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2018

NEET|JEE
ESSENTIALS

Class XI

Maximise your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 7 — Organic Chemistry — Some Basic Principles and Techniques

INTRODUCTION

Organic chemistry is the chemistry of carbon compounds as all organic compounds contain carbon as their essential constituent. Organic compounds may be regarded as hydrocarbons *i.e.*, compounds of carbon and hydrogen only. A large number of organic compounds also contain elements like N, O, S, *X,* etc. which are derived from hydrocarbons by replacing one or more hydrogen atoms in their molecules with these atoms. Thus, the modern definition of the organic chemistry is "the chemistry of the hydrocarbons and their derivatives."

ORGANIC COMPOUNDS

Tetravalency of Carbon
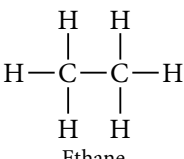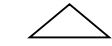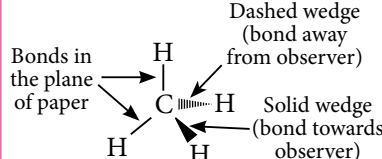
Carbon can complete its octet by sharing its valence electrons with the electrons of other atoms, by virtue of which it forms four covalent bonds, is generally referred to as tetracovalency of carbon. The unique capacity of carbon atom to form bonds with other carbon atoms, is called catenation.

Shapes

Type of hybridisation	Orbitals used	Geometry of the hybrid orbitals formed	Bond angle	Percentage of *s*- and *p*-characters
sp^3	one *s* + three *p*	Tetrahedral	109.5°	25% *s* + 75% *p*
sp^2	one *s* + two *p*	Trigonal planar	120°	33.3% *s* + 66.7% *p*
sp	one *s* + one *p*	Linear	180°	50% *s* + 50% *p*

Structural Representation

Complete formula	Condensed formula	Bond-line formula	Polygon formula	3D Representation
H—C—C—H (Ethane)	$CH_3—CH_3$ Ethane	*n*-Pentane	Cyclopropane	Bonds in the plane of paper; Dashed wedge (bond away from observer); Solid wedge (bond towards observer)
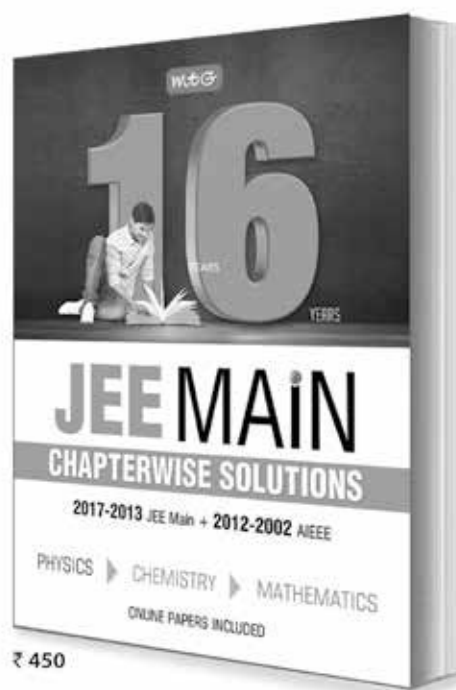
Classification

```
                          Organic Compounds
        ┌──────────────────────┴──────────────────────┐
Acyclic or Open chain or Aliphatic        Closed chain or Cyclic or Ring
      ┌──────────┴──────────┐                 ┌──────────┴──────────┐
 Saturated          Unsaturated       Homocyclic (Carbocyclic)    Heterocyclic
 (Alkanes)      (Alkenes, Alkynes)      ┌──────┴──────┐          ┌────┴────┐
                                    Alicyclic   Aromatic    Alicyclic  Aromatic
                                          ┌────────┴────────┐
                                     Benzenoid        Non-benzenoid
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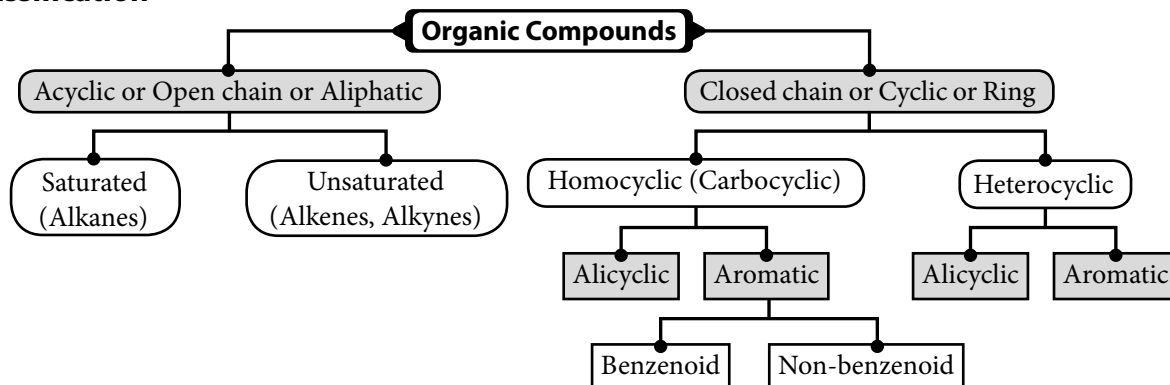
Homologous Series

A series of organic compounds, each containing a characteristic functional group, forms a homologous series in which each successive member differs by a —CH_2 unit or by $12 + 2 \times 1 = 14$ mass units.

Functional Groups

An atom or a group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compounds *e.g.*, hydroxyl group (—OH), aldehyde group (—CHO), carboxylic acid group (—COOH), etc.

IUPAC Nomenclature

IUPAC name = **2° prefix** + **1° prefix** + **word root** + **1° suffix** + **2° suffix**

2° prefix / 1° prefix:
Some functional groups are always treated as substituents whether organic compound is monofunctional or polyfunctional *e.g.*, Fluoro (–F), Chloro (–Cl), Bromo (–Br), Iodo (–I), Nitro (–NO_2), Nitroso (–NO), Diazo (–$\overset{+}{N}\equiv N$), Alkoxy (–O*R*), Alkyl (–*R*), Phenyl (–C_6H_5), etc.

Cyclo is used for carbocyclic compounds. If cyclo is not used, it indicates acyclic or open chain compound.
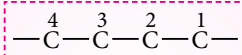
word root:
Principal chain
$$\overset{4}{—C}—\overset{3}{C}—\overset{2}{C}—\overset{1}{C}—$$
If no. of C atoms is 1-meth, 2-eth, 3-prop(*a*), 4-but(*a*), 5-pent(*a*), 6-hex(*a*), 7-hept(*a*), 8-oct(*a*), 9-non(*a*), 10-dec(*a*), 11-undec(*a*), 12-dodec(*a*). Extra '*a*' is added to word root if 1° suffix begins with a consonant.

Single bond only – ane
1 (=)bond –ene	1 (≡)bond –yne
2 (=)bonds –diene	2 (≡)bonds –diyne
3 (=)bonds –triene	3 (≡)bonds –triyne

1° suffix / 2° suffix:
Indicates functional group,
—OH(-ol), —CHO(-al)
$>$CO(-one),
—COOH (-oic acid),
—$CONH_2$ (-amide),
—COCl (-oyl chloride),
—COO*R* (alkyl ······-oate),
—CN (nitrile), —SH (thiol),
—NH_2 (-amine).
If 2° suffix begins with a vowel, the terminal '*e*' is dropped.

Compound	IUPAC name	Compound	IUPAC name
$CH_3CH_2CH_2CH_3$	Butane	CH_3CH_2OH	Ethanol
$CH\equiv CH$	Ethyne	$CH_3CH_2CH_2NH_2$	Propanamine
CH_3COOH	Ethanoic acid	$HC\equiv CCOOH$	Prop-2-yn-1-oic acid
CH_3CH_2Br	Bromoethane	$CH_3CH_2COCH_3$	Butan-2-one
$C_2H_5OC_2H_5$	Ethoxyethane	$CH_3—\overset{\underset{\|}{CH_3}}{CH}—CH_3$	2-Methylpropane

CH$_3$ CH$_3$ (1,2-dimethylcyclopentane structure)	1, 2-Dimethylcyclopentane	(cyclohexene structure)	Cyclohexene
OH CH$_3$ (2-methylphenol structure)	2-Methylphenol	OH O$_2$N NO$_2$ NO$_2$ (trinitrophenol structure)	2, 4, 6-Trinitrophenol

Isomerism

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. It is classified broadly into structural isomerism and stereoisomerism.

Types of structural isomerism :

Isomerism	Description	Example
Chain isomerism	Arises due to different arrangements of C-atoms. The chain isomers have almost similar chemical properties but different physical properties.	$H_3C-CH_2-CH_2-CH_3$, Butane $\quad$ $H_3C-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$ Isobutane
Position isomerism	Arises due to different positions of side chains, substituents, functional groups, double bonds, triple bonds, etc. on the parent chain.	$H_2C=CH-CH_2-CH_3$, But-1-ene $\quad$ $H_3C-CH=CH-CH_3$ But-2-ene
Functional isomerism	Arises due to presence of different functional groups. These isomers differ in both physical and chemical properties.	H_3C-CH_2-OH, Ethyl alcohol $\quad$ $H_3C-O-CH_3$ Dimethyl ether
Metamerism	Arises due to different alkyl groups on either side of the functional group.	$H_3C-CH_2-O-CH_2-CH_3$ Diethyl ether or Ethoxyethane $\quad$ $H_3C-O-CH_2-CH_2-CH_3$ Methyl propyl ether or Methoxypropane
Tautomerism	Tautomers have different functional groups and exist in dynamic equilibrium with each other due to rapid interconversion from one form to another.	$H_3C-\overset{\overset{O}{\Vert}}{C}-CH_3$ Acetone (keto form) $\rightleftharpoons$ $H_3C-\overset{\overset{OH}{\vert}}{C}=CH_2$ Prop-1-en-2-ol (enol form) Keto-enol tautomerism

INFO SHOTS

Antiaromatic molecules display record electrical conductance !
Antiaromatic compounds featuring planar rings of carbon atoms sharing a number of electrons that is a multiple of four, have been predicted to be excellent conductors. Researchers demonstrate high electrical conductance for an antiaromatic nickel complex-an order of magnitude higher than for a similar aromatic complex. Since, the conductance is also tunable by electrochemical gating, antiaromatic complexes are promising materials for future electronic devices.

Types of stereoisomerism :

Geometrical isomerism	• Isomers have the same structural formula but differ in the spatial arrangement of atoms or groups of atoms about double bond.
	• Compounds containing $C=N$ and $N=N$ bonds also show geometrical isomerism. In these cases, '*syn*' (for *cis*) and '*anti*' (for *trans*) are more commonly used.
	• *E* and *Z* system of nomenclature is used for highly substituted alkenes, having four different atoms or groups, attached to $C=C$ bond.
	  – *E* is assigned to an isomer in which high priority atoms or groups are on the opposite sides.
	  – *Z* is assigned to an isomer in which high priority atoms or groups are on the same side.

Diagrams for geometrical isomerism:

$$x \diagdown C = C \diagup x$$ *cis* (Similar groups on the same side of the double bond)

$$y \diagdown C = C \diagup x$$ *trans* (Similar groups on the different sides of the double bond)

$$HO \diagdown N = N \diagup OH$$ *syn*

$$HO \diagdown N = N \diagdown OH$$ *anti*

$$a \diagdown C = C \diagup d$$
$$b \diagup \qquad \diagdown e$$

Optical isomerism	• Compounds having similar physical and chemical properties but differing only in the behaviour towards polarised light are called optical isomers and the phenomenon is called optical isomerism. • Some substances have the ability to rotate the plane polarised light either to the right (clockwise) *i.e.*, dextrorotatory or to the left (anticlockwise) *i.e.*, laevorotatory are optically active substances and the property is called optical activity. • In order to exhibit optical activity, an object must be chiral. • The compound is said to have chirality if the central carbon atom is attached to four different groups and this centre is called chiral (asymmetric) centre or stereogenic centre or stereocentre. • If the central carbon atom has at least two identical groups then this centre is called achiral (symmetric) centre. • If molecule has a plane of symmetry, it is achiral and if molecule has no plane of symmetry, it is chiral. • Enantiomers or *d*-and *l*-isomers are the optical isomers which are non-superimposable mirror images (or dissymmetric). Equimolecular mixture of *d*- and *l*-forms is known as racemic mixture (*dl*-form). This is optically inactive due to external compensation. • Diastereomers are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation. • Meso compounds are those compounds which have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal compensation.

Diagrams for optical isomerism:

$$q - \textcircled{C} - s$$
Chiral centre (asymmetric)

$$r - \textcircled{C} - r$$
Achiral centre (symmetric)

FUNDAMENTAL CONCEPTS IN REACTION MECHANISM

Reaction Intermediates

Intermediates	Definition	Hybridisation of carbon and shape	Stability order
Carbocation : Formed by heterolytic cleavage of the covalent bond in which the leaving group takes away the shared pair of electrons.	Carbon species carrying positive charge on carbon.	sp^2-Hybridised carbon and trigonal planar shape.	$3° > 2° > 1°$
Carbanion : Formed by heterolytic cleavage of the covalent bond in which the shared pair of electrons remains with the carbon atom.	Carbon species carrying negative charge on carbon.	sp^3-Hybridised carbon and pyramidal shape.	$1° > 2° > 3°$

Free radical : Formed by homolytic cleavage of a covalent bond.	Atom or group of atoms having odd or unpaired electrons.	sp^2-Hybridised carbon and trigonal planar shape.	3° > 2° > 1°

ATTACKING REAGENTS

Attacking Reagents

Electrophiles
Positively charged or neutral molecules, having electron deficient atom

Nucleophiles
Negatively charged or neutral molecules, having electron rich atom with unshared electron pair

Ambiphiles
Behave like both electrophiles as well as nucleophiles

Charged	**Neutral**	**Charged**	**Neutral**	**Charged**	**Neutral**
H_3O^+, NO_2^+, NH_4^+, RCO^+, etc.	BF_3, $BeCl_2$, CO_2, $\diagup\!\!\!C\!=\!O$, etc.	H^-, OH^-, R^-, etc.	$\ddot{N}H_3$, $H_2\ddot{O}$:, $R\ddot{O}H$, etc.	$H_3\ddot{O}^+$, RNH_3^+, RCO_2^-, RSO_3^-, etc.	$R\ddot{O}H$ $\diagup\!\!\!C\!=\!O$, $R\!-\!CN$, etc.

ELECTRON DISPLACEMENT EFFECTS IN COVALENT BOND

Inductive effect : Displacement of σ-electrons along a saturated carbon chain when an electron donating (+I effect) or electron withdrawing (–I effect) group is attached at the end of the carbon chain.	• **–I effect :** $R_3\overset{+}{N}$— , —NO_2, —SO_2R, —CN, —COOH, —F, —Cl, —Br, —I, —OR, —COR, —OH, —C_6H_5, —CH = CH, etc. • **+I effect :** $(CH_3)_3C$— , $(CH_3)_2CH$— , CH_3CH_2— , CH_3 —, —COO^-, etc.
Electromeric effect : It involves complete transfer of π-electrons of a multiple bond towards one of the bonded atoms in the presence of an attacking reagent.	• **+E effect :** When electron transfer takes place towards the atom to which the attacking reagent gets attached. • **–E effect :** When electron transfer takes place away from the atom to which the attacking reagent gets attached.
Resonance or mesomeric effect : It is defined as the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and a lone pair of electrons present on adjacent atom.	• **+R effect :** —Cl, —Br, —I, —NH_2, —NHR, —NR_2, —$NHCOR$, —OH, —OR, —SR, —SH, —OCH_3, —$OCOR$, etc. • **–R effect :** —NO_2, —CN, —CHO, —COOH, —COR, etc.
Hyperconjugation : It involves delocalisation of σ-electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom having vacant p-orbital.	• For an alkyl group attached to unsaturated system, it decreases with decrease in number of α-hydrogens : CH_3— > CH_3CH_2— > $(CH_3)_2CH$— > $(CH_3)_3C$—

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Method	Used for separating	Examples
Crystallisation	Mixtures with difference in the solubility of the organic compound and its impurities in a solvent.	• Sugar with impurity of common salt can be crystallised from hot ethanol at 348 K (sugar dissolves but salt does not). • Benzoic acid and naphthalene from hot water (benzoic acid dissolves but naphthalene does not).

Sublimation	Mixtures of sublimable volatile compounds and non-sublimable impurities.	• Purification of camphor, anthracene, naphthalene, benzoic acid, etc.
Simple distillation	Mixtures of liquids having sufficient difference in their boiling points and contain non-volatile impurities.	• Chloroform (b.pt. 334 K) and aniline (b.pt. 457 K). • Ether (b.pt. 308 K) and toluene (b.pt. 384 K).
Fractional distillation	Mixtures of two or more miscible liquids which have b.pt. close to each other.	• Acetone (b.pt. 329 K) and methyl alcohol (b.pt. 338 K). • Benzene (b.pt. 353 K) and toluene (b.pt. 383 K).
Steam distillation	Mixtures of substances which are (i) volatile in steam, (ii) not miscible with water, (iii) possess a vapour pressure of about 10-15 mm of Hg, and (iv) contain non-volatile impurities.	• Aniline and water. • Purification of nitrobenzene, o-nitrophenol, bromobenzene, etc.
Azeotropic distillation	Mixtures with constant boiling points $i.e.$, azeotropic mixtures.	• Ethanol and water in ratio 95.87 : 4.13.
Vacuum distillation	Mixtures of high boiling liquids which decompose at or below their boiling points.	• Glycerol from spent-lye in soap industry (at 453 K under 12 mm Hg). • Concentration of sugarcane juice.
Chromatography	Mixtures with difference in the rates at which the components of the mixture move through a porous medium.	• $ortho$ and $para$ nitroaniline. • Blue and red dyes. • Plant pigments and other natural products.
Differential extraction	Mixtures of organic compounds from their aqueous solutions using a solvent that should (i) be immiscible with water, (ii) dissolve the organic compound.	• Benzoic acid from its aqueous solution using benzene.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Element	Detection	Confirmatory test	Reaction
Carbon	Copper(II) oxide test $2CuO + C \xrightarrow{\Delta} 2Cu + CO_2\uparrow$	CO_2 gas turns lime water milky.	$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$ Lime water $\quad$ Milkiness
Hydrogen	$CuO + 2H \xrightarrow{\Delta} Cu + H_2O$	Water droplets appear on the cooler part of the ignition tube and also turns anhydrous $CuSO_4$ blue.	$CuSO_4 + 5H_2O \rightarrow CuSO_4{\cdot}5H_2O$ White $\qquad\qquad$ Blue
Nitrogen	Lassaigne's extract (L.E.) $Na + C + N \xrightarrow{\Delta} NaCN$ (L.E.)	L.E. + $FeSO_4$ + NaOH, boil and cool + $FeCl_3$ + conc. HCl $\rightarrow$ blue or green colour.	$FeSO_4 + 2NaOH \rightarrow$ $\qquad Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaCN \rightarrow$ $\qquad Na_4[Fe(CN)_6] + 2NaOH$ $3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow$ $\qquad Fe_4[Fe(CN)_6]_3 + 12NaCl$ Prussian blue

Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (L.E.)	• L.E. + sodium nitroprusside → deep violet colour. • L.E. + CH$_3$COOH + (CH$_3$COO)$_2$Pb → black ppt.	$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow$ Sodium nitroprusside $Na_4[Fe(CN)_5NOS]$ Deep violet $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH}$ $PbS\downarrow + 2CH_3COONa$ Black ppt.
Halogens	$Na + X \xrightarrow{\Delta} NaX$ (L.E.)	L.E. + HNO$_3$ + AgNO$_3$, if • white ppt. soluble in aq. NH$_3$ (or NH$_4$OH) confirms Cl. • dull yellow ppt. partially soluble in aq. NH$_3$ (or NH$_4$OH) confirms Br. • yellow ppt. insoluble in aq. NH$_3$ (or NH$_4$OH) confirms I.	$NaX + AgNO_3 \xrightarrow{HNO_3} AgX\downarrow$ ppt. $AgCl + 2NH_{3(aq.)} \rightarrow [Ag(NH_3)_2]Cl$ White ppt. Soluble $AgBr + 2NH_{3(aq.)} \rightarrow [Ag(NH_3)_2]Br$ Dull yellow ppt. Partially soluble $AgI + 2NH_{3(aq.)} \rightarrow [Ag(NH_3)_2]I$ Yellow ppt. Insoluble
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} NaSCN$ Sodium thiocyanate (L.E.)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$NaSCN + FeCl_3 \rightarrow$ $[Fe(SCN)]Cl_2 + NaCl$ Blood red colour
Phosphorus	$P \xrightarrow[\Delta]{Na_2O_2,\ boil} Na_3PO_4$	Solution is boiled with nitric acid and then treated with ammonium molybdate (NH$_4$)$_2$MoO$_4$. Formation of yellow ppt. indicates the presence of phosphorus in organic compound.	$Na_3PO_4 + 3HNO_3 \rightarrow$ $H_3PO_4 + 3NaNO_3$ $H_3PO_4 + 12(NH_4)_2MoO_4$ $+ 21HNO_3$ $\rightarrow (NH_4)_3PO_4 \cdot 12MoO_3$ Ammonium phosphomolybdate (yellow ppt.) $+ 21NH_4NO_3 + 12H_2O$

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Element	Method
Carbon and Hydrogen	**Liebig's combustion method :** $\% \text{ of C} = \dfrac{12}{44} \times \dfrac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100 \qquad \% \text{ of H} = \dfrac{2}{18} \times \dfrac{\text{mass of H}_2\text{O formed}}{\text{mass of compound taken}} \times 100$
Nitrogen	**Dumas method :** $\% \text{ of N} = \dfrac{28}{22400} \times \dfrac{\text{vol. of N}_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$ **Kjeldahl's method :** $\% \text{ of N} = \dfrac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}}$

Halogens	**Carius method :**
	% of $X = \dfrac{\text{At. mass of } X}{108 + \text{At. mass of } X} \times \dfrac{\text{mass of Ag}X \text{ formed}}{\text{mass of compound taken}} \times 100$
Sulphur	**Carius method :**
	% of $S = \dfrac{32}{233} \times \dfrac{\text{mass of BaSO}_4 \text{ formed}}{\text{mass of compound taken}} \times 100$
Phosphorus	**Ignition method :**
	% of $P = \dfrac{62}{222} \times \dfrac{\text{mass of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{mass of compound taken}} \times 100$
Oxygen	**Iodine method :**
	% of $O = \dfrac{16}{44} \times \dfrac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$ or % of $O = \dfrac{5 \times 16}{2 \times 127} \times \dfrac{\text{mass of I}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$

SPEED PRACTICE

1. In Lassaigne's test for nitrogen, the blue colour is due to the formation of
   (a) ferric ferrocyanide
   (b) potassium ferrocyanide
   (c) sodium ferrocyanide
   (d) sodium cyanide.

2. The IUPAC name of the compound

    is

   (a) 3,4-dimethyl-1-penten-3-ol
   (b) isopropyl–3–methylvinylcarbinol
   (c) 2,3-dimethyl-4-penten-3-ol
   (d) none of the above.

3. The number of structural isomers for C_6H_{14} is

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

4. The IUPAC name of the compound

    is

   (a) 5-formylhex-2-en-3-one
   (b) 5-methyl-4-oxohex-2-en-5-al
   (c) 3-keto-2-methylhex-5-enal
   (d) 3-keto-2-methylhex-4-enal.   **(NEET 2017)**

5. The Lassaigne's extract is boiled with conc. HNO_3 while testing for halogens. Because it
   (a) decomposes Na_2S and NaCN, if formed
   (b) helps in the precipitation of AgCl
   (c) increases the solubility product of AgCl
   (d) increases the concentration of NO_3^- ions.

6. Hyperconjugation is most useful for stabilising which of the following carbocations?
   (a) Neopentyl   (b) *tert*-Butyl
   (c) Isopropyl   (d) Ethyl

7. Which of the following statements is not true about partition chromatography?
   (a) Mobile phase can be a gas or liquid.
   (b) Separation depends upon equilibration of solute between a mobile and a stationary phase.
   (c) Stationary phase is a finely divided solid adsorbent.
   (d) None of the above.

8. The less reactivity of chlorine atom in, $CH_2 = CH—Cl$ is due to
   (a) inductive effect   (b) resonance stabilisation
   (c) electromeric effect   (d) electronegativity.

9. Among the following, the least stable resonance structure is

10. The polarisation of electrons in acrolein may be written as
    (a) $\overset{\delta-}{CH_2}=CH-\overset{\delta+}{CH}=O$
    (b) $\overset{\delta-}{CH_2}=CH-CH=\overset{\delta+}{O}$
    (c) $\overset{\delta-}{CH_2}=\overset{\delta+}{CH}-CH=O$
    (d) $\overset{\delta+}{CH_2}=CH-CH=\overset{\delta-}{O}$

11. Which one of the following carbanions is least stable?
    (a) $CH_3CH_2^-$ (b) $(C_6H_5)_3C^-$
    (c) CH_3^- (d) $(CH_3)_3C^-$

12. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is
    (a) simple distillation
    (b) fractional distillation
    (c) steam distillation
    (d) distillation under reduced pressure.
    (JEE Main 2016)

13. The correct stability order for the following species is

    (I)   (II)   (III)   (IV)

    (a) (II) > (IV) > (I) > (III)
    (b) (I) > (II) > (III) > (IV)
    (c) (II) > (I) > (IV) > (III)
    (d) (I) > (III) > (II) > (IV)

14. Homolytic fission of a covalent bond leads to the formation of
    (a) nucleophile   (b) free radical
    (c) carbocation   (d) carbanion.

15. In hexa-1, 3-diene-5-yne, the number of C—C σ, C—C π and C—H σ bonds respectively are
    (a) 5, 4 and 6   (b) 6, 3 and 5
    (c) 5, 3 and 6   (d) 6, 4 and 5

16. Which of the following organic compounds has same hybridisation as its combustion product (CO_2)?
    (a) Ethane   (b) Ethyne
    (c) Ethene   (d) Ethanol

17. Which of the following statements is not correct for a nucleophile?
    (a) Ammonia is a nucleophile.
    (b) Nucleophiles attack low electron density sites.
    (c) Nucleophiles are not electron seeking.
    (d) Nucleophile is a Lewis acid.   **(AIPMT 2015)**

18. Liquids which decompose below their normal boiling points can be distilled at lower temperature by
    (a) increasing the pressure
    (b) decreasing the pressure
    (c) heating in water bath
    (d) heating in sand bath.

19. A substance containing an equal number of primary, secondary and tertiary carbon atoms is
    (a) mesityl oxide   (b) mesitylene
    (c) maleic acid   (d) malonic acid.

20. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is
    (a) $-SO_3H$, $-COOH$, $-CONH_2$, $-CHO$
    (b) $-CHO$, $-COOH$, $-SO_3H$, $-CONH_2$
    (c) $-CONH_2$ $-CHO$, $-SO_3H$, $-COOH$
    (d) $-COOH$, $-SO_3H$, $-CONH_2$, $-CHO$

21. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (At. mass Ag =108; Br =80)
    (a) 48   (b) 60
    (c) 24   (d) 36   **(JEE Main 2015)**

22. A gaseous hydrocarbon upon combustion gives 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is
    (a) C_3H_4 (b) C_6H_5
    (c) C_7H_8 (d) C_2H_4

23. In allene (C_3H_4), the type(s) of hybridisation of the carbon atom is (are)
    (a) sp and sp^3 (b) sp and sp^2
    (c) only sp^2 (d) sp^2 and sp^3

24. The best method for the separation of naphthalene and benzoic acid from their mixture is
    (a) sublimation   (b) chromatography
    (c) crystallisation   (d) distillation.

25. On complete combustion, 0.246 g of an organic compound gave 0.198 g of CO_2 and 0.1014 g of H_2O. The ratio of carbon and hydrogen atoms in the compound is
    (a) 1 : 3   (b) 1 : 2   (c) 2 : 5   (d) 2 : 7

26. Which among the given molecules can exhibit tautomerism?

    I   II   III

    (a) III only   (b) Both I and III
    (c) Both I and II   (d) Both II and III
    (NEET Phase-II 2016)

27. The principle involved in paper chromatography is
    (a) adsorption   (b) partition
    (c) solubility   (d) volatility.

28. The increasing order of the boiling points for the following compounds is

$$\underset{\text{(I)}}{C_2H_5OH} \quad \underset{\text{(II)}}{C_2H_5Cl} \quad \underset{\text{(III)}}{C_2H_5CH_3} \quad \underset{\text{(IV)}}{C_2H_5OCH_3}$$
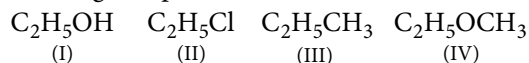
(a) (IV) < (III) < (I) < (II)
(b) (III) < (II) < (I) < (IV)
(c) (II) < (III) < (IV) < (I)
(d) (III) < (IV) < (II) < (I)

(JEE Main Online 2017)

29. Identify the compound that exhibits tautomerism.
(a) Lactic acid (b) 2-Pentanone
(c) Benzaldehyde (d) 2-Butene

30. Which of the following is a non-benzenoid aromatic compound?
(a) Benzoic acid (b) Naphthalene
(c) Tropolone (d) Anthracene

SOLUTIONS

1. (a) : In Lassaigne's test, substance is heated strongly with sodium metal then the extract is boiled with freshly prepared alkaline $FeSO_4$ solution and after cooling, $FeCl_3$ solution and excess of HCl is added in it. If prussian blue or green ppt. is obtained then nitrogen is confirmed.
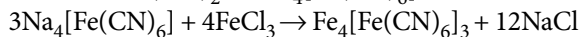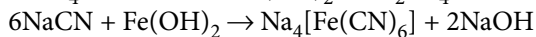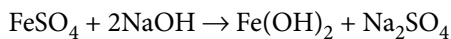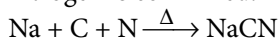
$Na + C + N \xrightarrow{\Delta} NaCN$
$FeSO_4 + 2NaOH \rightarrow Fe(OH)_2 + Na_2SO_4$
$6NaCN + Fe(OH)_2 \rightarrow Na_4[Fe(CN)_6] + 2NaOH$
$\underset{\text{Sodium ferrocyanide}}{3Na_4[Fe(CN)_6]} + 4FeCl_3 \rightarrow \underset{\substack{\text{Ferric ferrocyanide}\\\text{(prussian blue or green)}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$

2. (a)

3. (c) : (1) $CH_3 — CH_2 — CH_2 — CH_2 — CH_2 — CH_3$

(2) $CH_3 — CH_2 — CH_2 — \underset{\underset{CH_3}{|}}{CH} — CH_3$

(3) $CH_3 — CH_2 — \underset{\underset{CH_3}{|}}{CH} — CH_2 — CH_3$

(4) $CH_3 — \underset{\underset{CH_3}{\overset{\overset{CH_3}{|}}{|}}}{C} — CH_2 — CH_3$

(5) $CH_3 — \underset{\underset{CH_3}{|}}{CH} — \underset{\underset{CH_3}{|}}{CH} — CH_3$

4. (d):

$H—\underset{1}{\overset{\overset{O}{\|}}{C}}—\underset{2}{C}—\underset{3}{C}\underset{\overset{5}{\overset{\|}{6}}}{\overset{\overset{O}{\|}}{}}{}^4$
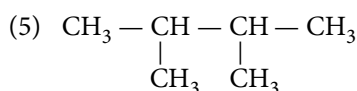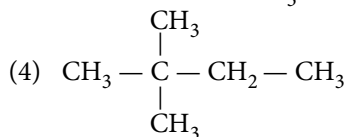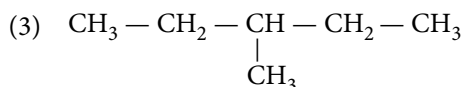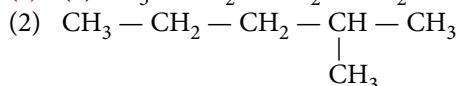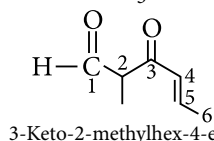
3-Keto-2-methylhex-4-enal

5. (a) : Conc. HNO_3 decomposes Na_2S and NaCN, if formed.
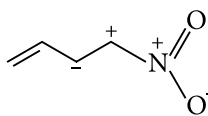
6. (b): $(CH_3)_3C^+$ has the maximum number of α-hydrogens (*i.e.* ; 9) and hence, hyperconjugation is most useful in explaining its stability.

7. (d)

8. (b): Due to resonance stabilisation, C—Cl bond acquires partial double bond character.

$H_2C{=}CH{-}\ddot{\underset{..}{Cl}}: \longleftrightarrow H_2\bar{C}{-}CH{=}\overset{+}{\underset{..}{Cl}}:$ (+*R*-effect)
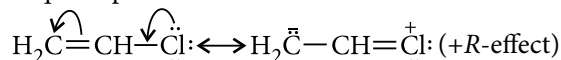
Due to shortening of bond, Cl is firmly attached to carbon and is not easily substituted.

9. (a) : In this, positive charges are present on the adjacent atoms, would be the least stable.

10. (d): Because of –*R* effect of — CHO group, oxygen has $\delta-$ charge and the terminal carbon atom has $\delta+$ charge as :

$$\overset{\delta+}{C}H_2{=}CH — CH{=}\overset{\delta-}{O}$$
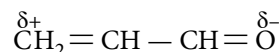
11. (d): More the alkyl groups, lesser is the stability of carbanions.

12. (d): Glycerol is separated from spent-lye by distillation under reduced pressure because under normal distillation glycerol having boiling point of 290 °C may decompose.

13. (d): Carbocation (I) is stabilized by +*R*-effect of O-atom as well as +*I*-effect of two —CH_3 groups, carbocation (II) is stabilized by +*I*-effect of —CH_3 and —$CH_2CH(CH_3)_2$ groups, carbocation (III) is stabilized by +*R*-effect of O-atom and +*I*-effect of one —CH_3 group while carbocation (IV) is stabilized by +*I*-effect of —$CH_2CH_2CH(CH_3)_2$ group. Thus, decreasing order of stability of these carbocations is : I > III > II > IV.

14. (b)

15. (a) :

$$\overset{\overset{H}{|}}{C}{=}C{-}C{=}C{-}C{\equiv}C{-}H$$

with H substituents
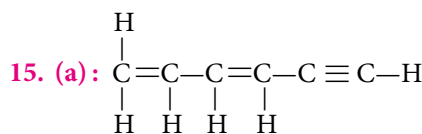
C—C σ bonds = 5
C—C π bonds = 4
C—H σ bonds = 6

16. (b): The hybridisation of 'C' in CO_2 is sp. Therefore, the organic compound having same hybridisation as CO_2, is ethyne.

17. (d): Nucleophiles are electron rich species hence, they are Lewis bases.

18. (b): Boiling point gets lowered at low pressure.

19. (b):
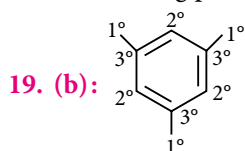
1° – carbon = 3
2° – carbon = 3
3° – carbon = 3

20. (d): $-COOH > -SO_3H > -CONH_2 > -CHO$

21. (c): % of Br $= \dfrac{80}{188} \times \dfrac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$

$= \dfrac{80}{188} \times \dfrac{141}{250} \times 100 = 24\%$

22. (c): $C_xH_y + \left(x + \dfrac{y}{4}\right)O_2 \longrightarrow xCO_2 + \dfrac{y}{2}H_2O$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 3.08 g $\quad$ 0.72 g
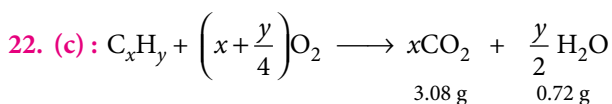
$\dfrac{3.08}{44} = 0.07 \quad \dfrac{0.72}{18} = 0.04$

$\therefore \quad \dfrac{x}{\dfrac{y}{2}} = \dfrac{0.07}{0.04} \quad$ or $\quad \dfrac{x}{y} = \dfrac{7}{8}$

Hence, the empirical formula is C_7H_8.

23. (b): $\overset{sp^2}{H_2C} = \overset{sp}{C} = \overset{sp^2}{CH_2}$
$\quad\quad\quad\quad$ Allene
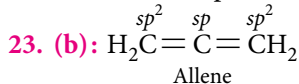
24. (c): Both benzoic acid and naphthalene sublime on heating and hence, cannot be separated by sublimation. Benzoic acid is soluble in warm water but naphthalene is not. Therefore, they can be separated by crystallisation.

25. (c): $C_xH_y + \left(x + \dfrac{y}{4}\right)O_2 \rightarrow xCO_2 + \dfrac{y}{2}H_2O$

$\quad\quad\quad\quad\quad\quad$ 0.198 g $\quad\quad$ 0.1014 g

$\dfrac{0.198}{44} = 0.0045 \quad \dfrac{0.1014}{18} = 0.0056$
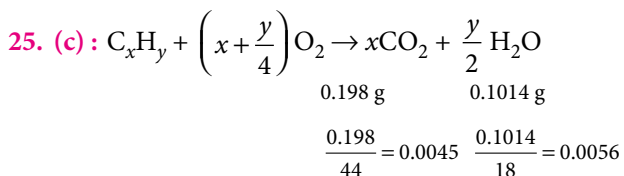
$\therefore \quad \dfrac{x}{\dfrac{y}{2}} = \dfrac{0.0045}{0.0056} \quad$ or $\quad \dfrac{x}{y} = \dfrac{2}{5}$

26. (a): α-Hydrogen at bridge carbon never participate in tautomerism. Thus, only (III) exhibits tautomerism.

keto-form
(III)

enol-form
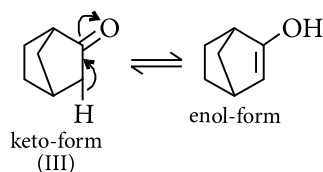
27. (b)

28. (d): B.pt. $\propto$ dipole moment
$\quad\quad\quad\quad \propto$ H-bonding

$\therefore$ The increasing order of boiling points will be :
$C_2H_5CH_3 < C_2H_5OCH_3 < C_2H_5Cl < C_2H_5OH$
$\quad$ (III) $\quad\quad\quad$ (IV) $\quad\quad\quad$ (II) $\quad\quad\quad$ (I)
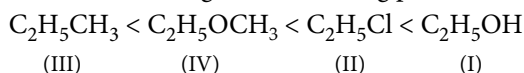
29. (b): 2-Pentanone $\quad$ *i.e.,* $\quad CH_3COCH_2CH_2CH_3$ contains α-hydrogens on a saturated carbon hence, shows tautomerism.

30. (c): Only tropolone is non-benzenoid aromatic compound rest all are benzenoid aromatic compounds.
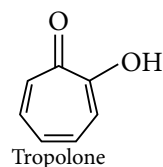
Tropolone

EXAMiNER'S MiND CLASS XI
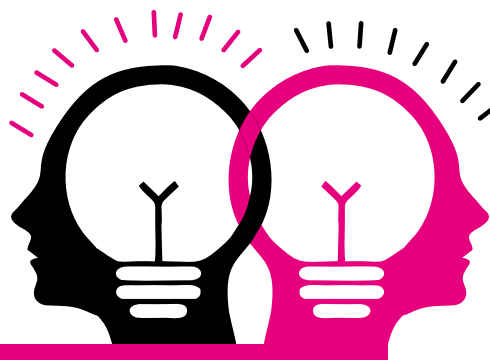
The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

REDOX REACTIONS

SECTION - I
Only One Option Correct Type

1. In the following reaction :

$$M^{x+} + MnO_4^- \longrightarrow MO_3^- + Mn^{2+} + \frac{1}{2} O_2,$$

if one mole of MnO_4^- oxidises 2.5 moles of M^{x+}, then the value of x is
(a) 5 (b) 3 (c) 4 (d) 2

2. A compound contains atoms X, Y and Z. The oxidation number of X is +2, Y is +5 and Z is –2. The possible formula of the compound is
(a) XYZ_2 (b) $Y_2(XZ_3)_2$
(c) $X_3(YZ_4)_2$ (d) $X_3(Y_4Z)_2$

3. Which of the following is not a redox reaction?
(a) $CaCO_3 \longrightarrow CaO + CO_2$

(b) $Na + H_2O \longrightarrow NaOH + \frac{1}{2} H_2$

(c) $MnCl_3 \longrightarrow MnCl_2 + \frac{1}{2} Cl_2$

(d) $O_2 + 2H_2 \longrightarrow 2H_2O$

4. Which of the following statements is not correct?
(a) The oxidation number of S in $(NH_4)_2S_2O_8$ is +6.
(b) The oxidation number of Os in OsO_4 is + 8.
(c) The oxidation number of S in H_2SO_5 is + 8.
(d) The oxidation number of O in KO_2 is –1/2.

5. What volume of 0.01 M $K_2Cr_2O_7$ would be required to oxidise Fe (II) in 50 mL of 0.03 M solution of ferrous ammonium sulphate in acidic medium?
(a) 150 mL   (b) 75 mL
(c) 50 mL   (d) 25 mL

6. When a piece of copper wire is immersed in a solution of aqueous silver nitrate, the solution becomes blue. This is a consequence of
(a) oxidation of silver
(b) oxidation of copper
(c) formation of copper complex
(d) reduction of copper.

7. The complex $[Fe(H_2O)_5NO]^{2+}$ is formed in the ring test for nitrate ion (NO_3^-), when freshly prepared $FeSO_4$ solution is added to aqueous solution of NO_3^- followed by the addition of conc. H_2SO_4. This complex is formed by charge transfer in which
(a) Fe^{2+} changes to Fe^{3+} and NO^+ changes to NO
(b) Fe^{2+} changes to Fe^{3+} and NO changes to NO^+
(c) Fe^{2+} changes to Fe^+ and NO changes to NO^+
(d) none of these.

8. The correct balanced ionic equation for the reaction that occurs when a solution of acetic acid is mixed with a solution of sodium carbonate is :

(a) $CH_3COOH_{(aq)} + CO_{3(aq)}^{2-} \rightleftharpoons CH_3COO_{(aq)}^- + HCO_{3(aq)}^-$

(b) $H_3O_{(aq)}^+ + CO_{3(aq)}^{2-} \rightleftharpoons HCO_{3(aq)}^- + H_2O_{(l)}$

(c) $CH_3COOH_{(aq)} + Na_2CO_{3(aq)} \rightleftharpoons CH_3COO_{(aq)}^- + NaHCO_{3(aq)} + Na_{(aq)}^+$

(d) $CH_3COOH_{(aq)} + OH_{(aq)}^- \rightleftharpoons CH_3COO_{(aq)}^- + H_2O_{(l)}$
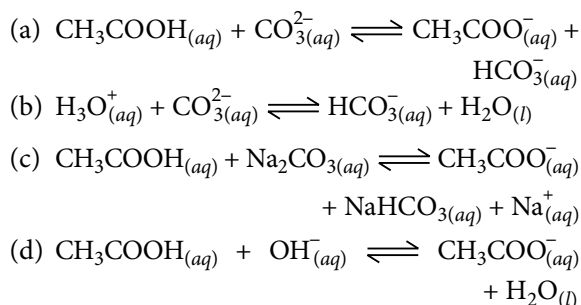
9. The standard reduction potential values of three metallic cations of X, Y and Z are 0.52 V, – 3.03 V and –1.18 V respectively. The correct order of reducing power of the corresponding metals is

(a) $Y > Z > X$ (b) $X > Y > Z$

(c) $Z > Y > X$ (d) $Z > X > Y$

10. In an oxidation process for a cell,

$$M_1 \rightarrow M_1^{n+} + ne^-,$$
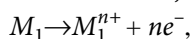
the other metal (M_2) being univalent showing reduction, takes up____electrons to complete redox reaction.

(a) $(n - 1)$ (b) 1   (c) n (d) 2

SECTION - II

More than One Options Correct Type

11. The correct statements for the given reaction

$x Cu_3P + y Cr_2O_7^{2-} \longrightarrow Cu^{2+} + H_3PO_4 + Cr^{3+}$ are

(a) Cu in Cu_3P is oxidised to Cu^{2+} and P in Cu_3P is also oxidised to PO_4^{3-}

(b) Cu in Cu_3P is oxidised to Cu^{2+} whereas, P in Cu_3P is reduced to H_3PO_4

(c) eleven electrons are involved in the conversion of Cu_3P to Cu^{2+} and H_3PO_4

(d) the value of x is 6.

12. During development of a photographic paper, following reaction takes place :

$2AgBr + 2OH^- +$ $\longrightarrow$ $+ 2Ag + 2H_2O + 2Br^-$
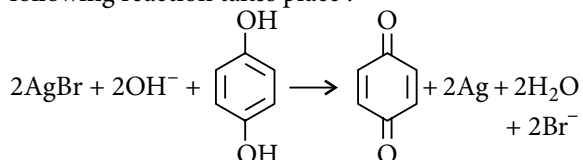
Select the incorrect statements.

(a) Hydroquinone is the oxidant.

(b) Ag^+ is the oxidant.

(c) Br^- is the oxidant.

(d) Ag^+ is the reductant.

13. Which of the following elements show fractional oxidation state in any of their compounds?

(a) P   (b) S   (c) I   (d) N

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

In redox systems, the titration method can be adopted to determine the strength of a reductant/ oxidant using a redox sensitive indicator. The usage of indicators in redox titrations is illustrated below :

In one situation, the reagent itself is intensely coloured *e.g.*, permanganate ion, MnO_4^- acts as the self indicator. If there is no dramatic auto-colour change (as with MnO_4^- titration), there are indicators which are oxidised immediately after the last drop of the reactant is consumed, producing a dramatic colour change. The best example is afforded by $Cr_2O_7^{2-}$, which is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

14. What suitable substance and its amount will be needed to prepare 100 mL of 0.1 N standard solution for the estimation of $KMnO_4$ solution?

(a) Oxalic acid, 0.63 g

(b) Oxalic acid, 0.90 g

(c) $FeSO_4.7H_2O$, 2.8 g

(d) Mohr's salt, 3.92 g

15. What is the final product of Mn in the redox reaction of oxalic acid with $KMnO_4$ in acidic medium?

(a) MnO_4^{2-} (b) MnO_2

(c) Mn^{2+} (d) Mn_2O_3

Paragraph for Questions 16 and 17

In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be represented as :

$$X + YZ \rightarrow XZ + Y$$
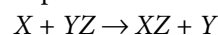
In metal displacement, a metal in a compound can be displaced by another metal in the uncombined state.

The non-metal displacement redox reactions include hydrogen displacement and rarely oxygen displacement.

16. The reaction, $CuSO_{4(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$ belongs to which of the following types of redox reactions?

(a) Combination reaction

(b) Decomposition reaction

(c) Metal displacement reaction

(d) Non-metal displacement reaction

17. Identify the redox reaction taking place in the beaker.

Initial stage — Metal rod, Colourless solution

Final stage — Shiny silvery deposit, Blue solution
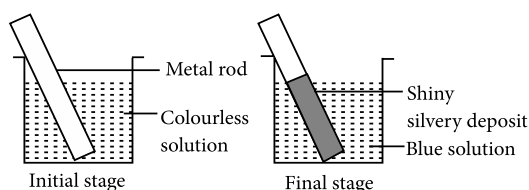
(a) $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(b) $Cu_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

(c) $Cu_{(s)} + Zn^{2+}_{(aq)} \rightarrow Zn_{(s)} + Cu^{2+}_{(aq)}$

(d) $2Ag_{(s)} + Cu^{2+}_{(aq)} \rightarrow 2Ag^{+}_{(aq)} + Cu_{(s)}$

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

List I		List II	
(P)	$2Cu^{+} \rightarrow Cu^{+} + Cu$	(i)	Auto-oxidation
(Q)	$NaOH + HCl \rightarrow NaCl + H_2O$	(ii)	Displacement reaction
(R)	2-Ethylanthraquinol $\xrightarrow[H_2/Pd]{O_2} H_2O_2 +$ oxidised product	(iii)	Neutralisation
(S)	$Zn + 2HCl \rightarrow ZnCl_2 + H_2$	(iv)	Disproportion-ation

	P	Q	R	S
(a)	(iii)	(iv)	(i)	(ii)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iv)	(iii)	(i)	(ii)
(d)	(ii)	(i)	(iv)	(iii)

19. Match the List I with List II and select the correct answer using the codes given below the lists :

List I (Reagent)		List II (Equivalent weight)	
(P)	$KMnO_4$ in acidic medium	(i)	$M/3$
(Q)	$KMnO_4$ in basic medium	(ii)	M
(R)	$FeC_2O_4 \rightarrow Fe^{3+}$	(iii)	$M/10$
(S)	$I_2 \rightarrow HIO_3$	(iv)	$M/5$
(T)	$N_2 \rightarrow 2NH_3$	(v)	$M/6$

	P	Q	R	S	T
(a)	(i)	(ii)	(iv)	(iii)	(v)
(b)	(iv)	(i)	(ii)	(iii)	(v)
(c)	(ii)	(iv)	(i)	(iii)	(v)
(d)	(v)	(iii)	(ii)	(i)	(iv)

SECTION - V

Assertion Reason Type

20. Assertion : In the following half reaction :
$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$
Equivalent weight of $Cr_2O_7^{2-} = \dfrac{\text{Molar mass}}{3}$

Reason : Change in oxidation number of chromium is 6 per atom.

21. Assertion : Lithium ion is a poor oxidising agent.

Reason : Lithium ion has the lowest electrode potential.

22. Assertion : The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Reason : The oxygen of peroxide is in –1 oxidation state and it is converted to zero oxidation state in O_2 and –2 oxidation state in H_2O.

SECTION - VI

Integer Value Correct Type

23. Among the following, the number of underlined elements having +6 oxidation state is
$\underline{P}O_4^{3-}$, $H_2\underline{S}_2O_8$, $H_2\underline{S}O_5$, $O\underline{F}_2$, $\underline{Cr}_2O_7^{2-}$, $\underline{Cr}O_5$
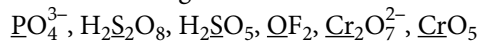
24. If the following is balanced reaction,
$4O_2^{x-} + 2H_2O \longrightarrow 4OH^{-} + 3O_2$, then x is
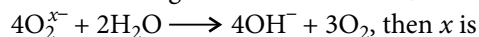
25. 2.496×10^{-x} g of pyrolusite containing 89.21% of MnO_2 will oxidise the same amount of oxalic acid as 37.12 mL of permanganate solution, one mL of which liberates 0.0175 g of I_2 from KI. The value of x is

ENVIRONMENTAL CHEMISTRY

1. SO_2 and NO_2 cause pollution by increasing
   (a) alkalinity   (b) neutrality
   (c) acidity   (d) buffer action.

2. Which of the following gases does not contribute to greenhouse effect?
   (a) O_3 (b) H_2O vapour
   (c) O_2 (d) N_2O

3. In Antarctica, ozone depletion is due to the formation of which of the following compounds?
   (a) Acrolein   (b) Peroxyacetyl nitrate
   (c) SO_2 and SO_3 (d) Chlorine nitrate

4. Which of the following statements is not correct?
   (a) CO is the main air pollutant.
   (b) All pollutants are not waste.
   (c) Water is polluted if BOD is less.
   (d) Lichens are pollution indicators.

5. Which of the following statements is incorrect?
   (a) The average residence time of NO is one month.
   (b) Limestone acts as a sink for SO_x.
   (c) SO_x can be removed from flue gases by passing through a solution of citrate ions.
   (d) Ammonia acts as a sink for NO_x.

6. When rain is accompanied by thunderstorm, the collected rainwater will have a pH value
   (a) slightly lower than that of rainwater without thunderstorm
   (b) slightly higher than that when the thunderstorm is not there
   (c) uninfluenced by the occurrence of thunderstorm
   (d) depends upon the amount of dust in air.

7. Which of the following substances are regulated by the Kyoto Protocol?
   I. Argon   II. Carbon dioxide
   III. Nitrogen   IV. Nitrous oxide
   V. Sulphur hexafluoride
   (a) I, II and III only (b) I and III only
   (c) II and V only   (d) II, IV and V only

8. Which of the following statements about polar stratospheric clouds (PSCs) is not correct?
   (a) PSCs do not react with chlorine nitrate and HCl.
   (b) Type I clouds are formed at about −77 °C and contain solid $HNO_3.3H_2O$.

(c) Type II clouds are formed at about −85 °C and contain some ice.
   (d) Due to presence of PSCs a tight whirlpool of wind called polar vortex is formed which surrounds Antarctica.

9. Living in the atmosphere of CO is dangerous, because it
   (a) combines with O_2 present inside to form CO_2
   (b) reduces organic matter of tissues
   (c) combines with haemoglobin and makes it incapable to absorb oxygen
   (d) dries up the blood.

10. Green chemistry means such reactions which
    (a) are related to the depletion of ozone layer
    (b) study the reactions in plants
    (c) produce colour during reactions
    (d) reduce the use and production of hazardous chemicals.

11. Which of the following conditions show the polluted environment?
    (a) pH of rain water is 5.6.
    (b) Amount of carbon dioxide in the atmosphere is 0.03%.
    (c) Biochemical oxygen demand is 10 ppm.
    (d) Eutrophication

12. Components of photochemical smog are
    (a) oxygen   (b) acrolein
    (c) peroxyacetyl nitrate (d) nitric oxide.

13. Man-made sources of air pollution are
    (a) population increase (b) deforestation
    (c) automobiles   (d) pollen grains.

Paragraph for Questions 14 and 15

The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world. There are two types of smog :

Classical smog occurs in cool humid climate. Photochemical smog occurs in warm, dry and sunny climate. The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories.

14. The brown hazy fumes of photochemical smog are due to
(a) nitrogen dioxide   (b) PAN formation
(c) aldehydes   (d) SO_2.

15. PAN present in the photochemical smog stands for
(a) polyacrylonitrile   (b) peroxyacetyl nitrate
(c) both (a) and (b)   (d) none of these.

Paragraph for Questions 16 and 17

In 1980s atmospheric scientists working in Antarctica reported about depletion of ozone layer commonly known as ozone hole over the south pole. In summer season, nitrogen dioxide and methane react with chlorine monoxide and chlorine atoms forming chlorine sink, preventing much ozone depletion, whereas in winter, special type of clouds are formed over Antarctica.

16. Which one of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere?
(a) Polyhalogens   (b) Ferrocene
(c) Fullerenes   (d) Freons

17. Ozone layer of stratosphere requires protection from indiscriminate use of
(a) pesticides   (b) atomic explosions
(c) aerosols and high flying jets
(d) balloons.

SECTION - IV
Matching List Type

18. Match the activity given in List I with their effect given in List II and select the correct answer using the codes given below the lists :

	List I		List II
(P)	Using carbamates as pesticides	(i)	Water pollution
(Q)	Using synthetic detergents for washing clothes	(ii)	Photochemical smog, damage to plant life, induce breathing problems
(R)	Releasing gases produced by automobiles and factories in the atmosphere	(iii)	Damaging ozone layer
(S)	Using chlorofluoro-carbon compounds for cleaning computer parts	(iv)	May cause nerve diseases in humans

	P	Q	R	S
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(i)	(ii)	(iii)
(c)	(iv)	(ii)	(i)	(iii)
(d)	(iii)	(iv)	(i)	(ii)

19. Match the List I with List II and select the correct answer using the codes given below the lists :
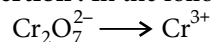
	List I		List II
(P)	Biodegradable pollutant	(i)	DDT
(Q)	Non-biodegradable pollutant	(ii)	SO_2
(R)	Primary pollutant	(iii)	PAN
(S)	Secondary pollutant	(iv)	Sewage

	P	Q	R	S
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(ii)	(i)	(iii)
(c)	(iv)	(i)	(ii)	(iii)
(d)	(iv)	(i)	(iii)	(ii)

SECTION - V
Assertion Reason Type

20. **Assertion :** Lower the concentration of D.O., more polluted is the water.
Reason : Oxygen is consumed by microbes for the decomposition of organic matter present in water.

21. **Assertion :** Photochemical smog is produced by nitric oxides.
Reason : Vehicular pollution is a major source of nitric oxides.

22. **Assertion :** Greenhouse effect was observed in houses used to grow plants and these are made of transparent glass.
Reason : Greenhouse name has been given because glass houses are made of green glass.

SECTION - VI
Integer Value Correct Type

23. Fluoride ion concentration in drinking water above x ppm would cause brown mottling of teeth. The value of x is

24. Of the following compounds : CF_2Cl_2, Ozone, Sulphuric acid, Nitric oxide, Nitric acid, Hydrocarbons, Formaldehyde, Acrolein, PAN, Carbonic acid, number of compounds responsible for photochemical smog is

25. In measurement of BOD_x, x is generally taken as

SOLUTIONS

REDOX REACTIONS

1. **(b):** $\overset{+7}{Mn}O_4^- + 5e^- \longrightarrow Mn^{2+}$

   Since 1 mole of MnO_4^- accepts 5 moles of electrons, therefore, 5 moles of electrons are lost by 2.5 moles of M^{x+}.

   $\therefore$ 1 mole of M^{x+} will lose electrons = 5/2.5 = 2 moles

   Since, M^{x+} changes to MO_3^- (where O.N. of $M = +5$) by accepting 2 electrons.

   $\therefore$ Oxidation state of M i.e. $x = +5 - 2 = +3$

2. **(c):** The possible formula of the compound will be $X_3(YZ_4)_2$, since sum of oxidation number of all the atoms in a neutral compound must be equal to zero.

3. **(a):** In redox reaction, oxidation and reduction takes place simultaneously.

   $$\overset{+2\,+4\,-2}{CaCO_3} \longrightarrow \overset{+2\,-2}{CaO} + \overset{+4\,-2}{CO_2}$$

   Since, in this reaction, no oxidation or reduction takes place thus, it is not a redox reaction.

4. **(c):** Oxidation state of S in $(NH_4)_2\overset{+1}{S_2}O_8 = +6$

   (Since $S_2O_8^{2-}$ has one peroxide bond)

   Oxidation state of Os in $OsO_4 = +8$

   Oxidation state of S in $H_2SO_5 = +6$

   (Since it has one peroxide bond)

   Oxidation state of O in $KO_2 = -1/2$

5. **(d):** Fe (II) $\to$ Fe (III) $+ e^-$; 'n' factor = 1

   $Cr_2O_7^{2-} + 14H^+ + 6e^- \to 2Cr^{3+} + 7H_2O$; '$n$' factor = 6

   Hence, $6 \times 0.01 \times V = 1 \times 0.03 \times 50 \Rightarrow V = 25$ mL

6. **(b):** Solution turns blue due to oxidation of Cu to Cu^{2+} ions in the solution.

   $Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$

7. **(c):** $NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$

   $Fe^{2+} + NO + 5H_2O \longrightarrow [Fe(H_2O)_5NO]^{2+}$

   Brown ring

8. **(d):** Na_2CO_3 solution is alkaline due to hydrolysis

   $CO_3^{2-} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$

   OH^- neutralises CH_3COOH.

9. **(a):** More negative or lower the reduction potential, more is the reducing property. Thus, the correct order of reducing power is $Y > Z > X$.

10. **(c):** The reaction shows $nM_2^+ + ne^- \to nM_2$

    i.e., electrons released at anode

    = electrons used at cathode.

11. **(a, c, d):** $4H_2O + \overset{+1}{Cu_3}\overset{-3}{P} \longrightarrow 3Cu^{2+} + H_3PO_4 + 11e^- + 5H^+] \times 6$

    $$\frac{6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O] \times 11}{6Cu_3P + 124H^+ + 11Cr_2O_7^{2-} \longrightarrow 18Cu^{2+} + 6H_3PO_4 + 22Cr^{3+} + 53H_2O}$$

12. **(a, c, d):** Ag^+ is reduced hence, it is an oxidant. Hydroquinone is oxidised hence, it is a reductant.

13. **(c, d):** I in KI_3 and N in N_3H show fractional oxidation state.

14. **(d):** Although oxalic acid is oxidised by $KMnO_4$ in acidic medium, it cannot be used to prepare the standard solution because the sample is impure. $FeSO_4 \cdot 7H_2O$ is not a substance of primary standard because it gets oxidised by atmospheric oxygen and its composition is not known. Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ is not prone to oxidation by atmospheric oxygen and is a substance of primary standard, and can be used to prepare a standard solution of Fe (II) which reduces acidified $KMnO_4$.

    Mass of Mohr's salt required

    $$= \frac{392 \times 0.1 \times 100}{1000} = 3.92\,g$$

15. **(c):** $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

16. **(c)**

17. **(b):** Since, copper is more reactive than silver, it displaces Ag^+ ions from its salt solution which get deposited on the copper rod.

18. **(c)**   19. **(b)**

20. **(d):** Equivalent weight of $Cr_2O_7^{2-} = \dfrac{\text{Molar mass}}{6}$

    Decrease in oxidation number of chromium is 3 per atom.

21. **(a):** Greater the standard electrode potential, powerful is the oxidising agent while lower the electrode potential, weaker is the oxidising agent.

22. **(a):** $2\overset{-1}{H_2}\overset{}{O_2} \longrightarrow 2\overset{-2}{H_2O} + \overset{0}{O_2}$

    Oxidation (top), Reduction (bottom)

23. (4): $\underline{P}O_4^{3-} \rightarrow x + 4(-2) = -3, \Rightarrow x = +5$

$H_2\underline{S}_2O_8 \rightarrow 2(+1) + 2x + 2(-1) + 6(-2) = 0$

$\Rightarrow \quad x = +6$ (two oxygen atoms with peroxide linkage).

$H_2\underline{S}O_5 \rightarrow 2(+1) + x + 2(-1) + 3(-2) = 0$

$\Rightarrow \quad x = +6$ (two oxygen atoms with peroxide linkage)

$\underline{O}F_2 \rightarrow x + 2(-1) = 0, \Rightarrow x = +2$

$\underline{Cr}_2O_7^{2-} \rightarrow 2x + 7(-2) = -2, \Rightarrow x = +6$

$\underline{Cr}O_5 \rightarrow x + 4(-1) + (-2) = 0,$

$\Rightarrow x = +6$

(four oxygen atoms with peroxide linkage).

24. (1): Reaction is balanced.

Thus, $-4x = -4 \qquad \therefore \quad x = 1$

Thus, O_2^{x-} is O_2^- (superoxide ion).

25. (1): The reactions involved are :

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; n factor = 2

$H_2C_2O_4 \longrightarrow 2H^+ + 2CO_2 + 2e^-$; n factor = 2

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; n factor = 5

$2I^- \longrightarrow I_2 + 2e^-$; n factor of I_2 = 2

No. of eq. of pure MnO_2 = No. of eq. of oxalic acid = No. of eq. of $KMnO_4$ = No. of eq. of I_2

$\Rightarrow \dfrac{0.0175}{127} \times 37.12 = 5.12 \times 10^{-3}$

Equivalent weight of $MnO_2 = \dfrac{87}{2} = 43.5$

Weight of MnO_2 in pyrolusite

$= 5.12 \times 10^3 \times 43.5 = 0.2227$ g

Weight of pyrolusite $= \dfrac{100 \times 0.2227}{89.21} = 0.2496$ g

$= 2.496 \times 10^1$ g

ENVIRONMENTAL CHEMISTRY

1. (c): SO_2 and NO_2 when dissolve in water, form H_2SO_4 and HNO_3 respectively.

$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$

$2SO_2 + O_2 \xrightarrow{\text{Particulate}} 2SO_3$

$SO_3 + H_2O \longrightarrow H_2SO_4$

Thus, they cause the pollution by increasing acidity.

2. (c)   **3. (d)**

4. (c): Polluted water has BOD value of more than 17 ppm.

5. (a): The average residence time of NO is 4 days.

6. (a): Normal rainwater has pH 5.6. Thunderstorm results in the formation of NO and HNO_3 which lowers the pH.

7. (d)

8. (a): PSCs react with chlorine nitrate and HCl to give HOCl and Cl_2.

9. (c): Carbon monoxide combines with haemoglobin of blood to form a complex called carboxy-haemoglobin. Formation of this complex makes the haemoglobin incapable of oxygen transport. Due to which there will be oxygen deficiency in the blood.

10. (d)

11. (c, d): BOD value more than 5 ppm shows water is polluted.

The process in which nutrient enriched water bodies support a dense plant population, which kills aquatic life by depriving them of oxygen and results in subsequent loss of biodiversity is known as eutrophication.

12. (b, c, d): Oxygen is not the component of photochemical smog.

13. (a, b, c)   **14.** (a)

15. (b): Peroxyacetyl nitrate

$$\left(\begin{array}{c} \quad\quad\text{O} \\ \quad\quad\| \\ CH_3-C-O-O-NO_2 \end{array} \right)$$

16. (d)

17. (c): Aerosols use CFCs and high flying jets release NO which are responsible for depletion of ozone layer.

18. (b)   **19. (c)**   **20. (a)**   **21. (b)**

22. (c): Houses used to grow plants are not made up of green glasses. The glasses are transparent.

23. (2)

24. (6): Photochemical smog contains neither smoke nor fog. It is a mixture of compounds like O_3, NO_2, PAN, hydrocarbons, aldehydes, ketones, acrolein and CO.

25. (5): We generally measure BOD_5 where 5 represents number of days for which the sample is kept, i.e., amount of O_2 consumed in 5 days.

···◈◈

ACE
YOUR WAY CBSE XI

Series 7

CHAPTERWISE PRACTICE PAPER : HYDROCARBONS | ENVIRONMENTAL CHEMISTRY

Time Allowed : 3 hours   Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q.no.1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q.no.6 to 10 are short answer questions and carry 2 marks each.
(iv) Q.no.11 to 22 are also short answer questions and carry 3 marks each.
(v) Q.no.23 is a value based question and carries 4 marks.
(vi) Q.no.24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log table if necessary, use of calculators is not allowed.

1. What is Lindlar's catalyst? Give its use.

2. Suggest the name of Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

3. What would happen if the greenhouse gases were totally missing in the earth's atmosphere?

4. Give IUPAC name of the following compound :

$$CH_3-CH_2CH_2-\underset{\underset{CH_3-CH-CH_2CH_3}{|}}{CH}-\underset{\underset{HC(CH_3)_2}{|}}{CH}-CH_2CH_2CH_2CH_2CH_3$$
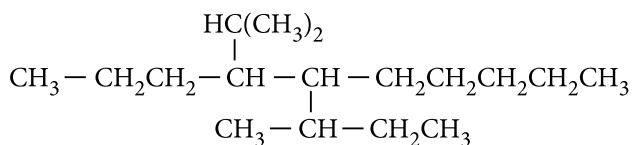
5. Why are alkanes called paraffins?

6. Is it possible to isolate pure staggered or eclipsed form of ethane at room temperature? Explain your answer.

7. Which of the following has larger dipole moment 1-butyne or 1-butene? Explain.

8. How will you demonstrate that double bonds of benzene are somewhat different from that of olefins?

9. What is Minamata disease?

10. Explain why the following systems are not aromatic :

(i) =CH$_2$ (ii)
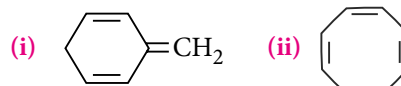
OR

Define resonance energy. What is resonance energy of benzene?

11. How will you prepare *cis*-pent-2-ene and *trans*-pent-2-ene by starting with ethyne?

12. (a) Will the butene formed on reduction with sodium in liquid ammonia of 2-butyne show the geometrical isomerism?

(b) Acetylene is acidic but it does not react with NaOH or KOH. Give reason.

OR

Ethene dissolves in conc. H_2SO_4, but ethyne does not. Explain. What do you conclude about $CH_3C{\equiv}CCH_3$?

13. Tetrachloroethene ($Cl_2C{=}CCl_2$) is non-reactive towards Cl_2 but addition of $AlCl_3$ makes it reactive. Explain.

14. An alkene 'A' contains three C—C, eight C—H σ-bonds and one C—C π-bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Deduce IUPAC name of 'A'.

15. Ethyne reacts with dil. H_2SO_4 in presence of mercury salts to give acetaldehyde but with dil. HCl under similar conditions, it gives vinyl chloride. Explain why.

16. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is 430.5 kJ mol^{-1}, 363.7 kJ mol^{-1} and 296.8 kJ mol^{-1} respectively. What will be the order of reactivity of these halogen acids? Give reason.

17. Chlorination at C–2 of pentane yields a racemic mixture of 2-chloropentane. Explain.

18. (a) On the basis of chemical reactions involved, explain how do chlorofluorocarbons cause thinning of ozone layer in stratosphere.
    (b) What are the sources of dissolved oxygen in water?

19. Two isomeric cyclic dienes X and Y having molecular formula C_6H_8 on hydrogenation give cyclohexane as the only product. A mixture of these two dienes on reductive ozonolysis gives succinaldehyde, propane-1, 3-dial and glyoxal. Deduce the structures of dienes X and Y.

20. What is COD? Which chemical substance is generally used in its measurement? Out of BOD and COD which one is better and why?

21. Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

22. Complete the following reactions with reason :
    (i) $CH_2\!=\!CH_2 \xrightarrow{\text{EtONa + EtOH}}$
    (ii) $F_2C\!=\!CF_2 \xrightarrow{\text{EtONa + EtOH}}$

23. Heaps of garbage are seen at different places in our country. With the passage of time, it starts stinking thereby causing pollution in the atmosphere. For this, nobody else but we ourselves are responsible. If we dispose off our garbage in a proper way, we can keep our environment clean. Smoking in public places not only affects the health of the smoker, but also it pollutes the air around him and affect the health of others. Disposal of industrial waste into rivers and lakes causes pollution of water which affects the aquatic life.

After reading the given paragraph, answer the following questions :
(a) What values are expressed in the given paragraph?
(b) What should be done to manage
    (i) household waste
    (ii) industrial waste?

24. (a) Define substitution reactions. Why does benzene undergo substitution reactions even though it contains double bonds?
    (b) What happens when benzene is treated with
        (i) conc. H_2SO_4 at 330 K
        (ii) mixture of conc. H_2SO_4 and conc. HNO_3 at 330 K
        (iii) ethanoyl chloride in presence of anhydrous $AlCl_3$?

OR

(a) Complete the given reactions sequence with proper explanation :

$$C \xleftarrow[\text{Zn/H}_2\text{O}]{\text{O}_3/\text{CH}_2\text{Cl}_2} \; \bigcirc \; \xrightarrow[\text{KMnO}_4]{\text{Cold alk.}} A$$
$$\xrightarrow[\text{KMnO}_4]{\text{Hot alk.}} B$$
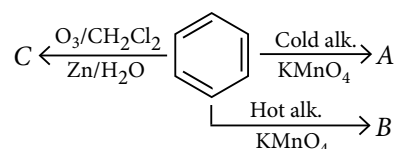
(b) Predict the major product of the following reaction and explain its formation :

$$H_3C\!-\!CH\!=\!CH_2 \xrightarrow[\text{HBr}]{(\text{PhCO})_2\text{O}_2}$$
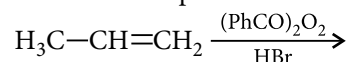
25. The relative reactivity of 1°, 2°, 3° hydrogen towards chlorination is 1 : 3.8 : 5. Calculate the percentage of all monochlorinated products obtained from 2-methylbutane.

OR

Identify A, B and C.
$$A, B \text{ and } C \; (C_6H_{10}) \xrightarrow{\text{CCl}_4} \text{All decolourises Br}_2 \text{ solution}$$

$$\xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{Cold}} \text{All are soluble}$$

$$(A) \xrightarrow[\text{AgNO}_3]{\text{Ammoniacal}} \text{White precipitate}$$

$$(B \text{ and } C) \xrightarrow[\text{AgNO}_3]{\text{Ammoniacal}} \text{No reaction}$$

$$(A \text{ and } B) \xrightarrow[\text{of H}_2/\text{Pt}]{\text{Excess}} \text{Hexane}$$

$$(C) \xrightarrow[\text{H}_2/\text{Pt}]{1 \text{ mol}} D(C_6H_{12})$$

$$(A) \xrightarrow[\text{KMnO}_4]{\text{Hot alk.}} \text{Pentanoic acid only}$$

(B) $\xrightarrow[\text{KMnO}_4]{\text{Hot alk.}}$ Propanoic acid only

(C) $\xrightarrow[\text{KMnO}_4]{\text{Hot alk.}}$ Adipic acid only
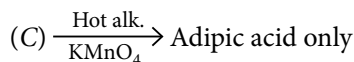
26. (a) Define eutrophication, primary and secondary pollutants.

(b) Write differences between photochemical and classical smog.

OR

(a) Give three examples in which green chemistry has been applied.

(b) What is pneumoconiosis? How does it occur?

(c) Why does water covered with excessive algal growth become polluted?

SOLUTIONS

1. Pd/BaSO_4 is known as Lindlar's catalyst. It is used in the conversion of alkynes to *cis*-alkenes with the help of H_2.

2. Lewis acids like anhy. AlCl_3, BF_3, etc., can be used in ethylation of benzene by Friedel—Crafts alkylation.

3. The solar energy radiated back from the earth's surface, is absorbed by greenhouse gases, which keeps the earth's surface and lower atmosphere warm. If there were no greenhouse gases, the temperature on the earth would be chilling.

4.
$$\overset{1}{\text{CH}_3}-\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}-\overset{\overset{\displaystyle\text{HC(CH}_3)_2}{|}}{\overset{4}{\text{CH}}}-\overset{\overset{\displaystyle|}{}}{\overset{5}{\text{CH}}}-\overset{6}{\text{CH}_2}\overset{7}{\text{CH}_2}\overset{8}{\text{CH}_2}\overset{9}{\text{CH}_2}\overset{10}{\text{CH}_3}$$
$$\text{CH}_3-\overset{2}{\text{CH}}-\overset{3}{\text{CH}_2}\text{CH}_3$$

5-*sec*-Butyl-4-isopropyldecane or
4-(1- Methylethyl)-5-(1-methylpropyl)decane
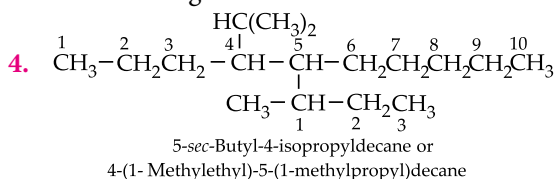
5. Alkanes are called paraffines because under normal conditions of temperature and pressure, alkanes are inert and do not react with general reagents.

6. The energy difference between staggered and eclipsed conformations of ethane is just 12.5 kJ mol^{-1}. Thus, the interconversion between different conformations is very rapid. Therefore, it is not possible to isolate either pure staggered or pure eclipsed form at room temperature.

7. The direction of dipole moment of individual bonds in 1-butyne and 1-butene, can be shown as follows :

$$\underset{\text{1-Butyne}}{\overset{sp^3 \quad sp \quad sp}{\text{CH}_3\text{CH}_2 \rightarrow \text{C} \equiv \text{C} \leftarrow \text{H}}} \qquad \underset{\text{1-Butene}}{\text{CH}_3\text{CH}_2 \, \text{C} = \text{C} \, \text{H}}$$
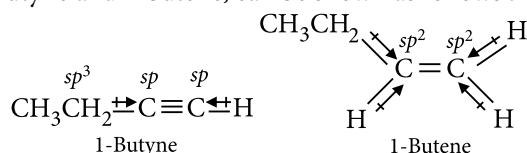
The resultant dipole moment of 1-butene and 1-butyne is due to the dipole moment of CH_3CH_2— C and C—H

bonds which oppose each other. Since, *sp*-hybridised carbon is more electronegative than a sp^2-hybridised carbon, therefore, polarity of $\text{CH}_3\text{CH}_2(sp^3)$—$\text{C}(sp)$ bond in 1-butyne is more than that of $\text{CH}_3\text{CH}_2(sp^3)$—$\text{C}(sp^2)$ bond in 1-butene. Therefore, 1-butyne has larger dipole moment than 1-butene.

8. The double bonds of olefins decolourise bromine water and discharge the pink colour of Baeyer's reagent while those of benzene not. This is because Br_2 gets added across olefinic double bond but not across the benzene double bond. It happens because double bonds in benzene are delocalised.

9. Minamata disease is a neurological syndrome caused by severe mercury poisoning. It was first discovered in Minamata city, Japan in 1956. It was caused by release of methylmercury in the industrial waste water from a chemical company. This chemical was accumulated in shellfish and fish in Minamata bay which was eaten by local populace resulted in mercury poisoning.

10. (i) Due to the presence of sp^3 hybridised carbon, the system is not planar hence, it is not aromatic.

$$sp^3 \quad \diagup\!\!\!\diagdown = \text{CH}_2$$
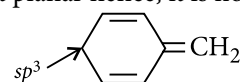
(ii) Cyclooctatetraene is tub-shaped *i.e.*, not planar and has 8π electrons. Therefore, the system is not aromatic.
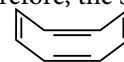
OR

Resonance energy is defined as the difference in internal energy of the resonance hybrid and that of the most stable canonical form. The more nearly the contributing structures are equal in stability, the greater is the resonance energy. The resonance energy of benzene is $150.62 \text{ kJ mol}^{-1}$ ($36.0 \text{ kcal mol}^{-1}$).

11. $\underset{\text{Ethyne}}{\text{HC} \equiv \text{CH}} \xrightarrow{\text{NaNH}_2} \text{HC} \equiv \text{C}^-\text{Na}^+ \xrightarrow[-\text{NaI}]{\text{CH}_3\text{I}}$

$\underset{\text{Sodium propynide}}{\text{CH}_3-\text{C} \equiv \text{C}^-\text{Na}^+} \xleftarrow{\text{NaNH}_2} \underset{\text{Propyne}}{\text{CH}_3-\text{C} \equiv \text{CH}}$

$\xrightarrow[-\text{NaI}]{\text{CH}_3\text{CH}_2\text{I}} \underset{\text{Pent-2-yne}}{\text{CH}_3-\text{C} \equiv \text{C}-\text{CH}_2\text{CH}_3}$

$\text{H}_2/\text{Pd-BaSO}_4 +$ quinoline (Lindlar's catalyst)   Na/liq. NH_3, 196 K (Birch reduction)

$$\underset{\text{cis-Pent-2-ene}}{\overset{\text{CH}_3 \quad \text{CH}_2\text{CH}_3}{\text{C} = \text{C}}} \qquad \underset{\text{trans-Pent-2-ene}}{\overset{\text{CH}_3 \quad \text{H}}{\text{C} = \text{C}}}$$
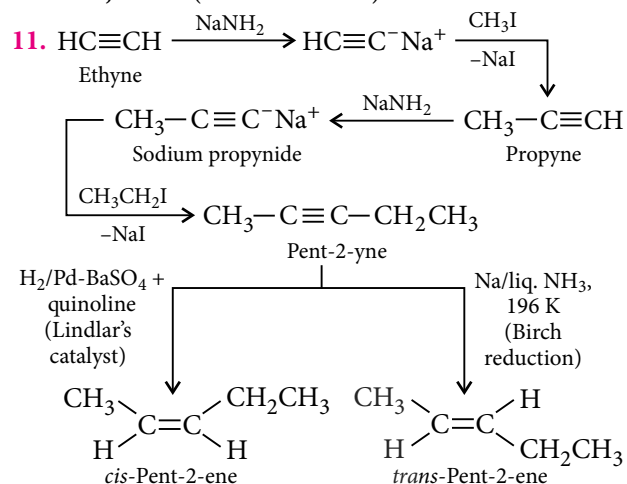
12. (a) $CH_3CH = CHCH_3$ (*trans*-2-butene) is formed by reduction of 2-butyne in the presence of sodium in liquid ammonia. It shows geometrical isomerism.

cis-2-Butene   trans-2-Butene
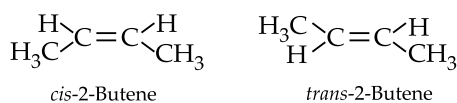
(b) Due to sp-hybridisation, the electrons of C—H bond are held more strongly by carbon atom thus, acetylene is a very weak acid and it does not react with NaOH or KOH but reacts with a very strong base such as $NaNH_2$.

OR

$$CH_2 = CH_2 + \text{conc. } H_2SO_4 \longrightarrow (CH_3\overset{+}{C}H_2)(HSO_4^-)$$
Ethene   I (sp^2)

$$CH \equiv CH + \text{conc. } H_2SO_4 \longrightarrow (CH_2 = \overset{+}{C}H)(HSO_4^-)$$
Ethyne   II (sp)
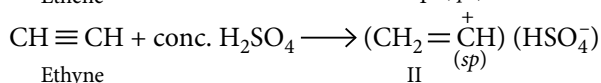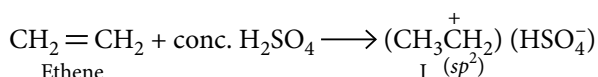
A vinylic carbocation carries the positive charge on an sp-hybridised carbon, which is more electronegative than an sp^2-hybridised carbon of an alkyl carbocation. Therefore, a vinylic carbocation is less stable than a primary alkyl carbocation. Hence, $CH \equiv CH$ is not soluble in conc. H_2SO_4.

$$CH_3C \equiv CCH_3 + \text{conc. } H_2SO_4 \longrightarrow CH_3CH = \overset{+}{C}CH_3$$
2-Butyne   (III)
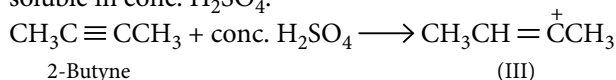
III is more stable than II due to electron donating groups. Hence, 2-butyne can be soluble in conc. H_2SO_4 but less than ethene.
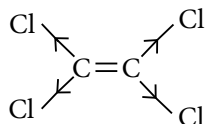
13.

Cl atoms are electron attractive hence, they decrease nucleophilic nature of alkene, hence no reaction with Cl_2 takes place. In presence of $AlCl_3$, electrophilic nature of Cl_2 is increased as :

$$AlCl_3 + Cl_2 \longrightarrow AlCl_4^- + Cl^+$$
                           Chloronium ion

$$Cl_2C = CCl_2 + Cl^+ \longrightarrow Cl_3C - \overset{+}{C}Cl_2$$

$$Cl_3C - \overset{+}{C}Cl_2 + AlCl_4^- \longrightarrow Cl_3C - CCl_3 + AlCl_3$$
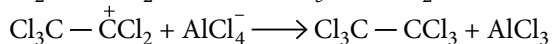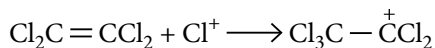
14. The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms.

There are eight C — H σ-bonds. Hence, there are 8 hydrogen atoms in '*A*'. Also, there are three C—C σ-bonds. Hence, there are four carbon atoms present in the structure of '*A*'.

Ozonolysis of '*A*' takes place as :

$$H_3C - CH = CH - CH_3 + O_3 \longrightarrow$$
           (*A*)
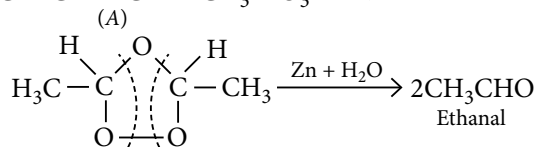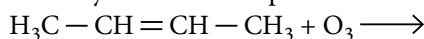
The final product has molecular mass = 44 u
Therefore, the IUPAC name of '*A*' is but-2-ene.

15. First of all, mercury ions form a complex (I) with acetylene. Since, H_2O is more nucleophilic than SO_4^{2-} ion, it attacks the complex (I) to form first vinyl alcohol which then tautomerises to give acetaldehyde.
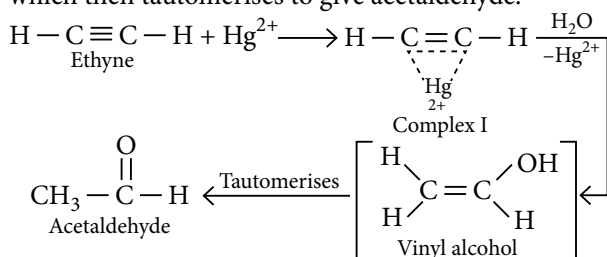
In case of dil. HCl, since, Cl^- ion is more nucleophilic than H_2O, it reacts with complex (I) to form vinyl chloride.
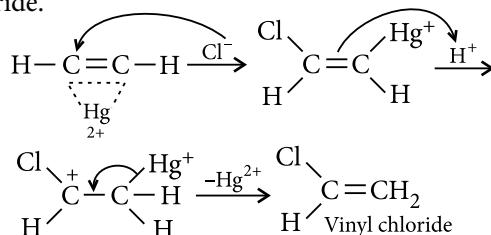
16. In the reaction of propene with HCl, HBr or HI, first H^+ adds to give the same carbocation intermediate (I) which then undergoes nucleophilic attack by the halide ion (X^-) to give the addition product. Here, first step is slow and hence, is the rate-determining step of the reaction while the second step is fast and hence, does not affect the rate of the reaction.
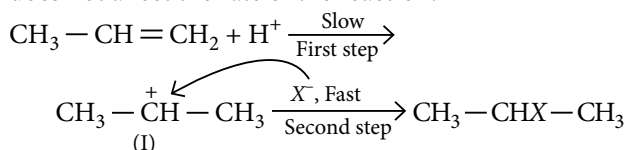
The rate of the first step depends upon how easily is the proton available. The availability of the proton, in turn, depends upon the bond dissociation energy of the $H - X$ molecule. Since the bond dissociation energy decreases in the order : HCl (430.5 kJ mol^{-1}) > HBr (363.7 kJ mol^{-1}) > HI (296.8 kJ mol^{-1}), therefore, the reactivity of the halogen acids decreases in the reverse order : HI > HBr > HCl.

17. Abstraction of hydrogen atom from C – 2 produces a trigonal planar radical. This radical then reacts with chlorine at either face [by path (a) or path (b)].
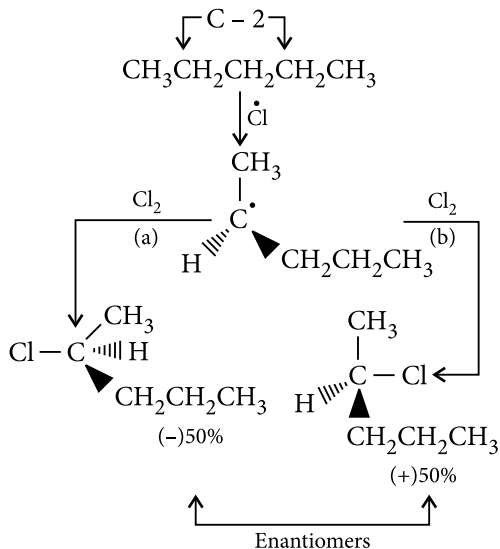
Enantiomers

Because the radical is achiral, the probability of reaction by either path is the same. Therefore, the two enantiomers with a chirality centre are produced in equal amounts and thus, mixture is racemic.

18. (a) CFCs are stable compounds they undergo decomposition in presence of sunlight. The reactions can be shown as :

$$CF_2Cl_2 \xrightarrow{h\upsilon} \dot{C}l + \dot{C}F_2Cl$$

$$\dot{C}l + O_3 \xrightarrow{h\upsilon} Cl\dot{O} + O_2$$

$$Cl\dot{O} + O \longrightarrow \dot{C}l + O_2$$
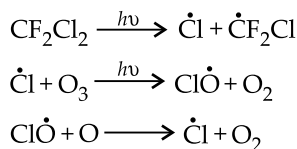
Since the free radicals are used by ozone and convert it to oxygen, they cause thinning of ozone layer in stratosphere.

(b) Sources of dissolved oxygen in water are :
(i) Photosynthesis (ii) Natural aeration (iii) Mechanical aeration.

19. Since, X and Y on hydrogenation give cyclohexane as the only product, therefore, X and Y must be cyclohexadienes. The two possible cyclohexadienes are :

Cyclohexa-1,4-diene,(X)   Cyclohexa-1,3-diene, (Y)
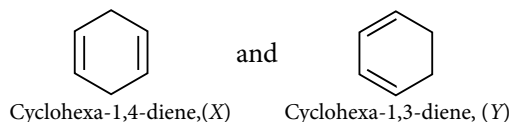
Whereas reductive ozonolysis of X will give two molecules of propane-1, 3-dial, reductive ozonolysis of Y will give succinaldehyde and glyoxal as shown :
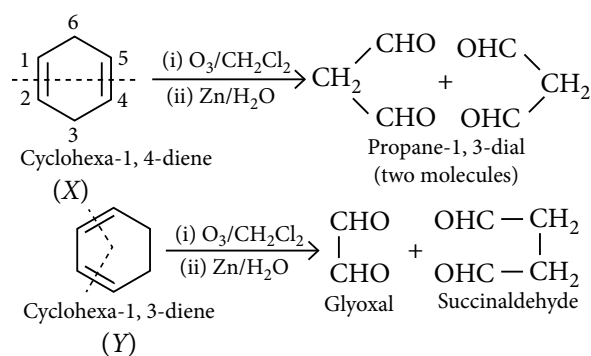
20. Chemical Oxygen Demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. It is measured by treating the given sample of water with an oxidizing agent, generally $K_2Cr_2O_7$ in presence of dilute H_2SO_4. COD is better estimate of organic matter which needs no saponification and is time saving.

21. Ethane contains carbon-carbon sigma (σ) bond. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C—C bond which is not disturbed due to rotation about its axis. This permits free rotation about C—C single bond. However, rotation around a C—C single bond is not completely free. It is hindered by a small energy barrier due to weak repulsive interaction between the adjacent bonds. Such type of repulsive interaction is called torsional strain. Of all the conformations of ethane, the staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}, which is very small. It has not been possible to separate and isolate different conformational isomers of ethane.

22. (i) No reaction. Nucleophile (EtO$^-$) does not add to alkenes because it is repelled by the π-electrons of the alkenes.

(ii) The electron withdrawing groups such as F atoms are attached to C=C bond, they reduce the electron density of the π-bond and stabilise the intermediate carbanions.

Ethoxy-1,1,2,2-tetrafluoroethane

23. (a) (i) We should not throw our household garbage in the open. We should show concern towards environment.

(ii) Smoking in public places should be punishable under law.

(iii) Industries should not be allowed to throw their waste into rivers and lakes.

(b) (i) We should keep two garbage bins in our house, one for recyclable waste and the other for non-recyclable waste.

(ii) Burning and incineration : The combustible industrial waste should be burnt at a far off place so that it is reduced to ash which can be used as a land filling material.

Dumping : The biodegradable waste including sewage sludge and waste of chemical industries containing compounds of nitrogen and phosphorus should be dumped into land so that with the passage of time, it is converted into manure.

24. (a) Substitution reactions are those reactions in which an atom or group of atoms directly attached to carbon in the substrate molecule is replaced by another atom or group of atoms, for example,

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H + Cl_2 \xrightarrow[\text{light}]{UV} H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-Cl + HCl$$
Methyl chloride

Benzene undergoes electrophilic substitution reactions because benzene ring has delocalized π-electrons thus, is an electron rich system. It is attacked by electrophiles giving substitution products.

(b) (i)

Benzene + conc. H_2SO_4 $\xrightarrow{330\ K}$ Benzene sulphonic acid (SO_3H) + H_2O

(ii)

Benzene + conc. HNO_3 $\xrightarrow{\text{Conc. } H_2SO_4}{330\ K}$ Nitrobenzene (NO_2) + H_2O

(iii)

Benzene + CH_3COCl (Ethanoyl chloride) $\xrightarrow[\text{AlCl}_3]{\text{Anhyd.}}$ Acetophenone ($COCH_3$) + HCl

OR

(a) Although benzene has three $C{=}C$ bonds, it still does not react either with cold alkaline $KMnO_4$ (Baeyer's test) or with hot alkaline $KMnO_4$ or acidic $KMnO_4$ or acidic $K_2Cr_2O_7$, *i.e.*, it does not undergo oxidation due to the delocalisation of $\pi\ e^-$s.

However, it undergoes ozonolysis reaction due to the formation of *tri*-ozonides, thereby the delocalisation of π-electrons does not take place.

$$\text{(benzene)} \xrightarrow[\text{Hot alk. KMnO}_4]{\text{Cold alk. KMnO}_4 \text{ or}} \text{No reaction } (A, B)$$

$$\text{(benzene)} \xrightarrow[\substack{\text{at - 78°C}\\ \text{Zn/H}_2\text{O}}]{\text{O}_3 + \text{CH}_2\text{Cl}_2} 3\ \underset{\underset{CHO}{|}}{CHO}$$
Glyoxal
(*C*)

(b) In presence of peroxide, addition of HBr to propene follows anti-Markovnikov's rule and hence, gives 1-bromopropane as the major product. The reaction occurs through a free radical mechanism *via* a more stable free radical intermediate as shown in the reaction :

$$CH_3-CH{=}CH_2 + \dot{B}r \xrightarrow[\text{(PhCO)}_2O_2]{\text{Slow}} CH_3-\dot{C}H-CH_2Br \xrightarrow[\text{Fast}]{H-Br}$$
Propene   More stable (2° free radical)

$$CH_3-CH_2-CH_2Br + \dot{B}r$$
1-Bromopropane

25.
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \xrightarrow{Cl_2}$$
2-Methylbutane

$$ClCH_2-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}$$

(*A*) Primary (9 positions for Cl group possible)

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_3$$

(*B*) Secondary (2 positions for Cl group possible at – CH_2)

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2CH_3$$

(*C*) Tertiary (1 position for Cl group possible).

Relative amounts of *A*, *B* and *C* compounds
= Number of hydrogen atoms × Relative reactivity

Relative amount :

$A(1°)$	$B(2°)$	$C(3°)$
$9 \times 1 = 9$	$2 \times 3.8 = 7.6$	$1 \times 5 = 5$

Total amount = 9 + 7.6 + 5 = 21.6

$$\% \text{ of } A = \frac{9}{21.6} \times 100 = 41.7\%$$

$$\% \text{ of } B = \frac{7.6}{21.6} \times 100 = 35.2\%$$

$$\% \text{ of } C = \frac{5}{21.6} \times 100 = 23.1\%$$

OR

Degree of unsaturation in A, B and $C = \dfrac{(2 \times 6 + 2) - 10}{2} = 2$

Structure of (A) : (A) reacts with ammoniacal $AgNO_3$ solution, which shows that it is a terminal alkyne with straight chain of six carbon atoms because on hydrogenation it gives hexane. Therefore, (A) is hex-1-yne.

(A) Hex-1-yne

Hexane

$[Ag(NH_3)_2]^+OH^-$ → White precipitate (silver hexynide)

[O] → Pentanoic acid + [HCOOH] → CO_2
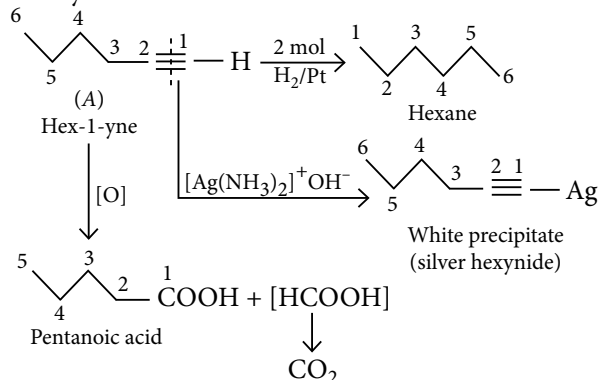
Structure of (B) : (B) does not react with $[Ag(NH_3)_2]^+$ and hence, it must be internal alkyne with straight chain of six carbon atoms because on hydrogenation it also gives hexane.

Location of triple bond is determined by oxidative cleavage. As it gives propanoic acid (3C-atom acid), it should be symmetrical internal alkyne.

Therefore, (B) is hex-3-yne.

(B) Hex-3-yne

Hexane

[O] → Propanoic acid (2 moles)
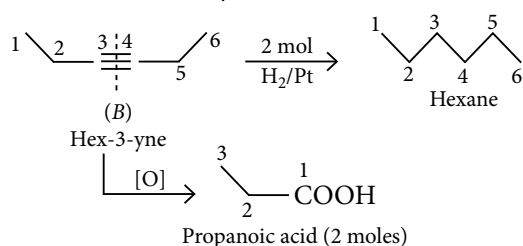
Structure of (C) : It absorbs one mol of H_2 and the product (D) (C_6H_{12}) after catalytic hydrogenation has 1 degree of unsaturation. So, (D) must be 6 C-atoms cyclic compound. Therefore, (C) is cyclohexene.

(C) Cyclohexene → 1 mol H_2/Pt → (D) Cyclohexane

[O] → Adipic acid (COOH, COOH)
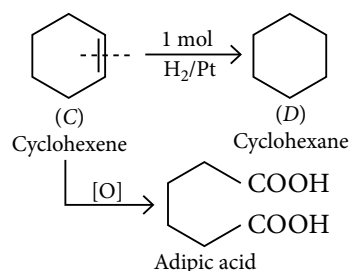
26. (a) Eutrophication : When the growth of algae increases in the surface of water, dissolved oxygen in water is reduced. This phenomenon is known as eutrophication. Due to this growth of fish gets inhibited.

Primary pollutants : Pollutants which enter directly into atmosphere due to natural or human activity, *e.g.*, NO.

Secondary pollutants : Pollutants which are formed as a result of reaction between primary pollutants, *e.g.*, PAN (Peroxyacetyl nitrates).

(b)

	Photochemical smog	Classical smog
(i)	It is formed as a result of photochemical decomposition of nitrogen dioxide and chemical reactions involving hydrocarbons.	It is formed due to condensation of SO_2 vapours on particles of carbon in cold climate.
(ii)	It takes place during dry warm season in presence of sunlight.	It is generally formed during winter when there is severe cold.
(iii)	It is oxidising in nature.	It is reducing in nature.

OR

(a) (i) In dry cleaning, use of liquefied CO_2 in place of tetrachloroethene ($Cl_2C = CCl_2$).

(ii) In bleaching of paper using H_2O_2 in place of chlorine gas.

(iii) In the manufacture of chemicals like ethanal using environment-friendly chemicals and conditions.

(b) Pneumoconiosis is a disease of lungs such as lung cancer, bronchital asthma, chronic bronchitis, etc. It is caused by small sized particulates which enter into lung through nose and provide a large surface area for adsorption of carcinogenic compounds such a polynuclear hydrocarbons, asbestos, etc.

(c) Water containing algae have a very less amount of oxygen as the algae consume most of the dissolved oxygen and thus deprive aquatic plants and oxygen of it and hence kill them. This results in eventual loss of biodiversity.

◈◈

MPP-9 | MONTHLY Practice Problems

Class XI

This specially designed column enables students to self analyse their extent of understanding of specified chapter. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Organic Chemistry-Some Basic Principles and Techniques

Total Marks : 120   **Time Taken : 60 Min.**

NEET / AIIMS
Only One Option Correct Type

1. Which of the following contain(s) both an aldehyde and an ether functional group?

    (i)   (ii)

    (iii)   (iv)

    (v)
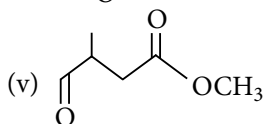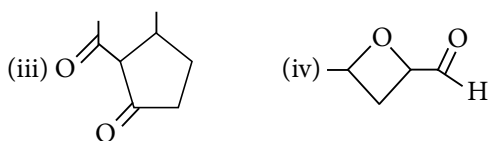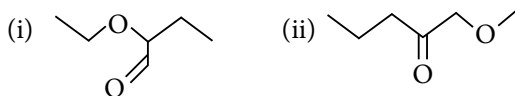
    (a) (i) only
    (b) (i) and (iv) only
    (c) (ii) and (v) only
    (d) (iii) and (iv) only

2. Which of the following is correct about ionisation enthalpy and electron affinity of methyl free radical?
    (a) $IE = EA$
    (b) $IE > EA$
    (c) $IE < EA$
    (d) None of these

3. Which one of the following behaves as a nucleophile as well as an electrophile?
    (a) CH_3NH_2
    (b) CH_3Cl
    (c) CH_3CN
    (d) CH_3OH

4. 0.257 g of an organic substance was heated with conc. H_2SO_4 and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 mL of N/10 HCl which required 23.2 mL of N/10 NaOH for neutralisation at the end of the process. The percentage of nitrogen in the compound is
    (a) 14.6
    (b) 18.0
    (c) 17.0
    (d) 15.5

5. In Dumas method, the gas which is collected in nitrometer is
    (a) N_2
    (b) NO
    (c) NH_3
    (d) H_2

6. Which of the following molecules will exhibit inductive, mesomeric and Baker-Nathan effects?
    (a) C_2H_5Cl
    (b) $CH_3 — CH = CH_2$
    (c) $CH_2 = CH — CH = CH_2$
    (d) $CH_3 — CH = CH — \underset{\substack{\| \\ O}}{C} — CH_3$

7. Out of the following reagents, electrophiles are
    (i) R_3N (ii) :CCl_2
    (iii) CH_3^+ (iv) H_2O
    (v) H_3O^+ (vi) Na^+
    (a) (i), (ii), (iii), (iv), (v)
    (b) (ii), (iii), (v)
    (c) (ii), (iii), (iv)
    (d) (ii), (iii), (iv), (v), (vi)

8. Absolute alcohol cannot be obtained by simple fractional distillation of solution of ethanol and water because
    (a) their boiling points are very near
    (b) ethanol remains dissolved in water
    (c) they form a constant boiling mixture
    (d) ethanol molecules are solvated.

9. The IUPAC name of the following structure

$$[(CH_3)_2CH]_2C(CH_2CH_3)\overset{CH_3}{\underset{|}{C}}=C(CH_2CH_3)_2 \text{ is}$$
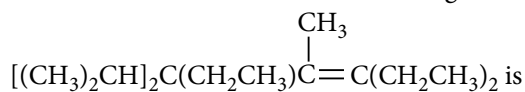
(a) 3, 5-diethyl-4,6-dimethyl-5-[1-methylethyl]-hept-3-ene

(b) 3,5-diethyl-5-isopropyl-4,6-dimethylhept-2-ene

(c) 3,5-diethyl-5-propyl-4,6-dimethylhept-3-ene

(d) none of the above.

10. Liebig's method is used for the estimation of
(a) nitrogen   (b) sulphur
(c) carbon and hydrogen
(d) halogens.

11. Which of the following carbocations undergoes rearrangement?

(a)   (b) $CH_3-\overset{+}{C}H-CH_3$

(c)   (d)
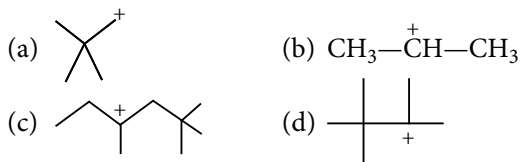
12. Which of the following shows minimum heat of combustion?
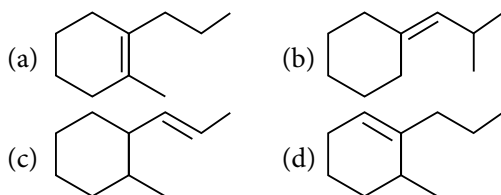
(a)   (b)

(c)   (d)

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. Assertion : In organic layer test, Cl_2 water is added to the sodium extract, which oxidises Br^- and I^- ions to Br_2 and I_2, respectively.
Reason : Reduction potential of Cl_2 is greater than that of Br_2 and I_2.

14. Assertion : Relative reactivity order towards electrophilic addition is
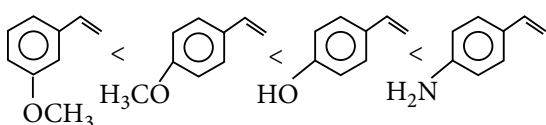
Reason : Electron releasing group stabilizes carbocation. More the $+M$ effect, more is stability of carbocation.

15. Assertion : p-Methylbenzyl carbocation is more stable than benzyl carbocation.
Reason : $—CH_3$ group at *para*-position increases the stability due to no bond resonance.

JEE MAIN / JEE ADVANCED
Only One Option Correct Type

16. In which of the following reactions, the principal group loses its preferences?
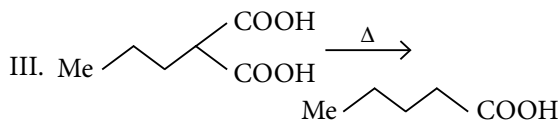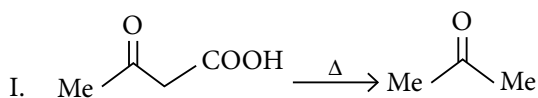
(a) I only   (b) I and II only
(c) I and III only   (d) All of these

17. Which can be said about degree of unsaturation?
(a) $DU = 1$ means one olefinic bond or one ring.
(b) $DU = 2$ means two olefinic bonds or one triple bond or two rings or one ring with one olefinic bond.
(c) $DU = 0$ means no unsaturation.
(d) All of the above.

18. The product (P) formed during the reaction

 $+ :CH_2 \longrightarrow P$; is

(a)   (b)
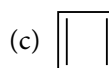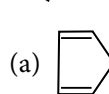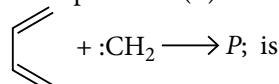
(c)   (d) none of these.

19. The correct name of the given compound is
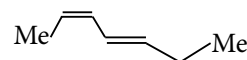
(a) (E-2), (E-4), hepta-2, 4-diene
(b) (Z-2), (Z-4), hepta-2,4-diene
(c) (E-2), (Z-4), hepta-2,4-diene
(d) (Z-2), (E-4), hepta-2, 4-diene.

More than One Options Correct Type

20. Which of the following orders regarding the stability of intermediates are not correctly arranged?

(a) $F_2\ddot{C} > Cl_2\ddot{C} > Br_2\ddot{C} > I_2\ddot{C}$ (singlet carbene)

(b) $(C_6H_5)_3\dot{C} > (C_6H_5)_2C\dot{H} > CH_2{=}CH{-}\dot{C}H_2$

(c) $R{-}C{\equiv}C^- < R_2C{=}\bar{C}H < R_3C{-}\bar{C}H_2$

(d)
$$\text{[ring]}^+ > (C_6H_5)_3C^+ >$$
$$(C_6H_5)_2CH^+ > \overset{+}{C}H_2{-}CH{=}CH_2$$

21. The correct statements concerning the structures E, F and G are

(E)
$$H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$
with H_3C on the left carbon

(F)
$$H_3C\overset{OH}{\underset{\displaystyle H_3C}{}}C{=}C{-}CH_3$$

(G)
$$H_3C\overset{CH_3}{\underset{\displaystyle H_3C}{}}C{=}C{-}OH$$
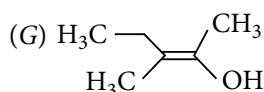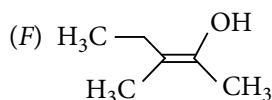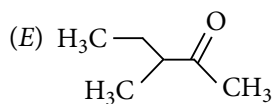
(a) E, F and G are resonance structures

(b) E, F and E, G are tautomers

(c) F and G are geometrical isomers

(d) F and G are diastereomers.

22. Which of the following statements are true?

(a) Protonation increases electrophilic nature of carbonyl group.

(b) $CF_3SO_3^-$ is better leaving group than $CH_3SO_3^-$.

(c) Benzyl carbonium ion is stabilised by resonance.

(d) $Cl_3C{-}CH\overset{OH}{\underset{\displaystyle OH}{}}$ is stable *gem*-diol.

23. Which of the following are not in accordance with given IUPAC name of the compound?
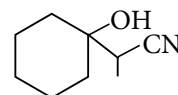
1-(1-Cyanoethyl)cyclohexanol
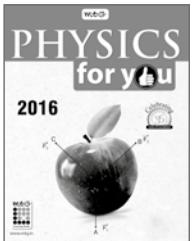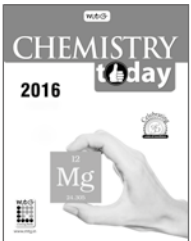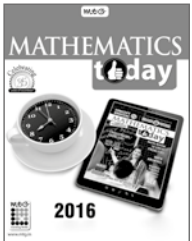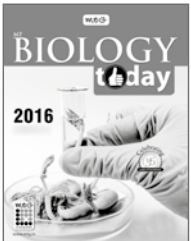
(a) Parent chain is incorrectly selected.

(b) Parent chain has only three carbons.

(c) Its IUPAC name is 1-(1-hydroxycyclohexyl)-1-methylenthanenitrile.

(d) Its IUPAC name is 2-(1-hydroxycyclohexyl) propanenitrile.

Integer Answer Type

24. Number of different functional groups in the given compound is

25. In the reaction,

$$\underset{H_3C}{\overset{CH_3}{\diagdown}}\underset{OH}{\diagup} \xrightarrow{+H^+} [F] \xrightarrow{Br_2, CCl_4} \underbrace{C_4H_8Br_2}_{\substack{5 \text{ such products} \\ \text{are possible}}}$$

how many structures of *F* are possible?

26. When the following compound is named correctly according to IUPAC convention, what would be the sum of positions of two chlorine atoms?
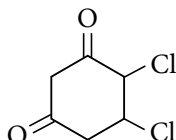
Comprehension Type

Carbene intermediates are produced by the photolysis of diazomethane (CH_2N_2) or ketene ($CH_2=C=O$). They are also produced by the reaction of CHX_3 with base or by Simmons–Smith reaction. There are two types of carbenes, singlet and triplet. They are so called due to their spin states.

27. In which reaction, the insertion of methylene increases potential energy?

(a) $CH_2=CH_2 + :CH_2 \longrightarrow CH_3-CH=CH_2$

(b)

(c) $Me-CH=CH_2 + :CH_2 \longrightarrow$
$$Me-CH=CH-CH_3$$

(d) $Me \diagdown Me + :CH_2 \longrightarrow Me \diagdown \diagup \diagdown Me$
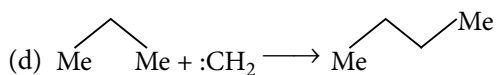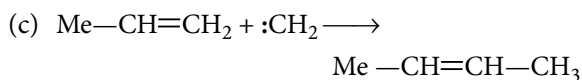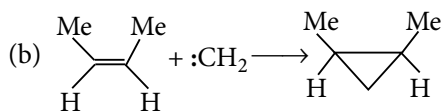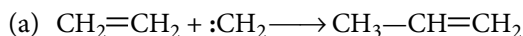
28. Which carbene is produced in the following reaction sequence?

$$Me_3C\bar{O} + H-\underset{I}{\overset{Cl}{\underset{|}{C}}}-Br \rightarrow Me_3COH + \underset{I}{\overset{Cl}{\underset{|}{\bar{C}}}}-Br \rightarrow \underline{?}$$
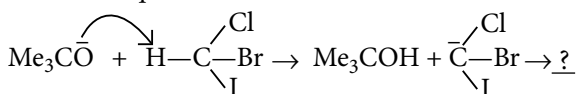
(a) **:CClBr**   (b) **:CBrI**

(c) **:CClI**   (d) All of these

Matrix Match Type

29. Match the structures given in Column I with common names mentioned in Column II and choose the correct answer using the codes given below :

Column I	Column II
P. Me⌢⌣COOH	1. Carbinol
Q. CH_3OH	2. Valeric acid
R. PhOH	3. Malonic acid
S. ⟨COOH / COOH	4. Carbolic acid

	P	Q	R	S
(a)	2	1	4	3
(b)	4	1	3	2
(c)	2	4	1	3
(d)	3	4	1	2

30. Match the reactions given in Column I with the intermediates mentioned in Column II and choose the correct answer using the codes given below :

Column I	Column II
P. Ph⌢Me $\xrightarrow[\text{Peroxide}]{\text{HCl}}$	1. Radical anion
Q. $F_3C-CHCl_2 \xrightarrow{EtO^-}$	2. Nitrene
R. $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2 + KOH}$	3. Carbocation
S. $\underset{Me}{\overset{Me}{\diagdown}}=O \xrightarrow[H_2O]{Mg/Hg}$	4. Carbanion

	P	Q	R	S
(a)	4	1	2	3
(b)	3	4	2	1
(c)	3	1	2	4
(d)	4	1	3	2

❀❀

Keys are published in this issue. Search now! ☺

SELF CHECK ✎

No. of questions attempted	……
No. of questions correct	……
Marks scored in percentage	……

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CONCEPT MAP
CLASS XI

Le Chatelier's Principle

If a system in dynamic equilibrium is disturbed, the position of equilibrium will shift so as to cancel out the effect of change and a new equilibrium can be established again.

Mechanistic Approach to Some Name Reactions

A mechanistic approach to any reaction classifies the reaction according to mechanism rather than by functional group. It explains the stereochemistry involved in a particular reaction, which can either be regioselective, stereoselective or stereospecific.

CONCEPT MAP
CLASS XII

Effect of Concentration Change

- Increase in conc. of reactants or decrease in conc. of products shifts the equilibrium to forward direction.
- Increase in conc. of products or decrease in conc. of reactants shifts the equilibrium to backward direction.

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$$
(yellow)   (orange)
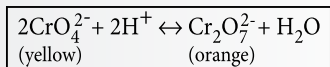
Increase H⁺ conc.	Decrease H⁺ conc.
• By adding H^+ • Equilibrium shift towards right. • Formation of $Cr_2O_7^{2-}$ (orange)	• By adding OH^- • Equilibrium shift towards left. • Formation of CrO_4^{2-} (yellow)

Effect of Pressure Change

- Applicable only in case of gaseous reactions and reactions which proceed with a change in number of moles of gaseous reactants and products.
- Increase in pressure shifts the equilibrium towards lesser number of gaseous molecules.
- Decrease in pressure shifts the equilibrium towards larger number of gaseous molecules.

Pressure-volume changes do not change the value of equilibrium constant as long as the temperature remains constant.

Effect of Volume Change

- The effect of change of volume will be exactly reverse to that of pressure.
- Decrease in volume shifts the equilibrium towards lesser number of gaseous molecules.
- Increase in volume shifts the equilibrium towards larger number of gaseous molecules.

Effect of Catalyst

- Catalyst has no effect on equilibrium, it simply helps to achieve the equilibrium quickly.
- Position of equilibrium and K_c unchanged.
- Provides an alternative pathway with lower activation energy.
- Increases forward and reverse rates to the same extent.
- Catalyst shortens the time to reach equilibrium.

Effect of Temperature Change

- **Endothermic reaction** is favoured with increase in temperature.

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B; \; \Delta H = +ve, K_c = \frac{[B]}{[A]} = \frac{k_f}{k_r}$$

Temp.↑
- Equilibrium shift to right → Absorb heat → Temp. decrease ↓
- $k_f > k_r \rightarrow K_c = \dfrac{k_f}{k_r}$
- More product, less reactant $\rightarrow K_c = \dfrac{[B]}{[A]}$ → $K_c \uparrow$

Temp.↓
- Equilibrium shift to left → Release heat → Temp. increase ↑
- $k_f < k_r \rightarrow K_c = \dfrac{k_f}{k_r}$
- More reactant, less product $\rightarrow K_c = \dfrac{[B]}{[A]}$ → $K_c \downarrow$
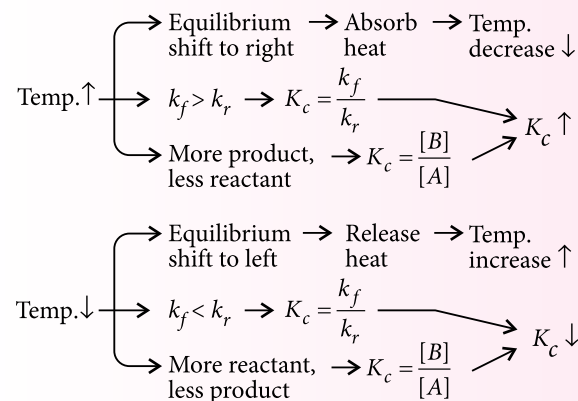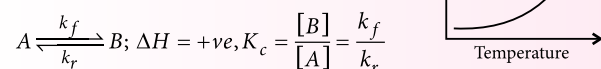
- **Exothermic reaction** is favoured with decrease in temperature.

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B; \; \Delta H = -ve, K_c = \frac{[B]}{[A]} = \frac{k_f}{k_r}$$

Temp.↑
- Equilibrium shift to left → Absorb heat → Temp. decrease ↓
- $k_f < k_r \rightarrow K_c = \dfrac{k_f}{k_r}$
- More reactant, less product $\rightarrow K_c = \dfrac{[B]}{[A]}$ → $K_c \downarrow$

Temp.↓
- Equilibrium shift to right → Release heat → Temp. increase ↑
- $k_f > k_r \rightarrow K_c = \dfrac{k_f}{k_r}$
- More product, less reactant $\rightarrow K_c = \dfrac{[B]}{[A]}$ → $K_c \uparrow$
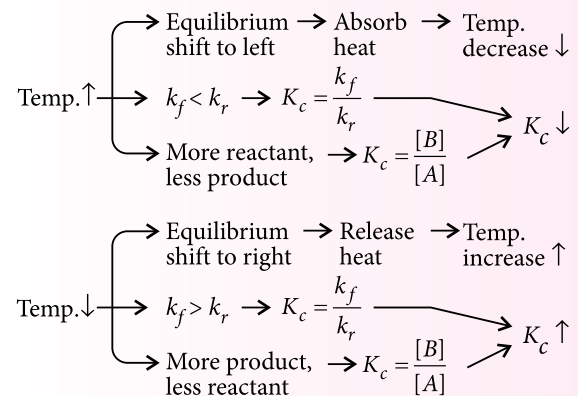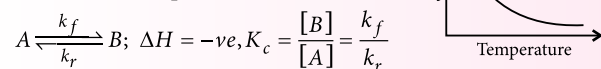
Effect of Inert Gas Addition

- Addition of an inert gas at constant volume has no effect on equilibrium.
- Addition of an inert gas at constant pressure will shift the equilibrium towards larger number of gaseous molecules.

Condition		Effect
$\Delta V = 0, V = $ Constant	$\Delta n = 0, +ve$ or $-ve$	No effect
At constant pressure	$\Delta n = 0$	No effect
	$\Delta n > 0$	Forward shift
	$\Delta n < 0$	Backward shift

I   Aldol Condensation

- In this reaction, an enolate ion (strong nucleophile) reacts with a carbonyl compound to form β-hydroxyaldehyde (aldol) or β-hydroxyketone (ketol) followed by dehydration to give a conjugated enone.
- Aldol condensation provides a good way to form carbon-carbon bond.
- This reaction is diastereoselective because of the way in which two prochiral reagents come together.
- Enolate is an important factor controlling the diastereoselectivity, in many examples *cis*-enolates give *syn*-aldols and *trans*-enolates give *anti*-aldols preferentially.
- Some enolates can only exist as *trans*-enolate because they are derived from cyclic ketones.

II   Reimer—Tiemann Reaction
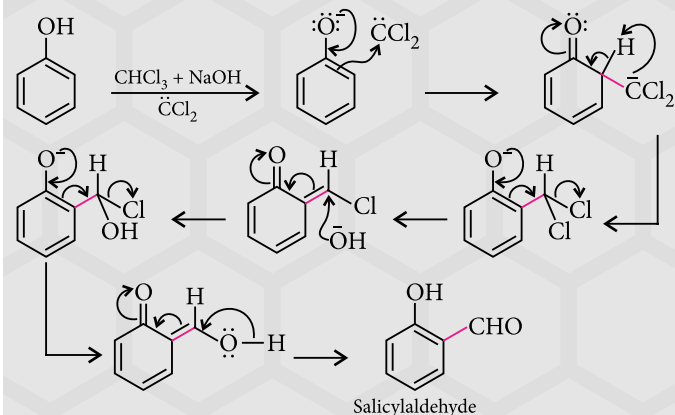
Salicylaldehyde

- Phenol on refluxing with chloroform and aqueous sodium hydroxide at 340 K followed by acid hydrolysis yields salicylaldehyde.
- This reaction is an example of carbene based reactions where it is also considered to be an electrophilic attack on benzene.
- The electrophile is :CCl_2, (dichlorocarbene) which does not add to benzene, but does attack the electron rich aromatic ring of phenol.
- If CCl_4 is used instead of $CHCl_3$, salicylic acid is formed.
- The Reimer—Tiemann reaction is an important way of making *ortho*-substituted phenols, but the yields are often poor.

III   Hoffmann Bromamide Degradation Method

Step - I :

$$R-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \xrightarrow[-HBr]{Br_2/KOH} R-\overset{O}{\overset{\|}{C}}-\ddot{N}HBr$$

Amide   N-Bromoamide

Step - II :

$$R-\overset{O}{\overset{\|}{C}}-\ddot{N}-Br \xrightarrow{\overline{O}H} \left[R-\overset{\overline{O}}{\overset{|}{C}}=N-Br \right] \xrightarrow[-Br^-]{Rearrangement}$$

$$O=C=\ddot{N}-R$$
Alkyl isocyanate

Step - III :

$$R-\ddot{N}=C=O \xrightarrow[Hydrolysis]{KOH} R-\ddot{N}H_2 + K_2CO_3$$
Alkyl isocyanate   1°-Amine
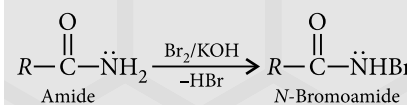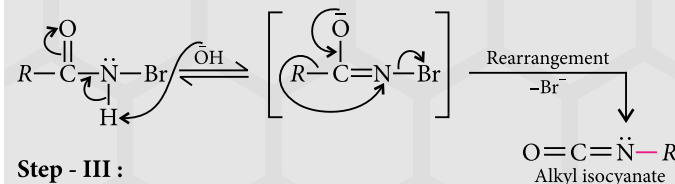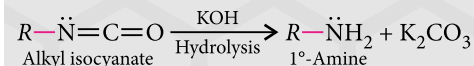
- In this reaction, amide gets converted to primary amine by the action of Br_2 and KOH / NaOH.
- This method is used for stepping down the series as the amine formed contains one carbon atom less than the parent amide.
- This reaction involves the migration of alkyl group from carbonyl in the precursor to nitrogen with the elimination of carbon dioxide.
- This method is limited to amides of the type $RCONH_2$.
- The step that leads to the formation of isocyanate through rearrangement is the slow and the rate determining step.
- The rearrangement proceeds with complete retention of configuration in the migrating group. The migrating group is never completely detached from the substance.

NEET | JEE
ESSENTIALS

Class XII

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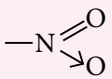
Unit 7	Organic Compounds Containing Nitrogen | Biomolecules

ORGANIC COMPOUNDS CONTAINING NITROGEN

INTRODUCTION

- Nitrogen is an important constituent of many organic compounds. The important classes of organic compounds containing nitrogen as a part of functional group are :
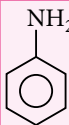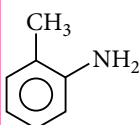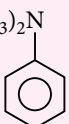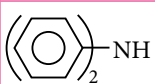
Functional group	Class of compounds
$-NH_2$	Amines
$-C\equiv N$	Cyanides
$-N\equiv C$	Isocyanides
$-N\underset{O}{\overset{O}{\diagdown}}$	Nitro compounds
$-O-N=O$	Nitrites
$-N_2^+X^-$	Diazonium salts

AMINES

- Amines are regarded as derivatives of ammonia in which one, two or all three hydrogen atoms are replaced by alkyl and/or aryl groups.

$$NH_3 \xrightarrow[-H]{+R} RNH_2 \xrightarrow[-H]{+R} R_2NH \xrightarrow[-H]{+R} R_3N \xrightarrow{RX} R_4\overset{+}{N}X^-$$

Ammonia — 1°-Amine — 2°-Amine — 3°-Amine — Quaternary ammonium salt
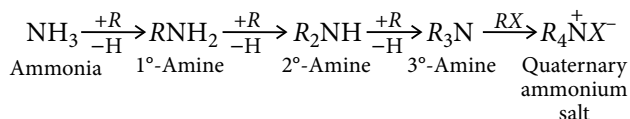
Nomenclature

Aliphatic amine	Common name	IUPAC name
CH_3NH_2	Methylamine	Methanamine
$(CH_3)_2CHNH_2$	Isopropylamine	Propan-2-amine
$CH_3NHC_2H_5$	Ethylmethylamine	N-Methylethanamine
$(CH_3)_3N$	Trimethylamine	N, N-Dimethylmethan-amine

Aromatic amine	Common name	IUPAC name
NH₂ (benzene ring)	Aniline	Benzenamine
CH₃, NH₂ (benzene ring)	o-Toluidine	2-Methylbenzenamine
$(CH_3)_2N$ (benzene ring)	N,N-Dimethylaniline	N, N-Dimethylbenzen-amine
(two benzene rings)₂—NH	Diphenylamine	N-Phenylbenzenamine

Structure

- N-atom in amines is sp^3-hybridised with tetrahedral structure where one position of the tetrahedral is occupied by a lone pair. Thus, the actual geometry is pyramidal with bond angle little less than 109.5°.

Pyramidal shape of trimethylamine

Optical Activity

- Amines containing different substituents on nitrogen are chiral. 2° and 3° amines exhibit optical activity or enantiomerism. However, unlike chiral carbon compounds, most chiral amines cannot be resolved as two enantiomeric forms rapidly interconvert into one another by **nitrogen inversion** or **amine inversion**. This is also known as **flipping**, (resembles an umbrella turning inside out) which occurs very rapidly (rate = 2.3×10^{10} s^{-1}).

Planar transition state

Preparation

Methods of Preparation

Ammonolysis of alkyl halides
(Hoffmann's ammonolysis method)

$$NH_3 \xrightarrow{RX} R - NH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N$$

$\quad$ 1° amine $\qquad$ 2° amine $\qquad$ 3° amine

$$\xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

Quaternary ammonium salt (4°)
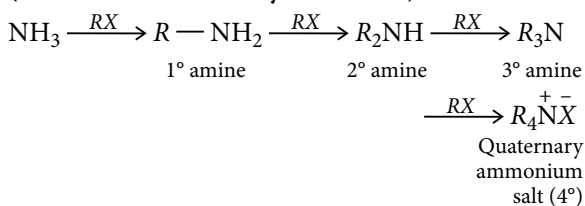
(Reactivity order : $R - I > R - Br > R - Cl$)

Reduction of nitriles
(Mendius reduction)

$$R - C \equiv N \xrightarrow[\text{or Na(Hg)/C}_2\text{H}_5\text{OH}]{\text{H}_2/\text{Raney Ni}} R - CH_2 - NH_2$$

Reduction of amides

$$R - CONH_2 \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) LiAlH}_4} R - CH_2 - NH_2$$
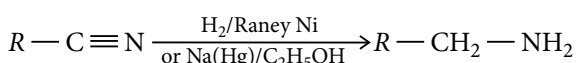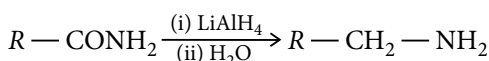
Reduction of nitro compounds
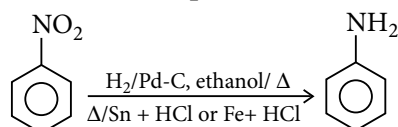
(Fe/HCl is preferred because $FeCl_2$ formed gets hydrolysed to release HCl gas.)

Hoffmann bromamide degradation reaction

$$RCONH_2 + Br_2 + 4KOH \longrightarrow R - NH_2 + K_2CO_3 + 2KBr + 2H_2O$$
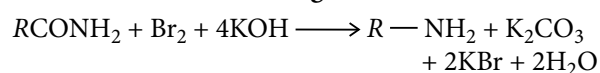
(Migration of alkyl group from carbonyl to nitrogen)

Gabriel phthalimide synthesis
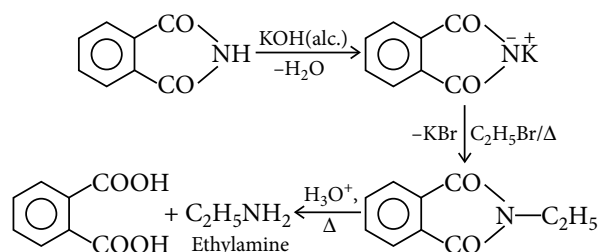
(Only for preparation of aliphatic primary amines)

Schmidt reaction

$$R - COOH \xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{N}_3\text{H}} R - NH_2 + CO_2 + N_2$$
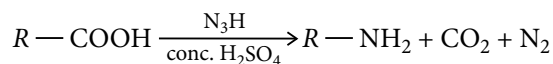
Industrial preparation

$$C_2H_5OH + NH_3 \xrightarrow[\text{Al}_2\text{O}_3]{723 \text{ K}} C_2H_5NH_2 \xrightarrow{C_2H_5OH}$$

$$(C_2H_5)_3N \xleftarrow{C_2H_5OH} (C_2H_5)_2NH$$

(Mixture is separated by fractional distillation)
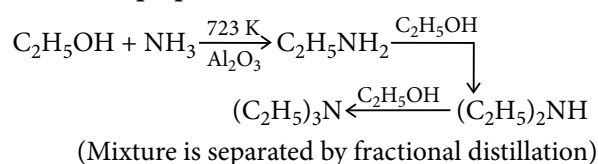
Physical Properties

- Pure amines are almost colourless but develop colour on keeping in air due to oxidation.

- Amines have higher b.pt. than hydrocarbons due to hydrogen bonding but have lower b.pt. than alcohols and carboxylic acids as electronegativity of nitrogen is lower than that of oxygen.

- Lower aliphatic amines are soluble in water due to hydrogen bonding, solubility decreases with increase in molar mass of amines.

Basic Character

Aliphatic amines :

- All aliphatic amines are stronger bases than ammonia due to $+I$ effect of alkyl groups.

- In aqueous solutions, the basicity of methylamines follows the order : $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$ (*i.e.,* 2° > 1° > 3°) but for ethylamines and all other higher amines basicity follows the order : $R_2NH > R_3N > RNH_2$ (*i.e.,* 2° > 3° > 1°).

- In non-aqueous solvents (*e.g.,* chlorobenzene) and in gaseous phase, the order of basicity is : 3° amine > 2° amine > 1° amine.

- Greater the value of K_b or smaller the value of pK_b, stronger is the base.

Chemical Properties

Aliphatic amines :
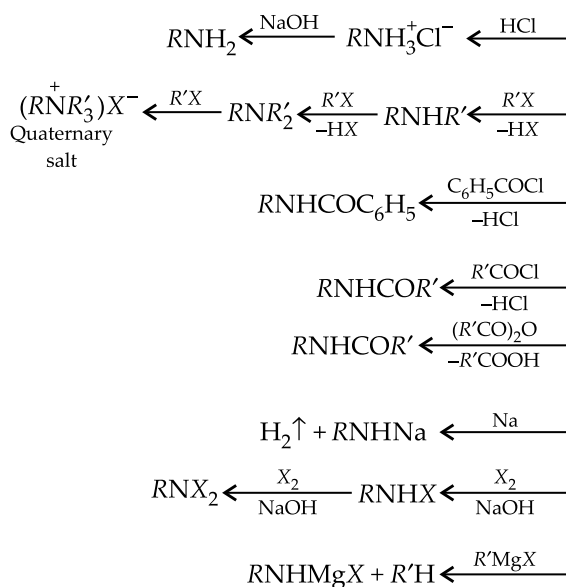
Aromatic amines :

- All aromatic amines are weaker bases than ammonia due to the $-I$ effect of aryl groups.

- Electron donating groups such as $-CH_3$, $-OCH_3$, $-NH_2$, etc., increase the basicity while electron withdrawing groups such as $-NO_2$, $-CN$, $-SO_3H$, $-COOH$, halogens, etc. decrease the basicity of amines. The effect of these substituents is more pronounced at *p*-positions than at *m*-positions.

- *o*-Substituted anilines are weaker bases than aniline regardless of the nature of the substituent whether electron donating or electron withdrawing. This is called *ortho*-effect.
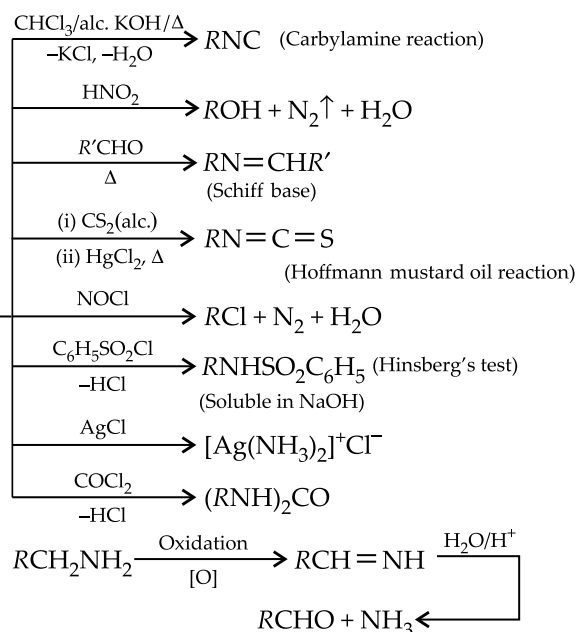
Aniline :
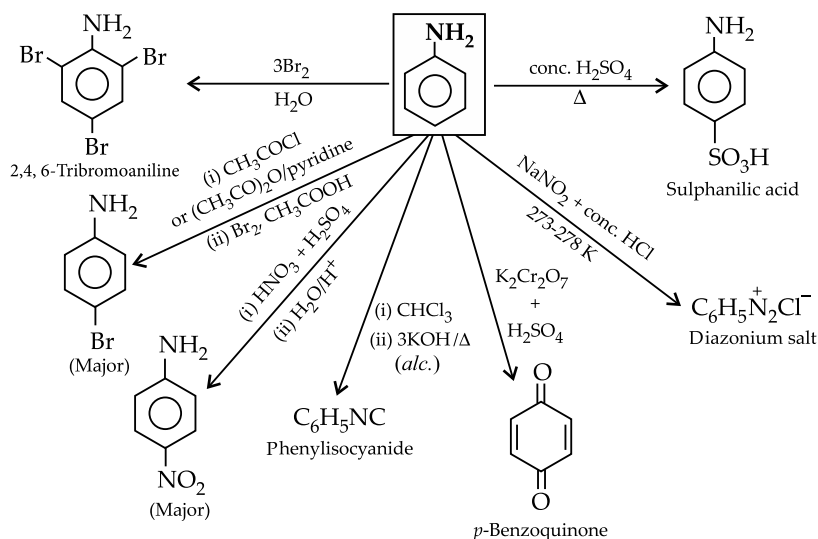
Identification of 1°, 2°, 3° Amines

Test	Primary amines	Secondary amines	Tertiary amines
Action of alkyl halides	Combine with three molecules of alkyl halides to form the quaternary salts.	Combine with two molecules of alkyl halides to form the quaternary salts.	Combine with one molecule of alkyl halide to form the quaternary salts.
Reaction with acid chlorides and acid anhydrides	Form monoalkyl substituted amide.	Form dialkyl substituted amide.	No reaction
Reaction with nitrous acid	Form mixture of alcohols and alkenes with evolution of nitrogen gas.	Form yellow oily nitrosoamine characterised by Liebermann's nitroso test.	Form nitrite salt which on decomposition gives mixture of nitrosoamine, alcohols and aldehydes or ketones.
Hinsberg's test with benzenesulphonyl chloride ($C_6H_5SO_2Cl$)	Form monoalkyl benzenesulphonamide which on treatment with alkali gives a water soluble salt.	Form dialkylbenzene-sulphonamide which does not dissolve in alkali.	No reaction

DIAZONIUM SALTS

- General formula of arenediazonium salts is :

$$Ar \overset{+}{-} N_2 \, X^-$$

  Aryl   Diazo   Anion (Cl^-, Br^-, HSO_4^-, BF_4^-, etc.)
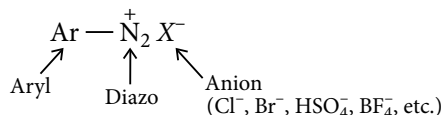
- Primary aliphatic amines form highly unstable alkanediazonium salts.

- Arenediazonium salts are more stable than alkanediazonium salts. The stability of arenediazonium ion is explained on the basis of resonance.

Method of Preparation (Diazotisation)

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\ K}$$

$$C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$
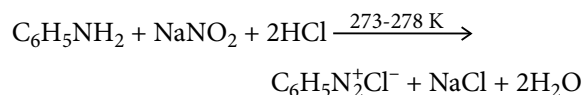
- Prepared in situ and used immediately after preparation.

Physical Properties

- Colourless crystalline solid, soluble in water.
- Stable only between 273-278 K.

Chemical Properties

Reactions involving displacement of diazo group :

$$\boxed{ArN_2^+ X^-}$$

- $\xrightarrow{KI} ArI$
- $\xrightarrow{HBF_4} ArN_2^+BF_4^- \begin{cases} \xrightarrow[\Delta]{} ArF \text{ (Balz-Schiemann reaction)} \\ \xrightarrow[\Delta]{NaNO_2/Cu} ArNO_2 \end{cases}$
- $\xrightarrow[> 278\ K]{H_2O} ArOH$
- $\xrightarrow[NaOH,\ \Delta]{C_6H_6} Ar-C_6H_5$ (Diphenyl) (Gomberg-Bachmann reaction)
- $\xrightarrow[Cu_2O,\ \Delta]{NaNO_2} ArNO_2$
- $\xrightarrow[Cu^+]{H_3PO_2/H_2O} ArH$
- $\xrightarrow[\Delta]{CH_3CH_2OH} ArH$
- $\xrightarrow[\substack{CuCl/HCl \\ or \\ CuBr/HBr \\ or \\ CuCN/KCN}]{} \left.\begin{array}{l} ArCl \\ or \\ ArBr \\ or \\ ArCN \end{array}\right\}$ Sandmeyer reaction
- $\xrightarrow[\substack{Cu/HCl \\ or \\ Cu/HBr \\ or \\ Cu/KCN}]{} \left.\begin{array}{l} ArCl \\ or \\ ArBr \\ or \\ ArCN \end{array}\right\}$ Gattermann reaction
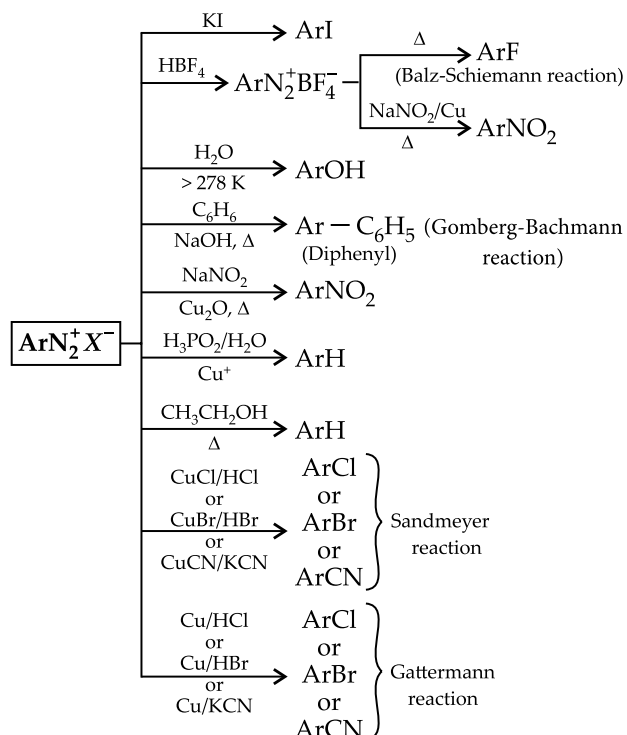
Reactions involving retention of diazo group :

$$\boxed{ArN_2^+ X^-}$$

Coupling reactions:
- $\xrightarrow[pH = 9\text{-}10,\ 0\text{-}5°C]{C_6H_5OH/OH^-} ArN = NC_6H_4OH$
- $\xrightarrow[pH = 4\text{-}5,\ 0\text{-}5°C]{C_6H_5NH_2/H^+} ArN = NC_6H_4NH_2$
- $\xrightarrow{C_6H_5N(CH_3)_2} ArN = NC_6H_4N(CH_3)_2$
- $\xrightarrow{\beta\text{-Naphthol, NaOH}} ArN = N-\text{(naphthol ring)}$ Azo dye

Reduction:
- $\xrightarrow[HCl]{SnCl_2} ArNH-NH_2$ Arylhydrazine
- $\xrightarrow[HCl]{Zn} ArNH-NH_2 \xrightarrow[HCl]{Zn} ArNH_2$
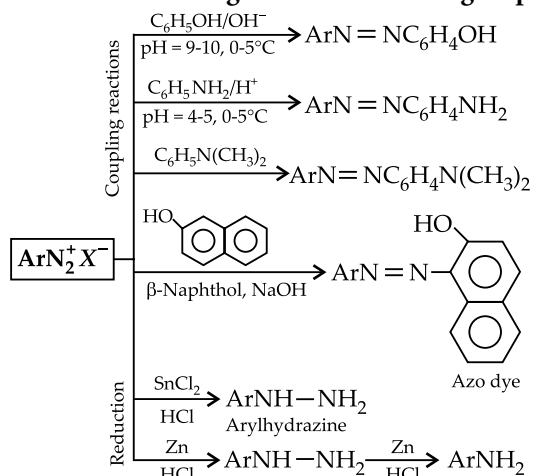
Uses

- There are large number of groups which can be attached to aromatic rings by the replacement of diazo group.
- Aryl fluorides and iodides cannot be prepared by direct halogenation but can be easily prepared by diazonium salts.
- Coupling reactions of diazonium salts are highly important in dye industry.

BIOMOLECULES

CARBOHYDRATES

- The polyhydroxy aldehydes or polyhydroxy ketones or substances which yield such products on hydrolysis, are known as saccharides. Their general formula is $C_x(H_2O)_y$ where, x and y can be 3, 4, 5, ... etc. They occur naturally in animal and plant kingdom and are composed of carbon, hydrogen and oxygen only.

Classification

Carbohydrates — Based on taste →

- **Non-sugar** (tasteless) → **Polysaccharides** : Give large number of monosaccharides on hydrolysis. General formula, $(C_6H_{10}O_5)_n$, where $n = 100$ to 3000. e.g., starch, cellulose, glycogen, etc.

- **Sugar** (sweet in taste)
  - Based on reducing property →
    - **Reducing :** Reduces Fehling's solution and Tollens' reagent. Contains free aldehyde or ketone groups. e.g., maltose, glucose, lactose, fructose, etc.
    - **Non-reducing :** Aldehyde and ketone groups are bonded. e.g., sucrose.
  - Based on hydrolysis →
    - **Monosaccharides**
      – Cannot be hydrolysed.
      – General formula, $(CH_2O)_n$; $n = 3-7$
      - Based on functional groups →
        - **Aldoses** (aldehyde group present) e.g., glucose
        - **Ketoses** (ketone group present) e.g., fructose
    - **Oligosaccharides**
      – Give 2 to 10 monosaccharides.
      – General formula, $(C_6H_{10}O_5)_n$; $n = 2-10$
      - Based on number of monosaccharides obtained →
        - **Disaccharides** e.g., sucrose, maltose
        - **Trisaccharides** e.g., raffinose
        - **Tetrasaccharides** e.g., stachyrose

MONOSACCHARIDES

Glucose ($C_6H_{12}O_6$)

- An aldohexose as it contains six carbon atoms and aldehydic group.

- **Structure :** During hemiacetal formation, C_5—OH of glucose combines with the C_1-aldehydic group. As a result, C_1 becomes chiral or asymmetric and thus, has two possible arrangements of H and OH groups around it. So, D-glucose exists in two stereoisomers $i.e.$, α-D-glucose and β-D-glucose. Such a pair of stereoisomers which differs in conformation only around C_1 are called anomers.

Fischer projection of D-(+)-Glucose

α-D-(+)-Glucopyranose   β-D-(+)-Glucopyranose

Haworth structures
(Anomers)

- **Preparation :**

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

Sucrose   Glucose   Fructose

(*Laboratory method*)

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393 \text{ K, 2-3 atm}]{H^+/\Delta} nC_6H_{12}O_6$$

Starch or Cellulose   Glucose

(*Commercial method*)

- **Open chain structure on the basis of following evidences :**

$CH_3\text{---}(CH_2)_4\text{---}CH_3$
n-Hexane
$\xleftarrow{HI, \Delta}$ (six carbon atoms are linked in a straight chain)

$\begin{matrix} CH=NOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix}$ Glucose oxime $\xleftarrow{NH_2OH}$ (confirms the presence of a carbonyl group)

$\begin{matrix} CH{<}^{CN}_{OH} \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix}$ Glucose cyanohydrin $\xleftarrow{HCN}$ (confirms the presence of a carbonyl group)

$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \textbf{Glucose} \end{matrix}$

$\xrightarrow{[O]/Br_2\text{-water}}$ (indicates aldehydic group) $\begin{matrix} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix}$ Gluconic acid

$\xrightarrow{5(CH_3CO)_2O}$ (confirms the presence of five —OH groups) $\begin{matrix} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{matrix}$ Glucose pentaacetate

$\xrightarrow{HNO_3/\text{Oxidation}}$ (indicates the presence of a primary alcoholic (—OH) group) $\begin{matrix} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{matrix}$ Glucaric acid or Saccharic acid

- **Chemical reactions :**

Reduction:

$\begin{matrix} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix}$ D-Sorbitol $\xleftarrow{Na\text{-}Hg}$

Oxidation :

$Cu_2O\downarrow$ + Gluconic acid
Red ppt.
$\xleftarrow{\text{Fehling's solution}}$

$2Ag\downarrow$ + Gluconic acid
Silver mirror
$\xleftarrow[Ag_2O]{\text{Tollens' reagent}}$

Due to —CHO group ← **Glucose** → Due to —OH group

$\begin{matrix} CHO \\ | \\ (CHCl)_4 \\ | \\ CH_2Cl \end{matrix}$ Pentachloroglucose (Glucose pentachloride) $\xleftarrow{PCl_5}$

$\xrightarrow[\text{Pyridine}]{CH_3COCl}$ $\begin{matrix} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{matrix}$ Glucose pentaacetate (mixture of α- and β-forms)

$\xrightarrow[\text{dry HCl gas}]{CH_3OH}$

α-D-Methylglucoside   +   β-D-Methylglucoside

Fructose ($C_6H_{12}O_6$)

- A ketohexose as it contains six carbon atoms and ketonic group.
- **Structure :**

$$CH_2OH$$
$$C=O$$
HO ———— H
H ———— OH
H ———— OH
$$CH_2OH$$

D-(–)-Fructose

α-*D*-(–)-Fructofuranose   β-*D*-(–)-Fructofuranose

Haworth structures
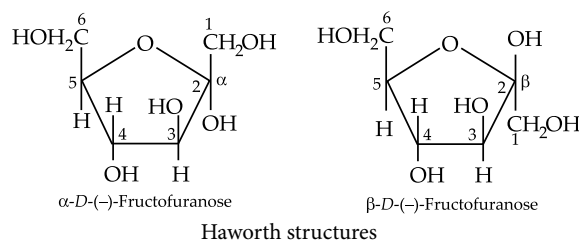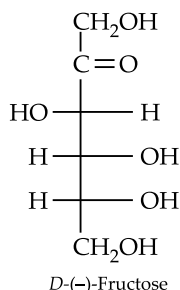
Mutarotation

- The spontaneous change in specific rotation of an optically active compound with time, to an equilibrium value, is called mutarotation.

α-*D*-(+)-Glucose $\rightleftharpoons$ Equilibrium $\rightleftharpoons$ β-*D*-(+)-Glucose
mixture
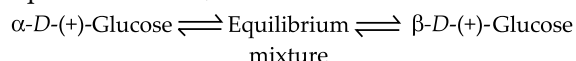
$$[\alpha]_D^{298\ K} = +112° \qquad [\alpha]_D^{298\ K} = +52.5° \qquad [\alpha]_D^{298\ K} = +19.2°$$

DISACCHARIDES

Maltose

- Maltose is composed of two α-*D*-glucose units in which C1 of one glucose is linked to C4 of another glucose unit.
- Reducing sugar.

α-*D*-Glucose   1,4-α-Glycosidic   α-*D*-Glucose
(Non-reducing unit)   linkage   (Reducing unit)
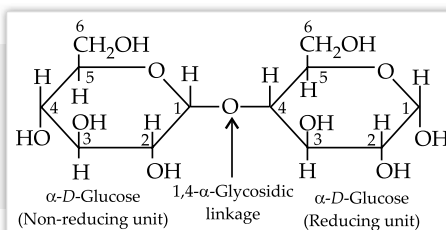
Lactose

- Known as milk sugar.
- It is composed of β-*D*-galactose and β-*D*-glucose in which linkage is between C1 of galactose and C4 of glucose.
- Reducing sugar.

β-*D*-Galactose   β-Glycosidic   β-*D*-Glucose
(Non-reducing unit)   linkage   (Reducing unit)
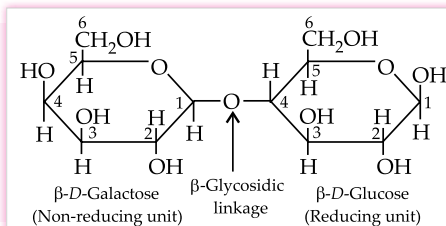
Sucrose

- On hydrolysis gives equimolar mixture of α-*D*-(+)-glucose and β-*D*-(–)-fructose.
- Glycosidic linkage between C1 of α-glucose and C2 of β-fructose.
- Non-reducing sugar.

α-*D*-Glucose   β-*D*-Fructose

Glycosidic linkage
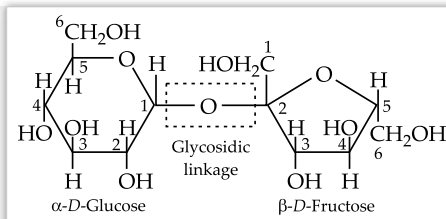
INFO SHOTS

Folding biomolecule model !

Proteins are fundamental macromolecules for life, with a diversity of functions. To perform these functions, what matters is the layout of these proteins secondary branches. Scientists have developed a theoretical method to calculate the most stable deposition that biomolecules try to adopt when they are together, or in close contact in cases where the bond is weak.

POLYSACCHARIDES

Starch

- Polymer of α-*D*-glucose units and consists of two components amylose and amylopectin.
- Amylose is water soluble, long unbranched chain of α-*D*-(+)-glucose units held by 1,4-α-glycosidic linkage.
- Amylopectin is water insoluble, branched chain polymer of α-*D*-glucose units held by 1,4-α-glycosidic linkage whereas branching occurs by 1,6-α-glycosidic linkage.

Glycogen

- Known as animal starch because its structure is similar to amylopectin and is more highly branched.

Cellulose

- Most abundant organic substance in plant kingdom.
- Straight chain polysaccharide of β-*D*-glucose units joined together by 1,4-β-glycosidic linkage.
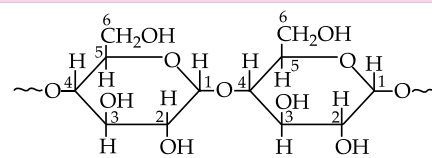
Amylose
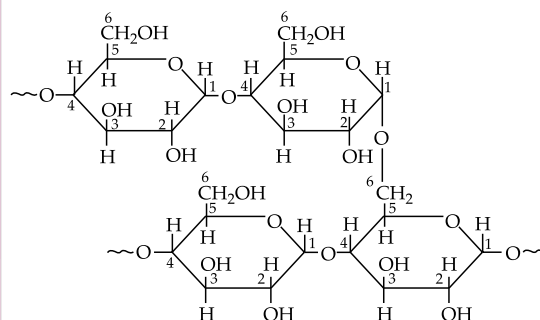
Amylopectin
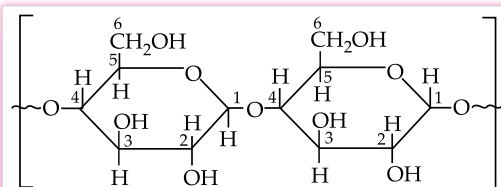
Cellulose

PROTEINS

- Proteins are condensation polymers of α-amino acids which are essential for the growth and maintenance of life.

$$R - \overset{\overset{\displaystyle NH_2}{\underset{\alpha}{|}}}{\underset{\underset{\displaystyle H}{|}}{C}} - COOH \quad (R = \text{side chain})$$
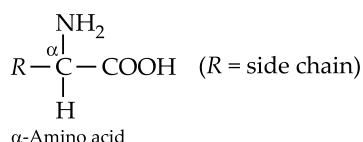
α-Amino acid

Classification of Amino Acids

- On the basis of relative number of amino ($-NH_2$) and carboxyl ($-COOH$) groups in the molecule :
    - **Neutral :** No. of $-COOH$ groups = No. of $-NH_2$ groups *e.g.*, glycine, alanine, valine, etc.
    - **Acidic :** No. of $-COOH$ groups > No. of $-NH_2$ groups *e.g.*, aspartic acid, asparagine, glutamic acid, etc.
    - **Basic :** No. of $-NH_2$ groups > No. of $-COOH$ groups *e.g.*, lysine, arginine, histidine, etc.

- On the basis of their synthesis in the body :
    - **Essential amino acids :** Cannot be synthesised in the body and must be obtained through diet *e.g.*, valine, leucine, lysine, isoleucine, arginine, phenylalanine, methionine, tryptophan, threonine and histidine.
    - **Non-essential amino acids :** Can be synthesised in the body. *e.g.*, glycine, alanine, glutamic acid, aspartic acid, etc.

Properties of Amino Acids

- In aqueous solution, the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as zwitter ion.

$$R - \underset{\underset{\displaystyle :NH_2}{|}}{CH} - \underset{\underset{\displaystyle O}{\|}}{C} - OH \rightleftharpoons R - \underset{\underset{\displaystyle ^+NH_3}{|}}{CH} - \underset{\underset{\displaystyle O}{\|}}{C} - O^-$$

Zwitter ion

- **Isoelectric point :** The pH at which no net migration of amino acid under the influence of applied electric field, is called isoelectric point.

- They exist in both *D*- and *L*-forms. Most naturally occurring α-amino acids have *L*-configuration.

- **Peptide bond :** During amide formation, the bond formed between two amino acids by the elimination of a water molecule, is called peptide linkage or peptide bond.

$$-\underset{\underset{O}{\|}}{C}-\boxed{OH + H}-\underset{\underset{H}{|}}{N}- \xrightarrow{-H_2O} -\underset{\underset{O\ \ H}{\underbrace{\|\ \ |}}}{C}-N-$$

Peptide bond
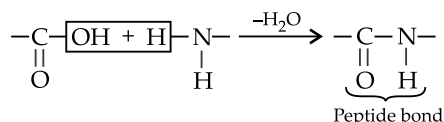
- Peptides are further divided into *di*, *tri*, *tetra* depending upon the number of amino acids combined.

- **Polypeptides :** Product which are formed by more than ten amino acids are known as polypeptides.

- A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u, is called a protein.

Classification of Proteins

- **Fibrous proteins :** In fibrous proteins, polypeptide chains run parallel and held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin (in hair, wool) and myosin (in muscles).

- **Globular proteins :** In globular proteins, polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, *e.g.*, insulin and albumins.

Structure of Proteins

- **Primary structure :** It refers to the specific sequence of α-amino acids held together in a protein.
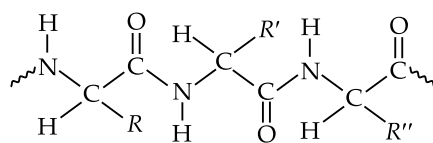
- **Secondary structure :** Due to folding or coiling of the peptide chain, these are of two types :
  - α-**helix :** Coils are stabilized by hydrogen bonds between carbonyl oxygen of first amino acid to amide nitrogen of fourth amino acid.
  - β-**pleated sheet structure :** Intermolecular H-bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains, giving a β-pleated sheet structure *e.g.*, silk fibroin.

Individual polypeptide chains →

α-helix   β-pleated sheet
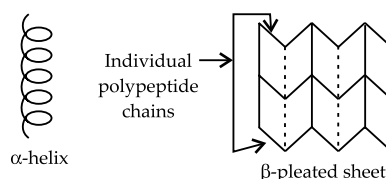
- **Tertiary structure :** Refers to overall folding of the polypeptide chains or its complete 3-D structure.

- **Quaternary structure :** Refer to spatial arrangement of two or more polypeptide chains with respect to each other.

Denaturation of Proteins

- When a protein in its native form, is subjected to physical changes (like temperature) or chemical changes (like pH), the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

- The denaturation causes change in secondary and tertiary structures but primary structure remains intact *e.g.*, coagulation of egg white on boiling, curdling of milk, formation of cheese, etc.

ENZYMES

- Enzymes are biocatalysts produced by living cells which catalyse the following biochemical reactions in living organisms :

Enzyme	Reaction catalysed
Maltase	Maltose → Glucose + Glucose
Lactase	Lactose → Glucose + Galactose
Amylase	Starch → $n \times$ Glucose
Invertase	Sucrose → Glucose + Fructose
Pepsin	Proteins → α-Amino acids
Trypsin	Proteins → α-Amino acids
Urease	Urea → $CO_2 + NH_3$
Nuclease	DNA, RNA → Nucleotides

Properties

- Required in very small amount.
- They reduce magnitude of activation energy.
- They are highly specific.
- They work at specific pH.
- They work well at moderate temperature.

Mechanism

- Binding of the enzyme (E) to substrate (S) to form a complex called the enzyme-substrate complex.

$$E + S \longrightarrow ES$$
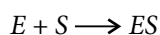
- Formation of complex of enzyme and product.

$$ES \longrightarrow EP$$
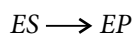
- Release of product from the enzyme-product complex.

$$EP \longrightarrow E + P$$
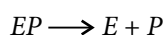
VITAMINS

- Required for normal growth and maintenance of the body. They cannot be produced in the body and hence must be supplied in diet.

Classification

- **Water soluble vitamins :** These are water soluble and must be supplied regularly in diet. *e.g.*, vitamin - B_1, B_2, B_6, B_{12} and C.
- **Fat soluble vitamins :** These are soluble in fat and oils and stored in liver and adipose tissues. *e.g.*, vitamin - A, D, E and K.

Vitamin name	Chemical name	Solubility	Sources	Deficiency disease
Vitamin A	Retinol	Fat	Milk, butter, eggs, fish, cod liver oil, green vegetables, etc.	Night-blindness, xerophthalmia.
Vitamin B_1	Thiamine	Water	Pulses, nuts, cereals, yeast, egg yolk, green vegetables, etc.	Beri-beri, loss of appetite.
Vitamin B_2	Riboflavin	Water	Milk, green vegetables, egg white, meat, liver, kidney, etc.	Anaemia, inflammation of tongue, dermatitis, cheilosis.
Vitamin B_6	Pyridoxine	Water	Rice bran, whole cereal, yeast, fish, meat, eggs, etc.	Affects central nervous system, weakness, convulsions, etc.
Vitamin H	Biotin	Water	Milk, yeast, liver, kidney, etc.	Dermatitis.
Vitamin B_2	Cyanocobalamin	Water	Eggs, milk, liver of ox, sheep, fish, etc.	Pernicious anaemia.
Vitamin C	Ascorbic acid	Water	Citrus fruits, chillies, sprouted pulses, etc.	Pyorrhea, scurvy (bleeding of gums).
Vitamin D (a mixture of vitamins D_1 and D_3)	Ergocalciferol and cholecalciferol	Fat	Butter, milk, eggs, fish liver oil, liver and meat etc.	Rickets (bending of bones) and osteomalacia.
Vitamin E	Tocopherol	Fat	Wheat germ oil, milk, nuts, peanut oil, cotton seed oil, eggs, fish, etc.	Loss of fertility in males, muscles degeneration.
Vitamin K	Phylloquinone	Fat	Leafy vegetables like cabbage, spinach, etc.	Haemorrhages and lengthens time of blood clotting.

NUCLEIC ACIDS

- Nucleic acids are the polymers of nucleotides present in nucleus of all living cells and play an important role in transmission of the hereditary characteristics and biosynthesis of proteins.

Classification

Nucleic acids → Deoxyribonucleic acid (DNA), Ribonucleic acid (RNA)
RNA → Messenger RNA (*m*-RNA), Ribosomal RNA (*r*-RNA), Transfer RNA (*t*-RNA)
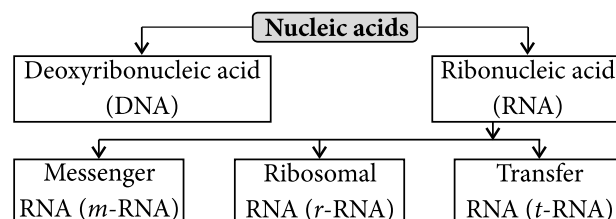
Structure

- A unit formed by attachment of a base to 1′ position of sugar is known as nucleoside. When nucleoside is linked to phosphoric acid at 5′ position of sugar moiety, a nucleotide is formed.
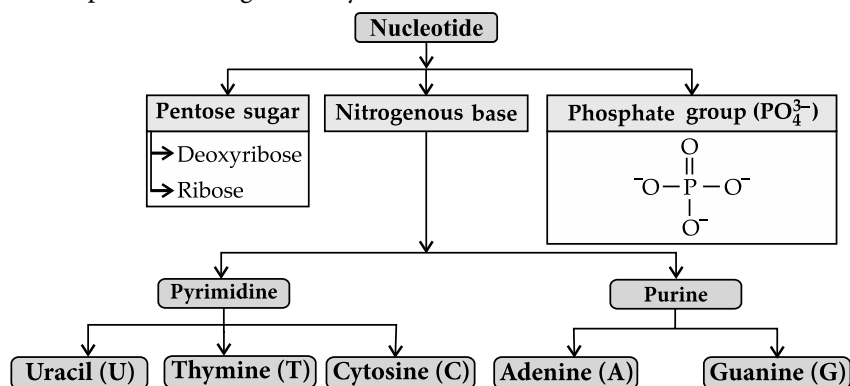
- Nucleotides are joined together by phosphodiester linkages between 5′ and 3′ carbon atoms of pentose sugar.

Nucleoside
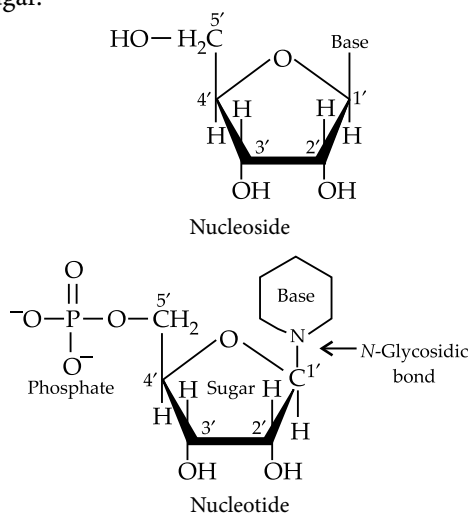
Nucleotide

- **Primary structure :** Refers to the sequence of nucleotides in the chain of nucleic acid.
- **Secondary structure :** Two strands of polynucleotides coil around each other in the form of double helix. James Watson and Francis Crick gave a double strand helix structure for DNA.
- **Chargaff's rule :** Amount of purine bases is always equal to pyrimidine bases. Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand. Adenine (A) pairs with thymine (T) through two H-bonds (A = T) and guanine (G) pairs with cytosine (C) through three H-bonds (G ≡ C).
  In case of RNA, adenine (A) pairs with uracil (U), (A = U).

Differences between DNA and RNA

Components	DNA	RNA
Sugar	2-deoxy-*D*-(–) ribose	*D*-(–)ribose
Pyrimidine base	Cytosine and thymine	Uracil and cytosine
Structure	Double stranded α-helix	Single stranded α-helix
Replication	Possible	Not possible

Biological Functions
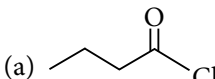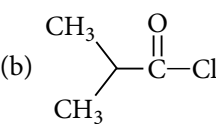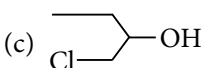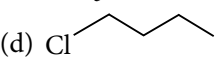
- **Replication :** Single DNA molecule produces two identical copies of itself.
- **Protein synthesis :** It is carried out by RNA molecules in two steps :
  - **Transcription :** Synthesis of RNA from DNA in the cytoplasm of the cell.
  - **Translation :** Protein synthesis by RNA molecules.

DNA Fingerprinting

- Every individual has unique fingerprints.
- The unique fingerprints are due to unique sequences of bases on DNA for every person.
- The technique for identifying individual person based upon the uniqueness of their DNA pattern is called DNA fingerprinting.
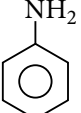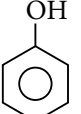
SPEED PRACTICE

1. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is
   (a) diethylamine   (b) ethylamine
   (c) aniline   (d) methylamine.

2. In the reaction,

$$C_4H_7OCl \xrightarrow{NH_3} \underset{(X)}{C_4H_9ON} \xrightarrow[KOH]{Br_2} CH_3CH_2CH_2NH_2$$

   compound (X) is

   (a) (structure: CH₃CH₂CH₂—C(=O)—Cl)

   (b) (structure: (CH₃)₂CH—C(=O)—Cl)

   (c) (structure: Cl—CH(CH₃)—OH)

   (d) (structure: Cl—CH₂CH₂CH₂—CHO)

3. For 'invert sugar', the correct statement(s) is(are) (Given : specific rotations of (+)-sucrose, (+)-maltose, L-(–)-glucose and L-(+)-fructose in aqueous solution are +66°, +140°, –52° and +92° respectively)
   (a) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose
   (b) 'invert sugar' is an equimolar mixture of D-(+)-glucose and D-(–)-fructose
   (c) specific rotation of 'invert sugar' is –20°
   (d) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products.
   [JEE Advanced 2016]

4. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is
   (a) 5   (b) 4   (c) 6   (d) 2

5. Identify the correct statement about lactose.
   (a) It consists of one galactose and one glucose unit.
   (b) Mutarotation is not possible.
   (c) Anomeric carbon of galactose is attached to carbon-1 of glucose which is β-1, 4-glycosidic bond.
   (d) All of the above.

6. Which of the following reactions is appropriate for converting acetamide to methanamine?
   (a) Hoffmann hypobromamide reaction
   (b) Stephen's reaction
   (c) Gabriel phthalimide synthesis
   (d) Carbylamine reaction   **[NEET 2017]**

7. The pH value of a solution at which a polar amino acid does not migrate under the influence of an electric field is called
   (a) isoelectronic point   (b) isoelectric point
   (c) neutralisation point   (d) none of these.

8. The structure of intermediate acetyl nitrene is
   (a) $CH_3—CO—\overset{+}{N}:$ (b) $CH_3—CO—\overset{-}{N}:$
   (c) $CH_3—CO—\underset{..}{N}:$ (d) $CH_3—CO=N:$

9. In hypobromite reaction of amide, carbonyl carbon atom is lost as
   (a) CO (b) CO_2
   (c) CO_3^{2-} (d) none of these.

10. In which of the following sequences of reactions the end product does not exhibit tautomerism?
    (a) $CH_3CH_2NH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$
    (b) $(CH_3)_2CHNH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$
    (c) $(CH_3)_3CNH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$
    (d) $CH_3CH(NH_2)C_2H_5 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$

11. The primary structure of polypeptide is determined by
    (a) the number of disulphite bonds in the polypeptide
    (b) the number of amino acids in the polypeptide
    (c) the order of amino acids in the polypeptide
    (d) the length of the polypeptide.

12. When a 2° aromatic amine hydrochloride is heated, it leads to the formation of 1° aromatic amine hydrochloride. The reaction is known as
    (a) Hoffmann degradation
    (b) Fries rearrangement
    (c) Hoffmann—Martius rearrangement
    (d) None of the above.

13. The correct statement regarding RNA and DNA, respectively is
(a) the sugar component in RNA is a arabinose and the sugar component in DNA is ribose
(b) the sugar component in RNA is 2′-deoxyribose and the sugar component in DNA is arabinose
(c) the sugar component in RNA is arabinose and the sugar component in DNA is 2′-deoxyribose
(d) the sugar component in RNA is ribose and the sugar component in DNA is 2′-deoxyribose.

[NEET Phase-I 2016]

14. A compound (X) has the molecular formula C_3H_7NO. With Br_2 and KOH, (X) gives (Y). (Y) responds to mustard oil reaction. (Y) upon treatment with HNO_2 evolves N_2 and gives an alcohol (Z) which gives iodoform test. (X) is likely to be
(a) $C_2H_5CONH_2$
(b) $CH_3COCH_2NH_2$
(c) CH_3COONH_4
(d) $CH_3CONHCH_3$

15. Which of the following will yield phenylhydrazine hydrochloride?
(a) Benzene and hydrazine
(b) Hydrazine and HCl
(c) Benzenediazonium chloride and $SnCl_2$/HCl
(d) Nitrobenzene and $SnCl_2$/HCl

16. When $C_6H_5N_2Cl$ is reduced with H_3PO_2, the product is

(a) NH_2 (substituted benzene)
(b) benzene
(c) OH (substituted benzene)
(d) $NHNH_2$ (substituted benzene)

17. The incorrect statement among the following is
(a) α-D-glucose and β-D-glucose are anomers
(b) the pentaacetate of glucose does not react with hydroxylamine
(c) cellulose is a straight chain polysaccharide made up of only β-D-glucose units
(d) α-D-glucose and β-D-glucose are enantiomers.

[JEE Main Online 2017]

18. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture, HNO_3 acts as a/an
(a) base
(b) acid
(c) reducing agent
(d) catalyst.

19. Ethyl isocyanide on hydrolysis in acidic medium generates
(a) ethanoic acid and ammonium salt
(b) methylamine salt and ethanoic acid
(c) ethylamine salt and methanoic acid
(d) propanoic acid and ammonium salt.

20. The charring product when glucose is heated with conc. H_2SO_4 is due to
(a) oxidation
(b) reduction
(c) dehydration
(d) dehydrogenation.

21. The correct statement regarding the basicity of arylamines is
(a) arylamines are generally more basic than alkylamines because of aryl group
(b) arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is sp-hybridised
(c) arylamines are generally less basic than alkylamines because the nitrogen lone pair electrons are delocalised by interaction with the aromatic ring π-electron system
(d) arylamines are generally more basic than alkylamines because the nitrogen lone pair electrons are not delocalised by interaction with the aromatic ring π-electron system.

[NEET Phase-II 2016]

22. Which statement is not true for describing enzymes?
(a) They are polypeptides.
(b) There are glycosidic linkages between the molecules.
(c) They are specific for a particular reaction.
(d) They catalyze biological reactions.

23. What is the end product in the following sequence of reactions :
$$\text{Acetamide} \xrightarrow[\text{Heat}]{P_2O_5} A \xrightarrow[\text{Zn/HCl}]{[H]} B \text{ ?}$$
(a) Methylamine
(b) Ethylamine
(c) Methyl isocyanide
(d) Ammonium acetate

24. When diethylamine is shaken with the cold solution of $NaNO_2$/HCl the product formed will be
(a) $(C_2H_5)_2NNO$
(b) $C_2H_5NO_2$
(c) $(C_2H_5)_2\overset{+}{N}H_2NO_2^-$
(d) C_2H_5OH

25. The pairs of optical isomers which differ in the configuration only around C-1 atom are called
(a) enantiomers
(b) anomers
(c) epimers
(d) diastereomers.

26. In the reaction,

the product (E) is

(a), (b), (c)

(d) H_3C—⟨O⟩—⟨O⟩—CH_3　　**[JEE Main 2015]**
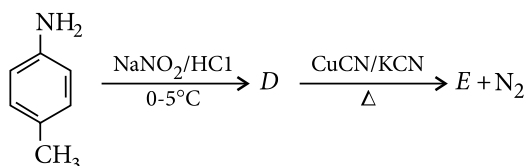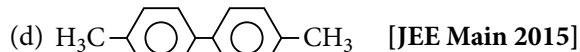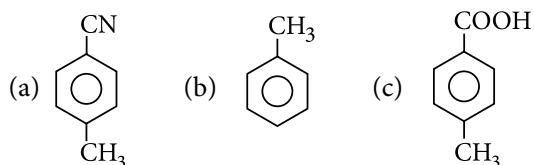
27. Deep blue colour formed by addition of copper (II) sulphate solution to ethylamine is due to formation of
(a) free Cu^{2+} ions in solution
(b) $(NH_4)_2SO_4$
(c) $[Cu(C_2H_5NH_2)_4]^{2+}$ ions
(d) $Cu(OH)_2$

28. The "N" which does not contribute to the basicity

for the compound

 is
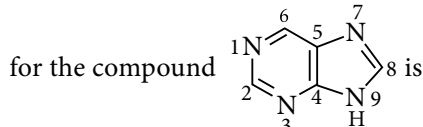
(a) N 9　　(b) N 3　　(c) N 1　　(d) N 7
[JEE Main Online 2016]

29. The acid used for the determination of molecular weights of amines is
(a) H_2PtCl_6　　　　(b) picric acid
(c) $HAuCl_4$　　　　(d) H_2SO_4

30. The configuration of the C-2 epimer of *D*-glucose is
(a) 2*R*, 3*S*, 4*R*, 5*S*　　(b) 2*S*, 3*S*, 4*R*, 5*R*
(c) 2*S*, 3*R*, 4*S*, 5*R*　　(d) 2*R*, 3*S*, 4*R*, 5*R*

SOLUTIONS

1. **(a) :** Secondary amines on treatment with HNO_2 gives yellow oily nitrosoamine.

$$R_2NH + HONO \rightarrow R_2NNO + H_2O$$
　　　　　　　　　　Nitrosoamine
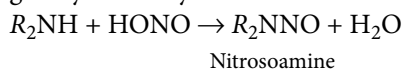
2. **(a)**

3. **(b, c) :** Invert sugar is prepared by acid catalyzed hydrolysis of sucrose.

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

Sucrose　　　　　　　*D*-(+)-Glucose　*D*-(−)-Fructose
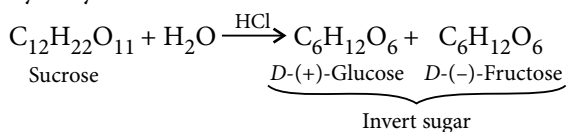
Invert sugar

Specific rotation of invert sugar is
$[\alpha]_{mix} = 0.5 \times (+52) + 0.5 \times (-92) = +26 - 46 = -20°$
On reaction with Br_2 water, invert sugar forms gluconic acid as one of the products. Br_2 water oxidises glucose into gluconic acid and fructose is not oxidised by it.

4. **(a) :** Molecular mass of compound = 180
Molecular mass after acetylation = 390
Increase in molecular mass = 210

$$R—NH_2 + CH_3—\overset{O}{\overset{||}{C}}—Cl \longrightarrow R—NH—\overset{O}{\overset{||}{C}}—CH_3 + HCl$$
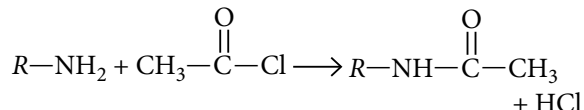
Increase in molecular mass for one $—NH_2$ group is 42 so, total 5 amino groups are present in the intial compound.

5. **(a)**

6. **(a) :**

$$CH_3—\overset{O}{\overset{||}{C}}—NH_2 + Br_2 + 4KOH \xrightarrow[\Delta]{\text{Hoffmann hypobromamide reaction}}$$
　　　　Acetamide

$$CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$
Methylamine
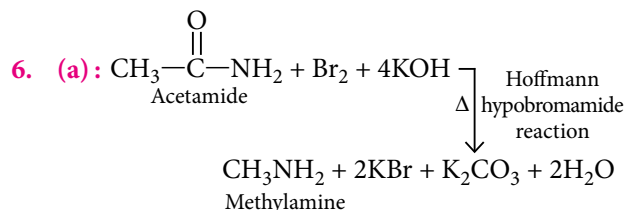
7. **(b) :** Isoelectric point is the pH at which structure of amino acid has equal positive and negative charges. At this point, the amino acids do not migrate in an electric field.

8. **(c) :** The structure of intermediate acetyl nitrene is
$CH_3—CO—\ddot{N}.$
It is formed by the following reaction :

$$CH_3—\overset{\overset{\ddot{N}H_2}{|}}{C}=O \xrightarrow[KOH]{Br_2} CH_3—\overset{\overset{\ddot{N}H—Br}{|}}{C}=O$$

$$\xrightarrow{KOH} CH_3—\overset{\overset{:\ddot{N}}{|}}{C}=O + HBr$$
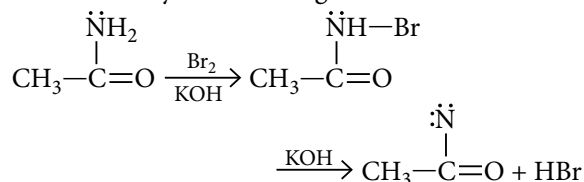
9. **(c) :** In hypobromite reaction of amide, carbonyl carbon atom is lost as CO_3^{2-} ion. The reaction takes place as follows :
$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$
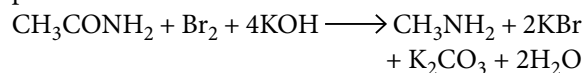
10. **(c) :** In the option (c) the end product is a 3° nitro compound.
$(CH_3)_3CNO_2$ it does not have α-hydrogen as such tautomerism is not possible.

11. **(c) :** The primary structure of a polypeptide is the information of the order of different amino acids in that polypeptide.

12. (c):

N(CH₃)₂·HCl → (Δ) → NHCH₃·HCl (with CH₃) → (Δ) → NH₂·HCl (with CH₃ and CH₃)

(then with $\overline{O}H$) →

NH₂ (with CH₃ and CH₃)
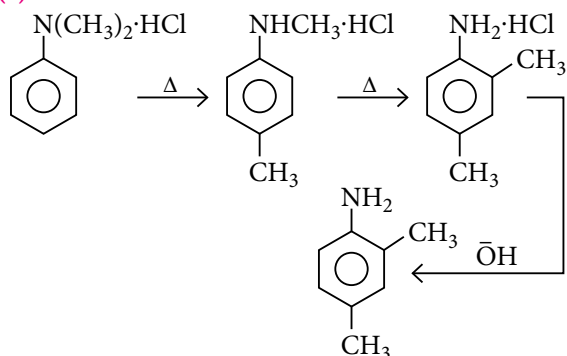
The above reaction is an example of Hoffmann—Martius rearrangement.

13. (d)

14. (a): Reaction of (X) with Br₂ + KOH suggests that (X) is an amide. Evolution of N₂ and formation of alcohol suggest that (Y) is a 1° aliphatic amine. Iodoform test of (Z) suggests that it is an alcohol of

the type $\left[\begin{array}{c} CH_3-CH- \\ | \\ OH \end{array} \right]$.

$C_2H_5CONH_2 \xrightarrow{Br_2 + KOH} C_2H_5NH_2 \xrightarrow{HNO_2}$
(X) .... (Y)

Hoffmann mustard oil reaction (i) S=C=S (ii) HgCl₂ → CH₃CH₂OH + N₂ (Z)

$C_2H_5-N=C=S$
Ethyl isothiocyanate

(Z) → I₂ + NaOH Iodoform test → CHI₃ + HCOONa

15. (c): $Ph-\overset{+}{N}\equiv N\overline{Cl} \xrightarrow{SnCl_2 / HCl} PhNHNH_2 \xrightarrow{HCl}$

$PhNHN\overset{+}{H}_3Cl^-$
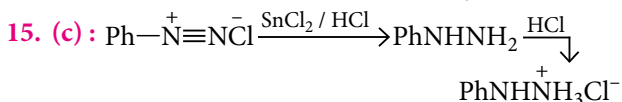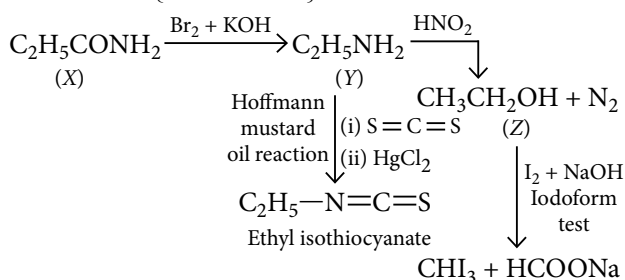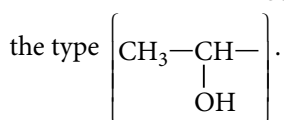
16. (b): Diazo group can be replaced by H on reduction with H₃PO₂.

17. (d)

18. (a): H₂SO₄ is a stronger acid than HNO₃.

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2\overset{+}{N}O_3$
Acid ...... Base ...... Conjugate base ...... Conjugate acid

$H_2\overset{+}{N}O_3 \rightarrow H_2O + NO_2^+$ (acts as electrophile)

19. (c): $C_2H_5-\overset{+}{N}\equiv C^- \xrightarrow{H_3O^+} C_2H_5\overset{+}{N}H_3 + HCOOH$
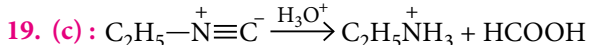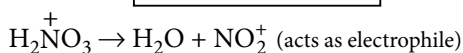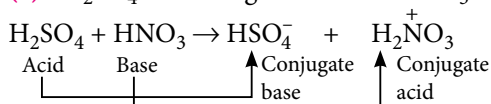
20. (c): Glucose is a hydrate of carbon $C_6(H_2O)_6$ and undergoes dehydration on heating with conc. H₂SO₄.

21. (c): In arylamines, lone pair of electrons on nitrogen atom is delocalised over the benzene ring,

thus, not available for donation. So, arylamines are less basic than alkylamines.

22. (b): Glycosidic linkages are present in carbohydrates.

23. (b):

$CH_3-\overset{O}{\overset{||}{C}}-NH_2 \xrightarrow[-H_2O]{P_2O_5, \Delta} CH_3-C\equiv N \xrightarrow[4[H]]{Zn/HCl}$
Acetamide

$CH_3-CH_2-NH_2$
Ethylamine
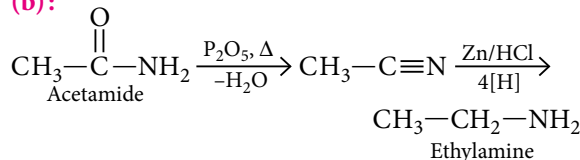
24. (a): $(C_2H_5)_2NH + HONO \longrightarrow (C_2H_5)_2N-NO + H_2O$
Nitrosoamine

25. (b)

26. (a):

NH₂ (with CH₃) $\xrightarrow[0-5°C]{NaNO_2/HCl}$ $\overset{+}{N}_2Cl^-$ (with CH₃) $\xrightarrow[\Delta]{CuCN/KCN}$

(D)

CN (with CH₃) + N₂

(E)
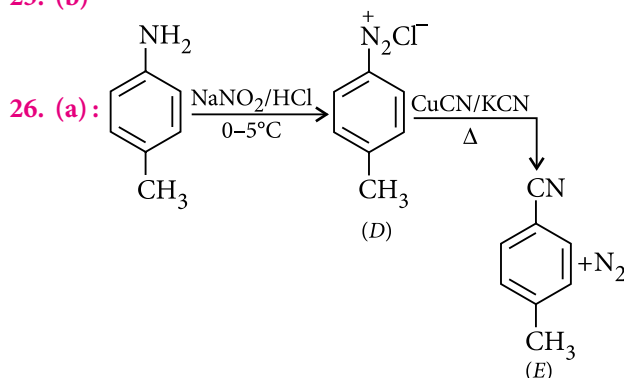
27. (c): $Cu^{2+} + 4C_2H_5NH_2 \longrightarrow [Cu(C_2H_5NH_2)_4]^{2+}$
Tetraethylaminecopper (II) ion
(Deep blue complex)

28. (a): Lone pair of electrons on N-9 are involved in resonance so, it is not basic in nature.

29. (a): The acid used is H₂PtCl₆. It is a solution of platinic chloride, PtCl₄ in conc.HCl
$2RNH_2 + H_2[PtCl_6] \longrightarrow [RNH_3]_2^+[PtCl_6]^{2-}$
Chloroplatinates on ignition leave a residue of metallic Pt. This reaction is employed in determining molecular weight of amines.

30. (b):

$\overset{1}{C}HO$
$HO-\overset{2}{C}-H$
$HO-\overset{3}{C}-H$
$H-\overset{4}{C}-OH$
$H-\overset{5}{C}-OH$
$\overset{6}{C}H_2OH$

D-Mannose
(epimer of glucose at C-2)
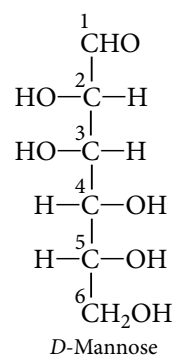
Configuration is 2S, 3S, 4R, 5R [by CIP rules].

◆◆

EXAMINER'S MIND CLASS XII
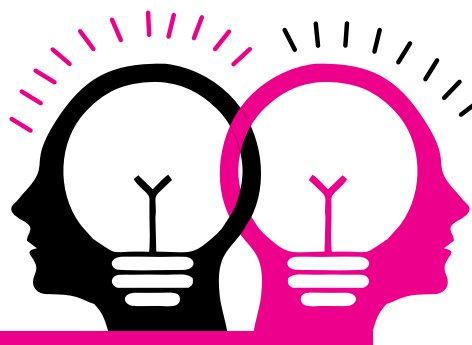
The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

SURFACE CHEMISTRY

SECTION - I

Only One Option Correct Type

1. The name aqua dag is given to the colloidal sol of
   (a) copper in water   (b) platinum in water
   (c) graphite in water   (d) none of these.

2. Softening of hard water is done using sodium aluminium silicate (zeolite). This causes
   (a) adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing Na^+ ions
   (b) adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing Al^{3+} ions
   (c) both (a) and (b)
   (d) none of the above.

3. Following are the properties related to adsorption :
   I.   Reversible
   II. Results into unimolecular layer
   III. Low heat of adsorption
   IV. Occurs at low temperature and decreases with increasing temperature.
   Which of the above properties are for physical adsorption?
   (a) I, II, III only   (b) I, III, IV only
   (c) II, III, IV only   (d) I, III only

4. Which is not the example of coagulation?
   (a) Curdling of milk
   (b) Purification of water by addition of alum
   (c) Rubber plating
   (d) Formation of deltas at the river beds

5. For the coagulation of 50 mL of ferric hydroxide sol, 10 mL of 0.5 M KCl is required. The coagulation value of KCl is
   (a) 5   (b) 10
   (c) 100   (d) none of these.

6. Which of the following has largest protecting power?
   (a) Gelatin (Gold no. = 0.01)
   (b) Dextrin (Gold no. = 15)
   (c) Potato starch (Gold no. = 25)
   (d) Albumin (Gold no. = 0.25)

7. Associated colloids
   (a) raise both the surface tension and viscosity of water
   (b) lower both the surface tension and viscosity of water
   (c) lower the surface tension and raise the viscosity of water
   (d) have greater concentration at the surface layer than the bulk of the solution.

8. The volumes of gases H_2, CH_4, CO_2 and NH_3 adsorbed by 1 g of activated charcoal at 298 K are in the order
   (a) $H_2 > CH_4 > CO_2 > NH_3$
   (b) $CH_4 > CO_2 > NH_3 > H_2$
   (c) $CO_2 > NH_3 > H_2 > CH_4$
   (d) $NH_3 > CO_2 > CH_4 > H_2$

9. Amongst the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient condition is
   (a) $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
   (b) $CH_3(CH_2)_{11}OSO_3^-Na^+$
   (c) $CH_3(CH_2)_6COO^-Na^+$
   (d) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$

10. Although, nitrogen does not adsorb on iron surface at room temperature but it get adsorbed at 83 K. Which one of the following statements is correct?
    (a) At 83 K, there is formation of monolayer.
    (b) At 83 K, nitrogen is adsorbed as atoms.
    (c) At 83 K, nitrogen molecules are held by chemical bonds.
    (d) At 83 K, there is formation of multimolecular layers.

SECTION - II
More than One Options Correct Type

11. On adding $AgNO_3$ solution into KI solution, a negatively charged colloidal sol is obtained on mixing
    (a) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.1 M KI
    (b) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.2 M KI
    (c) 100 mL of 0.2 M $AgNO_3$ + 100 mL of 0.1 M KI
    (d) 100 mL of 0.15 M $AgNO_3$ + 100 mL of 0.25 M KI

12. Which of the following statements are correct?
    (a) Physical adsorption is multilayer, non-directional, and non-specific.
    (b) In some cases, solvent may be adsorbed in preference to the solute on the surface of the adsorbent.
    (c) Chemical adsorption increases with increase in temperature.
    (d) Due to adsorption, surface energy increases.

13. Choose the correct reasons for the stability of lyophobic colloidal particles.
    (a) Preferential adsorption of ions on their surface from the solution.
    (b) Preferential adsorption of solvent on their surface from the solution.
    (c) Attraction between different particles having opposite charges on their surface.

(d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

SECTION - III
Paragraph Type

Paragraph for Questions 14 and 15

A chemist studied the phenomenon of adsorption by putting blood charcoal in KCl solution. He observed difference in the behaviour with dilute KCl solution and with concentrated KCl solution. He also studied the adsorption of different gases on solid adsorbent and the effect of temperature on adsorption. He put forward a mathematical relationship relating x/m with equilibrium pressure.

14. The correct order of the adsorption of gases studied will be
    (a) $NH_3 > SO_2 > CO_2 > HCl$
    (b) $CO_2 > SO_2 > NH_3 > HCl$
    (c) $SO_2 > NH_3 > HCl > CO_2$
    (d) $HCl > SO_2 > NH_3 > CO_2$

15. Which of the following result is observed with the experiment of KCl solution?
    (a) Dilute KCl solution shows no adsorption whereas concentrated KCl shows adsorption.
    (b) Concentrated KCl solution shows positive adsorption whereas dilute KCl solution shows negative adsorption.
    (c) Concentrated KCl solution shows no adsorption whereas dilute KCl solution shows adsorption.
    (d) Dilute KCl solution shows positive adsorption whereas concentrated KCl solution shows negative adsorption.

Paragraph for Questions 16 and 17

Coagulation is the process by which the dispersed phase of a colloid is made to aggregate and thereby separate from the continuous phase. The minimum concentration of an electrolyte in millimoles per litre of the electrolyte solution which is required to cause the coagulation of colloidal sol is called coagulation value.

$$\text{Coagulation value} \propto \frac{1}{\text{Coagulating power}}$$

The coagulation values of different electrolytes are different. This behaviour can be easily understood by Hardy—Schulze rule.

16. As_2S_3 sol is negatively charged. Capacity to precipitate it is highest in
    (a) K_2SO_4 (b) Na_3PO_4
    (c) $AlCl_3$ (d) $CaCl_2$

17. The ability of an ion to bring coagulation of a given colloid depends upon
(a) the sign of charge
(b) magnitude of charge
(c) both magnitude and sign of charge
(d) none of the above.

18. Match the List-I with List-II and select the correct answer using the codes given below the lists:

List I (Colloids)	List II (Classification)
(P) Rain cloud	(1) Sol
(Q) Paint	(2) Aerosol
(R) Soapsuds	(3) Gel
(S) Butter	(4) Foam

	P	Q	R	S
(a)	1	2	3	4
(b)	1	4	2	3
(c)	2	1	4	3
(d)	2	1	3	4

19. Match the List-I with List-II and select the correct answer using the codes given below the lists :

List I	List II
(P) Electrophoresis	(1) Movement of molecules of dispersion medium
(Q) Electroosmosis	(2) Determination of Avogadro's number
(R) Tyndall effect	(3) Ultramicroscope
(S) Brownian motion	(4) Determination of charge on colloidal particles

	P	Q	R	S
(a)	4	1	3	2
(b)	1	4	2	3
(c)	3	4	2	1
(d)	2	1	4	3

20. Assertion : Alcohols are dehydrated to hydrocarbons in the presence of acidic zeolites.
Reason : Zeolites are porous catalysts.

21. Assertion : Activity of an enzyme is pH-dependent.
Reason : Change in pH affects the solubility of the enzyme in water.

22. Assertin : Fe^{3} can be used for coagulation of As_2S_3 sol.
Reason : Fe^{3} reacts with As_2S_3 to give Fe_2S_3.

23. 526.3 mL of 0.5 m HCl is shaken with 0.5 g of activated charcoal and filtered. The concentration of the filtrate is reduced to 0.4 m. The amount of adsorption (x/m) is

24. For soaps critical micelle concentration (CMC) is 10^{-x} (min.) to 10^{-y} (max.) mol/L. What is the value of x?

25. 10% sites of catalyst bed have adsorbed by H_2. On heating H_2 gas is evolved from sites and collected at 0.03 atm and 300 K in a small vessel of 2.46 cm^3.
No. of sites available is 5.4×10^{16} per cm^2 and surface area is 1000 cm^2. Find out the number of surface sites occupied per molecule of H_2.

POLYMERS AND CHEMISTRY IN EVERYDAY LIFE

1. Which of the following statements is not correct?
(a) Soap acts by lowering surface tension between water and oil/insoluble material.
(b) The soap forms insoluble salt with Ca^{+2} ions.
(c) The COO^- group in soaps acts as hydrophilic and alkyl chain as hydrophobic parts.
(d) Soaps work more efficiently in hard water than in soft water.

2. Plexiglas is a commercial name of
(a) glyptal
(b) polyacrylonitrile
(c) polymethylmethacrylate
(d) polyethylacrylate.

3. Di-n-butylphthalate is
(a) plasticizer   (b) thermoplastic
(c) polymer   (d) thermosetting plastic.

4. The structural formula of monomer of PMMA is
(a) $CH_2\!=\!CHCOOCH_3$

(b) $CH_2 = \overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C} - COOCH_3$

(c) $CH_3COOCH = CH_2$

(d) $CH_3COOC = CH_2$ with CH_3 below
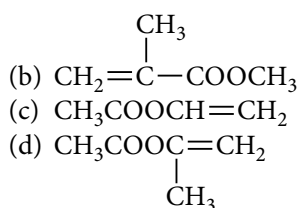
5. The incorrect statement about detergents is
   (a) inorganic phosphate is added to the detergents for the removal of calcium salts
   (b) sodium peroxoborate added to the detergents acts as bleaching agent
   (c) sodium sulphate is added to the detergents to increase bulk
   (d) fluorescers added to the detergents as foaming agents.

6. Structures of some common polymers are given. Which one is not correctly represented?
   (a) Neoprene : $\left[CH_2 - \overset{\overset{\displaystyle }{\displaystyle |}}{C} = CH - CH_2 - CH_2 \right]_n$ with Cl below
   (b) Terylene :
      $\left[OC - \langle \bigcirc \rangle - COOCH_2 - CH_2 - O \right]_n$
   (c) Nylon 6, 6 : $[NH(CH_2)_6 NHCO(CH_2)_4 - CO]_n$
   (d) Teflon : $[F_2C - CF_2]_n$

7. A catalyst used for the polymerisation of olefin is
   (a) Zeigler-Natta catalyst
   (b) Wilkinson's catalyst
   (c) Pd-catalyst
   (d) Zeise's salt catalyst.

8. A drug that is antipyretic as well as analgesic is
   (a) chlorpromazine hydrochloride
   (b) *para*-acetamidophenol
   (c) chloroquine
   (d) penicillin.

9. Which of the following is an incorrect statement?
   (a) Non-ionic detergents are neutral.
   (b) The hydrophilic portion of a non-ionic detergent functions by a hydrogen bonding mechanism.
   (c) Cationic detergents have a positively charged water soluble portion.
   (d) LABS detergents are non-biodegradable.

10. Which of the following acts as an antioxidant in edible oils?
    (a) Vitamin B   (b) Vitamin C
    (c) Vitamin D   (d) Vitamin E

SECTION - II
More than One Options Correct Type

11. Which of the following pairs are correctly matched?
    (a) Terylene–condensation polymer of terephthalic acid and ethylene glycol.
    (b) Teflon–thermally stable cross linked polymer of phenol and formaldehyde.
    (c) Plexiglas–homopolymer of methylmethacrylate.
    (d) Synthetic rubber–copolymer of butadiene and styrene.

12. The polymers which do not contain hydrogen bond are
    (a) teflon   (b) nylon 6, 6
    (c) polystyrene   (d) natural rubber.

13. Which of the following are correct about barbiturates?
    (a) Hypnotics or sleep producing agents
    (b) Tranquilizers
    (c) Non-narcotic analgesics
    (d) Pain reducing without disturbing the nervous system

SECTION - III
Paragraph Type

Paragraph for Questions 14 and 15

Polymerisation involves various mechanism depending upon the initiator. If initiator generates free radical, addition polymerisation takes place through free radical mechanism. If H^+ is initiator and electron releasing group is present, cationic polymerisation takes place. If electron withdrawing group is present and KNH_2 is initiator, anionic polymerisation takes place.

14. Which of the following will induce anionic polymerisation?
    (a) KNH_2 (b) *n*-Butyl lithium
    (c) KOH   (d) All of these

15. Which of the following will undergo cationic polymerisation in presence of H^+?
    (a) $CH_2 = CH$ with Cl below   (b) $CH_2 = CH$ with CN below
    (c) $CH_2 = CH$ with NO_2 below (d) $CH_2 = CH$ with CH_3 below

Paragraph for Questions 16 and 17

Synthetic tranquilizers are mostly barbituric acid derivatives (*e.g.*, veronal, luminal, seconal, amytal and nembutal). Other tranquilizers which are not barbituric

acid derivatives are chlordiazepoxide, equanil, meprobamate, valium, *etc.* Opium alkaloids such as morphine and codeine are powerful analgesics. Heroin which is morphine diacetate is a widely used narcotic analgesic. Drugs which are used to cure diseases caused by microbes are called antimicrobials. These may be either sulphadrugs such as sulphapyridine, sulphadiazine, sulphaguanidine or they may be antibiotics. Antibiotics which inhibit or arrest the growth of microbes are called bacteriostatic while others which kill the microbes are called bactericidal antibiotics.

16. Among the following the narcotic analgesic is
   (a) codeine   (b) ibuprofen
   (c) naproxen   (d) aspirin.

17. The bactericidal and bacteriostatic antibiotics respectively are
   (a) penicillin and ofloxacin
   (b) erythromycin and tetracycline
   (c) penicillin and chloramphenicol
   (d) tetracycline and penicillin.

SECTION - IV

Matching List Type

18. Match List-I (Polymer) with List-II (Monomer) and select the correct answer using the codes given below the lists :

List I		List II	
P.	Bakelite	1.	Ethylene glycol
Q.	Dacron	2.	Phenol
R.	Glyptal	3.	Phthalic acid
S.	Nylon-6	4.	Formaldehyde
		5.	Terephthalic acid
		6.	Caprolactam

	P	Q	R	S
(a)	1, 2	1, 3	1, 5	6
(b)	2, 4	1, 5	1, 3	6
(c)	2, 4	1, 6	1, 5	3
(d)	1, 2	1, 5	4, 6	3

19. Match List-I with List-II and select the correct answer using the codes given below the lists :

List I		List II	
P.	Urea formaldehyde resin	1.	Unbreakable cups
Q.	Nylon - 6	2.	TV cabinets
R.	Polystyrene	3.	Safety helmets
S.	Polyesters	4.	Tyre cords

	P	Q	R	S
(a)	1	4	2	3
(b)	1	2	4	3
(c)	4	2	3	1
(d)	4	3	2	1

SECTION - V

Assertion Reason Type

20. Assertion : 2-Methyl-1,3-butadiene is a monomer of natural rubber.
   Reason : Natural rubber is formed through anionic addition polymerisation.

21. Assertion : The cleansing action of soaps or detergents involve the formation of a stable emulsion of oil in water.
   Reason : The dispersed dirt particles in the solution or over the fibres are organic substances.

22. Assertion : 1,3-Butadiene is the monomer of Gutta percha.
   Reason : Gutta percha have all '*cis*' configuration.

SECTION - VI

Integer Value Correct Type

23. The total number of lone pairs of electrons in melamine is

24. How many of the following are thermosetting polymers?
   Bakelite, polyester, polyvinyl acetate, urea-formaldehyde resin, nylon-6,6, polypropylene, and melamine-formaldehyde resin

25. How many of the following compounds are artificial sweeteners?
   (i) BHT   (ii) BHA
   (iii) Chlorpheniramine (iv) Aspartame
   (v) Sucralose   (vi) Alitame
   (vii) Saccharin   (viii) Seldane
   (ix) Sodium benzoate   (x) Salts of sorbic acid

....

MPP-9 CLASS XI ANSWER KEY

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

SURFACE CHEMISTRY

1. **(c)**

2. **(a):** Hardness of water is due to carbonates or sulphates of Ca^{2+} and Mg^{2+} ions. When sodium aluminium silicate is added Na^+ replaces Ca^{2+} and Mg^{2+} by adsorption and hence, water becomes soft.

3. **(b):** Physical adsorption results into multimolecular layers on adsorbent surface under high pressure. While chemical adsorption results into unimolecular layer.

4. **(c):** Rubber plating does not involve coagulation process.

5. **(c):** Coagulation value

$$= \frac{\text{Number of millimoles of electrolyte required}}{\text{Volume of colloidal solution (in litre)}}$$

$$= \frac{10 \times 0.5}{50} \times 1000 = 100$$

6. **(a)**

7. **(c):** Associate colloids decrease surface tension and increase viscosity.

8. **(d):** The more easily liquefiable gases are more strongly adsorbed.

9. **(a):** Longer the carbon chain, *i.e.*, greater the size of the hydrophobic tail, lesser is the solubility in water and greater is the tendency of surfactant molecules to associate to form micelles. Therefore, critical concentration for micelle formation decreases.

10. **(d):** At 83 K physical adsorption takes place effectively so, multimolecular layers are formed.

11. **(b,d):** Solutions having higher concentration of I^- ions than Ag^+ ions will result in the formation of a negatively charged colloidal sol.

12. **(a,b):** (c) is wrong because chemical adsorption first increases and then decreases with increase in temperature.
(d) is wrong because as a result of adsorption, there is a decrease in surface energy.

13. **(a,d):** Adsorption of same type of ions on their surface causes repulsion between them and thus, stabilises the colloid. Also, the potential difference between the fixed and diffused layers

of opposite charges results in stabilisation of colloid.

14. **(c):** The critical temperature of the given gases is in the order : $SO_2 > NH_3 > HCl > CO_2$. Hence, their adsorption is in the same order.

15. **(b)**

16. **(c):** Al^{3+} has highest positive charge and as charge increases coagulating power also increases.

17. **(c):** Coagulation depends upon charge and magnitude.

18. **(c)**   19. **(a)**

20. **(b):** Dehydration is not due to porous nature but due to the acidic group present in zeolites.

21. **(b):** Activity of enzyme is maximum at pH = 7.4 (physiological pH). In fact, as pH is increased, the rate rises to a maximum and then falls off.

22. **(c):** Fe^{3} is positively charged whereas As_2S_3 is negatively charged sol. Their charges are neutralised on mixing hence, mutual precipitation (coagulation) occurs.

23. (4): Mass of HCl acid adsorbed by 0.5 g charcoal
$= 526.3 \times 10^{-3}(0.5 - 0.4) \times 36.5 \approx 2$

(Mol. wt. of HCl = 36.5 g mol^{-1})

The amount of adsorption,

$$\frac{x}{m} = \frac{2}{0.5} = 4$$

24. (4): CMC of soap is about 10^{-4} to 10^{-3} mol L^{-1}. Thus, $x = 4$.

25. (3): Adsorbed moles of $H_2 = \dfrac{0.03 \times 2.46 \times 10^{-3}}{0.0821 \times 300}$

$= 3 \times 10^{-6}$

$\therefore$ No. of molecules of H_2 adsorbed

$= 3 \times 10^{-6} \times 6 \times 10^{23}$

$= 18 \times 10^{17}$

Total number of surface sites available

$= 5.4 \times 10^{16} \times 1000 \Rightarrow 5.4 \times 10^{19}$ cm^2

No. of surface sites that is occupied by adsorption

of $H_2 = \dfrac{10}{100} \times 5.4 \times 10^{19} \Rightarrow 5.4 \times 10^{18}$

No. of surface sites occupied by one molecule of

$H_2 = \dfrac{5.4 \times 10^{18}}{18 \times 10^{17}} = 3$

POLYMERS AND CHEMISTRY IN EVERYDAY LIFE

1. (d): Soaps actually do not give foams in hard water due to formation of insoluble salts like calcium stearate and magnesium stearate with hard water containing impurities of Ca and Mg carbonates and bicarbonates.

2. (c)

3. (a): Di-*n*-butylphthalate is plasticizer added to PVC to make it soft.

4. (b)

5. (d): Fluorescers are optically whitening agents. These are generally added to laundry detergents to make the clothes appear cleaner. These are also known as fluorescent brighteners. They are stilbene derivatives.

6. (a): Correct representation of neoprene is

$$\left[CH_2 - \underset{\underset{Cl}{|}}{C} = CH - CH_2 \right]_n$$

7. (a): In polymerisation of ethylene, Ziegler-Natta catalyst (triethylaluminium and titanium tetrachloride) is used.

8. (b): *para*-Acetamidophenol (paracetamol) is used as an antipyretic as well as an analgesic.

9. (d): LABS (Linear alkylbenzene sulphonate) detergents are biodegradable.

10. (d): Vitamin E is an antioxidant present in edible oils.

11. (a,c,d)

12. (a,c,d): Nylon-6,6, the polymer of adipic acid and hexamethylenediamine, has strong H-bonds between the polymer units.

13. (a,b)

14. (d): All of these can induce anionic polymerisation because they are strong bases.

15. (d): In $CH_2 = \underset{\underset{CH_3}{|}}{CH}$, methyl group is electron-releasing, therefore, stabilises carbocation. (a), (b) and (c) have electron withdrawing groups which will destabilise carbocations.

16. (a) **17. (c)**

18. (b) **19. (a)**

20. (c): Butadiene derivatives undergo polymerisation by free radical addition reaction.

21. (a)

22. (d): Gutta percha is polymer of isoprene with all '*trans*' configuration.

23. (6): Melamine has 6 lone pairs of electrons.

24. (3): The three thermosetting polymers are :
(i) bakelite
(ii) urea-formaldehyde resin and
(iii) melamine-formaldehyde resin.

25. (4): Aspartame, sucralose, alitame and saccharin are artificial sweeteners.
i and ii are antioxidants.
iii and viii are antihistamines.
ix and x are preservatives.

◈ ◈

CLASS XII

ACE YOUR WAY CBSE

Practice Paper 2018

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q.no.1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q.no.6 to 10 are short answer questions and carry 2 marks each.
(iv) Q.no.1 to 22 and also short answer questions and carry 3 marks each.
(v) Q.no.23 is a value based question and carry 4 marks.
(vi) Q.no.24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log table if necessary, use of calculators is not allowed.

1. Calculate the overall dissociation constant for the complex $[Cu(NH_3)_4]^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

2. Arrange the following sets of compounds in order of their increasing boiling points :
Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol

3. Define 'order of a chemical reaction'.

4. Give a chemical test to distinguish between 2-propanol and 2-methyl-2-propanol.

5. How does the addition of alum purify water?

6. How ammonia is prepared on the large scale? Name the process and mention the optimum conditions for the production of ammonia by this process.

7. Two solutes X and Y in equal amounts are dissolved separately in 10 moles of solvent C. If X molecule is heavier than Y molecule, which solution will have larger relative lowering of vapour pressure?

8. Which is stronger reducing agent Cr^{2+} or Fe^{2+} and why?

9. Suggest three substances that can oxidise ferrous ions under suitable conditions.

10. (i) Identify the chiral molecule in the following :

 and Cl
Cl

(ii) Out of S_N1 and S_N2, which reaction occurs with :
(a) inversion of configuration
(b) racemisation.

OR

Give one reaction each to convert benzyl bromide into :
(i) benzyl ethyl ether
(ii) benzyl cyanide.

11. What is the freezing point of 0.2 molal solution of acetic acid in benzene in which it dimerises to the extent of 60%? Freezing point of benzene is 278.4 K and its molar heat of fusion is 10.042 kJ mol^{-1}.

12. Write the chemical equations for the preparation of 1-bromobutane from :
(i) 1-butanol (ii) 1-chlorobutane
(iii) but-1-ene.

13. Outline the principles for the refining of metals by the following methods :

(i) Distillation   **(ii)** Zone refining

(iii) Electrolysis

14. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

15. Identify the end products, A to C in the following transformations :

(i) $CH_3CH_2CH-CH=CH_2 \xrightarrow[H_2O_2, \, OH^-]{BH_3, \, THF} A$
   with C_2H_5 branch on the CH

(ii) (cyclohexane ring)$-CH_2-CHCH_3 \xrightarrow[170\,°C]{H^+} B$
   with OH on the CH

(iii) (cyclohexanone, ring with O) $\xrightarrow[H_3O^+]{CH_3CH_2MgBr/ether} C$
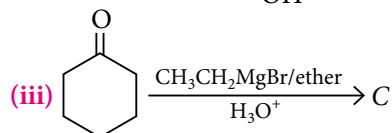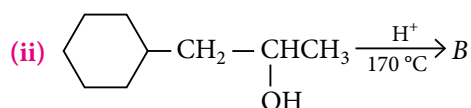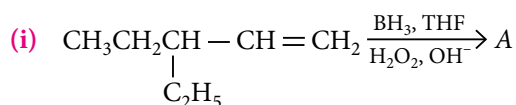
16. Answer the following questions on the basis of curve for a first order reaction :

plot of $\log \dfrac{[R]_0}{[R]}$ versus Time $\longrightarrow$
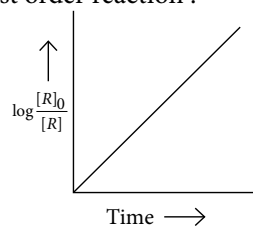
(i) What is the relation between slope and rate constant?

(ii) Calculate the rate constant if the slope is $2 \times 10^{-4}\ s^{-1}$.

(iii) Derive the relationship between half life and rate constant.

17. Convert benzene to aniline using the following reagents in correct order :
Alkaline $KMnO_4$ followed by HCl ; Br_2/KOH ; NH_3, heat ; CH_3Cl/Anhy. $AlCl_3$.

18. Explain the following observations :

(i) Lyophilic colloid is more stable than Lyophobic colloid.

(ii) Coagulation takes place when sodium chloride solution is added to hydrated ferric oxide sol.

(iii) Sky appears blue in colour.

19. Give reasons :

(i) Why silver and gold are known as coinage metals?

(ii) How do the oxides of transition elements in lower oxidation states differ from those in higher oxidation states and why?

20. **(i)** Is diet consisting mainly of rice, an adequate diet? Why or why not?

(ii) Can the acid chloride of an α-amino acid be made by treating it with $SOCl_2$?

OR

(i) Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.

(ii) How do you explain the presence of an aldehydic group in a glucose molecule?

21. Explain each of following observations :

(i) Tetrahedral Ni (II) complexes are paramagnetic but square planar Ni (II) complexes are diamagnetic.

(ii) Only transition metals are known to form π-complexes.

22. **(i)** Write formulae of the monomers of polythene and teflon.

(ii) Write the name and structure of one of the common initiators used in free radical addition polymerization.

(iii) What is the role of sulphur in the vulcanisation of rubber?

23. Mr. Praveen was living a life full of tension and anxiety due to work load in his office and hectic schedule. This made his nights sleepless due to which he started taking sleeping pills. One day, he discussed all this with his friend, who is a doctor by profession. His friend advised him not to take sleeping pills but prescribed him some mild tranquilizers and asked him to change his lifestyle by doing yoga, meditation and some physical exercises. After a few days, he started feeling better. After reading the above passage, answer the following :

(i) What is the main ingredient of sleeping pills and how does it work?

(ii) Name two mild tranquilizers.

(iii) What values are expressed by the doctor?

24. (i) An alloy of gold and cadmium crystallises with a cubic structure in which gold atoms occupy the corners and cadmium atoms fit into the face centres. Assign formula for this alloy.

(ii) The density of copper is 8.95 g cm^{-3}. It has a face centred cubic structure. Calculate the radius of copper atom.

OR

(i) Give reason :
(a) Silicon on doping with phosphorus forms *n*-type semiconductor.
(b) Ferrimagnetic substances show better magnetism than antiferromagnetic substances.

(ii) The radius of Na$^+$ ion is 95 pm and that of Cl$^-$ ion is 181 pm. Predict whether the coordination number of Na$^+$ ion is 6 or 4.

25. (i) Why do noble gases have comparatively large atomic sizes?

(ii) Give the formula and describe the structure of a noble gas species which is isostructural with :
(a) ICl$_4^-$ **(b)** IBr$_2^-$ **(c)** BrO$_3^-$

OR

(i) Write the structure of pyrophosphoric acid.

(ii) How do you account for the reducing behaviour of H$_3$PO$_2$ on the basis of its structure?

(iii) Account for the following :
(a) Bond dissociation energy of F$_2$ is less than that of Cl$_2$.
(b) Both NO and ClO$_2$ are odd electron species but NO dimerises while ClO$_2$ does not.
(c) Bleaching of flowers by chlorine is permanent while that by sulphur dioxide is temporary.

26. (i) Dipole moments of aldehydes and ketones are higher than those of alcohols. Explain.

(ii) Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid.

(iii) Fluorine is more electronegative than chlorine even then *p*-fluorobenzoic acid is a weaker acid than *p*-chlorobenzoic acid. Explain.

OR

(i) Write the structures of main products when benzenediazonium chloride reacts with the following reagents :

(a) HBF$_4$/Δ
(b) Cu/HBr

(ii) Write the structures of *A*, *B* and *C* in the following reactions :

(a) $C_6H_5NO_2 \xrightarrow{\text{Sn + HCl}} A \xrightarrow[273\ K]{\text{NaNO}_2 + \text{HCl}} B \xrightarrow[\text{H}_2\text{O}]{\Delta} C$

(b) $CH_3Cl \xrightarrow{\text{KCN}} A \xrightarrow{\text{LiAlH}_4} B \xrightarrow[273\ K]{\text{HNO}_2} C$

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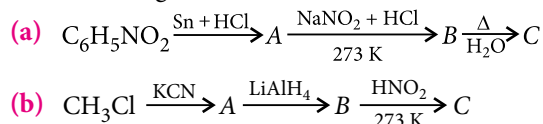
SOLUTIONS

</div>

1. The overall dissociation constant is the reciprocal of the overall stability constant. Overall dissociation constant = $\dfrac{1}{\beta_4} = \dfrac{1}{2.1 \times 10^{13}} = 4.8 \times 10^{-14}$

2. Methanol < ethanol < propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol

3. The order of a chemical reaction is equal to the sum of the powers (exponents) to which the various concentration terms are raised in the rate law expression of the reaction.

4. 2-Propanol will give yellow precipitate of iodoform on addition of I$_2$ and NaOH while 2-methyl-2-propanol will not.

5. Addition of alum coagulates the suspended impurities and makes water fit for drinking purpose.

6. Ammonia is manufactured industrially by Haber's process :
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}; \Delta_f H^\circ = -46.1$ kJ mol^{-1}
This is a reversible exothermic reaction. High pressure about 200 atm, low temperature about 700 K and use of catalyst such as iron oxide with small amounts of Al$_2$O$_3$ and K$_2$O would favour the formation of ammonia, according to Le Chatelier's principle.

7. Molar mass of *Y* is less than that of *X*, therefore, for the same mass of *X* and *Y*, moles of *Y* will be more than the moles of *X*. Thus, mole fraction of *Y* will be more than that of *X*. Hence, relative lowering of vapour pressure will be larger in case of *Y*.

8. Cr^{2+} is stronger reducing agent than Fe^{2+}. This can be explained in terms of $E^\circ_{(M^{3+}/M^{2+})}$ values. $E^\circ_{(Cr^{3+}/Cr^{2+})}$ has negative value (–0.41 V), indicating that Cr^{3+} would change into Cr^{2+} with difficulty whereas reverse would take place readily.

9. Oxidation of ferrous ions :
Fe^{2+} $\longrightarrow$ Fe^{3+} + e^-; $E^\circ_{Fe^{3+}/Fe^{2+}}$ = +0.77 V

Only those substances can oxidise Fe^{2+} to Fe^{3+} which are stronger oxidising agents and have positive reduction potentials greater than 0.77 V, so that EMF of the cell reaction is positive. For example, Br_2, Cl_2 and F_2.

10. (i)

2-Chlorobutane

(ii) (a) S_N2 **(b)** S_N1

OR

(i) $C_6H_5CH_2Br + NaOC_2H_5 \rightarrow C_6H_5CH_2-O-C_2H_5$

(ii) $C_6H_5CH_2Br + KCN \rightarrow C_6H_5CH_2CN$
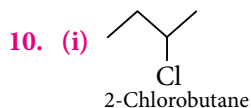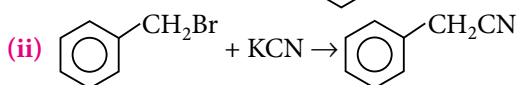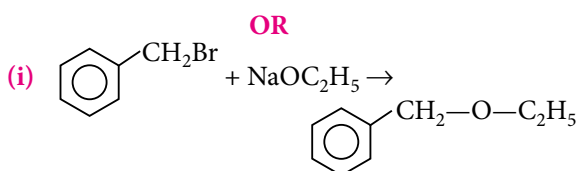
11. $K_f = \dfrac{RT_f^2 M}{1000 \times \Delta_{fus}H}$

$= \dfrac{8.314 \times 10^{-3} \times (278.4)^2 \times 78}{1000 \times 10.042}$

$= 5.0$ K kg mol^{-1}

$2CH_3COOH \longrightarrow (CH_3COOH)_2$
Dimer
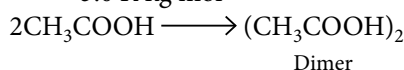
Degree of association (α)

$= \dfrac{i-1}{(1/n)-1} = \dfrac{i-1}{(1/2)-1}$

or $\quad 0.6 = \dfrac{i-1}{-0.5} \quad$ or $\quad i = 1 - 0.3 = 0.7$

$\Delta T_f = i \cdot K_f \cdot m = 0.7 \times 5.0 \times 0.2 = 0.7$ K

Freezing point of solution = 278.4 – 0.7 = 277.7 K

12. (i) $3CH_3CH_2CH_2CH_2OH + PBr_3 \longrightarrow$
1-Butanol

$\qquad 3CH_3CH_2CH_2CH_2Br + H_3PO_3$
1-Bromobutane

(ii) $CH_3CH_2CH_2CH_2Cl + NaBr \xrightarrow[\text{(Finkelstein reaction)}]{\text{Acetone, heat}}$
1-Chlorobutane

$\qquad CH_3CH_2CH_2CH_2Br + NaCl$
1-Bromobutane

(iii) $CH_3CH_2CH=CH_2 + HBr \xrightarrow[\substack{\text{Anti-Markownikoff's} \\ \text{addition}}]{\text{Peroxide}}$
But-1-ene

$\qquad CH_3CH_2CH_2CH_2Br$
1-Bromobutane
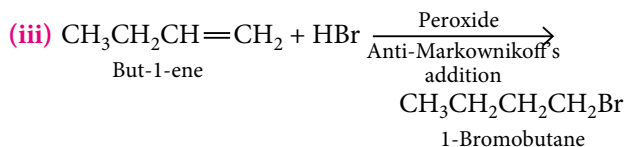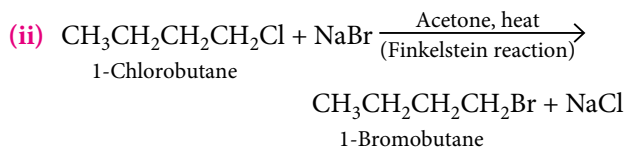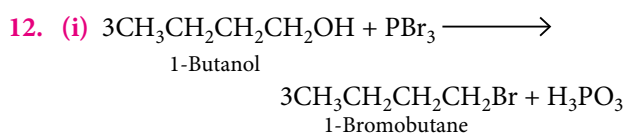
13. (i) Distillation is used for volatile metals. Impure metal is heated in a retort and its vapours are separately condensed in a receiver. The non-volatile impurities are left behind. Zn, Cd, Hg, etc. are purified by this method.

(ii) Zone refining is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. Extremely pure metal like silicon, germanium, etc. are refined by this method.

(iii) In electrolytic refining method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. On passing current, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while equivalent amount of metal dissolves from anode in the electrolyte in the form of metal ions.

At anode : $Zn \rightarrow Zn^{2+} + 2e^-$

At cathode : $Zn^{2+} + 2e^- \rightarrow Zn$
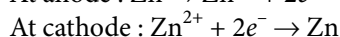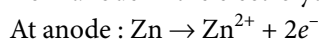
14. $A = \pi r^2 = 3.14 \times (0.5 \text{ cm})^2 = 0.785 \text{ cm}^2$

Resistivity, $\rho = R \times \dfrac{A}{l} = \dfrac{5.55 \times 10^3 \, \Omega \times 0.785 \text{ cm}^2}{50 \text{ cm}}$

$\qquad\qquad = 87.135 \, \Omega \text{ cm}$

Conductivity, $\kappa = \dfrac{1}{\rho} = \dfrac{1}{87.135 \, \Omega \text{ cm}} = 0.01148$ S cm^{-1}

Molar conductivity, $\Lambda_m = \dfrac{\kappa \times 1000}{\text{Molarity}}$

$= \dfrac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}} = 229.6$ S cm^2 mol^{-1}

15. (i) $CH_3CH_2\underset{\underset{C_2H_5}{|}}{CH}-CH=CH_2 \xrightarrow[H_2O_2,\ OH^-]{BH_3,\ THF} CH_3CH_2\underset{\underset{C_2H_5}{|}}{CH}CH_2CH_2OH$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (A)$

(ii) Cyclohexyl$-CH_2-\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[170\,°C]{H^+}$ Cyclohexyl$-CH=CHCH_3$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (B)$

(iii) Cyclohexanone $\xrightarrow[H_3O^+]{CH_3CH_2MgBr}$ 1-ethylcyclohexan-1-ol
$\qquad\qquad\qquad\qquad\qquad\qquad (C)$
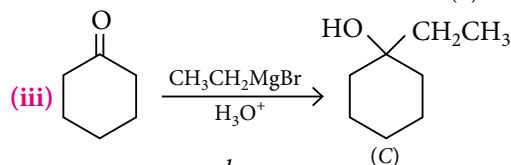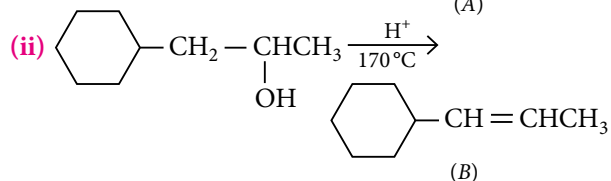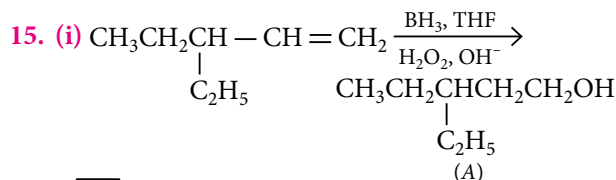
16. (i) Slope $= \dfrac{k}{2.303}$

(ii) As slope $= 2 \times 10^{-4}$ s^{-1}

$\therefore \quad k = 2.303 \times 2 \times 10^{-4}$ s$^{-1} = 4.606 \times 10^{-4}$ s^{-1}

(iii) For a first order reaction,

$t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]} \quad \Rightarrow \quad$ At $t_{1/2}, [R] = \dfrac{[R]_0}{2}$

$$t_{1/2} = \frac{2.303}{k} \log 2 \implies t_{1/2} = \frac{0.693}{k}$$

17.

Benzene $\xrightarrow{\text{CH}_3\text{Cl/Anhy. AlCl}_3}$ Toluene (CH$_3$)

$\xrightarrow[\text{(Oxidation)}]{\text{alk. KMnO}_4, \Delta}$ Potassium benzoate (COŌK$^+$) $\xrightarrow[\text{(–KCl)}]{\text{HCl}}$ Benzoic acid (COOH)

$\xrightarrow{\text{NH}_3}$ Ammonium benzoate (COOŌNH$_4^+$) $\xrightarrow[\text{(–H}_2\text{O)}]{\text{Heat}}$ Benzamide (CONH$_2$)

$\xrightarrow[\substack{\text{(Hoffmann bromamide} \\ \text{reaction)}}]{\text{Br}_2/\text{KOH}}$ Aniline (NH$_2$)
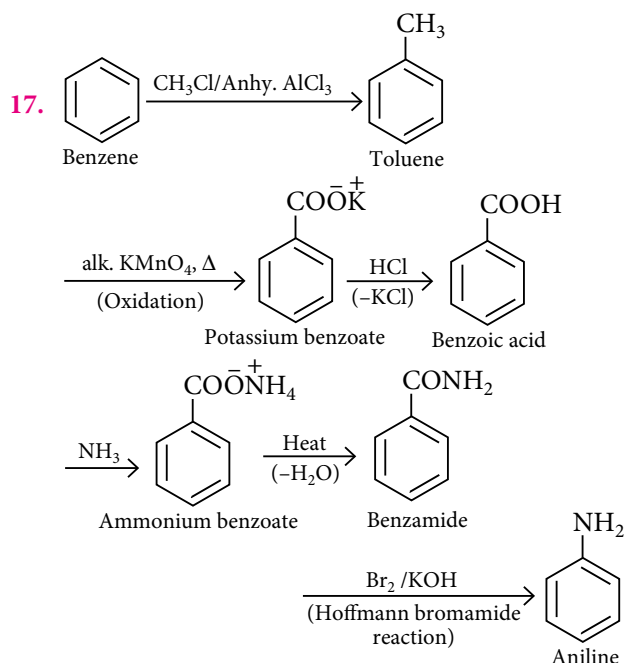
18. (i) A lyophilic sol is stable due to charge and hydration of the sol particles, such a sol can only be coagulated by removing the water and adding solvents like alcohol, acetone, etc. and then an electrolyte. On the other hand, a lyophobic sol is stable due to charge only and hence, can be easily coagulated by adding small amount of an electrolyte.

(ii) When the electrolyte NaCl is added to the sol of hydrated ferric oxide, the charge on the colloidal particles is neutralised by the oppositely charged ions provided by NaCl resulting in its coagulation.

(iii) The atmospheric particles of colloidal range scatter blue component of the sunlight preferentially. That is why the sky appears blue.

19. (i) Since they are noble metals, they are resistant to atmospheric and environmental chemical effects. Hence, they are used in the making of coins.

(ii) In the lower oxidation state, the transition metal oxides are basic and they are acidic if the metal is in higher oxidation state. The oxides are amphoteric when the metal is in intermediate oxidation state.

For example,

$\overset{+3}{\text{Mn}_2\text{O}_3}$	$\overset{+4}{\text{MnO}_2}$	$\overset{+7}{\text{Mn}_2\text{O}_7}$
Basic	Amphoteric	Acidic
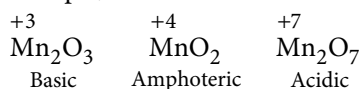
In case of lower oxide of a transition metal, the metal atom has a low oxidation state. This means some of the valence electrons of the metal atom are not involved in bonding, hence, these can be used for donation. Thus, these are act as bases.

20. (i) A diet consisting mainly of rice is not an adequate diet because it is deficient in lysine and threonine which are essential amino acids required for growth and maintenance of health and hence, their deficiency has to be supplemented by other protein rich diets like pulses, etc.

(ii) No, two molecules of the initially formed α-amino acid chloride react with each other to form a dipeptide acid chloride which, in turn, reacts further to form polypeptide acid chloride.

$$\text{NH}_2\text{CH}R\text{COOH} + \text{SOCl}_2 \rightarrow \text{NH}_2\text{CH}R\text{COCl} + \text{SO}_2 + \text{HCl}$$
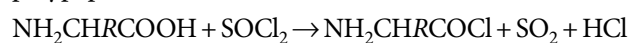
$$\underset{\substack{\text{α-Amino acid chloride} \\ \text{(two molecules)}}}{\text{NH}_2\text{CH}R\text{COCl} + \text{NH}_2\text{CH}R\text{COCl}} \xrightarrow{-\text{HCl}}$$

$$\underset{\substack{\text{Dipeptide acid} \\ \text{chloride}}}{n\text{NH}_2\text{CH}R\text{CONHCH}R\text{COCl}} \xrightarrow{-n\text{HCl}} \underset{\text{chloride}}{\text{Polypeptide acid}}$$
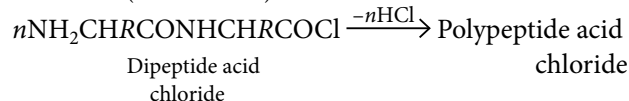
OR

(i) When egg white is boiled, the soluble globular protein, albumin present in it, is converted into insoluble rubber like mass. During this denaturation (i) globules unfold and helix get uncoiled and protein losses its biological activity and (ii) secondary and tertiary structures of albumin protein are destroyed while the primary structure (representing the sequence of α-amino acids) remains intact.

(ii) Glucose reacts with hydroxylamine (NH$_2$OH) to form an oxime and adds one molecule of hydrogen cyanide (HCN) to give cyanohydrin. Therefore, glucose contains a carbonyl group. On mild oxidation with bromine water, glucose gives a carboxylic acid, *i.e.*, gluconic acid containing the same six carbon atoms as present in glucose. This indicates that the carbonyl group present in glucose is an aldehydic group.

21. (i) Tetrahedral Ni (II) complexes involve sp^3-hybridisation. During their formation, two electrons are left unpaired in $3d$-orbitals of Ni^{2+} ion which makes the complex paramagnetic. Because tetrahedral Ni(II) complexes are high spin complexes.

Ni^{2+} (in tetrahedral complex)
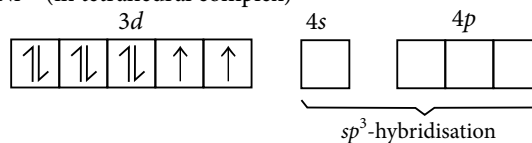
Square planar Ni (II) complexes involve dsp^2-hybridisation. During their formation, no unpaired electrons left in the complexes of this type and thus, they are diamagnetic. Because square planar Ni(II) complexes are low spin complexes.

Ni^{2+} (in square planar complex)

dsp^2-hybridisation
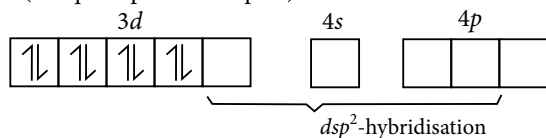
(ii) π-Complexes are the compounds of transition metals with ligands of the type carbon monoxide, alkenes, alkynes, benzene and other unsaturated ring systems. In such compounds, metal-carbon bond arises from interaction between π-electron cloud of ligand and partially filled d-orbitals which are present on metal atoms or their ions. For example, bonding of metal carbonyls. Since, the transition metal atoms or their ions have partially filled d-orbitals hence, these can form π-bond with unsaturated ligands.

22. (i) Monomer of polythene : $H_2C = CH_2$ (ethene)
Teflon : $F_2C = CF_2$ (tetrafluoroethene)

(ii) Benzoyl peroxide *i.e.*,
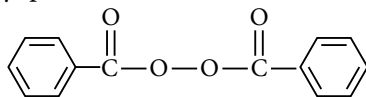
(iii) Vulcanisation is a process of heating natural rubber with sulphur and an appropriate additive to modify its properties. It gives greater elasticity and ductility. Sulphur forms cross linked network which gives mechanical strength to the rubber.

Natural rubber   Vulcanized rubber
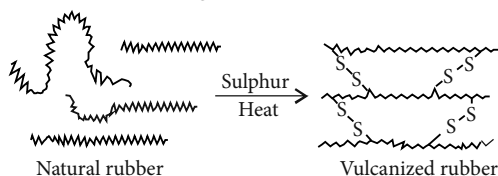
23. (i) The main ingredient of most of the sleeping pills is barbiturates. These chemicals make you breathe slowly and less deeply. That can be dangerous for people who have asthma or some other heart problems.

(ii) Chlordiazepoxide and diazepam are mild tranquilizers.

(iii) The doctor expressed concern about the health of his friend and made him aware of the harmful effects of sleeping pills, overdose of which acts as a poison and may even cause death.

24. (i) When the particles are present not only at corners but also at the centre of each face of the unit cell. It is called face centred unit cell.

Number of atoms in a unit cell of the face centred cubic (fcc) $\Rightarrow$ 8 atoms on the corners (gold) and 6 atoms on each face (cadmium).

Contribution by gold atoms on the corners $= \dfrac{1}{8} \times 8 = 1$

Contribution by cadmium atoms on the faces $= \dfrac{1}{2} \times 6 = 3$

Hence, formula for the given alloy = $AuCd_3$

(ii) As copper has fcc structure, $Z = 4$

$$d = \frac{Z \times M}{a^3 \times N_A}$$

$$8.95 = \frac{4 \times 63.5}{a^3 \times 6.02 \times 10^{23}}$$

$$a^3 = 47.143 \times 10^{-24} \text{ cm}^3$$

$$a = \sqrt[3]{47.143 \times 10^{-24}}$$

$$a = 3.612 \times 10^{-8} \text{ cm} = 361.2 \text{ pm}$$

For fcc, $4r = \sqrt{2}a$

$$r = \frac{a}{2\sqrt{2}} = \frac{361.2}{2 \times 1.414} = 127.7 \text{ pm}$$

OR

(i) (a) Since, group 15 elements (*e.g.*, phosphorus) have one electron excess to group 14 elements (*e.g.*, silicon) after forming four covalent bonds. Thus, the extra free electron is responsible for the formation of n-type semiconductors.

(b) Ferrimagnetic substances have a net dipole moment due to unequal parallel and antiparallel alignment of magnetic moments whereas antiferromagnetic substances have zero dipole moment due to compensatory alignment of magnetic moments. Therefore, ferrimagnetic substances show better magnetism than antiferromagnetic substances.

(ii) Radius of Na^+ = 95 pm
Radius of Cl^- = 181 pm

Radius ratio, $\dfrac{r_+}{r_-} = \dfrac{r_{(Na^+)}}{r_{(Cl^-)}} = \dfrac{95}{181} = 0.524$

The radius ratio lies between 0.414 – 0.732. Hence, Na^+ ions prefer to occupy octahedral holes, having coordination number 6.

25. (i) Noble gases have only van der Waals radii while others have covalent radii and van der Waals radii, by definition are larger than covalent radii.

(ii) (a) Structure of ICl_4^- : I in ICl_4^- has four bond pairs and two lone pairs. Therefore, according to VSEPR

theory, it should be square planar as shown in the figure. Here, ICl_4^- has $(7 + 4 \times 7 + 1 =)$ 36 valence electrons. A noble gas species having 36 valence electrons is $XeF_4(8 + 4 \times 7 = 36)$. Therefore, like ICl_4^-, XeF_4 is also square planar.

Square planar
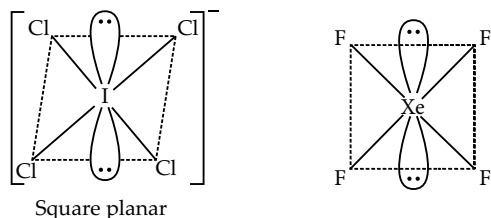
(b) **Structure of IBr_2^- :** I in IBr_2^- has two bond pairs and three lone pairs. So, according to VSEPR theory, it should be linear. Here, IBr_2^- has 22 $(= 7 + 2 \times 7 + 1)$ valence electrons. A noble gas species having 22 valence electrons is XeF_2 $(8 + 2 \times 7 = 22)$.

Thus, like IBr_2^-, XeF_2 is also linear.

Linear   Linear
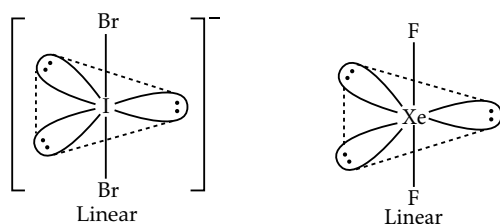
(c) **Structure of BrO_3^- :** Br atom in BrO_3^- has three bond pairs and one lone pair. Therefore, according to VSEPR theory, BrO_3^- should be pyramidal.

Here, BrO_3^- has $26(= 7 + 3 \times 6 + 1)$ valence electrons. A noble gas species having 26 valence electrons is $XeO_3(8 + 3 \times 6 = 26)$. Thus, like BrO_3^-, XeO_3 is also pyramidal.

Pyramidal   Pyramidal

OR

(i)

Pyrophosphoric acid
$(H_4P_2O_7)$
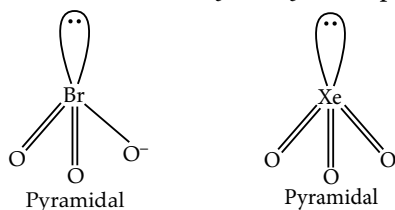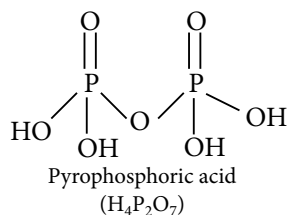
(ii) In H_3PO_2, two H atoms are bonded directly to P atom which imparts reducing character to the acid.

Hypophosphorous acid
(H_3PO_2)
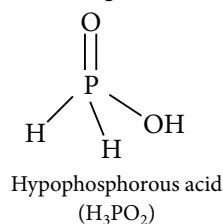
(iii) **(a)** Fluorine atom being smaller in size, the interelectronic repulsions between the non-bonding electrons present in the 2p-orbitals of fluorine atoms are much larger than similar interelectronic repulsion in the 3p-orbitals of chlorine atoms.

(b) In NO, the odd electron on N is attracted by only one O-atom but in ClO_2, the odd electron on Cl is attracted by two O-atoms. Thus, the odd electron on N in NO is localised while the odd electron on Cl in ClO_2 is delocalised. Consequently, NO has a tendency to dimerise but ClO_2 does not.

(c) Cl_2 bleaches coloured material by oxidation :
$$Cl_2 + H_2O \longrightarrow 2HCl + O$$
Coloured material + [O] $\longrightarrow$ Colourless
and hence, bleaching is permanent.
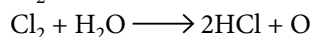
In contrast, SO_2 bleaches coloured material by reduction and hence, bleaching is temporary since, when the bleached colourless material is exposed to air, it gets oxidised and the colour is restored.
$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$
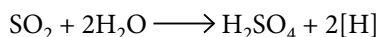
EXAM CORNER 2018

Exam	Date
VITEEE	4th April to 15th April
JEE Main	8th April (Offline), 15th & 16th April (Online)
SRMJEEE	16th April to 30th April
Karnataka CET	18th April & 19th April
WBJEE	22nd April
Kerala PET	23rd April & 24th April
AMU (Engg.)	29th April
COMEDK (Engg.)	13th May
BITSAT	16th May to 31st May
JEE Advanced	20th May
AIIMS	27th May

Coloured material + [H] $\longrightarrow$ Colourless material $\xrightarrow[\text{Oxidation}]{\text{Aerial}}$ Coloured material.
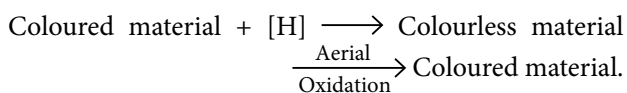
26. (i) π-electrons of the $\overset{}{\underset{}{C}} = O$ are loosely held and hence, can be shifted towards O-atom more readily than the more tightly held σ-electrons of the $C - O$ bond in alcohols. Consequently, partial +ve and –ve charge developed on $\overset{}{\underset{}{C}} = O$ bond of aldehyde is higher and than those on $C - O$ bond of alcohol. As a result, the dipole moment of aldehydes and ketones (2.3 – 2.8 D) is much higher than that of alcohols (1.6 – 1.8 D).

(ii) Due to intramolecular H-bonding (chelation), o-hydroxybenzaldehyde exists as discrete molecules while due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules.
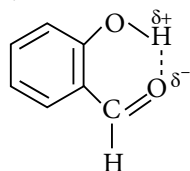
o-Hydroxybenzaldehyde
(Intramolecular H-bonding)
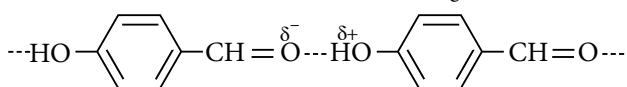
p-Hydroxybenzaldehyde (Intermolecular H-bonding)

To break these intermolecular H-bonds, a large amount of energy is required. Consequently, p-hydroxybenzaldehyde has a much higher m.pt. and b.pt. than the o-hydroxybenzaldehyde. As a result, o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

(iii) Since, halogens are more electronegative than carbon and also possess lone pairs of electrons, therefore, they exert both $-I$- and $+R$-effect. Now in F, the lone pairs of electrons are present in $2p$-orbitals but in Cl, they are present in $3p$-orbitals. Since, $2p$-orbitals of F and C are of almost equal size, therefore, the $+R$-effect is more pronounced in p-fluorobenzoic acid than in p-chlorobenzoic acid

Stronger $+R$-effect   Weaker $+R$-effect
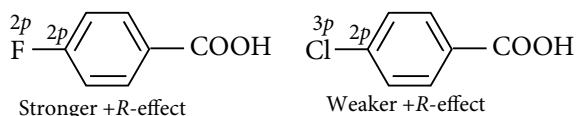
Thus, in p-fluorobenzoic acid, $+R$-effect outweighs the $-I$-effect but in p-chlorobenzoic acid, it is the $-I$-effect which outweighs the $+R$-effect. Consequently, p-fluorobenzoic acid is a weaker acid than p-chlorobenzoic acid.

OR
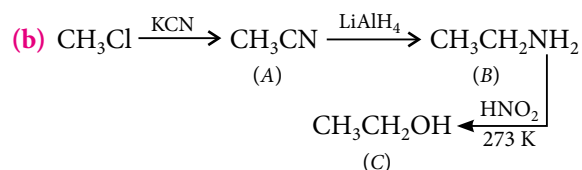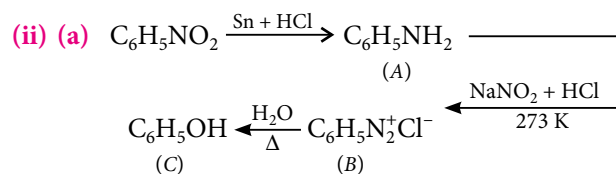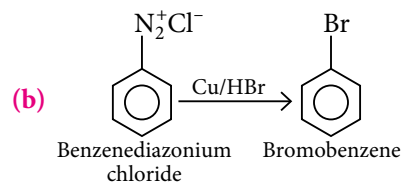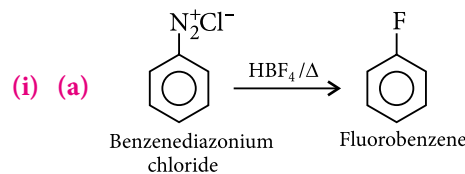
(i) (a)

Benzenediazonium chloride $\xrightarrow{\text{HBF}_4/\Delta}$ Fluorobenzene

(b)

Benzenediazonium chloride $\xrightarrow{\text{Cu/HBr}}$ Bromobenzene

(ii) (a) $C_6H_5NO_2 \xrightarrow{\text{Sn + HCl}} C_6H_5NH_2$ (A)

$\xrightarrow[\text{273 K}]{\text{NaNO}_2 + \text{HCl}}$

$C_6H_5OH \xleftarrow[\Delta]{H_2O} C_6H_5N_2^+Cl^-$
(C)   (B)

(b) $CH_3Cl \xrightarrow{\text{KCN}} CH_3CN \xrightarrow{\text{LiAlH}_4} CH_3CH_2NH_2$
                          (A)   (B)

$CH_3CH_2OH \xleftarrow[\text{273 K}]{\text{HNO}_2}$
(C)

MPP-9 | MONTHLY Practice Problems | Class XII

This specially designed column enables students to self analyse their extent of understanding of specified chapter. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Organic Compounds Containing Nitrogen

Total Marks : 120　　　　　　　　　　　　**Time Taken : 60 Min.**

NEET / AIIMS
Only One Option Correct Type

1. An amine forms salt with BF_3, if the alkyl group in amine is CH_3-, the order of basicity towards BF_3 is
   (a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
   (b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
   (c) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
   (d) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2$

2. Aniline is treated with $NaNO_2/HCl$ at 0 °C to give compound 'X' which on treatment with cuprous cyanide gives another compound 'Y'. When compound 'Y' is treated with H_2/Ni, compound 'Z' is obtained. Compound 'Z' is
   (a) benzyl alcohol　　(b) benzylamine
   (c) N-ethylaniline　　(d) phenol.

3. Identify the product Z in the given sequence of reactions :
   $$CH_3CN \xrightarrow{Na/C_2H_5OH} X \xrightarrow{HNO_2} Y \xrightarrow[\text{reagent}]{\text{Baeyer's}} Z$$
   (a) CH_3CHO　　(b) CH_3CONH_2
   (c) CH_3COOH　　(d) CH_3CH_2NHOH
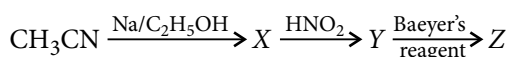
4. Consider the following ions :

   I. $Me_2N-\langle\rangle-\overset{+}{N}\equiv N$

   II. $O_2N-\langle\rangle-\overset{+}{N}\equiv N$

   III. $CH_3O-\langle\rangle-\overset{+}{N}\equiv N$

   IV. $CH_3-\langle\rangle-\overset{+}{N}\equiv N$
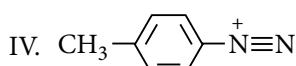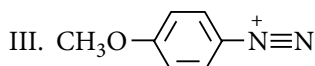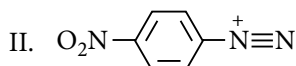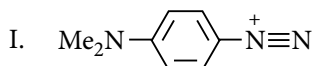
The reactivity of these ions towards azo coupling reactions under similar conditions is
(a) I < IV < II < III　　(b) I < III < IV < II
(c) III < I < II < IV　　(d) III < I < IV < II

5. Butanenitrile may be prepared by heating
   (a) propyl alcohol with alc. KCN
   (b) butyl alcohol with alc. KCN
   (c) butyl chloride with alc. KCN
   (d) propyl chloride with alc. KCN.

6. Which of the following is not a nitro-derivative?
   (a) $CH_3CH-N\overset{O}{\underset{O}{\diagup\diagdown}}$ | CH_3　　(b) CH_3CH_2ONO
   (c) $C_6H_5NO_2$　　(d) $C_6H_4(OH)NO_2$

7. Identify X and Y in the given reactions,
   $$CH_3-CH-CONH_2 \xrightarrow{Br_2/NaOH} X \xrightarrow{HNO_2} Y.$$ | CH_3
   (a) $CH_3-CH-CH_2NH_2$; $CH_3-CH-CH_2OH$ | CH_3 | CH_3
   (b) $CH_3CH=CHNH_2$; $CH_3CH=CHOH$
   (c) $CH_3-CH-NH_2$; $CH_3-CH-OH$ | CH_3 | CH_3
   (d) $CH_3CH_2CH_2NH_2$; $CH_3CH_2CH_2OH$
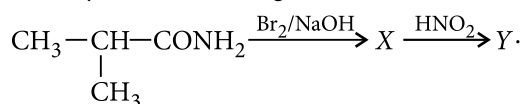
8. 59 g of an amide obtained from a carboxylic acid, RCOOH, upon heating with alkali liberated 17 g NH_3. The acid is
   (a) formic acid　　(b) acetic acid
   (c) propionic acid　　(d) benzoic acid.

9. Identify the compound 'Y' in the following reaction.

$$\underset{273\text{-}278\ K}{\xrightarrow{NaNO_2 + HCl}} \xrightarrow{Cu_2Cl_2} Y + N_2$$

(a)

(b)

(c)

(d)
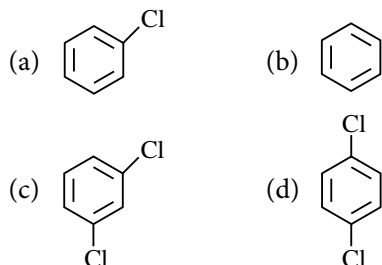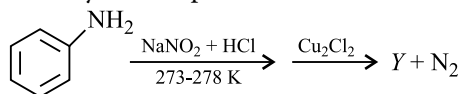
10. Aromatic nitriles are not prepared by which of the following reaction?
(a) $ArX + KCN$
(b) $ArN_2^+Cl^- + CuCN$
(c) $ArCONH_2 + P_2O_5$
(d) $ArCONH_2 + SOCl_2$
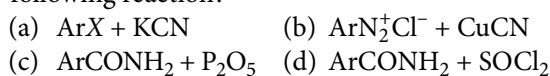
11. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. The final product is
(a) p-bromoaniline
(b) p-bromofluorobenzene
(c) 1, 3, 5-tribromobenzene
(d) 2, 4, 6-tribromofluorobenzene.

12. When aniline reacts with oil of bitter almonds condensation takes place and benzal derivative is formed. This is known as
(a) iodide of Millon's base
(b) Hinsberg's reagent
(c) acetanilide
(d) Schiff's base.

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. Assertion : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Reason : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is available for resonance.

14. Assertion : Gabriel phthalimide synthesis can be used to convert alkyl chlorides into primary amines.

Reason : With proper choice of reagent, Gabriel synthesis can be used to prepare primary, secondary and tertiary amines.

15. Assertion : p-Methoxyaniline (p-anisidine) is a stronger base than m-methoxyaniline (m-anisidine).

Reason : At m-position, methoxy group can exert only $-I$ effect but not $+R$ effect.

JEE MAIN / JEE ADVANCED
Only One Option Correct Type

16. Identify the final product.

(a)

(b)

(c)

(d)
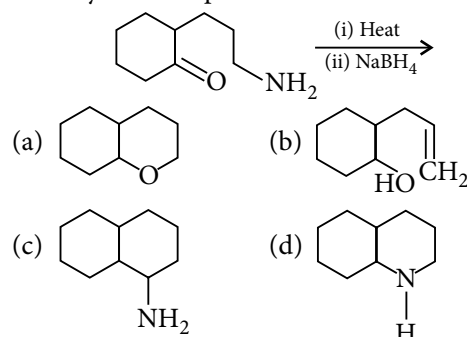
17. Which of the following is the strongest acid?
(a) 4-Nitrobenzoic acid
(b) 4-Methylbenzoic acid
(c) 4-Methoxybenzoic acid
(d) 4-Ethylbenzoic acid

18. A compound 'A' has a molecular formula, C_7H_7NO. On treatment with Br_2 and KOH, 'A' gives an amine 'B' which gives carbylamine test. 'B' upon diazotisation and coupling with phenol gives an azo dye. 'A' can be
(a) $C_6H_5CH=NOH$
(b) $C_6H_5CONH_2$
(c) $C_6H_5CH_2NO$
(d) o-, m- or p-$C_6H_4(NH_2)CHO$

19. Identify 'X' in the given reactions sequence.

$$\xrightarrow{(CH_3CO)_2O} A \xrightarrow{Br_2 / CH_3COOH} B$$

$$\xrightarrow{H^+ / H_2O} X$$

(a)

(b)

(c)

(d)
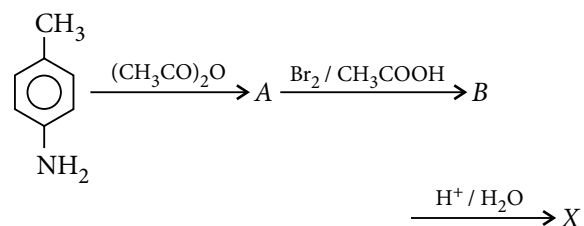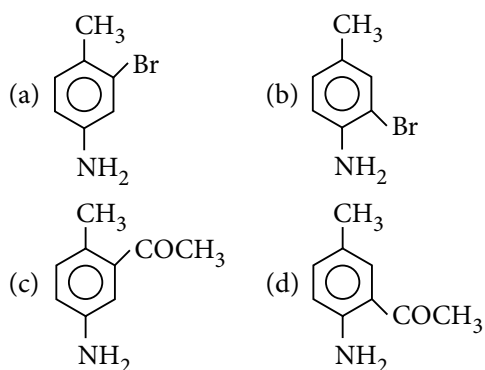
More than One Options Correct Type

20. Select the correct statements.
   (a) Most alkyl amines are more basic than ammonia in aqueous solution.
   (b) pK_a of $Me_3\overset{+}{N}H$ is higher than that of NH_4^+.
   (c) Aniline is more stable than anilinium ion.
   (d) pK_b of CH_3NH_2 is higher than that of NH_3.

21. Which of the following statements are correct?

$$CH_3 - N\rangle \qquad HN\langle - CH_3$$

N-Methylpiperidine   4-Methylpiperidine
(A)   (B)
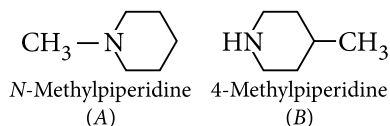
   (a) *A* has higher boiling point than *B*.
   (b) *B* has higher boiling point than *A*.
   (c) *A* and *B* have same boiling points being isomeric amines.
   (d) *B* reacts with benzenesulphonyl chloride while *A* does not.

22. A positive carbylamine test is given by
   (a) *N, N*-dimethylaniline
   (b) 2, 4-dimethylaniline
   (c) *N*-methyl-*o*-methylaniline
   (d) *p*-methylbenzylamine.

23. The reagents that can be used to convert benzenediazonium chloride to benzene are
   (a) $SnCl_2/HCl$ (b) CH_3CH_2OH
   (c) H_3PO_2, H_2O (d) HBF_4

Integer Answer Type

24. The total number of optically active compounds which can be resolved from the following list is
$C_2H_5NHCH_3$, $CH_3CH_2CH(CH_3)N(CH_3)C_2H_5$,

$[Ph(CH_3)(C_2H_5)\overset{+}{N}H]I^-$,

$[(C_2H_5)(CH_3)_2\overset{+}{N}H]I^-$,

$C_6H_5(CH_3)(C_2H_5)\overset{+}{N} - O^-$,

$(CH_3)(C_2H_5)NCH(CH_3)_2$
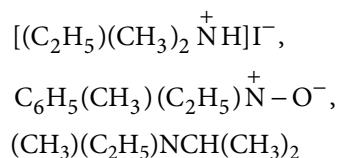
25. Number of amines out of the following which will react with CS_2 is
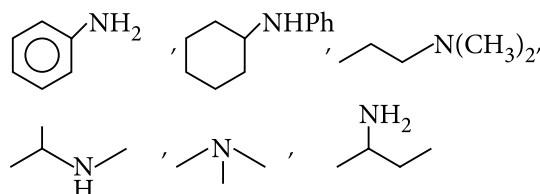
26. $C_4H_{11}N$ on reaction with HNO_2 forms 3° alcohol. Thus, amine is $x°$. x is _____.

Comprehension Type

A compound '*X*' (C_4H_5N) exists in two stereoisomeric forms. Compound (*X*) on reduction with H_2 in the presence of Ni gives a compound (*Y*). Compound '*Y*' ($C_4H_{11}N$) exists in only one form. Compound (*X*) on treatment with alk. $KMnO_4$ followed by acidification gives acetic acid and oxalic acid. When compound (*X*) is reacted with NaOH followed by acidification gives a compound (*Z*) with molecular formula, $C_4H_6O_2$. Compound (*Z*) on reaction with alk. $KMnO_4$ followed by acidification gives again oxalic acid and acetic acid. Compound (*Y*) on reaction with $CHCl_3$ and KOH forms a compound '*A*' (C_5H_9N). Compound (*Y*) on treatment with HNO_2 followed by reaction with PCC gives a compound (*B*) which gives positive Tollens' test.

27. The compound (*X*) must be
   (a) $CH_2 - CH = CH_2$
           |
           CN
   (b) $CH_3 - C = CH_2$
               |
               CN
   (c) $CH_3 - CH = CH - CN$
   (d) $CH_3 - CH = CH - NC$

28. The compound (*Z*) must be
   (a) $CH_2=CH-COOCH_3$
   (b) $CH_3-CH=CH-COOH$
   (c) $CH_3-CH=CH-NC$
   (d) $OHCCH_2-CH=CH_2$
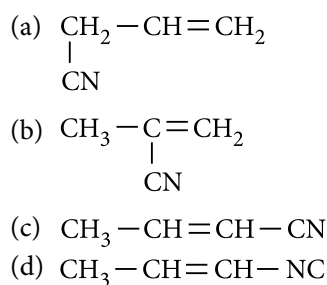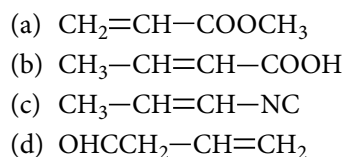
Matrix Match Type

29. Match the List I with List II and select the correct answer using the code given below the lists :

List I	List II
(Compounds)	(pK_b value)
P. Ammonia	1. 8.92
Q. Methanamine	2. 9.38
R. Benzenamine	3. 3.38
S. N,N-Dimethylaniline	4. 4.75

	P	Q	R	S
(a)	2	1	3	4
(b)	1	2	3	4
(c)	4	1	2	3
(d)	4	3	2	1

30. Match the List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. Benzenesulphonyl chloride	1. Zwitter ion
Q. Sulphanilic acid	2. Hinsberg's reagent
R. Alkyldiazonium salts	3. Dyes
S. Aryldiazonium salts	4. Conversion to alcohols

	P	Q	R	S
(a)	4	1	2	3
(b)	3	2	4	1
(c)	2	1	4	3
(d)	4	2	3	1

Keys are published in this issue. Search now! ☺

SELF CHECK

Check your score! If your score is

No. of questions attempted ......
No. of questions correct ......
Marks scored in percentage ......

> 90%	**EXCELLENT WORK !**	You are well prepared to take the challenge of final exam.
90-75%	**GOOD WORK !**	You can score good in the final exam.
74-60%	**SATISFACTORY !**	You need to score more next time.
< 60%	**NOT SATISFACTORY!**	Revise thoroughly and strengthen your concepts.

CHEMISTRY MUSING

PROBLEM SET 54

*C*hemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. Which of the following complexes is an example of strongest reducing agent?
   (a) $[Co(CN)_6]^{4-}$ (b) $[Co(CN)_6]^{3-}$
   (c) $[Ag(CN)_2]^-$ (d) $[Cu(CN)_4]^{3-}$

2. $H_4P_4O_{12}$ (tetrametaphosphoric acid) and $H_6P_4O_{13}$ (tetrapolyphosphoric acid) have same
   (a) no. of $P—O—P$ bonds
   (b) no. of $P—O—H$ bonds
   (c) no. of $P=O$ bonds
   (d) all of these.

3. A compound [structure], shows a large dipole moment. Which of the following resonance structures can be used to adequately explain this observation?

   (i) [structure]   (ii) [structure]

   (iii) [structure]   (iv) [structure]

   (a) (i) only   (b) (iii) and (iv) only
   (c) (ii) and (iii) only   (d) (iv) only

4. Which of the following statements is false about 1,3-dithiane, [structure] ?
   (a) It can react with RLi.
   (b) It can be alkylated by $CH_3CH_2CH_2Br$.
   (c) It can be alkylated by Me_2CHX.
   (d) It can be used for preparing aldehydes and ketones.

5. The value of $\dfrac{t_{0.875}}{t_{0.50}}$, for n^{th} order reaction is
   (a) $2^{(2n-2)}$ (b) $2^{(2n-2)}-1$
   (c) $\dfrac{8^{n-1}-1}{2^{n-1}-1}$ (d) none of these.

JEE ADVANCED

6. In the given reaction,

   [structure] $\xrightarrow{\text{dil. } H_2SO_4} P_1 + P_2$
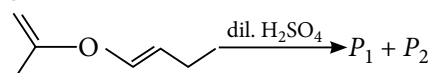
   P_1 and P_2 products are identified by
   (a) Tollens' reagent   (b) 1% alkaline $KMnO_4$
   (c) bromine-water test   (d) none of these.

COMPREHENSION

A terpene that is contained in the oil of citronella is α-farnesene. Refer to the structure of α-farnesene to answer the following questions :

[structure: α-farnesene]
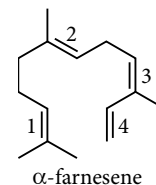
7. What reaction conditions could be used to produce acetone from α-farnesene?
   (a) H_2SO_4 and heat
   (b) HBr
   (c) O_3 and $(CH_3)_2S$
   (d) Dilute acid and cold conditions

8. In the reaction of α-farnesene with excess HBr, which double bond would be slowest to react?
   (a) The bond labelled 1   (b) The bond labelled 2
   (c) The bond labelled 3   (d) The bond labelled 4

INTEGER VALUE

9. The atomic masses of He and Ne are 4 and 20 amu respectively. The value of the de Broglie wavelength of He gas at –73 °C is 'M' times that of the de Broglie wavelength of Ne at 727 °C. The value of 'M' is

10. Assuming covalent radii to be additive property; calculate the iodine-iodine distances in *p*-diiodobenzene. The benzene ring is regular hexagon and each $C—I$ bond lies on a line passing through the centre of hexagon. The $C—C$ bond length in C_6H_6 is 1.40 Å and covalent radius of iodine and carbon atoms are 1.33 Å and 0.77 Å. Also neglect different overlapping effect.

❁❁

CONCEPT
BOOSTER

Hello Students!! Like the last article this article is also giving you an opportunity to learn and apply your conceptual knowledge to solve a little bit tough problems. As I say, problem solving approach is the most important key to be successful in competitive examinations. This article will show you the correct path for the same. Keep practicing and enjoy learning. Merry Christmas and Happy New Year to all of you. Wish you a lovely year ahead.

*Arunava Sarkar

VERY IMPORTANT PROBLEMS

1.

2.

3.

4.

5.

6.

SOLUTIONS

1.

$$\longrightarrow CH_2=CH-CH_2-CH=CH-COOH$$
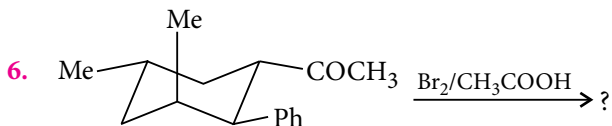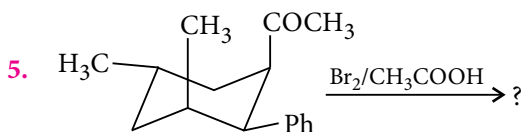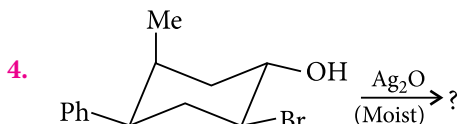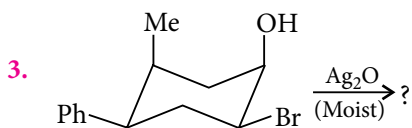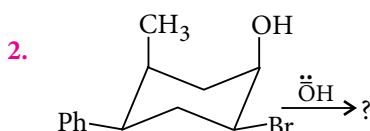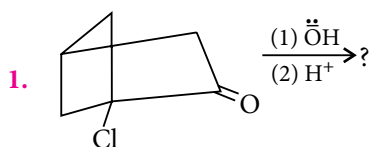
Remember that here semi-benzilic Favoroskii rearrangement takes place as there is difficulty in alkalisation.

2.

3.
(No proper arrangement is possible)
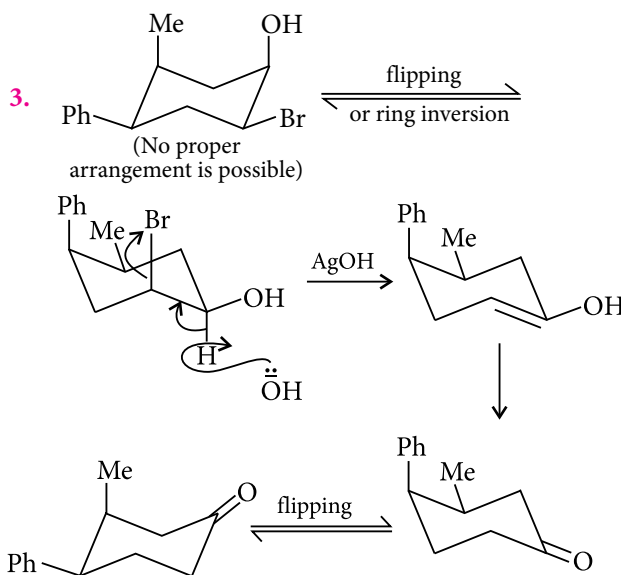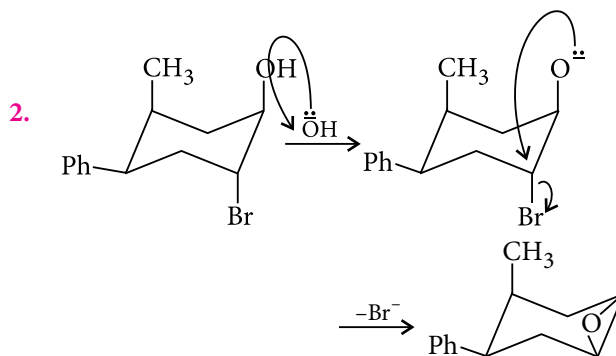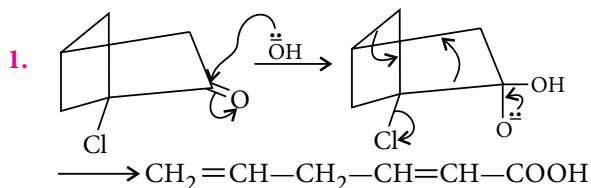
*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

4.

5.

Before, I answer this question a very important concept to be discussed and that is A-strain.

If we consider this segment in equatorial conformation then the allylic segment is coplanar and R_3 and R_2 are found to be coplanar and this gives strong steric repulsion. This is why an exocyclic $\text{C}=\text{C}$ prevent an equatorial substitutent at the adjacent carbon.

This 1, 3-interaction between R_2 and R_3 is called A-strain. Now, the given compound is

unstable due to A-strain

That is why strain enolisation does not take place. So, the compound will undergo flipping.
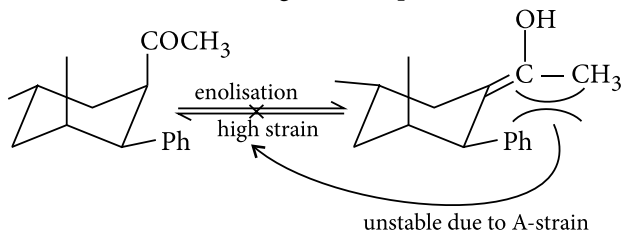
(W) does not undergo any kind of strain.

6.
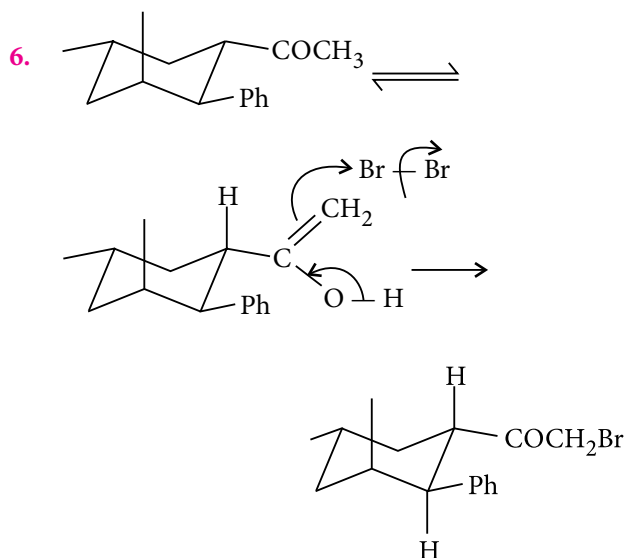
ADVANCED CHEMISTRY BLOC

(RE-READING ORGANIC CHEMISTRY)

Mk C.R ay, Oi sh

SOME IMPORTANT REACTIONS OF HYDROCARBONS

1. Addition of HOCl, HOBr, NOCl, Cl_2/H_2O :

The mechanism of HO*X* addition is electrophilic, with the initial attack by the positive halogen end of the HO*X* dipole. Following Markovnikov's rule, the positive halogen goes to the side of the double bond that has more hydrogens.

There is evidence that the mechanism with Cl_2 and H_2O is different from that with HOCl.
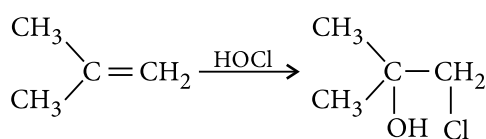
And,
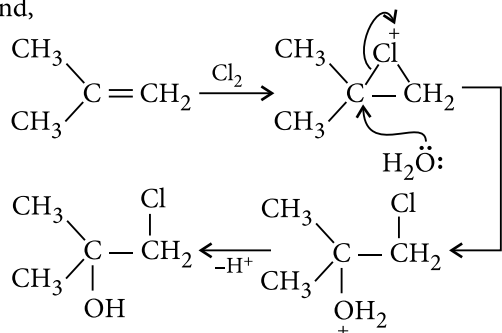
Addition products of NOCl are stable only if the carbon atom bearing the nitrogen has no hydrogen.
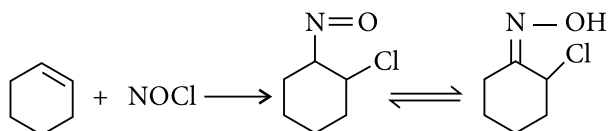
2. Water addition in alkenes :

Three different ways of water addition are :
Acid catalysed hydration involves carbocation and hence rearrangement.

So,
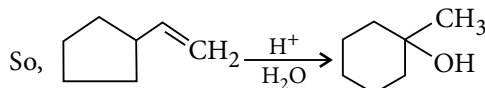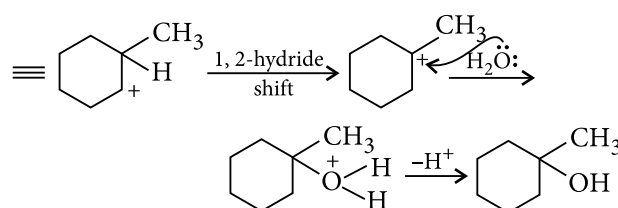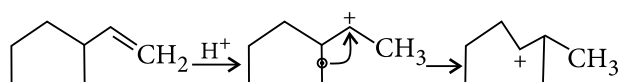
There is no specific stereochemistry of addition in this reaction.

In hydroboration-oxidation, there is no carbocation. So, no rearrangement takes place. —OH of water goes to the side that is less crowded. It's a *syn* addition.
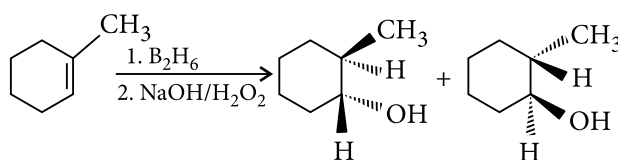
Another example
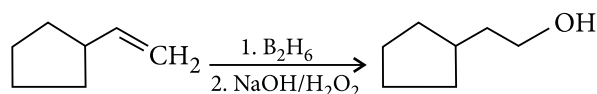
Oxymercuration-demercuration occurs with Markovnikov's regiochemistry and results in hydration of alkenes without complication from carbocation rearrangement. The overall stereochemistry of addition is not controlled here also like acid catalysed hydration results a mixture of both *cis* and *trans* products.
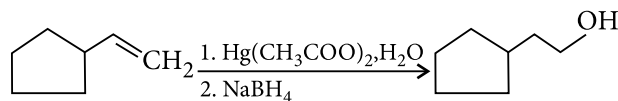
3. Alkyne preparation :

Double dehydrohalogenation is a common process. While $NaNH_2$ favours terminal alkyne, KOH favours non-terminal ones as is evident from the following :

$$CH_3 - \underset{Br}{CH} - \underset{Br}{CH}CH_2CH_3,$$

$$Br - \underset{Br}{CH}CH_2CH_2CH_2CH_3,$$

$$CH_3 - \underset{Br}{\overset{Br}{C}} - CH_2CH_2CH_3,$$

$$CH_2 - \underset{Br}{CH}CH_2CH_2CH_3$$
$$\underset{Br}{}\quad\underset{Br}{}$$

$$\xrightarrow[200°C]{KOH} CH_3C \equiv CCH_2CH_3$$
Pent-2-yne
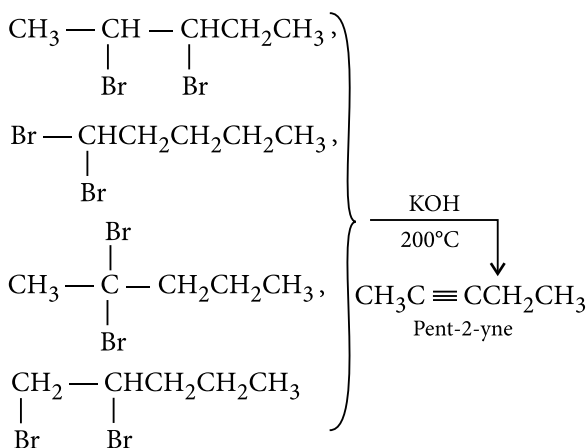
4. Water addition in alkynes :

Alkynes are less reactive than alkenes towards electrophilic addition reactions. So in acid catalysed hydration of alkynes, you require an additional catalyst Hg^{2+}. The result is Markovnikov's addition of water.

$$CH_3 - C \equiv CH + H_2O \xrightarrow[Hg^{2+}]{Dil.\ H_2SO_4} CH_3 - \underset{OH}{\overset{}{C}} = CH_2$$

$$\rightleftharpoons CH_3 - \overset{O}{\overset{||}{C}} - CH_3$$
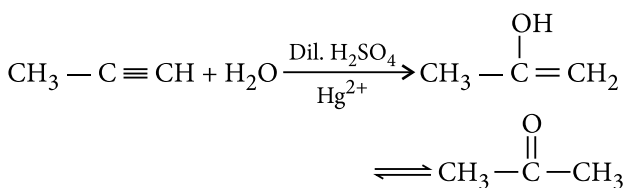
Anti-Markovnikov's water addition can be executed by hydroboration oxidation.

$$CH_3 - C \equiv CH \xrightarrow[2.\ H_2O_2/OH^-]{1.\ B_2H_6} CH_3 - CH = \underset{OH}{\overset{}{CH}}$$

$$\rightleftharpoons CH_3 - CH_2 - \overset{O}{\overset{||}{C}} - H$$
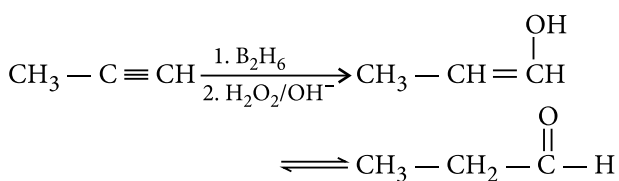
To prevent further addition of B_2H_6 at the alkene stage diamylborane is more recommended.

5. Oxidation of alkenes :

There are different oxidation products :

(i) $\overset{>}{\underset{}{}}C = C\overset{<}{\underset{}{}} \longrightarrow \overset{>}{\underset{}{}}\overset{O}{C - C}\overset{<}{\underset{}{}}$
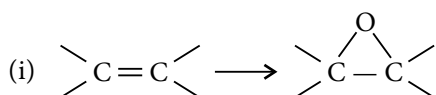
Oxidising agents : O_2, Ag, Δ
or $RCOOOH$ (per acid)

(ii) $\overset{>}{\underset{}{}}C = C\overset{<}{\underset{}{}} \longrightarrow \overset{>}{\underset{OH}{}}C - \underset{OH}{C}\overset{<}{\underset{}{}}$
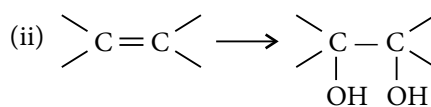
Reagents :
1. OsO_4 2. Na_2SO_3/H_2O
or MnO_4^-/OH^- (dilute and cold)
or 1. $RCOOOH$ 2. H_3O^+

While the first two reagents cause *syn*-addition of two —OH groups, the last one results *anti*-hydroxylation.

(iii) Oxidation cleavage can be executed by ozonolysis or even by Lemieux reagent or strong and hot alkaline $KMnO_4$. For examples :

$$\text{(cyclohexene)} \xrightarrow[\substack{CH_2Cl_2 \\ low\ temp.}]{O_3} Ozonide$$

with branches:
- $\xrightarrow[\substack{H_2O \\ (or\ Me_2S)}]{Zn}$ → CH=O, CH=O
- $\xrightarrow[(or\ H_2O_2)]{H_2O}$ → COOH, COOH
- $\xrightarrow{NaBH_4}$ → CH_2OH, CH_2OH

And,

$$CH_3 - \underset{CH_3}{\overset{}{C}} = CH - CH_3 \xrightarrow[[OH^-],\Delta]{KMnO_4}$$

$$CH_3 - \underset{CH_3}{\overset{}{C}} = O + CH_3 - COOH$$
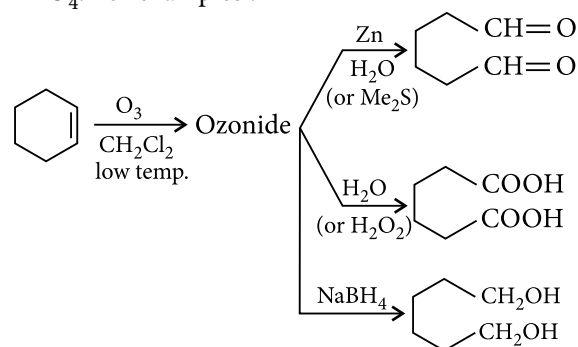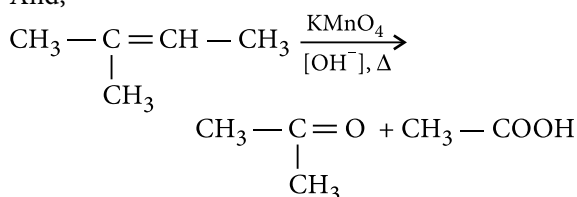
6. In the aromatic hydrocarbon section, you must note, the five most common electrophilic substitution reactions.

(i) Conc. HNO_3 and conc. H_2SO_4 (Nitration)
(ii) SO_3 in H_2SO_4 (Sulphonation)
(iii) Br_2 in $FeBr_3$ or Cl_2 in $FeCl_3$ (Halogenation)
(iv) RX in $AlCl_3$ (Friedel-Crafts alkylation)
(v) $RCOCl$ in $AlCl_3$ (Friedel-Crafts acylation)

MPP-9 CLASS XII		**ANSWER**	**KEY**	
1. (c)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (d)
6. (b)	**7.** (c)	**8.** (b)	**9.** (a)	**10.** (a)
11. (d)	**12.** (d)	**13.** (d)	**14.** (c)	**15.** (a)
16. (d)	**17.** (a)	**18.** (b)	**19.** (b)	**20.** (a,b,c)
21. (b,d)	**22.** (b, d)	**23.** (b,c)	**24.** (3)	**25.** (4)
26. (1)	**27.** (c)	**28.** (b)	**29.** (d)	**30.** (c)

All these reagents develop an electrophile, which then reacts in two steps mechanism :

The general SArE2 mechanism considering, E^+ as electrophile and B as base is :
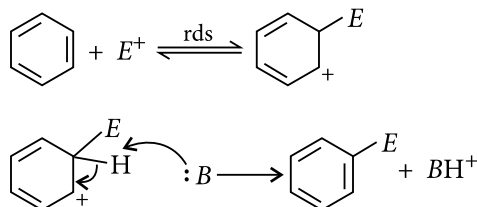
When you carry out further substitution on mono or polysubstituted benzenes, the concept of activating/deactivating groups and *ortho*/*para* directive influence becomes the point of attention.

Some activating groups in decreasing order :

$$—\bar{O} > —NH_2 > —NHR > —NR_2 > —OH$$
$$> —OR > —NHCOR > —Ph > —R$$

Some deactivating groups in decreasing order :

$$—NR_3 > —NO_2 > —CN > —COOH > —COOR$$
$$> —SO_3H > —CHO > —COR$$
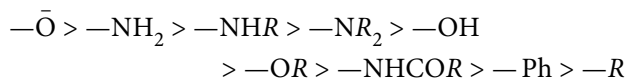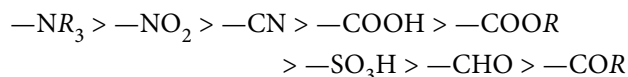
The substitution on a disubstituted benzene is guided by the two basic principles :

(i) Activator wins over deactivator

(ii) Strong activator wins over weaker activator.

The substitution positions are shown by arrow mark :
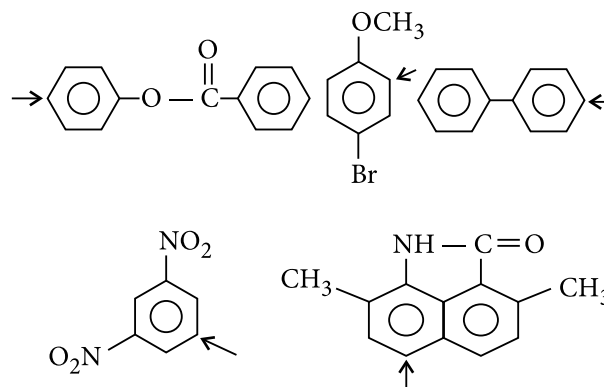
SRM University AP - Amaravati announces the setting up of School of Liberal Arts and Basic Sciences (SLABS)

B.A., B.B.A, B.Com. & B.Sc. courses will be offered from 2018 in 12 subjects

President of SRM University, Dr. P. Sathyanarayanan, announced the setting up of School of Liberal Arts and Basic Sciences (SLABS) at its University in Amaravati in the presence of the Honorary Pro Chancellor of SRM University, AP - Amaravati, Prof. Nicholas Dirks (Chancellor Emeritus, University of California, Berkley), and Dr. D Narayana Rao, Pro Vice Chancellor of SRM University, AP – Amaravati. SLABS will be SRM Amaravati's home for fundamental research, where free, open, and critical inquiry is pursued across disciplines, finding answers and solutions to world's most challenging problems and daunting issues. SLABS will have its first intake of students in 2018 and will offer B.A., B.B.A., B.Com and B.Sc. programs across 12 departments –Economics, English, History, Journalism, Psychology, Business Studies, Commerce, Physics, Chemistry, Mathematics, Biology and Computer Science.

"Today, we face increasingly complex issues and challenges, and tackling these, calls for multi-dimensional thought processes and problem solving skills. Education needs to focus on this and much more. We aim to help students develop such skills through the liberal arts and basic sciences education offered at SRM SLABS. For this, we are looking at hands-on guidance from Prof. Nicholas Dirks, given his background as a renowned anthropologist, and his rich experience in Liberal Arts. SRM SLABS also has a strong faculty base of international caliber who will bring a global perspective to liberal arts education." They will assist in creating a holistic approach to education, which will become, we hope, the calling card for SRM Amarvati's SLABS", says Dr. P Sathyanarayanan, President SRM Amaravati.

"I am very pleased to be involved with SRM Amaravati as it establishes its School of Liberal Arts and Basic Sciences. In our program, students will learn the skills of critical thinking and knowledge creation in a range of fields in the humanities, social sciences, and sciences. They will have an innovative multi-disciplinary education, in close proximity as well to breaking new teaching and research in areas ranging from machine learning and data science to public policy and social analysis", says Prof. Nicholas Dirks, Honorary Pro Chancellor, SRM Amaravati.

"SRM is committed to offering a distinctive form of learning empowering young students and thinkers with historical and cultural perspectives, as well as language, critical thinking, and communication skills— ideal traits to survive the modern world. The multi-disciplinary focus of SLABS will ensure that the students would have both breadth as well as depth of knowledge about a wide range of subjects", says Dr. D Narayana Rao, Pro. Vice Chancellor, SRM Amaravati.

About SRM University, AP-Amaravati

SRM University, AP – Amaravati, is envisaged to be a multi-disciplinary institution starting off with programs in engineering, followed by liberal arts and later on in fields of management, law, medical sciences, and pure sciences. SRM envisions to emerge as a world-class university in creating and disseminating knowledge and providing students a unique learning experience in their chosen field of scholarship that would best serve the society. The focus is on developing into an inter-disciplinary institution combining academic rigour, excitement of discovery, creativity and entrepreneurship that delivers cutting-edge research based education, creating new knowledge and innovations. The School of Engineering and Applied Sciences is already functional with the first batch of engineering students having commenced their courses in August 2017.

For more information, please visit: www.srmap.edu.in

FACT SHEET:

School of Liberal Arts and Basic Sciences (SLABS), at SRM University, AP-Amaravati

Beginning from	2018 session
Courses Offered	B.A., BBA, B. Com., B. Sc.
Program Duration	3 years + 1 Additional year (Optional) resulting in a Diploma / Certificate
Disciplines	Physical and Natural Sciences, Arts, Humanities, Social Sciences, Business Studies, Commerce
Subjects	Economics, English, History, Journalism, Psychology, Business Studies, Commerce, Physics, Chemistry, Mathematics, Biology and Computer Science.
Admission Criterion	Merit, based on Std. XII Exam Results
Faculty Profile	Top in the category from India and Abroad. 100% PhDs 75% have international Exposure in Research/Teaching 15% Foreign nationals Visiting faculty comprising of local and global experts/ academics
SLABS Approach	Multi-disciplinary. No restriction on courses across disciplines In class discussions, Field Trips Presentations / Movies / Hands on Assignments

At a Glance CHEMISTRY today 2017

MONTHS	Solved Papers (2017)	Practice Papers (2017 & 2018)	Examiner's Mind	JEE Accelerated Learning series/ NEET	JEE Essentials	Concept Map	Others
JANUARY	—	ACE Your Way CBSE (Class XI) Series-7, (Hydrocarbons, Environmental chemistry), ACE Your Way CBSE (Class XII) (2017)	Redox reactions, Environmental chemistry (Class XI), Surface chemistry, Polymers and Chemistry in everyday life (Class XII)	Unit-7 : Organic chemistry: Some basic principles and techniques (Class XI), Unit-7 : Organic compounds containing nitrogen, Biomolecules (Class XII)	Gaseous state (Class XI), Bonding in coordination compound (Class XII)	MPP-7 : Organic chemistry: Some basic principles and techniques (Class XI), MPP-7 : Aldehydes, ketones and carboxylic acids, Organic compounds containing nitrogen (Class XII), Chemistry Musing Problem Set-42, Concept Booster, Advanced Chemistry Bloc (Thermodynamics), Chemistry Musing Set-41, Crossword
FEBRUARY		JEE Main (Model Test Paper), NEET, JEE Main, ACE Your Way (Class XI), ACE Your Way (Class XII) (2017)	—	Unit-8 : Hydrocarbons, Environmental chemistry (Class XI), Unit-8 : Polymers, Chemistry in everyday life (Class XII)	Thermodynamics (Class XI), Detection of organic functional groups (Class XII)	MPP-8 : Hydrocarbons, Environmental Chemistry (Class XI), MPP-8 : Biomolecules, Polymers, Chemistry in everyday life (Class XII), Chemistry Musing Problem Set-43, Concept Booster, Advanced Chemistry Bloc (Thermochemistry), Chemistry Musing Solution Set-42, Crossword
MARCH	—	JEE Main, NEET, BITSAT, JEE Advanced, AIIMS ACE Your Way CBSE (Class XII) (2017)	—	Unit-9 : Practical chemistry (Class XI), Unit-9 : Practical chemistry (Class XII)	Some important compounds of group-13 and group-14 (Class XI) Stereochemistry (Class XII)	MPP (Class XI), MPP (Class XII), Chemistry Musing Problem Set-44, Chemistry Musing Solution Set-43, Crossword
APRIL	—	NEET, JEE Advanced (Model Test Paper), JEE Advanced (full length), BITSAT, AIIMS (2017)	—	—	Periodicity in properties (Class XI), Halogen derivatives (Class XII)	MPP (Class XI), MPP (Class XII), Chemistry Musing Problem Set-45, Chemistry Musing Solution Set-44, Advanced Chemistry Bloc (Thermodynamics), Concept Booster, Crossword
MAY	JEE Main, CBSE Board (Class XII)	NEET, JEE Advanced, BITSAT, AIIMS (2017)	—	—	Acyclic hydrocarbons (Class XI), The Solid State (Class XII)	MPP-1 : Some basic concepts of chemistry (Class XI), MPP-1 : The solid state, Solutions (Class XII), Chemistry Musing Problem Set-46, Advanced Chemistry Bloc (The wave theory of the atom), Concept Booster, Learn Fast (Some important halides of group-13 and group-14 elements), Crossword
JUNE	NEET, Karnataka CET, Kerala PET, WB JEE	ACE Your Way Series-1 (The Solid state, Solutions) (Class XII) (2018)	—	—	Acid-base titrations (Class XI), Extraction of some metals (Class XII)	MPP-2 : Structure of atom, Classification of elements and periodicity in properties (Class XI), MPP-2 : Electrochemistry, Chemical kinetics (Class XII), NCERT Corner, Exam Prep, Chemistry Musing Problem Set-47, Concept Booster, Advanced Chemistry Bloc (Acidic strength, an analysis), JEE Advanced Practice Problems, Chemistry Musing Solution Set-46
JULY	JEE Advanced	ACE You Way CBSE Series-1, Some basic concepts of chemistry, Structure of atom (Class XI), ACE Your Way CBSE Series-2 (Class XII), Electrochemistry, Chemical kinetics, Surface chemistry	Some basic concepts of chemistry, Classification of elements and periodicity in properties (Class XI), Solutions, The solid state, General principles and processes of isolation of elements (Class XII)	Unit-1 : Some basic concepts of chemistry, Structure of atom (Class XI), Unit-1 : The solid state, Solutions (Class XII)	Thermodynamic processes (Class XI), Substitution reactions (Class XII)	MPP-3 : Chemical bonding and molecular structure (Class XI), MPP-3 : Surface chemistry, General principles and processes of isolation of elements (Class XII), Success Story, Concept Booster (Heating effects), Chemistry Musing Problem Set-48, Chemistry Musing Solution Set-47
AUGUST	—	ACE Your Way CBSE Series-2, Classification of elements and periodicity in properties, Chemical bonding and molecular structure, ACE Your Way CBSE series-3, General principles and processes of isolation of elements, p-block elements (group-15 to 18)	Structure of atom, Organic chemistry: Some basic principles and techniques (Class XI), Solutions, Haloalkanes and haloarenes (Class XII)	Unit-2 : Classification of elements and periodicity in properties, Chemical bonding and molecular structure (Class XI), Unit-2 : Electrochemistry, Chemical kinetics, Surface chemistry (Class XII)	Molecular orbital Theory (MOT) (Class XI), Oxidation reactions (Class XII)	MPP-4 : States of matter, Thermodynamics (Class XI), MPP-4 : The p-block elements (group-15 to 18) (Class XII), Chemistry Musing Problem Set-49, JEE Advanced Practice Problems, Concept Booster (Heating effects), Advanced chemistry Bloc (basic strength of common compounds), Chemistry Musing Solution Set-48)
SEPTEMBER	—	ACE Your Way CBSE Series-3; States of matter, Thermodynamics, ACE Your Way CBSE (Series-4), The d- and f-block elements, Coordination compounds	Chemical bonding and molecular structure, Hydrogen (Class XI), The p-block elements (group-15 to 18), Alcohols, phenols and ether (Class XII)	Unit-3 : States of matter : Gases and Liquids, Thermodynamics (Class XI), Unit-3 : General principles and processes of Isolation of elements, The p-block elements (Group-15 to 18) (Class XII)	Titrimetric/volumetric analysis (Class XI), Redox reactions (Class XII)	MPP-5 : Equilibrium (Class XI), MPP-5 : The d-and f-block elements, Coordination compounds (Class XII), Chemistry Musing Problem Set-50, JEE Advanced Practice Problems, Concept Booster (Heating effects), Advanced Chemistry Bloc (An insight to MOT), Chemistry Musing Solution Set-49, Crossword
OCTOBER	—	ACE Your Way CBSE Series-4 : Equilibrium, Redox reactions (Class XI). ACE Your Way CBSE Series-5 Haloalkanes and haloarenes, Alcohols, phenols and ethers	States of matter, The s-block elements (Class XI), The d-and f-block elements, Electrochemistry (Class XII)	Unit-4 : Equilibrium, Redox reactions (Class XI), Unit-4 : The d- and f-block elements, Coordination compounds	Trends and anomalies in s-and p-block elements (Class XI), Surface chemistry (Class XII)	MPP-6 : Hydrogen, Redox reaction (Class XI), MPP-6 : Haloalkanes and haloarenes (Class XII), Chemistry Musing Problem Set-51, JEE Advanced Practice Problems, Chemistry Musing Solution Set-50
NOVEMBER	—	ACE Your Way CBSE Series-5 : Hydrogen, The s-block elements (Class XI). ACE Your Way CBSE Series-6 : Aldehydes, ketones and carboxylic acids, Amines	Hydrocarbons, Thermodynamics (Class XI) Aldehydes, ketones and carboxylic acids, coordination compounds (Class XII)	Unit-5 : Hydrogen, The s-block elements (Class XI), Unit-5 : Haloalkanes and haloarenes, Alcohols, phenols and ethers (Class XII)	Gaseous State (Class XI), Diazonium salt (Class XII)	MPP-7 : The s-block elements (Class XI), MPP-7 : Alcohols, phenols and ethers (Class XII), Chemistry Musing Problem Set-52, Nobel Prize-2017, Concept Booster (Special topic of coordination chemistry), Advanced Chemistry Bloc (Re-reading organic chemistry), Chemistry Musing Solution Set-51
DECEMBER	—	ACE Your Way CBSE Series-6 : The p-block elements, Organic chemistry: Some basic principles and techniques (Class XI), ACE Your Way CBSE Series-7 : Biomolecules, Polymers, Chemistry in everyday life	Equilibrium, The p-block elements (Class XI), Chemical kinetics, Amines and Biomolecules (Class XII)	Unit-6 : The p-block elements (Group-13 and 14), Unit-6: Aldehydes, ketones and carboxylic acids (Class XII)	Mechanistic approach to some name reactions (Class XI), The f-block elements (Class XII)	MPP-8 : The p-block elements (Class XI), MPP-8 : Aldehydes, ketones and carboxylic acids (Class XII), Chemistry Musing Problem Set-53, Concept Booster, JEE Advanced Practice Problems, Chemistry Musing Solution Set-52

CHEMISTRY MUSING

SOLUTION SET 53

1. (d) : Epoxidation is stereospecific as both new C—O bonds form to the same face of the alkene. If one face of the ring is blocked with a substituent, epoxidation becomes stereoselective, for the face which is anti to the substituent already present there.

2. (c)

3. (c) :
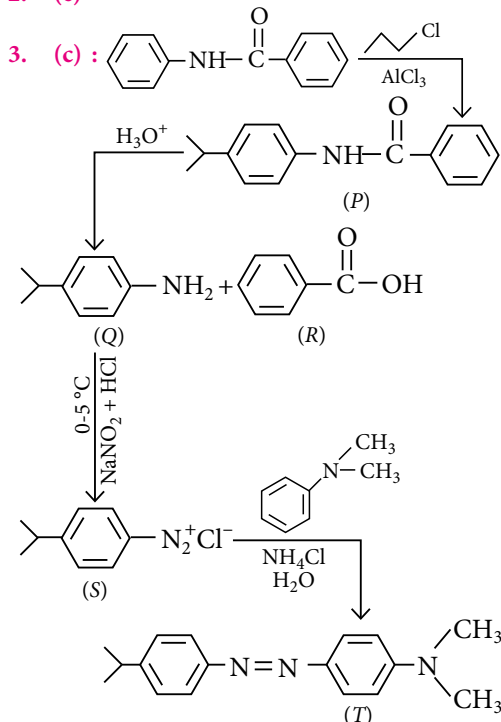
Diazonium salts (S) are unstable and explosive substances, they are not isolated in solid form but are used directly from the solution.

4. (a) : $KO_2 + CO_2 + H_2O \xrightarrow{\Delta} \underset{(P)}{KHCO_3} + O_2\uparrow$
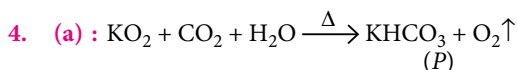
5. (b) : $W_{\text{Rev. isothermal (II)}} > W_{\text{Rev. adiabatic (I)}}$ and $W_{\text{Rev.}} > W_{\text{irr.}}$
$\Rightarrow W_{\text{Rev. isothermal (II)}} > W_{\text{Rev. adiabatic (I)}} > W_{\text{Irr. adiabatic (III)}}$
In isothermal expansion, T = constant

In adiabatic expansion, T decreases as the work is being done at the expense of internal energy. More is the work done by the gas, more is the decrease in T.

Thus, $(T_f)_{\text{Rev. isothermal (II)}} > (T_f)_{\text{Irr. adiabatic (III)}} > (T_f)_{\text{Rev. adiabatic (I)}}$

6. (b) : For the reaction,

	$X_{(g)}$	+	$2Y_{(g)}$	$\rightleftharpoons$	$Z_{(g)}$
Initial moles	1		2		0
Moles at equilibrium	$1 - x$		$2 - 2x$		x
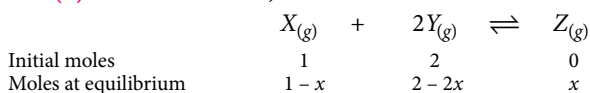
$\Delta n_g = n_p - n_r = 1 - (2 + 1) = -2$
$K_p = K_c(RT)^{\Delta n_g} = 0.35 \times (0.0821 \times 473)^{-2} = 2.32 \times 10^{-4}$

The expression for $K_p = \dfrac{p_Z}{p_X(p_Y)^2}$

$\Rightarrow$ Total moles (n_T) at equilibrium = $3 - 2x$
Let P be the equilibrium pressure, then partial pressures of X, Y and Z are :

$\Rightarrow p_X = \dfrac{1-x}{3-2x}P, \; p_Y = \dfrac{2-2x}{3-2x}P, \; p_Z = \dfrac{x}{3-2x}P$

$K_p = \dfrac{\dfrac{x}{3-2x}P}{\left(\dfrac{1-x}{3-2x}P\right)\left(\dfrac{2-2x}{3-2x}P\right)^2} = \dfrac{x(3-2x)^2}{P^2(1-x)(2-2x)^2}$

$\therefore \; K_p = \dfrac{0.6(3-1.2)^2}{P^2(1-0.6)(2-1.2)^2} = 2.32 \times 10^{-4}$
$\hspace{4cm} (\because x = 0.6)$

$\Rightarrow P^2 = 3.27 \times 10^4 \Rightarrow P \approx 180 \text{ atm}$

7. (a) : Given, mixture of (A) and (B) $\xrightarrow[\text{KOH}(aq.)]{\text{CHCl}_3}$ organic layer (A) + alkaline aqueous layer(B)
Organic layer on treating with $KOH_{(alc.)}$ produces C_7H_5N (C) of unpleasant odour, thus (C) is C_6H_5NC. Therefore, (A) is $C_6H_5NH_2$.

8. (d) : Alkaline layer on treating with $CHCl_3$ followed by acidification gives two isomers having formula, $C_7H_6O_2$. This is Reimer—Tiemann reaction, thus (B) is C_6H_5OH.
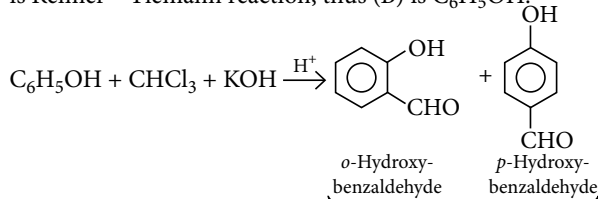
9. (1) : $KE = h\nu - h\nu_0 = h(\nu - \nu_0)$
$KE_1 = h(\nu_1 - \nu_0)$ ...(i) $KE_2 = h(\nu_2 - \nu_0)$ ...(ii)
Dividing equation (ii) by (i), we get

$\dfrac{KE_2}{KE_1} = \dfrac{h(\nu_2 - \nu_0)}{h(\nu_1 - \nu_0)} = \dfrac{(\nu_2 - \nu_0)}{(\nu_1 - \nu_0)}$. Given that, $\dfrac{KE_2}{KE_1} = 3$

$\therefore \; 3 = \dfrac{\nu_2 - \nu_0}{\nu_1 - \nu_0} \Rightarrow 3(\nu_1 - \nu_0) = \nu_2 - \nu_0$

$\Rightarrow 3\nu_1 - \nu_2 = 3\nu_0 - \nu_0 = 2\nu_0 \Rightarrow 3 \times 2.0 \times 10^{16} - 4 \times 10^{16} = 2\nu_0$

$\Rightarrow \nu_0 = \dfrac{2 \times 10^{16}}{2} = 1 \times 10^{16} \text{ s}^{-1}$

Comparing with $x \times 10^{16}$ s^{-1}, $x = 1$

10. (5) : Specific conductance (κ) = conductance $\times$ cell constant

$= \dfrac{1}{\text{resistance}} \times \text{cell constant}$

$= \dfrac{1}{2.5 \times 10^3} \times 1.25 = 5 \times 10^{-4} \; \Omega^{-1}\text{cm}^{-1}$

Equivalent conductance,

$(\Lambda_{eq}) = \text{sp. conductance } (\kappa) \times \dfrac{1000}{\text{Normality}}$

$\therefore \; \Lambda_{eq} = 5 \times 10^{-4} \times \dfrac{1000}{1/10} = 5 \; \Omega^{-1}\text{cm}^2 \text{ equiv}^{-1}$

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