

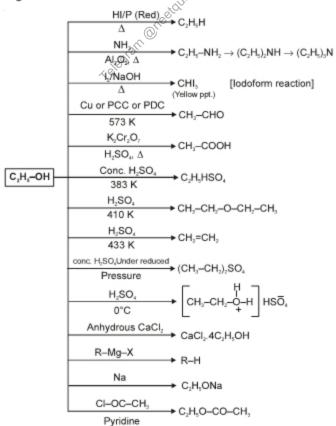
(b)
$$CH_3 - CH = CH_2 \xrightarrow{(1)B_2H_6, H_2O} CH_3 - CH_2 - CH_2 - OH$$
 [Hydroboration oxidation, Anti-markovnikov addition]

R-COOR' + NaOH (aq.) → R-COONa + R'OH [Saponification]

Physical Properties: In alcohols, the boiling point decrease with increase of branching in carbon chain. Boiling points of alcohols are higher in comparison to hydrocarbons, ethers, haloalkanes and haloarenes of comparable masses.

e.g.,	CH₃CH₂OH	$H_3C - O - CH_3$	CH ₃ - CH ₂ - CH ₃
	Ethanol	Methoxymethane	Propane
Molecular mass	46	46	44
Boiling point	351 K	248 K	231 K

Chemical Properties: Alcohols are acidic in nature due to polar O - H bond Alcohols are weaker acid than water except methyl alcohol. Electron donating group decreases the acidic strength while electron withdrawing groups increases the acidic strength 1° alcohol > 2° alcohol > 3° alcohol.



1°, 2°, 3° alcohols can be distinguished by Lucas test.

Uses

- Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.
- Ethanol is used as a solvent in paint industry and in the preparation of a number of carbon compounds.
- The commercial alcohol is made unfit for drinking by mixing in it some CuSO₄ (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

PHENOLS

Nomenclature

Compound	Common name	IUPAC name
CH ₃ OH	o-Cresol	2-Methylphenol
ОН	Catechol	Benzene-1,2-diol
ОН	Resorcinol (included in the control of the control	Benzene-1,3-diol
OH OH	Hydroquinone or quinol	Benzene-1,4-diol

Methods of Preparation

Hydrolysis of benzenediazonium salt

$$\mathsf{C_6H_6N_2CI} \underset{\vartriangle}{\overset{\mathsf{H_2O/H_2SO_4(dil)}}{\longrightarrow}} \mathsf{C_6H_6OH}$$

2. Alkalifusion of benzene sulphonates

$$C_6H_5SO_3H \xrightarrow{NaOH/\Delta} C_6H_5OH$$

From Grignard reagent

$$C_6H_5 - Mg - Br \xrightarrow{O_2} C_6H_5 - OH$$

On Industrial scale it is prepared by

$$\text{(a)} \quad \text{C}_6\text{H}_5 - \text{CH}(\text{CH}_3)_2 \xrightarrow{\text{(ii) O}_2} \text{C}_6\text{H}_5\text{OH} + (\text{CH}_3)_2\text{CO} \ [\text{Cumene process}]$$

(b)
$$C_6H_6 \xrightarrow{O_2,V_2O_5} C_6H_5 - OH$$

(c) $C_6H_5Cl \xrightarrow{NaOH, 300 \text{ atm}} C_6H_5 - OH \text{ (Dow's process)}$

Chemical Properties

Phenols are more acidic than alcohols. pK_a values of some phenols are given below : Electron donating group decreases the acidic strength while electron withdrawing group increases the acidity.

Compound	Formula	pK_a
o-Nitrophenol	$0-O_2N - C_6H_4 - OH$	7.2
m-Nitrophenol	m - O_2N $ C_6H_4$ $ OH$	8.3
p-Nitrophenol	$p-O_2N-C_6H_4-OH$	7.1
Phenol	C ₆ H ₅ OH	10.0
o-Cresol	$\mathrm{o\text{-}CH}_3 - \mathrm{C}_6\mathrm{H}_4 - \mathrm{OH}$	10.2
m-Cresol	m - $CH_3 - C_6H_4 - OH$	10.1
p-Cresol	$\operatorname{p-CH}_3-\operatorname{C}_6\operatorname{H}_4-\operatorname{OH}$	10.2
cidic strength of Acid	∞ 1 pK _a	

Ac 3 Br₂/H₂O 2, 4, 6-tribromophenol (white ppt) FeCI, ▶ [Fe(OC,H₅)₂] Purple colour NaOH C,H,<0H + 82H,<0H Br₂/CS₂ (Ortho) (Para) C,H,COCI C,H,QCOC,H, [Schotten-Baumann reaction] NaOH (aq.) dil. HNO OH + C_cH₄ OH NO₂ (Ortho) (Para) Major (Ortho) Conc. HNO. conc. H₂SO₄ NO₂ (Picric acid) C,H,N,CI C,H,-OH OH [Orange azo dye] CHCl₃, NaOH [Reimer Tiemann reaction] 340K, dil HCI CCI, NaOH 340K, HCI (dil) (i) NaOH, CO2, dil HCl CrO3 or air Phenoquinone

(Pink)

ETHERS

Nomenclature

Compound	IUPAC name
H ₃ COCH ₂ CH ₂ CH ₃	1-Methoxypropane
C ₆ H ₅ OCH ₃	Methoxybenzene (Anisole)
CH ₃ - O - CH ₂ - CH ₂ - OCH ₃	1,2-Dimethoxyethane
H ₃ C CH ₃ OC ₂ H ₅	2-Ethoxy-1,1-dimethylcyclohexane

Methods of Preparation

$$\text{1.} \quad \mathsf{CH_3CH_2OH} \xrightarrow{\quad \mathsf{H_2SO_4} \quad } \mathsf{C_2H_5OC_2H_5}$$

2.
$$RX + RONa \xrightarrow{Williamson} R - O - R + NaX$$

Physical Properties

Boiling Point:

Formula
$$CH_3(CH_2)_3CH_3$$
 $C_2H_5 - OC_2H_5$ $CH_3(CH_2)_3 - OH$ B.P./K 309.1 307.6 390

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

Chemical Properties:

(I) Reaction with hydrogen halide.

Rate: HI > HBr > HCl

(a)
$$R - O - R + HX \longrightarrow RX + R \circ OH$$

(b)
$$R - O - R + HX (excess) \longrightarrow 2RX + H_2O$$

(c)
$$C_6H_5OR + HX \longrightarrow C_6H_5OH + R - X$$

(II) Electrophilic aromatic substitution reaction – OR group is ring activating and o, p-directing group.

(a)
$$OCH_3$$
 OCH_3 OCH_4 OCH_5 OCH_5

(b)
$$CH_3$$
 + CH_3CI $Anhyd. AlCl_3$ CS_2 CH_3 + CH_3 + CH_3 (Minor) CH_3 (Major)

(c)
$$OCH_3$$
 OCH_3 OCH_3



Try Yourself

SECTION - A

Objective Type Questions

- 1. IUPAC name of OH i
 - (1) Carbinol
- (2) 2-hydroxy phenol
- (3) Benzene-1, 2-diol
- (4) o-phenol
- 2. Carbolic acid is
 - (1) Phenol
- (2) Phenyl benzoate
- (3) Phenyl acetate
- (4) Salol
- The oxidation in air of cumene followed by hydrolysis yields
 - (1) OH
- (2) CH₃-C-CH
- СН,-СН-СНС
- (3)
- (4) Both (1) & (2)

Product of the reaction is

- (1) CH₃ CH(CH₃) CH₂ CH₂OH
- (2) CH₃ C CH₂ CH₃
- (3) CH₃ CH₂ CH₂ CH₂ CH₂OH CH₃
- (4) CH₃ C CH₂OH CH₃
- When ethyl alochol is treated with H₂SO₄ at 0°C product will be
 - (1) Ethyl oxonium hydrogen sulphate
 - (2) Diethyl ether
 - (3) Ethyl hydrogen sulphate
 - (4) Ethene

6. What is the correct order of dehydrating tendency in acidic medium of following alcohols?

CH₂-CH₂-CH₂-OH CH₃-CH-CH₃
OH
II

- (1) | > || > |||
- (2) ||| > || > |
- (3) || > | > ||
- (4) ||| > | > ||
- Which is most reactive with HBr?
 - (1) 2-methyl propan-2-ol (2) Propan-1-ol
 - (3) Propan-2-ol
- (4) 2-methyl propan-1-ol
- Decreasing order of reactivity of alcohols towards sodium metal is
 - (1) 1° > 2° > 3°
- (2) 3° > 2° > 1°
- (3) 2° > 1° > 3°
- (4) 2° > 3° > 1°
- 9. Which of the following can work as a dehydrating agent for alcohols?
 - (1) H₂SO₄
- (2) Al₂O₃
- (3) H₃PO₄
- (4) All of these
- Arrange the following alcohols according to decreasing order of reactivity in dehydration reaction (if reaction follows E₁cb mechanism)

- (1) | > | | > | | > | V
- (2) I > II > III > IV
- (3) ||| > | > || > |V
- (4) | | | > | | > | | > |

- (1) IV > III > I > II
- (2) | > || > || > |V
- (3) || > || > | > |V
- (4) |V > || > || > |

- 20. Which of the following is the simple ether?
 - (1) CH₃-O-CH₃
- (2) CH₃-O-C₂H₅
- (3) C₆H₅O-CH₃
- (4) C₆H₅O-C₂H₅
- 21. In ethers the C-O-C bond angle is
 - (1) 180°
- (2) 90°
- (3) 110°
- (4) 160°
- 22. From Willamson's synthesis which of following ethers can be prepared?
 - Only symmetrical ethers
 - (2) Only unsymmetrical ethers
 - (3) Cyclic ether
 - (4) All of these

23.
$$CH_3 - CH_2 - O - C_6H_5 \xrightarrow{HI/\Delta} A + B$$

Product (A) and (B) are

- The O CH₃ group in anisole for an electrophilic aromatic substitution is
 - o-directing
- (2) p—directing
- (3) m-directing
- (4) o & p directing
- 25. Which of the following gives negative iodoform test?
 - CH₃-CH₃-OH
- (2) CH₃-CH₂-CH₂-OH

SECTION - B

Previous Years Questions

In the following sequence of reactions

$$CH_3-Br \xrightarrow{KCN} A \xrightarrow{H_3 \overset{+}{O}} B \xrightarrow{EiAlH_4} C,$$

the end product (C) is

[AIPMT 2012]

- Acetaldehyde
- (2) Ethyl alcohol
- (3) Acetone
- (4) Methane

- Which of the following compounds will give a yellow precipitate with I2 and alkali?
 - CH₃-CHOH-CH₃
 - (2) CH₃-C
 - (4) CH,-C-O-CH,-CH,-CH,
- 12. At room temperature the alcohol that does not react with Lucas reagent is
 - (1) Primary alcohol
- (2) Secondary alcohol
- (3) Tertiary alcohol
- (4) All of these
- Phenol is
 - A weaker acid than H₂O
 - (2) Stronger acid than carbonic acid
 - (3) Weaker acid than carbonic acid
 - (4) Neutral compound
- 14. At low temperature phenol reacts with Br2 in CS2 to form
 - m-bromophenol
- (2) o & p-bromophenol
- (3) p-bromophenol
- (4) 2,4,6-tribromophenol
- Which of the following produce violet colour with neutral FeCl₃ solution?
 - (1) Phenol
- (2) Ethanol
- (3) Ethanal
- (4) Alkyl halides
- Br₂ water reacts with phenol to form
 - 2-bromophenol
- (2) 4-bromophenol
- (3) 2, 4-dibromophenol (4) 2,4,6-tribromophenol
- Which of the following does not give effervescence with NaHCO₃?
 - (1) Phenol
- (2) Benzoic acid
- (3) Acetic Acid
- (4) 2, 4, 6 trinitrophenol
- CHO

Above reaction is known as

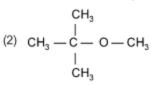
- Kolbe's reaction
- (2) Reimer Tiemann reaction
- (3) Dow's process
- (4) Schmidt reaction
- In the following compounds



Ш

 Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI? [NEET 2013]

(1) CH₃ - CH₂ - CH - O - CH₃



(3) CH₃ - CH - CH₂ - O - CH₃ | CH₃

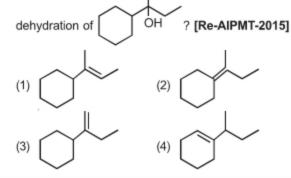
- (4) CH₃—CH₂—CH₂—CH₂—O—CH₃
- Among the following sets of reactants which one produces anisole? [AIPMT 2014]
 - CH₃CHO; RMgX
 - (2) C₆H₅OH; NaOH; CH₃I
 - (3) C₆H₅OH; neutral FeCl₃
 - (4) C₆H₅ CH₃; CH₃COCI; AICI₃
- Which of the following will not be soluble in sodium hydrogen carbonate? [AIPMT 2014]
 - (1) 2,4,6-trinitrophenol
- (2) Benzoic acid
- (3) o-Nitrophenol
- (4) Benzenesulphonic acid
- 5. Identity Z in the sequence of reactions,

 $CH_3CH_2CH = CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$ [AIPMT 2014]

- (1) CH₃ (CH₂)₃ O CH₂CH₃
- (2) (CH₃)₂CH₂ O CH₂CH₃
- (3) CH₃(CH₂)₄ O CH₃
- (4) CH₃CH₂ CH(CH₃) O CH₂CH₃
- 6. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group?

[Re-AIPMT-2015]

- (1) –CHCl₂
- (2) –CHO
- (3) –CH₂CI
- (4) -COOH
- Which of the following is not the product of



- 8. Which of the following reaction(s) can be used for the preparation of alkyl halides?
 - (I) CH₃CH₂OH+HCI anh. ZnCl₂ →
 - (II) CH₃CH₂OH + HCI →
 - (III) (CH₃)₃COH + HCI →
 - (IV) $(CH_3)_2CHOH+HCI \xrightarrow{anh. ZnCl_2}$

[Re-AIPMT-2015]

- (1) (IV) only
- (2) (III) and (IV) only
- (3) (I), (III) and (IV) only (4) (I) and (II) only
- The reaction

is called

[AIPMT-2015]

- (f) Gatterman Koch reaction
- (2) Williamson synthesis
- (3) Williamson continuous etherification process
- (4) Etard reaction
- The reaction

can be classified as

[NEET-2016]

- Williamson alcohol synthesis reaction
- (2) Williamson ether synthesis reaction
- (3) Alcohol formation reaction
- (4) Dehydration reaction
- 11. Which of the following reagents would distinguish cis-cyclopenta-1, 2-diol from the trans-isomer?

[NEET-2016]

- (1) Aluminium isopropoxide
- (2) Acetone
- (3) Ozone
- (4) MnO₂

12. Which one is the most acidic compound?

[NEET-2017]

(4)
$$O_2N \longrightarrow OH NO_2$$

 NO_2

- 13. The heating of phenyl-methyl ethers with HI [NEET-2017]
 - (1) Ethyl chlorides
 - (2) lodobenzene
 - (3) Phenol
 - (4) Benzene
- and with PCl₅ gives C. B and C react together to give diethyl ether. A, B and C are in the order 14. The compound A on treatment with Na gives B,

[NEET 2018]

- (1) C₂H₅OH, C₂H₆, C₂H₅CI
- (2) C₂H₅OH, C₂H₅CI, C₂H₅ONa
- (3) C₂H₅OH, C₂H₅ONa, C₂H₅CI
- (4) C₂H₅Cl, C₂H₆, C₂H₅OH
- 15. In the reaction

[NEET-2018]

The electrophile involved is

- (1) Dichloromethyl cation (⊕HCI₂)
- (2) Formyl cation ([⊕]_{CHO})
- (3) Dichlorocarbene (: CCl₂)
- (4) Dichloromethyl anion (⊕HCI₂)

16. Identify the major products P, Q and R in the following sequence of reactions: [NEET-2018]

+
$$CH_3CH_2CH_2CI \xrightarrow{Anhydrous \\ AlCl_3}$$

P $\xrightarrow{(i) O_2}$ Q + R

R

CH,CH,CH,

The structure of intermediate A in the following reaction, is [NEET-2019]

18. The compound that is most difficult to protonate is:

 The reaction that does not give benzoic acid as the major product is [NEET-2019 (Odisha)]

(1)
$$CH_2OH \xrightarrow{KMnO_4/H^+}$$
(2) $CH_2OH \xrightarrow{K_2Cr_2O_7}$

 The major products C and D formed in the following reaction respectively are

$$\mathsf{H_3C} - \mathsf{CH_2} - \mathsf{CH_2} - \mathsf{O} - \mathsf{C} \big(\mathsf{CH_3}\big)_3 \xrightarrow{-\mathsf{excessH}} \mathsf{C} + \mathsf{D}$$

[NEET-2019 (Odisha)]

- (1) H₃C CH₂ CH₂ OH and HO C(CH₃)₃
- (2) H₃C CH₂ CH₂ I and I C(CH₃)₃
- (3) H₃C CH₂ CH₂ OH and I C(CH₃)₃
- (4) H₃C CH₂ CH₂ I and HO C(CH₃)₃

Chapter 5

Aldehydes, Ketones and Carboxylic Acids

Sub-topics

Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties; and mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes; uses. Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

NOMENCLATURE

Structure	Common name	IUPAC name
НСНО	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
CH ₂ = CHCHO	Acrolein	Prop-2-enal
СНО	Acetaldehyde Acrolein	
СНО	Phthaldehyde	Benzene-1, 2-dicarbaldehyde.
(H ₃ C) ₂ C = CHCOCH ₃	Mesityloxide	4-Methylpent-3-en-2-one

Nature of Carbonyl group

Carbonyl carbon atom is sp^2 -hybridised and forms three sigma bonds and a π - bond with oxygen. The carbonoxygen double bond is polarized due to higher electronegativity of oxygen relative to carbon.

Aldehydes and Ketones

Preparation:

(I) Oxidation of alcohol

(II) Hydrogenation of acid chloride

(III) Dry distillation of calcium salt of acid

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\text{distillation} \\ -CaCO_3} + R - CHO$$

$$(HCOO)_2Ca \xrightarrow{\text{distillation}} + HCHO$$

$$(RCOO)_2Ca \xrightarrow{\text{distillation}} R - C-R$$

(IV) From alkene

$$\begin{split} \mathsf{CH}_2 &= \mathsf{CH}_2 + \mathsf{CO} + \mathsf{H}_2 \xrightarrow{\quad [\mathsf{Co}(\mathsf{CO})_4]_2 \quad} \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CHO} \quad \text{(oxo process)} \\ \mathsf{CH}_2 &= \mathsf{CH}_2 + \mathsf{PdCl}_2 \xrightarrow{\quad \mathsf{H}_2\mathsf{O} \quad} \mathsf{CH}_3 - \mathsf{CHO} \quad \text{(Wacker's method)} \end{split}$$

(V) Aromatic aldehyde

 $C_6H_6 + CO + HCI \xrightarrow{Anhy. \ AlCl_3} C_6H_5 CHO$ (Gatterman Koch Synthesis). In this reaction Electrophile is Formyl Carbocation $[H - C \oplus]$.

 $C_6H_6 + HCN + HCI \xrightarrow{Anhy.\ AlCl_5} C_6H_5CHO$ (Gatterman Aldehyde Synthesis). In this reaction Electrophile is Immine carbocation [H-C=N-H].

(VI) From hydrolysis of dihalide

$$R - CX_2 - R \xrightarrow{\text{aq. NaOH}} R - CO - R$$

Physical Properties

Methanal is a gas at room temperature. Ethanal is a volatile fiquid. Other Aldehydes and ketones are liquid or solid at room temperature. The boiling points of aldehydes and ketones are higher then hydrocarbons and ethers of comparable molecular masses. Also, their boiling points are lower than those of alcohol of similar molecular masses.

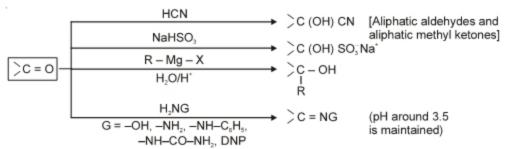
Compound	Molecular mass	B.P. (K)
n-Butane	.58	273
Methoxyethane	60	281
Propanal	58	322
Acetone	58	329
Propan-1-ol	60	370

Chemical Properties: Carbonyl compounds are highly reactive compounds due to C=O group.

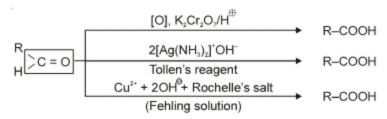
(I) Nucleophilic addition reaction: Aldehydes are more reactive than ketones.

Rate of nucleophilic addition reaction is controlled by given factors.

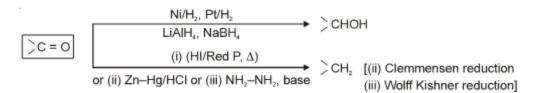
- (a) Steric factor
- (b) Inductive effect



(II) Oxidation reactions: Aldehydes are readily oxidised to carboxylic acid but ketones are oxidised by strong oxidising agents only.



(III) Reduction reaction: Carbonyl compounds can be reduced to alcohol or alkane depending upon the condition.



(IV) Polymerisation

(i) nHCHO ^{373K} → (CH₂O), Paraformaldehyde

(V) Aldol Condensation

Aldehydes and ketones containing α -hydrogen atom undergo condensation reactions in the presence of dilute base, e.g. NaOH, Ba(OH)₂, Ca(OH)₂, K₂CO₃ etc. to form β -hydroxy aldehydes (aldols) and ketones(ketols).

$$\begin{array}{c} \text{OH} \\ \text{CH}_3-\text{CHO}+\text{CH}_3-\text{CHO} \xrightarrow{\text{dil NaOH}} \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CHO} \xrightarrow{\Delta} \\ \text{CH}_3-\text{CH}=\text{CH}-\text{CHO} \\ \text{Crotanaldehyde} \end{array}$$

(VI) Cannizzaro's Reaction

In Cannizzaro reaction, one molecule of the aldehyde (having no α -hydrogen) is oxidised to acid at the expense of the other which is reduced to alcohol. The reaction occurs in the presence of concentrated solution of NaOH.

This reaction is also given by $(CH_3)_2$ CHCHO at 200°C (exception) which has an α -hydrogen.

(VII) Condensation of Acetone

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \\ C = O + H_{2}CH - C - CH_{3} \xrightarrow{dry\ HCl} \xrightarrow{CH_{3}} C = CH - C - CH_{2}O = C \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ C = CH - C - CH = C \\ CH_{3} \\$$

CARBOXYLIC ACIDS



Preparation

(I) From Grignard reagent

$$R - Mg - X \xrightarrow{(i) CO_2} R - COOH$$

(II) Hydrolysis of acid halide/acid amide/cyanides

$$R - COCI \xrightarrow{H_2O/\overset{\circ}{H}} R - COOH$$

$$R - CONH_2 \xrightarrow{H_2O/\overset{\circ}{H}} R - COOH$$

$$R - CN \xrightarrow{H_2O/\overset{\circ}{H}} R - COOH$$

(III) From carbon monoxide

(a)
$$CO + NaOH \xrightarrow{8-10 \text{ atm}} HCOONa \xrightarrow{HCI} HCOOH$$

(b)
$$\text{CH}_2 = \text{CH}_2 + \text{CO} + \underset{\text{(steam)}}{\text{H}_2\text{O}} \xrightarrow{\text{H}_3\text{PO}_4} \text{CH}_3 - \text{CH}_2 - \text{COOH} \text{(Koch reaction)}$$

(IV) From oxidation of alkyl benzene- Given by only those compounds which have benzylic H-atom.

Chemical Properties

Acidic Nature: Weak acids, partially ionised in aqueous medium

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

Higher the value of Ka, stronger will be acid.

Acidic strength of aliphatic carboxylic acid depends upon following factors.

- (i) Nature of group : EDG decreases the acidic strength while EWG increases the acidic strength HCOOH > CH₃COOH > CH₃CH₂COOH
- (ii) Position of group :
 CH₃ CH₂(CI) COOH > CH₂(CI) CH₂-COOH
- (iii) Number of groups : ${\rm CH_2CICOOH < CHCl_2COOH < CCl_3COOH}$

Aromatic acid:

- Presence of EDG decreases the acidic strength while EWG increases the acidic strength.
- Ortho effect

 Ortho substituted acids are stronger acid than benzoic acid irrespective of the nature of group.

(I) Decarboxylation reaction :

(II) Reduction reaction:

$$R$$
-COOH \longrightarrow R -CH $_3$ \longrightarrow R -CH $_2$ OH

(III) Halogenation : Carboxylic acids containing $\alpha-H$ atom can be halogenated in presence of red P and X_2 . $CH_\alpha COOH \xrightarrow{CI_2/P} CH_2(CI)-COOH \text{ (HVZ reaction)}$

(IV) Electrophilic aromatic substitution reaction :

-COOH group is ring deactivating group hence it is m-directing group.



Try Yourself

SECTION - A

Objective Type Questions

- IUPAC name of cinnamaldehyde is
 - (1) 3-phenylprop-2en-1-al
 - (2) 1-phenylprop-2-en-1al
 - (3) 2-phenylprop-2en-1-al
 - (4) 1-phenylprop-2-en-3-al
- Strong heating of calcium acetate gives
 - Acetaldehyde
- (2) Ethane
- (3) Acetic acid
- (4) Acetone
- Carbonyl compound obtained by reductive ozonolysis of benzene is
 - CH₃CHO
 - (2) CH₂CH₂CHO
 - (3) CH₂ C— C— CHO Ш 0

CHO

- Catalyst used in Rosenmund reduction is
 - Pd/BaSO₄
- (2) Zn Hg couple
- (3) LiAlH₄
- (4) Ni / H₂
- The reagent with which both aldehyde and ketone react easily is
 - (1) Fehling's reagent
- (2) Grignard reagent
- (3) Schiff's reagent
- (4) Tollen's reagent
- Which of the following will undergo aldol condensation?
 - (1) CCI₃CHO
- (2) HCHO
- (3) (CH₃)₃CCHO
- (4) CH₃-CH₂-CHO
- In Cannizzaro reaction, aldehyde molecules undergo
 - (1) Oxidation only
 - (2) Reduction only
 - (3) Self oxidation and reduction both
 - (4) Decomposition

- HCHO and CH3-CHO differ from each other in reaction with
 - (1) Schiff's reagent
- (2) Fehling solution
- (3) Ammonical AgNO₃
- (4) I₂ and NaOH
- Paraldehyde is
 - A trimer of formaldehyde
 - (2) A trimer of acetaldehyde
 - (3) A hexamer of formaldehyde
 - (4) A hexamer of acetaldehyde
- 10. Benzaldehyde reacts with ammonia to form
 - (1) Benzaldehyde ammonia

 - (3) Hydrobenzamide
- (3) Hydrobe (4) A Which of the following compound gives a ketone with Grignard reagent?
 - Formaldehyde
- (2) Ethyl alcohol
- (3) Methyl iodide
- (4) Methyl cyanide
- 12. On heated with dry HCI, acetone gives
 - (1) Mesityl oxide
- (2) Phorone
- (3) Both (1) & (2)
- (4) None of these
- In the reaction

$$C_6H_5CHO + C_6H_5NH_2 \longrightarrow [A] \xrightarrow{Ni/H_2} [B]$$
 the product [B] is

- (1) $C_6H_5-NH-CH_2-C_6H_5$ (2) $C_6H_5-N=CH-C_6H_5$
- (3) $(C_6H_5NH)_2CHC_6H_6$ (4) $C_6H_5-NH-CH-C_6H_5$
- 14. C2H5CHO and (CH3)2CO can be distinguished by testing with
 - Fehling solution
- (2) Hydroxylamine
- (3) Sodium bisulphite
- (4) Phenyl hydrazine
- 15. Formaldehyde when react with methyl magnesium bromide followed by hydrolysis gives
 - (1) CH₃-CH₂-OH
- (2) CH₃-COOH
- (3) CH₃-CHO
- (4) HCOOH

- 16. Which of the following is optically active?
 - Ethylene glycol
- (2) Glycerol
- Oxalic acid
- (4) Tartaric acid
- Cannizzaro reaction is given by
 - (1) HCHO
- (2) (CH₃)₃CCHO
- (3) C₆H₅CHO
- (4) All of these
- 18. A monobasic acid is
 - Oxalic acid
- (2) Tartaric acid
- (3) Lactic acid
- (4) Malonic acid
- Kolbe-Schmidtt reaction is used for the preparation
 - Salicylic acid
- (2) Salicylaldehyde
- (3) Phenol
- (4) Hydrocarbon
- 20. The reaction

$$\mathsf{CH_3-CH=CH_2} \xrightarrow{\begin{array}{c} \mathsf{CO+H_2O} \\ \mathsf{H} \end{array}} \xrightarrow{CH_3-\mathsf{CH-CH_3}} \xrightarrow{\mathsf{COOH}}$$

is known as

- Koch reaction
- (2) Kolbe's reaction
- (3) Clemmensen reduction
- (4) Wurtz reaction
- Palmitic acid is
 - (1) C₁₆H₃₁COOH
- (2) C₁₇H₃₅COOH
- (3) C₁₅H₃₁COOH
- (4) C₁₇H₃₁COOH
- 22. CH2-COOH is reacted with CH=CH in presence of Hg**, the product is
 - CH₂=CH(OOC-CH₂)
 - CH,-O COCH,
 - (3) CH₃-CH₂-CH₂-O COCH₃
 - (4) (CH₃-COO)₂Hg
- 23. Treatment of benzoic acid and Cl2 / FeCl3 will give
 - p-chlorobenzoic acid
 - o-chlorobenzoic acid
 - (3) 2. 4 dichlorobenzoic acid
 - (4) m-chlorobenzoic acid
- - Carboxylic acid
- (2) Alcohol
- (3) Ketone
- (4) Carbohydrate
- The acid which reduces Tollens reagent
 - Methanoic acid
- (2) Ethanoic acid
- (3) Butanoic acid
- (4) Propanoic acid

26. Product [P] will be

$$CH_3-CH_2-COOH \xrightarrow{HI/P_4} [P]$$

- Ethane
- (2) Propane
- (3) Butane
- (4) Hexane
- 27. Which of the following dibasic acids on strong heating gives CO, CO, H,O?
 - Formic acid
- (2) Oxalic acid
- (3) Malonic acid
- (4) Succinic acid
- 28. Which of the following compounds will not give salt of benzoic acid with KMnO₄/OH?
 - C₆H₅(CH₃)₂CCH₂OH (2) C₆H₅CH(CH₃)₂
 - (3) C₆H₅CH₂OH
- (4) C₆H₅CH₃
- In given reaction

- [X] will not be
- PCI₆
- (2) PCI₂
- (3) SOCI,
- (4) Anhy. ZnCl₂/HCl
- 30. Which has least pK_a value?
 - (1) CI3CCOOH
- (2) CHCl₂COOH
- (8) CICH, COOH
- (4) CH₃-COOH
- When sodium formate is heated with sodalime it
 - Hydrogen
- (2) Ethylene
- (3) Ethane
- (4) Methane
- Which of the following groups is/are m-directing?
 - (1) –CHO
- (2) -OH
- (3) –COOH
- (4) Both (1) & (3)
- Benzoic acid may be converted into ethyl benzoate by reaction with
 - Methyl chloride
- (2) Dry HCl, C₂H_eOH
- (3) Propanol
- (4) None of these
- Consider the following reaction sequences

$$C_4H_6O_4 \xrightarrow{\Delta} C_3H_6O_2 \xrightarrow{CaO} C_2H_6$$
 [B] [B] [C] , [A] and [B]

are respectively

- CH₃-CH(COOH)₂, CH₃-CH₂-COOH
- (2) CH₂-COOH , CH₃-CH₂-COOH
- (3) COOCH, CH₃-COOCH₃
- (4) COOH CH2 COOH

Starting from propanoic acid the following reactions were carried out

$$CH_3-CH_2-COOH \xrightarrow{SOCI_2} [X] \xrightarrow{NH_1} [Y]$$

$$\xrightarrow{Br_2} [Z]$$

Product [Z] will be

- (1) CH₃-CH₂-Br
- (2) CH₃-CH₂-NH₃
- (3) CH₃-CH₂-COBr
- (4) CH₃-CH₂-CH₂-NH₂
- 36. Which of the following does not contain an acyl group?
 - (1) Acid chloride
- (2) Amide
- (3) Ester
- (4) Ether
- 37. Acetamide is
 - (1) Acidic
- (2) Basic
- (3) Amphoteric
- (4) Neutral
- 38. Hexamethylene tetramine is used as
 - (1) Analgesic
- (2) Antipyretic
- (3) Urinary antiseptic
- (4) All of these
- Strongest acid among the following
 - (1) HCOOH
- (2) CH₃COOH

40.
$$+ HCN \longrightarrow x \xrightarrow{H,O^+} y$$

Product 'x' and 'y' in the above reaction are

SECTION - B

Previous Years Questions

 The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is

[AIPMT 2012]

- (1) A > B > C > D
- (2) A > C > B > D
- (3) B > A > D > C
- (4) B > D > C > A
- 2. Predict the products in the given reaction.

[AIPMT 2012]

- Which of the following acids does not exhibit optical isomerism? [AIPMT 2012]
 - Lactic acid
 - (2) Tartaric acid
 - (3) Maleic acid
 - (4) α-amino acids
- CH₃CHO and C₆H₅CH₂CHO can be distinguished chemically by: [AIPMT 2012]
 - (1) Tollen's reagent test
 - (2) Fehling solution test
 - (3) Benedict test
 - (4) Iodoform test

 Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is: [AIPMT 2012]

Consider the following reaction

The product 'A; is

[AIPMT 2012]

- (1) C₆H₅CHO
- (2) C₆H₆OH
- (3) C₆H₅COCH₃
- (4) C₆H₅Cl
- 7. Which of the following compounds will give a yellow precipitate with iodine and alkali?

[AIPMT 2012]

- (1) Acetophenone
- (2) Methyl acetate
- (3) Acetamide
- (4) 2-hydroxypropane
- Reaction by which Benzaldehyde cannot be prepared [NEET 2013]

(4)
$$CH_3 + CrO_2CI_2$$
 in CS_2 followed by H_3O^+

Which one is most reactive towards Nucleophilic addition reaction? [AIPMT 2014]

 Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is

[Re-AIPMT-2015]

- (1) Hydrocyanic acid
- (2) Sodium hydrogen sulphite
- (3) A Grignard reagent
- (4) Hydrazine in presence of feebly acidic solution
- 11. Which one of the following esters gets hydrolysed most easily under alkaline conditions?

[Re-AIPMT-2015]

- The oxidation of benzene by V₂O₅ in the presence of air produces [Re-AIPMT-2015]
 - (1) Benzoic acid
 - (2) Benzaldehyde
 - (3) Benzoic anhydride
 - (4) Maleic anhydride

- 13. Treatment of cyclopentanone
 - O with

methyl lithium gives which of the following species?

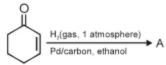
[AIPMT-2015]

- Cyclopentanonyl biradical
- (2) Cyclopentanonyl anion
- (3) Cyclopentanonyl cation
- (4) Cyclopentanonyl radical
- 14. An organic compound "X" having molecular formula C₅H₁₀O yields phenyl hydrazone and gives negative response to the lodoform test and Tollen's test. It produces n-pentane on reduction. 'X' could be :

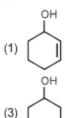
[AIPMT-2015]

- n-amyl alcohol
- (2) Pentanal
- (3) 2-pentanone
- (4) 3-pentanone
- The correct statement regarding a carbonyl compound with a hydrogen atom on its alphacarbon, is [NEET-2016]
 - A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its
 - carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol

 A carbonyl compound with its alpha. (2) A carbonyl compound with a hydrogen atom on
 - (3) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration
 - (4) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
- The correct structure of the product A formed in the reaction



[NEET (Phase-2) 2016]



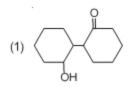


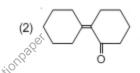
17. The correct order of strengths of the carboxylic acids

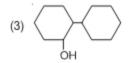
is

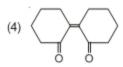
[NEET (Phase-2) 2016]

- (1) | > || > |||
- (2) || > || > |
- (3) III > II > I
- (4) || > | > ||
- Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating? [NEET-2017]

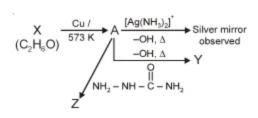








Consider the reactions :



Identify A, X, Y and Z

[NEET-2017]

- A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine
- (2) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide
- A-Ethanal. X-Ethanol. Y-But-2-enal. Z-Semicarbazone
- (4) A-Ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydrazone

 Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

- (1) Formation of intramolecular H-bonding
- (2) Formation of carboxylate ion
- (3) Formation of intermolecular H-bonding
- (4) More extensive association of carboxylic acid via van der Waals force of attraction
- Compound A, C₈H₁₀O, is found to react with NaOI (produced by reacting Y with NaOH) and yields a yellow precipitate with characteristic smell.

A and Y are respectively

[NEET-2018]

- When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is [NEET-2019 (Odisha)]
 - (1) An alkene
- (2) A carboxylic acid
- (3) An aldehyde
- (4) A ketone



Chapter 6

Amines

Sub-topics

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary secondary and tertiary amines. Cyanides and Isocyanides- will be mentioned at relevant places. Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Nomenclature



$$\begin{array}{c} \operatorname{CH_3} - \operatorname{N} - \operatorname{CH_3} \\ | \\ \operatorname{CH_3} \end{array}$$

Common Name

n-Propylamme Isopropylamine

Ethylmethylamine

Trimethylamine

IUPAC name

Propan-1-amine Propan-2-amine

N-methylethanamine

N,N-Dimethylmethanamine



Aniline

Aniline or Benzenamine

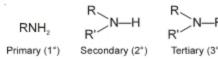


o-Toluidine

2-Aminotoluene

Classification

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.



Structure

N-atom of amines is trivalent and carries an unshared pair of electrons, having sp^3 - hybridisation. Due to the presence of unshared pair of electrons, the angle C—N—E, (where E is C or H)is less than 109.5°; for example it is 108° in case of trimethylamine.

Preparation

1. Hofmann's exhaustive alkylation of ammonia

$$\mathsf{R-I+HNH_2} \to \mathsf{R-NH_2+I-R} \to \mathsf{R_2NH+I-R} \to \mathsf{R_3N+I-R} \to \mathsf{R_4N} \ \mathsf{I}$$

2. Gabriel's phthalimide synthesis

Aromatic amines cannot be formed from this reaction,

3. Hofmann's bromamide reaction

$$R - CONH_2 \xrightarrow{Br_2 + KOH} R - NH_2$$
 (Only for 1° emines)

4. Reduction of nitrogenous compounds

(a)
$$R - CH = NOH \xrightarrow{Na/C_2H_3OH} R - CH_2 - NH_2$$
 (Only for 1° amines)

(b)
$$R - CO - NH_2 \xrightarrow{\text{LiAlH}_4} R - CH_2 - NH_2$$

(c)
$$R - CN \xrightarrow[\text{LIAIH}_4]{\text{Na/C}_2H_5OH}$$
 $R - CH_2 - NH_2$ [Use of Na/C $_2H_5OH$ is Mendius reaction]

(f)
$$C_6H_5NO_2 \xrightarrow{\text{Electrolytic reduction}} C_6H_5 - NH_2$$

5. From acid chloride

$$R - COCI \xrightarrow{NaN_3/NaOH} R - NH_2$$
 [Curtius reaction]

6. From carboxylic acid

$$R - COOH \xrightarrow{N_2H} R - NH_2$$
 [Schmidt reaction]

Physical Properties

- Lower aliphatic amines are gases with fishy odour.
- Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between N of one and H of another molecule.
- The order of boiling points of isomeric amines follow the order:

Primary > Secondary > Tertiary

Chemical Properties: Amines are basic in gaseous state as well as in aqueous medium.

Amines: CH₃NH₂, (CH₃)₂NH, (CH₃)₃N, C₂H₅NH₂, (C₂H₅)₂NH, (C₂H₅)₃N
 pK_b: 3.38, 3.27, 4.22, 3.29, 3.00, 3.25

More the value of pK, lesser is the basic strength.

Aniline is less basic than aliphatic amines and ammonia, due to resonance.

Chemical Properties

(i) Basic nature

$$R - NH_{2} \xrightarrow{H_{2}O} RNH_{3}^{*} + OH^{-}$$

$$R - NH_{2} \xrightarrow{HCI} R - NH_{3}CI^{-}$$

$$BF_{3} \longrightarrow R - N \rightarrow BF_{3}$$

$$H$$

$$Ag^{*} \longrightarrow [Ag(NH_{2} - R)_{2}]^{*} \otimes^{OJ}^{OJ}^{OJ}$$

(ii) Reaction with HNO₂

1° amine:

$$R - NH_2 \xrightarrow{HNO_2} ROH + N_2 \uparrow$$

$$NH_2 \xrightarrow{NaNO_2/HCI} O \xrightarrow{N_2CI} N_2CI$$

2° amine: forms yellow oily liquid.

3° amine:

$$R_3N \xrightarrow{HNO_2} [R_3NH]^*NO_2$$

$$CH_3 \xrightarrow{HNO_2} NO \xrightarrow{CH_3} CH_3$$

(iii) Acylation reaction

(iv) Reaction with Grignard reagent

$$R'Mg X + R - NH_2 \longrightarrow R'H + R - NH - Mg X$$

$$R'Mg X + R_2 - NH \longrightarrow R'H + R_2 - N Mg X$$

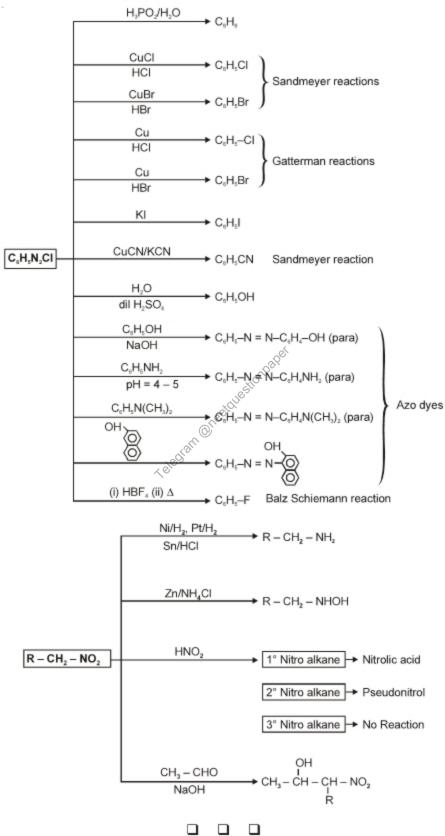
(v) Carbylamine reaction

$$R - NH_2 + CHCI_3 + KOH \longrightarrow R - NC$$
1° amine Pungent smell

(vi) Electrophilic aromatic substitution reaction

-NH₂ group is highly ring-activating group hence it becomes difficult to stop the reaction at monosubstitution stage and in most of the cases trisubstituted product is obtained.

Chemical Properties of Benzene Diazonium Chloride





Try Yourself

SECTION - A

Objective Type Questions

- N, N dimethyl propanamine, N-methyl aniline and aniline respectively can be classified in which family of amines?
 - Primary, Secondary, Tertiary
 - (2) Primary, Tertiary, Secondary
 - Tertiary, Primary, Secondary
 - (4) None of these
- Identify the end product

- (1) Aniline
- (2) Nitrobenzene
- (3) Phenol
- (4) Benzenediazonium salt
- Identify the final product [Z] in the following sequence of reactions

$$CH_3-NH_2 \xrightarrow{CH_3I} [X] \xrightarrow{AgOH (aq.)} [Y] \xrightarrow{\Delta} [Z] + CH_3-OH$$

- (1) (CH₂)₂N
- (2) CH3-CH2-CH2-NH2
- (3) (CH₂)₂NH
- (4) (CH₃)₄ ⊕ ⊖ OH
- Hydrolysis of phenyl isocyanide forms
 - (1) Benzoic acid
- (2) Formic acid
- (3) Aniline
- (4) Both (2) & (3)
- Grabiel phthalimide synthesis cannot be used for the preparation of

(1)
$$(CH_3)_3 C - NH_2$$
 (2) NH_2

(4) All of these

Aniline can be prepared by

Mentify [Z] in the following sequence of reactions

$$C_6H_{13}COCI \xrightarrow{H_2, Pd/BaSO_4} [X] \xrightarrow{C_0H_{13}NH_2} [Y]$$

$$\frac{Ni/H_2}{\Delta}$$
 [Z]

- C₆H₁₃CH₂-NH-C₆H₁₃
- (2) C₁₂H₂₅-CH₂-NH₂

- (4) (C₆H₁₃)₂CHN
- The final product [P] obtained in the reaction sequence is

Toluene
$$\xrightarrow{(1) \text{ KMnO}_{\ell}/\text{OH}/\Delta} \rightarrow [A] \xrightarrow{\text{SOCl}_2} [B]$$

$$\frac{NH_3}{OH^-}$$
 [C] $\frac{NaOBr}{}$ [D]

- (1) C₆H₅CONH₂
- (2) p-CH₂C₆H₄NO₂
- (3) C₆H₅CH₂NH₂
- (4) C₆H₅NH₂
- When C2H5Br is treated with excess of NH3 followed by the treatement with alkali, the major product formed will be
 - (1) C₂H₅NH₂
- (2) C₂H₄
- (3) [(C₂H₅)₄N]⁺
- (4) (C₂H₅)₃N

- 10. Acetone oxime on catalytic hydrogenation gives
 - (1) 1-propanamine
 - (2) Isopropyl amine
 - (3) Ethyl methyl amine
 - (4) CH₄ and ethanamine
- Arrange the following
 - (I) Methyl amine
- (II) Dimethylamine
- (III) Aniline (IV) N-methylaniline in order of decreasing basicity (in gas phase)
- (1) || > | > |V > |||
- (2) I > II > III > IV
- (3) IV > III > II > I
- (4) | | | > | > | V
- The order of basic strength among the following amines in aqueous solution is
 - (1) CH₃-NH₂ > (CH₃)₃N > (CH₃)₂NH
 - (2) (CH₃)₂NH > CH₃-NH₂ > (CH₃)₃N
 - (3) CH₃-NH₂ > (CH₃)₂NH > (CH₃)₃N
 - (4) (CH₃)₃N > CH₃NH₂ > (CH₃)₂NH
- The basic character of ethyl amine, diethylamine, triethylamine and ammonia in vapour phase is
 - (1) 3° > 2° > 1° > NH₃
 - (2) 2° > 3° > 1° > NH,
 - (3) 1° > 2° > 3° > NH₃
 - (4) None of these
- The amine which does not react with acetyl chloride is
 - (1) CH₃-NH₂
- (2) (CH₃)₂NH
- (3) (CH₃)₃N
- (4) CH₃CH₂-NH₃
- 15. Which of the following amine produces alcohol upon reaction with HNO₂ acid?
 - (1) CH₃ CH₂ NH₂
- (2) CH₃- CH- NH₂
- (3) CH₃ C NH₂ CH₃
- (4) All of these
- 16. CH₃Mg Br C₂H₃NH₂ → alkane + Mg Br
 - (1) CH,
- (2) C₂H₆
- (3) C₃H₈
- (4) C₄H₁₀

- The correct decreasing order of basicities of following compound is in vapour phase
 - (I) CH₃-C NH₃
- (II) CH₃-CH₂-NH₂
- (III) (CH₃)₂ NH
- (IV) CH₃-C-NH₂
- (1) || > | > ||| > |V
- (2) I > III > II > IV
- (3) III > II > I > IV
- (4) | > || > || > |V
- 18. The value of K_b is highest in case of
 - (1) p-methoxyaniline
- (2) p-chloroaniline
- (3) p-nitroaniline
- (4) p-methylaniline
- The compound which on reaction with cold HNO₂ gives nitrosoamine is
 - (1) CH₃-NH₂
- (2) (CH₃)₂NH
- (3) (CH₃)₃N
- (4) (CH₃-CH₂)₃N
- An amine reacts with C₆H₅SO₂Cl and the product is soluble in alkali, amine is
 - Primary
- (2) Secondary
- (3) Tertiary
- (4) All of these
- 21 Aniline on heating with conc. H₂SO₄ at 180°C gives
 - (1) Benzene sulphonic acid
 - (2) Sulphanilic acid
 - (3) Both (1) & (2)
 - (4) None of these

What will be the minor product of the abovereaction?

- (2) NH₂
- 3) NH₂
- (4) All are formed in equal percentage

CH₂CH₂- CH₂- CH - CN H₃O^{*} → Product, product ĊH.

is

- Acid
- (2) Amine
- (3) Nitro compound
- (4) Cyanide
- 24. p-chloro aniline and anilinium hydrochloride can be distinguished by
 - Sandmeyer reaction (2) NaOH
 - (3) AgNO₃
- (4) Carbylamine test

What is the organic product of the above reaction?

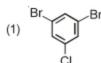
Final product [C] obtained in this reaction would be

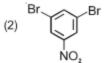
- Unpleasant smelling carbyl amines are formed by heating alkali and chloroform with
 - (1) Any amine
 - (2) Any aliphatic amine
 - (3) Any aromatic amine
 - (4) Any primary amine

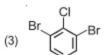
- Which of the following amine will not give carbylamine reaction?
 - Ethyl amine
- (2) Methyl amine
- (3) Aniline
- (4) Dimethyl amine
- In the following reaction product B is

$$ArNH_2 \xrightarrow{NaNO_2+HCI} [A] \xrightarrow{CuBr} [B]$$

- (1) ArBr
- (2) ArNO₂
- (3) ArCl
- (4) Ar–Ar
- Benzene diazonium chloride can be converted into phenol by treating it with
 - (1) H₃PO₃
- (2) H2O, H2SO4
- (3) Alcohol, heat
- (4) HBF, heat
- 31. The final product [C] obtained in the reaction sequence is







- In the reaction between C2H5Br and alcoholic AgNO2, the major product obtained is
 - Nitro ethane
- (2) Ethane
- (3) Ethyl nitrite
- (4) Ethyl isocyanide
- 33. Reduction of nitrobenzene with Zn + NaOH in CH₃OH produces
 - (1) Aniline
- (2) Azoxy benzene
- (3) p-aminophenol
- (4) Azobenzene
- Which of the following on reaction with nitrous acid, followed by treatment with NaOH produces a blue colouration?
 - (1) R-CH2-NO2
- (2) R2CHNO2
- (3) R₃CNO₂
- (4) PhNO₂

The main product [P] in the reaction is

- R-CN
- (2) RNC
- (3) RCNO
- Which reactants and reagents are involved in Mendius reaction?
 - (1) R-CN & Na/C2H5OH (2) R-CN & H2O/HCI
 - (3) R-CN & Zn/NH₄Cl (4) R-CN & SnCl₂/HCl
- 37. In the reaction sequence, product [B] will be

$$\text{CH}_3\text{-CHO} \xrightarrow{\quad \text{NH}_2\text{OH} \quad } [\text{A}] \xrightarrow{\quad P_2\text{O}_5 \quad } [\text{B}]$$

- CH₃-CH=NOH
- (2) CH₂=NOH
- (3) CH₃-CN
- (4) CH₂-CH₂-NH₂
- 38. Butanenitrile may be prepared by heating
 - Pentyl alcohol with KCN
 - (2) Butyl alcohol with KCN
 - (3) Butyl chloride with KCN
 - (4) Propyl chloride with KCN
- 39. Identify [X] in the following sequence

$$[X]$$
 $\xrightarrow{HNO_2}$ C_3H_8O $\xrightarrow{K_2Cr_2O_7}$ C_3H_6O

- (1) CH₃-NH-CH₂-CH₃ (2) CH₃-CH₂-CH₂-NH₃
- (3) (CH₃)₃N
- (4) CH₂CH₂CN
- 40. The action of nitrous acid on primary aliphatic amine at 0-5°C gives
 - (1) Nitro alkane
- (2) Alkyl nitrite
- (3) Alcohol
- (4) Secondary amine

SECTION - B

Previous Years Questions

Consider the reaction

$$RCHO + NH_2NH_2 \longrightarrow RCH = N - NH_2$$

What sort of reaction is it?

[AIPMT 2012]

- (1) Electrophilic addition elimination reaction
- (2) Free radical addition elimination reaction
- (3) Electrophilic substitution elimination reaction
- (4) Nucleophilic addition elimination reaction
- An organic compound (C₃H₉N) (A), when treated with nitrous acid, gave an alcohol and N2 gas was evolved. (A) on warming with CHCl3 and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A).

[AIPMT 2012]

$$CH_3$$
 $CH-NH_2$ (2) C

In the reaction
$$\bigoplus_{\mathbf{P},\mathbf{Cl}^{\Theta}}^{\mathbf{NO}_2} \xrightarrow{\mathbf{A}} \bigoplus_{\mathbf{Bl}}^{\mathbf{NO}_2}$$

A is

[NEET 2013]

- Cu₂Cl₂
- (2) H₃PO₂ and H₂O
- (3) H⁺/H₂O
- (4) HgSO₄/H₂SO₄
- In the following reaction, the product (A)

[AIPMT 2014]

$$\stackrel{\stackrel{\bullet}{N} = NCI^{-}}{\longrightarrow} NH_{2}$$

$$\stackrel{\bullet}{\longrightarrow} (A)$$
Yellow dye

- Which of the following will be most stable diazonium salt RN₂⁺X⁻? [AIPMT 2014]
 - (1) CH₃N₂⁺X⁻
- (2) $C_6H_5N_2^+X^-$
- (3) CH₃CH₂N₂⁺X⁻
- (4) $C_6H_5CH_2N_2^+X^-$
- Nitrobenzene on reaction with conc. HNO₃/H₂SO₄ at 80-100°C forms which one of the following products? [NEET 2013]
 - (1) 1, 3-Dinitrobenzene
 - (2) 1, 4-Dinitrobenzene
 - (3) 1, 2, 4-Trinitrobenzene
 - (4) 1, 2-Dinitrobenzene

7. The following reaction

is known by the name

[Re-AIPMT-2015]

- Acetylation reaction
- (2) Schotten-Baumen reaction
- (3) Friedel-Craft's reaction
- (4) Perkin's reaction
- Method by which Aniline cannot be prepared is

[Re-AIPMT-2015]

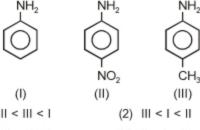
- (1) Reduction of nitrobenzene with H2/Pd in ethanol
- (2) Potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
- (3) Hydrolysis of phenylisocyanide with acidic solution
- (4) Degradation of benzamide with bromine in alkaline solution
- The electrolytic reduction of nitrobenzene strongly acidic medium produces [AIPMT-2015]
 - Aniline
- p-Aminophenol
- (3) Azoxybenzene
- (4) Azobenzene
- 10. The product formed by the reaction of an aldehyde with a primary amine is [NEET-2016]
 - (1) Aromatic acid
- (2) Schiff base
- (3) Ketone
- (4) Carboxylic acid
- The correct statement regarding the basicity of arylamines is [NEET-2016]
 - (1) Arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is sp-hybridized
 - (2) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring π electron system
 - (3) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring π electron system
 - (4) Arylamines are generally more basic than alkylamines because of aryl group

12. A given nitrogen-containing aromatic compound A reacts with Sn/HCl, followed by HNO2 to give an unstable compound B. B, on treatment with phenol, forms a beautiful coloured compound C with the molecular formula C₁₂H₁₀N₂O. The structure of compound A is [NEET (Phase-2) 2016]

Which one of the following nitro-compounds does not react with nitrous acid?

[NEET (Phase-2) 2016]

The correct increasing order of basic strength for the following compounds is [NEET-2017]



- (1) || < || < |
- (3) | | | < | | < |
- (4) | | < | < | | |
- Which of the following reactions is appropriate for converting acetamide to methanamine?

[NEET-2017]

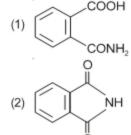
- Carbylamine reaction
- (2) Hoffmann hypobromamide reaction
- Stephens reaction
- (4) Gabriels phthalimide synthesis

- Nitration of aniline in strong acidic medium also gives m-nitroaniline because [NEET-2018]
 - Inspite of substituents nitro group always goes to only m-position.
 - (2) In electrophilic substitution reactions amino group is meta directive.
 - (3) In acidic (strong) medium aniline is present as anilinium ion.
 - (4) In absence of substituents nitro group always goes to m-position.
- The correct order of the basic strength of methyl substituted amines in aqueous solution is

[NEET-2019]

- (1) (CH₃)₂NH > CH₃NH₂ > (CH₃)₃N
- (2) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$
- (3) (CH₃)₃N > (CH₃)₂NH > CH₃NH₂
- (4) CH₃NH₂ > (CH₃)₂NH > (CH₃)₃N
- 18. The major product of the following reaction is

[NEET-2019]



- (3) COOH
- (4) NH₂
- The amine that reacts with Hinsberg's reagent to give an alkali insoluble product is

[NEET-2019 (Odisha)]

- (2) CH₃ CH NH CH CH₃ CH₃ CH₃
- CH₂CH₃ | (3) CH₃ — CH₂ — N — CH₂CH₃
- (4) CH₃ CH₂CH₂CH₂CH₃ CH₃

Chapter 7

Biomolecules

Sub-topics

Carbohydrates- Classification (aldoses and ketoses), monosaccharide (glucose and fructose), D.L. configuration, oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen): importance. Proteins- Elementary idea of – amino acids, peptide bond, polypeptides, proteins, primary structure, secondary structure, tertiary structure and quaternary structure (qualitative idea only), denaturation of proteins; enzymes. Hormones- Elementary idea (excluding structure). Vitamins- Classification and function. Nucleic Acids: DNA and RNA

CARBOHYDRATES

- Carbohydrates are mainly compounds of carbon, hydrogen and oxygen.
- 2. General molecular formula initially considered was $C_{12}(\hat{H}_{2}O)_{y}$ e.g., glucose $-C_{6}H_{12}O_{6}$, sucrose $C_{12}H_{22}O_{11}$ etc.

But many of the compounds which behave as carbohydrates, do not follow the general molecular formula C_v(H₂O)_v.

- Thus carbohydrates are the class of compounds that include polyhydroxy aldehydes or polyhydroxy ketones.
- 4. Carbohydrates are also known as saccharides.

Classification

The carbohydrates are classified into three major classes

- (i) Monosaccharides
- (ii) Oligosaccharides
- (iii) Polysaccharides

Monosaccharides

- Monosaccharides are simple sugars with single unit of polyhydroxy aldehyde or polyhydroxy ketones.
- (ii) General molecular formula C_nH_{2n}O_n (with some exceptions).

Oligosaccharides

- Oligosaccharides are made up of 2-10 units of monosaccharides or simple sugars.
- Oligosaccharides with two, three and four monosaccharides respectively known as disaccharides, trisaccharides and tetrasaccharides.
- (iii) Sucrose is the example of this class.

Polysaccharides

- Polysaccharides are made up of 'n' number of monosaccharide units (above 10 units).
- (ii) Starch, cellulose and glycogen are the examples of this class.

(iii)
$$(C_6H_{10}O_5)_n \xrightarrow{nH_2O} nC_6H_{12}O_6$$

starch H^+ glucose

(iv) Homopolysaccharides are made up of single type of monosaccharides. Heteropolysaccharide is made up of two or more different types of monosaccharides.

Monosaccharide-Glucose

Glucose is known as dextrose and also known as grape sugar.

Preparation

Hydrolysis of cane sugar in presence of an acid or enzyme gives glucose (alongwith fructose)

Glucose and Fructose have same molecular formula but different structural formula.

Structure of D-Glucose

(i) Open chain structure :

The reaction of glucose with

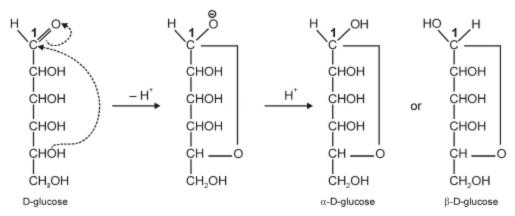
- (a) HI to give hexane
- (b) Hydroxylamine to form monoxime
- (c) HCN to form cyanohydrin, gives the existence of the open chain structure of glucose

(ii) Cyclic structure of glucose :

The open chain structure of glucose fails to explain

- (a) No reaction of glucose with NaHSO₃ and NH₃, even though CHO group is present.
- (b) No reaction of glucose with 2, 4-DNP
- (c) Negative test (for aldehydes) with Schiff's base.

All the above observations indicates that free aldehydic group is not present.



α-D-glucose and β-D-glucose are anomers of each other.

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Mutarotation : The α and β anomers of glucose are obtained by crystallisation at 30°C and 98°C respectively. When solution of the either form of two forms are allowed to stand, the specific rotation of the solution changes slowly and reaches a constant value.

The gradual change in specific rotation of an optically active compound is called mutarotation.

$$\alpha$$
-D-glucose \rightleftharpoons Eq. mixture \rightleftharpoons β -D-glucose +111° +52.5° +19°

Disaccharides

- (i) Disaccharides are composed of two molecules of monosaccharides linked by glycosidic linkage.
- (ii) The disaccharides may be reducing or non reducing in nature depending upon linkage.

Sucrose
$$(C_{12}H_{22}O_{11}) \xrightarrow{H_2O/H^+} Glucose + Fructose$$

Lactose $(C_{12}H_{22}O_{11}) \xrightarrow{H_2O/H^+} Glucose + Galactose$

Maltose $(C_{12}H_{22}O_{11}) \xrightarrow{H_2O/H^+} Glucose + Glucose$

Structure of Sucrose, Lactose and Maltose

(i) Sucrose

(ii) Lactose

HO H OH H OH H H OH
$$\frac{3}{5}$$
 OH $\frac{3}{1}$ OH $\frac{3}{1}$

(iii) Maltose

Polysaccharides:

(i) In polysaccharides, thousands of monosaccharide units are joined together by glycosidic linkage.

$$(C_6H_{10}O_5)_n \xrightarrow{H^*/H_2O} C_{12}H_{22}O_{11} \longrightarrow C_6H_{12}O_6$$
Starch Maltose D-glucose

- (ii) Starch does not reduce Fehling's solution or Tollen's reagent.
- (iii) Starch does not form an Osazone.
- (iv) Starch is a mixture of two polysaccharides i.e., amylose and amylopectin.

Cellulose : (C₆H₁₀O₅)_n

- (i) Cellulose is a straight chain polysaccharide composed of only D-glucose units.
- (ii) Cellulose does not reduce Tollen's reagent or Fehling's solution.

Reducing and Non-reducing sugars

Carbohydrate which gives red precipitate with Fehling solution is known as reducing sugar. All monsaccharides and disaccharides (except sucrose) are reducing sugars. Carbohydrate which does not give red precipitate with Fehling solution is known as non-reducing carbohydrate, sucrose is a non-reducing sugar and polysaccharides are non-reducing carbohydrates.

AMINO ACIDS

Proteins are made up of amino acids. All naturally occurring amino acids are α -amino acids, where amine group is connected with α -carbon of carboxylic acid. Amino acids have amphoteric character. A free amino group is basic, a free carboxyl group is acidic. Lysine and Arginine are Basic Amino Acids because they carry two amino groups and one carboxyl group. Glutamic acid (glutamate) and Aspartic acid (aspartate) contain one amino and two carboxyl groups each and are classified as Acidic Amino Acids. Alanine, glycine, valine and phenylalanine are Neutral Amino Acids as these contain one amino and one carboxyl group.

$$R - CH - COOH$$

$$NH_{2}$$

$$Amino acid (R = side chain)$$

$$COOH$$

$$H_{2}N - C - H$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$COOH$$

$$CH_{2}$$

$$COOH$$

$$CH_{2}$$

$$COOH$$

$$CH_{2}$$

$$COOH$$

$$CH_{2}$$

$$COOH$$

$$CH_{3}$$

$$COOH$$

$$CH_{4}$$

$$COOH$$

$$CH_{5}$$

$$CH$$

Side chain of a basic and an acidic amino acids

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Amino Acids which occur in Proteins

Glycine, alanine, serine, cysteine, aspartic acid, glutamic acid, asparagine, glutamine, methionine, threonine, valine, leucine, isoleucine, lysine, histidine, arginine, phenylalanine, tyrosine, tryptophan and proline.

PROTEINS

Proteins are polyamides formed from amino acids. The α -carbon atom of the amino acids is asymmetric and show optical isomerism (stereo). Proteins consist mainly of l isomers of amino acids. There are 20 commonly occurring amino acids in proteins. Amino acids form zwitter ion. Lack of essential amino acids in diet can cause diseases such as Kawashiorkar.

Peptide Bond and Structure of Proteins

Amino acids are joined together by an amide linkage called **peptide bond**.

Proteins are long polymers of amino acids linked by peptide bonds (polypeptides). The sequence in which the amino acids are arranged in a protein is called the primary structure.

The secondary structure arises due to the regular folding of the backbone of the polypeptide chain due to intramolecular hydrogen bonding between the carboxyl and amino groups.

The tertiary structure is the three-dimensional structure of globular and fibrous proteins. It arises due to folding and superimposition of various secondary structural elements.

ENZYMES

Enzymes are biological catalysts which increase the rate of biochemical reactions even under mild conditions of temperature and pH without taking part in reaction.

Properties of Enzymes:

- (i) They speed up reactions up to ten million times compared to the uncatalyzed reactions.
- (ii) They are very specific in their action on substrates and each enzyme catalyzes only specific type of reaction.
- (iii) They are active at moderate temperature and pH.
- (iv) The action of enzymes are inhibited by various organic and inorganic molecules.

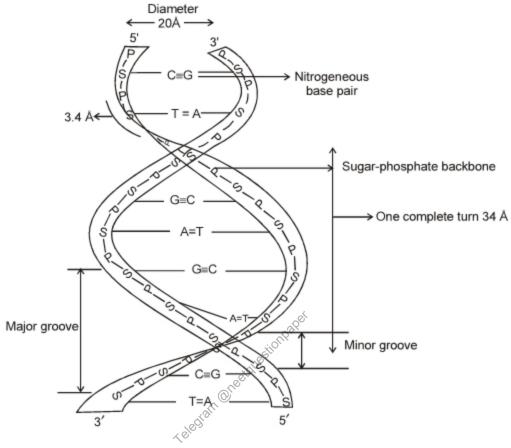
NUCLEIC ACIDS

- Nucleic acids play an essential role in transmission of the hereditary characteristics and the biosynthesis of proteins.
- There are two classes of nucleic acids: DNA (deoxyribonucleic acid) and RNA (ribonucleic acid).
 Nucleic acids are the long polymers in which the monomeric units are nucleotides. The structural units of nucleotides are made up of three essential components; a nitrogenous base, a pentose sugar (5-carbon sugar), and a phosphate group.
- In nucleic acids, the individual nucleotides are linked through phosphate groups to give rise to long polynucleotide structures.

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Structure of DNA

DNA consists of two strands of polynucleotides coiled around each other in the form of a double helix.



Functions of Nucleic Acids

Replication: The genetic information of the cell is contained in the sequence of the bases A, T, G and C in the DNA molecule.

The DNA sequence that codes for a specific protein or polypeptide is called a **Gene** and thus every protein in a cell has a corresponding gene. The relation between the nucleotide triplets and the amino acids is called the **GENETIC CODE**.

VITAMINS

Vitamins are organic compounds necessary for normal health but cannot be synthesised in human body. Deficiency of vitamins causes many disorders and diseases. Vitamins B and C are water soluble while vitamins A, D, K and E are fat soluble.



Try Yourself

SECTION - A

Objective Type Questions

- 1. The main structural feature of proteins is
 - (1) The ester linkage
- (2) The ether linkage
- (n) The color minage
- (3) The peptide linkage (4) All of these
- 2. Glucose can not be classified as
 - (1) A hexose
 - (2) A carbohydrate
 - (3) An oligo saccharides
 - (4) An aldose
- 3. Which of the following is an acidic amino acid?
 - (1) Lysine
- (2) Arginine
- (3) Aspartic acid
- (4) Histidine
- Acid hydrolysis of sucrose causes
 - (1) Esterification
- (2) Saponification
- (3) Inversion
- (4) Rosenmund reduction
- Molecular formula C₆H₁₂O₆ is of
 - Glucose
- (2) Fructose
- (3) Both (1) & (2)
- (4) None of these
- Adenine is
 - (1) A nucleotide
- (2) An enzyme
- (3) An amino acid
- (4) Purine base
- Which of the following monosaccharide is a pentose?
 - (1) Galactose
- (2) Glucose
- (3) Fructose
- (4) Arabinose
- 8. The disaccharide present in milk is
 - (2) Lactose
 - Maltose
 Sucrose
- (4) Cellobiose
- 9. General formula for many carbohydrates is
 - (1) $C_n H_{2n} O_{2n+2}$
- (2) $C_x(H_2O)_{2x}$
- (3) $C_x(H_2O)_y$
- (4) $C_n H_{2n} O_{2n}$
- 10. Molish test is used for
 - Monosaccharides
- (2) Disaccharides
- (3) Polysaccharides
- (4) All of these

- Glucose gives silver mirror with Tollens reagent tests, it shows the presence of
 - (1) An acidic group
- (2) An alcoholic group
- (3) A ketonic group
- (4) An aldehydic group
- 12. Insulin is
 - (1) Amino acid
- (2) Protein
- (3) Carbohydrate
- (4) A lipid
- Starch is changed into disaccharide in the presence of
 - (1) Diastase
- (2) Lactase
- (3) Maltase
- (4) Zymase
- Peptides are
- (1) Esters
- (2) Salt
- (3) Amides
- (4) Ketones
- 15. Which one is disaccharide?
 - (1) Glucose
- (2) Fructose
- (3) Galactose
- (4) Sucrose
- 16. Product [P] in the following reaction will be

- (1) 2 CHOH
- (2) 2C=O CH,OH

CH,OH

- ĊH₂OH CHO
- ÇH₂OH
- (3) (CHOH), CH,OH
- (4) (CHOH)₄ CH₅OH
- 17. Cellulose is
 - (1) $(C_6H_{10}O_5)_n$
- (2) (C₃H₃N₃)_n
- (3) $(C_3H_6N_6)_n$
- (4) (C₁₂H₂₂O₁₁)_n

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- Vitamin B₁₂ contains metal
 - (1) Pb
- (2) Zn
- (3) Fe
- (4) Co
- 19. Amino acids are
 - (1) Liquids
 - (2) Volatile solids
 - (3) Non-volatile crystalline compounds
 - (4) Mixture of amines and acids
- On treating glucose with Fehling's solution we get a precipitate, whose colour is
 - (1) Yellow
- (2) Red
- (3) Black
- (4) White
- 21. Which one of the following is not present in RNA?
 - (1) Uracil
- (2) Thymine
- (3) Ribose
- (4) Phosphate
- 22. On complete hydrolysis all proteins yield
 - (1) α-Aminoacids
- (2) Monohydric alcohol
- (3) Mono haloalkanes
- (4) Enzymes
- 23. Sugar can be tested in urine by
 - (1) Molish test
- (2) Dunstan's test
- (3) Benedict's test
- (4) Legal's test
- 24. Which of the following is correct about fructose?
 - (1) It has furanose structure
 - (2) It is hexose
 - (3) It has open chain structure
 - (4) All of these
- 25. -NH-CO- group is characteristic of
 - Cellulose
- (2) Nucleic acid
- (3) Proteins
- (4) Phospholipids
- 26. Which of the following undergoes charring on heating with conc. H₂SO₄?
 - (1) Nucleic acids
- (2) Proteins
- (3) Fats
- (4) Carbohydrates
- 27. Nicotine present in tobacco is a/an
 - Alkaloid
- (2) Terpene
- (3) Steroid
- (4) Protein
 - ЙH
- An aqueous solution of CH₃—CH—COOH at isoelectric point migrates
 - (1) Towards anode
 - (2) Towards cathode
 - (3) No migration towards any electrode
 - (4) None of these

- Number of moles of PhNHNH₂ required to form osazone from fructose is
 - (1) 2

(2) 3

(3) 1

- (4) 4
- 30. Glucose __HNO₃ → P, Product 'P' is
 - (1) Gluconic acid
- (2) Glucaric acid
- (3) Aspartic acid
- (4) All of these

SECTION - B

Previous Years Questions

1. Deficiency of vitamin B, causes the disease

[AIPMT 2012]

- (1) Cheilosis
- (2) Sterility
- (3) Convulsions
- (4) Beri-Beri
- Which one of the following sets of monosaccharides forms sucrose? [AIPMT 2012]
 - β-D-Glucopyranose and α-D-fructofuranose
 - (2) α-D-Glucopyranose and β-D-fructopyranose
 - (3) α–D–Galactopyranose and α–D–Glucopyranose
 - (4) α-D-Glucopyranose and β-D-fructofuranose
- 3. Which of the following hormones is produced under the condition of stress which stimulates glycogenolysis in the liver of human beings?

[AIPMT 2014]

- (1) Thyroxin
- (2) Insulin
- (3) Adrenaline
- (4) Estradiol
- D(+) glucose reacts with hydroxyl amine and yields an oxime. The structure of the oxime would be

[AIPMT 2014]

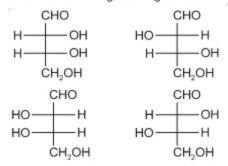
- In a protein molecule, various amino acids are linked together by [NEET-2016]
 - (1) Dative bond
- (2) α-glycosidic bond
- (3) β-glycosidic bond
- (4) Peptide bond
- Which one given below is a non-reducing sugar?

[NEET-2016]

- (1) Sucrose
- (2) Maltose
- (3) Lactose
- (4) Glucose
- The correct statement regarding RNA and DNA, respectively is [NEET-2016]
 - The sugar component in RNA is 2'-deoxyribose and the sugar component in DNA is arabinose
 - (2) The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose
 - (3) The sugar component in RNA is ribose and the sugar component in DNA is 2'-deoxyribose
 - (4) The sugar component in RNA is arabinose and the sugar component in DNA is ribose
- The central dogma of molecular genetics states that the genetic information flows from

[NEET (Phase-2) 2016]

- (1) Amino acids → Proteins → DNA
- (2) DNA → Carbohydrates → Proteins
- (3) DNA → RNA → Proteins
- (4) DNA → RNA → Carbohydrates
- The correct corresponding order of names of four aldoses with configuration given below



respectively, is

[NEET (Phase-2) 2016]

- (1) L-erythrose, L-threose, L-erythrose, D-threose
- (2) D-threose, D-erythrose, L-threose, L-erythrose
- (3) L-erythrose, L-threose, D-erythrose, D-threose
- (4) D-erythrose, D-threose, L-erythrose, L-threose

10. Which of the following statements is not correct?

[NEET-2017]

- Insulin maintains sugar level in the blood of a human body
- (2) Ovalbumin is a simple food reserve in eggwhite
- Blood proteins thrombin and fibrinogen are involved in blood clotting
- (4) Denaturation makes the proteins more active
- The difference between amylose and amylopectin is [NEET-2018]
 - (1) Amylopectin have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 α -linkage
 - (2) Amylose have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 β -linkage
 - (3) Amylose is made up of glucose and galactose
 - (4) Amylopectin have 1 \rightarrow 4 $\alpha\text{-linkage}$ and $^{\circ}$ 1 \rightarrow 6 $\beta\text{-linkage}$
- 12 Which of the following compounds can form a zwitterion? [NEET-2018]
 - (1) Aniline
 - (2) Acetanilide
 - (3) Glycine
 - (4) Benzoic acid
- The non-essential amino acid among the following is [NEET-2019]
 - (1) Valine
- (2) Leucine
- (3) Alanine
- (4) Lysine
- 14. Which structure(s) of proteins remain(s) intact during denaturation process?

[NEET-2019 (Odisha)]

- Tertiary structure only
- (2) Both secondary and tertiary structures
- (3) Primary structure only
- (4) Secondary structure only

Chapter 8

Polymers

Sub-topics

Classification- Natural and synthetic, methods of polymerization (addition and condensation), copolymerization. Some important polymers: natural and synthetic like polyesters, bakelite; rubber, Biodegradable and non-biodegradable polymers.

Classification

Polymers are defined as high molecular mass macromolecules, which consist of repeating structural units derived from the corresponding monomers. Based on source polymers can be of three types.

- (i) Natural polymers: Found in plants and animals. e.g., Proteins, Cellulose, Starch etc.
- (ii) Semi-synthetic polymers: Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are examples of semi-synthetic polymers.
- (iii) Synthetic polymers: Examples are : Polyethene inylon 6, 6, Buna-S etc.

Important Synthetic Polymers

Addition Polymers :

Polymer	Monomer	Application	
Polyethylene	Ethene CH ₂ = CH ₂	Packing material carry bags, insulation for electrical wires and cables, etc.	
Polypropylene	Propene CH ₃ -CH = CH ₂	Packing of textiles and foods, liners for bags, heat shrinkage wraps, carpet fibres, etc.	
Polystyrene or Styron	C ₆ H ₂ -CH = CH ₂ Styrene	Plastic toys, house hold wares, radio and television bodies	
Neoprene	CH ₂ = C-CH = CH ₂ Chloroprene CI	Hoses, shoe heels, stoppers, conveyer belts for mines, etc.	
Buna-s	Styrene CH = CH ₂ , butadiene CH ₂ = CH–CH = CH ₂ , Na as catalyst	Manufacture of tyres, rubber sole, water proof shoes, etc.	
Polyacrylates PMMA	Methyl metha acrylate CH ₃ CH ₂ = C-COOCH ₃	Lenses, light covers, light shades, air craft windows, etc.	
Polyethyl acrylate	CH ₂ = CH–COOC ₂ H ₅	Latex paints adhesives	
Polyacrylonitrile (PAN)(orlon)	Acrylonitrile CH ₂ = CH–CN	For making clothes, carpets, blankets, etc.	
Polyvinyl chloride (PVC)	Vinyl chloride CH ₂ = CH–Cl	Good electrical insulator, hose pipes, rain coats, hand bags, etc.	
Polytetrafluoro ethylene (PTFE) (Teflon)	Tetrafluoro ethylene CF ₂ = CF ₂	For nonstick utensils coating, etc.	

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Condensation Polymers:

Polymer	Monomer	Application
Terylene or dacron	(i) Ethylene glycol HO-CH ₂ -CH ₂ -OH	For wash and wear fabric, tyre cords, seat belts and sails
	(ii) terephthalic acid	
	ноос-{_}соон	
Glyptal or Alkyd resin	(i) Ethylene glycol HO-CH ₂ -CH ₂ -OH	Paints and Lacquers
	(ii) Phthalic acid COOH	
Nylon-6, 6	Adipic acid $HOOC-(CH_2)_z-COOH$ $H_2N-(CH_2)_q-NH_2$ Hexamethylenediamine	Textile fabrics, bristols of brushes, etc.

Polymer	Monomer	Application
Nylon-6, 10	Adipic acid HOOC –(CH ₂) ₄ –COOH Sebacic acid HOOC –(CH ₂) ₈ –COOH	Textile abrics, carpets, bristles for brushes
Nylon-6	HOOC –(CH ₂) ₀ –COOH Caprolactam	Mountainering ropes, tyre cords fabrics
Bakelite (Thermosetting polymer)	Phenol and Formaldehyde OH , HCHO	As binding glue for wood, varnishes, lacquers
Melamine Formaldehyde resin (Thermosetting polymer)	Melamine and Formaldehyde NH2 NH2 N N and HCHO NH2 NH2	Break-resistant crockery
Kevlar	(i) 1, 4-diamino benzene NH₂-V_NH₂ (ii) Terephthaloyl chloride CIOC-V_COCI	Light weight personal armor (bullet-resistant vests)
Urea formaldehyde resin	(i) Urea NH ₂ –C–NH ₂ (ii) Formaldehyde HCHO	Buttons, bottle caps, surgical items, etc.

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Biodegradable polymers

In view of the potential environmental hazards of synthetic polymeric wastes, certain biodegradable polymers such as PHBV and Nylon-2-Nylon-6 are developed as alternatives.

Poly β-hydroxybutyrate-co-β-hydroxy valerate (PHBV)





Try Yourself

SECTION - A

Objective Type Questions

- Glycol on reacting with terephthalic acid gives
 - (1) Glycerol
- (2) Glycollic acid
- (3) Glyptal
- (4) Dacron / Terylene
- Bakelite is polymer of the reaction between
 - (1) Formaldehyde and NaOH
 - (2) Aniline and Urea
 - (3) Phenol and methanal
 - (4) Phenol and methanol
- Natural rubber is a polymer of
 - Ethylene
- (2) Vinyl chloride
- (3) Phenol
- (4) Isoprene
- Gun-cotton is
 - Nitro sucrose
- (2) Nitro cellulose
- (3) Nitro glucose
- (4) Nitro picrin
- Glyptal is classified as a
 - (1) Polyolefin
 - (2) Polyester
 - (3) Polyamide
 - (4) Polyether
- Acrilan fibre used for cloth, carpets and blankets, is the polymer of
 - (1) Acrylonitrile
 - (2) Ethyl acrylate
 - (3) Styrene
 - (4) Mono chloro trifluoro ethane
- Orlon fibers are made from
 - Nylon–6 6
 - (2) Terylene
 - (3) Acrylonitrile
 - (4) Polyethyl acrylate

- Polythene is
 - Thermosetting polymer
 - (2) Thermoplastic
 - (3) Elastomer
 - (4) None of these
- When ethylene diamine is heated with dicarboxylic acid which of the following is obtained?
 - Polythenes
- (2) Polystyrenes
- (3) Polyesters
- (4) Polyamides
- 10 Rayon is
 - (1) Natural silk
 - (2) Artificial silk
 - (3) Natural plastic or rubber
 - (4) Synthetic plastic
- Glyptal is a
 - (1) Viscose rayon
- (2) Nylon
- (3) Polyamide
- (4) Alkyd resin
- 12. Which is not a polymer?
 - (1) Ice
- (2) Starch
- (3) Protein
- (4) Cellulose
- 13. Product of addition polymerisation reaction is
 - (1) PVC
- (2) Nylon
- (3) Terylene
- (4) Polyamide
- 14. Adipic acid with Hexamethylenediamine gives
 - (1) Glycerol
- (2) Glycollic acid
- (3) Glyptal
- (4) Nylon-6,6
- (1) Synthetic rubber

Chloroprene is used in making

- (2) Plastic
- (3) Petrol

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- The synthetic polymers which resembles natural rubber is
 - (1) Neoprene
- (2) Chloroprene
- (3) Glyptal
- (4) Nylon
- 17. Nylon-66 is not a
 - (1) Fibre
 - (2) Condensation polymer
 - (3) Homopolymer
 - (4) Polyamide
- 18. Styrene is the monomer of
 - (1) Buna-S
- (2) Glyptal
- (3) PTFE
- (4) Orlon
- 19. Buna-S is a polymer of
 - (1) Butadiene and Styrene
 - (2) Butadiene and Acrylonitrile
 - (3) Styrene
 - (4) Butadiene and Chloroprene
- Triethyl aluminium and titanium chloride used in plastic industry is a
 - (1) Vulcaniser
 - (2) Plasticiser
 - (3) Ziegler-Natta catalyst
 - (4) Wilkinson's catalyst
- When ethylene is polymerised under very high pressure then product is
 - (1) Low density polyethylene
 - (2) High density polyethylene
 - (3) Unbranched polyethylene
 - (4) None of these
- 22. Which one of the following is used to make 'non-stick' cookware?
 - (1) PVC
- (2) PMMA
- (3) PAN
- (4) PTFE
- 23. Which one of the following is a linear polymer?
 - (1) Amylopectin
 - (2) Glycogen
 - (3) Starch
 - (4) Amylose
- 24. Gutta percha rubber is
 - (1) A trans 1,4-polyisoprene polymer
 - (2) A very hard material
 - (3) A synthetic polymer
 - (4) All of these

- 25. PMMA is the polymer of
 - (1) Methyl methacrylate (2) Methyl acrylate
 - (3) Methacrylate
- (4) Ethylacrylate

SECTION - B

Previous Years Questions

- Which one of the following is **not** a condensation polymer? [AIPMT 2012]
 - Dacron
- (2) Neoprene
- (3) Melamine
- (4) Glyptal
- Which of the following statements is false?

[AIPMT 2012]

- The repeat unit in natural rubber is isoprene.
- (2) Both starch and cellulose are polymers of glucose.
- (3) Artificial silk is derived from cellulose.
- (4) Nylon-66 is an example of elastomer.
- 3. Which one of the following sets forms the biodegradable polymer? [AIPMT 2012]
 - (1) CH₂ = CH CN and CH₂ = CH - CH = CH₂
 - (2) H₂N CH₂ COOH and H₂N - (CH₂)₅ - COOH
 - (3) HO CH2 CH2 OH and

(4)
$$CH_2 = CH - CH = CH_2$$
 and

Which is the monomer of Neoprene in the following? [NEET 2013]

(2)
$$CH_2 = C - CH = CH_2$$

- (3) CH₂ = CH C = CH
- (4) CH2 = CH -- CH = CH2

5. Nylon is an example of

[NEET 2013]

- (1) Polysaccharide
- (2) Polyamide
- (3) Polythene
- (4) Polyester
- Which one of the following is an example of a thermosetting polymer? [AIPMT 2014]

(3)
$$\stackrel{\text{H}}{=}$$
 $\stackrel{\text{CI}}{=}$ $\stackrel{\text{H}}{=}$ $\stackrel{\text{O}}{=}$ $\stackrel{\text{O}}{=}$

7. Which of the following organic compounds polymerizes to form the polyester Dacron?

[AIPMT 2014]

- (1) Propylene and para HO (C₆H₄) OH
- (2) Benzoic acid and ethanol
- (3) Terephthalic acid and ethylene glycol
- (4) Benzoic acid and para HO (C₆H₄) → OH
- Caprolactam is used for the manufacture of

[Re-AIPMT-2015]

- (1) Terylene
- (2) Nylon-6, 6
- (3) Nylon-6
- (4) Teflon
- Biodegradable polymer which can be produced from glycine and aminocaproic acid is [AIPMT-2015]
 - (1) Nylon 6.6
- (2) Nylon 2 nylon 6
- (3) PHBV
- (4) Buna N
- Natural rubber has
- [NEET-2016]
- (1) Random cis and trans-configuration
- (2) All cis-configuration
- (3) All trans-configuration
- (4) Alternate cis and trans-configuration

 Which one of the following structures represents nylon 6,6 polymer? [NEET (Phase-2) 2016]

(1)
$$\begin{pmatrix} H_2 & H_2 & H_3 \\ C & C & C & C \\ NH_2 & CH_3 \end{pmatrix}_{66}$$

Regarding cross-linked or network polymers, which of the following statements is incorrect?

[NEET 2018]

- They contain covalent bonds between various linear polymer chains.
- (2) They are formed from bi- and tri-functional monomers.
- (3) They contain strong covalents bonds in their polymer chains.
- (4) Examples are bakelite and melamine.
- 13. The biodegradable polymer is
- [NEET-2019]

- (1) Nylon-6,6
- (2) Nylon-2-Nylon 6
- (3) Nylon-6
- (4) Buna-S
- The polymer that is used as a substitute for wool in making commercial fibres is

[NEET-2019 (Odisha)]

- (1) Buna-N
- (2) melamine
- (3) nylon-6,6
- (4) polyacrylonitrile

Chapter 9

Chemistry in Everyday Life

Sub-topics

Chemicals in medicines- analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines. Chemicals in food- preservatives, artificial sweetening agents, elementary idea of antioxidants. Cleansing agents- soaps and detergents, cleansing action.

Medicines

Chemicals in Medicine: Chemical substances used for treatment of diseases and for reducing the suffering from pain are called medicines or drugs. Chemotherapy is the science in which chemicals are used for the treatment of diseases.

Chemicals used in chemotherapy are frequently classified according to their action. Thus analgesics relieve pain, antipyretics reduce temperature, anti-inflammatories control inflammation and antibiotics kill bacteria and other micro-organisms.

1. Antipyretics: Antipyretics are substances used to bring down body temperature in high fever. e.g., Aspirin, Phenacetin and Paracetamol.

Aspirin is a common antipyretic. It should not be taken empty-stomach as it generates salicylic acid which may ulcerate stomach wall and can cause bleeding. Calcium and sodium salts of aspirin are more soluble and less harmful.

2. Analgesics: There are drugs used for relieving pain. Aspirin and some other antipyretics act as analgesics also. Certain narcotics (which produce sleep and unconsciouness) are also used as analgesics. Examples of narcotics are morphine, marijuane, codeine, pethidine and heroin. Heroin is morphine diacetate. They are known to be habit-forming.

RO
$$Codeine$$

R'O $Codeine$

R'O $Codeine$

R'O $Codeine$

R'O $Codeine$

R' = H, Morphine
R = CH₃, Codeine

Pethidine hydrochloride

3. Antiseptics and Disinfectants: Antiseptics are the chemicals which kill or prevent the growth of micro-organisms. Antiseptics are applied to living tissues. They can be applied to wounds, cuts, ulcers and diseased skin surfaces. Antiseptics are also employed to reduce odours resulting from bacterial decomposition on the body or in the mouth.

Disinfectants kill micro-organisms but are not safe for contact with living tissues. These are applied to inanimate objects such as floor, instruments, etc.

The same substance can act as an antiseptic as well as a disinfectant by varying the concentration of the solution used. Thus a 0.2 percent solution of phenol acts as an antiseptic, 1 percent solution is a disinfectant and 1.2 percent solution acts as germicide.

Chlorine is used for making water fit for drinking. Low concentration of sulphur dioxide is used for sterilizing squashes for preservation. Commonly used antiseptic, dettol is a mixture of chloro-xylenol and terpineol in a suitable solvent. Bithional is added to soap to impart antiseptic properties. It reduces undesirable odours resulting from bacterial decomposition of organic matter on the skin.

lodine is a powerful antiseptic. It is employed as tincture of iodine. Iodoform (CHI₃) is used as an antiseptic for wound powder.

Some organic dyes, gentian violet and methylene blue are used as antiseptic.

4. Antibiotics: Antibiotics are chemical substances produced by micro-organisms (bacteria, fungi and moulds) that can inhibit the growth or even destroy other micro-organisms. Penicillin is used against large number of infections caused by various bacteria. It is an effective drug for pneumonia, bronchitis, sore throat and abcesses. Other antibiotics like streptomycin and tetracycline are used against diseases caused by bacteria.

Some antibiotics are specific for certain diseases, for example, streptomycin for tuberculosis and chloramphenicol for typhoid.

Broad spectrum antibiotics are medicines effective against several different types of harmful micro-organisms, e.g., tetracycline, chloramphenicol. Penicillin has a narrow spectrum. Ampicillin and amoxicillin are derivatives of penicillin.

Chloramphenicol is a broad spectrum antibiotic. It is rapidly absorbed from the gastro-intestinal tract and hence can be given orally in case of typhoid, dysentry, acute fever, certain form of urinary infections, meningitis and pneumonia.

Sulpha drugs like sulphanilamide and its derivatives sulphadiazine and sulphaguanidine, etc., act against micro-organisms like antibiotics and have been used in place of them.

- 5. Tranquilizers: The chemical substances which act on the central nervous system and have a calming effect to reduce anxiety are specified as tranquilizers. They are basically of two types:
 - (i) Sedative and hypnotics
 - (ii) Mood elevators or antidepressants
 - (i) Sedative and hypnotics: sedatives are central nervous system depressants that reduce nervous tension and promote relaxation without inducing sleep whereas hypnotics are central nervous system depressants

that induce sleep. Synthetic compounds used as sedative and hypnotics are barbituric acid and its derivatives such as **luminal** and **seconal**.

(ii) Antidepressants: A drug used for the treatment of highly depressed patient, who has lost his confidence, to improve his efficiency is known as antidepressant or mood elevator.

- Anaesthetics: These are chemical substances administered for producing general or local insensibility to pain and other sensation. As evident from the definition, anaesthetics are of two types.
 - (i) General anaesthetics; (ii) Local anaesthetics
 - (i) General anaesthetics: These produce unconsciousness and are given when major surgical operations are to be performed. Some of the common general anaesthetics are listed below.

Liquid form: Nitrous oxide, cyclopropane, ethylene, etc.

(ii) Local anaesthetics: These produce loss of sensation on a small portion of the body where the drug is applied. Local anaesthetics are used for minor operations.

Jelly form: xylocaine

Spray form : Ethyl chloride Injection form : Procaine

7. Sulpha drugs: Sulpha drugs were the first chemotherapeutic agents having great antibacterial powers. These are a group of drugs which are derivatives of sulphanilamide. These are widely used as substitute medicines against cocci infection (streptococci, gonococci and pneumonococci, etc.) to the patients who are allergic to antibiotics

$$H_2N$$
 \longrightarrow SO_2NH_2

Sulphanilamide (p-Aminobenzenesulphonamide)

Artificial Sweetening Agents

Artificial sweetener	Structural Formula	Sweetness value in comparison to cane sugar
Aspartame	HO—C—CH ₂ —CH—C—NH—CH—C—OCH ₃ NH ₂ —CH ₂ Aspartic acid part Phenylalanine methyl ester part	100
Saccharin	SO ₂ NH	550
Sucralose	CI H HO H HO CIH ₂ CI	600
Alitame	O CH, CH, C	2000

Food Preservatives:

Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives include table salt, sugar, vegetable oils and sodium benzoate, CeHaCOONa. Sodium benzoate is used in limited quantities and is metabolised in the body. Salts of sorbic acid and propanoic acid are also used as preservatives.

Soaps:

Soaps used for cleaning purpose are sodium or potassium salts of long chain fatty acids, e.g., stearic, oleic and palmitic acids. Soaps containing sodium salts are formed by heating fat (i.e., glycerl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as saponification.

Why do soaps not work in hard water?

Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium soaps respectively when sodium or potassium soaps are dissolved in hard water.

These insoluble soaps separate as scum in water and are useless as cleansing agent. In fact these are hinderance to good washing, mass. Hair washed with hard water looks dull because of this sticky precipitate. Dye does not absorb evenly on cloth washed with soap using hard water, because of this gummy mass.



Try Yourself

SECTION - A

Objective Type Questions

- Class of chemical compounds which are used for the treatments of mental disease are called
 - (1) Analgesic
- (2) Antipyretic
- (3) Tranquilizers
- (4) Antiseptic
- 2. 0.2% solution of phenol acts as
 - (1) Antiseptic
- (2) Disinfectant
- (3) Antipyretic
- (4) Germicide
- 3. Which of the following will act as weak antiseptic for eyes?
 - (1) 0.2% phenol
 - (2) Iodoform
 - (3) Dilute solution of H₃BO₃
 - (4) H₂O₂
- Drug which arrests the growth of the organism is called
 - (1) Bactericidal
 - (2) Bacteriostatic
 - (3) Antihistamines
 - (4) Antifertility drug
- Allergic reactions are caused mainly due to libration of in the body
 - (1) Microbes
- (2) Histamines
- (3) Bacteria
- (4) Acid
- 6. Which of the following is a bacteriostatic?
 - (1) Penicillin
 - (2) Aminoglycosides
 - (3) Ofloxacin
 - (4) Erythromycin

- 7. Which of the following is used as alternative of antibiotic?
 - (1) Sulphadrug
 - (2) Antihistamine
 - (3) Tranquilizer
 - (4) Antipyretic
- 8. Which of the following is a preservative?
 - (1) Sodium benzoate
 - (2) Boric acid
 - (3) Alitame
 - (4) Penicillin

Which of the following is used as an antiseptic under the name Perhydrol?

- (1) Hydrogen peroxide
- (2) Bithional
- (3) lodoform
- (4) Boric acid
- Compounds which retard the action of oxygen on the food and thereby help in preservation are called as
 - (1) Antioxidants
 - (2) Antimicrobials
 - (3) Antifertility drug
 - (4) Sweetener
- Which of the following is cationic detergent?

- (2) CH₃(CH₂)₁₆CH₂-SO₃-Na
- (3) CH₃(CH₂)₁₆COO(CH₂CH₂O)_nCH₂CH₂OH
- (4) All of these

(3) Disinfectants harm the living tissues

(4) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant

Aspirin is Artificial sweetener which is stable under cold [AIPMT 2014] conditions only is (2) Antibiotic Antiseptic Saccharine (2) Sucralose (3) Tranquilizer (4) Analgesic (3) Aspartame (4) Alitame Antiseptic present in dettol is Nitrogen dioxide and sulphur dioxide have some (1) Quodine (2) Chloroxylenol properties in common. Which property is shown by (3) Bithional (4) None of these one of these compounds, but not by the other? [AIPMT-2015] COOH is the structure of (1) Is used as a food-preservative OCOCH (2) Forms 'acid-rain' (1) Aspirin (2) Salol (3) Is a reducing agent (3) Phenolphthalein (4) Ibrufen (4) Is soluble in water 15. Substances which are used to bring down Bithional is generally added to the soaps as an temperature in high fever are called additive to function as a/an [AIPMT-2015] (1) Analgesic (2) Tranquilizers (1) Antiseptic (2) Softener (3) Antipyretic (4) Antimicrovial (3) Dryer (4) Buffering agent Which of the following is an analgesic? **SECTION - B** [NEET-2016] **Previous Years Questions** Chloromycetin Novalgin Chloroamphenicol is an [AIPMT 2012] (3) Penicillin (4) Streptomycin Antifertility drug Mixture of chloroxylenol and terpineol acts as (2) Antihistaminic [NEET-2017] (3) Antispetic and disinfectant Analgesic (2) Antiseptic (4) Antibiotic-broad spectrum (3) Antipyretic (4) Antibiotic Antiseptics and disinfectants either kill or prevent Among the following, the narrow spectrum antibiotic growth of microorganisms. Identify which of the is [NEET-2019] following statements is not true? [NEET 2013] Penicillin G (2) Ampicillin Chlorine and lodine are used as strong (3) Amoxycillin (4) Chloramphenicol disinfectants The artificial sweetener stable at cooking (2) Dilute solutions of Boric acid and Hydrogen, temperature and does not provide calories is Peroxide are strong antiseptics [NEET-2019 (Odisha)]

Alitame

(3) Aspartame

(2) Saccharin

(4) Sucralose

Chapter 10 Hydrogen

Sub-topics

Occurrence, isotopes, preparation, properties and uses of hydrogen; hydrides-ionic, covalent and interstitial; physical and chemical properties of water, heavy water; hydrogen peroxide-preparation, reactions, uses and structure.

Hydrogen is the most abundant element in the universe.

Atomic Number

1s¹ Electronic configuration

Protium 1H1, Deuterium 2H1, Tritium 3H1 [Mixture is Hydron] Isotopes

Orthohydrogen, o-H2 (75% at 25°C) Allotropes

Parahydrogen, PH₂ (25% at 25°C)

H₂, D₂, T₂ Molecular forms

Oxidation state

Note: (i) Nucleus of hydrogen contains only proton.

(ii) Physical properties of isotopes are different whereas their chemical properties are same (Physical constant: T > D > H).

Preparation of H₂

(a) Water gas shift reaction (Bosch Process)-Reaction of steam on hydrocarbons or coke at high temperature.

$$C_nH_{2n+2(g)} + nH_2O \xrightarrow{-1270 \text{ K}} nCO + (2n+1)H_2$$

e.g.
$$CH_4 + H_2O_{(g)} \xrightarrow{-1270 \text{ K}} CO_{(g)} + 3H_{2(g)}$$

$$\mathsf{C(s)} + \mathsf{H_2O_{(g)}} \xrightarrow{-1270\,\mathsf{K}} \; \mathsf{CO_{(g)}} + \; \mathsf{H_{2(g)}}$$

CO is converted to CO2 by passing steam over iron oxide to form more H2:

$$CO_{(g)} + H_2O_{(g)} \xrightarrow{-673 \text{K}} CO_2 + H_{2(g)}$$

(b) Lane's process

1st step : $3Fe(s) + 4H_2O(g) \xrightarrow{\Delta} Fe_3O_4 + 4H_2$

2nd step: It is reduction of Fe₃O₄ using water gas.

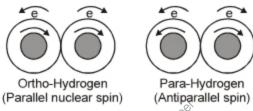
- (c) By electrolysis of water, 2H₂O → 2H₂ + O₂
 In laboratory acid is added while in industry Ba(OH)₂.
- (d) Laboratory preparation
 - (i) Zn + H₂SO₄ → ZnSO₄ + H₂
 - (ii) $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$
 - (iii) NaH + H₂O → NaOH + H₂

Note: Concentrated H2SO4 is an oxidising reagent.

Properties of Hydrogen

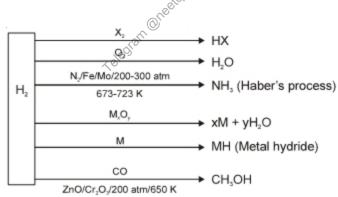
A. Physical Properties

- Colourless, odourless and tasteless gas.
- (ii) Dihydrogen has two nuclear spin isomers called ortho and para-dihydrogen.



At high temperature maximum of 75% ortho-H₂ can be present. Ortho-H₂ and para-H₂ have 1 and 0 nuclear spin respectively.

B. Chemical Properties



Compounds of Hydrogen

Hydrides

(a) Saline/Ionic hydrides

Hydrogen combines mostly with s-block metals

e.g. NaH, CaH2 (except BeH2 and MgH2)

(b) Metallic hydrides/Interstitial hydrides/Non-stoichiometric

Hydrogen combines with d-block and f-block metals.

e.g., ScH2, LaH2

(c) Molecular/Covalent hydrides

Hydrogen combines with p-block elements (Exception: MgH2, BeH2)

Note: (i) Molecular hydrides are further divided as - electron deficient (e.g., B₂H₈), electron precise (e.g., CH_d) and electron rich (e.g., NH₂)

(ii) The elements of group 7, 8, 9 do not form hydrides. This is known as Hydride Gap region.

Water

Water is universal polar solvent because of permanent dipole moment (1.84).

Hard Water and Soft Water: Water containing soluble calcium and magnesium salts like bicarbonates, chlorides and sulphates is called hard water. Water free from the above salt is known as soft water.

The hardness of water may be of temporary or permanent in nature.

Temporary hardness: Due to presence of bicarbonates of Ca and Mg.

Permanent hardness: Due to presence of soluble calcium and magnesium sulphates and chlorides.

Removal of hardness is known as softening of water. Some important water softners are

- (i) By Na₂CO₃
- (ii) Calgon → Na₂ [Na₄(PO₃)₆]
- (iii) Permutit (Na₂Al₂Si₂O₈.xH₂O)

Hydrogen Peroxide (H₂O₂)

H₂O₂ is with open book like structure with polar O-H bond and non-polar O-O bond.



Preparation

- (A) Na₂O₂ + H₂SO₄ (20%, ice cold) → Na₂SO₄ + H₂O₂ (Merck's process)
- (B) $BaO_2 + CO_2 + H_2O \rightarrow H_2O_2 + BaCO_3$
- (C) By electrolysis of 50% H₂SO₄ (Industrial process).

The bottle of H_2O_2 labelled as "10 V H_2O_2 " means 10 ml of O_2 is obtained from 1 ml of H_2O_2 at STP after decomposition ($2H_2O_2 \rightarrow 2H_2O + O_2$). Similarly "20 V H_2O_2 ", "30 V H_2O_2 ".

Volume strength of $H_2O_2 = 11.2 \times M$ or $= 5.6 \times N$

Properties

- (A) It can act as both oxidising as well as reducing agent.
 - (i) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ In acid
 - (ii) $H_2O_2 + 2e^- \rightarrow 2OH^- In base$
- (B) H₂O₂ is a weak diprotic acid.



Try Yourself

SECTION - A

Objective Type Questions

- 1. Allotropes of hydrogen are
 - (1) Deuterium, Tritium
 - (2) Ortho-H₂, Meta-H₂
 - (3) Ortho-H₂, Para-H₂
- (4) Protonium, Deuterium
- 2. Lane's process is used for the preparation of
 - (1) H₂
- (2) H₂O
- (3) H,O,
- (4) D₂O
- 3. Enthalpy of vapourisation
 - (1) For H, is more than D,
 - (2) For D2 is more than H2
 - (3) For both H, and D, are same
 - (4) Value can't be determined
- 4. In Water gas shift reaction, water gas is
 - (1) H₂ + H₂O
- (2) H₂ + CO₂
- (3) H₂ + CO
- (4) H₂ + D₂
- In ortho and para hydrogen the nuclear spin respectively are
 - (1) Parallel and opposite
 - (2) Opposite and parallel
 - (3) It may be parallel or opposite
 - (4) They do not differ in nuclear spin
- 6. Take out the odd compound
 - (1) LiH
- (2) CaH₂
- (3) NaH
- (4) ScH₂
- The example of covalent hydride is
 - (1) TiH
- (2) NaH
- (3) CH,
- (4) All of these
- Interstial hydrides are formed by
 - (1) s-block metals
- (2) p-block metals
- (3) d-block metals
- (4) All of these

- 9. The group of elements responsible for hydride gap
 - (1) Mn, Ca, Ni
- (2) Mn, Fe, Li
- (3) Mn, Fe, Co
- (4) Mn, Cu, Cl
- 10. Group 7, 8, 9 are responsible for
 - (1) Covalent hydrides
 - (2) Ionic hydrides
 - (3) Metallic hydrides
 - (4) Hydride gap
- 11. Hardness of water is due to of Ca and Mg
 - (1) Sulphates, chlorides, bicarbonates
 - (2) Fluorides, sulphates, carbonates
 - (3) Only carbonates
 - (4) Carbonates, bromides
- 12. Temporary hardness is due to
 - (1) Bicarbonates of Ca and Mg
 - (2) Sulphates of Ca and Mg
 - (3) Carbonates of Ca and Mg
 - (4) Chlorides of Ca and Mg
- 13. Calgon is
 - (1) Na₂CO₃
- (2) Na,[Na,(PO,),]
- (3) Na₂[Na₄(PO₂)₆]
- (4) Na₄[Na₂(PO₃)₅]
- 14. Oxidation of 2-butyl anthraquinol by air gives
 - (1) H₂O
- (2) D₂O
- (3) H₂O₂
- (4) H₂
- Which of the following is correct for H₂O₂?
 - (1) H2O2 can act as oxidising agent
 - (2) H,O, is non-planar
 - H₂O₂ is prepared from Na₂O₃
 - (4) All of these

- The bottle labelled '30 V H₂O₂' means
 - (1) 30 ml of H₂O₂ on decomposition gives 30 ml of O₂ at STP
 - (2) 30 ml of H₂O₂ on decomposition gives 10 ml of O, at STP
 - (3) 1 ml of H₂O₂ on decomposition gives 30 ml of O, at STP
 - (4) 1 ml of H₂O₂ on decomposition gives 29 ml of O, at STP
- The normality of H₂O₂ labelled as "10 V H₂O₂" is
 - (1) 1.786 N
- (2) 3.4 N
- (3) 5.6 N
- (4) 11.2 N
- 18. Volume strength of 1.7 N H₂O₂ is
 - (1) 1.7 × 5.6
- (2) 1.7 × 11.2
- (3) 1.7
- (4) 0.17
- 19. CH₂D + Cl₂(one mole) → ?
 - CH,CI
- (2) CH, DCI
- (3) CD₂CI
- (4) CH₂CI₂
- 20. Ice starts floating on water due to its
 - (1) High density
- (2) Low density
- (3) Hydrogen bonding
- (4) Due to its solid nature
- 21. The correct order of boiling point is
 - (1) H₂ > D₂
- (2) D₂ > T₂
- (3) D,O > H,O
- (4) H₂O > D₂O
- Hydrogen with negative oxidation state is in
 - (1) CH₄
- (2) SiH₂
- (3) NH₃
- (4) LiH
- Hybridisation of oxygen in H₂O and H₃O₅ is
 - sp² and sp³
 - (2) sp³ and sp²
 - (3) sp² and sp²
 - (4) sp³ and sp³

- 24. Which of the following is correct?
 - (1) D2O is known as heavy water
 - (2) Hydride gap is due to group 7, 8, 9
 - (3) Ortho and para-H, are allotopes of hydrogen
 - (4) All of these
- 25. H,O, is manufactured these days
 - By the action of H₂O₂ on BaO₃
 - (2) By the action of H₂SO₄ on Na₂O₅
 - (3) By electrolysis of 50% H,SO,
 - (4) By burning hydrogen in excess of oxygen
- 26. The ease of adsorption of the hydrates alkali metal ions on an ion-exchange resins follows the order
 - (1) K⁺ < Na⁺ < Rb⁺ < Li⁺
 - (2) Na⁺ < Li⁺ < K⁺ < Rb⁺
 - (3) Li⁺ < K⁺ < Na⁺ < Rb⁺
 - (4) Rb⁺ < K⁺ < Na⁺ < Li⁺

SECTION - B

Previous Years Questions

Which of the following statements about hydrogen is incorrect? [NEET-2016]

- Dihydrogen does not act as a reducing agent
- (2) Hydrogen has three isotopes of which tritium is the most common
- (3) Hydrogen never acts as cation in ionic salts
- (4) Hydronium ion, H₂O⁺ exists freely in solution
- The method used to remove temporary hardness of water is [NEET-2019]
 - Calgon's method
 - (2) Clark's method
 - (3) Ion-exchange method
 - (4) Synthetic resins method

Chapter 11

s-Block Elements

Sub-topics

Group-I and group-II elements: General introduction, electronic configuration, occurrence, anomalous properties of the first element of each group, diagonal relationship, trends in the variation of properties (such as ionization enthalpy, atomic and ionic radii), trends in chemical reactivity with oxygen, water, hydrogen and halogens; uses. Preparation and Properties of Some important Compounds: Sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate, biological importance of sodium and potassium. Industrial use of lime and limestone, biological importance of Mg and Ca.

Alkali Metals (Group - I)

Element	Symbol	Atomic No.
Lithium	Li	9
Sodium	Na	11
Potassium	K	19
Rubidium	Rb	37
Cesium	cs	55
Francium	Fr	87

Alkaline Earth Metals (Group - II)

Element	Symbol	Atomic No.
Benyllium	Be	4
Magnesium	Mg	12
Calcium	Ca	20
Strontium	Sr	38
Barium	Ва	56
Radium	Ra	88

Physical Properties

A. Atomic Properties

Atomic Radii

- (a) The alkali metals have largest atomic radii in their period.
- (b) The alkaline earth metals are smaller than alkali metals.
- (c) The atomic radii increases down the group for both.
- (d) Ionic size also increases down the group for both.
- (e) Alkali metal cations are larger than those of the corresponding isoelectronic alkaline earth metal cations because of lesser positive charge.

B. Ionization Energy

(a) The Ist I.E. of alkali metals < Ist I.E of alkaline earth metals.

The IInd I.E. of alkali metals > IInd I.E of alkaline earth metals.

(b) The alkali metals have lowest I.E followed by alkaline earth metals.

This is due to

- Larger atomic radii.
- Greater screening effect due to presence of closed shell of electrons.

C. Flame colouration

Metal	Colour	Metal	Colour
Li	Crimson	Ca	Brick red
Na	Yellow	Sr	Crimson
K	Violet	Ва	Apple green
Rb	Red violet		
Cs	Blue	age ^s	

Alkali and Alkaline earth metals impart colours to the flame when they are heated, electron get excited to higher energy level due to absorption of heat and when e comes back to ground state emits energy of different wavelength, which falls under visible region.

Note: Be and Mg due to small size and high ionisation potential energy do not impart colour.

D. Reducing nature

Alkali metals and alkaline earth metals are good reducing agents due to low I.P. value and electropositive nature.

Alkali metals are strong reducing agents than alkaline earth metals.

As I.P decreases, reducing nature increases down the group for Gp-I and Gp-II.

Li is exceptionally strongest reducing agent due to small size, high hydration energy and highest negative E° value.

E. Conductivity: (Mobility of ions in aqueous solution)

Conductivity is higher if size of ion is smaller.

Down the group cationic size of alkali metals increases and hence Li* should show high mobility and hence high conductivity.

But exceptionally due to high hydration energy the ionic size of M* in aqueous solution decreases down the group from Li⁺ to Cs⁺ decreasing the mobility and hence Li⁺(aa) has least conductivity.

$$Li^{+}_{(g)} < Cs^{+}_{(g)}$$
 (radius)

F. Metallic Character

The metallic character increases down the group I and group II. The metallic lustre is due to the low I.E of valence electrons. Alkaline earth metals are less electropositive than the alkali metals hence they are less metallic than alkali metals.

The metallic character increases down the group in s-block.

Chemical Properties

A. Oxides

Li forms stable oxide (Li₂O), Na forms peroxide (Na₂O₂) and rest of the group-I metals form superoxides as stable oxides.

Be, Mg and Ca forms stable oxides whereas Ba and Sr forms peroxides.

Oxides and peroxides are colourless whereas superoxides are coloured.

Note: All oxides of group-I and group-II are basic except BeO which is amphoteric.

B. Hydroxides

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

 $M_2O_2 + H_2O \rightarrow 2M^+ + 2OH^- + \frac{1}{2}O_2$
 $2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$

Down the group the basic character of alkali and alkaline earth metal hydroxides increases, due to increase in ionic character.

Note: Be(OH), is amphoteric

Down the group solubility of hydroxides increases, group-I hydroxides are more soluble than group-II hydroxides.

C. Halides

The reactivity of group-I and group-II metals increases from Li to Cs and Be to Ba and that of halogen towards a particular group-I and group-II reactivity decreases from F₂ to I₂.

All halides are ionic except beryllium halide (which is covalent).

Percentage Ionic character and covalent character is given by Fajan's Rule.

Hybridisation of Be-atom in $BeCl_2$ may be sp^3 , sp^2 and sp in solid state, vapour phase (when exist as dimer) and sp above 1200 K temperature respectively.

D. Nitrates (Only decomposition reaction)

$$\begin{split} &\mathsf{MNO_3} \stackrel{\Delta}{\longrightarrow} \mathsf{MNO_2} + \frac{1}{2}\mathsf{O_2} \ \ [\mathsf{M} = \mathsf{Na}, \ \mathsf{K}, \ \mathsf{Rb}, \ \mathsf{Cs}] \\ &2\mathsf{M}(\mathsf{NO_3})_2 \stackrel{\Delta}{\longrightarrow} 2\mathsf{MO} + 4\mathsf{NO_2} + \mathsf{O_2} \ \ [\mathsf{M} = \mathsf{Be}, \ \mathsf{Mg}, \ \mathsf{Ca}, \ \mathsf{Sr}, \ \mathsf{Ba}] \end{split}$$

Note: Exceptionally LiNO3 decomposes to Li2O + NO2 + O2

E. Carbonates/Bicarbonates

All carbonates of group-I do not decompose, except Li2CO3.

NEET s-Block Elements 103

Carbonates of group-II decomposes to give metal oxide and CO2.

$$MCO_3 \rightarrow MO + CO_2 [M = Be, Mg]$$

Down the group for group-I and group-II carbonates thermal stability increases.

$$M(HCO_3)_2 \rightarrow MCO_3 + CO_2 + H_2O$$
 [M = group-II metal]
 $MHCO_3 \rightarrow M_2CO_3 + CO_2 + H_2O$ [M = group-I metal]

Note: Na2CO3 is prepared by Solvay's process but not K2CO3 because KHCO3 is highly soluble in water.

Solubility of carbonates decreases in aqueous solution down the group but that of bicarbonates increases down the group.

F. Reaction with N₂

In group-I, only Li reacts with N2 to give Li3N rest of them do not react.

group-II reacts with N2 to give M3N2 (e.g., Mg3N2, Ca3N2)

G. Reaction with liquid NH₃

- (a) All alkali metals and alkaline earth metals except Be and Mg dissolve in liquid NH₃ to give a deep blue solution.
- (b) Dilute metal ammonia solutions are blue. On increasing the concentration of NH₃ the blue colour starts changing to copper or bronze colour after which metals does not dissolve.
- (c) The dissolution of metal yields ammoniated sation and electron.

For alkali metals

$$M \longrightarrow M^+ \mbox{ (in liq. ammonia)} \mbox{$\stackrel{\circ}{\mathscr{L}}$$^-$} \mbox{(ammoniated)}$$

$$M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

solvated electron

For alkaline earth metal

$$M \longrightarrow M^{+2} + 2e^{-}$$

$$2NH_3 + 2e^- \longrightarrow 2NH_2^- + H_2$$

$$M^{2+} + 2NH_2^- \longrightarrow M(NH_2)_2$$

As electropositivity increases, the stability of ammoniated metal cation increases. Alkali metal ammonia solution have

- blue colour due to the presence of ammoniated electron which absorb energy in visible region.
- very high electrical conductivity due to ammoniated electrons and solvated cation.
- (iii) paramagnetic behaviour.
- (iv) very strong reducing property.

Solution is blue in colour, conductive in nature and is paramagnetic due to ammoniated electron.

Important Points

- 1. Li and Mg shows diagonal relationship due to comparable size and similar polarising power.
- Lithium is extracted from important minerals spodumene LiAlSi₂O₆, lepidolite (Li, Na, K)₂Al₂(SiO₃)₃ F(OH) and amblygonite LiAl(PO₄)F.

Extraction

- (a) Preparation of lithium chloride from the above minerals
- (b) Electrolysis of LiCl, consists of mixture of 55% LiCl and 45% KCl as electrolyte.
- Sodium is extracted by electrolysis of fused mixture of sodium chloride (40%) and calcium chloride (60%) in Down's cell.
- 4. Sodium hydroxide is prepared by using following cells
 - (a) The mercury cathode cell (Castner-Kellner cell)

- (b) Diaphragm cell: Alkali and chlorine are kept separate by using diaphragm, electrolysis of which liberates Cl₂(anode) and NaOH (cathode).
- (c) Nafion membrane cell: NaCl is electrolysed

$$2NaCl_{(aq)} + H_2O_{(I)} \xrightarrow{electrolysis} 2NaOH_{(aq)} + H_2 + Cl_2$$

Solvay's process: (Preparation of Na₂CO₃·10H₂O)

(b)
$$NH_3 + H^+ \rightarrow NH_4^+$$

(c)
$$NH_4^+ + HCO_3^- \rightarrow NH_4HCO_3$$

(d)
$$NH_4HCO_3 + NaCI \rightarrow NaHCO_3 \xrightarrow{\triangle} Na_2CO_3$$

Note: K2CO3 can't be prepared as KHCO3 formed, is highly soluble in water.

- 6. Magnesium is extracted from
 - (a) (i) Magnesite (MgCO₃) or Dolomite (MgCO₃.CaCO₃)

$$MgCO_3 \xrightarrow{\Delta} MgO + O_2$$

$$CaCO_3 \cdot MgCO_3 \longrightarrow CaO \cdot MgO + 2CO_2$$

(ii) MgO is treated with C and Cl2 whereas CaO-MgO is treated with ferrosilicon

$$MgO + C + Cl_2 \rightarrow MgCl_2 + CO$$

$$\downarrow electrolysis$$
 Mg

(b) From carnallite

The ore is dehydrated in a current of hydrogen chloride and the fused chloride is electrolysed to give Mg.

(c) From sea water (Main industrial method)

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \xrightarrow{\Delta} MgO \xrightarrow{C + Cl_2} MgCl_2 \xrightarrow{Electrolysis} Mg$$

NEET s-Block Elements 105

7. Compositions

Quicklime - CaO

Slaked lime - Ca(OH)₂

Epsom salt – MgSO₄·7H₂O

Plaster of paris $- CaSO_4 \cdot \frac{1}{2}H_2O$

Lime stone - CaCO₃

Portland cement - CaO, SiO $_2$, Al $_2$ O $_3$, Fe $_2$ O $_3$, etc.

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Try Yourself

SECTION - A

Objective Type Questions

- The metallic lustre exhibited by sodium is explained by
 - (1) Diffusion sodium ions
 - (2) Oscillation of loose electrons
 - (3) Excitation of free protons
 - (4) Existence of body centred cubic lattice
- Alkali metals readily dissolve in liquid ammonia to give blue coloured solutions. The blue colour is believed to be due to
 - (1) Ammoniated cations
 - (2) Ammoniated anions
 - (3) Ammoniated electrons
 - (4) Ammoniated cations and ammoniated electrons
- 3. Alkali metals are powerful reducing agents because
 - (1) These are metals
 - (2) These are non-metals
 - (3) Their ionic radii are large
 - (4) Their ionization potentials are low
- 4. Molecular formula of Glauber's salt is
 - (1) MgSO, 7H,O
 - (2) CuSO₄·5H₂O
 - (3) FeSO, 7H,O
 - (4) Na,SO, 10H,O
- 5. Which of the following oxides is formed when potassium metal is burnt in excess air?
 - (1) K₂O
- (2) KO
- (3) KO₂
- (4) K₂O₂
- 6. KNO, on heating gives
 - (1) O₂
- (2) NO₂
- (3) O, + NO,
- (4) NO + O₂

- 7. Which of the following is correct for thermal stability?
 - (1) K2CO3 < MgCO3 < CaCO3 < BeCO3
 - (2) BeCO₃ < MgCO₃ < CaCO₃ < K₂CO₃
 - (3) BeCO, < MgCO, < K,CO, < CaCO,
 - (4) CaCO₃ < MgCO₃ < BeCO₃ < K₂CO₃
- 8. Which of the following has the smallest size ?
 - (1) Na+
- (2) Mg²⁺
- (3) Al3+
- (4) P5+
- The ionization potential of Li, Na and K follows the order Li > Na > K. The oxidation potential of these elements follows the order
 - (1) Li > Na > K
- (2) Li > K > Na
- (3) K > Na > Li
- (4) Na > K > Li
- The correct order of melting points of Be, Mg and Ca is
 - (1) Be > Mg > Ca
- (2) Be > Ca > Mg
- (3) Ca > Mg > Be
- (4) Ca > Be > Mg
- 11. Which one of the following has lowest first ionisation energy?
 - (1) Li
- (2) Na
- (3) Rb
- (4) Cs
- 12. Alkali metals are usually prepared by
 - (1) Reduction of their oxides with aluminum
 - (2) Reduction of their oxides with carbon
 - (3) Electrolysis of their molten chlorides
 - (4) Thermal decomposition of their carbonates
- 13. Which compound possesses the highest lattice energy?
 - Csl
 - (2) KF
 - (3) LiF
 - (4) NaCl

- The alkali metals are strong reducing agents due to
 - Low ionization energy
 - (2) Large ionic radii
 - High enthalpy of hydration
 - (4) High reduction potential value
- Which of the following compounds has the highest melting point?
 - NaF
- (2) NaCl
- (3) NaBr
- (4) Nal
- Li(s) → Li* (aq) + e⁻ iE° = +3.07 V. Li is the best reducing agent due to its
 - Low I.E.
- (2) Small ionic radius
- (3) High ∆H_{Hyd}. of Li⁺
- (4) Low ΔH sublimation
- Portland cement is prepared by using
 - (1) Limestone, clay and gypsum
 - (2) Limestone, gypsum and alumina
 - (3) Limestone, clay and sand
 - (4) Limestone, gypsum and sand
- 18. Which metals are radioactive in the s-block?
 - Cs and Fr
- (2) Cs and Ra
- (3) Fr and Ra
- (4) Ba and Ra
- Reason for alkali metals to be soft is
 - They are less metallic in nature
 - (2) There is only one valency electron per atom
 - (3) They do not have close-packed structures
 - (4) They have high I.E.
- 20. The thermal stability of alkaline earth metal carbonates increases from Be to Ba. This is because
 - (1) Covalent nature decreases and ionic nature increases
 - (2) Size increases
 - (3) Electropositive nature increases
 - (4) Ionization potential decreases
- 21. Which of the following decreases on descending from Be to Ba?
 - (1) Solubility of hydroxides in water
 - (2) Basic strength of oxides
 - (3) Thermal stabilities of the carbonates
 - (4) Sum of the first two ionisation energies

- 22. Which of the following is most soluble in water?
 - Be(OH),
- (2) Mg(OH),
- (3) Ca(OH),
- (4) Ba(OH),
- 23. Which of these give oxide on heating?
 - LiNO₃
- (2) NaNO_a
- (3) KNO₃
- (4) CsNO₃
- 24. Which of these is thermally unstable?
 - Li,CO,
 - (2) Na,CO,
 - (3) K₂CO₃
 - (4) Rb₂CO₃
- Diagonal relationship in periodic table is shown by the elements of
 - First with second period
 - (2) Second with third period
 - (3) Third with fourth period
 - (4) None of these
- The thermal stability of the carbonates are
 - (1) Na,CO, > K,CO, > BeCO, > BaCO,
 - (2) K₂CO₃ > Na₂CO₃ > BaCO₃ > BeCO₃
 - (3) BaCO₃ > BeCO₃ > K₂CO₃ > Na₂CO₃
 - (4) None of these
- 27. With respect to alkaline earth metals, the alkali metals show
 - Greater hardness
 - (2) Higher melting point
 - Smaller ionic radii
 - Lower ionization energy
- 28. Sodium when dropped in water catches fire because
 - (1) It has higher atomic mass
 - (2) It is a metal
 - (3) It is highly electropositive in nature
 - (4) The hydrogen gas evolved in the reaction is combustible in nature
- Hybridisation of Be in BeCl, can be
 - sp
 - (2) sp²
 - (3) sp³
 - (4) All of these

SECTION - B

Previous Years Questions

Which one of the alkali metals, forms only, the normal oxide, M2O on heating in air?

[AIPMT 2012]

- (1) Li
- (2) Na
- (3) Rb
- (4) K
- On heating which of the following releases CO. most easily? [Re-AIPMT-2015]
 - (1) MgCO₃
- (2) CaCO.
- (3) K₂CO₃
- (4) Na₂CO₂
- The function of "Sodium pump" is a biological process operating in each and every cell of all animals. Which of the following biologically important ions is also a constituent of the pump?

[AIPMT-2015]

- (1) Fe2+
- (2) Ca2+
- (3) Mq²⁺
- (4) K⁺
- Solubility of the alkaline earth's metal sulphates in water decreases in the sequence [AIPMT-2015]
 - (1) Ba > Mg > Sr > Ca (2) Mg > Ca > Sr > Ba &

 - (3) Ca > Sr > Ba > Mg (4) Sr > Ca > Mg > √8a
- Which of the following statements is false?

[NEET-2016]

- (1) Mg2+ ions are important in the green parts of plants
- (2) Mg²⁺ ions form a complex with ATP
- (3) Ca2+ ions are important in blood clotting
- (4) Ca2+ ions are not important in maintaining the regular beating of the heart
- The suspension of slaked lime in water is known [NEET (Phase-2) 2016]
 - (1) Limewater
 - (2) Quicklime
 - (3) Milk of lime
 - (4) Aqueous solution of slaked lime

- In context with beryllium, which one of the following statements is incorrect? [NEET (Phase-2) 2016]
 - (1) It is rendered passive by nitric acid
 - (2) It forms Be₂C
 - (3) Its salts rarely hydrolyze
 - (4) Its hydride is electron-deficient and polymeric
- 8. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field? [NEET-2017]
 - (1) Na
- (2) K
- (3) Rb
- (4) Li
- Which of the following oxides is most acidic in nature? [NEET-2018]
 - MgO
- (2) BeO
- (3) CaO
- (4) BaO
- Among CaH2, BeH2, BaH2, the order of ionic character is [NEET-2018]
 - BeH₂ < CaH₂ < BaH₃
 - (2) CaH₂ < BeH₂ < BaH₃
 - (3) BaH₂ < BeH₂ < CaH₂
 - (4) BeH₂ < BaH₂ < CaH₂
 - Enzymes that utilize ATP in phosphate transfer require an alkaline earth metal (M) as the cofactor. M is: [NEET-2019]
 - Be
- (2) Mg
- (3) Ca
- (4) Sr
- 12. Which of the following is an amphoteric hydroxide? [NEET-2019]
 - Sr(OH)₂
- (2) Ca(OH)₂
- (3) Mg(OH)₂
- (4) Be(OH)₂
- Crude sodium chloride obtained by crystallisation of brine solution does not contain

[NEET-2019 (Odisha)]

- CaSO₄
- (2) MgSO₄
- (3) Na₂SO₄
- (4) MgCl₂
- 14. Which of the alkali metal chloride (MCI) forms its dihydrate salt (MCI · 2 H₂O) easily?

[NEET-2019 (Odisha)]

- KCI
- (2) LiCl
- (3) CsCl
- (4) RbCl

Chapter 12

p-Block Elements

Sub-topics

General Introduction to p-Block Elements. Group 13 elements: General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous properties of first element of the group; Boron, some important compounds: borax, boric acids, boron hydrides. Aluminium: uses, reactions with acids and alkalies. group 14 elements: General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous behaviour of first element. Carbon, allotropic forms, physical and chemical properties: uses of some important compounds: oxides. Important compounds of silicon and a few uses: silicon tetrachloride, silicones, silicates and zeolites, their uses. Group - 15, 16 and 17 elements: General introduction, electronic configuration, variations of properties, oxidations states, Hydrides, Halides, oxides and oxyacids, interhalogen compounds. Group 18 elements: General introduction, electronic configuration, occurrence, some compounds of xenon.

BORON FAMILY (GROUP - 13)

Element	Symbol	Atomic No.
Boron	В	5
Aluminium	Al	13
Galium	Ga	31
Indium	In	49
Thallium	TI	81

Boron is the first member of group 13 and is the only non-metal of the group. Boron occurs in two isotopic forms B¹⁰ and B¹¹.

The important mineral of boron are

Boron is prepared from:

- (i) Reduction of B₂O₃
 - $B_2O_3 + 3Mg \rightarrow 2B + 3MgO$
- (ii) Electrolytic reduction of fused borates
- (iii) Reduction of volatile boron compound by dihydrogen at high temperature

$$2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$$

Physical properties

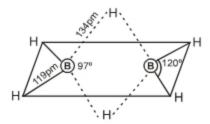
- (a) The atomic radius increases from Boron to Aluminium, decreases from Aluminium to Gallium and again increases from Indium to Thalium.
- (b) All elements are soft metal with low melting point and high electrical conductivity except Boron.

- (c) Down the group stability of +3 oxidation state decreases whereas stability of +1 state increases due to inert pair effect.
- (d) Only Boron shows allotropy.

Note: Al(OH)3, Tl(OH)3 and Tl(OH) is known but not Al(OH).

Compounds of Boron

(1) B₂H₆ (Diborane)



Boron in B₂H₆ is sp³ hybridised.

Two bridging B - H > Terminal B - H bond

Boron hydride is dimerised by Banana bond known as **3-centred-2electron** (3c – 2e) **bond** or banana bond or hydrogen bridge bond.

(2) Oxides and Hydroxides

Note: (i) B(OH)₃ i.e., H₃BO₃ is orthoboric acid. (i) white crystalline, in which planar H₃BO₃ units are joined by hydrogen bonds. It is a weak monobasic lewis acid. B(OH)₃ + 2HOH → [B(OH)₄]⁻ + H₃O⁺.

(3) Borax : Na₂B₄O₇·10H₂O

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} NaBO_2 + B_2O_3$$
 (used in borax-bead test)
Borax Glassy bead

Borax-bead + Transition metal salt → Coloured bead

Metal oxide + B₂O₃ → Metal(BO₂)₂

Metal metaborate (coloured)

Where metal is transition metal (In metal metaborate metal will show given colours, Cu-green, Co-deep blue, Fe-yellow, Ni-brown)

 $B_3N_3H_6$ – **Borazole** also known as **Borazine** or **Inorganic Benzene**. It is isoster of benzene. Hybridisation of B and N-atoms is same i.e. sp^2 .

(4) Boron trihalides (BX₃)

The number of electrons around BX₃ is only six i.e. BX₃ is electron deficient having tendency to accept a pair of electrons and thus behave as Lewis acids.

In BX_3 , $p\pi$ - $p\pi$ back-bonding is possible and the extent of back-bonding decreases with increase in the size of halogen. So the acidic strength follows the order $BF_3 < BCI_3 < BBr_3 < BI_3$.

CARBON FAMILY (GROUP - 14)

Element	Symbol	Atomic No.	
Carbon	С	6	
Silicon	Si	14	
Germanium	Ge	32	
Tin	Sn	50	
Lead	Pb	82	

Allotropes of Carbon

Crystalline - Diamond, Graphite, Fullerenes

Amorphous - Charcoal, Coke, lamp black

Note: All except Pb shows allotropy.

Properties:

- (a) Down the group +4 oxidation state becomes unstable whereas +2 oxidation state becomes stable.
- (b) Down the group catenation property decreases due to decrease in the bond dissociation energy.
- (c) The ability to form $p\pi$ – $p\pi$ multiple bonds to itself and to other elements, decreases down the group.
- (d) Tetrahalides of type MX₄ are covalent and are with tetrahedral geometry. The thermal stability of the halides decreases down the group.
- (e) Sn2+ is less stable than Sn4+ and Pb2+ is more stable than Pb4+

Note: Pbl4 does not exist

- (a) Dihalides stability increases in order, CX2 < SiX2 < GeX2 < SnX2 < PbX2
- (b) Catenation property decreases down the group due to decrease in strength of bond.
- (c) Conversion of β-tin (white) to α-tin (grey) in cold countries is known as Tin plague, Tin-pest or Tin-disease.
- (f) Carbides (i) Ionic carbides → CaC₂
 - (ii) Covalent carbides → SiC, B₄C
 - (iii) Interstitial carbides → WC, TiC

Note: SiCl₄, can be hydrolysed to silicic acid H₂SiO₃.H₂O but not CCl₄ due to unavailability of vacant d-orbital in CCl₄.

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Oxides

- (a) CO is neutral oxide whereas CO₂ is acidic oxide.
- (b) SiO₂, GeO₂, SnO₂ and PbO₂ are amphoteric.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

- (c) CO2 is a gas whereas rest all are solids.
- (d) Quartz, cristobalite and tridymite are three crystalline form of SiO₂.

Silicates

The basic structural unit of silicates is the SiO₄ tetrahedron. Depending on the number of corner shared various kind of silicates are known.

Orthosilicates – SiO_4^{4-} unit; Pyrosilicates – $Si_2O_7^{6-}$; chain, cyclic or linear single chain silicates –[$(SiO_3)^{2-}$]_n, sheet silicates [$(Si_2O_5)^{2-}$]_n and 3D silicates.

Silicones

Synthetic polymer with Si-O-Si linkage.

Silicones are polymers containing R₂SiO repeating units. These are not affected by light, water, heat and electricity.

RSiCl₃ gives sheet structure to silicones.

Note: Due to strong Si-O linkage SiO, forms giant petwork solid with high melting point.

Some Important Reaction

(i)
$$CO_2 + 2NH_3 \rightarrow NH_2CO_2NH_4 \rightarrow CO(NH_2)_2$$
ammonium carbamate

(ii)
$$CaC_2 + N_2 \rightarrow \underbrace{CaNCN + C}_{Nitrolim}$$

NITROGEN FAMILY (GROUP - 15)

Element	Symbol	Atomic No.
Nitrogen	N	7
Phosphorous	Р	15
Arsenic	As	33
Antimony	Sb	51
Bismuth	Bi	83

(a) Down the group metallic character increases.

N and P - non-metals, As and Sb - metalloids, Bi-metallic.

- (b) All elements except nitrogen have low and almost similar electronegatives.
- (c) N₂ is gas whereas P, As, Sb and Bi are solids under normal condition.
- (d) N₂ is less reactive due to high bond dissociation energy.

Multiple bonding is present $(p\pi - p\pi)$ in $N \equiv N$.

Down the group $p\pi$ – $p\pi$ bond formation tendency decreases but $p\pi$ – $d\pi$ bond formation increases with other atoms.

Properties:

Hydrides

NH₃ PH₃ AsH₃ SbH₃ BiH₃

- (i) Bond angle decreases
- (ii) Thermal stability decreases
- (iii) Basic character decreases
- (iv) Reducing nature increases

Note: BiH₃ > SbH₃ > NH₃ > AsH₃ > PH₃ - boiling point NH₃ is exception due to H-bonding

Halides

- (i) Two series of halides of the type MX₃ and MX₅
- (ii) Bonding in trihalides is covalent except in case of BiF₃ which is ionic.
- (iii) All trihalides except NBr₃ and NI₃are stable.

Note: NX₅ does not exist, due to unavailability of d-orbital in the valence shell.

Oxides

£١	Acid	lic strength	n decreas	es →	d.
cidic strength creases	M_2O_3	N_2O_3	P_2O_3	As_2O_3	@neetulestinpaper
creas	M_2O_4	N_2O_4	P_2O_4	As ₂ O ₄	idlesit
Ä	$M_2O_{\scriptscriptstyle 5}$	N_2O_5	P_2O_6	As ₂ O ₅	Ores
Ψ					-M

Note: N₂O & NO are neutral oxides.

Oxides of Nitrogen

Oxide	Structure	Preparation
(a) N ₂ O	N≡N→O	$NH_4NO_3 \xrightarrow{ \Delta} N_2O + H_2O$
(b) NO ₂	OKNIO	$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + \frac{1}{2}O_2$
(c) N ₂ O ₃	0//N-N 0	${\rm NO} + {\rm NO_2} \xrightarrow{-30^{\circ}{\rm C}} {\rm N_2O_3}$
(d) N ₂ O ₄	N-N-N	$2NO_2 \xrightarrow{-23^{\circ}C} N_2O_4$
(e) N ₂ O ₅	0 N-O-N 0	$\mathrm{4HNO_3} + \mathrm{P_4O_{10}} \rightarrow \mathrm{2N_2O_5} + \mathrm{4HPO_3}$

Oxyacids of Phosphorus

Hypophosphorous acid → H₃PO₂

Phosphorous acid → H₃PO₃

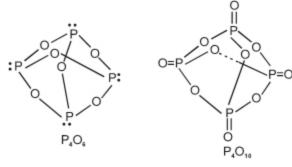
Orthophosphoric acid → H₃PO₄

Metaphosphoric acid → HPO₃

Hypophosphoric acid → H₄P₂O₆

Pyrophosphoric acid → H₄P₂O₇

Structure of P₄O₆ & P₄O₁₀



Reactions to Remember

(ii)
$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

(iv)
$$NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$$

(v)
$$NH_4NO_2 \xrightarrow{\Delta} N_2 + H_2O$$

(vi)
$$AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + O_2$$

(vii)
$$\operatorname{HgNO_3} \xrightarrow{\Delta} \operatorname{Hg} + \operatorname{NO_2} + \operatorname{O_2}$$

(viii) NH₃ is prepared by hydrolysis of
$$Mg_3N_2$$
: $Mg_3N_2 + 6H_2O \rightarrow Mg(OH)_2 + 2NH_3$

(x) In lab., ammonia is prepared by the reaction of NH4Cl with Ca(OH)2.

$$2NH_4CI + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + H_2O$$

(xi) Ostwald process: Nitric acid is manufactured by the catalytic oxidation of ammonia.

$$4NH_3 + 5O_2 \xrightarrow{Pt/Rh} 4NO + 6H_2O$$

 $2NO + O_2 \xrightarrow{1120K} 2NO_2$
 $3NO_2 + H_2O \rightarrow 2HNO_3 + NO(g)$

OXYGEN FAMILY (GROUP - 16)

Element	Symbol	Atomic No.	
Oxygen	0	8	
Sulphur	S	16	
Selenium	Se	34	
Tellurium	Te	52	
Polonium	Po	84	

NEET p-Block Elements 115

Only oxygen has tendency to form double bond (O=O), i.e., $p\pi$ - $p\pi$ bonding among the group elements.

Down the group $p\pi$ – $p\pi$ bonding between same element decreases but $p\pi$ – $p\pi$ bonding among other elements increases.

Sulphur exist mainly in two allotropic form: rhombic sulphur and monoclinic sulphur.

Properties:

Hydrides

 $\begin{array}{c|c} H_2O \\ H_2S \\ H_2Se \\ H_2Te \end{array}$ Down the group, bond angle decreases, acidic strength increases, thermal stability decreases.

Oxides

 $SO_3 > SO_2$ - acidic strength $SO_3 > SeO_3$ - acidic strength

Oxyacids of sulphur

Sulphuric acid is prepared by Contact process.

Steps: (i) Sulphur or sulphide ores are heated in air to generate SO2.

- (ii) Conversion of SO2 to SO3 by reaction with O2 in the presence of V2O5.
- (iii) Absorption of SO₃ in H₂SO₄ to give oleum, which on hydrolysis gives H₂SO₄ back.

Halogen Family (Group - 17)

Element	Symbol	Atomic No.
Fluorine	F	9
Chlorine	CI	17
Bromine	Br	35
lodine	- 1	53
Astatine	Αt	85

The name **halogens** is derived from the Greek word meaning sea salt producers because its three members occur as salts (chlorides, bromides and iodides) in sea water.

- (a) Atomic and ionic radii: The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge.
- (b) Ionization energies: The ionization energies of halogens are very high. It decreases from Fluourine to lodine.
- (c) Melting and boiling points: The melting and boiling points of halogens increases with increase in atomic number as we go down the group.

(d) Electron affinities

- (i) All these have maximum electron affinities in their respective periods. This is due to the fact that the atoms of these elements have only one electron less than the stable noble gas (ns²np6) configurations. Therefore, they have maximum tendency to accept an additional electron.
- (ii) In general, electron affinity decreases from top to bottom in a group. This is due to the fact that the effect of increase in atomic size is much more than the effect of increase in nuclear charge and thus, the additional electron feels less attraction by the large atom. Consequently, electron affinity decreases.
- (iii) Fluorine has unexpectedly low electron affinity than chlorine. Therefore, chlorine has the highest electron affinity in this group. The lower electron affinity of fluorine as compared to chlorine is due to very small size of the fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p subshell of fluorine and thus, the incoming electron does not feel much attraction. Therefore, its electron affinity is small.

Thus, electron affinity among halogens varies as :

(e) Colour: All the halogens are coloured. The colour of different halogens are given below:

Halogens	Fluorine	Chlorine	Bromine (I)	lodine (s)
Colour	Light yellow	Greenish yellow	Reddish brown	Dark violet

(f) Low dissociation energies: All the halogen have very low dissociation energies. As a result, they can readily dissociate into atoms and react with other substance. As shown below, the dissociation energies of halogens are quite low in comparison to common molecules such as H₂, O₂ and N₂. The decreasing order is Cl₂ > Br₂ > F₂ > I₂.

Molecule	F ₂	Cl ₂	Br ₂	l ₂	H ₂	02	N ₂
Dissociation energies	159	243 ₅ 2577	193	151	458	495	941

(g) Oxidising power: Halogens have high electron affinity values and therefore they have strong tendency to take up the electron.

$$\frac{1}{2}X_2 + e^- \longrightarrow X^-$$

As a result, they act as powerful oxidising agents.

The decreasing oxidising power of the halogen as we go down the group is shown by their decreasing reduction potentials.

X ₂	F ₂	Cl2	Br ₂	l ₂	At ₂	
E° (volts) Reductions	2.87	1.40	1.09	0.62	- 0.3	

(h) Formation of hydrides

- (i) Physical state: Hydrogen fluoride is a low boiling liquid (b.p. 292 K) while HCl, HBr and HI are gases. The anomalous property of HF is due to presence of hydrogen bonding in the molecules. Due to hydrogen bonding in HF molecules it exists as associated molecule (HF)_n.
- (ii) Thermal stability: The thermal stability of the hydrides decreases from HF to HI. HF is most stable whereas HI is least stable. Decrease in stability of the hydrides is due to decrease in bond strength which decreases as we go down the group.

(iii) Reducing character: The decreasing thermal stability of hydrogen halides from HF to HI indicates that the reducing character increases down the group as

(iv) Acidic strength: The acidic strength of these acids increases down the group

Thus, HF is the weakest acid and HI is the strongest acid among these halogen hydrides.

Fluorine is the most electronegative halogen. Thus, HF should be more ionic in nature and consequently it should be strongest acid. The major factor is the bond dissociation energy. The bond dissociation energy decreases from HF to HI so that HF has maximum bond dissociation energy and HI has the lowest value.

(i) Oxides of halogens: Fluorine forms two oxides OF₂ and O₂F₂ which are called oxygen fluorides. In this case fluorine is more electronegative than oxygen. On the other hand the oxides of CI, Br and I are called oxides. They form oxides from +1 to +7 oxidation states.

Oxidation State	Fluorine	Chlorine	Bromine	lodine
-1	OF ₂			
+1	-	Cl ₂ O	Br ₂ O	
+2				
+4		CIO ₂	BrO ₂	I ₂ O ₄
+5		ar a Nagor		I ₂ O ₅
+6		Cl ² O ⁶ C/2	Br ₂ O ₅	
+7		Cl ₂ Q ₈		I ₂ O ₇

Note: All these oxides are powerful oxidising agents and decompose explosively when subjected to mechanical shock or heat.

(j) Oxyacids of halogens: The oxyacids of halogens are given in table may be noted that fluorine forms only one unstable oxoacid HOF as because fluorine is more electronegative than oxygen.

Oxidation State	Chlorine	Bromine	lodine
+1	HCIO	HBrO	HIO
	Hypochlorous acid	Hypobromous acid	Hypoiodous acid
+3	HCIO ₂		
	Chlorous acid		
+5	HCIO ₃	HBrO ₃	HIO ₃
	Chloric acid	Bromic acid	lodic acid
+7	HClO₄	HBrO ₄	HIO₄
	Perchloric acid	Perbromic acid	Periodic acid

Note :
$$\mathrm{HOCl} < \mathrm{HClO_2} < \mathrm{HClO_3} < \mathrm{HClO_4} \rightarrow \mathit{acidic strength}$$

 $\mathrm{HClO} > \mathrm{HBrO} > \mathrm{HIO} \rightarrow \mathit{acidic strength}$

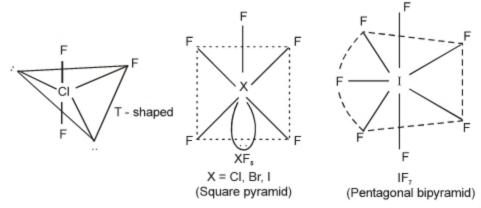
(k) Interhalogen compounds

Halogens may react to form binary interhalogen compounds of the types XY (CIF, BrF, BrCl, ICI, IBr) (Linear) XY_3 (CIF₃, BrF₃, IF₃, ICI₃) **T-shaped**

XY5 - CIF5, BrF5, IF5 (Square pyramidal)

XY, - IF, (Pentagonal bi-pyramidal)

Shapes:



They are essentially covalent due to less difference in their electronegativity. They are more reactive than halogens due to less effective overlapping (except fluorine).

NOBLE GASES (GROUP - 18)

Eleme	nt	Symbol	Atomic No.
Helium		He	2
Neon		Ne	10
Argon		Ar	18
Krypto	n	Kr	36
Xenon		Xe	54
Rador	1	Rn	86



- (a) Down the group from He to Xe solubility increases due to increase in dipole induced dipole interaction.
- (b) Polarizability increases down the group.
- (c) As van der Waal forces increases down the group liquefication increases down the group.
- (d) He exists in two liquid phases He-I & He-II. He-I is normal liquid while He-II is super fluid.
- (e) The m. p and b. p. of noble gases are very low and increase with increase of atomic number due to the increase in size (van der Waals' forces).

Chemical Properties

In general, noble gases are not very reactive. Their inertness to chemical reactivity is attributed to the following reasons :

- (a) The noble gases have completely filled ns2np6 electronic configurations in their valence shells.
- (b) The noble gases have very high ionisation energies.
- (c) The electron affinities of noble gases are almost zero.

In 1962, N. Bartlett noticed that platinum hexafluoride, PtF₆ is a powerful oxidising agent which combines with molecular oxygen to form ionic compound, dioxygenyl hexafluoroplatinate (V), O₂*[PtF₆]⁻.

$$O_2(g) + PtF_6(g) \longrightarrow O_2^+[PtF_6]^-$$

- (d) The first ionisation energy of xenon gas [1170 kJ mol-1] is fairly close to that of oxygen (1166 kJ mol-1).
- (e) The molecular diameter of oxygen and atomic radius of xenon are similar (4Å)

On this assumption, Bartlett reacted xenon and platinum hexafluoride in gas phase and an orange yellow solid of the composition $XePtF_{\epsilon}$ was obtained.

$$Xe(g) + PtF_6(g) \longrightarrow Xe^+[PtF_6]^-(s)$$
Orange yellow

(i) Preparation of fluorides: The common fluorides of xenon such as XeF₂, XeF₄ and XeF₆ can be prepared by the direct combination of xenon and fluorine under different conditions:

$$Xe+F_2 \xrightarrow{Ni \text{ vessel}} XeF_2$$

[Xenon in excess]

$$Xe+2F_2$$
 $\xrightarrow{\text{Ni vessel}}$ XeF_4

$$\begin{array}{cccc} Xe + 3F_2 & \xrightarrow{Ni \ vessel} & XeF_6 \\ \text{(1:20)} & & 573 \ K, \ 50-60 \ atm \end{array}$$

(ii) Preparation of oxides: XeO₃ is the most common oxide and it is prepared by the hydrolysis of XeF₄ or XeF₆.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 3O_2 + 24HF$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

(iii) Preparation of oxyfluorides: The oxyfluorides of xenon are prepared by the partial hydrolysis of XeF₄ or XeF₆.

$$XeF_4 + H_2O \xrightarrow{-80^{\circ}C} XeOF_2 + 2HF$$

Xenon dayoffluoride

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Xenon oxytetrafluoride

(f) Structure of xenon compounds: The type of hybridisation and structures of some common compounds of xenon are given in table.

Compound	Formula	Oxidation	State of hybridisation	Structure
Xenon difluoride	XeF ₂	+2	sp³d	Linear
Xenon tetrafluoride	XeF ₄	+4	sp³d²	Square planar
Xenon hexafluoride	XeF ₆	+6	sp ³ d ³	Distorted octahedral
Xenon oxydifluoride	XeOF ₂	+4	sp³d	Tshaped
Xenon oxytetrafluoride	XeOF ₄	+6	sp ³ d ²	Square pyramidal
Xenon trioxide	XeO ₃	+6	sp³	Pyramidal



Try Yourself

SECTION - A

Objective Type Questions

- Boric acid when burnt with ethyl alcohol gives a green edged flame due to the combustion of
 - (1) Boric anhydride
- (2) Metaboric acid
- (3) Ethyl borate
- (4) Orthoboric acid
- 2. Amorphous boron on burning in air forms
 - (1) B(OH),
 - (2) Mixture of B2O3 and BN
 - (3) Only B₂O₃
 - (4) Only BN
- Boron compounds behave as lewis acids because of their
 - (1) Acidic nature
 - (2) Covalent nature
 - (3) Ionisation energy
 - (4) Electron deficient nature
- 4. Ozone, on reaction with KI solution finally produces
 - (1) Cl₂
- (2) l₂
- (3) HI
- (4) IO₄-
- 5. Two electron three centred bond is present in
 - (1) NH₃
- (2) B₂H₆
- (3) BCI,
- (4) AICI,
- 6. Which of the following compound is actually isoelectronic and isostructural with benzene?
 - (1) Diborane
- (2) Toluene
- (3) Borazole
- (4) Metaboric acid
- The formula of compounds of boron and hydrogen may be
 - (1) B₀H₀₊₁
- (2) B₀H₀₊₄
- (3) B₀H₀₀₀
- (4) Both (2) & (3)
- 8. The first ionisation enthalpies of Li, Be, B and C are given below. Which of these corresponds to Boron?
 - (1) 520 kJ mol⁻¹
- (2) 800 kJ mol-1
- (3) 899 kJ mol-1
- (4) 1086 kJ mol⁻¹

- BCI, does not exist as dimer because
 - (1) Due to back bonding
 - (2) B has low electronegativity
 - (3) B has low electron affinity
 - (4) B has no vacant orbitals
- 10. In B₂H₆
 - (1) There is a B-B-B bond
 - (2) The structure is similar to C,H,
 - (3) The boron atoms are linked through hydrogen bridges
 - (4) All the atoms lie in one plane
- 11 The compound which is commonly known as inorganic benzene is
 - (1) B₆H₆
- (2) B₃N₃H₃
- (3) B₃N₃H₆
- (4) C_sH_sB
- 12. Carborundum is the commercial name of
 - (1) Al₂O₃
- (2) SiC
- (3) SiO,
- (4) HPO₃
- 13. Which does not exist?
 - (1) [CCI_a]²⁻
- (2) [SiCl_e]²⁻
- (3) [GeF_c]²⁻
- (4) [SnCl_a]²⁻
- The geometry of (SiO₄)⁴ ion is
 - (1) Tetrahedral
- (2) Square planar
- (3) Octahedral
- (4) Planar triangular
- The silicates which contain discrete tetrahedral units are
 - (1) Sheet silicates
 - (2) Ortho silicates
 - (3) Three dimensional silicates
 - (4) Pyrosilicate
- Poisonous gas present in the exhaust fumes of car is
 - (1) CH,
- (2) C,H,
- (3) CO
- (4) CO₂

NEE	T					
17.	Al, Cr and Fe remains of	uneffe	cted with conc. HNO ₃			
	(1) Strong oxidising na	ture				
	(2) Less reactivity of metal					
	(3) Formation of passiv	ve lay	er of metal oxide			
	(4) Low reactivity of HN	NO ₃				
18.	NO ₂ is anhydride of					
	(1) HNO ₃	(2)	HNO ₂			
	(3) HNO ₂ and HNO ₃	(4)	H ₂ N ₂ O ₂			
19.	NH ₄ NO ₃ on heating give	es				
	(1) N ₂ O	(2)	NO			
	(3) N ₂	(4)	N_2O_3			
20.). (NH ₄) ₂ Cr ₂ O ₇ on heating gives					
	(1) $N_2 + Cr_2O_3 + H_2O$	(2)	CrO ₃ + N ₂ + H ₂ O			
	(3) CrO ₅ + N ₂ + H ₂ O	(4)	None of these			
21.	NH ₃ reacts with excess	of Cl	₂ to give			
	(1) NCl ₃	(2)	NH₄CI			
	(3) N ₂	(4)	NCI ₅			
22.	Excess of NH ₃ reacts v	vith C	₂ to give			
	(1) NH ₄ Cl		NCI ₃			
	(3) N ₂ O	(4)	NCI ₅			
23.	NH ₃ is dried over					
	(1) Conc. H ₂ SO ₄	(2)	P ₂ O ₅			
	(3) CaO	(4)	CaCl ₂			
24.	CO ₂ is isoelctronic with	1	P ₂ O ₅ © O			
	(1) NO ₂ +	(2)	NO			
	(3) N ₂		NO ₂			
25.	Distillation of conc. HN	O ₃ wit	h P₂O₅ gives			
	(1) N ₂ O ₅		NO ₂			
	(3) N ₂ O ₃		N ₂ O ₄			
26.	NH₄+ is a conjugate aci					
	(1) NH ₃		NH ₂ -			
	(3) HN ₃	, ,	None of these			
27.	$2NH_3 + 3CuO \rightarrow N_2 + 3$	3Cu +	3H₂O, NH₃ is			

(1) Reducing agent

(3) Both (1) & (2)

(1) Calcium nitride

(1) NO

give

(3) N₂O₄

30. Which of the following flourides does not exist? NF_e (2) PF_s (3) AsF₅ (4) SbF₂ 31. Which of the following compounds evolves N2 on heating? (1) NH₄NO₃ (2) NaNO, (3) NH, NO, (4) Pb(NO₃), NO, can not be prepared by heating (1) KNO, (2) Pb(NO₃), (3) Cu(NO₃), (4) AgNO, Oxygen is prepared in laboratory from (1) Sodium and water (2) Electrolysis of water (3) KCIO, and MnO, (4) HNO, Oxygen can be prepared from solid KMnO₄ by Dissolving the solid in FeSO, solution (2) Dissolving the solid in dilute HCI (3) Treating the solid with H₂ gas (4) Strongly heating the solid (3) Water Oxegen is denser than air so it is collected over (2) Spirit (3) Mercury (4) Kerosene oil 36. The formula of ozone is O, it is An allotrope of oxygen (2) Compound of oxygen (3) Isotope of oxygen (4) Isobar of oxygen There is no S-S bond in (1) S₂O₄²⁻ (2) S₂O₆ ²⁻ (3) S₂O₃2-(4) S₂O₇²⁻ 38. When thiosulphate ion is oxidised by iodine, which one of the following ion is produced? (1) SO₃²⁻ (2) SO₄2-(3) S₄O₆²⁻ (4) S₂O₆²⁻ 39. What is formed when Cl, is bubbled through molten sulphur? (1) SOCI, (2) SCI, (3) S₂Cl₂ (4) SCI₄ 40. Which one is known as Caro's acid? H,SO. (2) H₂SO₂ (3) H,S,O, (4) H,S,O, 41. Which one is known as Marshall's acid?

(2) H₂SO₆

(4) H₂S₂O₇

(1) H₂S₂O₃

(3) H,S,O,

(2) Oxidizing agent

(2) Calcium cyanide

(4) None of these

(2) N₂O₃

(4) N₂O₈

28. Which of the following oxides of nitrogen is

Nitrogen reacts with calcium oxide and carbon to

(3) Calcium cyanamide (4) Calcium nitrate

anhydride of HNO2 (Nitrous acid)?

- When moist coloured flowers are added into SO, gas the flowers are decolourised because
 - SO, absorbs colouring matter
 - (2) SO₂ oxidises vegetable colouring matter
 - (3) SO, reduces vegetable colouring matter
 - (4) SO₂ gives colourless product
- 43. Which of the following is best oxidizing agent?
 - (1) F₂
- (2) Cl₂
- (3) O₂
- (4) Br₂
- 44. Out of the hydrogen halides which one has the highest boiling point
 - (1) HI
- (2) HBr
- (3) HCI
- (4) HF
- 45. Which of the following reaction is possible?
 - I, + 2NaBr → Br, + 2Nal
 - (2) I₃ + 2NaCl → Cl₃ + 2Nal
 - (3) Br₂ + 2NaCl → Cl₂ + 2NaBr
 - (4) Cl₂ + 2NaBr → Br₂ + 2NaCl
- 46. Which of the hydrogen halides forms salts like KHX, (where X is a halogen atom)?
 - (1) HF
- (2) HCI
- (3) HI
- (4) HBr
- Iodine will be able to displace chlorine from
 - KCIO₃
- (2) KCI
- (3) HCI
- (4) BaCl,
- 48. HF is not stored in glass bottles because
 - (1) It reacts with visible part of light
 - (2) It reacts with sodium oxide of the glass
 - (3) It reacts with the aluminium oxide of the glass
 - (4) It reacts with SiO, of the glass
- 49. Which noble gas compound was made by N. Bartlet?
 - XeF₂
- (2) XePtF,
- (3) O, Pt F,
- (4) XeF₄
- Hybridisation of Xe in XeO₃, XeF₆, XeO₃F₃ respectively
 - sp³, sp³d³, sp³d
- (2) sp³, sp³d², sp³d
- (3) sp², sp³d, sp³d²
- (4) sp², sp³, sp

SECTION - B

Previous Years Questions

- In which of the following compounds, nitrogen exhibits highest oxidation state? [AIPMT 2012]
 - (1) N₃H
- (2) NH₂OH
- (3) N₂H₄
- (4) NH₂

- 2. A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. During the reaction which element undergoes maximum change in the oxidation number? [AIPMT 2012]
 - (1) CI
- (2) C
- (3) S
- (4) H
- Sulphur trioxide can be obtained by which of the following reaction [AIPMT 2012]

 - (1) $S + H_2SO_4 \xrightarrow{\Delta}$ (2) $H_2SO_4 + PCI_6 \xrightarrow{\Delta}$
 - (3) CaSO₄ + C → ∆ (4) Fe₂(SO₄)₂ → ∆
- Which of the following statements is not valid for oxoacids of phosphorus? [AIPMT 2012]
 - All oxoacids contain tetrahedral four coordinated phosphorus
 - (2) All oxoacids contain atleast one P = O unit and one P - OH group
 - Orthophosphoric acid is used in the manufacture of triple superphosphate
 - (4) Hypophosphorous acid is a diprotic acid
- In which of the following arrangements the given sequence is not strictly according to the property indicated against it? [AIPMT 2012]
 - (1) HF < HCI < HBr < HI : increasing acidic strenath
 - (2) H₂O < H₂S < H₂Se < H₂Te : increasing pK_a
 - (3) NH₃ < PH₃ < AsH₃ < SbH₃ : increasing acidic
 - (4) CO₂ < SiO₂ < SnO₂ < PbO₂ : increasing oxidising power
- Which of the following structure is similar to graphite? [NEET 2013]
 - (1) B

- (2) B₄C
- (3) B₂H₆
- (4) BN
- Which of these is not a monomer for a high molecular mass silicone polymer? [NEET 2013]
 - Me₂SiCl₂
- (2) Me₃SiCl
- (3) PhSiCl₂
- (4) MeSiCl₂
- The basic structural unit of silicates is [NEET 2013]
 - SiO⁴₄
- (2) SiO₃²
- (3) SiO₄²⁻
- (4) SiO-
- Which is the strongest acid in the following?

[NEET 2013]

- HCIO₂
- (2) HCIO,
- (3) H₂SO₃
- (4) H₂SO₄

XeF₂ is isostructural with

[NEET 2013]

- (1) ICI₂
- (2) SbCl₂
- (3) BaCl₂
- (4) TeF₂
- 11. Acidity of diprotic acids in aqueous solutions increases in the order [AIPMT 2014]
 - (1) H₂S < H₂Se < H₂Te (2) H₂Se < H₂S < H₂Te
 - (3) H₂Te < H₂S < H₂Se (4) H₂Se < H₂Te < H₂S
- 12. The variation of the boiling points of the hydrogen halides is in the order HF > HI > HBr > HCl.

What explains the higher boiling point of hydrogen fluoride? [Re-AIPMT-2015]

- The bond energy of HF molecules is greater than in other hydrogen halides
- (2) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule
- (3) The electronegativity of fluorine is much higher than for other elements in the group
- (4) There is strong hydrogen bonding between HF molecules
- The stability of +1 oxidation state among Al, Ga, In and TI increases in the sequence

[Re-AIPMT-2015]

- (1) TI < In < Ga < Al
- (2) In < TI < Ga < Al
- (3) Ga < In < Al < Tl (4) Al < Ga < In < Tl ⊙</p>
- 14. Which of the statements given below is incorrect?

[Re-AIPMT-2015]

- ONF is isoelectronic with O₂N⁻
- (2) OF2 is an oxide of fluorine
- (3) Cl₂O₇ is an anhydride of perchloric acid
- (4) O₃ molecule is bent
- Strong reducing behaviour of H₃PO₂ is due to

[Re-AIPMT-2015]

- (1) High oxidation state of phosphorus
- (2) Presence of two –OH groups and one P H bond
- (3) Presence of one –OH group and two P H
- (4) High electron gain enthalpy of phosphorus
- When copper is heated with conc. HNO₃, it produces [NEET-2016]
 - Cu(NO₂)₂ and N₂O
 - (2) Cu(NO₃)₂ and NO₂
 - (3) Cu(NO₃)₂ and NO
 - (4) Cu(NO₃)₂, NO and NO₂

- Which is the correct statement for the given [NEET-2016]
 - Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid
 - (2) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid
 - (3) Both are diprotic acids
 - (4) Both are triprotic acids
- Among the following, the correct order of acidity is [NEET-2016]
 - (1) HCIO₄ < HCIO₂ < HCIO < HCIO₃
 - (2) HCIO₃ < HCIO₄ < HCIO₂ < HCIO</p>
 - (3) HCIO < HCIO₂ < HCIO₃ < HCIO₄
 - (4) HCIO₂ < HCIO < HCIO₃ < HCIO₄
- The product obtained as a result of a reaction of nitrogen with CaC, is [NEET-2016]
 - (1) Ca₂CN
- (2) Ca(CN)₂
- (3) CaCN
- (4) CaCN₂
- Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules?

[NEET-2016]

- (\$) F₂ > Cl₂ > Br₂ > l₂ (2) l₂ > Br₂ > Cl₂ > F₂
- (3) Cl₂ > Br₂ > F₂ > I₂ (4) Br₂ > I₂ > F₂ > Cl₂
- Match the compounds given in Column-I with the hybridisation and shape given in Column-II and mark the corect option. [NEET-2016]

Column-I

Column-II

- (a) X₃F₆
- (i) Distorted octahedral
- (b) XeO₂
- (ii) Square planar
- (c) XeOF,
- (iii) Pyramidal
- (d) XeF₄
- (iv) Square pyramidal

(d)

(ii)

(iii)

- (a)
- (b) (c)
- (1) (iv)
- (ii) (iii)
- (2) (i)
- (iii)
- (iv)
- (3) (i)
- (ii)
- (4) (iv)
- (iii) (i) (ii) 22. AIF3 is soluble in HF only in presence of KF. It is due to the formation of [NEET (Phase-2) 2016]
 - (1) K₃[AIF₃H₃]
- (2) K₃[AIF₆]
- (3) AIH₂
- (4) K[AIF₂H]
- 23. Name the gas that can readily decolourises acidified KMnO₄ solution [NEET-2017]
 - (1) CO₂
- (2) SO₂
- (3) NO₂
- (4) P₂O₅
- 24. In which pair of ions both the species contain S-S bond? [NEET-2017]
- (2) S₄O₆²⁻, S₂O₃²⁻
- (1) S₂O₇²⁻, S₂O₃²⁻ (3) S₂O₇²⁻, S₂O₈²⁻
- (4) S₄O₆²⁻, S₂O₇²⁻

It is because of inability of ns2 electrons of the valence shell to participate in bonding that

[NEET-2017]

- Sn²⁺ is reducing while Pb⁴⁺ is oxidising
- (2) Sn2+ is oxidising while Pb4+ is reducing
- (3) Sn2+ and Pb2+ are both oxidising and reducing
- (4) Sn⁴⁺ is reducing while Pb⁴⁺ is oxidising
- 26. Match the interhalogen compounds of column I with the geometry in column II and assign the correct code [NEET-2017]

Column I

Column II

- (a) XX"
- (i) T-shape
- (b) XX²₃
- (ii) Pentagonal bipyramidal
- (c) XX₆
- (iii) Linear
- (d) XX₇
- (iv) Square-pyramidal
- (v) Tetrahedral
- a(iii), b(iv), c(i), d(ii)
 a(iii), b(i), c(iv), d(ii)
- (3) a(v), b(iv), c(iii), d(ii) (4) a(iv), b(iii), c(ii), d(i)
- 27. The element which does not disproportionate in NaOH solution?
 - (1) F₂
- (2) Cl₂
- (3) P_x
- (4) S
- The correct order of atomic radii in group 13
 - (1) B < Al < In < Ga < Tl (2) B < Al < Ga ≼√m < Tl
 - (3) B < Ga < Al < In < Tl (4) B < Ga < Al < Tl < In
- Which one of the following elements is unable to form MF₆³⁻ ion? [NEET-2018]
 - Ga
- (2) AI
- (3) In
- (4) B
- Which of the following statements is **not** true for [NEET-2018]
 - (1) All form monobasic oxyacids
 - (2) All are oxidizing agents
 - Chlorine has the highest electron-gain enthalpy
 - (4) All but fluorine show positive oxidation states
- 31. Which of the following is incorrect statement?

[NEET-2019]

- PbF_a is covalent in nature
- (2) SiCl₄ is easily hydrolysed
- (3) GeX₄ (X = F, Cl, Br, I) is more stable than GeX,
- (4) SnF₄ is ionic in nature

32. Which of the following species is not stable?

[NEET-2019]

- [SiF₆]²⁻
- (2) [GeCl₆]²
- (3) [Sn(OH)₆]²⁻
- (4) [SiCl_e]²⁻
- Which is the correct thermal stability order for H_2E (E = O, S, Se, Te and Po)? [NEET-2019]
 - (1) H₂S < H₂O < H₂Se < H₂Te < H₂Po
 - (2) H₂O < H₂S < H₂Se < H₂Te < H₂Po
 - (3) H₂Po < H₂Te < H₂Se < H₂S < H₂O
 - (4) H₂Se < H₂Te < H₂Po < H₂O < H₂S
- Match the following :

[NEET-2019]

- (a) Pure nitrogen
- (i) Chlorine
- (b) Haber process
- (ii) Sulphuric acid
- (c) Contact process
- (iii) Ammonia
- (d) Deacon's process
- (iv) Sodium azide or

Barium azide

Which of the following is the correct option?

(a) (b) (c)

(iv)

(iii)

- (ii)
 - (iii) (iv)
- (ii) (īv)
- (i)
- (3)(iii)
- (i) (ii)

(iii)

- (4)(iv)
- Identify the incorrect statement related to PCIs from the following: [NEET-2019]
 - Three equatorial P-Cl bonds make an angle of 120° with each other
 - (2) Two axial P-Cl bonds make an angle of 180° with each other
 - (3) Axial P-Cl bonds are longer than equatorial P-CI bonds
 - (4) PCI_s molecule is non-reactive
- Aluminium chloride in acidified aqueous solution forms a complex 'A', in which hybridisation state of Al is 'B'. What are 'A' and 'B', respectively?

[NEET-2019 (Odisha)]

- (1) $[AI(H_2O)_6]^{3+}$, d^2sp^3 (2) $[AI(H_2O)_6]^{3+}$, sp^3d^2
- (3) $[AI(H_2O)_4]^{3+}$, sp³ (4) $[AI(H_2O)_4]^{3+}$, dsp²
- Which of the following compounds is used in cosmetic surgery? [NEET-2019 (Odisha)]
 - Zeolites
- (2) Silica
- (3) Silicates
- (4) Silicones

Chapter 13

General Principles and Processes of Isolation of Elements

Sub-topics

Principles and methods of extraction- concentration, oxidation, reduction electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron.

Minerals

The naturally occuring chemical substances in the earth's crust which are obtained by mining are known as minerals.

Ores: Minerals which can be used as source of commercial receivery of a desired substance are termed as ores.

Gangue or Matrix: Ores are associated with earthy materials or impurity known as gangue or matrix particles.

Metallurgy

The scientific and technological processes used for separation of metal from their ores are collectively called metallurgy.

Three Steps: (1) Concentration, (2) Isolation of metal, (3) Purification of metal.

Some Important ores :

Bauxite : Al₂O₃.2H₂O
 Diaspore : Al₂O₃.H₂O
 Zinc blende (sphalerite) : ZnS
 Galena : PbS

5. Malachite : CuCO₃.Cu(OH)₂

6. Azurite : 2CuCO₃.Cu(OH)₂

 7. Zincite
 : ZnO

 8. Calamine
 : ZnCO₃

 9. Pyrolusite
 : MnO₂

 10. Haematite
 : Fe₂O₃

 11. Magnetite
 : Fe₃O₄

Dolomite : MgCO₃.CaCO₃

13. Casseterite : SnO₂
 14. Siderite : FeCO₃
 15. Argentite (Silver glance) : Ag₂S
 16. Cinnabar : HgS

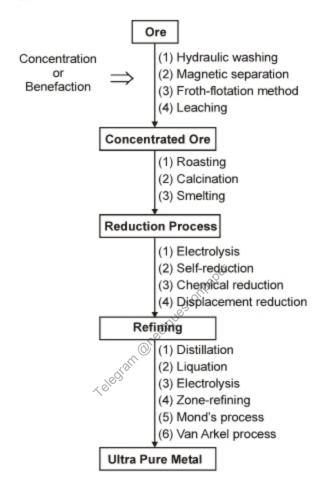
Corundum : Al₂O₃

18. Carnallite : KCI.MgCl₂.6H₂O

Spodumene : LiAl(Si₂O₆)

Lepidolite : (Li, Na, K)₂ Al₂(SiO₃)₃.F(OH)

Flow Sheet for Metallurgy



Some Important Terms

- (a) Hydraulic Washing: Method is based on the difference in specific gravities of ore and gangue particles. Also known as gravity separation method.
- (b) Magnetic Separation: This method is based on magnetic and non-magnetic properties of two components of the ore.
- (c) Froth-Floatation Method: The principle of the process is that the mineral particles are wetted by oils and gangue particles by water (oil - pine oil, collector - xanthates, fatty acid, froth stabilizer - cresol and aniline, some activator).
- (d) Leaching: Method useful in case if ore is soluble in suitable solvent. Mostly used for Bauxite ore, silver glance, etc.
- (e) Calcination: The concentrated ore is heated below its melting point in the absence of air, where volatile matter leaves away. Surface area of ore increases.

$$2AI(OH)_3 \rightarrow AI_2O_3 + 3H_2O$$

 $CaCO_3 \rightarrow CaO + CO_2$

(f) Roasting: The concentrated sulphide ore is heated in regular supply of air at a temperature below the melting point of the metal. Surface area of ore increases and it gives oxide form generally.

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

(g) Goldschmidt Thermite Process: All is used as reducing agent. BaO₂ and Mg form ignition mixture.

$$Cr_2O_3 + 2AI \rightarrow AI_2O_3 + 2Cr$$

(h) Auto Reduction: The partly oxidized metal can reduce the ore.

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

- (i) Zone Refining: The method is based on the principle that impurities are more soluble in the melt than in the pure metal. Mostly used for semiconductors Ge, Si, Ga.
- (j) Mond's Process: Also known as vapour phase refining

(k) Van Arkel Process: Used for ultrapurification of Zr, Hf

$$Zr + 2I_2 \xrightarrow{\Delta} ZrI_4 \xrightarrow{T \text{ (temperature)}} Zr + 2I_2$$

Extraction of Some Elements

A. Iron: Haematite Fe₂O₃, Magnetite Fe₃O₄, Limonite Fe₂O₃.3H₂O, Iron pyrites FeS₂, Siderite FeCO₃.

Types:

- (i) Pig iron or cast iron: 2 to 4.5% C with some impurities like S, Si, P, Mn. It cannot be welded.
- (ii) Wrought iron: purest variety .0.2 0.5% C.
- (iii) Steel: 0.1 to 1.5% C alongwith some other elements like Cr, Mn, Ni, etc. metals in alloy steels.

Extraction from haematite: It is concentrated by washing with water. Then it is roasted with a little of coal in a reverberatory furnace. During roasting moisture is removed. Impurities of As, S and P are converted into their gaseous oxides. Roasted mass is then reduced by heating with coke and limestone in a blast furnace of about 150 feet height in the ratio of 8:4:1.

Reactions in blast furnace :

(i) Combustion zone – just near the bottom temperature is 2100 K.

$$C + O_2 \rightarrow CO_2$$
; $\Delta H = -393.5 \text{ kJ}$

(ii) As the CO₂ goes upward temperature falls to about 1575 K due to the the endothermic nature of the reaction.

CO₂ + C
$$\rightarrow$$
 2CO; Δ H = +163 kJ

(iii) Any ferric oxide which might have been left as such, may be reduced to iron by coke above 1125 K temperature.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

After this, Fe melts in this zone of fusion at about 1575 K.

(iv) At about 1275 K slag is formed

$$\begin{aligned} \operatorname{CaCO_3} &\longrightarrow \operatorname{CaO} + \operatorname{CO_2} \\ \operatorname{CaO} &+ \operatorname{SiO_2} &\longrightarrow \operatorname{CaSiO_3} \text{ (slag)}. \end{aligned}$$

Calcium silicate

(v) At temperature upto 1125 K near the top Fe₂O₃ is reduced by CO to Fe.

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$
; $FeO + CO \rightarrow Fe + CO_2$

Iron, thus obtained is called pig iron. Fast cooling converts it to grey cast iron while slow cooling converts it to white or light grey cast iron that has Fe₃C cementite.

B. Copper: Copper pyrite CuFeS2, Azurite 2CuCO3, Cu(OH)2, Malachite CuCO3, Cu(OH)2,

Extraction: Copper is generally extracted from copper pyrites. It is concentrated by froth-floatation process.

The principle of extraction involves the following steps:

(i) Roasting: S, P, As are removed as volatile impurities.

$$\begin{split} & \mathsf{2CuFeS_2} + \mathsf{O_2} \to \mathsf{Cu_2S} + \mathsf{2FeS} + \mathsf{SO_2} \\ & \mathsf{2FeS} + \mathsf{3O_2} \to \mathsf{2FeO} + \mathsf{2SO_2} \text{ (Partial)} \end{split}$$

(ii) Smelting: Roasted ore is mixed with some coke and sand and heated strongly in blast furnace of about 30 feet height. The material obtained is rich in copper and is called 'Matte'.

$$\begin{aligned} & 2\text{FeS} + 3\text{O}_2 \rightarrow 2\text{FeO} + 2\text{SO}_2 \\ & \text{FeO} + \text{SiO}_2 \rightarrow 2\text{FeSiO}_3 \text{ (slag)} \\ & 2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2 \\ & \text{Cu}_2\text{O} + \text{FeS} \rightarrow \text{Cu}_2\text{S} + \text{FeO}. \end{aligned}$$

(iii) Bessemerisation: Molten matte (containing Cu₂O, Cu₂S) is heated in Bessemer converter and a blast of hot air is passed through it.

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

This reaction is exothermic and keeps the mass in molten state. Copper obtained is called blister copper and is about 98-99% pure.

- (iv) Refining
 - (a) Poling: Hydrocarbons present in the freshly cut poles reduce cuprous oxide to copper.
 - (b) Electrolytic refining: Copper sulphate solution is made electrolyte. Anode is made up of impure Cu while pure Cu strip is used as cathode.

At anode :
$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

At cathode : $Cu^{2+} + 2e \rightarrow Cu^{3/2}$

C. Silver: Ag (47). Its outer electronic configuration is 5s¹ 4d¹¹⁰, oxidation state is +1. Argentite (silver glance) Ag₂S; Horn silver-AgCl; Pyrargyrite or Ruby silver-Ag₂S.Sb₂S₃ are the important ores of Ag. It also occur in free state. Its density is 10.5 g cm⁻³. Its melting point is 1233K and boiling point is 2485K. It is silvery white lustrous metal.

Extraction from Argentite:

- (i) Ore is concentrated by froth floatation process.
- (ii) Now it is treated with 0.5% NaCN solution and O₂ is passed to consume Na₂S otherwise the reaction is reversible.

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

 $4Na_2S + 2H_2O + 5O_2 \rightarrow 2Na_2SO_4 + 4NaOH + S$

(iii) The above solution is treated with Zn dust. Silver being less electropositive deposits first.

Na
$$[Ag(CN)_a] + Zn \rightarrow Na_a [Zn(CN)_a] + 2Ag$$

- (iv) Now it is refined by electrorefining process.
- D. Gold: Atomic No. 79, At. mass 197, outer electronic configuration 6s¹sd¹0. Gold occurs in the native state also. It is yellow in colour. It is less reactive, so it is called noble metal. It oxidation state is + 1, + 3, density = 19.3 g cm⁻³, m.pt 1333 K, b.pt 3239 K. It is lustrous. It is highly malleable and ductile.

Extraction

 Concentrated by hydraulic washing. Gold particles are then passed over amalgamated copper where gold amalgam is formed. Gold amalgam on distillation in iron retrorts, leaves behind gold. (ii) From sulphide ore — After concentrating the ore by froth flotation process, it is roasted well to remove As, S, Te, etc.

Then the gold is obtained by Mac-Arther-Forest cyanide process :

4Au + KCN +
$$2H_2O$$
 + $O_2 \rightarrow$ 4K [Au(CN)₂] + 4KOH
2K [Au (CN)₂] + Zn \rightarrow K₂ [Zn (CN)₄] + 2Au

Purification of Au

- (i) Parting process: The impure gold is boiled with conc. H₂SO₄ when Ag and Cu dissolve leaving behind Au.
- (ii) Cupellation: Impure Au is melted in the presence of borax, silica and air in a cupel when impurities of Pb, Cu, Zn are oxidised and removed as vapours.
- (iii) Electrolytic refining: Electrolyte AuCl₃.

Properties: Gold is very little reactive and is not affected by air, water, acids and bases – Noble metal. It is soluble in aqua regia (3 parts conc. HCl and 1 part conc. HNO₃).

$$3 \times [3HCI + HNO_3 \longrightarrow NOCI + H_2O + 2CI]$$

 $2 \times [Au + 3CI \longrightarrow AuCl_3]$

Carat: Pure gold is 24 carat. It is very soft. To make jewellary some Ag or Cu is mixed in it. 14 carat gold means 14 parts of gold while the rest is copper. Usually 22 carat gold is used to make jewellary. Copper is good conductor of heat and electricity. Ag is best conductor of electricity but it is expensive. Cu, Ag, Au are less reactive than hydrogen, they are called coinage metals. Au and Ag are used in jewellery.

Cu, Ag, Au belong to group 11 of periodic table.

E. Zinc: Atomic No. 30, At. mass 65. Outer electronic configuration is 4s² 3d¹⁰, oxidation state is +2. Zn, Cd, Hg are not considered as transition metals because neither they nor their ions have incompletely filled d-orbital. Zn does not show variable oxidation state. Its m.pt is 692 K, b.pt 1180K, density = 7.1 g cm⁻³. Zinc blende (sphalerite) ZnS; Calamine ZnCO₄; Zincite ZnO are the important ores of Zn.

Extraction: It is usually extracted from zinc blende

- (i) Concentration: by froth floatation process.
- (ii) Roasting:

(iii) Reduction : ZnO + C $\xrightarrow{\text{coke}}$ Zn + CO

It is strongly heated in vertical fire clay retorts with coke when the vapours of Zn are collected and condensed.

- (iv) Refining
 - (a) Fractional distillation to remove low boiling Cd (B.P. 1073 K), which Zn has higher boiling point (1180 K).
 - (b) Electrolytic refining using ZnSO₄ as electrolyte.

Zn is good conductor of heat and electricity. Zn is readily oxidised to ZnO. ZnO becomes yellow on heating. Zn is more reactive than H₂. ZnO is amphoteric. It is also called **Philospher's wool.**



Try Yourself

SECTION - A

Objective Type Questions

- The process of extracting a metal in pure form from its ore is known as
 - Refining
- (2) Purification
- (3) Metallurgy
- (4) None of these
- The process by which the sulphide ore is concentrated by
 - Froth floatation process
 - (2) Leaching
 - (3) Gravity separation
 - (4) Magnetic separation method
- The lighter impurities can be removed from the ore by
 - Magnetic separation
 - (2) Froth floatation process
 - (3) Gravity separation
 - (4) Leaching
- The ore of a metal which can be easily attracted by a magnetic field can be best separated by
 - (1) Magnetic separation (2) Froth floatation
- - Gravity separation
- (4) None of these
- The process by which Al(OH), is converted into Al,O, is known as
 - (1) Roasting
- (2) Calcination
- (3) Ignition
- (4) None of these
- The sulphide ores are converted into their oxides by roasting which is heating in the presence of air. The carbonate ores are converted into their oxides by
 - Roasting
- (2) Calcination
- (3) Smelting
- (4) None of these
- The reaction Cu,S + 2Cu,O 6Cu + SO, which is very important in the metallurgy of copper is an example of
 - (1) Oxidation
- (2) Reduction
- (3) Autoreduction
- (4) None of these
- Na[Ag(CN),] can be converted into Ag by
 - Treating it with Zn
- (2) Electrolysis
- (3) Either (1) or (2)
- (4) None of these

- An ore which is concentrated by magnetic separation is
 - Galena
- (2) Wolframite
- (3) Alumina
- (4) Cinnabar
- 10. The process in which a sulphide ore is heated in air below its melting point is known as
 - Roasting
- (2) Calcination
- (3) Reduction
- (4) Distillation
- 11. Heating a pyrite ore in air to remove sulphur is known as
 - Calcination
- (2) Fluxing
- (3) Smelting
- (4) Roasting
- Froth floatation process for the concentration of ores is an illustration of the practical application of
 - Adsorption
- (2) Absorption
- (3) Coagulation
- (4) Sedimentation
- Carbon reduction method is used in the extraction of
 - (1) Sn
- (2) Zn
- (3) Pb
- (4) All of these
- Reducing metal required in Goldschmidt Alumino Thermic process is
 - Chromium powder
- (2) Zinc powder
- Aluminium powder
- (4) Silver powder
- Calamine, an ore of zinc is
 - (1) ZnSO₄
- (2) ZnS
- (3) ZnCO,
- (4) ZnO
- The composition of diaspore is
 - (1) Al₂O₃·2H₂O
- (2) Al₂O₃·3H₂O
- (3) Al₂O₃
- (4) Al₂O₃·H₂O
- Consider the following
 - (A) Willemite Zn,SiO,
 - (B) Chromite Magnetic separation
 - (C) Bauxite Alumina
 - (D) Liquation Metals, e.g., Fe

Which is/are not correctly matched?

- A only
- (2) B only
- (3) C only
- (4) D only

- 18. Lepidolite is an ore of
 - (1) K
- (2) Na
- (3) Li
- (4) Rb
- The main ore of iron is
 - (1) Chloride
- (2) Sulphate
- (3) Nitrate
- (4) Oxide
- Bauxite, an ore of Al is purified by
 - Serpeck's process
- (2) Baeyer's process
- (3) Hall's process
- (4) All of these
- In the Hall's process for purification of bauxite ore, the ore is fused with
 - NaHCO,
- (2) Na,CO,
- (3) NaF
- (4) Na,AIF,
- Aluminothermic process is used in the extraction of
 - Mn
- (2) Cr
- (3) Co
- (4) All of these
- 23. Which of the following metals is obtained by Mond's process?
 - Ni
- (2) Co
- (3) Fe
- (4) All of these
- 24. Leaching process is used to concentrate
 - (1) Bauxite
- (2) Galena
- (3) Cinnabar
- (4) Haematite
- The froth floatation process is based upon
 - Magnetic properties of gangue
 - (2) Specific gravity of ore particles
 - (3) Preferential wetting of ore particles by oil
 - (4) Preferential adsorption of gangue particles by oil

SECTION - B

Previous Years Questions

- Aluminium is extracted from alumina (Al₂O₂) by electrolysis of a molten mixture of [AIPMT 2012]
 - Al₂O₃ + Na₃AlF₆ + CaF₂
 - (2) Al₂O₃ + KF + Na₃AlF₆
 - (3) Al₂O₃ + HF + NaAlF₄
 - (4) Al₂O₃ + CaF₂ + NaAlF₄
- In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with [AIPMT 2012]
 - Iron sulphide (FeS)
 - (2) Carbon monoxide (CO)
 - (3) Copper (I) sulphide (Cu₂S)
 - (4) Sulphur dioxide (SO₂)

Which one of the following is a mineral of iron?

[AIPMT 2012]

- Pyrolusite
- (2) Magnetite
- (3) Malachite
- (4) Cassiterite
- Roasting of sulphides gives the gas X as a byproduct. This is a colorless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic acts as a reducing agent and its acid has never been isolated. The gas X is

[NEET 2013]

- SO₂
- (2) CO₂
- (3) SO₃
- (4) H₂S
- Match items of Column I with the items of Column II and assign the correct code :

	Column I		Column II
(a)	Cyanide process	(i)	Ultrapure Ge
(b)	Froth floatation process	(ii)	Dressing of ZnS
(c)	Electrolytic reduction	(iii)	Extraction of Al
(d)	Zone refining	(iv) (v)	Extraction of Au Purification of Ni

[NEET-2016]

- a(iii), b(iv), c(v), d(i)
 a(iv), b(ii), c(iii), d(i)
- (3) a(ii), b(iii), c(i), d(v) (4) a(i), b(ii), c(iii), d(iv)
- Extraction of gold and silver involves leaching with CN⁻ ion. Silver is later recovered by [NEET-2017]
 - (1) Liquation
- (2) Distillation
- (3) Zone refining
- (4) Displacement with Zn
- 7. Considering Ellingham diagram, which of the following metals can be used to reduce alumina?

[NEET-2018]

- (1) Fe
- (2) Zn
- (3) Cu
- (4) Mg
- Which one is malachite from the following?

[NEET-2019]

- CuFeS₂
- (2) Cu(OH)₂
- (3) Fe₃O₄
- (4) CuCO₃.Cu(OH)₂
- Identify the incorrect statement.

[NEET-2019 (Odisha)]

- Gangue is an ore contaminated with undesired materials
- (2) The scientific and technological process used for isolation of the metal from its ore is known as metallurgy
- (3) Minerals are naturally occurring chemical substances in the earth's crust
- (4) Ores are minerals that may contain a metal

Chapter 14

d-and f-Block Elements

Sub-topics

General introduction, electronic configuration, characteristics of transition metals, general trends in properties of the first row transition metals- metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation. Preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$. Lanthanoids- electronic configuration, oxidation states, chemical reactivity, and lanthanoid contraction and its consequences. Actinoids: Electronic configuration, oxidation states and comparison with lanthanoids.

The **transition elements** may be defined as elements whose atoms or simple ions in their common oxidation state contain partially filled *d*-orbitals. This definition does not cover zinc, cadmium and mercury. However, these are studied with transition elements.

The general electronic configuration of these elements is $(n-1)d^{1-10} ns^{1-2}$. These are divided into four transition series.

(i) The first transition series: (3d-series) involves the filling of 3d orbitals and has 10 elements from scandium (Z = 21) to zinc (Z = 30).

Sc	Ti	٧	Cr	Mn	Fe	Со	Ni	Cu	Zn
$3d^14s^2$	$3d^24s^2$	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d84s2	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²

(ii) The second transition series: (4d series) involves the filling of 4d orbitals and has 10 elements from ytterium (Z = 39) to cadmium (Z = 48).

	Υ	Zr	Nb	Мо	Te	Ru	Rh	Pd	Ag	Cd
Ī	4d ¹ 5s ²	4d ² 5s ²	4d ⁴ 5s ¹	4d ⁵ 5s ¹	4d ⁵ 5s ²	4d ⁷ 5s ¹	4d ⁸ 5s ¹	4d ¹⁰ 5s ⁰	4d ¹⁰ 5s ¹	4d ¹⁰ 5s ²

(iii) The third transition series: (5d series) involves the filling of 5d orbitals and has 10 elements. The first element of this series is lanthanum (Z = 57). It is followed by 14 elements (lanthanides, involving filling of 4f orbitals). The next nine elements are from hafnium (Z = 72) to mercury (Z = 80).

La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg
5d ¹ 6s ²	5d ² 6s ²	5d ³ 6s ²	5d ⁴ 6s ²	5d ⁵ 6s ²	5d ⁶ 6s ²	5d ⁷ 6s ²	5d86s2	5d ¹⁰ 6s ¹	5d ¹⁰ 6s ²

(iv) The fourth transition series : It contains $_{89}\mathrm{Ac},~_{104}\mathrm{Rf}$ to $_{112}\mathrm{Uub}.$

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Metallic Character

Transition elements exhibit good mechanical properties, *i.e.*, they are hard, malleable and ductile. They have high enthalpies of atomization, high melting and boiling points: have high thermal and electrical conductivity as well as lustre. Their mechanical properties and high melting, as well as boiling points indicate the presence of strong metallic bond.

The transition elements exhibit all the three types of structures; face centred cubic (fcc), hexagonal close packed (hcp)and body centred cubic (bcc).

The bond strength in these metals can be traced to the presence of unpaired d-electrons. An unpaired d-electron tends to form a covalent bond. The number of such bonds will determine the overall bonds strength and thus reflect in the hardness of these metals.

Ionisation Energies

The ionisation energies of transition metals increase as we move across each series through not quite regularly.

Reason: The shrinking atomic size and increased nuclear charge results in a strong attraction between the nucleus and the electrons. Consequently, ionisation energies increase.

It is evident that first ionisation energies of most of the 5d elements are higher than those of 3d and 4d-elements. This is due to the fact that the outer valence electrons of 5d- elements of experience greater effective nuclear charge due to poor shielding of the nucleus by 4f-electrons, effect of Lanthanide contraction.

Electrode Potential

Transition elements have low negative values of standard reduction electrode potential values due to high ionisation energies, high heats of sublimation which are more than offset with large heats of hydration. Consequently, transition elements are **weak reducing agents** and are **less reactive**.

It must be noted that greater the reduction electrode potential more unstable the oxidized state and hence the metal in that oxidized state will be a strong oxidising agent.

Oxidation State

Oxidation state is due to the participation of ns and (n-1)d electrons. Oxidation state increases till middle of series and then starts decreasing. Transition element mostly with lower oxidation state are ionic and that with higher oxidation state are covalent. Maximum oxidation state of +8 is shown by Osmium (Os)

Melting Point

The melting point increases to the maximum in middle of series and then falls with increase in atomic number. [Exception: Mn have abnormally low m.pt]. M.pt. depends on strength of attractive forces among metals and presence of additional covalent bonding due to unpaired electrons present in *d*-orbital (*d*-*d* overlapping)

Oxides

General formula of oxides are MO, M₂O₃, M₃O₄, MO₂, M₂O₅. The oxides of transition element in lower oxidation states (1 and 2) are basis while those with higher oxidation states are acidic.

Formation of Complexes

By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant d-orbitals of suitable energy, these metals exert strong electrostatic attraction on the ligands. The species formed on interaction of metal and the ligand (or ligands) is known as a complex.

The transition metal ions form complexes because of the following reasons:

- (i) Their small cation size
- (ii) High effective nuclear charge
- (iii) Availability of vacant (n−1) d-orbitals of appropriate energy

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Formation of Coloured Compounds

The transition metal ions have unpaired *d*-electrons, which on absorbing visible light can jump from one *d*-orbital to another, *i.e.*, intra *d*-*d* transitions take place. Thus when light falls certain visible wavelengths are absorbed. The transmitted light appears coloured and gives the colour of compound. The ions having no *d*-*d* transitions are colourless.

Note: KMnO₄ and K₂Cr₂O₂ are coloured not due to d-d transition but because of charge transfer spectra.

Catalytic Properties

Most of the transition metals and their compounds are found to act as catalysts.

- (a) Transition metals as catalyst: Catalytic power of transition metals is believed to operate either by the formation of interstitial compounds to adsorb and activate the reacting substances, e.g., hydrogenation of alkenes in presence of palladium or platinum is thought to take place through this mechanism.
- (b) Transition metal compounds as catalysts: Catalysis by metal compounds results from their ability to provide low energy pathways for reactions by either of the following two ways:
 - (i) By the formation of appropriate intermediates. For example, the reaction between substance A and B in presence of transition metal X as catalyst takes place as shown below:

$$\begin{array}{c} A \\ \text{Reactant} + X \\ \text{Catalyst} \end{array} \longrightarrow \begin{array}{c} AX \\ \text{unstable} \end{array} \longrightarrow AB + A \\ \text{Catalyst} \end{array}$$

(ii) By the change of oxidation states of transition metals. For example, V₂O₅ acts as a catalyst for the conversion of SO₂ to SO₃ because of the ability of vanadium to have several oxidation states as:

Solid V_2O_5 adsorbs a SO_2 molecule on the surface, gives it an oxygen atom to convert it to SO_3 and is itself reduced to V_2O_4 .

$$SO_2 + V_2O_5 \longrightarrow V_2O_4 + SO_3$$
Divanadium tetraoxide

The divanadium tetraoxide is reconverted to V2O5 by reaction with oxygen

$$2V_2O_4 + O_2 \longrightarrow 2V_2O_5$$

Magnetic properties

Most of the transition elements show paramagnetism. Paramagnetism arises from the presence of unpaired electrons in atoms, ions or molecules. The magnetic character is comparable in terms of magnetic moment given as $\mu = \sqrt{n(n+2)}$ Bohr magnetons. In general, more is the number of unpaired electrons greater is the magnetic character. The maximum paramagnetism is seen in d⁵ cases, having the maximum unpaired electrons. 1 BM = eh/4 π mc

Magnetic moments of some lons of first transition series

lon	Outer electronic Configuration	Number of unpaired electrons	Magnetic mome	ent, m, (BM)
			Calculated	Observed
			$\mu = \sqrt{n(n+2)}$	
Sc3+	3d ⁰	0	0.0	0.0
Ti ³⁺	3d ¹	1	1.73	1.75
V3+	3d²	2	2.84	2.76

Potassium Dichromate $(K_2Cr_2O_7)$ [Equivalent weight in acidic medium = $\frac{M}{6}$; M is molecular weight]

Preparation

It is prepared by chromite ore.

$$\text{(i)} \quad \text{4FeO.Cr}_2 \text{O}_3 + \text{16NaOH} + \text{7O}_2 \rightarrow \underset{\text{Sod. chromate}}{\text{8Na}_2 \text{CrO}_4} + \text{2Fe}_2 \text{O}_3 + \text{H}_2 \text{O}$$

Properties

(i)
$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

$$\text{(ii)} \quad \mathsf{K_2Cr_2O_7} + \mathsf{Cold.} \; \mathsf{H_2SO_4} \rightarrow \; \mathsf{CrO_3} \\ \text{(red)} \\ \text{$^{(\mathsf{red)}^{(\mathsf{c})}}$} \\ \text{$^{(\mathsf{red)}^{(\mathsf{c})}$}$} \\ \text{$^{(\mathsf{red)}^{(\mathsf{c})}}$} \\ \text{$^{(\mathsf{$$

(iii)
$$\text{K}_2\text{Cr}_2\text{O}_7$$
 + Hot $\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4$ + $\underset{\text{Chromic sulphate}}{\text{Cr}_2(\text{SO}_4)_3}$ + O_2

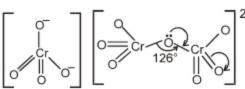
(iv) Chromyl Chloride test :

$$K_2Cr_2O_7 + 4KCI + 6H_2SO_4 \rightarrow CrO_2CI_2 + KHSO_4 + H_2O$$

$$Value Value Value$$

(v)
$$K_2Cr_2O_7 + 4H_2O_2 + 2H^* \rightarrow 2Cr_0_5 + H_2O_3$$

Structure :



Chromate ion

Dichromate ion

In CrO₄2- ion, all bond lengths are equal.

In Cr₂O₇²⁻ ion, outer six Cr-O bonds are equal while inner two Cr-O bonds are equal.

Potassium Permanganate, KMnO₄

Equivalent weight of KMnO4

- (a) In acidic medium = $\frac{M}{5}$
- (b) In alkaline medium = $\frac{M}{3}$, (in the presence of reducing agent)
- (c) In neutral medium = $\frac{M}{3}$

Preparation

KMnO₄ is prepared from pyrolusite ore, MnO₂

(i)
$$2MnO_2 + 4KOH + O_2 \longrightarrow K_2MnO_4 + H_2O$$

pot. manganate (green)

[or MnO₂ is reacted with K₂CO₃/O₂ or KOH, KNO₃ or KClO₃, form K₂MnO₄]

(ii)
$$3MnO_4^{2(-)} + 4H^{(+)} \longrightarrow 2MnO_4^{(-)} + MnO_2 + 2H_2O$$

Note: By electrolytic oxidation MnO₄²⁻ is also converted to MnO₄⁻ ion.

Chemical Properties

(ii) KMnO₄ acts as good oxidising agent in acidic, alkaline and neutral media.

Lanthanides and Actinides

- (a) Oxidation State: The principal oxidation state exhibited by all the lanthanides is +3. Some of the elements exhibit +2 oxidation state, e.g., Sm²⁺, Eu²⁺, Tm²⁺, and Yb²⁺ exist in aqueous solutions and are good reducing agents. Some of the elements also exhibit +4 oxidation state, e.g., Pr⁴⁺, Ce⁴⁺, Tb⁴⁺ and Dy⁴⁺. An aqueous solution of Ce⁴⁺ is good oxidising agent.
 - Note: The usual oxidation states such as +2 or +4 exhibited by the lanthanides can be explained on the basis of extra stability associated with empty, half-filled and completely filled 4f subshell. For example Eu and Yb exhibit +2 oxidation state because they acquire the f⁷ and f¹⁴ configuration respectively. Similarly, Ce and Tb show +4 oxidation state by acquiring f⁰ and f⁷ configurations respectively.
- (b) Colour: Most of the lanthanide metal ions are coloured because they have partly filled f-orbitals in which f-f transitions are possible.
- (c) Melting and boiling points: Lanthanides have fairly high melting and boiling points. However, their melting and boiling points do not show any definite trend as we move from La to Lu.
- (d) Density: Lanthanides have high densities which range between 6.7 to 9.74 g cm⁻³. However, densities of lanthanides do not show definite trends with rise in atomic number.
- (e) Ionisation energies: Lanthanides have fairly low ionisation energy values due to fairly large atomic size which are quite comparable with those of alkaline earth metals particularly calcium.
- (f) Electropositive character: On account of low ionisation energy values and fairly large size lanthanides have high electropositive character.

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(g) Paramagnetism: Lanthanide metal ions show paramagnetism due to the presence of unpaired electrons in their f-orbitals.

- (h) Complex formation: On account of large size, lanthanides have much less tendency to form complexes.
- (i) Radioactivity: Of all the lanthanides, only promethium (Z = 61) is radioactive.

Use of lanthanides

- (i) A pyrophoric alloy which contains cerium (40.5%), lanthanum and neodymium (44%); iron (4.5%); calcium, carbon and silicon (10.5%) is used in cigarette lighters, toys, flame throwing tanks and tracer bullets as well as shells.
- (ii) Cerium oxide cuts off heat and untraviolet light and so is used in glare reducing spectacles.
- (iii) Cerium magnesium alloys are used in flash light powders.
- (iv) Cerium salts are used in analysis, dyeing cotton, lead accumulators, medicines as catalysts.
- (v) Ceria and thoria are used in gas lamp mantles.

Comparison of Lanthanide and Actinide Series

Elements of lanthanide and actinides resemble in many respects but they do differ in some respects as shown below:

Similarities

	Lanthanides	Actinides
1.	Mainly exhibit +3 oxidation state.	They also mainly exhibit +3 oxidation state.
2.	They exhibit lanthanide contraction.	They exhibit actinide contraction.
3.	They show ion-exchange behaviour.	3. They also show ion-exchange behaviour.

Differences:

- All actinoids are radioactive while among anthanoids only Pm(Z = 61) is radioactive.
- Actinoids show oxidation states 3 to 7. Lanthanoids show 2 to 4.
- After 92U all actinoids are synthetic. Among lanthanoids only Pm is synthetic.
- Actinoids form oxocations, e.g., UO₂⁺, lanthanoids do not form such ions.

Some Important Compositions

 $\begin{array}{lll} \mbox{Nessler's reagent} & : & \mbox{Alkaline solution of } \mbox{K}_2[\mbox{Hg}_4] \\ \mbox{Calomel} & : & \mbox{Hg}_2\mbox{Cl}_2 \mbox{ (mercurous chloride)} \end{array}$

Lunar Caustic : AgNO₃

Hypo solution : Na₂S₂O₃ (used in photography)

Corrossive sublimate : HgCl₂

Blue vitriol : $CuSO_4.5H_2O$ Green vitriol : $FeSO_4.7H_2O$ White vitriol : $ZnSO_4.7H_2O$



Try Yourself

SECTION - A

Objective Type Questions

- The highest oxidation state is shown by transition element with outer most configuration as
 - d²s²
- (2) d5s1
- (3) d⁶s²
- (4) d8s2
- Which one of the following ion has least magnetic moment?
 - (1) Cu+2
- (2) Ni+2
- (3) Co2+
- (4) Fe⁺²
- 3. Which one of the following ion has maximum magnetic moment?
 - (1) Co3+
- (2) Ti3+
- (3) Cr3+
- (4) V3+
- 4. Identify the correct statement. Transition metals
 - (1) Exhibit inert pair effect
 - (2) Exhibit variable oxidation state
 - (3) Have low melting points
 - (4) Do not show catalytic activity
- The most stable oxidation state of iron is
 - (1) +2
- (2) +3
- (3) -2
- (4) -3
- The highest oxidation state shown by any transition element is
 - (1) +2
- (2) +6
- (3) +7
- (4) +8
- 7. Which of the following compound is diamagnetic?
 - (1) ZnCl,
- (2) CrCl₃
- (3) CuSO,
- (4) NiCl,2-
- 8. Which oxide of manganese is most acidic in nature?
 - (1) MnO
- (2) Mn₂O₂
- (3) Mn₂O₃
- (4) MnO₂
- 9. Which metal has the highest melting point?
 - (1) Pt
- (2) W
- (3) Pd
- (4) Au

- 10. Which metal has the lowest melting point?
 - (1) Cs
- (2) Na
- (3) Hg
- (4) Sn
- 11. Which of the following ions should have highest magnetic moment?
 - (1) Fe2+
- (2) Fe3+
- (3) Zn²⁺
- (4) Sc²⁺
- 12. Which of the following is not coloured?
 - (1) Mn2+
- (2) Cr3+
- (3) Zn2+
- (4) Cu2+
- 13 Iron (III)
 - (1) Has a d⁶ configuration
 - (2) Has a d7 configuration
 - (3) Is isoelectronic with Co (II)
 - (4) Is isoelectronic with Mn (II)
- 14. The correct statement(s) among the following is/are
 - (a) All the d- and f-block elements are metals
 - (b) All the d- and f-block elements form coloured ions
 - (c) All the d-and f-block elements are paramagnetic
 - (1) (a) only
- (2) (a) and (b)
- (3) (b) and (c)
- (4) All of these
- When manganese dioxide is fused with KOH in air, it gives
 - (1) Potassium permanganate
 - (2) Potassium manganate
 - (3) Manganese hydroxide
 - (4) Mn₃O₄
- 16. $4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 3O_2 + X$, in this reaction X is
 - (1) CrO₃
- (2) Cr₂O₇
- (3) Cr,O,
- (4) CrO₅

- The blue colour produced on adding H₂O₃ to acidified K₂Cr₂O₂ is due to the formation of
 - (1) CrO₅
 - (2) Cr₂O₃
 - (3) CrO₂²
 - (4) CrO,
- When acidified solution of potassium dichromate is shaken with aqueous solution of ferrous sulphate
 - (1) Cr,O,2- ion reduced to Cr3+ ions
 - (2) Cr₂O₂²⁻ ion reduced to CrO₄²⁻ ions
 - (3) Cr₂O₂- ion oxidised to Cr
 - (4) Cr₂O₂- ion oxidised to CrO₃
- The equilibrium Cr₂O₂²-

 2CrO₄²- shift in forward direction
 - In acidic medium
 - (2) In basic medium
 - (3) In neutral medium
 - (4) Does not depend on change in pH
- 20. The reaction $MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$ takes place in O_4^{2-}
 - Basic medium
 - (2) Acidic medium
 - (3) Neutral medium
 - (4) Both acidic and basic medium
- Which of the following compounds is used as the starting material for the preparation of potassium dichromate?
 - K₂SO₄.Cr₂(SO₄)₃.24H₂O (chrom alum)
 - (2) PbCrO₄ (chrom yellow)
 - (3) FeCr₂O₄ (chromite)
 - (4) PbCrO,PbO (chrom red)
- 22. Which of the following statement is wrong?
 - An acidified solution, K,Cr,O, liberates iodine from iodides
 - (2) In acidic solution, dichromate ions are converted to chromate ions
 - (3) Ammonium dichromate on heating undergoes exothermic decomposition to give Cr2O3
 - (4) Potassium dichromate is used as titrant for Fe²⁺ ions

- Zn and Hg donot show variable valency because
 - They are soft
 - (2) Their inner d-orbitals are completely filled
 - (3) They have only 2- electrons in the outer most shell
 - (4) None of these
- 24. Mercury on heating with aqua regia gives
 - Hg(NO₃)₂
- (2) HgCl₂
- (3) Hg(NO₂)₂
- (4) Hg,Cl,
- Ammonium dichromate is used in fireworks. The green coloured powder blown in the air is
 - CrO.
- (2) Cr₂O₃
- (3) Cr
- (4) CrO(O)

SECTION - B

Previous Years Questions

Which of the statements is not true?

[AIPMT 2012]

- K₂Cr₂O₇ solution in acidic medium is orange
- (2) K₂Cr₂O₇ solution becomes yellow on increasing the pH beyond 7
- (3) On passing H₂S through acidified K₂Cr₂O₇ solution, a milky colour is observed
- (4) Na₂Cr₂O₇ is preferred over K₂Cr₂O₇ in volumetric analysis
- Identify the alloy containing a non-metal as a constituent in it [AIPMT 2012]
 - Bell metal
 - (2) Bronze
 - (3) Invar
 - (4) Steel
- Which one of the following does not correctly represent the correct order of the property indicated [AIPMT 2012] against it?
 - Ti < V < Cr < Mn : increasing number of oxidation states
 - (2) Ti3+ < V3+ < Cr3+ < Mn3+ : increasing magnetic moment
 - (3) Ti < V < Cr < Mn : increasing melting points</p>
 - (4) Ti < V < Mn < Cr : increasing 2nd ionization enthalpy

Four successive members of the first series of the transition metals are listed below. For which one of

them the standard potential (E_{M²⁺M}) value has a [AIPMT 2012] positive sign?

- (1) Co (Z = 27)
- (2) Ni (Z = 28)
- (3) Cu (Z = 29)
- (4) Fe (Z = 26)
- The catalytic activity of transition metals and their compounds is ascribed mainly to [AIPMT 2012]
 - (1) Their magnetic behaviour
 - (2) Their unfilled d-orbitals
 - (3) Their ability to adopt variable oxidation states
 - (4) Their chemical reactivity
- Which of the following exhibits only +3 oxidation state? [AIPMT 2012]
 - (1) U
- (2) Th
- (3) Ac
- (4) Pa
- 7. Identify the correct order of solubility in aqueous medium [NEET 2013]
 - (1) $ZnS > Na_2S > CuS$ (2) $Na_2S > CuS > ZnS$

 - (3) Na₂S > ZnS > CuS (4) CuS > ZnS > Na₂S
- Which of the following lanthanoid ions is diamagnetic? [NEET 2013]

- (1) Sm2+
- (2) Eu2+
- (3) Yb²⁺
- (4) Ce2+
- KMnO₄ can be prepared from K₂MnO₄ as per the reaction:

$$3MnO_4^{2-} + 2H_2O \Longrightarrow 2MnO_4^{-} + MnO_2 + 4OH^{-}$$

The reaction can go to completion by removing OH- ions by adding [NEET 2013]

- (1) KOH
- (2) CO₂
- (3) SO₂
- (4) HCI
- Which of the following statements about the interstitial compounds is incorrect? [NEET 2013]
 - (1) They are chemically reactive
 - (2) They are much harder than the pure metal
 - (3) They have higher melting points than the pure
 - (4) They retain metallic conductivity

- Which of the following does not give oxygen on heating? [NEET 2013]
 - (1) Zn(ClO₃)₂
- (2) K₂Cr₂O₇
- (3) (NH₄)₂Cr₂O₇
- (4) KCIO₂
- The pair of compounds that can exist together is

[AIPMT 2014]

- FeCl₃, SnCl₂
- (2) HgCl₂, SnCl₂
- (3) FeCl₂, SnCl₂
- (4) FeCl₃, KI
- Reason of lanthanoid contraction is

[AIPMT 2014]

- Negligible screening effect of 'f' orbitals
- (2) Increasing nuclear charge
- Decreasing nuclear charge
- (4) Decreasing screening effect
- The reaction of aqueous KMnO₄ with H₂O₂ in acidic conditions gives : [AIPMT 2014]
 - (1) Mn4+ and O2
- (2) Mn2+ and O2
- (3) Mn²⁺ and O₂
- (4) Mn4+ and MnO2
- Magnetic moment 2.83 BM is given by which of the following ions? [AIPMT 2014]
 - (At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28)
 - (1) Ti³⁺
- (2) Ni2+
- (3) Cr³⁺
- (4) Mn2+
- Gadolinium belongs to 4f series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

[Re-AIPMT-2015]

- (1) [Xe]4f⁷5d¹6s²
- (2) [Xe]4f⁶5d²6s²
- (3) [Xe]4f⁸6d²
- (4) [Xe]4f⁹5s¹
- Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Numbers in the parenthesis are atomic numbers) [AIPMT-2015]
 - Zr (40) and Ta (73)
 - (2) Ti (22) and Zr (40)
 - (3) Zr (40) and Nb (41)
 - (4) Zr (40) and Hf (72)

- 18. Which one of the following statements is corrected when SO₂ is passed through acidified K₂Cr₂O₇ solution? [NEET-2016]
 - Green Cr₂(SO₄), is formed
 - (2) The solution turns blue
 - (3) The solution is decolourized
 - (4) SO₂ is reduced
- The electronic configurations of Eu (Atomic no. 63), Gd (Atomic No. 64) and Tb (Atomic No 65) are

[NEET-2016]

- [Xe]4f²6s², [Xe]4f²5d¹6s² and [Xe]4f⁸6s²
- (2) [Xe]4f⁷6s², [Xe]4f⁸6s² and [Xe]4f⁸5d¹6s²
- (3) [Xe]4f⁶5d¹6s², [Xe]4f⁷5f¹ and [Xe]4f⁹6s²
- (4) [Xe]4f⁶5d¹6s², [Xe]4f⁷5d¹6s² and [Xe]4f⁸5d¹6s²
- 20. Which one of the following statements related to lanthanons is incorrect?

[NEET (Phase-2) 2016]

- (1) Europium shows +2 oxidation state
- (2) The basicity decreases as the ionic radius decreases from Pr to Lu
- (3) All the lanthanons are much more reactive than aluminium
- (4) Ce(+4) solutions are widely used as oxidizing agent in volumetric analysis
- 21. The reason for greater range of oxidation states in actinoids is attributed to [NEET-2017]
 - (1) The radioactive nature of actinoids
 - (2) Actinoid contraction
 - (3) 5f, 6d and 7s levels having comparable energies
 - (4) 4f and 5d levels being close in energies

 HgCl₂ and l₂ both when dissolved in water containing l⁻ ions the pair of species formed is

[NEET-2017]

- (1) Hgl₂, l₃
- (2) Hgl₂, I⁻
- (3) Hgl₄²⁻, l₃⁻
- (4) Hg₂I₂, I[™]
- 23. Which one of the following ions exhibits d-d transition and paramagnetism as well?

[NEET-2018]

- (1) CrO₄²⁻
- (2) Cr₂O₇²-
- (3) MnO₄²
- (4) MnO₄
- The manganate and permanganate ions are tetrahedral, due to : [NEET-2019]
 - The π-bonding involves overlap of p-orbitals of oxygen with d-orbitals of manganese
 - (2) There is no π -bonding
 - The π-bonding involves overlap of p-orbitals of oxygen with p-orbitals of manganese
 - (4) The π-bonding involves overlap of d-orbitals of oxygen with d-orbitals of manganese
- When neutral or faintly alkaline KMnO₄ is treated with potassium iodide, iodide ion is converted into 'X'. 'X' is [NEET-2019 (Odisha)]
 - (1) IO-
 - (2) l₂
 - (3) IO₄
 - (4) IO₃

Chapter 15

Coordination Compounds

Sub-topics

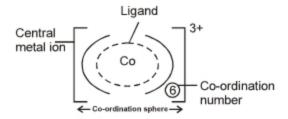
Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds, isomerism (structural and stereo) bonding, Werner's theory VBT,CFT; importance of coordination compounds (in qualitative analysis, biological systems).

Coordination Compound (or complex compound)

It is a complex substance which contains a central metal atom or ion surrounded by oppositely charged ions or neutral molecules (some cases have cations also) and retains identity in solutions although partial dissociation may occur.

Complex Ions

It is electrically charged radical which is formed by the union of simple cation with one or more neutral molecules or simple anion; e.g., complex ferrocyanide ions [Fe(CN)₆]^{4—}, is formed by the union of six CN[—] ions with one Fe²⁺ ion. The cluster of affions or molecules which surround the central metal ion are called ligands. The non bonded pairs of electrons on the ligand form co-ordinate bonds to the central ion by donating these unshared electron pairs into its vacant orbitals. It is because of this reason that the term coordinate compounds is coined for such substances.



Werner's Theory

Metals possess two types of valencies — Primary and Secondary. Primary valency is ionic and satisfied by anion while secondary is covalent and may be satisfied by anions as well as neutral molecules. It is directional in nature. It is verified by conductance data and the amount of precipitate. For example:

$$\begin{split} & [\text{Pt}(\text{NH}_3)_6]\text{Cl}_4 & \text{5 ions} & [\text{AgCI ppt maximum; conductance maximum}] \\ & [\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3\cdot\text{NH}_3 & \text{4 ions} \\ & [\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2\cdot2\text{NH}_3 & \text{3 ions} \\ & [\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}\cdot3\text{NH}_3 & \text{2 ions} \\ & [\text{Pt}(\text{NH}_3)_2\text{Cl}_4]\cdot4\text{NH}_3 & \text{No ions} & [\text{AgCI ppt minimum; no conductance}] \end{split}$$

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IUPAC Nomenclature

In order to name these compounds certain rules have been suggested by IUPAC.

- The positive part of a coordination compound is named first and is followed by the negative part.
- (ii) The ligands are named first followed by the central metal. The prefixes di- tri-, tetra- etc, are used to indicate the number of each kind of ligand present. The prefixes bis (two ligands) tris (three ligands) etc. are used when the polydentate ligands surround the central atom.
- (iii) The ligands are named in alphabetical order. Names of the anionic ligands end in O, those of cationic in ium. Neutral ligands have their regular names except that H2O is named aqua; NH3 ammine; NO nitrosyl; and CO carbonyl.
- (iv) The oxidation state of the central metal is indicated in roman numbers in a brackett.
- (v) When a complex species has negative charge, the name of the central metal ends in -ate. For some elements, the name of ion is based on the latin name of the metal (For example, argentate for silver).

Name of some of the complexes

[CrCl₂(H₂O)₄]Cl Tetraquadichloridochromium (III) chloride. [CoCl2(en)2]Cl Dichloridobis(ethylenediamine)cobalt (II) chloride K₄[Fe(CN)₆] Potassium hexacyanoferrate(II). Ni(CO), Tetracarbonylnickel (O)

K[Ag(CN)₂] Potassium dicyanoargentate (I)

 $K[BF_{a}]$ Potassium tetrafluoroborate (III)

 $K_3[Fe(C_2O_4)_3]$ Potassium trioxalatoferrate (III)

 $[Mn(H_2O)_6]^{2+}$ Hexaquamanganese(II) ion

[Ni(NH₃)₆]Cl₂ Hexamminenickel(II) chloride

[Co(NO₂)₃(NH₃)₃] Triamminetrinitrocobalt (III)

[NiCl₂(CH₃NH₂)₂] Dichloridobis(methylamine)nickel(II)

 $[CoBr(NH_3)_4 (H_2O)] (NO_3)_5$ Tetrammineaquabromidocobalt (III) nitrate

K₂ [SiF₆] Potassium hexafluorosilicate (IV)

K2[Ni(EDTA)] Potassium ethylenediaminetetracetatonickelate (II)

Fe₄[Fe(CN))₆]₃ Iron hexacyanoferrate(II)

LiAlH, Lithium tetrahydridoaluminate (III)

 $[Pt(Py)_4][PtCl_4]$ Tetrapyridinplatinum(II)tetrachloridoplatinate(II)

Na₂[SiF₆] Sodium hexafluorosilicate(IV)

Isomerism

(a) Structural isomerism

- (i) Hydrate isomerism
 - $e.g., [Co(H_2O)_6]Cl_3 \& [Co(H_2O)_4Cl_2]Cl.2H_2O$
- (ii) Ionisation isomerism

(iii) Linkage isomerism

(iv) Co-ordination isomerism

$$e.g., [Cr(NH_3)_6][Co(CN)_6] \& [Co(NH_3)_6] [Cr(CN)_6]$$

(v) Co-ordination position isomerism

$$e.g.$$
, $\left[(NH_3)_4 Co \left\langle \begin{array}{c} OH \\ CI \end{array} \right\rangle Co(NH_3)_2 CI_2 \right] SO_4$

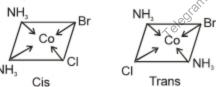
(b) Stereo isomerism

(i) Geometrical isomerism

Tetrahedral complexes do not show geometrical isomerism.

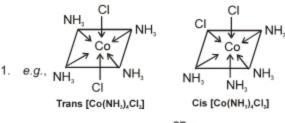
Square planer complexes with general formula: MA₂X₂, MA₂XY, MABX₂, MABXY, M(AB)₂ show geometrial isomerism.

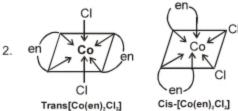




Note: MABCD shows special type of 3 geometrical isomerism.

Complexes with general formula, [MA₄X₂], [MA₄XY], [M(AA)₂X₂] shows geometrical isomerism.





The complex with formula [MA₃X₃] show geometrical isomerism of facial and meridonial type.





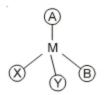
[with respect to A ligand]

Note: Complex with general formula [MABCDEF] shows 15 special geometrical isomerism but no such compound has been observed practically.

(ii) Optical isomerism

Case I: When C.N = 4

Possible hybridisations are dsp² and sp³, when cordination number of central atom is 4. In case of dsp²hybridisation optical isomerism is not possible. In case of sp3-hybridisation optical activity is possible only when all four linkages to the central metal are different.

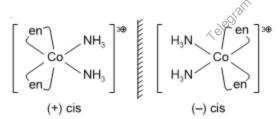


Optically active

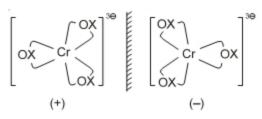
Case II: When C.N = 6

Type I : $[M(AA)_2B_2]$

 $\textit{e.g.}, \ [\text{Co(en)}_2(\text{NH}_3)_2]^{3\oplus}; \ \textit{cis form is optically active wheareas transform is optically inactive}$



Type II: [M(AA)₂]



E.A.N. Rule

(Effective atomic number rule): It states that E.A.N. of any element should be equal to atomic number of next inert gas (Many exceptions exist).

EAN = Own e⁻ of central metal atom/ion + electrons donated to it by ligands.

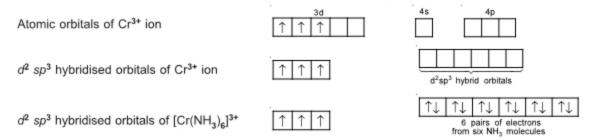
Hybridisation

(a) [Cr(NH₃)₆]³⁺ ion:

Electronic configuration of Cr = [Ar] 3d54s1

Electronic configuration of Cr3+ ion = [Ar] 3d3.

The chromium ion must make available six empty orbitals to accommodate six electron pairs from the six ammonia molecules. This can be achieved by the following hybridisation scheme:



A few examples of complex ions with the kind of hybridisation of central atom along with their geometries is tabelled below:

Name & formula of the complex ion	Nature of hybridisation of the metal ion	Geometry unpaired	No. of unpaired electrons	Nature of magnetism
[Ni(CN) ₄] ²⁻ [Cu(CN) ₄] ²⁻	dsp²	square planar	zero	diamagnetic
or [Cu(NH ₃) ₄] ²⁺	dsp²	square planar	one	paramagnetic
Ni(CO) ₄	sp³	tetrahedral	zero	diamagnetic
[Cr(NH ₃) ₆] ³⁺	of sp³ © Ses	octahedral	three	paramagnetic
[Fe(CN) ₆] ³⁻		octahedral	one	paramagnetic

(b) [Ni(CO)₄]:

In this complex, the oxidation state of nickel is zero. The electronic configuration of nickel in the zero oxidation state is [Ar] 3d⁸, 4s². In order to accommodate 4 electron pairs **donated** by four carbonyl ligands, the nickel atom must make available a set of four empty orbitals. This is achieved by pushing 4s electrons into 3d orbitals whereby pairing all the 3d electrons. This has been done because CO is a strong field ligand.

There will be no unpaired electron. Thereafter, nickel atom will undergo sp³ hybridization as shown below:

Atomic orbitals of nickel atom	3d ↑ ↑ ↑ ↑ ↑ ↑	4s	
sp3 hybridized orbitals of nickel atom	1		sp^3 hybridization
sp³ hybridized orbitals of [Ni(CO) ₄]	$\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow$		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Note: Depending upon the strength of the ligand either inner complex or outer complexes are formed.

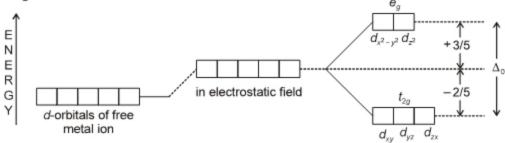
Also strong field causes maximum pairing whereas weak field ligands donot form maximum pairing. The strength of ligands according to spectrochemical series is

CRYSTAL FIELD THEORY

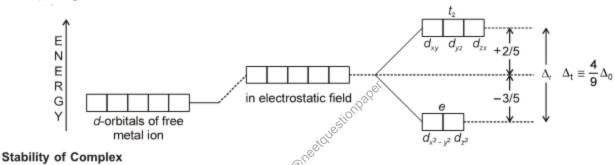
VBT fails to explain the magnetic properties and geometry of most of the complex compounds. Crystal field theory assumes the central metal as positively charged point and ligands are point negative charges. Electrostatic force of attraction between the central metal and ligands causes decrease in potential energy and formation of complex takes place.

In CFT, degeneracy of d-orbitals is lost.

Splitting of d-orbitals in octahedral field :



Splitting of d-orbitals in tetrahedral field :



Higher the stability constant, higher would be the stability of the complex.

Strong field complexes are more stable than weak field complexes.

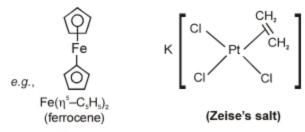
Inner d-orbital complex is more stable than outer -d-orbital complex.

Chelates are more stable. Moreover chelate of 5-member having no double bond and 6-member ring having double bond are more stable.

ORGANOMETALLIC COMPOUNDS

Compounds containing at least one metal carbon bond may be called as Organometallic compounds.

- (i) Sigma bonded compounds e.g., R-MgX, Al₂(CH₃)₆
- (ii) Pi-bonded organometallic compounds



(iii) σ & π-bonded organometallic compounds



Try Yourself

SECTION - A

Objective Type Questions

- 1. Which is not true for ligand metal complex?
 - Smaller the ligand, the more stable is the metal-ligand complex
 - (2) Highly charged ligands form stronger bonds
 - (3) Larger the permanent dipole moment of ligand, the more stable is the bond
 - (4) Greater the I.P. of central metal, stronger is the bond
- Which one of the following square planar complexes will be able to show cis-trans isomerism?
 - (1) MA, B
- (2) M (AA')₂
- (3) MA,
- (4) All of these

(AA': is unsymmetrical bidentate ligand ABCD are unidentate ligands)

- The correct IUPAC name of Fe(C₅H₅), is
 - (1) Cyclopentadienyl iron (II)
 - (2) Bis(η5-Cyclopentadienyl) iron (II)
 - (3) Dicyclopentadienyl Ferrate (II)
 - (4) Ferrocene
- The complex Hg[Co(CNS)] is correctly named as
 - (1) Mercury tetrathiocyanato cobaltate (II)
 - (2) Mercury cobalt tetra sulphocyano (II)
 - (3) Mercury tetra sulphocyanide cobaltate (II)
 - (4) Mercury sulphocyanato cobalt (II)
- 5. K₃ [Al(C₂O₄)₃] is called
 - (1) Potassium aluminooxalate
 - (2) Potassium alumino(III)oxalate
 - (3) Potassium trioxalatoaluminate
 - (4) Potassium trioxalatoaluminate(III)

The co-ordination number and oxidation number of X in the following compound

[X (SO₄) (NH₃)₅]CI will be

- (1) 10 and 3
- (2) 2 and 6
- (3) 6 and 3
- (4) 6 and 4
- How many ions are produced from [Co (NH₃)₆]Cl₃ in solution?
 - (1) 6
- (2) 4
- (3) 3

- (4) 2
- 8. Which of the following complex species involves sp³Ø² hybridisation?
 - (N) [CoF,]1-
- (2) [Co(NH₂)₂]3+
- (3) [Fe(CN)_e]3-
- (4) [Cr(NH₃)₆]³⁺
- The complex ion [Pt(NH3)4]+2 has structure
 - (1) Pyramidal
- (2) Tetrahedral
- (3) Square planar
- (4) Pentagonal
- 10. [CoF_c]3- is an
 - (1) Inner orbital, paramagnetic
 - (2) Outer orbital, paramagnetic
 - (3) Outer orbital, diamagnetic
 - (4) Inner orbital, diamagnetic
- The number of unpaired electrons in K_a[Fe(CN)_a] is
 - (1) 0
- (2) 1
- (3) 4

- (4) 5
- The Ni(CO)₄ complex is diamagnetic in nature. The hybrid state of Ni is
 - (1) sp3
- (2) sp²d
- (3) sp³d
- (4) spa³
- In hexacyanomanganate (II) ion, the Mn atom assume d²sp³ hybrid state. The number of unpaired electrons in the complex is
 - (1) 1

(2) 2

(3) 3

(4) Zero

- Hexaflurocobaltate (III) ion is found to be high spin complex. The probable hybrid state of cobalt in it is
 - (1) d^2sp^3
- (2) sp³
- (3) sp³d
- (4) sp³d²
- The two compounds Sulphatopentaamminecobalt (III) bromide and Sulphatopentaamminecobalt (III) chloride represent
 - Linkage isomerism
 - Ionisation isomerism
 - Co-ordination isomerism
 - (4) No isomerism
- 16. The compounds [Co(NO2)(NH3)2]Cl2 and [Co(ONO)(NH3)5]Cl2 are example of
 - Geometrical isomers (2) Linkage isomers
 - (3) Ligand isomers
- (4) Ionisation isomers
- 17. The kind of isomerism exhibited by [Rh(en), Cl,] [Ir(en)Cl,] and [Ir(en),][RhCl,] is

- (3) [Cr(NH_s)_eCl]SO_x
- (4) Both (1) & (2)
- The type of isomerism shown by

[Co(en),(NCS),]Cl and

[Co(en),(NCS)CI]NCS is

- (1) Co-ordination
- (2) Ionisation
- (3) Linkage
- (4) All of these
- 20. Which isomerism is exhibited by the compound $[Co(NH_x)_x(H_yO)_x]Cl_x?$
 - Linkage isomerism
 - (2) Cis-trans isomerism
 - Co-ordination isomerism
 - (4) Fac-Mer isomerism
- 21. Which of the following is most likely structure of CrCl, 6H,O if 1/3 of total chlorine of the compound is precipitated by adding AgNO, to its aqueous solution?
 - [Cr(H₂O)₆]Cl₂
- (2) [Cr(H,O),Cl,].3H,O
- (3) [CrCl₂(H₂O)₄]Cl₂H₂O (4) [CrCl₂(H₂O)₄]Cl₂H₂O

- 22. Atomic No. of Ni is 28. It forms a carbonyl having formula Ni(CO)₄. The EAN of Ni is
 - (1) 33
- (3) 30
- (4) 24
- Hybridisation of Ni in [Ni(CN)₄]²⁻ is
 - dsp²
- (3) sp²d
- (4) sp³
- Which of the following complex will show maximum paramagnetism?
 - (1) [Ni(CN),]2(-)
- (2) [Fe(CO),]
- (3) [FeF_e]³⁽⁻⁾
- (4) [Co(NH₃)₆]³⁹
- Which of the following complex can show optical activity?
 - (1) [MA,B,] (facial)
- (2) [M(AA),]
- (3) [M(AA)₂B₂] (trans)
- (4) All of these

SECTION - B

Which one of the following is an outer orbital

[AIPMT 2012]

- (1) [Cr(NH₃)₅SO₃]Cl Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is not true?

[AIPMT 2012]

- Red complex has a square planar geometry.
- (2) Complex has symmetrical H-bonding
- Red complex has a tetrahedral geometry
- (4) Dimethylglyoxime functions as bidentate ligand

$$\begin{cases}
dimethylglyoxime = \begin{cases}
H_3C - C = N \\
H_3C - C = N
\end{cases}
OH$$

- Low spin complex of d6-cation in an octahedral field will have the following energy: [AIPMT 2012]

 - (1) $\frac{-12}{5}\Delta_0 + P$ (2) $\frac{-12}{5}\Delta_0 + 3P$
 - (3) $\frac{-2}{5}\Delta_0 + 2P$ (4) $\frac{-2}{5}\Delta_0 + P$

 $(\Delta_0$ = Crystal Field Splitting Energy in an octahedral field, P = Electron pairing energy)

 Among the following complexes the one which shows Zero crystal field stabilization energy (CFSE) is [AIPMT 2012]

[AIPI

- (1) [Mn(H₂O)₆]³⁺
- (2) [Fe(H₂O)₆]³⁺
- (3) [Co(H₂O)₆]²⁺
- (4) [Co(H₂O)₆]³⁺
- 5. Which of the following complexes is used to be as an anticancer agent?
 - (1) mer-[Co(NH₃)₃Cl₃]
- (2) cis-[PtCl₂(NH₃)₂]
- (3) cis-K₂[PtCl₂Br₂]
- (4) Na₂[CoCl₄]
- 6. The name of complex ion, [Fe(CN)_c]3- is

[Re-AIPMT-2015]

- (1) Tricyanoferrate (III) ion
- (2) Hexacyanidoferrate (III) ion
- (3) Hexacyanoiron (III) ion
- (4) Hexacyanitoferrate (III) ion
- The hybridization involved in complex [Ni(CN)₄]²⁻ is (At. No. Ni = 28) [Re-AIPMT-2015]
 - (1) d^2sp^2
- (2) d^2sp^3
- (3) dsp2
- (4) sp3
- The sum of coordination number and oxidation number of the metal M in the complex [M(en)₂(C₂O₄)]Cl (where en is ethylenediamine) is

[Re-AIRMT-2015]

- (1) 7
- (2) 8
- (3) 9
- (4) 6
- Number of possible isomers for the complex [Co(en)₂Cl₂]Cl will be (en = ethylenediamine)

[Re-AIPMT-2015]

- (1) 3
- (2) 4
- (3) 2
- (4) 1
- Which of these statements about [Co(CN)₆]³⁻ is true? [AIPMT-2015]
 - [Co(CN)₆]³⁻ has no unpaired electrons and will be in a high-spin configuration
 - (2) [Co(CN)₆]³⁻ has no unpaired electrons and will be in a low-spin configuration
 - (3) [Co(CN)₆]³⁻ has four unpaired electrons and will be in a low-spin configuration
 - (4) [Co(CN)₆]³⁻ has four unpaired electrons and will be in a high-spin configuration

- Cobalt(III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C? [AIPMT-2015]
 - (1) CoCl₃.6NH₃
- (2) CoCl₃.3NH₃
- (3) CoCl₃.4NH₃
- (4) CoCl₃.5NH₃
- Magnetic moment 2.84 B.M. is given by (At. nos, Ni = 28, Ti = 22, Cr = 24, Co = 27) [AIPMT-2015]
 - (1) Co2+
- (2) Ni2+
- (3) Ti³⁺
- (4) Cr²⁺
- Which of the following has longest C O bond length? (Free C – O bond length CO is 1.128 Å)

[NEET-2016]

- (1) [Mn(CO)₆]*
- (2) Ni(CO),
- (3) [Co(CO)₄]⁰
- (4) [Fe(CO),]2-
- The correct increasing order of trans-effect of the following species is [NEET (Phase-2) 2016]
 - $(1) NH_3 > CN^- > Br^- > C_6H_5^-$
 - (2) $CN^- > C_6H_5^- > Br^- > NH_3$
 - (3) $Br^- > CN^- > NH_3 > C_6H_5^-$
 - (4) CN⁻ > Br⁻ > C₆H₅⁻ > NH₃
- Correct increasing order for the wavelengths of absorption in the visible region for the complexes of Co³⁺ is [NEET-2017]
 - [Co(en)₃]³⁺, [Co(NH₃)₆]³⁺, [Co(H₂O)₆]³⁺
 - (2) [Co(H₂O)₆]³⁺, [Co(en)₃]³⁺, [Co(NH₃)₆]³⁺
 - (3) [Co(H₂O)₆]³⁺, [Co(NH₃)₆]³⁺, [Co(en)₃]³⁺
 - (4) [Co(NH₃)₆]³⁺, [Co(en)₃]³⁺, [Co(H₂O)₆]³⁺
- The correct order of the stoichiometries of AgCI formed when AgNO₃ in excess is treated with the complexes: CoCl₃·6NH₃, CoCl₃·5NH₃, CoCl₃·4NH₃ respectively is [NEET-2017]
 - 1 AgCl, 3 AgCl, 2 AgCl
 - (2) 3 AgCl, 1 AgCl, 2 AgCl
 - (3) 3 AgCl, 2 AgCl, 1 AgCl
 - (4) 2 AgCl, 3 AgCl, 1 AgCl
- An example of a sigma bonded organometallic compound is [NEET-2017]
 - (1) Ruthenocene
- (2) Grignard's reagent
- (3) Ferrocene
- (4) Cobaltocene

- Pick out the correct statement with respect [Mn(CN)₆]³⁻ [NEET-2017]
 - It is sp³d² hybridised and octahedral
 - (2) It is sp3d2 hybridised and tetrahedral
 - (3) It is d2sp3 hybridised and octahedral
 - (4) It is dsp² hybridised and square planar
- Jahn-Teller effect is not observed in high spin complexes of [NEET (Phase-2) 2016]
 - (1) d^7
- (2) d8
- (3) d^4
- (4) d⁹
- 20. Iron carbonyl, Fe(CO), is

[NEET-2018]

- (1) Tetranuclear
- (2) Mononuclear
- (3) Dinuclear
- (4) Trinuclear
- The type of isomerism shown by the complex [CoCl₂(en)₂] is [NEET-2018]
 - (1) Geometrical isomerism
 - (2) Coordination isomerism
 - (3) Linkage isomerism
 - (4) Ionization isomerism
- The geometry and magnetic behaviour of the complex [Ni(CO)₄] are [NEET-2018]
 - (1) Square planar geometry and diamagnetic
 - (2) Tetrahedral geometry and diamagnetic
 - (3) Tetrahedral geometry and paramagnetic
 - (4) Square planar geometry and paramagnetic

 Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the correct code : [NEET-2018]

	Colum	n I		Column I
a.	Co3+		i.	√8 BM
b.	Cr3+		ii.	√35 BM
C.	Fe ³⁺		iii.	$\sqrt{3}$ BM
d.	Ni^{2+}		iv.	$\sqrt{24}$ BM
			V.	$\sqrt{15}$ BM
	а	b	С	d
(1)	iv	V	ii	i
(2)	i	ii	iii	N
(3)	iii	V	i	ii
(4)	iv	i	ii	iii

 What is the correct electronic configuration of the central atom in K₄[Fe(CN)₆] based on crystal field theory? [NEET-2019]

- (∮) t⁴₂g eੰ
- (2) $t_{2g}^6 e_g^0$
- (3) $e^3 t_2^3$
- (4) e⁴ t₂²
- The Crystal Field Stabilisation Energy (CFSE) for [CoCl₆]⁴⁻ is 18000 cm⁻¹. The CFSE for [CoCl₄]²⁻ will be [NEET-2019 (Odisha)]
 - (1) 8000 cm⁻¹
- (2) 6000 cm⁻¹
- (3) 16000 cm⁻¹
- (4) 18000 cm⁻¹

Chapter 16

Environmental Chemistry

Sub-topics

Introduction, Atmospheric Pollution, Tropospheric Pollution, Greenhouse Effect, Acid rain, Smog, Stratospheric Pollution, Water Pollution, Biochemical Oxygen Demand (BOD), Eutrophication, Soil Pollution, Strategies to Control Environmental Pollution, Green Fuel

Environmental chemistry makes an analysis of all the chemical species in the environment and studies its origin, reactions and effects on animate and inanimate objects.

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on living and non-living things.

A substance which causes pollution, is known as pollutant. Pollutants are of two types :

- (i) Primary pollutant: They enter the air as a result of natural events or human activities. For e.g., CO, SO, etc.
- (ii) Secondary pollutant: These are formed in the air due to chemical reactions between two or more primary pollutants e.g., SO₃, PAN, etc.

Atmospheric Pollution

The lowest region of atmosphere in which the organisms live is called troposphere which extends upto the height of 10 km from sea level. This region contains air, much water vapour and clouds.

The layer above the troposphere is called stratosphere which extends between 10 km and 50 km above sea level and contains N₂, O₃, O₃ and little water vapour.

Tropospheric Pollution

The major tropospheric pollutants are :

- (i) Gaseous air pollutants: These include oxides of carbon, nitrogen and sulphur, hydrocarbons, hydrogen sulphide, ozone etc.
- (ii) Particulate pollutants: These are the minute solid particles or liquid droplets in air. These may be viable (e.g., bacteria, fungi, moulds, algae, etc.) or non-viable (e.g., smoke, dust, mists and fumes)

Greenhouse Effect

About 25% of the solar energy reaching the earth is radiated back to the atmosphere. Some of this radiated heat energy is trapped by gases like CO₂, CH₄, O₃, N₂O water vapour and chlorofluoro carbon compounds in the atmosphere which result into global warming. This is called greenhouse effect. Usually CO₂ is not considered as pollutant but is the major contributor to global warming.

Acid Rain

The normal rain water has a pH of 5.6 due to the presence of H* ions formed as follows:

$$H_2O(I) + CO_2(g) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^*(aq) + HCO_3^-(aq)$$

When the pH of rain water drops below 5.6, it is called acid rain. It is due to the dissolution of acidic oxides present in atmosphere like SO_2 and NO_2 in rain water which produces the corresponding acids like H_2SO_4 and HNO_2 in rain water.

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NEET Environmental Chemistry 153

Smog

It is the most common form of air pollution. It is a dark fog having smoke, dust, gases and water vapours.

It is of two types:

- (i) Classical smog It is also called reducing smog or London smog and occurs in cool humid climate. It consists of smoke, fog and SO₂.
- (ii) Photochemical smog It is also called oxidising smog or Los Angles smog and occurs in warm, dry and sunny climate.

It contains oxides of nitrogen, O₃ and organic compounds such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).

Photochemical smog causes headache, chest and throat infections and also damages plant life.

Stratospheric Pollution

Ozone is present in the upper stratosphere which prevents the harmful ultraviolet radiations from the sun to reach the earth surface.

The main threat to this ozone layer is posed by the use of freons (CFCs) which are used in aerosol sprays, refrigerators and air-conditioners. They react with O₃ by free radical process. Also nitrogen oxides (particularly nitric oxide) combines very rapidly with ozone and depletes its concentration.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

Water Pollution

Any unwanted change that deteriorates the quality of water and makes it unfit for drinking purpose is called water pollution.

Sources of water pollution include pathogens, organic wastes and chemical pollutants (e.g. acids, detergents, fertilizers, PCBs, etc.).

Biochemical Oxygen Demand (BOD)

The amount of oxygen required by bacteria to breakdown the organic matter present in a certain volume of water is called BOD.

Clean water should have BOD value of less than 5 ppm whereas highly polluted water would have a BOD of 17 ppm or more.

Eutrophication

Presence of extra nutrients in water bodies brings about a dense plant population, which kills animal life by depriving it of oxygen is called eutrophication.

Some important chemicals and their international standards for drinking water are tabulated below:

Chemicals	Tolerable limit	Effects (due to
1. Fluoride	1. 1 ppm	Harmful effect for bones and teeth
2. Sulphate	2. 500 ppm	Laxative effect
3. Nitrate	3. 50 ppm	Blue-baby syndrome
4. Lead	4. 50 ppb	Damages kidney, liver, reproductive system, etc.

pH of drinking water should lie between 5.5 - 9.5

Soil Pollution

It is unfavourable alteration of soil by factors which decrease soil productivity, quality of plants and ground water is called soil pollution.

Major soil pollutants include insecticides (e.g. DDT), pesticides, herbicides (e.g. NaClO₃, Na₃AsO₃, etc.) and fertilizers which enter animal and human bodies through food chain. Some biodegradable insecticides like organo-phosphates and carbamates have been used but these are very harmful to humans.

Industrial waste, both biodegradable and non-biodegradable, also contribute towards water and soil pollution.

Biodegradable wastes are generated by cotton mills, food precessing units, paper mills and textile factories. Non-biodegradable wastes are generated by thermal power plants and iron and steel plants.

Strategies to Control Environmental Pollution

Strategies include waste management i.e., collection of domestic waste at the disposable site, recycling of non-biodegradable materials like plastic, glass, etc. and proper disposal of biodegradable wastes. 4R principle to reduce harmful effects of non-biodegradable materials is : reduce, reuse, recycle and recover.

Green Fuel

Fuel obtained from plastic waste contains no lead and is known as green fuel.

Green Chemistry

It means utilization of existing knowledge so as to bring about reduction in the production of pollutants, energy consumption and waste generation. For example replacement of tetrachloroethene (a water pollutant and a carcinogen) as solvent or dry-cleaning by liquid CO₂ which is less harmful; use of H₂O₂ for bleaching clothes which makes use of lesser amount of water.



Try Yourself

SECTION - A

Objective Type Questions

- 1. Which of the following is a primary pollutant?
 - (1) O₃
- (2) SO₂
- (3) SO₃
- (4) PAN
- 2. The lowest region of atmosphere is called
 - (1) Ionosphere
 - (2) Mesosphere
 - (3) Troposphere
 - (4) Stratosphere
- 3. The major tropospheric pollutants include
 - (1) Hydrocarbons
 - (2) Oxides of nitrogen
 - (3) Dust
 - (4) All of these
- 4. Which of the following samples of rain water with given pH would be called acid rain?
 - (1) pH = 6.0
- (2) pH = 7
- (3) pH = 4.2
- (4) pH = 5.8
- 5. Which of the following is not a component of reducing smog?
 - (1) Fog
- (2) Smoke
- (3) Acrolein
- (4) SO₂
- 6. Which of the following samples of water with given BOD would be qualified as highly polluted water?
 - (1) BOD less than 5
 - (2) BOD between 5 and 10
 - (3) BOD between 11 and 15
 - (4) BOD greater than 17
- 7. Which of the following is a greenhouse gas?
 - (1) SO₃
- (2) N₂O
- (3) Cl₂
- (4) CO

- 8. Which of the following components of photochemical smog are powerful eye irritants?
 - (1) HCHO and NO
 - (2) O₃ and PAN
 - (3) HCHO and acrolein
 - (4) Acrolein and NO
- 9. By which of the following reaction mechanisms does CFCs deplete ozone layer in the stratosphere?
 - (1) Free radical process
 - (2) Nucleophilic addition reaction
 - (3) Electrophilic substitution reaction
 - (4) Nucleophilic substitution process
- The main cause of eutrophication is
 - (1) Aquatic animals
 - (2) Nutrient rich water bodies
 - (3) Dissolved oxygen
 - (4) Dissolved carbon-dioxide
- 11. Which of the following water pollutant if present in excess can damage kidney and liver?
 - (1) Pb
- (2) F-
- (3) NO₂⁻
- (4) SO₄2-
- 12. Which of the following is a herbicide?
 - NaClO₃
 - (2) Na₃PO₄
 - (3) NaClO
 - (4) KMnO₄
- Fuel obtained from plastic waste is called
 - Plastic fuel
 - (2) Green fuel
 - (3) Lead fuel
 - (4) Biogas

(3) Recycling of non-biodegradable wastes

(4) All of these

Which of the following is a more biodegradable Green chemistry involves insecticide? (1) Reduction in the production of pollutants and DDT (2) Aldrin (2) Increased use of green chemicals (3) Increased use of green plants in atmosphere (3) Dieldrin (4) To study the effect of pollutants on green plants (4) Organo-phosphates 15. Which of the following is the tolerable limit of fluoride ion concentration in water? SECTION - B (2) 5 ppm 1 ppm **Previous Years Questions** (4) 100 ppm (3) 25 ppm Which oxide of nitrogen is not a common pollutant 16. The most serious water pollutants are introduced into the atmosphere both due to natural (1) Organic wastes (2) Pathogens and human activity? [NEET-2018] (3) Chemical pollutants (4) Fertilizers N₂O₅ (2) NO₂ 17. Which of the following substance is the main (3) NO (4) N₂O cause of ozone layer depletion? Among the following, the one that is not a green 2. Freons (2) CH₄ house gas is [NEET-2019] (3) O₂ (4) HCI Nitrous oxide (2) Methane Non-biodegradable industrial wastes are produced (3).⊘Ozone (4) Sulphur dioxide by (1) Steel plant (2) Paper mills with a suitable detergent is (3) Textile mills (4) Cotton mills [NEET-2019 (Odisha)] Waste management includes (1) CO₂ (1) Collection of domestic wastes (2) Water gas (2) Proper disposal of biodegradable wastes

(3) Petroleum gas

(4) NO₂

Sample Question Paper-1

Choose the correct answer:

- Which statement is correct for acetophenone?
 - (1) It is reduced to methylphenyl carbinol by Na
 - (2) It is oxidized to [O]
 - (3) It undergoes electrophilic substitution at ortho para position
 - (4) It undergoes iodoform reaction with iodine and strong alkali
- $\xrightarrow{\text{Conc. } H_2\text{SO}_4} X \xrightarrow{\text{Br}_2} Y$
 - (1) CH₃ CH₂ CH₃ (2) CH₃ CH CH₃
 - (3) $CH_3 C = CH_2$ (4) $CH_3C \equiv CH$
- Correct order of reactivity towards aromatic



- (1) | > || > || > |V
- (3) II > I > III > IV
- (4) III > I > II > IV
- Which of the following compounds possesses the highest melting point?

A on ozonolysis gives cyclohexanone and butan-2-one. Identify A

- Which compound is used for gravimetric estimation of Cu (II)?
 - (1) Cu₂O
- (2) Cu₂CO₃
- (3) Cu₂l₂
- (4) Cu₂(SCN)₂
- Colourless species is
 - (1) VCI₃
- (2) CrCl₂
- (3) Na₃VO₄
- (4) [V(H₂O)₆SO₄].H₂O
- Correct oxidizing power of perhalate ion is
 - (1) BrO₄ > IO₄ > CIO₄
 - (2) CIO₄ > BrO₄ > IO₄
 - (3) IO₄ > BrO₄ > CIO₄
 - (4) IO₄ > CIO₄ > BrO₄
- Which of the following has square planar geometry?
 - [PtCl₄]^{2−}
- (2) [CoCl₄]²⁻
- (3) [FeCl₄]²⁻
- (4) [NiCl₄]²⁻
- Aldol condensation between acetaldehyde and propanaldehyde will give how many products?
 - (1) Two
- (2) Four
- (3) Three
- (4) One
- 11. Ethylamine on heating with CS2 in presence of HgCl, forms
 - (1) C₂H₅NCS
- (2) (C₂H₅)₂S
- $(3) (C_2H_5)_2CS$
- (4) C₂H₅Cl₂

- On complete hydrolysis, the sugar produced by DNA and RNA respectively are
 - (1) β-D-ribose, β-D-2-deoxyribose
 - (2) Arabinose, β-D-2-ribose
 - (3) β-D-2-deoxyribose, β-D-2-ribose
 - (4) β-D-2-deoxyribose, Arabinose
- 13. Which of the following compounds will give dye test?
 - (1) C₆H₅NH₂
- (2) (C₆H₅)₂NH
- (3) CH₃NH₂
- (4) C₂H₅NH₂
- 14. Which of the following is floating agent?
 - (1) Pine oil
- (2) K-ethyl xanthate
- (3) Cresol
- (4) NaCN
- Reaction of nitrous acid with aliphatic primary amine will give
 - (1) Alcohol
- (2) Dye
- (3) Nitrile
- (4) Diazonium salt
- Correct order of increasing strength of C–O bond in the following carbonyls is
 - (1) $[Mn(CO)_6]^+ < [V(CO)_6]^- < [Fe(CO)_5]$
 - (2) $[V(CO)_6]^- < [Fe(CO)_5] < [Mn(CO)_6]^+$
 - (3) [V(CO)₆]⁻ < [Mn(CO)₆]⁺ < [Fe(CO)₅]
 - (4) [Mn(CO)₆]⁺ < [Fe(CO)₅] < [V(CO)₆]⁻
- 17. Identify the incorrect match
 - (1) Morphine, Heroin Analgesics
 - (2) Ranitidine, Cimetidine Antacids
 - (3) Penicillin, Chloramphenicol Antibiotics
 - (4) Novalgin, Streptomycin Antihistamines









19. Which one of the following structures represent Nylon-6 polymer?

- (1) $\left(\begin{array}{c} C (CH_2)_5 \begin{array}{c} H \\ N \end{array} \right)_n$
- (2) $\left(\begin{array}{c} H & H & O \\ N (CH_2)_6 N C (CH_2)_4 C \end{array}\right)_n$
- (3) $\left(\begin{array}{c} H \\ N (CH_2)_5 C N (CH_2)_6 N \end{array}\right)_{n}$
- (4) $\left(\begin{array}{c} O \\ C \\ C \end{array}\right) \left(\begin{array}{c} H \\ C \\ O \end{array}\right)_{n}$
- 20. Non-reducing sugar among the following is
 - Sucrose
- (2) Maltose
- (3) Lactose
- (4) Glucose
- 21. 2-Butyne $\xrightarrow{\text{Na/liq NH}_3}$ A $\xrightarrow{\text{Br}_2/\text{CCl}_4}$ B,

B is

- (1) 2,2-dibromobutane
- (2) Meso-2,3-dibromobutane
- (3) 2,3-dibromobutane
- (4) 1,4-dibromobutane
- In which of the following compounds S_N1 will occur easily?
 - (1) C₆H₅CH₂OH
- (2) CH₃OH
- (3) (CH₃)₂CHOH
- (4) C₂H₅OH
- 23. In which of following compounds H shifting in Cannizzaro reaction will occur easily?
 - (1) HCHO
- (2) C₆H₅CHO
- (3) (CH₃)₃C CHO
- (4) (C₆H₅)₃ C CHO
- 24. Which one of the following will not give cis diols?
 - (1) 1% Alkaline KMnO₄
- (2) OsO₄ Na₂CO₃
- (3) $\frac{RCO_3H}{H^*/H_2O}$
- (4) All of these
- 25. Consider the following carbanions
 - CH₃ ČH₂
 - II. CH, = CH
 - III. $HC \equiv C^{(i)}$

The correct order of stability is

- (1) | > || > |||
- (2) ||| > || > |
- (3) | = || = |||
- (4) || > ||| > |

$$CH_3$$
 $CH = CH_2 \xrightarrow{H_2O} X \text{ (major)}$

Which one of the following is incorrect match?

(1) Fe₄[Fe(CN)₆]₃

Prussian blue

(2) Na₄[Fe(CN)₅NOS]

Deep violet

(3) PbS

Red

(4) Fe(CNS)₂

Blood red

28. CH₃ - CH₂ - CH₃
$$\xrightarrow{Br_2}$$
 A Na Dry ether

$$\xrightarrow[\text{Ozonolysis}]{\text{Er}_2,\text{hv}} X \xrightarrow[\text{Dibromo derivative}){\text{Zn}} Y \xrightarrow[\text{Ozonolysis}]{\text{Reductive}} Z$$

'Z' is

- (1) Butanone
- (2) Acetone
- (3) Ethanal
- (4) 3-Methylcyclobutanone

29. Water zinc reacts with dilute nitric acid, it gives

- (1) Zn(NO₃)₂, NO₂, N₂O
- (2) Zn(NO₃)₂, N₂O
- (3) Zn(NO₃)₂, NO₂
- (4) Zn(NO₃)₂, NO

30. In which of the following, geometrical isomerism is possible?

- (1) CH₂ = CH₂
- (2) CH₃CH = CH CH₃
- (3) Cl₂C = CBr₂
- (4) $H-C \equiv C-Br$

31. Which one of the following compounds will not show tautomerism?





32.
$$CH_3 \xrightarrow{Br_2} A \xrightarrow{alc. KOH} B \xrightarrow{(ii) B_2H_6}$$

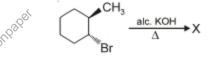
IUPAC name of X is

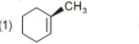
- 2-Methylcyclopentanol
- (2) 1-Methylcyclopentanol
- (3) 1-Cyclopentylmethanol
- (4) Cyclohexanol

Which one of the following compounds is antiaromatic?

(4) All of these

Identify the product 'X' in the reaction









Which of the following is a temporary effect?

- Hyperconjugation
- (2) Resonance
- (3) Transmission effect (4) Electromeric effect

In Williamson's synthesis, ethoxyethane is 36. prepared by

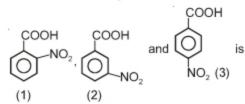
- (1) Heating sodium ethoxide with ethyl bromide
- (2) Passing ethanol over heated alumina
- (3) Treating ethyl alcohol with excess of conc. H₂SO₄ at 430-440 K
- (4) Heating ethanol with dry Ag₂O

37. Which of the following statement is correct?

- All halogens form oxyacids
- (2) HCIO₄ is better oxiydizing agent than HCIO₃
- (3) Polonium is radioactive halogen
- (4) I₂ dissolves in KI solution

- 38. K₂[Hgl₄] detects the ion/group
 - (1) NH₂-
- (2) NO
- (3) NH₄⁺
- (4) AICI₃
- 39. The magnetism of Ni2+ ion is
 - (1) $\frac{eh}{4\pi m}$
- (2) $\sqrt{6} \frac{eh}{4\pi m}$
- (3) $\sqrt{8} \frac{\text{eh}}{4\pi \text{m}}$
- (4) $\sqrt{10} \frac{\text{eh}}{4\pi \text{m}}$
- 40. Ammonia can be dried by
 - (1) Conc. H₂SO₄
 - (2) P₄O₁₀
 - (3) CaO
 - (4) Anhyd. CaCl₂
- - (1) Red liquid
- (2) Violet gas
- (3) Greenish yellow gas (4) Yellow-brown gas
- Gabriel phthalimide reaction is used for the synthesis of
 - (1) 1°-alcohol
- (2) 1°-amine
- (3) Aldehyde
- (4) Ketone

- Alanine has pK₈₁ = 9.6 and pK₈₂ = 2.4; isoelectric point will be at pH of
 - (1) 6
 - (2) 9
 - (3) pH > 9.6 or pH < 2.4
 - (4) pH = 9.6 or pH = 2.4
- 44. Order of acidic strength for



- (1) 1<2<3
- (2) 2 < 3 < 1
- (3) 3 < 1 < 2
- (4) 3 < 2 < 1
- For osazone formation, the effective structure unit necessary is
 - (1) CH₂OCH₃
- (2) CH₂Oŀ
- (3) CH₂OH

CHOCH,

(4) CHO

Sample Question Paper-2

Choose the correct answer:

- What would be the concentration of Cl⁻ ions when equal volumes of aqueous solutions of 0.01 M NH₄Cl and 0.02 M Al₂(SO₄)₃, are mixed?
 - (1) 0.005
- (2) 0.01
- (3) 0.001
- (4) 0.05
- The product obtained on the ozonolysis of acetylene is
 - (1) HCHO
- (2) CH₃CHO
- (3) CHO CHO
- (4) None of these
- 3. Which of the following has highest dipole moment?
 - (1) CH₃-Br
- (2) CH₃-CI
- (3) CH₃-F
- (4) CH₃--I
- The segment of DNA which acts as the instrumental manual for the synthesis of the protein is called
 - (1) Nucleotide
- (2) Nucleoside
- (3) Ribose
- (4) Gene
- 5. Which of the following fact is incorrect?
 - In case of a binary solution of two Volatile liquids, the vapour phase is always richer in more volatile component
 - (2) Molarity of a solution is temperature dependent
 - (3) Impurities lower the freezing point of a pure liquid substance
 - (4) ΔT_f measurement is preferred to determine molar mass of macromolecules
- 6. In which of the following compounds, in solid state, P exhibits two different oxidation states?
 - (1) PBr₅
- (2) PH
- (3) PCI₅
- (4) P₄O₁₀
- 7. HCI (limiting) →

Product of this process

- (1) / VCI
- (2)
- (3) CI >→≡
- (4) CI →=

- The treatment of benzene with isobutene in the presence of sulphuric acid gives
 - (1) Iso-butyl benzene
 - (2) n-butyl benzene
 - (3) Tert-butyl benzene
 - (4) No reaction
- 9. Which of the following matching is irrelevant?

(1)
$$C - CH_3 \longrightarrow COO^- + CH_3$$

$$\begin{array}{c} O \\ | \\ C_6H_5-CH=O \longrightarrow C_6H_5CH-C-C_6H_5 \\ | \\ OH \end{array}$$

(Aldol condensation)

(3)
$$CH_3-CH_2-COOH \xrightarrow{CI/P/hv} CH_3-CH-COOH \xrightarrow{(HVZ reaction)}$$

(4)
$$C - CI \xrightarrow{H_J/Pd/BaSO_J/S} CHO$$
(Rosenmund reduction)

10. In the following skeleton what would be the most likely situation for the highest stability of carbocation?

- (1) 2
- (2) 4

(3) 3

- (4) 1
- 11. In the following reaction, the product (A) is

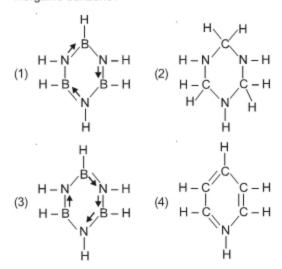
(2)
$$N = N - OH$$

(3)
$$\langle \bigcirc \rangle$$
 N = N $-\stackrel{+}{O}$ H

$$(4) \bigcirc N = N - \bigcirc OF$$

The compound D shall be

- The volume of H₂ gas produced at STP in Lane's process by 10 g Fe (44% impure) is
 - (1) 3L
- (2) 6L
- (3) 5L
- (4) 4L
- 14. Which of the following is the correct structure of inorganic benzene?



- 15. Which of the following has the highest value of magnetic moment?
 - (1) [Fe(CN)_e]3-
- (2) [CoCl₆]⁴
- (3) [NiCl₄]²⁻
- (4) [Cu(NH₃)₄]²⁺
- DDT can be obtained by combination of which two reactants in presence of H₂SO₄?

- 17. Optįcal isomerism is not shown by
 - (t) [Co(en)2Cl2]+
- (2) [Co(NH₃)₃Cl₃]
- (3) [Co(en₃)]
- (4) [CoCl₂(en)(NH₃)₂]*
- Base having highest pK_a
 - (1) KOH
- (2) NaOH
- (3) Be(OH)₂
- (4) LiOH
- 19. Which one of the following is not a peroxide?
 - BaO₂
- (2) SnO₂
- (3) Na₂O₂
- (4) H₂O₂
- 20. Among following which carbon hydrogen bond has least energy, for homolysis?
 - (1) Benzyl -H
- (2) 3° butyl -H
- (3) Methyl -H
- (4) Allyl -H
- 21. The equation related with nucleophilic addition

(1)
$$CH_2 = CH_2 \xrightarrow{(i) \text{ dil. } H_2SO_4/\Delta} C_2H_5OH$$

(2)
$$\bigcirc$$
 CH=0 CHCN

$$(4) \bigcirc CI + Cu_2(CN)_2 \longrightarrow CN$$

- In B₂H₆, the bond between Boron to Boron is
 - 2-center-2-electron bond
 - (2) Banana bond
 - (3) Co-ordinate bond
 - (4) π-bond
- 23. Number of monobromo products from methyl cyclopentane
 - (1) 3

(2) 4

(3) 5

- (4) 6
- 24. Which of the following formula of carbonyls is incorrect?
 - (1) [Ni(CO)₄]
- (2) [Fe(CO)₆]
- (3) [Co(CO)₄]
- (4) [Mn₂(CO)₁₀]
- Electrophilic substitution would be most favourable

- Number of moles of phenyl hydrazine required to convert one mole of glucose to glucosazone is,
 - (1) 3
- (3) 5

- (4) 6
- 27. The number of negative charge on the basic unit of pyrosilicate is
 - (1) 2
- (2) 4
- (3) 6
- (4) 3
- NaNO2 + HCI 28.



- c=0

- 29. +2 oxidation state would be most stable in
 - (1) Ge
- (2) Sn
- (3) C
- (4) Pb

- 30. The polymer which belongs to straight chain linear polymer class is
 - (1) Glycogen
 - (2) Amylopectin
 - (3) High density polythene
 - (4) Low density polythene
- 31. Carborundum is
 - (1) Al₂O₃
- (2) P₄O₁₀
- (3) C₃O₂
- (4) SiC
- 1 mol of which of the following would be equal to one gram equivalent?
 - (1) NaClO
- (2) H₂PO₂
- (3) Oxalic acid
- (4) Glauber's salt
- 33. Which of the following polymer contains N?
 - (1) Terylene
- (2) Oxytocin
- (3) Bakelite
- (4) Cellulose
- The correct molecular geometry and hybridization for PCI_s is
 - Pentagonal bipyramidal, sp³d
 - Trigonal bipyramidal, sp³d
 - (3) Square planar, sp³d²
 - (4) Octahedral, sp³d²
- Which of the following is an alum?
 - (1) FeSO₄(NH₄)₂SO₄.6H₂O
 - (2) MgCO₃.CaCO₃
 - (3) Na₂SO₄.Al₂(SO₄)₃.24H₂O
 - (4) 2PbCO₃.Pb(OH)₂
- LiAlH₄ cannot bring following reduction process
 - CH₃-CH-CH₃ to propane

 - -CH=CH2 to ethyl benzene

- 37. In which of the following, elements of d-block will generally exhibit their highest oxidation state?
 - (1) Oxides
- (2) Nitrates
- (3) Sulphates
- (4) Chlorides
- 38. Which does not form true anhydride on dehydration?
 - (1) HCOOH
- (2) CH₃OH
- (3) COOH COOH
- (4) All of these
- 39. Which of the following is monobasic acid?
 - (1) H₃BO₃
- (2) H₃PO₂
- (3) H₂S₂O₇
- (4) Both (1) & (2)
- Cis-trans isomerism is not exhibited by
 - (1) $(CH_3)_2C = NOH$
 - (2) [Co(NH₃)₄Br₂]⁺
 - (3) But-2-ene
 - (4) But-2-en-1, 4-dioic acid
- 41. Which one of the following structures represents terylene?

(2)
$$\left\{ \begin{array}{c} H \\ N - (CH_2)_6 - N - C - (CH_2)_4 - C \end{array} \right\}_{n}$$

(3)
$$\left\{ \begin{array}{c} C - (CH_2)_5 - \begin{array}{c} H \\ N \end{array} \right\}_n$$

(4)
$$\left\{ CH_2 - CH = CH - CH_2 - CH - CH_2 \right\}_n$$

- 42. Which one of the following forms micelle in aqueous solution above CMC and Kraft temperature?
 - Glucose
 - (2) Sodium stearate
 - (3) Urea
 - (4) Pyridinium chloride
- 43. Which of the following would be a square planar paramagnetic complex?
 - [Ni(CN)₄]²⁻
- (2) [Ni(CO)₄]
- (3) [Cu(NH₃)₄]²⁺
- (4) [CuCl₄]³-
- 44. Which of the following reactions will give diborane?
 - (1) NaBH₄ + I₂ →
- (2) BF₃ + LiAlH₄ → →
- (3) BF₃ + NaH → (4) All of these
- 45. Consider the following statements
 - H₂O₂ liberates O₂ on reaction with KMnO₄ in ⊘acidic medium
 - H2 gas is formed by action of Aluminium with dilute NaOH
 - III. Boiling water has pH = 7

Choose the correct statement(s)

- (1) Only I
- (2) II & III
- (3) I & II
- (4) I, II & III

NEET Answers 165

ANSWERS

Chapter 1: Organic Chemistry - Some Basic Principles and Techniques

		Chap	oter	: Organ	ic Cn	emistry ·	Som	ie Basic	Princ	ipies and	ı ieci	nniques		
Sect	tion	A : Object	tive T	ype Ques	tions									
	1.	(1)	2.	(1)	3.	(3)	4.	(4)	5.	(2)	6.	(1)	7.	(2)
	8.	(2)	9.	(1)	10.	(2)	11.	(1)	12.	(2)	13.	(3)	14.	(2)
	15.	(2)	16.	(1)	17.	(3)	18.	(4)	19.	(4)	20.	(3)	21.	(4)
- :	22.	(3)	23.	(2)	24.	(2)	25.	(3)	26.	(4)	27.	(2)	28.	(1)
2	29.	(4)	30.	(3)	31.	(1)	32.	(1)	33.	(3)	34.	(1)	35.	(4)
	36.	(3)	37.	(3)	38.	(1)	39.	(4)	40.	(2)				
Sect	tion	B : Previo	us Ye	ears Ques	tions									
	1.	(3)	2.	(1)	3.	(1)	4.	(4)	5.	(1)	6.	(4)	7.	(3)
	8.	(3)	9.	(4)	10.	(4)	11.	(3)	12.	(4)	13.	(1)	14.	(3)
	15.	(1)	16.	(1)	17.	(4)	18.	(1)	19.	(4)	20.	(4)	21.	(1)
-	22.	(1)	23.	(4)										
						Chapter	-							
Sect	tion	A : Object	tive T	ype Ques	tions			ages						
	1.	(4)	2.	(3)	3.	(1)	4.	(1) onpaper	5.	(1)	6.	(3)	7.	(1)
	8.	(3)	9.	(1)	10.	(3)	11. 👾	×(9)	12.	(1)	13.	(4)	14.	(3)
	15.	(4)	16.	(1)	17.	(3)	11. 18.	(1)	19.	(3)	20.	(1)	21.	(1)
:	22.	(1)	23.	(2)	24.	(3)	25.	(1)	26.	(2)	27.	(2)	28.	(1)
	29.	(4)	30.	(1)	31.	(3)	32.	(2)	33.	(4)	34.	(2)	35.	(2)
	36.	(4)	37.	(3)	38.	(1)	39.	(4)	40.	(4)	41.	(1)	42.	(4)
	43.	(4)	44.	(4)	45.	(1)								
Sect	tion	B : Previo	us Ye	ears Ques	tions									
	1.	(3)	2.	(1)	3.	(1)	4.	(2)	5.	(4)	6.	(3)	7.	(3)
	8.	(2)	9.	(2)	10.	(1)	11.	(2)	12.	(3)	13.	(4)	14.	(3)
	15.	(3)	16.	(1)	17.	(4)	18.	(2)	19.	(4)	20.	(3)	21.	(1)
:	22.	(2)	23.	(2)	24.	(2)	25.	(3)	26.	(2)				
				Ch	napte	r 3 : Halo	alkar	nes and I	Haloa	renes				
				0.	.apto		-							
		A : Object												
	1.	(3)	2.	(2)	3.	(1)	4.	(4)	5.	(4)	6.	(2)	7.	(4)
	8.	(1)	9.			(1)	11.	(4)	12.	(3)	13.	(2)	14.	(2)
	15.	(2)	16.	(2)	17.		18.	(3)	19.	(2)	20.	(2)	21.	(3)
	22.	(2)	23.	(2)	24.	(1)	25.	(2)						
		B : Previo							_				_	
	1.	(3)	2.	(3)	3.	(1)	4.	(4)	5.	(3)	6.	(3)	7.	(3)
	8.	(1)	9.	(1)	10.	(2)	11.	(3)	12.	(2)				

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Chapter 4: Alcohols, Phenols and Ethers

Section A: Objective Type Questions

1.	(3)	2.	(1)	3.	(4)	4.	(2)	5.	(1)	6.	(2)	7.	(1)
----	-----	----	-----	----	-----	----	-----	----	-----	----	-----	----	-----

Section B: Previous Years Questions

Chapter 5 : Aldehydes, Ketones and Carboxylic Acids

Section A: Objective Type Questions

Section B: Previous Years Questions

Chapter 6: Amines

Section A: Objective Type Questions

1. (4) 2. (4) 3. (1) 4. (4) 5. (4)	6. (1) 7. (1)
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Section B : Previous Years Questions

^{22.} (4)

NEET Answers 167

Chapter 7	7:	Biomo	lecul	es
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Section A: Objective Type Questions

1. (3) 2. (3) 3. (3) 4. (3) 5. (3) 6. (4)	4.	(3)	4.	4.		(3)		5.	(3)	6.	(4)	7.	. (4	4)
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29. (2) 30. (2)

Section B: Previous Years Questions

Chapter 8 : Polymers

Section A: Objective Type Questions

1.	(4)	2.	(3)	3.	(4)	4.	(2)	5.	(2)	6.	(1)	7.	(3)
----	-----	----	-----	----	-----	----	-----	----	-----	----	-----	----	-----

Section B: Previous Years Questions

Chapter 9 & Chemistry in Everyday Life

Section A: Objective Type Questions

1.	(3)	2. (1	3.	(3	4 (2) 5. (2	6. (4) 7. ((1	١
	(0)	× /		0.	100	, ,,	·	,	•	, ,,		, , ,	٠.	,

15. (3)

Section B: Previous Years Questions

8. (1) 9. (4)

Chapter 10 : Hydrogen

Section A: Objective Type Questions

22. (4) 23. (4) 24. (4) 25. (3) 26. (3)

Section B: Previous Years Questions

1. (1 & 2) 2. (2)

168 Answers NEET

Chapter 11: s-Block Elements

Section A: Objective Type Questions

1. (2) 2. (3) 3. (4) 4. (4) 5. (3) 6. (1) 7. (2)

8. (4) 9. (2) 10. (1) 11. (4) 12. (3) 13. (3) 14. (1)

15. (1) 16. (3) 17. (1) 18. (3) 19. (2) 20. (1) 21. (4)

22. (4) 23. (1) 24. (1) 25. (2) 26. (2) 27. (4) 28. (4)

29. (4)

Section B: Previous Years Questions

1. (1) 2. (1) 3. (4) 4. (2) 5. (4) 6. (3) 7. (3)

8. (4) 9. (2) 10. (1) 11. (2) 12. (4) 13. (2) 14. (2)

Chapter 12 : p-Block Elements

Section A: Objective Type Questions

1. (3) 2. (2) 3. (4) 4. (2) 5. (2) 6. (3) 7. (4)

8. (2) 9. (1) 10. (3) 11. (3) 12. (2) 13. (1) 14. (1)

15. (2) 16. (3) 17. (3) 18. (3) 19. (1) 20. (1) 21. (1)

22. (1) 23. (3) 24. (1) 25. (1) 26. (1) 27. (1) 28. (2)

29. (3) 30. (1) 31. (3) 32. (1) 33. (3) 34. (4) 35. (1)

36. (1) 37. (4) 38. (3) 39. (3) 40. (2) 41. (3) 42. (3)

43. (1) 44. (4) 45. (4) 46. (1) 47. (1) 48. (4) 49. (2)

50. (1)

Section B: Previous Years Questions

1. (1) 2. (1) 3. (4) 4. (4) 5. (2) 6. (4) 7. (2)

8. (1) 9. (2) 10. (1) 11. (1) 12. (4) 13. (4) 14. (2)

15. (3) 16. (2) 17. (2) 18. (3) 19. (2) 20. (3) 21. (2)

(2)

22. (2) 23. (2) 24. (2) 25. (1) 26. (2) 27. (1) 28. (3)

29. (4) 30. (4) 31. (1) 32. (4) 33. (3) 34. (4) 35. (4)

36. (2) 37. (4)

Chapter 13: General Principles and Processes of Isolation of Elements

Section A: Objective Type Questions

1. (3) 2. (1) 3. (3) 4. (1) 5. (2) 6. (2) 7. (3)

8. (1) 9. (2) 10. (1) 11. (4) 12. (1) 13. (4) 14. (3)

15. (3) 16. (4) 17. (4) 18. (3) 19. (4) 20. (4) 21. (2)

22. (4) 23. (1) 24. (1) 25. (3)

Section B: Previous Years Questions

1. (1) 2. (3) 3. (2) 4. (1) 5. (2) 6. (4) 7. (4)

8. (4) 9. (1)

NEET Answers 169

Chapter	14:	d-and	f-Block	Elements
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Section A: Objective Type Questions

	141	_		_			141	_	r 1	_		_	
1.	(3)	2.	(1)	3.	(1)	4.	(2)	5.	(2)	6.	(4)	7.	(1)

22. (2)23. (2)(2)24. 25. (2)

Section B: Previous Years Questions

22. (3)23. (3)24. (1) 25. (4)

Chapter 15: Coordination Compounds

Section A: Objective Type Questions

Section B: Previous Years Questions

22. (2)23. (1) 24. (2)25. (1)

Chapter 16: Environmental Chemistry

Section A: Objective Type Questions

(1) (1) 16. (2)17. (1) 18. (1) 19. (4)20.

Section B: Previous Years Questions

23.

(3)

24.

(3)

15.

22.

(1)

1. (1)2. (4)3. (1)

Sample Question Paper-1

(2)

26.

(3)

27.

(3)

28.

(2)

25.

170	An	swers												NEET
2	9.	(2)	30.	(2)	31.	(4)	32.	(1)	33.	(2)	34.	(4)	35.	(4)
3	6.	(1)	37.	(4)	38.	(3)	39.	(3)	40.	(3)	41.	(3)	42.	(2)
4	3.	(1)	44.	(2)	45.	(4)								
	Sample Question Paper-2													
1		(1)	2.	(3)	3.	(2)	4.	(4)	5.	(4)	6.	(3)	7.	(2)
8		(3)	9.	(2)	10.	(1)	11.	(2)	12.	(2)	13.	(1)	14.	(1)
1	5.	(2)	16.	(3)	17.	(2)	18.	(1)	19.	(2)	20.	(4)	21.	(2)
2	2.	(2)	23.	(2)	24.	(3)	25.	(2)	26.	(1)	27.	(3)	28.	(3)
2	9.	(4)	30.	(3)	31.	(4)	32.	(1)	33.	(2)	34.	(2)	35.	(3)
3	6.	(4)	37.	(1)	38.	(4)	39.	(4)	40.	(1)	41.	(1)	42.	(2)
4	3.	(3)	44.	(4)	45.	(3)								

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