NEET | JEE
Class XI | XII   ESSENTIALS

ACE YOUR WAY CBSE
Class XI-XII

CHEMISTRY
today

India's #1
CHEMISTRY MONTHLY FOR
JEE (Main & Advanced) & NEET

CHEMISTRY
MUSING

CONCEPT
MAP

EXAMINER'S
MIND

CONCEPT
BOOSTER

ADVANCED
CHEMISTRY BLOC

MONTHLY
PRACTICE
PROBLEMS
(XI & XII)

CHEMISTRY today

CONTENTS

Subscribe online at www.mtg.in

Individual Subscription Rates				Combined Subscription Rates			
	1 yr.	2 yrs.	3 yrs.		1 yr.	2 yrs.	3 yrs.
Mathematics Today	330	600	775	PCM	900	1500	1900
Chemistry Today	330	600	775	PCB	900	1500	1900
Physics For You	330	600	775	PCMB	1000	1800	2300
Biology Today	330	600	775				

CHEMISTRY TODAY
wishes all readers a very
Happy New Year
2017

NEET | JEE
ESSENTIALS

Class XI

Maximize 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

Organic chemistry deals with the study of hydrocarbons and their derivatives.

FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

✤ Functional groups are groups of atoms in organic compounds that are responsible for the characteristic chemical reactions of those compounds.

Alkane
Naming : -ane
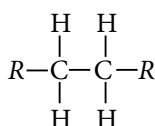*e.g.,* ethane
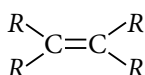
Alkene
Naming : -ene
e.g., ethene

Alkyne
Naming : -yne
e.g., ethyne

Alcohol
Naming : -ol
e.g., ethanol
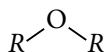
Ether
Naming : -oxy -ane
e.g., methoxyethane
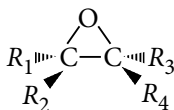
Epoxide
Naming : -ene oxide
e.g., ethene oxide

Haloalkane
Naming : halo-
e.g., chloroethane
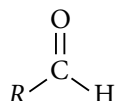
Aldehyde
Naming : -al
e.g., ethanal
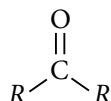
Ketone
Naming : -one
e.g., propanone

Carboxylic acid
Naming : -oic acid
e.g., ethanoic acid

Acid anhydride
Naming : -oic anhydride
e.g., ethanoic anhydride

Ester
Naming : -yl -oate
e.g., ethyl ethanoate

Amide
Naming : -amide
e.g., ethanamide

Acyl halide
Naming : -oyl halide
e.g., ethanoyl chloride

Amine
Naming : -amine
e.g., ethanamine

Nitrile
Naming : -nitrile
e.g., ethanenitrile

Imine
Naming : -imine
e.g., ethanimine

Isocyanate
Naming : -yl isocyanate
e.g., ethyl isocyanate

Azo compound
Naming : azo-
e.g., azoethane

Thiol
Naming : -thiol
e.g., methanethiol

Arene
Naming : -yl benzene
e.g., ethyl benzene

Naming of all these organic compounds can be done by using IUPAC Nomenclature System.

IUPAC Nomenclature

IUPAC Name : 2° prefix + 1° prefix + root word + 1° suffix + 2° suffix

Root word

The root word indicates the number of carbon atoms in the parent chain.

For C_1-meth, C_2-eth, C_3-prop(*a*), C_4-but(*a*), C_5-pent(*a*), C_6-hex(*a*), C_7-hept(*a*), C_8-oct(*a*), C_9-non(*a*), C_{10}-dec(*a*), C_{11}-undec(*a*), C_{12}-dodec(*a*).

Extra '*a*' is added to root word if 1° suffix begins with a consonant. In general, the root word for any carbon chain is alk.

Suffix

A suffix designates the functional groups present in the compound. The suffix is again divided into primary and secondary.

Prefix

The parts of the name that precede the root word are called prefixes. The prefix is again divided into primary and secondary.

Primary suffix

- Primary suffix indicates the degree of saturation or unsaturation in the parent chain and is added immediately after the root word.
- Root word + Primary suffix → saturated or unsaturated carbon chain.
  - Single bonds only —ane, e.g., $CH_3CH_2CH_3$, root word – prop primary suffix – ane
- 1(=) bond, – ene e.g., $CH_3—CH=CH—CH_3$, root word : but primary suffix : -ene 2(=) bonds, – diene 3(=) bonds, – triene
- 1 (≡) bond, – yne e.g., $CH≡C—CH_2—CH_3$, root word : but primary suffix : -yne 2(≡) bonds, – diyne

For example :

-
$$H_3C \overset{4}{\underset{3}{\boxed{}}} \overset{1}{\underset{2}{|||}} \quad \text{3-Methylcyclobutyne}$$
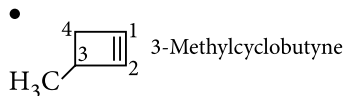
Secondary suffix

- A secondary suffix indicates the functional group present in the carbon compound.
- Functional group, —OH(-ol), —CHO(-al), >CO(-one), —COOH(-oic acid), —$CONH_2$ (-amide), —COCl (-oyl chloride), —COO*R* (oate), —CN (nitrile), —SH (thiol), —NH_2 (amine), —SO_3H (sulphonic acid).
- If 2° suffix begins with a vowel, the terminal '*e*' is dropped otherwise it is retained.

Primary prefix

A primary prefix is used to differentiate acyclic and cyclic compounds. But the rules for using these are slightly different. *e.g.,* in cyclic compounds, the prefix cyclo is added before the root word.

- $CH_3—\overset{}{\underset{\underset{\text{Br}}{|}}{CH}}—CH_2COOH$

  3-Bromobutanoic acid
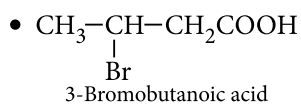
Secondary prefix

- Some functional groups are always treated as substituents whether organic compound is mono or polyfunctional *e.g.,* Fluoro (—F), Chloro (—Cl), Bromo (—Br), Iodo (—I), Nitro (—NO_2), Nitroso (—NO), Diazo (—$\overset{+}{N}≡N$), Alkoxy (—O*R*), Alkyl (—*R*), Phenyl (—C_6H_5), etc.
- When functional groups act as substituents in the presence of other principal functional group *e.g.,* Hydroxyl (—OH), Formyl (—CHO), Oxo or Keto (>CO), Cyano (—CN), Carboxy (—COOH), Alkoxycarbonyl (—COO*R*), Halocarbonyl (—CO*X*), Amino (—NH_2), Carbamoyl (—$CONH_2$), Sulpho (—SO_3H)

IUPAC Nomenclature of Benzene Derivatives

↳ For substituted benzene derivatives, the substituent is placed as prefix to the word benzene.

e.g., [benzene ring with CH₂CH₃] Ethyl benzene
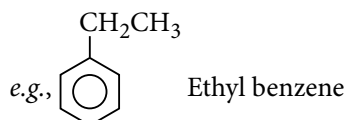
↳ In disubstituted benzene ring, the substituents are located at the lowest possible numbers while numbering the carbon atoms of the ring.

e.g., [benzene ring with CH₃ at position 1 and CH₃ at position 2] 1,2-Dimethyl benzene
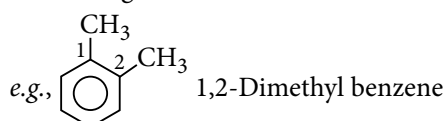
↳ In the trivial system of nomenclature, the prefix *ortho* (*o-*) indicates 1,2- *meta* (*m-*) indicates 1,3- and *para* (*p-*) indicates 1,4-disubstituted benzene ring.

e.g.,

o-Xylene   *m*-Xylene   *p*-Xylene
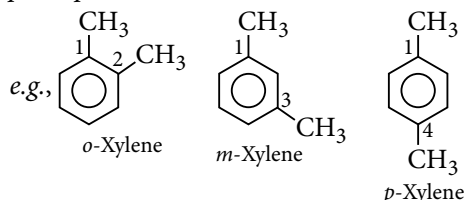
↳ In case of tri- or higher substituted benzene derivatives, common name of benzene derivatives is taken as the base compound. Number 1 position is assigned to the substituent of the base compound and lowest locant rule is followed for other substituents.

e.g., [benzene ring with NH_2 at position 1, CH_3 at position 2, C_2H_5 at position 4] 4-Ethyl-2-methylaniline
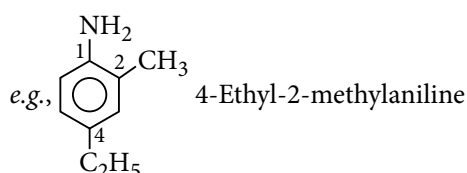
↳ Benzene ring is considered as substituent [Phenyl (Ph), $-C_6H_5$] when it is attached to an alkane with a functional group.

e.g., [benzene ring with CH_2CH_2CHO, numbered 3 2 1] 3-Phenylpropanal
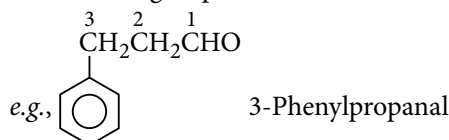
IUPAC Nomenclature of Bicyclic Compounds

↳ Bicyclic compounds are named by adding prefix bicyclo to the name of hydrocarbon corresponding to total number of carbon atoms in two rings.

In between the words bicyclo and alkane, an expression in the square brackets is placed that represents the number of carbon atoms in each bridge connecting two bridge heads, in descending order separated from one another by full stop.

$$CH_2-CH-CH_2$$
$$CH_2 \quad CH_2$$
$$CH_2-CH-CH_2$$

Bicyclo [3.2.1] octane
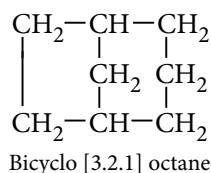
↳ If substituent is present, we number the bridged ring system beginning at one bridge head, proceeding first along the longest bridge to the other bridge head, then along the next longest bridge back to the first bridge head. The shortest bridge is numbered last.

8-Methyl bicyclo [3.2.1] octane
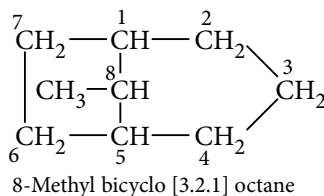
IUPAC Nomenclature of Spiro Compounds

↳ Spiro compounds are named by adding prefix spiro followed by bracket containing the number of carbon atoms in each ring in ascending order and then by the name of hydrocarbon corresponding to total number of carbon atoms in two rings. The numbering starts from the atom next to the spiro atom and proceeds through the smaller ring first.

Spiro[2.4]heptane   Spiro[2.2]pentane
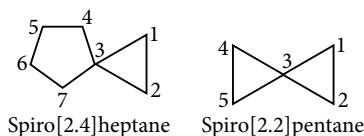
Isomerism

↳ The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as *isomerism*.

↳ Isomerism in an organic compound can be classified broadly into structural and stereoisomerism.

Chain isomerim

Different arrangement of carbon atoms in a carbon skeleton. *e.g.*,

$$H_3C{-}CH_2{-}CH_2{-}CH_3$$
Butane

$$H_3C{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3$$
2-Methylpropane
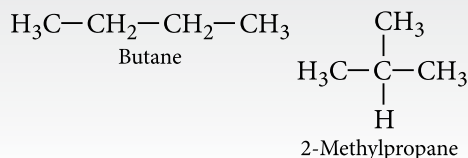
Position isomerism

Different position of the same functional group in the molecule. *e.g.*,

$$CH_3{-}CH{=}CH{-}CH_3 \quad CH_3{-}CH_2{-}CH{=}CH_2$$
But-2-ene   But-1-ene
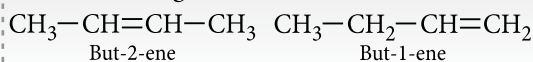
Functional isomerism

Different positions of atoms give a different functional group. *e.g.*,

$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH$$
Ethanoic acid

$$H{-}\overset{\overset{O}{\|}}{C}{-}OCH_3$$
Methyl methanoate

Metamerism

Different alkyl groups are attached to the same polyvalent functional group. *e.g.*,

$$H_3C{-}CH_2{-}O{-}CH_2{-}CH_3$$
Diethyl ether or Ethoxyethane

$$H_3C{-}O{-}CH_2{-}CH_2{-}CH_3$$
Methyl propyl ether or 1-Methoxypropane
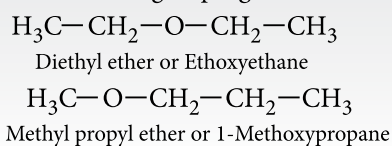
Tautomerism

Tautomers have different functional groups and exist in dynamic equilibrium with each other due to a rapid interconversion from one form to another. *e.g.*,
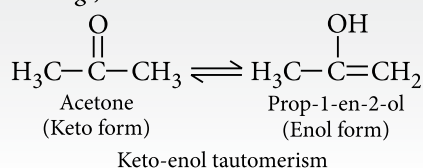
$$H_3C{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \rightleftharpoons H_3C{-}\overset{\overset{OH}{|}}{C}{=}CH_2$$
Acetone   Prop-1-en-2-ol
(Keto form)   (Enol form)
Keto-enol tautomerism

Geometrical isomerism

Different arrangement of substituents around a bond with restricted rotation. *e.g.*,

$$\underset{Cl}{\overset{H}{\diagdown}}C{=}C\underset{H}{\overset{Cl}{\diagup}}$$
(*E*) *trans*-1,2-Dichloroethene
E = High priority atoms or groups are on the opposite side

$$\underset{H}{\overset{Cl}{\diagdown}}C{=}C\underset{H}{\overset{Cl}{\diagup}}$$
(*Z*) *cis*-1,2-Dichloroethene
Z = High priority atoms or groups are on the same side
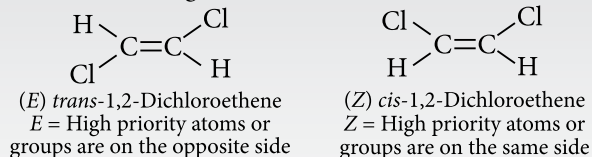
In addition to alkenes, compounds containing $C{=}N$ (aldoxime and ketoxime) and $N{=}N$ (azo compounds) bonds also show geometrical isomerism. However, in these cases, '*syn*' (for *cis*) and '*anti*' (for *trans*) are more commonly used.

Optical isomerism

- 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*.

$$q{-}\overset{\overset{p}{|}}{\underset{\underset{r}{|}}{ⓒ}}{-}s$$
chiral centre
(asymmetric)

$$r{-}\overset{\overset{p}{|}}{\underset{\underset{q}{|}}{ⓒ}}{-}r$$
achiral centre
(symmetric)

$$H{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C^*}}{-}OH$$
(*S*)

$$HO{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C^*}}{-}H$$
(*R*)

1-Chloroethanol
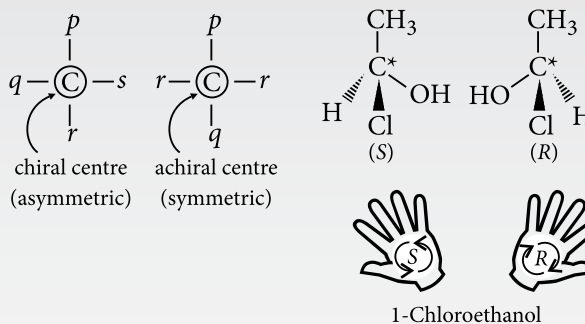
- *Enantiomers* or *d and l isomers* are the optical isomers which are non-superimposable mirror images (or dissymmetric) of each other.
- *Diastereomers* are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.
- *Meso 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*.

Fission of a Covalent Bond

↪ **Homolytic fission**

$$R\overset{\frown}{-}X \xrightarrow{\text{Heat/Light}} R^{\bullet} + X^{\bullet}$$
$$\text{Alkyl free radical}$$

↪ **Heterolytic fission**

$$CH_3\overset{\frown}{-}X \longrightarrow \overset{+}{C}H_3 + :X^-$$
(X is more electronegative) Carbocation
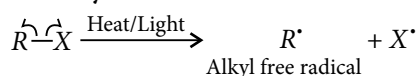
$$\overset{\frown}{CH_3}-Z \longrightarrow :\bar{C}H_3 + Z^+$$
(C is more electronegative) Carbanion
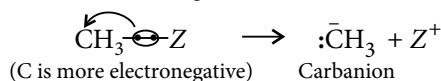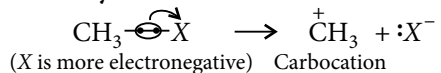
Reactions and Reaction Intermediates

↪ **Substitution reactions**

➢ **Free radical substitution reaction**

$$CH_4 + Cl_2 \xrightarrow[\text{or } 670\,K]{h\nu} CH_3Cl + HCl$$
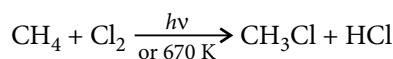
➢ **Electrophilic substitution reaction (S_E)**

– **Unimolecular (S_E1)**

$$CH_3CH_2MgBr + HBr \longrightarrow CH_3CH_3 + MgBr_2$$

– **Bimolecular (S_E2)**

$$:\ddot{C}l-\ddot{C}l: + AlCl_3 \longrightarrow :\ddot{C}l-\ddot{C}l^+ \bar{A}lCl_3$$

Slow

Cl
| ← Fast – Cl—ĀlCl₃+H
+ HCl + AlCl₃
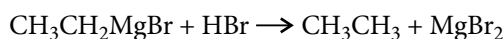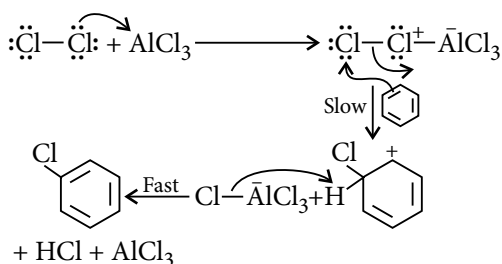
➢ **Nucleophilic substitution reaction (S_N)**

– **Unimolecular (S_N1)**

$$\underset{}{>}C\overset{\frown}{-}X \xrightarrow[]{\text{Slow}} {}^{(a)}\overset{Nu:^-}{\underset{(a)}{\overset{}{>}C^+}}{}^{(b)} \xrightarrow[(b)]{\text{Fast}} >C-Nu$$
Retention of configuration

(a) Fast

$$Nu-C\overset{}{-}$$
Inversion of configuration

– **Bimolecular (S_N2)**

$$Nu:^- + R''\overset{R'}{\underset{R'''}{\overset{|}{C}}}X \longrightarrow \left[Nu\cdots\overset{R'}{\underset{R''}{C}}\cdots X\right]$$

$$Nu\overset{R'}{\underset{R'''}{C}}R'' + X^-$$
Inversion of configuration
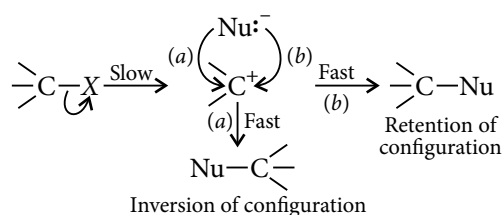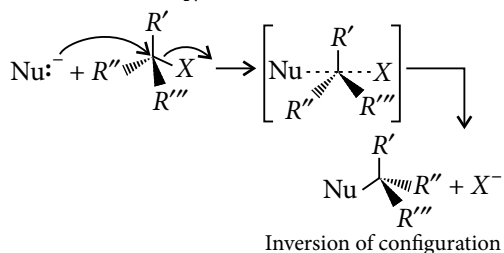
↪ **Addition reactions**

➢ **Nucleophilic addition reaction**

$$HO^- + H\overset{\frown}{-}CN \longrightarrow H_2O + CN^-$$
Nucleophile

$$\underset{R}{\overset{R}{>}}C=O + CN^- \longrightarrow \left[R-\underset{CN}{\overset{R}{\underset{|}{\overset{|}{C}}}}-O^-\right]\overset{H-CN}{\underset{-CN^-}{}}$$
Nucleophile

$$R-\underset{CN}{\overset{R}{\underset{|}{\overset{|}{C}}}}-OH$$
Ketone cyanohydrin (Addition product)

➢ **Electrophilic addition reaction**

$$CH_3CH\overset{\frown}{=}CH_2 + H^+ \xrightarrow{\text{Slow}} CH_3-\overset{+}{C}H-CH_3$$
Propylene   Isopropyl carbocation (2°)

$$CH_3-\overset{+}{C}H-CH_3 + Br^- \xrightarrow{\text{Fast}} CH_3-\underset{Br}{\overset{|}{C}H}-CH_3$$
2-Bromopropane (Addition product)
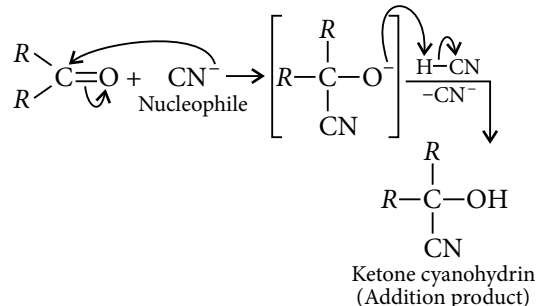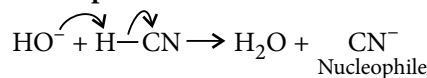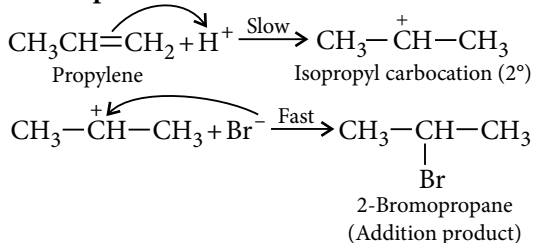
➢ **Free radical addition reaction**

$$CH_3CH=CH_2 + HBr \xrightarrow{\text{Peroxides}}$$
Propene

$$CH_3-CH_2-CH_2Br$$
n-Propyl bromide
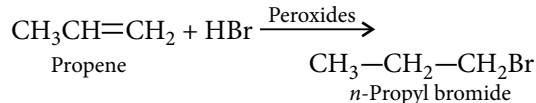
↪ **Elimination reactions**

➢ **α-Elimination**
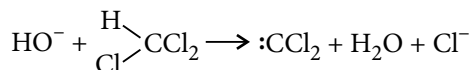
$$HO^- + \underset{Cl}{\overset{H}{>}}CCl_2 \longrightarrow :CCl_2 + H_2O + Cl^-$$

➢ **β-Elimination**

$$H-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-OH \xrightarrow{\text{Conc. } H_2SO_4} CH_2=CH_2 + H_2O$$

➢ **γ-Elimination**

$$BrCH_2-CH_2-CH_2Br \xrightarrow{\text{Zn dust}} \triangle$$
1,3-Dibromopropane   Cyclopropane

↪ **Condensation reaction**

$$CH_3-\overset{O}{\overset{||}{C}}-H + CH_3CHO \xrightarrow{\text{aq. NaOH}}$$
Two molecules of ethanal

$$CH_3-\underset{OH}{\overset{|}{C}H}-CH_2CHO$$
3-Hydroxybutanal

↪ **Isomerisation reaction**

$$\underset{H}{\overset{H_3C}{>}}C=C\underset{CH_3}{\overset{H}{<}} \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \underset{H}{\overset{H_3C}{>}}C=C\underset{H}{\overset{CH_3}{<}}$$
trans-But-2–ene   *cis*-But-2-ene
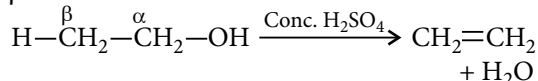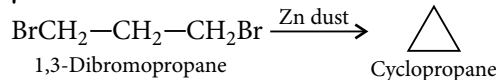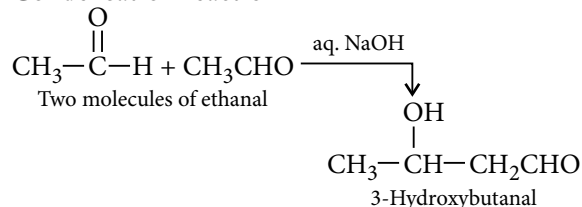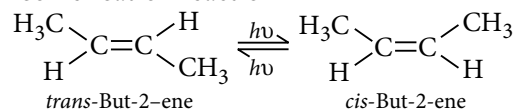
ATTACKING REAGENTS

Electrophiles	Nucleophiles	Ambiphiles
They are positively charged or neutral molecules having electron deficient atom, seeking a site of high electron density to attack. Electrophiles have incomplete outer shells and are also called *Lewis acids* (electron-pair acceptors). Charged : H_3O^+, X^+ (where X = Cl, Br, I), NO_2^+, NO^+, NH_4^+, $\overset{+}{S}O_3H$, $C_6H_5\overset{+}{N}_2$, R^+, RCO^+. Neutral : BF_3, $AlCl_3$, $FeCl_3$, $SiCl_4$, $BeCl_2$, $ZnCl_2$, SO_3, CO_2, CS_2, CX_4, $RCOCl$, $>\!C\!=\!O$, $:CCl_2$.	They are negatively charged or neutral molecules having electron-rich atom with unshared electron pair, seeking electron deficient site to attack. They are also called *Lewis bases* (electron-pair donors). Charged : H^-, OH^-, X^-, CN^-, N_3^-, RO^-, R^-, RS^-, SH^-, HSO_3^-, NO_2^-, NH_2^-, $RCOO^-$, $HC\equiv C^-$. Neutral : $\overset{..}{N}H_3$, $H_2\overset{..}{\underset{..}{O}}$, $R\overset{..}{\underset{..}{O}}H$, $R\overset{..}{\underset{..}{O}}R$, $R\overset{..}{\underset{..}{S}}H$, $RMgX$, $Ph_3\overset{..}{P}$, RLi, $LiAlH_4$, etc.	They behave both like electrophiles and nucleophiles hence, have dual nature. $R\overset{..}{\underset{..}{O}}H$, $H\overset{..}{\underset{..}{O}}H$ and $R\overset{..}{P}H_2$

ELECTRON DISPLACEMENT EFFECTS IN COVALENT BONDS

Types of Electronic Displacement Effects

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.

↳ *Decreasing order of –I effect* :
$$—NO_2 > —CN > —COOH > —F > —Cl > —Br > —I > —H$$

↳ *Decreasing order of +I effect* :
$$(CH_3)_3C— > (CH_3)_2CH— > CH_3CH_2— > CH_3— > D— > H—$$

Electromeric effect

It involves the complete transfer of π electrons of a multiple bond to one of the bonded atoms in presence of an attacking reagent.

↳ *+E effect* : When electron transfer takes place to the atom to which the attacking reagent gets finally attached.

↳ *–E effect* : When electron transfer takes place away from the atom to which the attacking reagent gets finally 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 or +M effect* : —OH, —OR, —SH, —SR, —NH_2, —NHR, —NR_2, —Cl, —Br, —I, etc.

↳ *–R or –M effect* : $>\!C\!=\!O$, —CHO, —COOR, —CN, —NO_2, etc.

↳ In case of the elements of the second period in the periodic table, such resonance structures which violate octet rule should not be considered. *e.g.*,

$$CH_2\!=\!CH\!-\!\overset{+}{N}H_3 \underset{I}{} \longleftrightarrow\!\!\!\times\!\!\!\longrightarrow \overset{+}{C}H_2\!-\!CH\!=\!NH_3 \underset{II}{}$$

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 with an unshared *p*-orbital. For an alkyl group attached to unsaturated system it decreases with decrease in number of α-hydrogens. Thus, the order of hyperconjugation effect decreases in the order :
$$CH_3— > CH_3CH_2— > (CH_3)_2CH— > (CH_3)_3C—$$

Methods of Purification of Organic Compounds

Methods

Distillation under reduced pressure : It is used to purify liquids
- having very high boiling points.
- which decompose at or below their boiling points.

  e.g., Glycerol is separated from spent-lye in soap industry.

Steam distillation : This method is used to separate substances which are steam volatile, insoluble in water, possess a vapour pressure of 10-15 mm Hg and contain non-volatile impurities.
- Aniline is separated from aniline-water mixture.
- Essential oils, *o*-nitrophenol, bromobenzene, nitrobenzene, etc. can be purified.

Differential extraction : This method involves the shaking of an aqueous solution of an organic compound with an organic solvent in which the organic compound is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they can form two distinct layers which can be separated by using separating funnel.
- Benzoic acid can be extracted from its water-benzoic acid mixture using benzene.

Chromatography : It involves differential movement of individual components of a mixture through a stationary phase under the influence of a mobile phase.
- Widely used for separation, purification, identification and characterisation of the components of a mixture, whether coloured or colourless.

Adsorption chromatography (stationary phase is solid)
- **Column chromatography :** It involves separation of a mixture over a column of adsorbent packed in a glass tube.
  Mixture of naphthalene and benzophenone can be separated by this.
- **Thin layer chromatography :** It involves the separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.
  Amino acids can be detected by spraying the plate with ninhydrin solution.

Crystallisation : Differential solubilities of a given organic compound and its impurities in the same solvent.
- Crystallisation of sugar (containing an impurity of common salt) is achieved by shaking the impure solid with hot ethanol at 348 K (sugar dissolves whereas common salt remains insoluble).

Sublimation : Some solid substances change from a solid to a vapour state without passing through the liquid state. Sublimable compounds get separated from non-sublimable impurities.
- Iodine from sodium chloride (as iodine sublimes readily leaving behind sodium chloride).
- Camphor, naphthalene, anthracene, benzoic acid, etc. are purified.

Distillation : It is used to separate
- volatile liquids from non-volatile impurities.
- liquids having sufficient difference in their boiling points.
- Hexane (b.p. 342 K) and toluene (b.p. 384 K)
- Chloroform (b.p. 334 K) and aniline (b.p. 457 K)

Fractional distillation : If the difference in boiling points of two liquids is not much, this method is used.
- Crude oil in petroleum industry is separated into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil, etc.

Partition chromatography : It is a liquid/liquid chromatography in which both the mobile phase and the stationary phase are liquids and used for the separation of sugars and amino acids.
- **Paper chromatography:** A special quality paper known as chromatographic paper is used. It contains water trapped in it, which acts as the stationary phase.
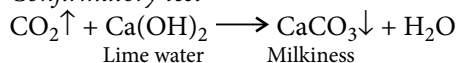
QUALITATIVE ANALYSIS

Detection of Elements and their Confirmatory Tests

↪ **Carbon (Copper oxide test)**

$$2CuO + C \xrightarrow{\Delta} 2Cu + CO_2\uparrow$$

Confirmatory test

$$\underset{\text{Lime water}}{CO_2\uparrow + Ca(OH)_2} \longrightarrow \underset{\text{Milkiness}}{CaCO_3\downarrow} + H_2O$$

↪ **Hydrogen (Copper oxide test)**

$$CuO + 2H \xrightarrow{\Delta} Cu + H_2O$$

Confirmatory test

$$\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4\cdot 5H_2O}$$

↪ **Nitrogen**

$$Na + C + N \xrightarrow{\Delta} \underset{\text{(Lassaigne's extract)}}{NaCN}$$

Confirmatory test

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$
$$Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$$
$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

↪ **Sulphur**

$$2Na + S \xrightarrow{\Delta} \underset{\text{(Lassaigne's extract)}}{Na_2S}$$

Confirmatory test

$$\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Deep violet}}{Na_4[Fe(CN)_5NOS]}$$
$$Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$$

↪ **Halogens**

$$Na + X \xrightarrow{\Delta} \underset{\substack{\text{(Lassaigne's extract)}\\(X = Cl, Br \text{ or } I)}}{NaX}$$

Confirmatory test

$$NaX + AgNO_3 \xrightarrow{HNO_3} \underset{\text{ppt.}}{AgX\downarrow}$$

— White ppt. soluble in aqueous NH_3 (or NH_4OH) confirms Cl.

$$\underset{\text{White ppt.}}{AgCl\downarrow + 2NH_{3(aq.)}} \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl}$$
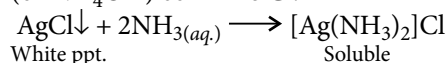
— Yellow ppt. partially soluble in aqueous NH_3 (or NH_4OH) confirms Br.
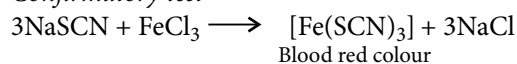
— Yellow ppt. insoluble in aqueous NH_3 (or NH_4OH) confirms I.

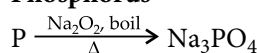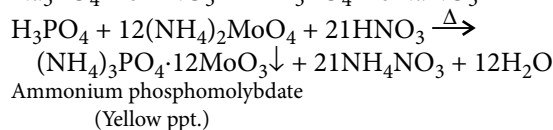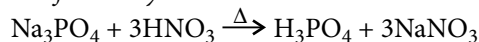↪ **Nitrogen and sulphur**

$$Na + C + N + S \xrightarrow{\Delta} \underset{\substack{\text{(Lassaigne's extract)}\\\text{Sodium thiocyanate}}}{NaSCN}$$

Confirmatory test

$$3NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red colour}}{[Fe(SCN)_3]} + 3NaCl$$

↪ **Phosphorus**

$$P \xrightarrow[\Delta]{Na_2O_2, \text{ boil}} Na_3PO_4$$

Confirmatory test

$$Na_3PO_4 + 3HNO_3 \xrightarrow{\Delta} H_3PO_4 + 3NaNO_3$$
$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \xrightarrow{\Delta}$$
$$\underset{\substack{\text{Ammonium phosphomolybdate}\\\text{(Yellow ppt.)}}}{(NH_4)_3PO_4\cdot 12MoO_3\downarrow} + 21NH_4NO_3 + 12H_2O$$

iNFO SHOTS
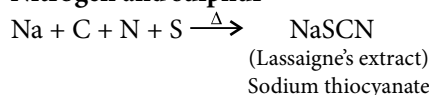
### Gas Chromatography(GC) – Sensor Can 'Smell' Prostate Cancer!

A Research team from the University of Liverpool has reached an important milestone towards creating a urine diagnostic test for prostate cancer. The use of a gas chromatography (GC) – sensor system combined with advanced statistical methods towards the diagnosis of urological malignancies', which describes a diagnostic test using a special tool to 'smell' the cancer in men's urine. The GC sensor system is able to successfully identify different patterns of volatile compounds that allow classification of urine samples from patients with urological cancers. The research team used a gas chromatography sensor system called Odoreader that was developed by a team led by Professor Probert and Professor Norman Ratcliffe at UWE Bristol. The test involves inserting urine samples into the Odoreader that are then measured using algorithms developed by the research team at the University of Liverpool and UWE Bristol. "The Odoreader has a 30 metre column that enables the compounds in the urine to travel through at different rates thus breaking the sample into a readable format. This is then translated into an algorithm enabling detection of cancer by reading the patterns presented. The positioning of the prostate gland which is very close to the bladder gives the urine profile a different algorithm if the man has cancer."

QUANTITATIVE ANALYSIS

Methods of Analysis

Estimation of carbon and hydrogen

Liebig's combustion method :

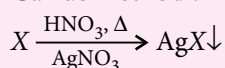$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$$
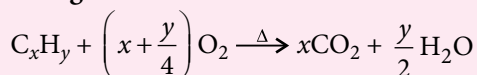
$$\% \text{ of C} = \frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of compound taken}} \times 100,$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{\text{Mass of H}_2O \text{ formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of halogen

Carius method :

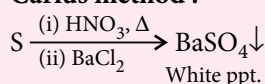$$X \xrightarrow[\text{AgNO}_3]{\text{HNO}_3, \Delta} AgX\downarrow$$

$$\% \text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of compound taken}} \times 100$$

$$\% \text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of compound taken}} \times 100$$

$$\% \text{ of I} = \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of sulphur

Carius method :

$$S \xrightarrow[\text{(ii) BaCl}_2]{\text{(i) HNO}_3, \Delta} \underset{\text{White ppt.}}{BaSO_4\downarrow}$$
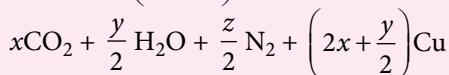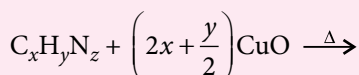
$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of carbon, hydrogen and nitrogen

The elements carbon, hydrogen and nitrogen present in a compound can be determined by an apparatus known as CHN elemental analyser. It requires only 1-3 mg of the compound and displays the values of the element on the screen. The results are accurate within ±0.03% error.
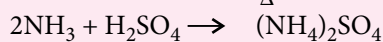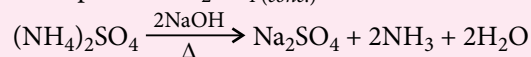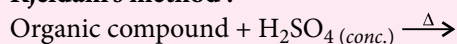
Estimation of nitrogen

Dumas method :

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \xrightarrow{\Delta}$$

$$xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

$$\% \text{ of N} = \frac{28}{22400} \times \frac{\text{Vol. of N}_2 \text{ at STP}}{\text{Mass of compound taken}} \times 100,$$

$$\text{Vol. of N}_2 \text{ at STP} = \frac{P_1V_1 \times 273}{760 \times T_1}$$

Kjeldahl's method :

Organic compound + $H_2SO_{4\,(conc.)} \xrightarrow{\Delta}$

$$(NH_4)_2SO_4 \xrightarrow[\Delta]{2\text{NaOH}} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$\% \text{ of N} = \frac{1.4 \times \text{Molarity of acid} \times \text{Vol. of acid used} \times \text{Basicity of acid}}{\text{Mass of compound taken}},$$

$$\% \text{ of N} = \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid used}}{\text{Mass of compound taken}}$$
$$\text{(for monobasic acid)}$$

Estimation of phosphorus

Ignition method :

$$P \xrightarrow[\text{Heat}]{\text{HNO}_3} H_3PO_4$$

$$H_3PO_4 + Mg^{2+} + NH_4Cl \xrightarrow{\Delta} \underset{\substack{\text{Magnesium ammonium} \\ \text{phosphate (white ppt.)}}}{MgNH_4PO_4} + HCl$$

$$2MgNH_4PO_4 \xrightarrow{\Delta} \underset{\text{Magnesium pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$
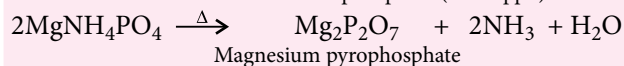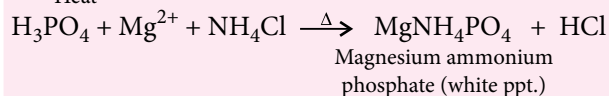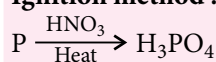
$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{Mass of Mg}_2P_2O_7 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of oxygen

% of oxygen in a compound = 100 – (Sum of the % of all other elements present in the compound).

SPEED PRACTICE

1. Which of the following represents the given mode of hybridisation sp^2–sp^2–sp–sp from left to right?
   (a) CH_2=CH—C≡N
   (b) CH≡C—C≡CH
   (c) CH_2=C=C=CH_2
   (d) [structure]

2. 2,4,6-Trinitroiodobenzene has three C—N bonds labelled as a, b and c. The correct bond length of the three bonds is
   (a) $a = b = c$
   (b) $a > b > c$
   (c) $a = b > c$
   (d) $a = b < c$

3. Lassaigne's extract of p-nitrochlorobenzene is acidified with dil. HNO_3 and then treated with silver nitrate solution, the white precipitate formed is due to
   (a) AgCl
   (b) AgCN
   (c) both (a) and (b)
   (d) no white ppt. is obtained.

4. A mixture of two organic compounds 'A' (b.pt. 80°C) and 'B' (b.pt. 110°C) can be separated by
   (a) sublimation
   (b) steam distillation
   (c) fractional distillation
   (d) fractional crystallisation.

5. 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)

6. Which of the following carbocations is least stable?
   (a) $C_6H_5\overset{+}{C}H_2$
   (b) p-NO_2—C_6H_4—CH_2^+
   (c) p-CH_3O—C_6H_4—CH_2^+
   (d) p-Cl—C_6H_4—CH_2^+

7. The stability of carbanions in the following compounds
   (i) $RC≡\overset{..}{\overset{..}{C}}$
   (ii) [structure]
   (iii) $R_2C=\overset{..}{C}H$
   (iv) $R_3C—\overset{..}{C}H_2$
   is in the order
   (a) (ii) > (iii) > (iv) > (i)
   (b) (iv) > (ii) > (iii) > (i)
   (c) (i) > (iii) > (ii) > (iv)
   (d) (i) > (ii) > (iii) > (iv)

8. IUPAC name of the following compound is
   [structure]
   (a) N,N-dimethylcyclopropanecarboxamide
   (b) N-methylcyclopropanamide
   (c) cyclopropanamide
   (d) none of the above.
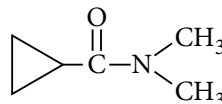
9. In the given conformation, C_2 is rotated about C_2—C_3 bond anticlockwise by an angle of 120°, then the conformation obtained is
   [structure]
   (a) fully eclipsed conformation
   (b) partially eclipsed conformation
   (c) gauche conformation
   (d) staggered conformation.
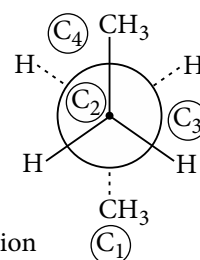
10. Consider the reaction,
    $$RCHO + NH_2—NH_2 \longrightarrow RCH=N—NH_2$$
    What sort of reaction is this?
    (a) Nucleophilic addition – elimination reaction
    (b) Electrophilic addition – elimination reaction
    (c) Free radical addition – elimination reaction
    (d) Electrophilic substitution – elimination reaction
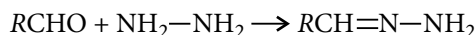
11. The total number of stereoisomers that can exist for 'M' is
    [structure]
    M
    (a) 1
    (b) 2
    (c) 3
    (d) 4
    (JEE Advanced 2015)
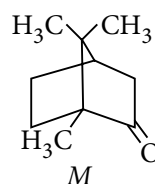
12. 0.25 g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralise 10 cm³ of 0.5 M H_2SO_4. The percentage of nitrogen in the compound is
    (a) 28
    (b) 56
    (c) 14
    (d) 112

13. Which of the following statements is incorrect?
   (a) Using Lassaigne's test nitrogen and sulphur present in organic compound can be tested.
   (b) Using Beilstein's test the presence of halogen in a compound can be tested.
   (c) In Lassaigne's filtrate the nitrogen present in an organic compound is converted into NaCN.
   (d) In the estimation of carbon an organic compound is heated with CaO in a combustion tube.

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

15. Which among the given molecules can exhibit tautomerism?
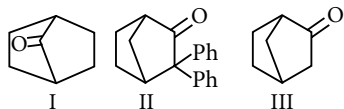
   (a) III only   (b) Both I and III
   (c) Both I and II   (d) Both II and III
   (NEET Phase-II 2016)

16. The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is
   (a) distillation
   (b) crystallisation
   (c) distillation under reduced pressure
   (d) steam distillation.

17. For the following reactions :
   (A) $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH = CH_2$
   $+ KBr + H_2O$
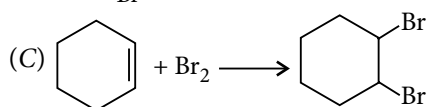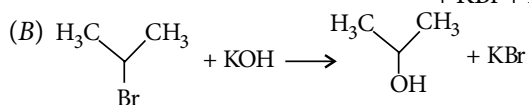
   Which of the following statements is correct?
   (a) (A) is elimination, (B) and (C) are substitution reactions.
   (b) (A) is substitution, (B) and (C) are addition reactions.
   (c) (A) and (B) are elimination reactions and (C) is addition reaction.

   (d) (A) is elimination, (B) is substitution and (C) is addition reaction.   **(NEET Phase-I 2016)**

18. 29.5 mg of an organic compound containing nitrogen was directed according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralisation. The percentage of nitrogen in the compound is
   (a) 59.0   (b) 47.4   (c) 23.7   (d) 2.37

19. The correct IUPAC name of the compound

 is
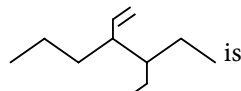
   (a) 3-(1-ethylpropyl) hex-1-ene
   (b) 4-ethyl-3-propylhex-1-ene
   (c) 3-ethyl-4-ethenylheptane
   (d) 3-ethyl-4-propylhex-5-ene.

20. The dihedral angles between the hydrogen atoms in Sawhorse and Newman staggered conformations of ethane respectively are
   (a) 60°, 120°   (b) 60°, 180°
   (c) 120°, 180°   (d) 180°, 60°

21. 0.1724 g of a volatile substance when vaporised displaced 60 cm^3 of air measured at 27°C and 746.7 mm pressure. The molecular mass of the substance (Aqueous tension at 27°C = 26.7 mm Hg) is
   (a) 74.66   (b) 72.33
   (c) 70.0   (d) 70.33

22. The correct order of basic strength of the following compounds is
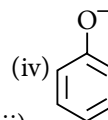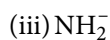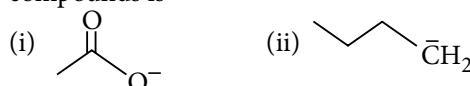
   (a) (iv) > (ii) > (i) > (iii)
   (b) (iii) > (ii) > (iv) > (i)
   (c) (ii) > (iii) > (iv) > (i)
   (d) (ii) > (iii) > (i) > (iv)

23. 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)**

24. C — H bond energy is about 101 kcal/mol for methane, ethane and other alkanes but is only 77 kcal/mol for C — H bond of CH_3 in toluene. This is because
(a) of inductive effect due to $—CH_3$ in toluene
(b) of the presence of benzene ring in toluene
(c) of resonance among the structures of benzyl radical in toluene
(d) of aromaticity of toluene.

25. 1.4 g of an organic compound was digested according to Kjeldahl's method and the ammonia evolved was absorbed in 60 mL of M/10 H_2SO_4 solution. The excess sulphuric acid required 20 mL of M/10 NaOH solution for neutralisation. The percentage of nitrogen in the compound is
(a) 3   (b) 5   (c) 10   (d) 24
(JEE Main 2015)

26. The number of stereoisomers formed by the catalytic hydrogenation of both double bonds in the following compound will be
(a) 1   (b) 2
(c) 3   (d) 4

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

(a) [structure with OH, COOH, CH₃]
(b) [structure with OH, COOH]
(c) [structure with OH, COOH]
(d) [structure with COOH, OH]

28. 9.9 g of an amide with molecular formula, $C_4H_5N_xO_y$ on heating with alkali liberated 1.7 g of ammonia. If the percentage of oxygen is 32.33%, then the ratio of N and O atoms in the compound is
(a) 1 : 1   (b) 1 : 2   (c) 2 : 3   (d) 3 : 2

29. The most stable conformation of 2-chloroethanol (chlorohydrin) is
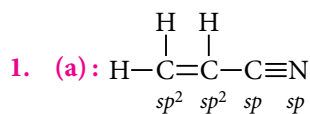(a) skew   (b) staggered
(c) eclipsed   (d) gauche.

**30.** 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)

SOLUTIONS

1. (a) :
$$H—\underset{sp^2}{C}=\underset{sp^2}{C}—\underset{sp}{C}\equiv\underset{sp}{N}$$
(with two H atoms on the first two carbons)

2. (c) : In resonance, only the group which is coplanar with the skeleton can participate in resonance. If the group is out of plane of the ring (skeleton), it cannot participate in resonance.

[chemical resonance structures of 2,4,6-Trinitroiodobenzene]
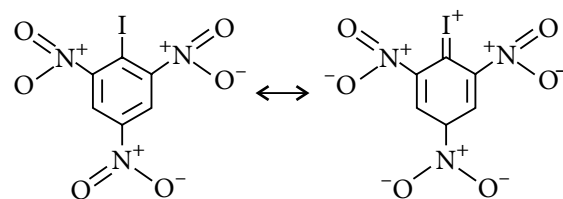
2, 4, 6-Trinitroiodobenzene
(Picryl iodide)

Only the *p*-nitro group is involved in resonance with the benzene, the *o*-nitro groups do not participate in resonance as they are pushed out of the plane of the ring by heavier iodine atom, hence the C — N bond length of the two *o*-nitro groups is equal and greater than that of *p*-nitro group. Thus, $a = b > c$.

3. (c) : Lassaigne's extract for the compound *p*-nitrochlorobenzene contains both NaCN as well as NaCl, so on treatment with $AgNO_3$, the extract gives precipitate of AgCN as well as AgCl unless it is boiled with HNO_3 which will remove NaCN as gaseous HCN.

4. (b): Steam distillation can be applied only when one of the components has boiling point lesser than boiling point of water.

5. (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.

6. (b): $p\text{-}NO_2 — C_6H_4 — \overset{+}{C}H_2$ is the least stable carbocation since electron withdrawing $–NO_2$ group destabilises the carbocation.

7. (d): The stability of the carbanion decreases as the electronegativity of the carbon carrying –ve charge decreases or the hybridisation of carbon carrying –ve charge changes from *sp* to sp^2 to sp^3. Thus, $RC\equiv C^-$ is the most stable while $R_3C—CH_2^-$ is the least stable carbanion. Out of $C_6H_5^-$ and $R_2C=CH^-$; $R_2C=CH^-$ is less stable due to +*I*-effect of the two *R* groups. Thus, the overall

stability decreases in the order :
$RC{\equiv}C^- > C_6H_5^- > R_2C{=}CH^- > R_3C{-}CH_2^-$

8. **(a) :**
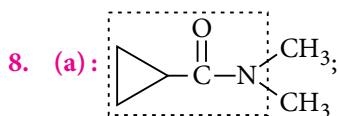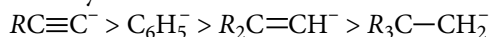
N,N-Dimethylcyclopropane carboxamide

9. **(c) :**

10. **(a) :**

11. **(b):**
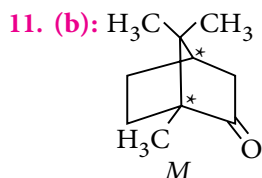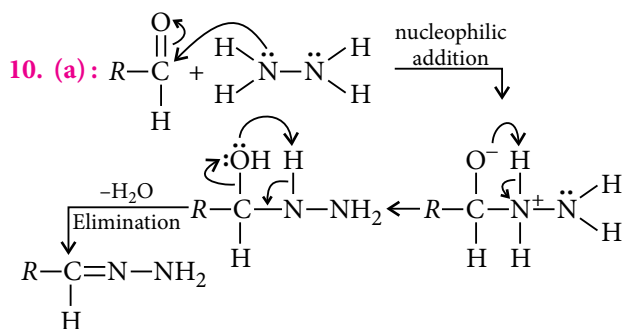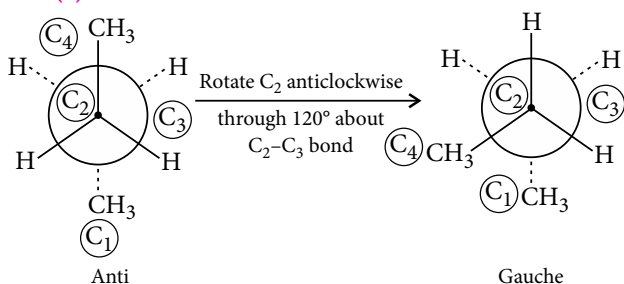
M has two chiral C-atoms thus, number of stereoisomers
$$= 2^n = 2^2 = 4.$$
But due to bridging, rotation is not possible so, only two stereoisomers exist.

12. **(b):** From Kjeldahl's method,

Percent of nitrogen $= \dfrac{1.4 \times N \times V}{W}$

$= \dfrac{1.4 \times 0.5 \times 2 \times 10}{0.25} = 56\%$

13. **(d):** In the estimation of carbon, an organic compound is heated with Cu(II) oxide in a combustion tube. Carbon present in the compound is oxidised to carbon dioxide and hydrogen to water.

$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$

$2H + CuO \xrightarrow{\Delta} Cu + H_2O$
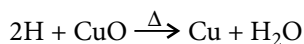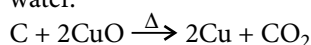
14. **(b):** Partition chromatography is based on continuous differential partition of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

15. **(a) :** α-Hydrogen at bridged carbon never participates in tautomerism. Thus, only (III) exhibits tautomerism.

keto-form   enol-form
(III)
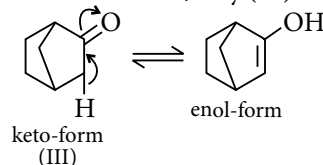
16. **(d):** As we know, essential oils are insoluble in water and have high vapour pressure at 373 K but are miscible with water vapour in vapour phase, it means these are steam volatile. Hence, steam distillation is used for the extraction of essential oils.

17. **(d):** $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH{=}CH_2$
$+ KBr + H_2O$
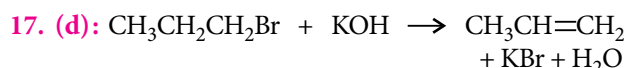
Saturated compound is converted into unsaturated compound by removal of group of atoms hence, it is an elimination reaction.
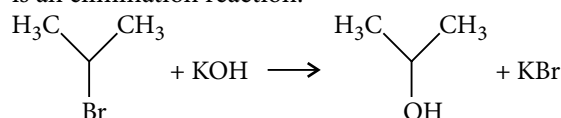
—Br group is replaced by —OH group hence, it is a substitution reaction.
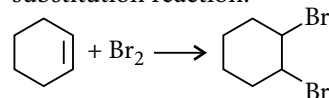
Addition of Br_2 converts an unsaturated compound into a saturated compound hence, it is an addition reaction.

18. **(c) :** Weight of organic compound = 29.5 mg
$NH_3 + HCl \longrightarrow NH_4Cl$
$HCl + NaOH \longrightarrow NaCl + H_2O$
Millimoles of HCl neutralised by 15 mL of 0.1 M
NaOH = 1.5
Total millimoles of HCl = $20 \times 0.1 = 2$
Millimoles used by $NH_3 = 2 - 1.5 = 0.5$
Weight of $NH_3 = 0.5 \times 17$ mg = 8.5 mg
Weight of nitrogen $= \dfrac{14}{17} \times 8.5$ mg $= 7$ mg
% of nitrogen $= \dfrac{7}{29.5} \times 100 = 23.7\%$
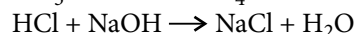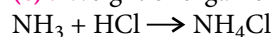
19. **(b):**

4-Ethyl-3-propylhex-1-ene
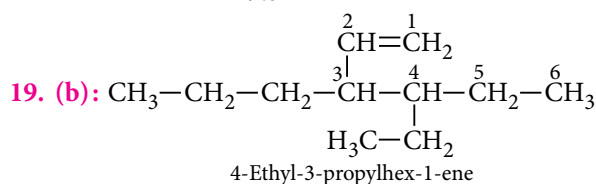
20. (d): In Sawhorse conformation, angle is 180° while in Newman conformation, angle is 60°.

21. (a): Let V_2 be the volume of air displaced or vapours formed at STP.

$$\therefore \quad V_2 = \frac{(746.7 - 26.7)\, mm \times 60\, cm^3 \times 273\, K}{300\, K \times 760\, mm}$$

$$= 51.72\, cm^3$$

Now $51.72\, cm^3$ of the vapours at STP weigh

$$= 0.1724\, g$$

$\therefore$ $22400\, cm^3$ of vapours at STP will weigh

$$= \frac{0.1724 \times 22400}{51.72} = 74.66\, g$$

$\therefore$ Molecular mass of the substance = $74.66\, g\, mol^{-1}$

22. (c): The corresponding acids of (i), (ii), (iii) and (iv) respectively are : CH_3COOH, $CH_3CH_2CH_2CH_3$, NH_3 and C_6H_5OH. Their acid character decreases in the order :

$CH_3COOH > C_6H_5OH > NH_3 > CH_3CH_2CH_2CH_3$

Now since a strong acid has a weak conjugate base, therefore, their basic strength decreases in the opposite order :

$CH_3CH_2CH_2CH_2^-$ (ii) $> NH_2^-$ (iii) $> C_6H_5O^-$ (iv) $>$ CH_3COO^- (i).

23. (c): % of Br

$$= \frac{80}{188} \times \frac{Mass\ of\ AgBr\ formed}{Mass\ of\ substance\ taken} \times 100$$

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

24. (c): $C_{(alkyl)}$—$C_{(aryl)}$ bond in toluene has partial double bond character due to resonance.

$\therefore$ C—H bond in toluene has less energy as compared to others.

25. (c): Milliequivalents of $H_2SO_4 = 60 \times \dfrac{1 \times 2}{10} = 12$

Milliequivalents of NaOH = $20 \times \dfrac{1}{10} = 2$

Milliequivalents of NH_3 = 12 – 2 = 10

% of nitrogen = $\dfrac{1.4 \times (N \times V)_{NH_3}}{W} = \dfrac{1.4 \times 10}{1.4} = 10$

26. (c): Hydrogen may add to both double bonds from the same face to form meso compound '*B*'. If H_2 adds to the two double bonds from opposite faces, the two enantiomers (*C* and *D*) are formed in equal amounts.

meso (*B*)   Racemic mixture (*C*) and (*D*)
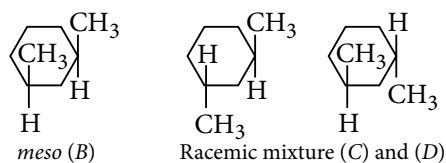
27. (b):
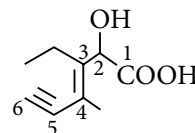
3-Ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid

28. (b): Since the molecular formula of the amide is $C_4H_5N_xO_y$, therefore, on heating with alkali, 1 mole of the amide will produce x moles of NH_3

$= 17x$ g of NH_3.

Now, 1.7 g of NH_3 is obtained from amide = 9.9 g

$\therefore$ $17x$ g of NH_3 will be obtained from amide

$$= \frac{9.9}{1.7} \times 17x\ g = 99x\ g$$

$\therefore$ Molecular weight of amide = $99x$

% of N = $\dfrac{14x}{99x} \times 100 = \dfrac{1400}{99}$

$\therefore$ Number of N atoms (x) in one molecule of amide

$$= \frac{1400}{99 \times 14} = 1.01$$

% of O = 32.33   (Given)

$\therefore$ Number of O atoms (y) in one molecule of amide

$$= \frac{32.33}{16} = 2.02$$

Ratio of N and O atoms, *i.e.*,

$x : y = 1.01 : 2.02 = 1 : 2$

29. (d): Due to H-bonding, most stable conformation of 2-chloroethanol is gauche.
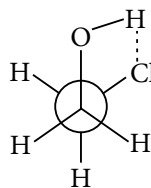
30. (d): Nucleophiles are electron rich species hence, they are Lewis bases.

....◈ ◈

MPP-7 CLASS XII   ANSWER KEY

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

At a Glance CHEMISTRY today 2016

MONTHS	Solved Papers (2016)	Practice Papers (2016 & 2017)	Examiner's Mind	JEE Accelerated Learning series/ NEET | JEE Essentials	Concept Map	Others
JANUARY	—	ACE Your Way CBSE XII Chapterwise Series -8 (2016)	Environmental Chemistry, Hydrocarbons (Class XI); Amines, Biomolecules, Polymers, Chemistry in Everyday Life (Class XII)	Unit-7 : Organic Compounds Containing Oxygen, Organic Compounds Containing Nitrogen (Class XII)	The s-Block Elements	Chemistry Musing Problem Set-30, Practice Questions for PMTs/PETs (Organic Chemistry), Practice Paper PMT (Class XII), Concept Booster (Biomolecules), Advanced chemistry Bloc (Specific conductance and Equivalent conductance), Chemistry Musing Solution Set-29, You ask we answer, Crossword
FEBRUARY	—	JEE Main & Advanced, AIPMT, ACE Your Way CBSE XII (2016)	—	Unit-8 : Biomolecules, Polymers, Chemistry in Everyday Life (Class XII)	The p-Block Elements (Group 13)	Chemistry Musing Problem Set-31, You ask we answer, AIIMS Special (Assertion & Reason), Olympiad Problems, Concept Booster (Mystery of Reduction), Chemistry Musing Solution Set-30, Learn fast (Hydrogen and its compounds), Advanced chemistry Bloc (Thermodynamics efficiency of fuel cell and temperature coefficient of cell), Crossword
MARCH	—	AIPMT, JEE Main, ACE Your Way CBSE XII, AIPMT (Model Test Paper) (2016)	—	Unit-9 : Principles Related to Practical Chemistry (Class XI-XII)	The p-Block Elements (Group 14)	Chemistry Musing Problem Set-32, Advanced chemistry Bloc (Chemical Bonding), Concept Booster (Dealing with Oxidation), Chemistry Musing Solution Set-31, Olympiad Problems, AIIMS Special (Assertion & Reason), You ask We answer, Crossword
APRIL	CBSE Board Class (XII)	JEE Advanced (Model Test Paper), AIPMT, JEE Main, AIPMT (Model Test Paper), AIIMS, BITSAT, JEE Advanced (2016)	—	—	Some Basic Concepts of Chemistry	Chemistry Musing Problem Set-33, Advanced Chemistry Bloc (Fischer Projection), You ask We answer, Chemistry Musing Solution Set-32, Olympiad Problems, Concept Booster (Dealing with oxidation), Exam Ready, Crossword
MAY	JEE Main	JEE Advanced, PMT, AIIMS, BITSAT, JIPMER (2016)	—	—	Alcohols, Phenols and Ethers	Chemistry Musing Problem Set-34, Concept Booster (Impact of electronic effects on Acidity and Basicity), Advanced chemistry Bloc (Sawhorse and Newman projections), Chemistry Musing Solution Set-33, Learn Fast (Chemical Bonding and Molecular Structure, d-and f-Block Elements), Olympiad Problems, You ask We answer, Crossword
JUNE	NEET Phase-I Kerala PET, Karnataka CET	NEET Phase-II (2016); ACE Your Way CBSE XII Chapterwise Series-1 (2017)	—	—	Aldehydes, Ketones and Carboxylic Acids	Chemistry Musing Problem Set-35, Concept Booster (Beware of Bases), NCERT Corner (Class XI - XII), Exam Prep (Questions for practice), Olympiad Problems, Advanced Chemistry Bloc (Geometrical isomers), You ask We answer, Chemistry Musing Solution Set-34, Crossword
JULY	JEE Advanced	NEET Phase-II (2016); ACE Your Way CBSE XI Chapterwise Series-1; ACE Your Way CBSE XII Chapterwise Series-2 (2017)	Some Basic Concepts of Chemistry, Classification of Elements and Periodicity in properties (Class XI); The solid state, General Principle 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)	Chemical Bonding (Class XI); Reaction mechanism (Class XII)	MPP-1 : Some Basic Concepts of Chemistry (Class XI); MPP-1 : The solid State (Class XII), Chemistry Musing Problem set-36, Chemistry Musing Solution Set-35, You ask We answer, Crossword
AUGUST	WB JEE	ACE Your Way CBSE XI Chapterwise Series-2; ACE Your Way CBSE XII Chapterwise Series-3 (2017)	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)	Concepts of Acids and Bases (Class XI); Drugs (Class XII)	You ask We Answer, MPP-2 : Structure of Atom, Classification of Elements and Periodicity in Properties (Class XI); MPP-2 : Solutions, Electrochemistry (Class XII), Advanced Chemistry Bloc (Reductions), Chemistry Musing Problem Set-37, Chemistry Musing Solution Set-36, Crossword
SEPTEMBER	NEET Phase-II	ACE Your Way CBSE XI Chapterwise Series-3; ACE Your Way CBSE XII Chapterwise Series-4 (2017)	Chemical Bonding and molecular structure, Hydrogen (Class XI); The p-Block Elements (Group 15 to 18) (Class XII)	Unit-3 : States of matter : Gases and Liquids, Thermodynamics (Class XI); Unit-3 : General Principles and processes of Isolation of Elements, p-Block Elements (Group 15 to 18) (Class XII)	Reactive Intermediates (Class XI); Some commercial Cells (Batteries) (Class XII)	MPP-3 : States of Matter, Chemical Bonding and Molecular structure (Class XI); MPP-3 : Surface Chemistry, Chemical Kinetics (Class-XII), Chemistry Musing Problem Set-38, Chemistry Musing Solution Set-37, Crossword
OCTOBER	—	ACE Your Way CBSE XI Chapterwise Series-4; ACE Your Way CBSE XII Chapterwise Series-5, JEE Advanced (2017)	States of Matter, s-Block Elements (Class XI); Electrochemistry, d-and f-Block Elements (Class XII)	Unit-4 : Equilibrium, Redox reactions (Class XI); Unit-4 : d- and f-Block Elements, Coordination compounds (Class XII)	Isomerism (Class XI); Name Reactions (Class XII)	MPP-4 : Thermodynamics, Equilibrium (Class-XI); MPP-4 : General Principles and processes of Isolation of Elements, The p-Block Elements (Group 15 to 18) (Class-XII), Chemistry musing Problem set-39, Concept Booster (Kinetic and thermodynamics Enolate), Advanced Chemistry Bloc (Limits of pH scale), Chemistry Musing Solution Set-38, Crossword
NOVEMBER	—	ACE Your Way CBSE XI Chapterwise Series-5; ACE Your Way CBSE XII Chapterwise Series-6 (2017)	Thermodynamics, hydrocarbons (Class XI); Coordination Compounds, Aldehydes, Ketones and Carboxylic Acids (Class XII)	Unit-5 : Hydrogen, The s-Block Elements (Class XI); Unit-5 : Haloalkanes and Haloarenes, Alcohols, Phenols and Ethers (Class XII)	Atomic models (Class XI); Name Reactions (Class XII)	News corner, MPP-5 : Hydrogen, Redox Reactions (Class XI); MPP-5 : The d-and f- Block Elements, Coordination Compounds (Class-XII), Chemistry Musing Problem set-40, Concept Booster, Advanced Chemistry Bloc (Thermodynamics), Chemistry Musing Solution Set-39, Crossword
DECEMBER	—	ACE Your Way CBSE XI Chapterwise Series-6; ACE Your Way CBSE XII Chapterwise Series-7, JEE Advanced (2017)	Equilibrium, The p-Block Elements (Class XI); Chemical Kinetics, Amines, Biomolecules (Class XII)	Unit-6 : The p-Block Elements (Group 13 and 14) (Class XI); Unit-6 : Aldehydes and Ketones, Carboxylic Acids (Class XII)	Some Basic Concepts of Chemistry (Class XI); Reaction Kinetics (Class XII)	MPP-6 : The s-Block Elements, The p-Block Elements (Class XI); MPP-6 : Haloalkanes and Haloarenes, Alcohols, Phenols and Ethers (Class XII), Chemistry Musing Problem set-41, Concept Booster, Chemistry Musing Solution Set-40, Crossword

ACE YOUR WAY **CBSE**

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 tables if necessary, use of calculators is not allowed.

1. Why do hydrocarbon molecules with an odd number of carbon atoms have lower melting points than those with an even number of carbon atoms?

2. What is the composition of photochemical smog?

3. Give the IUPAC name for the following compound :

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CH_3$$

4. Name any two compounds that damage ozone layer?

5. Write the structure of given compound :
'Tetra-*tert*-butylmethane'.

6. Ozone is a toxic gas and is a strong oxidising agent even then its presence in the stratosphere is very important. Explain what would happen if ozone from this region is completely removed.

7. Complete the reactions :

   (i) $CH_4 + O_2 \xrightarrow[\text{723-773 K}]{\text{Copper tube}}$

   (ii) $C_2H_5COONa + NaOH \xrightarrow{\text{CaO}}$

8. Once upon a time, hand pump water was considered to be pure and used freely for drinking in villages but not now. Why?

9. Suggest a route for the preparation of nitrobenzene starting from acetylene.

10. Draw *cis* and *trans* isomers of the following compounds. Also write their IUPAC names.

    (i) $CHCl = CHCl$

    (ii) $C_2H_5(CH_3)C = C(CH_3)C_2H_5$

    OR

    What happens when
    (i) bromoethane is treated with zinc and hydrochloric acid?
    (ii) hydrogen is passed into 2-bromopropane in the presence of palladium?

11. An organic compound, C_8H_{18} on monochlorination gives a single monochloride. Write the structure of the hydrocarbon.

12. (i) What are the reactions involved in removing SO_2 from the atmosphere by passing it through a solution containing citrate ions?

(ii) What is the most important sink of CO pollutant?

(iii) How are flue gases from industries freed from oxides of nitrogen and sulphur?

13. 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.

14. Write down the reactions involved during the formation of photochemical smog.

15. Give the structures of the compounds which on reductive ozonolysis form the following compounds :
(i) propane-1, 3-dial
(ii) glyoxal and formaldehyde
(iii) acetaldehyde, formaldehyde and carbon dioxide.

16. **(i)** Explain by giving reasons "the presence of CO reduces the amount of the haemoglobin available in the blood for carrying oxygen to the body cells".
(ii) Name four tropospheric pollutants.

OR

What are the harmful effects of photochemical smog and how can they be controlled?

17. **(i)** Despite their –I effect, halogens are *ortho, para* directing in haloarenes. Explain why?
(ii) How will you demonstrate that double bonds of benzene are somewhat different from that of olefines?

18. **(i)** What are biodegradable and non-biodegradable pollutants?
(ii) What is the importance of measuring BOD of a water body?

19. **(i)** In the following sequence of reaction :

$$CH_3COOH \xrightarrow{NaOH} CH_3COONa \xrightarrow[CaO]{\Delta}$$

$$B \xleftarrow[\text{(ii) Na/Dry ether}]{\text{(i) } Cl_2, h\upsilon,} A$$
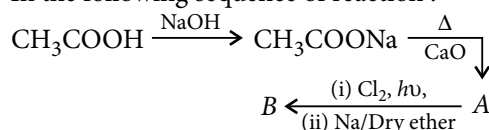
identify A and B.

(ii) Predict the major product in the following reaction :

$$C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$$

20. What are the major causes of water pollution? Explain.

21. Predict the major products of the following :

(i) $CH_3-C\equiv C-Ph \xrightarrow[H_2O]{Hg^{2+}, H^+}$

(ii) $PhCH=CH_2 \xrightarrow{HBr}$

(iii) $\begin{array}{c} CH_3 \\ CH_3 \end{array} C=CH_2 \xrightarrow[H_2O]{Br_2}$
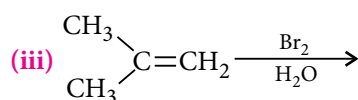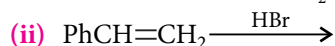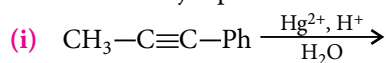
22. **(i)** Why COD is preferred over BOD?
(ii) (a) Differentiate between primary and secondary pollutants by giving example.
(b) Write the consequences of global warming.

23. Sonu and Nilesh were friends. In winters, one day when they were going to school at 10 : 00 am Sonu felt irritation in his eyes and throat. He was unable to breath. Nilesh immediately took him to the doctor. Doctor gave him the proper remedy. When he became well, Nilesh asked reason for this. Doctor answered him satisfactorily.
(i) Can you guess what reason was given by the doctor for the illness of Sonu?
(ii) Why is such smog formed?
(iii) What should be done to prevent the formation of smog?
(iv) What values are possessed by Nilesh?

24. **(i)** Arrange the following sets of compounds in order of their decreasing relative reactivity with an electrophile, E^+.
(a) Chlorobenzene, 2,4-dinitrochlorobenzene, *p*-nitrochlorobenzene
(b) Toluene, *p*-$H_3C-C_6H_4-CH_3$, *p*-$H_3C-C_6H_4-NO_2$,*p*-$O_2N-C_6H_4-NO_2$
(ii) Deduce the structures for the following :
(a) An alkyne 'X' has molecular formula, C_5H_8. It reacts neither with sodamide nor with ammoniacal cuprous chloride.
(b) A hydrocarbon 'Y' decolourises bromine water. On ozonolysis it gives 3-methyl butanal and formaldehyde.
(c) A hydrocarbon 'Z' has molecular formula C_8H_{10}. It does not decolourise bromine water and is oxidised to benzoic acid on heating with $K_2Cr_2O_7$. It can also have three other isomers A, B and C. Write the structures of Z, A, B and C.
Also give the name of the compounds.

OR

(i) Arrange the three isomeric pentanes in order of increasing stability at room temperature.
(ii) Give a method of preparation of propane from (a) an alkene (b) an alkyl halide.

(iii) Write the structures of all the alkenes that can be hydrogenated to form 2-methylbutane.

(iv) Why is light or heat necessary to initiate the chlorination reaction?

25. Account for the following :

(i) Ozone layer is necessary for life.

(ii) The temperature of thermosphere is 1500°C but a person would not feel warm in it.

(iii) Increased SO_2 concentration causes chlorosis.

(iv) CO_2 keeps the earth warm.

(v) The pH of normal rain water is 5.6.

OR

(i) How can you apply green chemistry for the following :

(a) to control photochemical smog?

(b) to avoid use of halogenated solvents in dry cleaning and that of chlorine in bleaching?

(c) to reduce the consumption of petrol and diesel?

(ii) For dry cleaning, in the place of tetrachloroethene, liquefied carbon dioxide with suitable detergent is an alternative solvent. What type of harm to the environment will be prevented by stopping use of tetrachloroethene? Will use of liquefied carbon dioxide with detergent be completely safe from the point of view of pollution? Explain.

26. (i) Name the reagents used to carry out the following conversions :

(a) $H_3CCH_2CH{=}CH_2 \longrightarrow$
$\qquad H_3CCH_2CH_2CH_2OH$

(b) $H_3CCH_2CH{=}CH_2 \longrightarrow$
$\qquad H_3CCH_2CH(OH)CH_2OH$

(c) $H_3CC{\equiv}CH \longrightarrow H_3CCOCH_3$

(d) $\underset{\qquad Br \ \ Br}{H_2C{-}CH_2} \longrightarrow HC{\equiv}CH$

(ii) A monosubstituted alkyl benzene of the formula, $C_{10}H_{14}$ resists vigorous oxidation to an aryl carboxylic acid. Name the compound and write its various monosubstituted isomers.

OR

Complete the following reactions :

(i) Isopropyl bromide $\xrightarrow[\text{Heat}]{\text{alc. KOH}} A \xrightarrow[\text{Peroxide}]{\text{HBr}} B$

(ii) n-Propyl alcohol $\xrightarrow[\text{443 K}]{\text{Conc. } H_2SO_4} A \xrightarrow[\text{Heat}]{O_2/Ag} B$

(iii) Propyne $\xrightarrow[\text{Quinoline}]{H_2/Pd/BaSO_4} A \xrightarrow[\text{(ii) Zn, } H_2O]{\text{(i) } O_3} B + C$

SOLUTIONS

1. Because, they do not fit into crystal lattice easily whereas, hydrocarbons with even number of carbon atoms can fit into crystal lattice easily.

2. It is a mixture of number of irritation causing compounds like NO_2, O_3, peroxyacetylnitrates (PAN), aldehydes, ketones, hydrocarbons and CO.

3. 3-Ethyl-5-methylheptane

4. NO and freons.

5. The expanded structure of the given alkane is
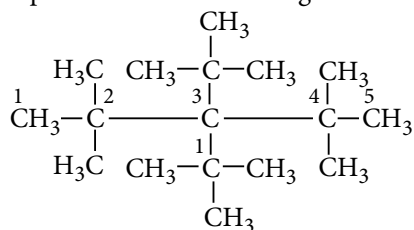
Tetra-*tert*-butylmethane

6. Ozone prevents harmful UV radiations of the Sun from reaching to the earth's surface, thereby it protects life from adverse effects of UV radiations. If ozone is removed completely from the stratosphere, the UV rays will reach to the earth and lead to several diseases like sunburn, skin infection, etc.

7. (i) $2CH_4 + O_2 \xrightarrow[\text{723-773 K}]{\text{Copper tube}} \underset{\text{Methanol}}{2CH_3OH}$

(ii) $C_2H_5COONa + NaOH \xrightarrow{CaO} \underset{\text{Ethane}}{C_2H_6} + Na_2CO_3$

8. Hand pump water is ground water. It collects water below the surface of the earth after passing through the pores of the earthy materials which act as a filter for it and is pure. Now due to disposal of domestic wastes and industrial effluents and use of fertilisers and pesticides, a number of harmful soluble substances dissolve into rain water and pass through the soil and enter into ground water resulting in water pollution.

9. Acetylene when passed through red hot iron tube at 500°C, undergoes cyclic polymerisation to give benzene which upon nitration gives nitrobenzene.

10. (i)

cis-1,2-dichloroethene $\qquad$ *trans*-1,2-dichloroethene

(ii)

cis-3,4-dimethylhex-3-ene   *trans*-3,4-dimethylhex-3-ene

OR

(i) Ethane is formed.

$$CH_3CH_2\!-\!Br + 2[H] \xrightarrow[\text{(Reduction)}]{Zn/HCl} \underset{\text{Ethane}}{CH_3CH_3}$$
$$+\, HBr$$
(Bromoethane)

(ii) Propane is obtained.

$$\underset{\text{2-Bromopropane}}{(CH_3)_2CH\!-\!Br} + H_2 \xrightarrow[\text{(Reduction)}]{Pd} \underset{\text{Propane}}{(CH_3)_2CH_2} + HBr$$

11. Since, the hydrocarbon (C_8H_{18}) on monochlorination gives a single monochloride, therefore, all the 18 H-atoms are equivalent. The only such hydrocarbon is 2, 2, 3, 3-tetramethylbutane, *i.e.*,

12. (i) $$SO_{2(g)} + H_2O_{(l)} \rightleftharpoons HSO_3^-{}_{(aq)} + H^+_{(aq)}$$
$$HSO_3^- + H_2Cit^- \longrightarrow \underset{\text{(Complex)}}{[HSO_3 \cdot H_2Cit]^{2-}}$$

(ii) Soil microorganisms

(iii) By scrubbing flue gases with conc. H_2SO_4 or with alkaline solutions like $Ca(OH)_2$ and $Mg(OH)_2$.

13. 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 vinylic alcohol which then tautomerises to give acetaldehyde.

Ethyne   Complex (I)

Acetaldehyde   Vinylic alcohol

In case of dil. HCl, since Cl^- ion is more nucleophilic than H_2O, it reacts with complex (I) to form vinyl chloride.

Vinyl chloride

14. $$NO_{(g)} + \frac{1}{2}O_{2(g)} \xrightarrow{h\upsilon} NO_{2(g)}$$
$$NO_{2(g)} \xrightarrow{h\upsilon} NO_{(g)} + O_{(g)}$$

These oxygen atoms react with O_2 to form ozone as :
$$O_{2(g)} + O_{(g)} \rightleftharpoons O_{3(g)}$$
$$O_{3(g)} + NO_{(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

These two gases formed, react with hydrocarbons to produce other chemicals.

$$3CH_4 + 2O_3 \longrightarrow \underset{\text{Formaldehyde}}{3CH_2\!=\!O} + 3H_2O$$

Other chemicals produced are :

Acrolein   Peroxyacetyl nitrate (PAN)

15. (i)

Cyclopropene   Propane-1, 3-dial

(ii) $$\underset{\text{1, 3-Butadiene}}{CH_2\!=\!CH\!-\!CH\!=\!CH_2} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} \underset{\text{Formaldehyde}}{HCHO}$$
$$+ \underset{\text{Glyoxal}}{OCH\!-\!CHO} + HCHO$$

(iii) Formation of CO_2 indicates that on either side of this carbon, there is a double bond. Since CH_3CHO and $HCHO$ are the two aldehydes obtained, therefore, this carbon is attached to $CH_3CH\!=$ group on one side and $=CH_2$ group on the other side. Therefore, the compound is 1, 2-butadiene.

$$\underset{\text{1, 2-Butadiene}}{CH_3CH\!=\!C\!=\!CH_2} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} \underset{\text{Acetaldehyde}}{CH_3CHO}$$
$$+ \underset{\text{Carbon dioxide}}{O\!=\!C\!=\!O} + \underset{\text{Formaldehyde}}{HCHO}$$

16. (i) CO is a poisonous gas and it binds to haemoglobin of the blood more readily (about 200 times) than oxygen to form carboxy haemoglobin.

$$Hb + CO \rightleftharpoons \underset{\text{Carboxyhaemoglobin}}{HbCO}$$

The presence of CO, therefore, reduces the amount of the haemoglobin available in the blood for the transport of oxygen to the body cells.

(ii) The tropospheric pollutants may be gaseous or particulate. For example,

Gaseous : Oxides of sulphur, Oxides of nitrogen, hydrogen sulphide, hydrocarbons, etc.

Particulate : Dust, Smoke, Fumes, Smog, etc.

Photochemical smog consists of O_3, NO, acrolein, formaldehyde and PAN. O_3 and NO irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough, difficulty in breathing. Aldehydes and PAN cause irritation in eyes. PAN is highly toxic substance to plants and causes bronzing of tender leaves. Ozone also affects the rubber articles and causes cracking and ageing.
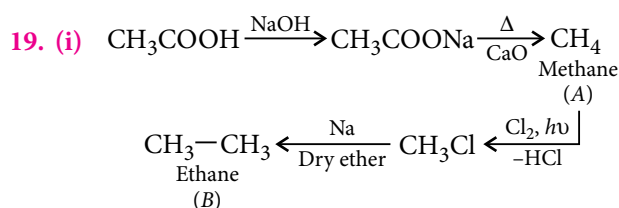
Control of photochemical smog : If primary precursors of photochemical smog such as hydrocarbons and NO_2 are controlled, the secondary precursors such as O_3 and PAN will automatically be reduced. In automobiles, catalytic converters are used to prevent the release of nitrogen oxide and hydrocarbons to the atmosphere.

Certain plants such as *Pinus*, *Juniparus*, etc., can metabolise nitrogen oxide and can help in reducing photochemical smog.

17. (i) Halogens are moderately deactivating group. Because of their strong $-I$ effect, overall electron density on benzene ring decreases. However, due to resonance the electron density on *ortho* and *para*-positions is greater than that at *meta*-position. Hence, they are also *o* and *p*-directing groups.
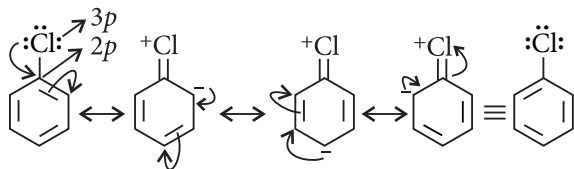
(ii) The double bonds of olefines decolourise Br_2 in CCl_4 and discharge the pink colour of Baeyer's reagent with simultaneous formation of a brown ppt. of MnO_2 while those of benzene do not.

18. (i) Biodegradable pollutants are those which can be decomposed by microorganisms such as bacteria. For example, dust particles, sewage, cow dung, etc.
Non-biodegradable pollutants are those which cannot be decomposed by microorganisms. For example, plastic materials, mercury, aluminium, DDT, etc.

(ii) Biochemical oxygen demand (BOD) is the measure of level of pollution caused by organic biodegradable material in a water body. The clean water would have a BOD value of less than 5 ppm whereas higher values of BOD indicate polluted water.
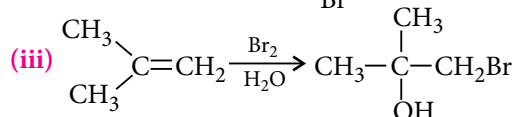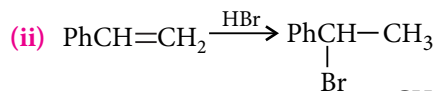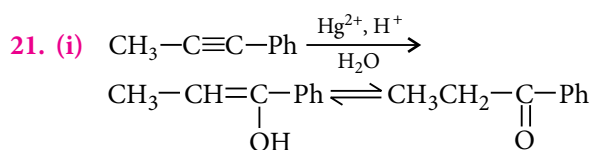
19. (i)

$$CH_3COOH \xrightarrow{NaOH} CH_3COONa \xrightarrow[CaO]{\Delta} \underset{\substack{\text{Methane}\\(A)}}{CH_4}$$

$$\underset{\substack{\text{Ethane}\\(B)}}{CH_3-CH_3} \xleftarrow[\text{Dry ether}]{Na} CH_3Cl \xleftarrow[-HCl]{Cl_2, h\upsilon}$$

(ii) In the presence of conc. H_2SO_4, isobutyl alcohol first forms 1° carbocation (I) which then undergoes rearrangement to the more stable 3° carbocation (II) by 1, 2-hydride shift. Carbocation (II) then reacts with benzene to form *tert*-butyl benzene as :

tert-butyl benzene
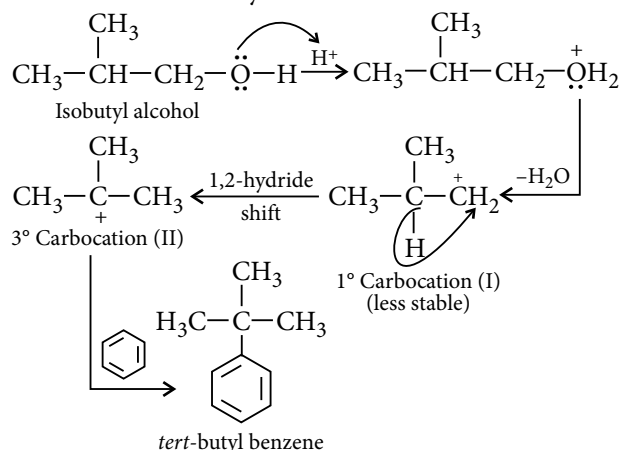
20. The major causes of water pollution may be enlisted as :

(i) Pathogens : Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta. Human excreta contains bacteria such as *Escherichia coli* and *Streptococcus faecalis* which cause gastrointestinal diseases.

(ii) Organic wastes : The other major water pollutants are organic matter such as leaves, grass, trash, etc. They pollute water as a consequence of runoff. Excessive phytoplankton growth within water is also a cause of water pollution. These wastes are biodegradable.

(iii) Chemical pollutants : Water soluble inorganic chemicals that include heavy metals such as cadmium, mercury, nickel, etc. constitute an important class of pollutants. These metals then can damage kidneys, central nervous system, liver, etc. Acids (like sulphuric acid) from mine drainage and salts from many different sources including raw salt used to melt snow and ice in the colder climates (sodium and calcium chloride) are water soluble chemical pollutants.

21. (i) $CH_3-C\equiv C-Ph \xrightarrow[H_2O]{Hg^{2+},\ H^+}$

$$CH_3-CH=\underset{OH}{C}-Ph \rightleftharpoons CH_3CH_2-\underset{O}{\overset{\|}{C}}-Ph$$

(ii) $PhCH=CH_2 \xrightarrow{HBr} PhCH-CH_3$ with Br substituent

$$PhCH=CH_2 \xrightarrow{HBr} PhCH-\underset{Br}{|}CH_3$$

(iii)
$$\underset{CH_3}{\overset{CH_3}{>}}C=CH_2 \xrightarrow[H_2O]{Br_2} CH_3-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2Br$$

22. (i) COD is preferred over BOD because COD can be found in a few minutes whereas BOD requires at least 5 days.

(ii) (a) Primary pollutants : These are simple molecules that persist in the environment in the form, they are formed. *e.g.*, oxides of carbon, nitrogen, sulphur (such as CO, NO_2, SO_2), hydrocarbons etc.

Secondary pollutants : These are the products of reactions of primary pollutants, which are more harmful than primary pollutants, *e.g.*, PAN (peroxyacetyl nitrate) which is formed when hydrocarbons react photochemically with oxides of nitrogen, ozone, aldehydes, phenols, etc.

(b) Global warming is the main consequence of disturbance of green house effect. Global warming had a drastic effect on climatic conditions. It may cause melting of polar ice caps and glaciers which result in floods of low lying areas. Moreover global warming also increases the incidence of several infectious diseases such as malaria, sleeping sickness, dengue, yellow fever, etc.

23. (i) Sonu became ill because of photochemical smog which caused irritation in his eyes and throat.

(ii) It is formed when sunlight is absorbed by O_3, oxides of nitrogen and hydrocarbons.

(iii) Formation of smog can be prevented by controlling the emission of oxides of nitrogen and sulphur.

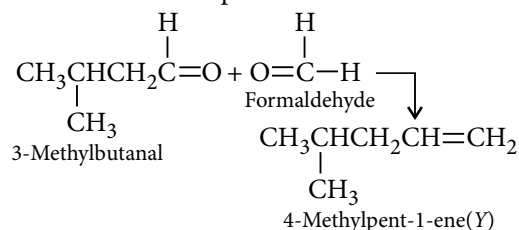**(iv)** Nilesh is helpful, intelligent and curious.

24. (i) (a) Chlorobenzene > *p*-nitrochlorobenzene > 2,4-dinitrochlorobenzene.

(b) *p*-$CH_3-C_6H_4-CH_3$ > toluene > *p*-$CH_3-C_6H_4-NO_2$ > *p*-$NO_2-C_6H_4-NO_2$

(ii) (a) Alkyne 'X' is C_5H_8. Since it does not react with sodamide or ammoniacal cuprous chloride, this alkyne can not be terminal.
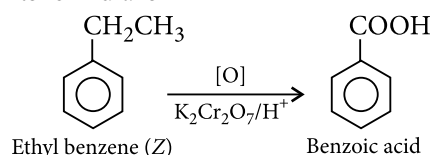
$\therefore CH_3CH_2C\equiv CCH_3$
Pent-2-yne(X)

(b) Hydrocarbon 'Y' is alkene because it decolourises bromine water. From the products of ozonolysis, the structure of alkene can be predicted.
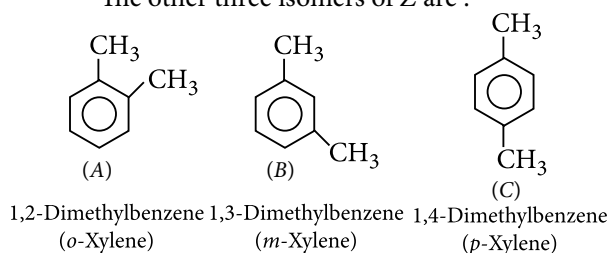
$$\underset{\underset{CH_3}{|}}{CH_3CHCH_2}\overset{\overset{H}{|}}{C}=O + O=\overset{\overset{H}{|}}{C}-H \rightarrow$$

Formaldehyde

3-Methylbutanal

$$CH_3\underset{\underset{CH_3}{|}}{CHCH_2}CH=CH_2$$
4-Methylpent-1-ene(Y)

(c) Since, the given hydrocarbon 'Z' does not decolourise bromine water so, it is arene. Its formula is

Ethyl benzene (Z) $\xrightarrow[K_2Cr_2O_7/H^+]{[O]}$ Benzoic acid (COOH)

The other three isomers of Z are :

(A) 1,2-Dimethylbenzene (*o*-Xylene)

(B) 1,3-Dimethylbenzene (*m*-Xylene)

(C) 1,4-Dimethylbenzene (*p*-Xylene)

OR

(i) The stability of structural isomers generally increases with increasing branching. Thus, Pentane $(CH_3(CH_2)_3CH_3)$ < *iso*-pentane $((CH_3)_2CHCH_2CH_3)$ < *neo*-pentane, $((CH_3)_4C)$

(ii) (a) $CH_3-CH=CH_2 + H_2 \xrightarrow[catalyst]{Pt,\ Pd\ or\ Ni} (CH_3)_2CH_2$

(b) $CH_3-CH_2-Cl + H_2 \xrightarrow{Zn/HCl}$
$CH_3-CH_3 + HCl$

(iii) Alkenes must have the same skeleton as 2-methylbutane. $C-\underset{\underset{C}{|}}{C}-C-C$

There are three different positions for the double bond; hence three different alkenes are :

$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3,\ CH_3-\underset{\underset{CH_3}{|}}{C}=CHCH_3,$

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH=CH_2$$
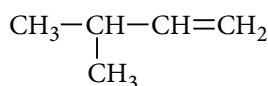
(iv) The Cl—Cl bond must be broken to form chlorine radical before the reaction with methane. This homolysis requires high energy, which is supplied either by heat or light.

25. (i) Ozone absorbs about 99% of harmful UV radiations coming from the sun and thus, protects human being from adverse effect of UV radiations. Thus, its presence is necessary for life.

(ii) This is because the pressure in the thermosphere is very low.

(iii) Because increased SO_2 concentration retards the rate of formation of chlorophyll.

(iv) CO_2 have tendency to absorb most of the heat radiation that are emitted by objects of the earth. Thus, it keeps the earth warm.

(v) This is because of the dissolution of CO_2 from atmosphere which furnishes H^+ ions to the rain water.

$$H_2O_{(l)} + CO_{2(g)} \rightleftharpoons H_2CO_{3(aq)}$$
$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}$$
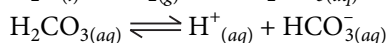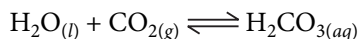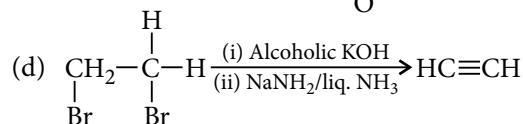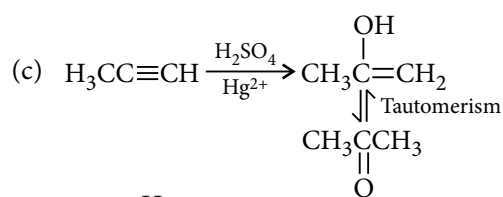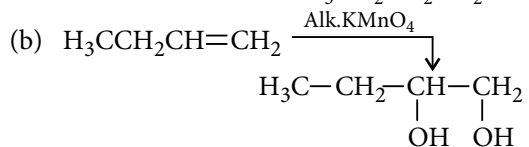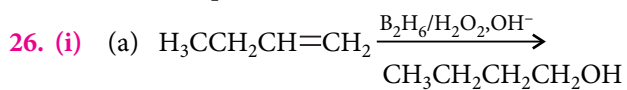
<div align="center">OR</div>

(i) (a) To control photochemical smog use environmental friendly chemicals, reduce factory waste and ensure complete combustion of fuels.

(b) Use of H_2O_2 in bleaching and replace halogenated solvents by liquefied CO_2 in drycleaning.

(c) Use of CNG and LPG instead of petrol and diesel.

(ii) Tetrachloroethene used as a solvent for drycleaning contaminates the ground water and is a suspected carcinogen. This process is now being replaced by a process where liquefied CO_2 with a suitable detergent is used. This will cause less harm to ground water. It will not be completely safe as the use of detergent will also cause pollution but the extent of pollution can be reduced.
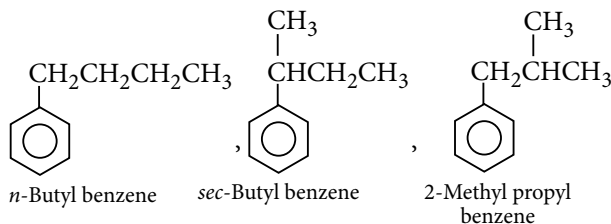
26. (i) (a) $H_3CCH_2CH=CH_2 \xrightarrow{B_2H_6/H_2O_2,\,OH^-} CH_3CH_2CH_2CH_2OH$

(b) $H_3CCH_2CH=CH_2 \xrightarrow{Alk.KMnO_4}$
$$H_3C-CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

(c) $H_3CC\equiv CH \xrightarrow[Hg^{2+}]{H_2SO_4} CH_3\underset{\underset{\displaystyle OH}{|}}{C}=CH_2$ $\Big\downarrow\Big\uparrow$ Tautomerism

$$CH_3\underset{\underset{\displaystyle O}{||}}{C}CH_3$$

(d) $\underset{\underset{\displaystyle Br}{|}}{CH_2}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-H \xrightarrow[\text{(ii) NaNH}_2/\text{liq. NH}_3]{\text{(i) Alcoholic KOH}} HC\equiv CH$

(ii) An alkyl group on benzene nucleus undergoes oxidation if it has at least one benzylic hydrogen atom. Since it resists oxidation, it means that it has no hydrogen at benzylic carbon. Therefore, it should be tertiary. So, the compound is *tert*-butyl benzene represented as
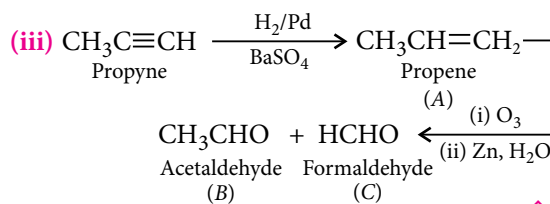
C(CH_3)_3
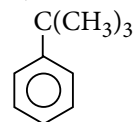
tert-Butyl benzene

Other monosubstituted isomers are :

$CH_2CH_2CH_2CH_3$ *n*-Butyl benzene ,

$\underset{\underset{\displaystyle CH_3}{|}}{CHCH_2CH_3}$ *sec*-Butyl benzene ,

$\underset{\underset{\displaystyle CH_3}{|}}{CH_2CHCH_3}$ 2-Methyl propyl benzene

<div align="center">OR</div>

(i) $CH_3\underset{\underset{\displaystyle Br}{|}}{CH}CH_3 \xrightarrow[\text{Heat}]{\text{alc. KOH}} CH_3CH=CH_2$
Isopropyl bromide , Propene (*A*)

$CH_3CH_2CH_2Br \xleftarrow[\text{Peroxide}]{\text{HBr}}$
1-Bromopropane (*B*)

(ii) $CH_3CH_2CH_2OH \xrightarrow[443\ K]{\text{conc. }H_2SO_4} CH_3CH=CH_2$
n-Propyl alcohol , Propene (*A*)

$CH_3CH\underset{\underset{\displaystyle O}{\diagdown\;\diagup}}{-}CH_2 \xleftarrow[575\ K]{O_2/Ag}$
Propylene oxide (*B*)

(iii) $CH_3C\equiv CH \xrightarrow[BaSO_4]{H_2/Pd} CH_3CH=CH_2$
Propyne , Propene (*A*)

$CH_3CHO + HCHO \xleftarrow[\text{(ii) Zn, }H_2O]{\text{(i) }O_3}$
Acetaldehyde (*B*) Formaldehyde (*C*)

❖❖
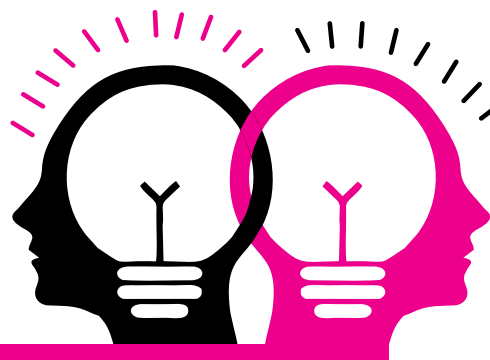
EXAMINER'S MIND CLASS XI

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. What is the equivalent mass of IO_4^- when it is converted into I_2 in acidic medium?
   (a) $\dfrac{M}{6}$ (b) $\dfrac{M}{7}$ (c) $\dfrac{M}{5}$ (d) $\dfrac{M}{4}$

2. Which of the following is a redox reaction?
   (a) $2CuSO_4 + 4KI \longrightarrow 2CuI + 2K_2SO_4 + I_2$
   (b) $SO_2 + H_2O \longrightarrow H_2SO_3$
   (c) $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$
   (d) $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$

3. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M $ZnSO_4$?
   (a) The copper metal will dissolve with evolution of oxygen gas.
   (b) The copper metal will dissolve with evolution of hydrogen gas.
   (c) No reaction will occur.
   (d) The copper metal will dissolve and zinc metal will be deposited.

4. Oxidation states of X, Y, Z are $+2, +5$ and respectively. Formula of the compound formed by these will be
   (a) X_2YZ_6 (b) XY_2Z_6 (c) XY_5 (d) X_3YZ_4

5. Oxidation states of the metal in the minerals haematite and magnetite, respectively are
   (a) II, III in haematite and III in magnetite
   (b) II, III in haematite and II in magnetite
   (c) II in haematite and II, III in magnetite
   (d) III in haematite and II, III in magnetite.

6. In the reaction,
   $As_2S_5 + xHNO_3 \longrightarrow 5H_2SO_4 + yNO_2$
   $\qquad\qquad\qquad\qquad + 2H_3AsO_4 + 12H_2O$
   the values of x and y are
   (a) 40, 40   (b) 10, 10   (c) 30, 30   (d) 20, 20

7. In the disproportionation reaction,
   $3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$
   the equivalent mass of the oxidising agent is (molar mass of $HClO_3 = 84.45$)
   (a) 16.89   (b) 32.22   (c) 84.45   (d) 28.15

8. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour of sulphuric acid?
   (a) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
   (b) $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$
   (c) $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$
   (d) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

9. Which gas is evolved when PbO_2 is treated with conc. HNO_3?
   (a) NO_2 (b) O_2 (c) N_2 (d) N_2O

10. To an acidic solution of an anion, a few drops of $KMnO_4$ solution is added. Which of the following, if present, will not decolourise the $KMnO_4$ solution?
    (a) CO_3^{2-} (b) NO_2^- (c) S^{2-} (d) Cl^-

SECTION - II

More than One Options Correct Type

11. When Cl_2 is passed through hot NaOH, oxidation number of Cl changes from
    (a) –1 to 0   (b) 0 to –1   (c) 0 to +7   (d) 0 to +5

12. For the given reactions, which of the following statements are true?

    $$KI + K_3[Fe(CN)_6] \xrightarrow[\text{(excess)}]{\frac{\text{Dilute}}{H_2SO_4}} \text{Brownish yellow solution}$$
    $$\downarrow ZnSO_4$$

    $$\text{White precipitate} + \underbrace{\text{Brownish yellow filtrate}}$$
    $$\downarrow Na_2S_2O_3$$
    $$\text{Colourless solution}$$

    (a) The first reaction is a redox reaction.
    (b) White precipitate is of $Zn_3[Fe(CN)_6]_2$.
    (c) Addition of starch solution to filtrate gives blue colour.
    (d) White precipitate is soluble in NaOH solution.

13. Which of the following statements are not true about the following decomposition reaction?
    $2KClO_3 \longrightarrow 2KCl + 3O_2$
    (a) Potassium is undergoing oxidation.
    (b) Chlorine is undergoing oxidation.
    (c) Oxygen is reduced.
    (d) None of the species are undergoing oxidation or reduction.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Redox equations are balanced either by ion-electron method or by oxidation number method. Both methods lead to the correct form of the balanced equation. The ion electron method has two advantages. So some chemists prefer to use the ion-electron method for balancing of redox reactions carried out in dilute aqueous solutions, where free ions have more or less independent existence.

The oxidation number method for balancing of redox reactions is mostly used for solid chemicals or for reactions in concentrated acidic media.

14. For the oxidation reaction,
    $K_4[Fe(CN)_6] \longrightarrow Fe^{3+} + CO_2 + NO_3^-$
    the n-factor is
    (a) 1   (b) 11   (c) $\frac{5}{3}$ (d) 61

15. For the oxidation reaction,
    $As_2S_3 \longrightarrow As^{5+} + SO_4^{2-}$
    the n-factor is
    (a) 11   (b) 28   (c) 61   (d) $\frac{5}{3}$

Paragraph for Questions 16 and 17

Oxidation is a process which involves addition of oxygen or any other electronegative element or removal of hydrogen or any other electropositive element or involves loss of electrons or results in the increase in oxidation number of atoms. Reduction is a process which involves addition of hydrogen or any other electropositive element or involves removal of oxygen or any other electronegative element or involves gain of electrons or results in the decrease in oxidation number of atoms.

16. In a reaction, 4 moles of electrons are transferred to one mole of HNO_3. The possible product obtained due to reduction is
    (a) 0.5 mole of N_2 (b) 0.5 mole of N_2O
    (c) 1 mole of NO_2 (d) 1 mole of NH_3

17. In which of the following reactions, nitrogen is not reduced?
    (a) $NO_2 \longrightarrow NO_2^-$ (b) $NO_3^- \longrightarrow NO$
    (c) $NO_3^- \longrightarrow NH_4^+$ (d) $NH_4^+ \longrightarrow N_2$

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)	$2Mg + O_2 \longrightarrow 2MgO$	1. Removal of hydrogen
(Q)	$Mg + Cl_2 \longrightarrow MgCl_2$	2. Removal of electropositive element, potassium
(R)	$2H_2S + O_2 \longrightarrow 2S + 2H_2O$	3. Addition of oxygen
(S)	$2KI + H_2O + O_3 \longrightarrow 2KOH + I_2 + O_2$	4. Addition of electronegative element, chlorine

	P	Q	R	S
(a)	2	3	4	1
(b)	3	4	1	2
(c)	3	4	2	1
(d)	3	2	1	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) $2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2$	1. Metal displacement reaction
(Q) $2NaH \xrightarrow{\Delta} 2Na + H_2$	2. Disproportionation reaction
(R) $V_2O_5 + 5Ca \xrightarrow{\Delta} 2V + 5CaO$	3. Decomposition reaction
(S) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$	4. Redox reaction

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

SECTION - I

Only One Option Correct Type

1. CO_2 is produced in atmosphere by
   I. respiration
   II. burning of fossil fuels
   III. volcanic eruptions
   Identify the correct option.
   (a) Only I and II   (b) Only II and III
   (c) I, II and III   (d) Only I

2. Photochemical smog is caused by a light mediated reaction between
   (a) NO_2 and unsaturated hydrocarbons
   (b) NO_2 and SO_2
   (c) SO_2 and unburnt hydrocarbons
   (d) SO_2 and O_3.

SECTION - V

Assertion Reason Type

20. Assertion : HNO_3 acts only as an oxidising agent, while HNO_2 acts both as an oxidising agent and a reducing agent.
   Reason : The oxidation number of N in HNO_3 is maximum.

21. Assertion : Sodium perxenate (Na_4XeO_6) reacts with NaF in acidic medium to give XeO_3 and F_2.
   Reason : XeO_6^{4-} is a stronger oxidant than F_2.

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. The difference in the oxidation numbers of two types of sulphur atoms in $Na_2S_4O_6$ is

24. The number of moles of oxalate ions oxidised by one mole of MnO_4^- ion is x/y. The value of $x + y$ is

25. Among the given list of compounds, total number of compounds having zero oxidation state of the underlined elements is
   (a) $\underline{S}O_3^{2-}$ (b) $H_2\underline{C}O$ (c) $\underline{C}H_2Cl_2$
   (d) $Na_2\underline{C}r_2O_7$ (e) $\underline{O}_3$

3. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was
   (a) phosgene   (b) methyl isocyanate
   (c) methylamine   (d) ammonia.

4. Growth of fish is not as healthy in warm water as in cold water because
   (a) the amount of D.O. in warm water is higher than in cold water
   (b) warm water is not liked by fish
   (c) cold water contains more marine plants
   (d) the amount of D.O. in warm water is less than in cold water.

5. Which of the following statements is not true about classical smog?

(a) Its main components are produced by the action of sunlight on emissions of automobiles and factories.
(b) It is produced in cold and humid climate.
(c) It contains compounds of reducing nature.
(d) It contains smoke, fog and sulphur dioxide.

6. Dinitrogen and dioxygen are main constituents of air but these do not react with each other to form oxides of nitrogen because _____
(a) the reaction is endothermic and requires very high temperature
(b) the reaction can be initiated only in presence of a catalyst
(c) oxides of nitrogen are unstable
(d) N_2 and O_2 are unreactive.

7. Which of the following statements is true about ozone layer?
(a) It is harmful because ozone is dangerous to living organism.
(b) It is beneficial because oxidation reaction can proceed faster in the presence of ozone.
(c) It is beneficial because ozone cuts-off the ultraviolet radiation of the sun.
(d) It is harmful because ozone cuts out the important radiations of the sun which are vital for photosynthesis.

8. Main pollutants released from iron and steel industry are
(a) CO, CO_2 and SO_2 (b) NO, SO_2 and H_2S
(c) CO_2, H_2S and NO_2 (d) CFCs, NO_2 and SO_2.

9. Excess nitrate in drinking water can cause
(a) methemoglobinemia
(b) kidney damage
(c) liver damage   (d) laxative effect.

10. Sewage containing organic wastes should not be disposed in water bodies because it causes major water pollution. Fishes in such a polluted water die because of
(a) large number of mosquitoes
(b) increase in the amount of dissolved oxygen
(c) decrease in the amount of dissolved oxygen
(d) clogging of gills by mud

SECTION - II
More than One Options Correct Type

11. Phosphate containing fertilisers cause water pollution. Addition of such compounds in water bodies causes

(a) enhanced growth of algae
(b) decrease in amount of dissolved oxygen in water
(c) deposition of calcium phosphate
(d) increase in fish population.

12. Which of the following are proper methods to dispose sludge?
(a) Incineration
(b) Dumping
(c) Anaerobic digestion by microbes
(d) Filtration

13. The consequences of global warming may be
(a) increase in average temperature of the earth
(b) melting of Himalayan Glaciers
(c) increased biochemical oxygen demand
(d) eutrophication.

SECTION - III
Paragraph Type
Paragraph for Questions 14 and 15

Water is one of the most common substance on earth. It covers 72% of the earth's surface. Water is essential for life and its pollution can cause serious problems. The effect of polluted water on health can be anything from an upset stomach to severe illness which may lead to death. Eutrophication is another effect of water pollution. It is the process that results when large quantities of phosphates and nitrates are released into aquatic ecosystem. High concentration of phosphates and nitrates causes rapid growth of bacteria and algae. These microorganisms consume so much oxygen that there is not enough dissolved oxygen, available for other organisms to use in respiration.

14. Which of the following does not cause water pollution?
(a) Heavy metals such as Cd, Pb, Hg
(b) Detergents
(c) Polychlorobiphenyls
(d) Freons

15. Eutrophication of a lake means, it
(a) is low in nutrients
(b) is high in nutrients
(c) has excess amount of organic matter
(d) has high temperature.

Tropospheric pollution is caused by gaseous air pollutants as well as particulate matter. Among the gaseous air pollutants, oxides of sulphur (SO_x), oxides of nitrogen (NO_x) and carbon monoxide play an important role towards pollution. Formation of acid rain, photochemical smog, greenhouse effect and global warming all are the results of various chemical and photochemical reactions taking place in the atmosphere. Various particulates including viable and non-viable are also responsible for causing serious air pollution.

16. Which of the following has largest concentration in acid rain?
   (a) HNO_3 (b) HCl   (c) H_2SO_4 (d) H_2CO_3

17. Which of the following does not contribute towards the formation of photochemical smog?
   (a) NO   (b) SO_2
   (c) O_3 (d) Hydrocarbons

SECTION - IV

Matching List Type

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

List I (Pollutants)	List II (Effects)
(P) Oxides of sulphur	1. Global warming
(Q) Nitrogen dioxide	2. 'Blue baby' syndrome
(R) Carbon dioxide	3. Respiratory diseases
(S) Nitrates in drinking water	4. Red haze in traffic and congested areas

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

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

List I (pollutants)	List II (Effect(s))
(P) Phosphate fertilisers in water	1. BOD level of water increases
(Q) Methane in air	2. Acid rain
(R) Excess organic matter in water	3. Global warming
(S) Oxides of nitrogen in air	4. Eutrophication

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

SECTION - V

Assertion Reason Type

20. Assertion : The pH of acid rain is less than 5.6.
   Reason : Carbon dioxide present in the atmosphere dissolves in rain water and forms carbonic acid.

21. Assertion : If BOD level of water in a reservoir is less than 5 ppm, it is highly polluted.
   Reason : High biological oxygen demand means low activity of bacteria in water.

22. Assertion : It has been found that one molecule of CFCs can destroy more than one thousand O_3 molecules in the stratosphere.
   Reason : Due to CFCs a massive ozone hole has been created in the ozone layer over Antarctica and northern hemisphere.

SECTION - VI

Integer Value Correct Type

23. The value of x in SO_x when the oxides of sulphur acts as a secondary pollutant is

24. In oxyhaemoglobin, the coordination number of Fe^{2+} is

25. Among the following, the total number of herbicides is
   DDT, BHC, sodium chlorate, organo-mercury compounds, sodium arsenite

SOLUTIONS

REDOX REACTIONS

1. (b): $2IO_4^- + 16H^+ + 14e^- \longrightarrow I_2 + 8H_2O$

Eq. wt. of $IO_4^- = \dfrac{2 \times Mol.wt}{14} = \dfrac{M}{7}$

2. (a): $2\overset{+2}{Cu}SO_4 + 4\overset{-1}{K}I \longrightarrow 2\overset{+1}{Cu}I + 2K_2SO_4 + \overset{0}{I_2}$

3. **(c)** : No reaction will occur. As reduction potential of Zn^{2+} ions to Zn atom is lower than that for Cu^{2+} ions. Hence, Cu metal cannot displace Zn^{2+} ions from $ZnSO_4$ solution.

4. **(b)** : The oxidation sates of X, Y and Z are +2, +5 and –2 respectively.
   In $X_2YZ_6 = 2 \times 2 + 5 + 6(-2) \neq 0$
   In $XY_2Z_6 = 2 + 5 \times 2 + 6(-2) = 0$
   In $XY_5 = 2 + 5 \times 5 \neq 0$
   In $X_3YZ_4 = 3 \times 2 + 5 + 4(-2) \neq 0$
   Hence, the formula of the compound is XY_2Z_6.

5. **(d)** : Haematite is Fe_2O_3, in which oxidation number of iron is III. Magnetite is Fe_3O_4 which is infact a mixed oxide ($FeO \cdot Fe_2O_3$), hence iron is present in both II and III oxidation states.

6. **(a)** : The balanced equation is
   $As_2S_5 + 40HNO_3 \longrightarrow 5H_2SO_4 + 40NO_2$
   $\qquad\qquad\qquad\qquad + 2H_3AsO_4 + 12H_2O$

7. **(a)** : $ClO_3^- \longrightarrow \overset{0}{Cl_2}$;
   In $ClO_3^- = x - 6 = -1$ or $x = +5$

   Eq. mass of $ClO_3^- = \dfrac{\text{Mol. mass of } ClO_3^-}{\text{Oxidation number change}}$

   $= \dfrac{84.45}{5} = 16.89$

8. **(d)** : $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$
   Here, the oxidation state of every atom remains the same so, it is not a redox reaction.

9. **(b)** : PbO_2 is a powerful oxidising agent and liberates O_2 when treated with acids.

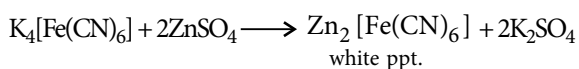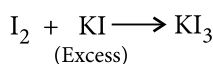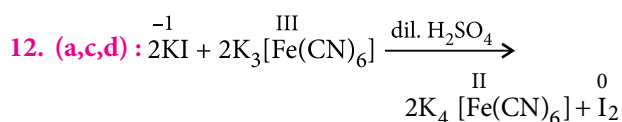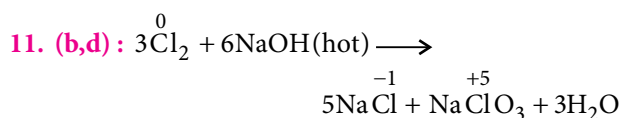 $PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \dfrac{1}{2}O_2$
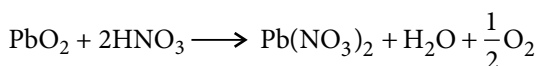
10. **(a)** : Oxidation state of C in CO_3^{2-} is +4, which is maximum. So, it will not be oxidised hence, does not decolourise $KMnO_4$ solution.

11. **(b,d)** : $\overset{0}{3Cl_2} + 6NaOH\,(hot) \longrightarrow$
    $\qquad\qquad \overset{-1}{5Na\,Cl} + \overset{+5}{Na\,ClO_3} + 3H_2O$

12. **(a,c,d)** : $2\overset{-1}{K}I + 2K_3\overset{III}{[Fe(CN)_6]} \xrightarrow{\text{dil. } H_2SO_4}$
    $\qquad\qquad\qquad\qquad 2K_4 \overset{II}{[Fe(CN)_6]} + \overset{0}{I_2}$

    $I_2 + KI \longrightarrow KI_3$
    $\quad\;\;$ (Excess)

    $K_4[Fe(CN)_6] + 2ZnSO_4 \longrightarrow Zn_2\,[Fe(CN)_6] + 2K_2SO_4$
    $\qquad\qquad\qquad\qquad\qquad\qquad$ white ppt.

$KI_3 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI + KI$
Brownish $\qquad\qquad\qquad\qquad\qquad$ Colourless
yellow filtrate $\qquad\qquad\qquad\qquad\;$ solution

$Zn_2[Fe(CN)_6] + 8NaOH \longrightarrow 2Na_2[Zn(OH)_4]$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ Soluble
$\qquad\qquad\qquad\qquad\qquad\qquad + Na_4[Fe(CN)_6]$

13. **(a,b,c,d)** :
$$\overset{+1\;+5\;-2}{2KClO_3} \longrightarrow \overset{+1\;-1}{2KCl} + \overset{0}{3O_2}$$
with Reduction over $KClO_3 \to KCl$ and Oxidation over O_2.

14. **(d)** : $\overset{+1 \times 4}{K_4}\left[\overset{-1 \times 6}{Fe^{2+}(CN)_6}\right]^{4-}$
    Oxidation state of Fe is +2.
    $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
    $6(CN)^- \longrightarrow 6CO_2 + 12e^-$
    $6(x - 3 = -1) \qquad 6(x - 4 = 0)$
    $6(x = 2) \qquad\qquad 6(x = 4)$
    $6(CN)^- \longrightarrow 6NO_3^- + 48e^-$
    $\left(\begin{array}{c}\text{O.N.} \\ \text{of N} = -3\end{array}\right)\quad \begin{array}{c} 6(x - 6 = -1) \\ 6(x = 5)\end{array}$
    n-factor = 61

15. **(b)** :
    $2As^{3+} \longrightarrow 2As^{5+} + 4e^-$
    $(2x = 6) \qquad\quad (2x = 10)$
    $3S^{2-} \longrightarrow 3SO_4^{2-} + 24e^-$
    $(3x = -6) \qquad (3x - 24 = -6)$
    $\qquad\qquad\qquad (3x = 18)$
    n-factor = 28

16. **(b)** : $HNO_3 + 4e^- \longrightarrow ?$
    O.N. of N in $HNO_3 = +5$
    Change in O.N. of N is 4.
    Therefore, oxidation number of N in product should be +1.
    $\therefore$ O.N. of N in $N_2 = 0$
    O.N. of N in $N_2O = +1$
    O.N. of N in $NO_2 = +4$
    O.N. of N in $NH_3 = -3$
    Thus, the possible product of reduction is N_2O.
    Now, $2\,HNO_3 \equiv N_2O \Rightarrow HNO_3 = 0.5\,N_2O$
    $\therefore$ 0.5 mole of N_2O is produced.

17. **(d)** : $\overset{+4}{NO_2} \longrightarrow \overset{+3}{NO_2^+}$, $\overset{+5}{NO_3^-} \longrightarrow \overset{+2}{NO}$,
    $\overset{+5}{NO_3^-} \longrightarrow \overset{-3}{NH_4^+}$, $\overset{-3}{NH_4^+} \longrightarrow \overset{0}{N_2}$

18. **(b)**

19. (a): $(P) \rightarrow 2, 4$; $(Q) \rightarrow 3, 4$; $(R) \rightarrow 1, 4$; $(S) \rightarrow 3$

20. (a)

21. (a): $\overset{+8}{Xe}O_6^{4-} + 2\overset{-1}{F^-} + 6H^+ \longrightarrow \overset{+6}{Xe}O_3 + \overset{0}{F_2} + 3H_2O$

22. (a):

$$\underset{\text{Reduction}}{\overset{\text{Oxidation}}{2H_2\overset{-1}{O_2} \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O_2}}}$$
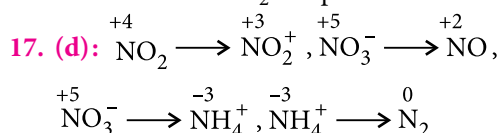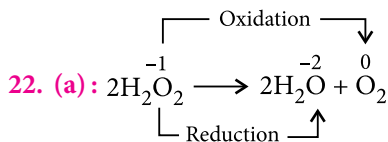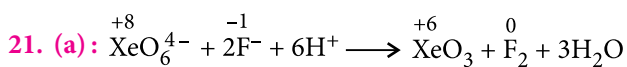
Thus, the above reaction is a disproportionation reaction.

23. (5): $S_4O_6^{2-}$:

$$\bar{O} - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\overset{+5}{} \overset{0}{S} - \overset{0}{S} - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\overset{+5}{} \bar{O}$$
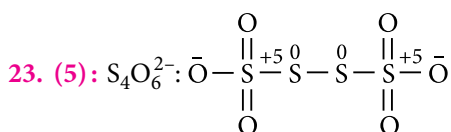
So, difference in oxidation numbers of two types of $S = (5 - 0) = 5$
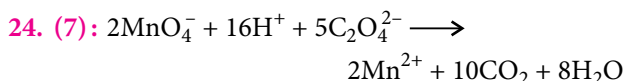
24. (7): $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow$
$$2Mn^{2+} + 10CO_2 + 8H_2O$$
As 2 moles of MnO_4^- oxidises 5 moles of $C_2O_4^{2-}$.
So, 1 mole of MnO_4^- will oxidise 5/2 moles of $C_2O_4^{2-}$.
i.e., $x = 5$ and $y = 2$
∴ $x + y = 5 + 2 = 7$

25. (3): The zero oxidation state of the underlined element is in (b), (c) and (e)
(a) +4, (b) 0, (c) 0, (d) +6, (e) 0

ENVIRONMENTAL CHEMISTRY

1. (c)

2. (a): Photochemical smog is caused by a light mediated reaction between nitrogen oxides and unsaturated hydrocarbons produced by automobiles and factories.

3. (b): The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was methyl isocyanate (MIC), $CH_3 - N = C = O$.

4. (d): Due to lesser amount of D.O. in warm water, the growth of fish in it is not as healthy as in cold water.

5. (a): Photochemical smog is produced by the action of sunlight on emissions of automobiles and factories.

6. (a): The reaction between dinitrogen and dioxygen occurs at a very high temperature hence, they do not react easily.

7. (c): Ozone layer in the stratospheres cuts off 99.5% of sun's harmful ultraviolet (UV) radiations from reaching the earth's surface.

8. (a): Iron and steel industry use coke as a reductant in blast furnace which contains C and S. On oxidation, these are converted to CO, CO_2 and SO_2 gases.

9. (a): Excess concentration of nitrate in drinking water is harmful and can cause methemoglobinemia (blue baby syndrome).

10. (c): If organic waste is disposed in water, it consumes the available oxygen and fishes in such polluted water will die due to decrease in amount of dissolved oxygen.

11. (a,b): Phosphate containing fertilisers support dense growth of plants and algae and decrease the amount of dissolved oxygen.

12. (a,b,c): Incineration, dumping and anaerobic digestion by microbes are the three proper methods used for the disposal of sludge.

13. (a,b): Global warming may results in increase in average temperature of earth causing melting of Himalayan glaciers.

14. (d): Freons do not cause water pollution.

15. (b): Eutrophication is caused by high concentration of phosphates and nitrates from fertilisers in aquatic ecosystems.

16. (c): H_2SO_4 has the largest concentration, HNO_3 has lesser and HCl has the least concentration in acid rain.

17. (b): SO_2 has no contribution in the formation of photochemical smog.

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

20. (b): Normally rain water has a pH of 5.6. CO_2 as well as oxides of nitrogen and sulphur dissolve in water to form acid rain which has pH < 5.6.

21. (d): Water is not polluted if BOD < 5 ppm. High BOD demand means high activity of bacteria.

22. (a)

23. (3): SO_x is a mixture of SO_2 (primary pollutant) and SO_3 (secondary pollutant).

24. (6): In oxyhaemoglobin, Fe^{2+} is coordinated to five donor groups and the sixth site is free which is coordinated with O_2.

25. (2): Sodium chlorate and sodium arsenite are herbicides.

◈ ◈

This specially designed column enables students to self analyse their extent of understanding of specified chapters. 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.

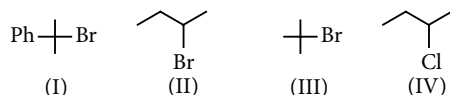## Organic Chemistry-Some Basic Principles and Techniques
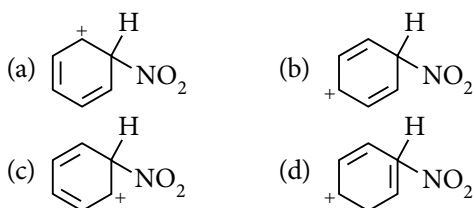
Total Marks : 120

Time Taken : 60 Min.

Only One Option Correct Type

**1.** Arrange these compounds in the order of increasing rate of S_N1 reaction.

Ph—Br (I), (II) with Br, (III) with Br, (IV) with Cl

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

2. Tautomerism is exhibited by
(a) $(CH_3)_3CNO$
(b) $(CH_3)_2NH$
(c) R_3CNO_2
(d) RCH_2NO_2

3. Which is not the resonance structure of a carbocation?

4. The IUPAC name of the compound is
(a) 2-formylmethyl propanoate
(b) 2-oxoethyl propanoate
(c) 2-propionyloxyethanal
(d) both (a) and (b) are correct.

5. Consider the following pairs of possible isomers

(IA) (IIA) (IIIA)

(IB) (IIB) (IIIB)
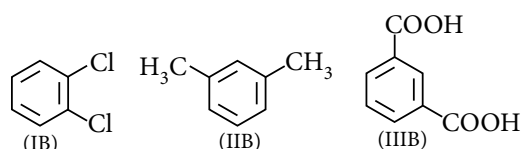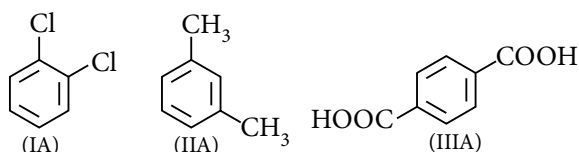
Which of the following statements is correct?
(a) All three pairs represent different compounds.
(b) IA and IB are identical; IIA and IIB are identical; and IIIA and IIIB are identical.
(c) IA and IB are isomers; IIA and IIB are identical; and IIIA and IIIB are isomers.
(d) IA and IB are identical; IIA and IIB are identical, and IIIA and IIIB are isomers.

6. The Lassaigne's extract of an organic compound after acidification with HNO_3 is mixed with a few mL of CCl_4 and then treated with chlorine water. The lower layer of CCl_4 develops a violet colour. This indicates that the organic compound contains
(a) nitrogen
(b) sulphur
(c) bromine
(d) iodine.

7. Which one of the following has all the effects, namely inductive, mesomeric and hyperconjugative?
(a) CH_3Cl
(b) $CH_3CH=CH_2$
(c) $CH_3CH=CHCCH_3$ (with $\overset{\|}{O}$)
(d) $CH_2=CH—CH=CH_2$

8. The number of isomers (geometrical and optical) possible for the compound with the following structure
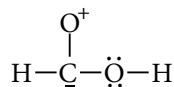$CH_3CH=CH—CH=CH—CH_2CHOHCH_3$ is
(a) 2
(b) 4
(c) 6
(d) 8

9. The correct order of reactivity for the following compounds in S_N2 reaction : CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is
   (a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
   (b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
   (c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
   (d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

10. For the detection of phosphorus, the organic compound after fusion with Na_2O_2 is extracted with water, boiled with HNO_3 and then ammonium molybdate is added to it. A yellow ppt. is obtained which is due to the formation of
    (a) ammonium phosphate
    (b) ammonium phosphomolybdate
    (c) ferric phosphate
    (d) disodium ammonium phosphate.

11. In E2 elimination, some compounds follow Hofmann's rule which means
    (a) the double bond goes to the most substituted position
    (b) the compound is resistant to elimination
    (c) no double bond is formed
    (d) the double bond goes mainly towards the least substituted carbon.

12. The empirical formula of a compound is CH_2. The mass of one mole of the compound is 42 g. Therefore, its structural formula is
    (a) $CH_3CH_2CH_3$
    (b) $CH_3—CH=CH_2$
    (c) $CH_2=CH—CH=CH_2$
    (d) $CH_3—C≡CH$

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 :** The central carbon atom in $H_2C=C=CH_2$ is *sp*-hybridised.
    Reason : In this molecule all the carbon atoms are attached to each other by double bonds.

14. **Assertion :** $H—\overset{\overset{O^-}{|}}{C}=\overset{+}{O}H$ is more stable than $H—\overset{\overset{O^+}{|}}{\underset{..}{C}}—\overset{..}{\underset{..}{O}}—H$
    Reason : Compound in which the positive and negative charges reside on the most electropositive and most electronegative atoms of the species respectively is more stable.
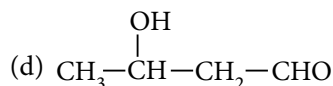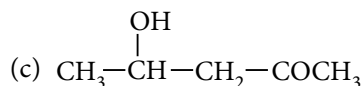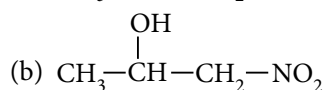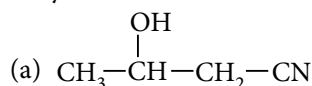
15. **Assertion :** The IUPAC name for the compound, $NCCH_2CH_2COOH$ is 4-carboxybutanenitrile.
    Reason : —COOH is considered as substituent group while —CN is considered as the principal functional group.

Only One Option Correct Type

16. Dichlorocarbene is generated by the action of potassium-1-butoxide on chloroform. This is an example of
    (a) α-elimination reaction
    (b) β-elimination reaction
    (c) addition reaction
    (d) rearrangement reaction.

17. In the following groups
    (I) – OAc   (II) –OMe
    (III) – OSO$_2$Me   (IV) – OSO$_2$CF$_3$
    the order of leaving group ability is
    (a) I > II > III > IV   (b) IV > III > I > II
    (c) III > II > I > IV   (d) II > III > IV > I

18. Which alcohol will be most reactive for dehydration?
    (a) $CH_3—\overset{\overset{OH}{|}}{CH}—CH_2—CN$
    (b) $CH_3—\overset{\overset{OH}{|}}{CH}—CH_2—NO_2$
    (c) $CH_3—\overset{\overset{OH}{|}}{CH}—CH_2—COCH_3$
    (d) $CH_3—\overset{\overset{OH}{|}}{CH}—CH_2—CHO$

19. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it?
    (a) The C=O bond is weaker than the C—O bond.
   (b) The anion $HCOO^-$ has two resonating structures.

(c) The anion is obtained by removal of a proton from the acid molecule.

(d) Electronic orbitals of carbon atom are hybridised.

More than One Options Correct Type

20. Reaction between neopentyl bromide and ethanol gives 2-methoxy-2-methyl butane as the major products because
(a) this involves a 1, 2-hydride shift
(b) this involves a 1, 2-alkyl shift
(c) this occurs through a S_N1 mechanism
(d) this is also accompanied with the formation of alkenes as by product.

21. Br has a low reactivity in $CH_2 = CH—Br$ because
(a) Br is electronegative
(b) of the $+M$ effect of bromine
(c) the C—Br bond has a partial double bond character
(d) Br shows $+I$ effect.

22. Which of the following species are planar?
(a) *Iso*-propyl carbanion
(b) Nitromethyl carbanion
(c) Singlet carbene
(d) Triphenylmethyl carbocation

23. Which of the following statements are correct?
(a) A *meso* compound is optically active because the rotation caused by any molecules is cancelled by an equal and opposite rotation caused by another molecules that is the mirror image of the first.
(b) A *meso* compound has chiral centres but exhibits no optical activity.
(c) A *meso* compound has a plane of symmetry and thus exhibits no optical activity.
(d) A *meso* compound has molecules which are superimposable on their mirror image even though they contain chiral centres.
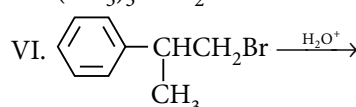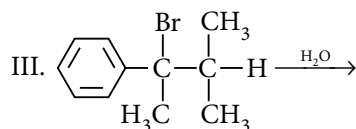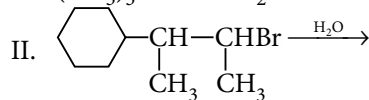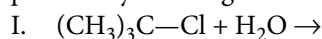
Integer Answer Type

24. On bromination of the following compound, Br goes to which position in the major product?
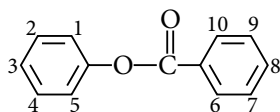
25. How many of the following S_N reactions will give

product by rearrangement?

I. $(CH_3)_3C—Cl + H_2O \rightarrow$

II. $\langle\hspace{-4pt}\bigcirc\hspace{-4pt}\rangle$—CH—CHBr $\xrightarrow{H_2O}$ with CH₃ CH₃

III. $\langle\hspace{-4pt}\bigcirc\hspace{-4pt}\rangle$—C—C—H $\xrightarrow{H_2O}$ with Br CH₃ / H₃C CH₃

IV. $(CH_3)_2CHCH_2Br \xrightarrow{H_2O/Ag^+}$

V. $(CH_3)_3CCH_2Br \xrightarrow{H_2O/Ag^+}$

VI. $\langle\hspace{-4pt}\bigcirc\hspace{-4pt}\rangle$—CHCH₂Br $\xrightarrow{H_2O^+}$ with CH₃

26. A conjugate system has at least .... π electrons.

Comprehension Type

The reaction of an electrophile with a nucleophile is the same as the reaction of a Lewis acid with a Lewis base and is termed as Lewis acid-base association reaction, as a result of which each atom in the product completes its octet (except H which completes its duplet).

27. Consider the following reaction between an electrophile and nucleophile,
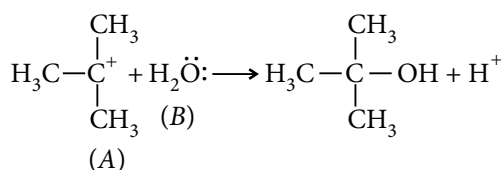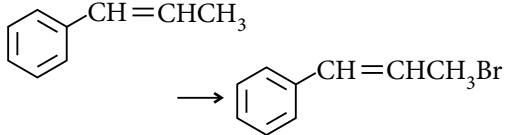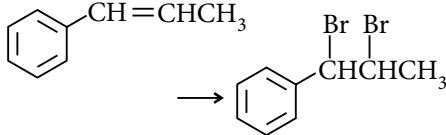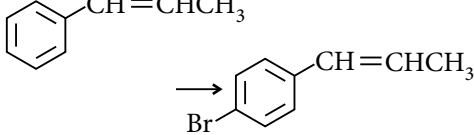
$$H_3C—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} + H_2\ddot{O}: \longrightarrow H_3C—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH + H^+$$
(A), (B)

Incorrect statement (s) is/are

(a) It is a Lewis acid-base association reaction.

(b) It is a Lowry-Bronsted acid-base reaction.

(c) Driving force that makes ΔG negative is the completion of the octet of C and O atoms in the product.

(d) A is an electrophile and B is a nucleophile.

28. In which case additional reagent is required to generate an electrophile?

(a)

(b)

(c)

(d) In all cases
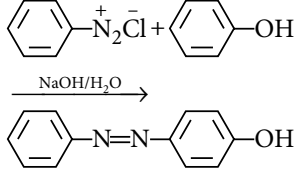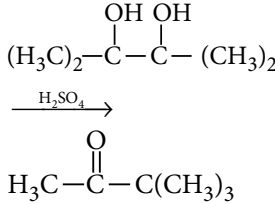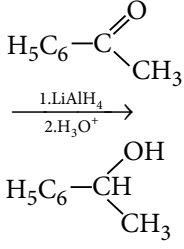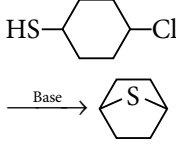
Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I		Column II	
(P)	1, 2-Dichloroethane	1.	Gauche conformation
(Q)	1, 2-Dimethyl-cyclopropane	2.	Geometrical isomerism
(R)	1, 2-Ethanediol	3.	Chair conformation
(S)	1, 2-Dimethyl-cyclohexane	4.	Conformational isomerism

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

30. Match the reaction in Column I with appropriate options in Column II.

Column I

(P)

(Q)

(R)

(S)

Column II

1. Racemic mixture

2. Addition reaction

3. Substitution reaction

4. Coupling reaction

5. Carbocation intermediate

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

◈◈

Keys are published in this issue. Search now! ☺

CONCEPT MAP

GASEOUS STATE

A substance exists in gaseous state if the thermal energy of molecules predominates over intermolecular forces, molecules are sufficiently apart from one another (intermolecular distances 10^{-7} – 10^{-5} cm), have large rotatory, vibratory and translatory motions and are most energetic.

Ideal gases

Gases which follow gas laws under all conditions of temperature and pressure.

Gas Laws

Boyle's law

$P \propto \dfrac{1}{V}$ (at constant T and n)

$\therefore P_1 V_1 = P_2 V_2 = $ constant $\Rightarrow \dfrac{P_1}{P_2} = \dfrac{V_2}{V_1}$

Avogadro's law

$V \propto n$ (at constant P and T)

$\Rightarrow \dfrac{V}{n} = $ constant

Charles' law

$V \propto T$ (at constant P and n)

$\therefore \dfrac{V_1}{T_1} = \dfrac{V_2}{T_2} = $ constant

Gay-Lussac's law

$P \propto T$ (at constant V, n)

$\dfrac{P}{T} = $ constant $\Rightarrow \dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

Ideal gas equation

$PV \propto nT$; $PV = nRT$

or $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$ [Equation of state]

Dalton's law of partial pressures

$P_{total} = p_1 + p_2 + p_3 + p_4 \ldots$ (at constant T, V)

where, $p_1 = x_1 P_{total}$

$p_2 = x_2 P_{total}$; $p_3 = x_3 P_{total}$

$P_{dry\,gas} = P_{moist\,gas} - $ aqueous tension

Molecular velocities of gaseous molecules

- **Average velocity :**

$U_{av} = \sqrt{\dfrac{8RT}{\pi M}} = \sqrt{\dfrac{8PV}{\pi M}}$

- **Root mean square velocity :**

$U_{rms} = \sqrt{\dfrac{3RT}{M}} = \sqrt{\dfrac{3PV}{M}}$

- **Most probable velocity :**

$U_{mp} = \sqrt{\dfrac{2RT}{M}} = \sqrt{\dfrac{2PV}{M}}$

- $U_{mp} : U_{av} : U_{rms} = 1 : 1.128 : 1.224$

Kinetic molecular theory of gases

- The actual volume of the molecules is negligible as compared to the space between them and hence they are considered as the point masses.
- Interaction between the particles is negligible.
- Particles of a gas are always in constant and random motion and the collisions between them are perfectly elastic.
- Pressure of the gas is due to the collisions of gaseous molecules with the walls of the container.

Kinetic gas equation

$PV = \dfrac{1}{3} mnu^2 \Rightarrow u = \sqrt{\dfrac{3PV}{M}} = \sqrt{\dfrac{3RT}{M}}$; Average K.E./ molecule $= \dfrac{3}{2}\dfrac{RT}{N} = \dfrac{3}{2}kT$

Real gases

Gases which do not follow gas laws under all conditions of temperature and pressure.

Van der Waal's equation

$\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT$

- a (atm $L^2 mol^{-2}$) is measure of intermolecular forces.
- b ($L\,mol^{-1}$) measure of effective size.

Compressibility factor, Z

- For ideal gas, compressibility factor i.e., $Z = PV/nRT = 1$
- For real gas, $Z = PV_{real}/nRT$, $Z \neq 1$. Hence, two cases arise :
  - When $Z < 1$, it is a negative deviation i.e., easily compressible.
  - When $Z > 1$, it is a positive deviation i.e., difficult to compress.

Liquefaction of gases

It is carried out by increasing pressure or decreasing temperature.

Critical temperature (T_c)

It is the highest temperature above which a gas cannot be liquefied ; $T_c = 8a/27Rb$

Critical volume (V_c)

Volume of one mole of a gas at critical temperature; $V_c = 3b$

Critical pressure (P_c)

Pressure of one mole a gas at its critical temperature ; $P_c = a/27b^2$.

BONDING IN COORDINATION COMPOUNDS

Apart from playing an important role in various life processes like photosynthesis, oxygen transportation and storage, coordination compounds have shown their usefulness in medicinal and analytical chemistry also such as treatment of metal toxicity, hardness of water etc.

CONCEPT **MAP**

Werner's theory
It gives an idea about the structures of complex compounds.

Postulates of Werner's theory
- Metals possess two types of valencies; primary valency (oxidation number) and the secondary valency (coordination number).
- A metal atom tends to satisfy both primary as well as secondary valencies.
- Secondary valencies satisfied by ligands are directional while primary valencies satisfied by negative ions are non-directional in nature.

Limitations of Werner's theory
- Werner's theory could not explain
  - the complex forming property of only certain elements.
  - directional characteristics of bonds.
  - characteristic magnetic and optical properties of complexes.

Valence bond theory
It describes the bonding in terms of hybridised orbitals of the central metal atom or ion, it explains the shapes of complexes and relation between the observed magnetic behaviour and bond type.

Postulates of VBT
- The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number which hybridise together.
- The vacant hybrid orbitals form coordinate bond with ligands. These bonds are of equal strength and directional in nature.

Hybridisation and geometry of complexes

Coordination no.	Type of hybridisation	Geometry of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

### Limitations of VBT
- It could not explain the colour and electronic spectra of complexes.
- It could not explain the structure of $[Cu(NH_3)_4]^{2+}$ ion.
- It could not explain why the pairing of electrons occurs in the presence of strong ligands.
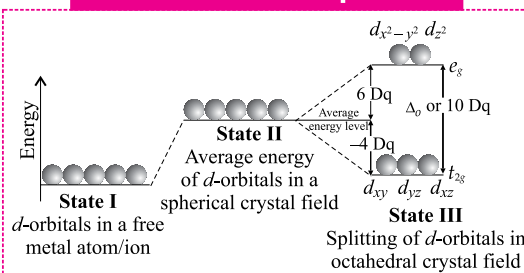
Crystal field theory (CFT)
According to CFT, under the influence of ligand field, degeneracy of d-orbitals is destroyed and they split into two or more energy levels. The extent of splitting depends upon the strength of ligand.
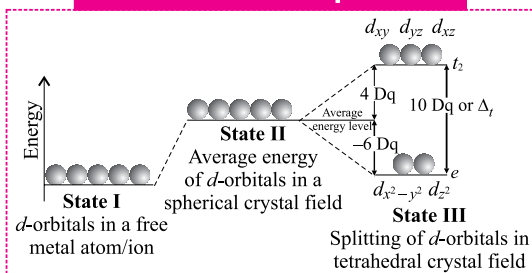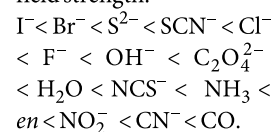
Spectrochemical series
Arrangement of ligands in the order of increasing field strength.
$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$.

Increasing order of CFSE (Δ_o) →

- If $\Delta_o < p$, then complex is high spin.
- If $\Delta_o > p$, then complex is low spin.

Tetrahedral complexes

State I — d-orbitals in a free metal atom/ion
State II — Average energy of d-orbitals in a spherical crystal field
State III — Splitting of d-orbitals in tetrahedral crystal field

$d_{xy}\ d_{yz}\ d_{xz}$ — t_2
4 Dq, –6 Dq, 10 Dq or Δ_t
$d_{x^2-y^2}\ d_{z^2}$ — e

Octahedral complexes

State I — d-orbitals in a free metal atom/ion
State II — Average energy of d-orbitals in a spherical crystal field
State III — Splitting of d-orbitals in octahedral crystal field

$d_{x^2-y^2}\ d_{z^2}$ — e_g
6 Dq, –4 Dq, Δ_o or 10 Dq
$d_{xy}\ d_{yz}\ d_{xz}$ — t_{2g}

Jahn-Teller distortion
- If the d-orbitals are asymmetrically filled, they will repel some ligands in the complex more than the others. This results in distortion of octahedral complexes.
- Distortion caused by asymmetric filling of t_{2g} is too small to measure.

- Asymmetric filling of e_g orbitals causes a significant distortion.

e_g: $d_{x^2-y^2}\ d_{z^2}$
Four long bonds and two short bonds.

e_g: $d_{x^2-y^2}\ d_{z^2}$
Two long bonds and four short bonds.
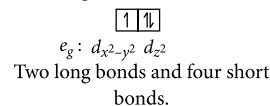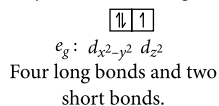
d^4 (high spin), d^7 (low spin) and d^9 configurations show Jahn Teller distortion.

Maximize 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.
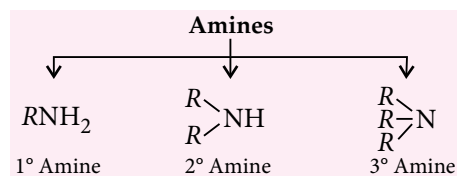
Unit 7 — ORGANIC COMPOUNDS CONTAINING NITROGEN
BIOMOLECULES

ORGANIC COMPOUNDS CONTAINING NITROGEN

AMINES

↳ The derivatives of ammonia formed by the replacement of one or more hydrogen atoms by the corresponding number of alkyl or aryl groups are known as *amines*. Like ammonia, nitrogen is sp^3-hybridised and the geometry is pyramidal in amines.

CLASSIFICATION

Amines

$R\mathrm{NH_2}$ — 1° Amine

$\begin{array}{c} R \\ R \end{array}\!\!>\!\mathrm{NH}$ — 2° Amine

$\begin{array}{c} R \\ R \\ R \end{array}\!\!>\!\mathrm{N}$ — 3° Amine

PHYSICAL PROPERTIES

Physical state and odour

↳ Lower aliphatic amines are gases which smell like ammonia and lower aromatic amines are liquids with characteristic unpleasant odour.

Solubility

↳ Amines are soluble in water due to hydrogen bonding while higher amines and aromatic amines are soluble in organic solvents such as benzene, ether, alcohol, etc.

↳ As the size of the alkyl group increases, solubility decreases.

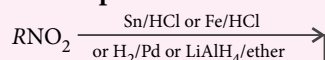**Physical Properties**

Boiling points

↳ Tertiary amines have the lowest boiling points as they do not have hydrogen atoms linked to the nitrogen atom.

↳ The intermolecular association is more in primary amines than in secondary amines due to the presence of two hydrogen atoms. Therefore, the order of boiling points of isomeric amines is 1° > 2° > 3°.
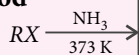
Colour

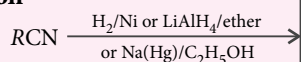↳ Pure amines are colourless but develop colour when exposed to air.
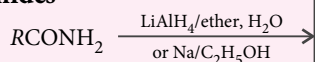
PREPARATION

Reduction of nitro compounds

$$RNO_2 \xrightarrow[\text{or } H_2/Pd \text{ or } LiAlH_4/\text{ether}]{\text{Sn/HCl or Fe/HCl}}$$

Hofmann's ammonolysis method

$$RX \xrightarrow[373 \text{ K}]{NH_3}$$

Mendius reduction

$$RCN \xrightarrow[\text{or Na(Hg)/C}_2H_5OH]{H_2/Ni \text{ or } LiAlH_4/\text{ether}}$$

Reduction of amides

$$RCONH_2 \xrightarrow[\text{or Na/C}_2H_5OH]{LiAlH_4/\text{ether, } H_2O}$$

Gabriel phthalimide synthesis

Phthalimide (benzene ring fused with CO–NH–CO)

$$\xrightarrow[\substack{(ii)\ RX, \Delta \\ (iii)\ H^+/H_2O \text{ or } OH^-/H_2O, \Delta}]{(i)\ KOH(alc.)}$$
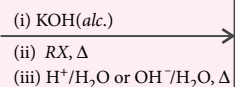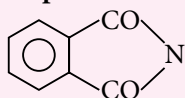
Hofmann's bromamide degradation

$$RCONH_2 \xrightarrow[KOH, \Delta]{Br_2}$$

Curtius reaction

$$RCOCl \xrightarrow[(ii)\ H_3O^+ \text{ or } NaOH, \Delta]{(I)\ NaN_3/C_2H_5OH, \Delta}$$
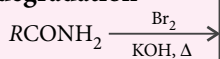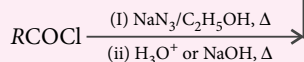
$$\boxed{R{-}NH_2}$$

Ammonolysis of alcohols

$$ROH + NH_3 \xrightarrow[\text{or ThO}_2, \Delta]{Al_2O_3}$$
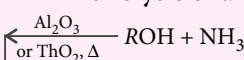
Schmidt reaction

$$RCOOH \xrightarrow[\Delta]{N_3H/H_2SO_4 (conc.)}$$
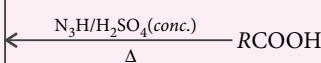
Reductive amination of aldehydes or ketones

$$O{=}C{<}_{R'}^{R} \xrightarrow[150°C, 300 \text{ atm}]{NH_3, H_2/Ni \text{ or } NaBH_3CN}$$

Reduction of oximes

$$RCH{=}NOH \xrightarrow[\text{or Na/C}_2H_5OH]{LiAlH_4/\text{ether}}$$
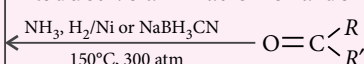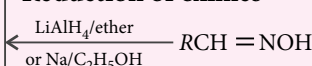
Decarboxylation of α-amino acids

$$\underset{\underset{NH_2}{|}}{RCHCOOH} \xrightarrow[\Delta]{Ba(OH)_2}$$
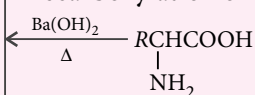
Hydrolysis of isocyanates

$$RNC \xrightarrow[HCl]{H_2O}$$
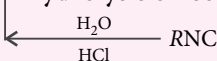
CHEMICAL PROPERTIES

✎ **Basic character**

- ➢ In gaseous phase, the order of basicity of amines is : 3° amine > 2° amine > 1° amine > NH_3.
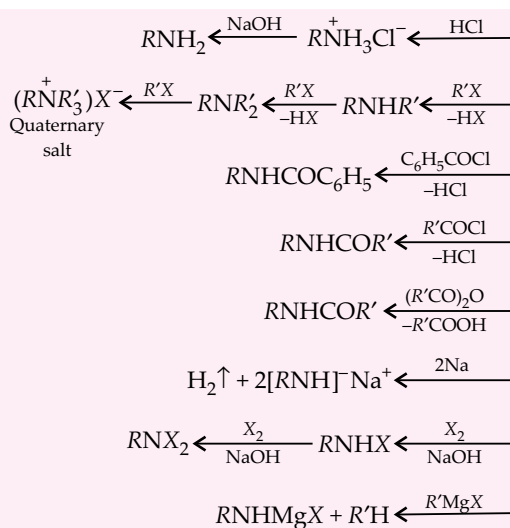- ➢ In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity in aqueous solution of amines is as follows :
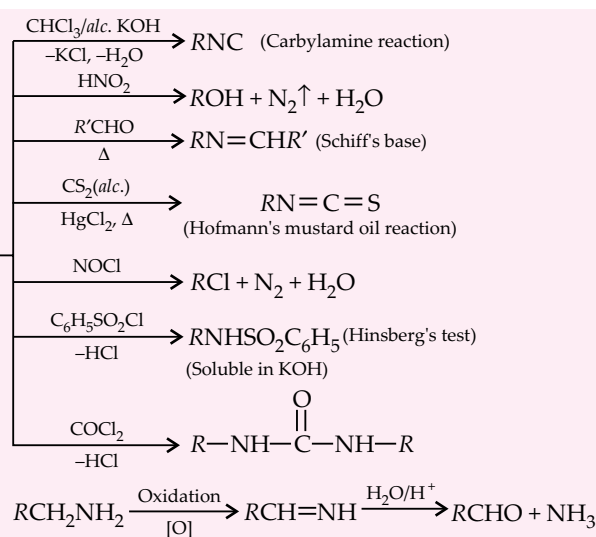
  - $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
  - $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

➢ Aniline is less basic than alkylamines due to the delocalization of lone pair of electrons of nitrogen atom over benzene ring. Moreover, the anilinium ion obtained by accepting a proton have only two resonating structures and is less stable than aniline.
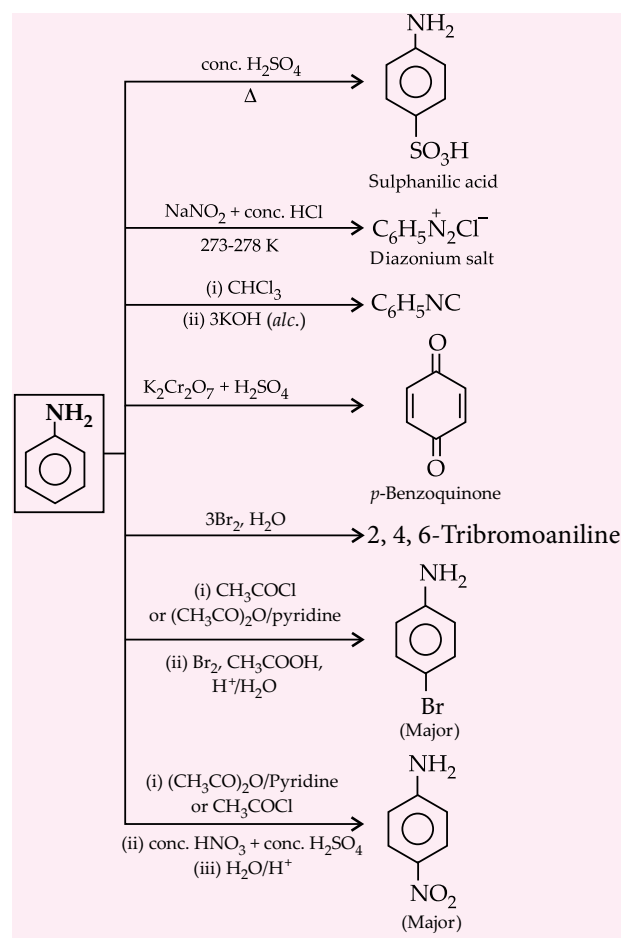
✎ **Chemical Reactions**

$$RNH_2 \xleftarrow{NaOH} R\overset{+}{N}H_3Cl^- \xleftarrow{HCl}$$

$$(R\overset{+}{N}R'_3)X^- \xleftarrow{R'X} RNR'_2 \xleftarrow[-HX]{R'X} RNHR' \xleftarrow[-HX]{R'X}$$
Quaternary salt

$$RNHCOC_6H_5 \xleftarrow[-HCl]{C_6H_5COCl}$$

$$RNHCOR' \xleftarrow[-HCl]{R'COCl}$$

$$RNHCOR' \xleftarrow[-R'COOH]{(R'CO)_2O}$$

$$H_2{\uparrow} + 2[RNH]^-Na^+ \xleftarrow{2Na}$$

$$RNX_2 \xleftarrow[NaOH]{X_2} RNHX \xleftarrow[NaOH]{X_2}$$

$$RNHMgX + R'H \xleftarrow{R'MgX}$$

$$\boxed{R{-}NH_2}$$

$$\xrightarrow[-KCl, -H_2O]{CHCl_3/alc.\ KOH} RNC \quad \text{(Carbylamine reaction)}$$

$$\xrightarrow{HNO_2} ROH + N_2{\uparrow} + H_2O$$

$$\xrightarrow[\Delta]{R'CHO} RN{=}CHR' \quad \text{(Schiff's base)}$$

$$\xrightarrow[HgCl_2, \Delta]{CS_2(alc.)} RN{=}C{=}S$$
(Hofmann's mustard oil reaction)

$$\xrightarrow{NOCl} RCl + N_2 + H_2O$$

$$\xrightarrow[-HCl]{C_6H_5SO_2Cl} RNHSO_2C_6H_5 \text{ (Hinsberg's test)}$$
(Soluble in KOH)

$$\xrightarrow[-HCl]{COCl_2} R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R$$

$$RCH_2NH_2 \xrightarrow[[O]]{\text{Oxidation}} RCH{=}NH \xrightarrow{H_2O/H^+} RCHO + NH_3$$

Distinction between 1°, 2° and 3° Amines

Test	Aliphatic			Aromatic
	1°	2°	3°	
Carbylamine test	Bad smelling carbylamine is formed.	No reaction	No reaction	Only aromatic primary amines give this test.
Mustard oil test	Alkyl isothiocyanate is formed.	No reaction	No reaction	Only aromatic primary amines give this test.
Hoffmann's test	Forms solid dialkyl oxamide.	Forms liquid dialkyl oxamic ester.	No reaction	
Hinsberg's test	Monoalkyl sulphonamide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No reaction	No reaction
Azo dye test	No reaction	No reaction	No reaction	Only primary aromatic amines give this test.

ANILINE

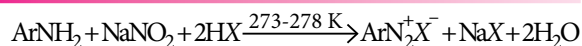↪ Aromatic amino compound in which the nitrogen atom of amino group is directly attached to aromatic ring.

CHEMICAL PROPERTIES

DIAZONIUM SALTS

↪ These have the general formula, $ArN_2^+X^-$, where Ar is abbriviated for the aryl group and X^- can be Cl^-, Br^-, HSO_4^-, NO_3^-, etc.
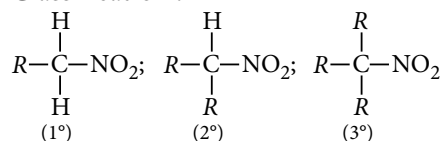
PREPARATION

$$ArNH_2 + NaNO_2 + 2HX \xrightarrow{273\text{-}278\ K} ArN_2^+X^- + NaX + 2H_2O$$

CHEMICAL PROPERTIES

D I A Z O N I U M S A L T S	
	Balz-Schiemann reaction $\xrightarrow[-HCl]{HBF_4} ArN_2^+BF_4^- \xrightarrow{\Delta} ArF + N_2 + BF_3$
	Gomberg Bachmann reaction $\xrightarrow[NaOH,\ \Delta]{C_6H_6} Ar-C_6H_5 + HCl + N_2\uparrow$ (Diphenyl)
	$\xrightarrow[\text{or } CH_3CH_2OH/\Delta]{H_3PO_2/Cu^+} ArH$
	Sandmeyer's reaction $\xrightarrow{CuBr/HBr} ArBr + N_2$
	Gattermann reaction $\xrightarrow{Cu/HBr} ArBr + N_2$
	Coupling reaction $\xrightarrow[pH = 9\text{-}10,\ 0\text{-}5°C]{C_6H_5OH/OH^-} ArN=NC_6H_4OH$
	Reduction $\xrightarrow[HCl]{SnCl_2} ArNH-NH_2$ Aryl hydrazine

NITRO COMPOUNDS

↪ **General formula :** RNO_2

↪ **Classification :**

$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-NO_2; \quad R-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-NO_2; \quad R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-NO_2$$

$(1°) \qquad\qquad (2°) \qquad\qquad (3°)$

SRM UNIVERSITY
(Under Section 3 of UGC Act 1956)

ONE ENTRANCE EXAMINATION
ONE COUNSELING

ONE COURSE
ONE FEE

ALL B.Tech PROGRAMMES
ALL CAMPUSES

SRMJEEE (UG) 2017

Online examination: 1st April to 30th April 2017

Aerospace Automobile Biomedical Biotechnology Chemical Civil CSE EEE ECE EIE Genetics IT Mech Mechatronics Nanotech Software

RANKED SRM AS No.1 Private Engineering University 2016

* No.1 Private Engineering University by Times Engineering, Times of India - i3 Research Consultant survey 2016 | 2015 | 2014

Academics

Choice-based Flexible Credit System (CFCS)
- Aggregation of credits through flexible ways
- Opportunity to enter Honours College
- Earn credits through MOOCs, Industry Modules, and International Competitions
- Choice of subjects, teacher and time of study
- Students are taught by Scientists of SRM Research Institute

National Level Facilities and Industry Partners
- UNESCO Bioethic India Nodal Center
- SRM DBT Platform for Advanced Life Science Technologies
- SRM-ZOLLER Professional Trainining Center for Tool Management Solutions
- Bosch Rexroth Hydraulic and Pneumatic Training Center

Center for Higher Order Thinking (CHOT)
e-Lab | e-Learn | e-Think

Center for Cultural and Language Studies (CCLS)
ELS English Language Center
Taiwan Education Center
European Language Center
Asia and Far East Language Center

Student Abroad and Transfer Program (SATP)

Semester Abroad
- Sponsored by SRM to study one semester abroad
- 500+ Students 13 Countries 25+ Universities such as MIT, CMU, CORNELL, HARVARD, UC Davis, Warwick, Kyushu University

Dual Degree

USA : University of Pittsburgh | Illinois Institute of Technology | Dayton | Virginia CW | Missouri State

UK : Warwick | Lancaster | Birmingham City

Australia : New South Wales | Royal Melbourne Institute of Technology (RMIT) | LaTrobe University

France : Polytechnic Tours

Germany : University of Applied Sciences Bochum

Twinning

USA : Carnegie Mellon University

UK : Lancaster University

MoUs 80+ with top ranked universities & Industries for exchanges & internships

---

Placement

- No. of companies - 244, No. of Offers - 6064
- International Offer:
  YKK, Japan (Highest pay ₹18 Lacs PA)
- Prime Offers - Amazon | CISCO | Deloitte | Verizon | Ericsson | Airbus | Alcatel | ABB | Fuji Xerox | Goldman Sachs | Honeywell | Vodafone | Schaffer | Siemens | Honda | Hyundai | Mahindra & Mahindra | INFOSYS | Wipro | Cognizant | TCS | Wabag | HP

Diversity of Students

Around 1500 students from 56 countries
Around 600 students are foreign nationals
Around 200 international students on study tours to SRM every year

Research Opportunities

More than ₹90 Crore worth of research projects for students to associate with
Journal publications: H-index of the institution stands at 46
SRMSAT fully designed by students and faculty

Ranking and Accreditation

Ranked in Indias top 30 by
Times Higher Education (THE), UK
Ranked Indias No. 1 by India Today (Factual) and Times of India

Accreditation of Kattankulathur Campus Programs

ABET — Computing Accreditation Commission
ABET — Engineering Accreditation Commission

B.Tech Programs Civil, Mech, EEE and ECE are accredited by Engineering Accreditation Commission and B.Tech IT Program by Computing Accreditation Commission of ABET, USA. http://www.abet.org

To Apply: Make e-payment or fill application online, download and courier with DD for ₹1060.

Scholarships: Founders Scholarship, Board Merit Scholarship

SRM UNIVERSITY AP — Amaravati —

SRM UNIVERSITY HARYANA Sonepat

SRM UNIVERSITY
Kattankulathur
Ramapuram
NCR, Delhi
Vadapalani

Online applications open from 18th November 2016 onwards

Please visit www.srmuniv.ac.in to know about courses offered, eligibility, fees, etc.
For any queries contact: +91-44-2745 5510, 4743 7500. Email: admissions.india@srmuniv.ac.in

Preparation

$$CH_3CH_2CH_3 \xrightarrow[673\,K]{HNO_3} CH_3CH_2CH_2NO_2 +$$

$$\overset{\displaystyle NO_2}{\underset{\displaystyle |}{CH_3CHCH_3}} + CH_3CH_2NO_2 + CH_3NO_2$$

$$RX + AgNO_2 \xrightarrow[(alc.)]{\Delta} RNO_2 + AgX$$

$$CH_2ClCOOH \xrightarrow[-NaCl]{NaNO_2} CH_2NO_2COOH$$

$$\xrightarrow{\Delta} CH_3NO_2 + CO_2$$

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{CH_3-C}}=CHNO_2 \xrightarrow[H^+ \text{or } OH^-]{HOH} \downarrow$$

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{CH_3-C}}=O + CH_3NO_2$$

$\boxed{R-NO_2}$

Chemical Properties

$$RNO_2 \xrightarrow[\text{ether}]{LiAlH_4} RNH_2$$

$$RNO_2 \xrightarrow[6[H]]{Sn/HCl} RNH_2 + 2H_2O$$

$$RCH_2NO_2 + H_2O \xrightarrow[\Delta]{H^+} RCOOH + NH_2OH$$

$$\underset{(1°)}{RCH_2NO_2} \xrightarrow[NaOH]{HNO_2} \overset{\displaystyle R-C=N\bar{O}\overset{+}{N}a}{\underset{\displaystyle NO_2}{|}}$$

(Red coloured sodium salt)

$$\underset{\underset{(2°)}{NO_2}}{\overset{|}{R_2CH}} + HNO_2 \xrightarrow[\Delta]{-H_2O} \underset{NO_2}{\overset{|}{R_2C-NO}} \xrightarrow[NaOH]{\text{Ether or}} \downarrow$$

Blue colour

$$\underset{(3°)}{R_3C-NO_2} \xrightarrow[NaOH]{HNO_2} \text{No reaction}$$

CYANIDES AND ISOCYANIDES

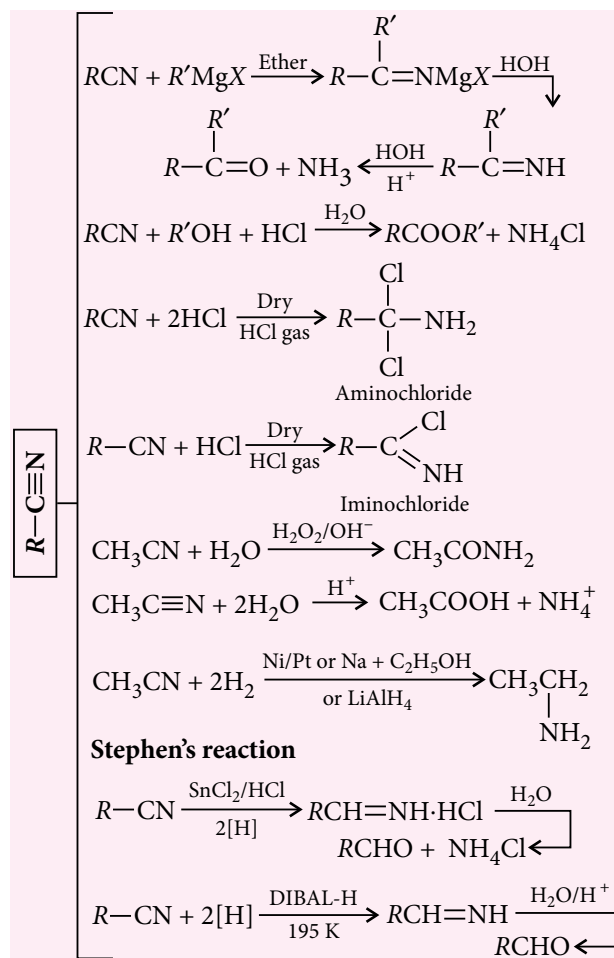↳ General Formula of cyanides is $R-C\equiv N$ or isocyanides is $R-N\rightleftharpoons C$.

↳ Cyanides are also called nitriles.
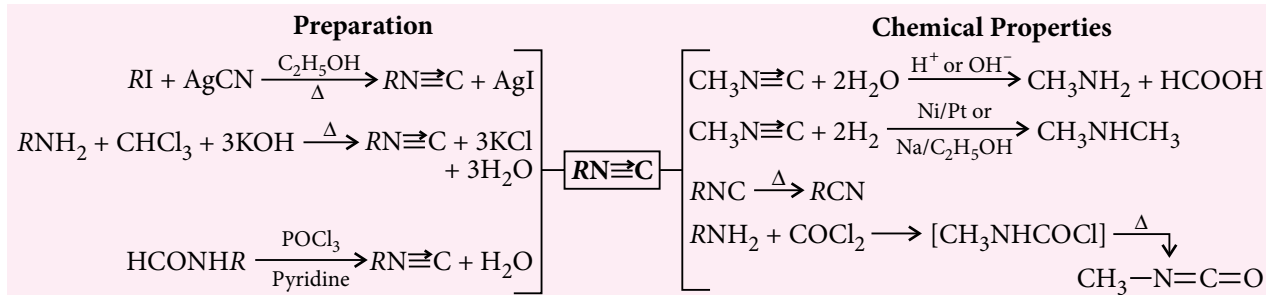Isocyanides are also called isonitriles or carbylamines.

PREPARATION OF CYANIDES

$\boxed{R-C\equiv N}$

$$RX + KCN \longrightarrow RCN + KX$$

$$RCONH_2 \xrightarrow[\Delta]{P_2O_5} RC\equiv N + H_2O$$

$$CH_3CH=NOH \xrightarrow[-H_2O]{P_2O_5} CH_3C\equiv N$$

$$RMgBr + Cl-CN \longrightarrow RCN + MgBrCl$$

$$RCH_2NH_2 \xrightarrow[773\,K]{Cu} RCN + 2H_2$$

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$

$$CH_3C\equiv N \xleftarrow[-H_2O]{Al_2O_3} CH_3CONH_2 \xleftarrow[773K, -H_2O]{Al_2O_3}$$

$$2CH_3CH_3 + 2NH_3 + 3O_2 \xrightarrow[773\text{-}873\,K]{\text{Catalyst}} \downarrow$$

$$2CH_3CN + 6H_2O$$
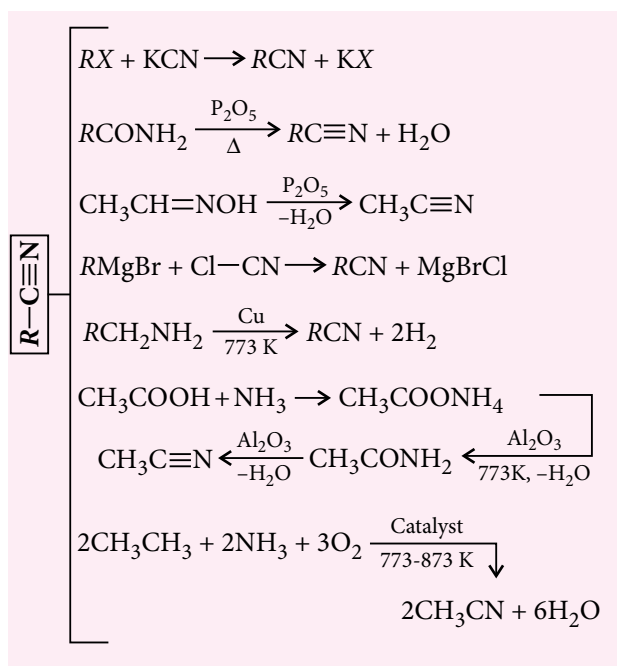
CHEMICAL PROPERTIES OF CYANIDES

$\boxed{R-C\equiv N}$

$$RCN + R'MgX \xrightarrow{\text{Ether}} \underset{R'}{\overset{\displaystyle R'}{R-C}}=NMgX \xrightarrow{HOH} \downarrow$$

$$\underset{R'}{\overset{|}{R-C}}=O + NH_3 \xleftarrow[H^+]{HOH} \underset{R'}{\overset{|}{R-C}}=NH$$

$$RCN + R'OH + HCl \xrightarrow{H_2O} RCOOR' + NH_4Cl$$

$$RCN + 2HCl \xrightarrow[\text{HCl gas}]{\text{Dry}} \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\overset{|}{R-C-NH_2}}}$$

Aminochloride

$$R-CN + HCl \xrightarrow[\text{HCl gas}]{\text{Dry}} R-C\!\!\overset{\textstyle Cl}{\underset{\textstyle NH}{\Big\backslash\!\!\!\Big/}}$$

Iminochloride

$$CH_3CN + H_2O \xrightarrow{H_2O_2/OH^-} CH_3CONH_2$$

$$CH_3C\equiv N + 2H_2O \xrightarrow{H^+} CH_3COOH + NH_4^+$$

$$CH_3CN + 2H_2 \xrightarrow[\text{or } LiAlH_4]{Ni/Pt \text{ or } Na + C_2H_5OH} \underset{NH_2}{\overset{|}{CH_3CH_2}}$$

Stephen's reaction

$$R-CN \xrightarrow[2[H]]{SnCl_2/HCl} RCH=NH\cdot HCl \xrightarrow{H_2O}$$

$$RCHO + NH_4Cl \longleftarrow$$

$$R-CN + 2[H] \xrightarrow[195\,K]{DIBAL-H} RCH=NH \xrightarrow{H_2O/H^+}$$

$$RCHO \longleftarrow$$

ISOCYANIDES

Preparation

$$RI + AgCN \xrightarrow[\Delta]{C_2H_5OH} RN{\equiv}C + AgI$$

$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RN{\equiv}C + 3KCl + 3H_2O$$

$$HCONHR \xrightarrow[\text{Pyridine}]{POCl_3} RN{\equiv}C + H_2O$$

$$RN{\equiv}C$$

Chemical Properties

$$CH_3N{\equiv}C + 2H_2O \xrightarrow{H^+ \text{ or } OH^-} CH_3NH_2 + HCOOH$$

$$CH_3N{\equiv}C + 2H_2 \xrightarrow[Na/C_2H_5OH]{Ni/Pt \text{ or}} CH_3NHCH_3$$

$$RNC \xrightarrow{\Delta} RCN$$

$$RNH_2 + COCl_2 \longrightarrow [CH_3NHCOCl] \xrightarrow{\Delta}$$
$$CH_3{-}N{=}C{=}O$$

iNFOSHOTS

Going against the grain : Nitrogen turns out to be hypersociable!

Nobody expected this. Computer simulations suggest that nitrogen, a very well-known element, with a reputation for being reluctant to react could, at a high enough pressure, break the chemical rules and become extremely gregarious : a single atom would then be able to form even six chemical bonds. This surprising discovery has been made by researchers at the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw and the New Technology Centre at the University of Warsaw (CeNT UW). Researchers analyzed thousands of crystal structures of nitrogen compounds with fluorine arising at high pressures, hoping to see some structures containing nitrogen pentafluoride NF_5 particles. They were completely unprepared for the fact that, in one of the crystal they ran into ions with the formula NF_6^- in which the nitrogen atom bonds with as many as six fluorine atoms. A reorganization takes place during which the molecular crystal, originally formed of a mixture of gases NF_3 and F_2, transforms into a complex ionic crystal constructed of NF_4^-, NF_2^+ and NF_6^- ions. The pressure required for the synthesis of crystals containing NF_6^- amounts to 400-500 thousand atmospheres which is within the reach of current experiment techniques.
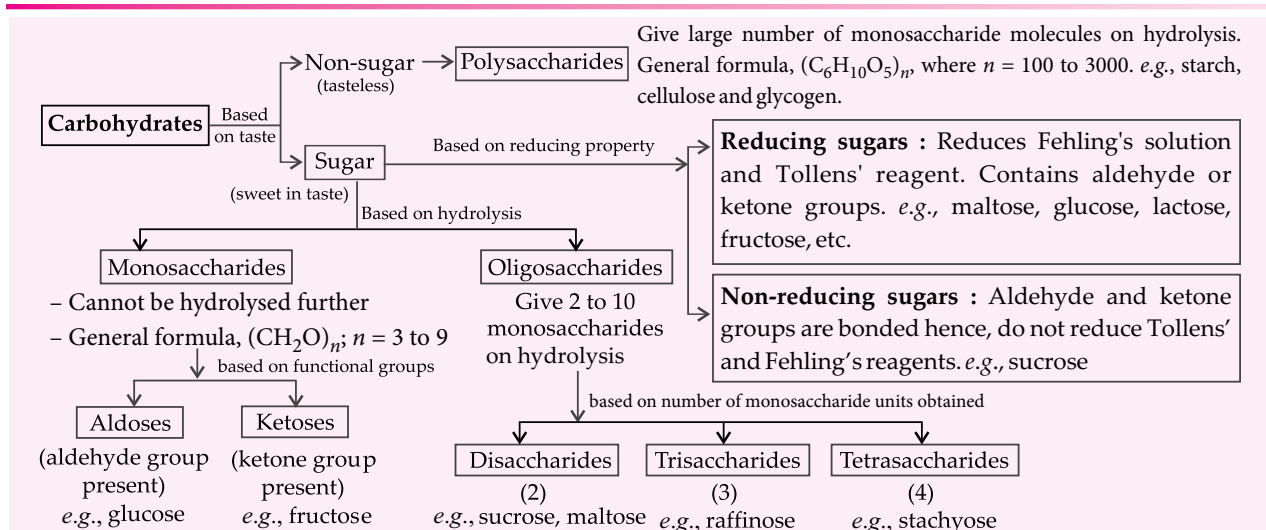
BIOMOLECULES

CARBOHYDRATES

⇨ These are polyhydroxy aldehydes or polyhydroxy ketones or compounds which yield such products on hydrolysis. These are also 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.
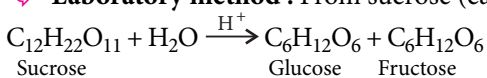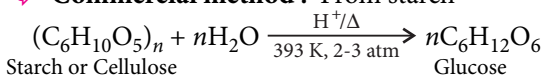
CLASSIFICATION

Give large number of monosaccharide molecules on hydrolysis. General formula, $(C_6H_{10}O_5)_n$, where n = 100 to 3000. *e.g.*, starch, cellulose and glycogen.

Reducing sugars : Reduces Fehling's solution and Tollens' reagent. Contains aldehyde or ketone groups. *e.g.*, maltose, glucose, lactose, fructose, etc.

Non-reducing sugars : Aldehyde and ketone groups are bonded hence, do not reduce Tollens' and Fehling's reagents. *e.g.*, sucrose

Carbohydrates — Based on taste
- Non-sugar (tasteless) → Polysaccharides
- Sugar (sweet in taste)

Based on reducing property

Based on hydrolysis

- Monosaccharides
  - Cannot be hydrolysed further
  - General formula, $(CH_2O)_n$; n = 3 to 9
  - based on functional groups
    - Aldoses (aldehyde group present) *e.g.*, glucose
    - Ketoses (ketone group present) *e.g.*, fructose

- Oligosaccharides
  - Give 2 to 10 monosaccharides on hydrolysis
  - based on number of monosaccharide units obtained
    - Disaccharides (2) *e.g.*, sucrose, maltose
    - Trisaccharides (3) *e.g.*, raffinose
    - Tetrasaccharides (4) *e.g.*, stachyose

MONOSACCHARIDES

Glucose ($C_6H_{12}O_6$), Aldohexose

Preparation

↳ **Laboratory method :** From sucrose (cane sugar)

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
Sucrose $\qquad\qquad$ Glucose $\quad$ Fructose

↳ **Commercial method :** From starch

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

Structure :

D-(+)-Glucose
Fischer projection

α-*D*-(+)-Glucopyranose $\quad$ β-*D*-(+)-Glucopyranose
Haworth structures
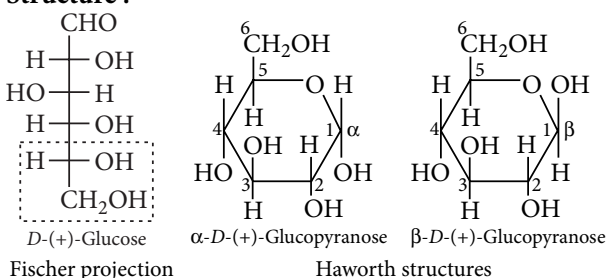
Evidences of open chain structure of glucose

↳ Glucose + HI $\xrightarrow[\text{Red P}]{\Delta}$ *n*-Hexane
confirms the presence of six carbon atoms linked in a straight chain.

↳ Glucose + $NH_2OH \longrightarrow$ Glucose oxime
confirms the presence of a carbonyl group.

↳ Glucose + HCN $\longrightarrow$ Glucose cyanohydrin
confirms the presence of a carbonyl group.

↳ Glucose + $[O]/Br_2$-water $\longrightarrow$ Gluconic acid
indicates aldehydic group.

↳ Glucose + $5(CH_3CO)_2O \longrightarrow$ Glucose pentaacetate
confirms the presence of five –OH groups.

↳ Glucose + HNO_3/oxidation $\longrightarrow$ Glucaric acid
indicates the presence of a primary alcoholic (–OH) group.

Physical Properties

↳ It is a colourless, crystalline solid, melts at 146°C and less sweet (three-fourth) than cane sugar.

↳ It is readily soluble in water, sparingly soluble in alcohol but insoluble in ether.

↳ It is optically active and the ordinary naturally occurring form is (+)-glucose or dextro form. It shows mutarotation.

Chemical Properties

Glucose

Due to –CHO group

Reduction

Na-Hg/H_2O or $NaBH_4$

CH$_2$OH
|
(CHOH)$_4$
|
CH$_2$OH
D-Sorbitol

Oxidation

Fehling's solution → $Cu_2O\downarrow$ + Gluconic acid
Red ppt.

Tollens' reagent Ag_2O → $2Ag\downarrow$ + Gluconic acid
Silver mirror

$5CH_3COCl$ / Pyridine →

CHO
|
(CHOCOCH$_3$)$_4$
|
CH$_2$OCOCH$_3$
Glucose pentaacetate
(a mixture of α and β)

Due to –OH group

CH_3OH / dry HCl gas →

α-*D*-Methylglucoside $\qquad$ β-*D*-Methylglucoside

$5PCl_5$ →

CHO
|
(CHCl)$_4$ + 5POCl$_3$ +5HCl
|
CH$_2$Cl
Pentachloroglucose
(Glucose pentachloride)

Mutarotation

↳ The change in specific rotation of an optically active compound with time to an equilibrium value is called *mutarotation*.

α-*D*-Glucose ⇌ Equilibrium mixture ⇌ β-*D*-Glucose
$[\alpha]_D = +112°$ $\qquad$ $[\alpha]_D = +52.7°$ $\qquad$ $[\alpha]_D = +19°$

Fructose ($C_6H_{12}O_6$), Ketohexose

Preparation

↳ **From sucrose (cane sugar)**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\Delta]{\text{dil. } H_2SO_4} C_6H_{12}O_6 +$$
Cane sugar   *D*-Glucose
(Dextrorotatory)   (Dextrorotatory)

$$C_6H_{12}O_6$$
D-Fructose
(Laevorotatory)
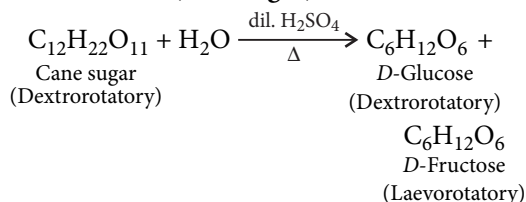
The solution containing equimolar mixture of *D*-(+)-glucose and *D*-(−)-fructose is called *invert sugar* and the process is known as *inversion*.
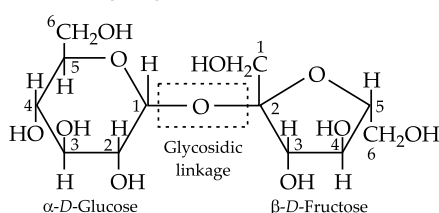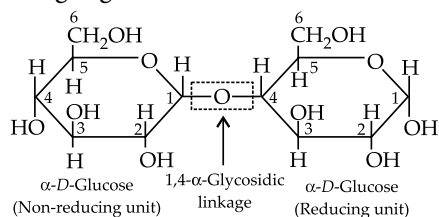
↳ **From inulin**

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{dil. } H_2SO_4} nC_6H_{12}O_6$$
Inulin   Fructose

Structure
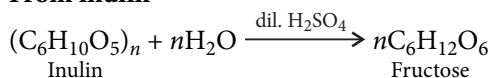
D-(−)-Fructose   α-*D*-(−)-Fructofuranose
Fischer structure   Haworth structure
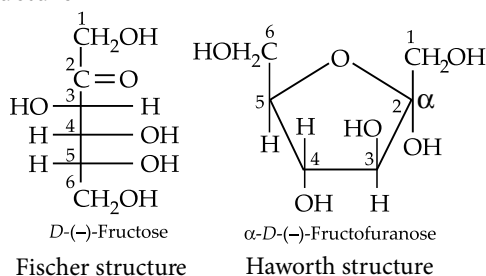
DISACCHARIDES

↳ **Sucrose ($C_{12}H_{22}O_{11}$)**

➢ Cane sugar and Dextrorotatory
➢ Non-reducing sugar

α-*D*-Glucose   β-*D*-Fructose

↳ **Maltose ($C_{12}H_{22}O_{11}$)**

➢ Malt sugar and Dextrorotatory
➢ Reducing sugar

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

↳ **Lactose ($C_{12}H_{22}O_{11}$)**

➢ Milk sugar and epimeric in nature
➢ Reducing sugar

β-*D*-Galactose   β-*D*-Glucose
(Non-reducing unit)   (Reducing unit)
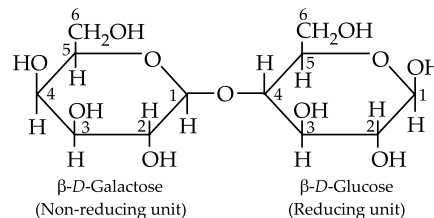
POLYSACCHARIDES

↳ **Starch :** It is a polymer of α-*D*-glucose units and consists of two components : amylose and amylopectin.

➢ **Amylose**
  – It is a long unbranched chain with 200-1000 α-*D*-(+)-glucose units held by 1,4-α-glycosidic linkage.
  – Water soluble
  – It constitutes about 15-20% of starch.
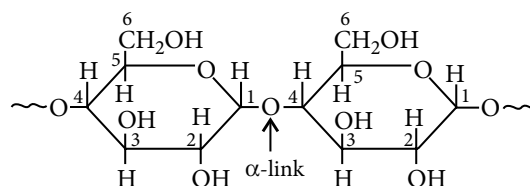
➢ **Amylopectin**
  – It is a branched chain polymer of α-*D*-glucose units in which chain is formed by 1,4-α-glycosidic linkage whereas branching occurs by 1,6-α-glycosidic linkage.
  – Insoluble in water
  – It constitutes 80-85% of starch.
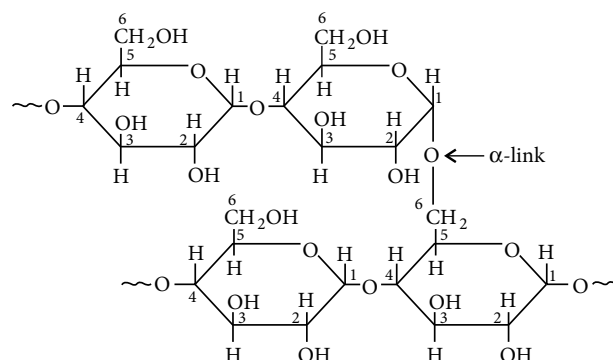
- **Cellulose $(C_6H_{10}O_5)_n$:** It is a straight chain polysaccharide composed only of β-D-glucose units joined together by 1,4-β-glycosidic linkages between C-1 of one glucose and C-4 of the next glucose unit.
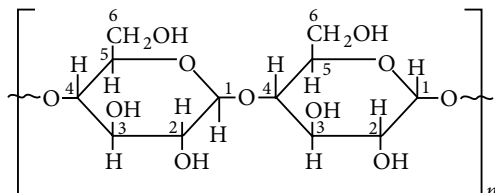
- **Glycogen $(C_6H_{10}O_5)_n$:** It is stored in liver and muscles and has a similar structure to that of amylopectin and consists of long chains of glucose units.

PROTEINS

- Proteins are fundamental basis of structure and functions of life. They are high molecular mass complex biopolymers of α-amino acids. They occur naturally in milk, cheese, pulses, peanuts, fish, meat, etc.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha\text{-Amino acids}$$
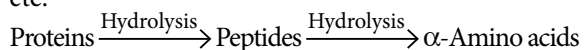
AMINO ACIDS

- Amino acids are the bifunctional molecules with both acidic carboxyl group (– COOH) and basic amino group (– NH$_2$).
- Amino acids can be further divided into three categories :
  - ➤ **Acidic :** No. of –COOH groups > No. of –NH$_2$ groups
  - ➤ **Basic :** No. of –COOH groups < No. of –NH$_2$ groups
  - ➤ **Neutral :** No. of –COOH groups = No. of –NH$_2$ groups

CLASSIFICATION OF PROTEINS

On the basis of molecular structure :

- **Globular proteins :** Globular proteins results when the polypeptide chains coil around itself to give three dimensional spherical shape. These are soluble in water, *e.g.*, insulin and albumins.
- **Fibrous proteins :** In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin and myosin.

- **Isoelectric point :** The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, +ve and –ve charges are equal and it does not migrate to either electrode, is called isoelectric point. The amino acids have least solubility in water at isoelectric point which helps in their separation.

STRUCTURE OF PROTEINS

- **Primary structure :** It refers to the number and linear sequence of amino acids held together by peptide bonds.
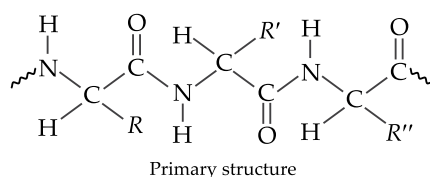
Primary structure

- **Secondary structure :** It is due to the folding or coiling of the peptide chain.
  It is mainly of two types :
  - ➤ **α-helix :** These coils are stabilised by intramolecular hydrogen bonds between carbonyl oxygen of first amino acid to amide hydrogen of fourth amino acid.
  - ➤ **β-pleated sheet :** β-pleated sheet structure is formed when hydrogen bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains. The bonding in β-pleated sheet structure is intermolecular H-bonding. The structure is not planar but is slightly pleated. Silk fibroin has β-pleated structure.
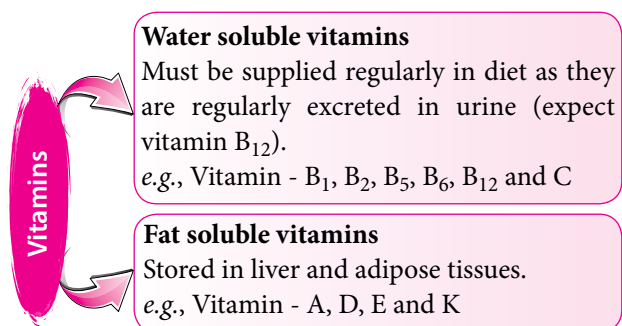

α-helix
e.g., myosin (nucleus), keratin (hair), etc.

β-pleated sheet
e.g., silk protein (fibroin)

Individual polypeptide chains
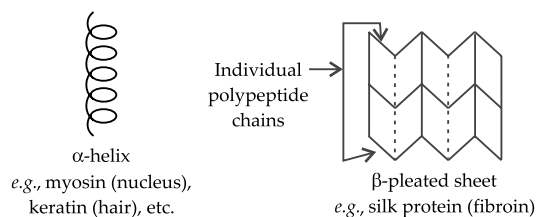
- **Tertiary structure :** It represents overall folding of the polypeptide chains, *i.e.*, further folding of the secondary structure and the bonds responsible for such interaction are hydrophobic interactions, hydrogen bonds, ionic interactions, van der Waals' forces and disulphide bonds.

⮆ **Quaternary structure :** The spatial arrangement of the subunits (two or more polypeptide chains) with respect to each other.

VITAMINS

⮆ These are the complex organic molecules which cannot be produced by the body and must be supplied in small amounts in diet to carry out essential metabolic reactions and biological functions which are required for normal growth and maintenance of the body.

CLASSIFICATION

Vitamins

Water soluble vitamins
Must be supplied regularly in diet as they are regularly excreted in urine (expect vitamin B_{12}).
e.g., Vitamin - B_1, B_2, B_5, B_6, B_{12} and C

Fat soluble vitamins
Stored in liver and adipose tissues.
e.g., Vitamin - A, D, E and K

NUCLEIC ACIDS

⮆ 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 (Sugar + base + phosphoric acid)		
DNA	**Components**	**RNA**
2-Deoxy-D-(–)-ribose	Sugar	*D*-(–)-ribose
Cytosine and thymine	Pyrimidine base	Uracil and cytosine
Adenine and guanine	Purine base	Adenine and guanine
H_3PO_4	Phosphoric acid	H_3PO_4
Double stranded α-helix	Structure	Single stranded α-helix
Possible	Replication	Not possible

ENZYMES

⮆ The enzymes are biocatalysts produced by living cells which catalyse biochemical reactions in living organisms. Chemically, they are naturally occurring simple or conjugated proteins.

⮆ **Importance**
➤ They play a vital role in living organisms as they catalyse many biological processes.
➤ Enzyme deficiency causes diseases *e.g.*, the deficiency of phenylalanine hydroxylase enzyme causes phenylketone urea (PKU) and the deficiency of tyrosinase causes albinism.
➤ They are used for the production of beer, wine, syrup and cheese, etc.

HORMONES

⮆ A hormone may be defined as a specific organic product of an endocrine gland secreted into the blood which carries it to some part of the body (target organ) where it regulates a definite physical effect. These are the molecules that act as intercellular messengers and are poured directly in the blood stream by endocrine glands.

CLASSIFICATION

Hormones

Amines
e.g., epinephrine, thyroxine

Peptides
e.g., oxytocin, vasopressin

Proteins
e.g., insulin, glucagon

Steroids
e.g., sex hormones

Female sex hormones
e.g., oestrogens, progesterone

Male sex hormones
e.g., androgens
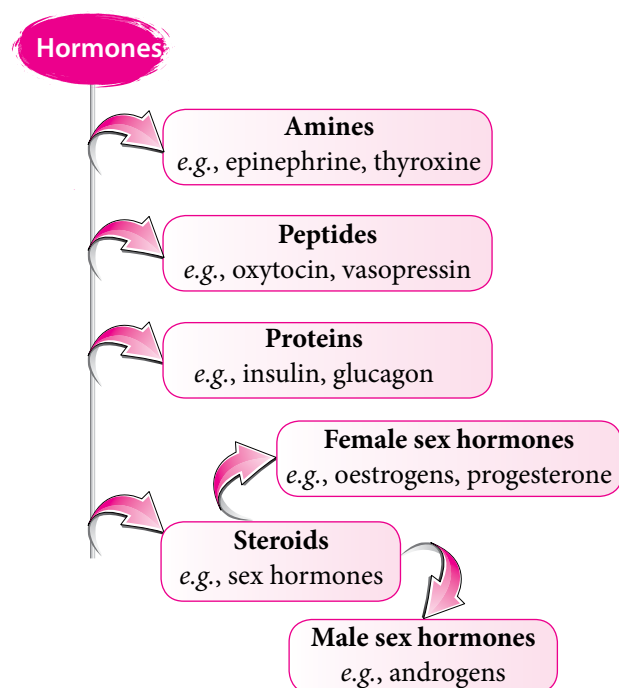
SPEED PRACTICE

1. Which of the following statements is true regarding the basicity of the two amines?

   CH_2NH_2 (I) CH_2NH_2 (II)
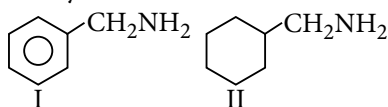
   (a) Both are equally basic because both are 1° amines.
   (b) I > II because it is an aromatic amine.
   (c) II > I because it is an aliphatic amine.
   (d) I < II because of difference in the nature of β-carbon.

2. When an aqueous solution of D-glucose is treated with a base, it is converted into D-fructose and D-mannose, this conversion (isomerisation) involves
   (a) enolisation
   (b) tautomerisation.
   (c) both (a) and (b)
   (d) none of these.

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

   NH₂
   (i) Acetic anhydride/pyridine
   (ii) KBrO₃/HBr
   (iii) H₃O⁺, heat
   (iv) NaNO₂/HCl, 273 – 278 K
   (v) Cu/HBr

   (a) [Br, Br benzene]   (b) [Br, Br benzene]
   (c) [Br, Br, Br benzene]   (d) [Br, Br, Br, Br benzene]
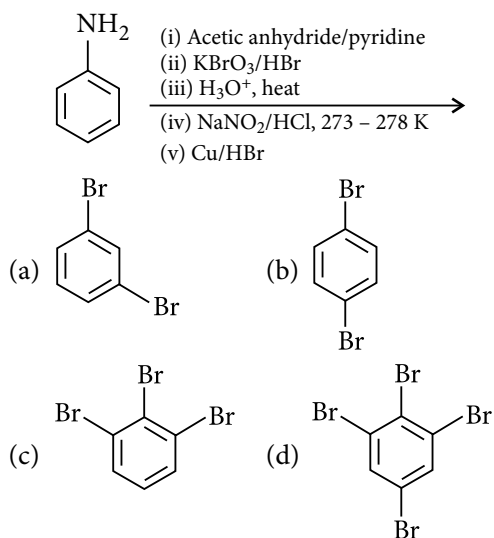
   (JEE Advanced 2016)

4. The pair in which both the species have iron is
   (a) nitrogenase, cytochromes
   (b) carboxypeptidase, haemoglobin
   (c) haemocyanin, nitrogenase
   (d) haemoglobin, cytochromes.

5. Which of the following statements is incorrect?
   (a) Aniline is more acidic than ammonia.
   (b) $F-\langle\rangle-\overset{+}{N}H_3$ is less acidic than $\langle\rangle-\overset{+}{N}H_3$
   (c) Amines are less acidic than alcohols of comparable molecular masses.
   (d) $RCONH_2$ is more acidic than RCH_2NH_2

6. Chagaff's rule states that in an organism
   (a) amount of adenine (A) is equal to that of thymine (T) and amount of guanine (G) is equal to that of cytosine (C).
   (b) amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C).
   (c) amount of adenine (A) is equal to that of cytosine (C) and the amount of the thymine (T) is equal to that of guanine (G).
   (d) amounts of all bases are equal.

7. Consider the following sequence for aspartic acid :

   $$H_3\overset{+}{N}-\overset{CO_2H}{\underset{CH_2CO_2H}{|}}-H \underset{1.88}{\overset{pK_1}{\rightleftharpoons}} H_3\overset{+}{N}-\overset{CO_2^-}{\underset{CH_2CO_2H}{|}}-H \underset{3.65}{\overset{pK_R}{\rightleftharpoons}}$$

   $$H_3\overset{+}{N}-\overset{CO_2^-}{\underset{CH_2CO_2^-}{|}}-H \underset{9.66}{\overset{pK_2}{\rightleftharpoons}} H_2N-\overset{CO_2^-}{\underset{CH_2CO_2^-}{|}}-H$$
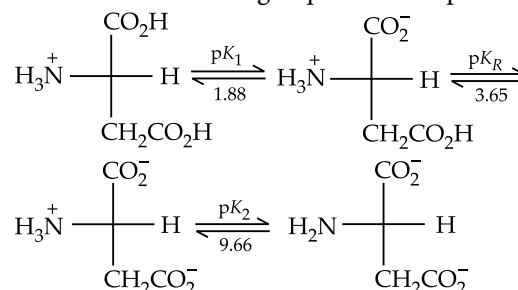
   The pI (isoelectric point) of aspartic acid is
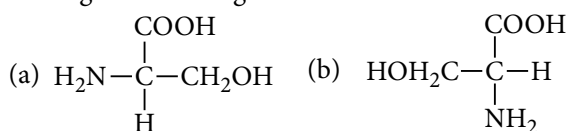   (a) 3.65   (b) 2.77
   (c) 5.74   (d) 1.88

   (JEE Main 2016 online)

8. In a reaction of aniline a coloured compound 'C' was obtained. The structure of 'C' would be

 $\langle\rangle-NH_2 \xrightarrow[HCl, 0-5°C]{NaNO_2} B \xrightarrow{\langle\rangle-N\langle{}^{CH_3}_{CH_3}} C$

   (a) $\langle\rangle-NH-NH-\langle\rangle-N\langle{}^{CH_3}_{CH_3}$
   (b) $\langle\rangle-N=N-\langle\rangle-N\langle{}^{CH_3}_{CH_3}$

(c)

(d)
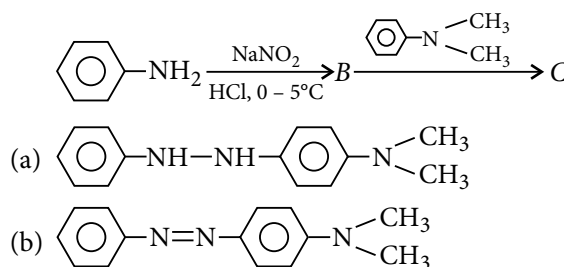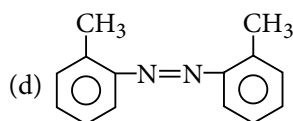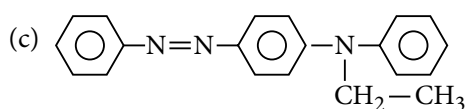
9. Among the following *L*-serine is

(a) $H_2N-\underset{\underset{H}{|}}{\overset{\overset{COOH}{|}}{C}}-CH_2OH$

(b) $HOH_2C-\underset{\underset{NH_2}{|}}{\overset{\overset{COOH}{|}}{C}}-H$

(c) $H-\underset{\underset{CH_2OH}{|}}{\overset{\overset{NH_2}{|}}{C}}-COOH$

(d) $H_2N-\underset{\underset{COOH}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-H$
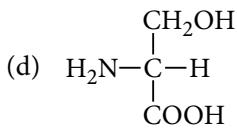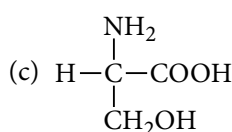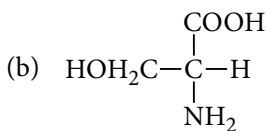
10. An organic compound '*A*' having molecular formula C_2H_3N on reduction gave another compound '*B*'. Upon treatment with nitrous acid, '*B*' gave ethyl alcohol. On warming with chloroform and alcoholic KOH, it formed an offensive smelling compound '*C*'. The compound '*C*' is
(a) $CH_3CH_2NH_2$ (b) $CH_3CH_2N{\rightleftharpoons}C$
(c) $CH_3C{\equiv}N$ (d) CH_3CH_2OH

11. The correct set of stereochemical relationship amongst the following monosaccharides is

I   II

III   IV
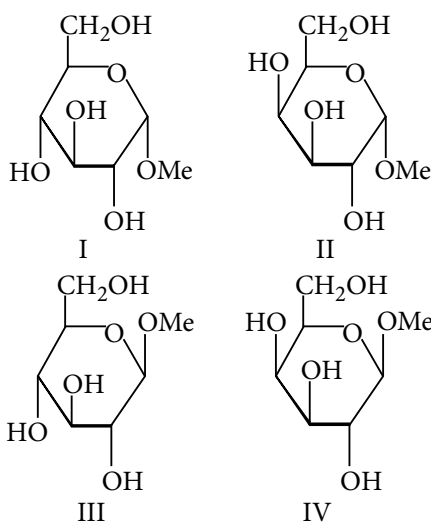
(a) (I) and (II) are anomers; (III) and (IV) are epimers.
(b) (I) and (II) are epimers ; (III) and (IV) are anomers.
(c) (I) and (III) are anomers; (I) and (II) are epimers.
(d) (I) and (III) are epimers; (II) and (IV) are anomers.

12. A given nitrogen containing aromatic compound '*A*' reacts with Sn/HCl, followed by HNO_2 to give an unstable compound '*B*'. '*B*', on treatment with phenol, forms a beautiful coloured compound '*C*' with the molecular formula, $C_{12}H_{10}N_2O$. The structure of compound '*A*' is

(a)
(b)
(c)
(d)
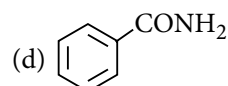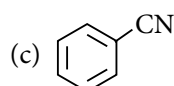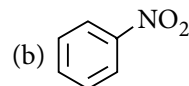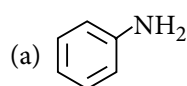
(**NEET Phase-II 2016**)

13. Which of the following statements about "Denaturation" of proteins are correct?
(i) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
(ii) Denaturation leads to the conversion of double strands of DNA into single strand.
(iii) Denaturation affects primary structure which gets distorted.
(a) (i) and (iii)   (b) (ii) and (iii)
(c) (i) and (ii)   (d) (i), (ii) and (iii)

14. The correct order of basicities of the following compounds is

$$CH_3-C{\underset{NH_2}{\overset{NH}{\diagup}}}$$
1

$$CH_3-CH_2-NH_2$$
2

$$(CH_3)_2NH$$
3

$$CH_3-\underset{}{\overset{\overset{O}{\|}}{C}}-NH_2$$
4

(a) 2 > 1 > 3 > 4   (b) 1 > 3 > 2 > 4
(c) 3 > 1 > 2 > 4   (d) 1 > 2 > 3 > 4
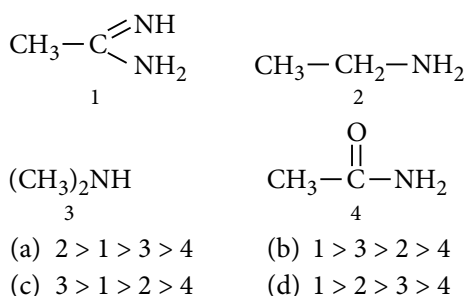
15. An electric current is passed through an aqueous solution (buffered at pH = 6.0) of alanine (pI = 6.0) and arginine (pI = 10.2). The two amino acids can be separated because
(a) alanine migrates to anode, and arginine to cathode.
(b) alanine migrates to cathode, and arginine to anode.
(c) alanine does not migrate, while arginine migrates to cathode.
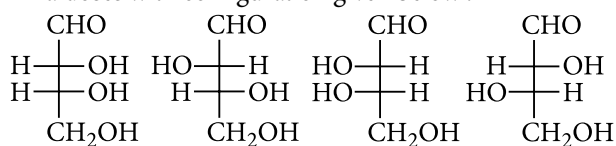(d) alanine does not migrate, while arginine migrates to anode.

16.

$$\underset{\text{(cyclohexanone)}}{\text{O}} \xrightarrow[\text{C}_2\text{H}_5\text{O}^-]{\text{CH}_3\text{NO}_2} [A] \longrightarrow [B] \xrightarrow[\text{H}^+]{\text{HONO}} \underset{\text{(cycloheptanone)}}{\text{O}}$$
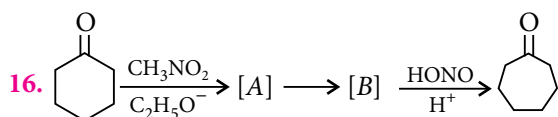
Which reaction is involved in the above conversion?
(a) Diazotisation and Beckmann rearrangement
(b) Diazotisation and Reimer–Tiemann reaction
(c) Aldol condensation and diazotisation
(d) Diazotisation and pinacol type of rearrangement.

17. Which one of the following statements is not true regarding (+)-lactose?
(a) (+)-Lactose, $C_{12}H_{22}O_{11}$ contains 8 —OH groups.
(b) On hydrolysis (+)-lactose gives equal amount of $D(+)$-glucose and $D(+)$-galactose.
(c) (+)-Lactose is a β-glycoside formed by the union of a molecule of $D(+)$-glucose and a molecule of $D(+)$-galactose.
(d) (+)-Lactose is a reducing sugar and does not exhibit mutarotation.

18. The correct corresponding order of names of four aldoses with configuration given below :

```
   CHO          CHO          CHO          CHO
H──OH      HO──H       HO──H       H──OH
H──OH      H──OH       HO──H       HO──H
  CH₂OH        CH₂OH        CH₂OH        CH₂OH
```

respectively, is
(a) L-erythrose, L-threose, L-erythrose, D-threose
(b) D-threose, D-erythrose, L-threose, L-erythrose
(c) L-erythrose, L-threose, D-erythrose, D-threose
(d) D-erythrose, D-threose, L-erythrose, L-threose.

(NEET Phase-II 2016)

19. An optically active amine (X) with molecular formula $C_5H_{13}N$ on treatment with aqueous $NaNO_2$/HCl gives a tertiary alcohol (Y) with evolution of N_2 gas. The compounds (X) and (Y) respectively are :
(a) 2-methylbutanamine, 2-methylbutan-1-ol
(b) 2-methylbutanamine, 2-methylbutan-2-ol
(c) 2-methylbutanamine, 3-methylbutan-2-ol
(d) neopentylamine, neopentyl alcohol

20. Which statement is incorrect about peptide bond?
(a) C—N bond length in proteins is longer than usual bond length of C—N bond.
(b) Spectroscopic analysis shows planar structure of $-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{NH}-$ bond.

(c) C—N bond length in proteins is shorter than usual bond length of C—N bond.
(d) None of these.

21. In the following sequence of reactions, what is D?

$$\underset{\text{CH}_3}{\bigcirc\!\!\text{I}} \xrightarrow{[O]} A \xrightarrow{SOCl_2} B \xrightarrow{NaN_3} C \xrightarrow{\text{Heat}} D$$
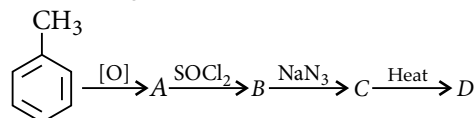
(a) Primary amine
(b) An amide
(c) Phenyl isocyanate
(d) Open chain hydrocarbon

22. Optical rotation of a freshly prepared solution of α-D-glucopyranose is +111° while that of β-D-glucopyranose is +19.2°. In solution, an equilibrium mixture of these two anomers is 52.5°. The percentage of α-form in the equilibrium mixture is
(a) 36%   (b) 64%
(c) 52.5%   (d) 19.2%

23. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are
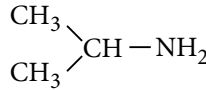(a) one mole of NaOH and one mole of Br_2
(b) four moles of NaOH and two moles of Br_2
(c) two moles of NaOH and two moles of Br_2
(d) four moles of NaOH and one mole of Br_2.
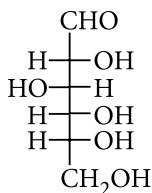
(JEE Main 2016 offline)

24. Which of the vitamins A, B, C, D, E, K are water soluble?
(a) Vitamin-A, B, C   (b) Vitamin-B complex, C
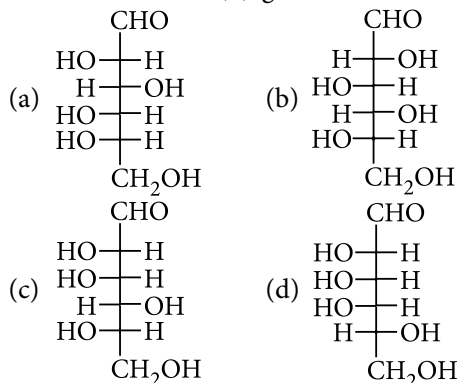(c) Vitamin-D, E   (d) Vitamin-A, D, E, K

25. An organic compound C_3H_9N(A) when treated with nitrous acid gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (B) which on reduction gave isopropyl methyl amine. Predict the structure of (A).
(a) $CH_3-CH_2-CH_2-NH_2$
(b) $\underset{CH_3}{\overset{CH_3}{>}}CH-NH_2$
(c) $CH_3-CH_2-NH-CH_3$
(d) $CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$

26. The structure of *D*-(+)-glucose is

$$
\begin{array}{c}
\text{CHO} \\
\text{H}\!-\!\text{OH} \\
\text{HO}\!-\!\text{H} \\
\text{H}\!-\!\text{OH} \\
\text{H}\!-\!\text{OH} \\
\text{CH}_2\text{OH}
\end{array}
$$

The structure of *L*-(–)-glucose is

(a)
$$
\begin{array}{c}
\text{CHO} \\
\text{HO}\!-\!\text{H} \\
\text{H}\!-\!\text{OH} \\
\text{HO}\!-\!\text{H} \\
\text{HO}\!-\!\text{H} \\
\text{CH}_2\text{OH}
\end{array}
$$

(b)
$$
\begin{array}{c}
\text{CHO} \\
\text{H}\!-\!\text{OH} \\
\text{HO}\!-\!\text{H} \\
\text{H}\!-\!\text{OH} \\
\text{HO}\!-\!\text{H} \\
\text{CH}_2\text{OH}
\end{array}
$$

(c)
$$
\begin{array}{c}
\text{CHO} \\
\text{HO}\!-\!\text{H} \\
\text{HO}\!-\!\text{H} \\
\text{H}\!-\!\text{OH} \\
\text{HO}\!-\!\text{H} \\
\text{CH}_2\text{OH}
\end{array}
$$

(d)
$$
\begin{array}{c}
\text{CHO} \\
\text{HO}\!-\!\text{H} \\
\text{HO}\!-\!\text{H} \\
\text{HO}\!-\!\text{H} \\
\text{H}\!-\!\text{OH} \\
\text{CH}_2\text{OH}
\end{array}
$$

(JEE Advanced 2015)

27.

$$\text{(cyclohexyl ethyl ketone)} \xrightarrow{\text{NH}_2\text{OH}} [\ ] \xrightarrow[\text{heat}]{\text{conc. H}_2\text{SO}_4} [\ ] \xrightarrow{\text{H}^+} [Z]; Z \text{ is}$$
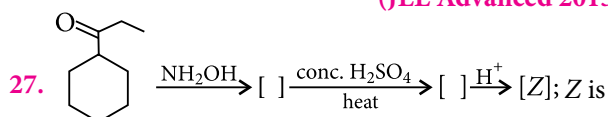
(a) a single compound
(b) a mixture of two compounds
(c) a mixture of three compounds
(d) a mixture of four compounds.

28. Structure of disaccharide formed by glucose and fructose is given below:
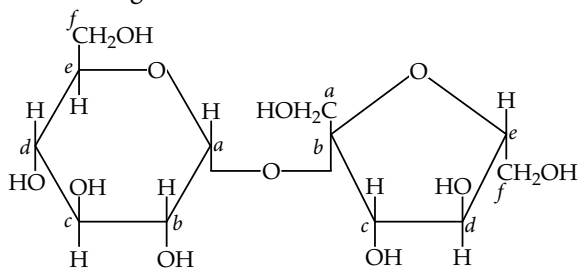
Identify anomeric carbon atoms in monosaccharide units.
(a) '*a*' carbon of glucose and '*a*' carbon of fructose
(b) '*a*' carbon of glucose and '*e*' carbon of fructose
(c) '*a*' carbon of glucose and '*b*' carbon of fructose
(d) '*f*' carbon of glucose and '*f*' carbon of fructose.

29. The correct statement regarding the basicity of arylamines is
(a) aryl amines are generally more basic than alkyl amines because of aryl group.
(b) aryl amines are generally more basic than alkyl amines, because the nitrogen atom in aryl amines is *sp*-hybridised.

(c) aryl amines are generally less basic than alkyl amines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π-electron system.
(d) aryl amines are generally more basic than alkyl amines because the nitrogen lone-pair electrons are not delocalised by interaction with the aromatic ring π-electron system.

(NEET Phase-I 2016)

30. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH₂-group in the carbon chain, the reagent used as source of nitrogen is
(a) sodium amide, $NaNH_2$
(b) sodium azide, NaN_3
(c) potassium cyanide, KCN
(d) potassium phthalimide $C_6H_4(CO)_2N^-K^+$.

SOLUTIONS

1. (d): Here the two amines differ in the nature of β-carbon atom.
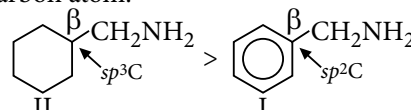
sp^3-hybridised carbon atom is more basic than sp^2-hybridised carbon atom. Hence, II > I.

2. (c): When an aqueous solution of *D*-glucose, *D*-mannose or *D*-fructose is treated with a base, it undergoes enolisation and a series of keto-enol tautomerisation to form a mixture of the three monosaccharides (*Lobry de Bruyn-van Ekenstein transformation*).
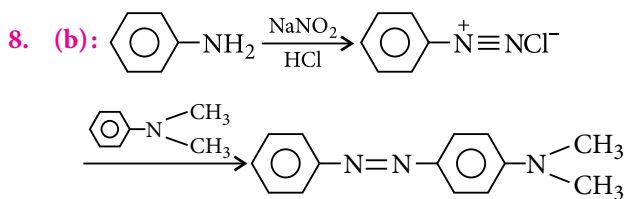
3. (b):
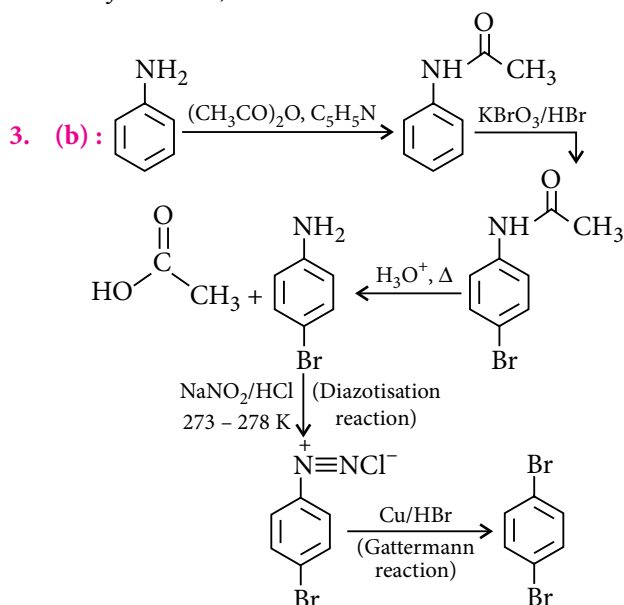
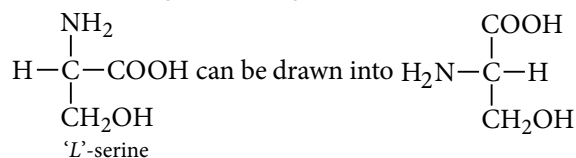4. **(d):** Both haemoglobin and cytochrome contain iron.

5. **(b):** Due to $-I$-effect of F, electron density in the N—H bond decreases and hence release of a proton becomes easier from p-fluoroanilinium ion than that from anilinium ion. All other statements are correct.

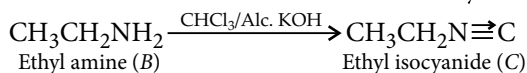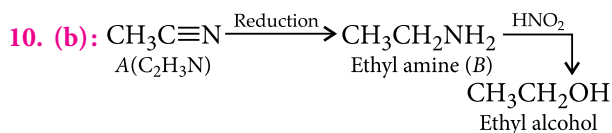6. **(a):** Amount (in moles) of $A = T$ and that of $G = C$.

7. **(b):** $pI = \dfrac{pK_1 + pK_R}{2} = \dfrac{1.88 + 3.65}{2} = \dfrac{5.53}{2}$

$$= 2.765 \approx 2.77$$

8. **(b):**

9. **(c):** According to exchange rule

Keeping —CH$_2$OH at base and rotating other three groups to bring COOH at the top.

10. **(b):**

$$\underset{A(C_2H_3N)}{CH_3C\equiv N} \xrightarrow{Reduction} \underset{\text{Ethyl amine }(B)}{CH_3CH_2NH_2} \xrightarrow{HNO_2}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\underset{\text{Ethyl amine }(B)}{CH_3CH_2NH_2} \xrightarrow{CHCl_3/Alc.\ KOH} \underset{\text{Ethyl isocyanide }(C)}{CH_3CH_2N\overset{\equiv}{=}C}$$

11. **(c):** (I) and (III) differ in configuration at C$_1$ and hence are anomers while (I) and (II) differ in configuration at C$_4$ and hence are epimers.

12. **(b):**
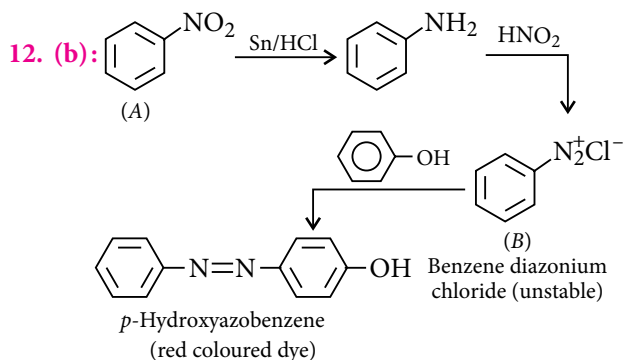
13. **(c):** Statements (i) and (ii) are correct.

14. **(b):**
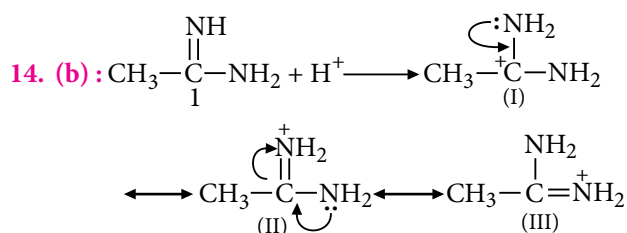
The conjugate acid (I) obtained by addition of a proton to (1) is stabilised by two equivalent resonating structures and hence, compound (1) is the most basic. Further 2° amines are more basic than 1° amines while amides are least basic due to delocalisation of lone pair of electrons of N over the C=O group. Thus, the order : 1 > 3 > 2 > 4

15. **(c):** At the given pH (6) of the solution, alanine (pI = 6.0), exists as a dipolar ion while arginine (pI = 10.2) exists as a cation. Hence on passing an electric current, alanine will not migrate to any electrode, while arginine will migrate to cathode.

16. **(d):**
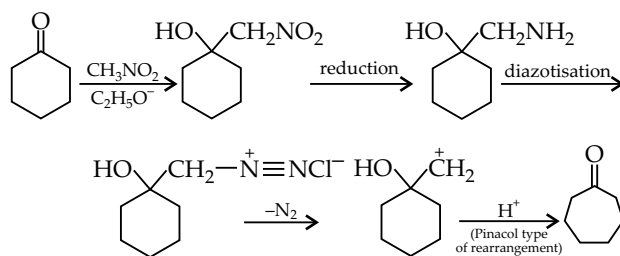
17. **(d):** (+)-Lactose is a reducing sugar and shows mutarotation.

18. **(d):**
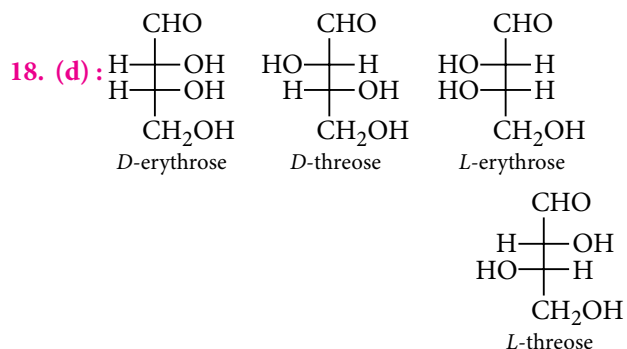
19. **(b):** Since, C$_5$H$_{13}$N on treatment with NaNO$_2$/HCl gives an alcohol, therefore, it must be a 1° amine. Since the amine is optically active, the —NH$_2$ group cannot be directly attached to the chiral centre because it will rapidly undergo recemisation due to nitrogen inversion. Therefore, the carbon skeleton must contain a chiral centre.
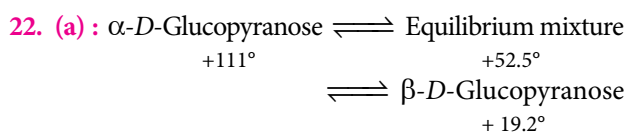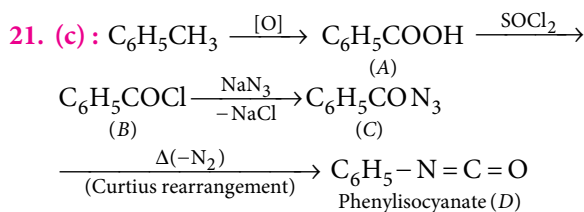
In other words, the amine is 2-methylbutanamine and the 3° alcohol must be 2-methylbutan-2-ol.

$$CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\text{2-Methylbutanamine}}{C^*H}}-CH_2NH_2 \xrightarrow[-N_2]{HNO_2} CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{H}{\overset{+}{C}}}-\overset{+}{C}H_2$$

$$\longrightarrow CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{}{\overset{+}{C}}}-CH_3 \xrightarrow[-H^+]{+H_2O} CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\text{2-Methylbutan-2-ol}}{OH}}{C}}-CH_3$$
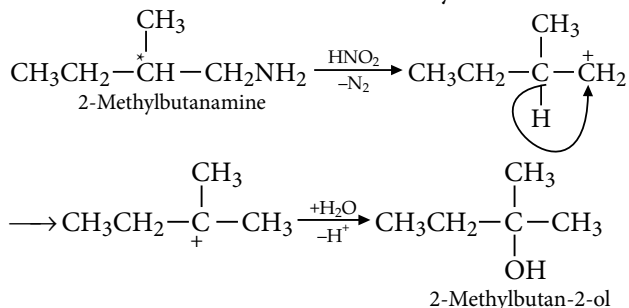
20. (a) : Due to resonance, C—N bond acquires some double bond character.

$$-\overset{\overset{\displaystyle \ddot{O}:}{||}}{C}-\ddot{N}H- \longleftrightarrow -\overset{\overset{\displaystyle :\ddot{O}:^-}{|}}{C}=\overset{+}{N}H-$$
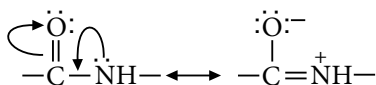
As a result, C—N bond in proteins is shorter than usual bond length of C—N bond,

21. (c) : $C_6H_5CH_3 \xrightarrow{[O]} \underset{(A)}{C_6H_5COOH} \xrightarrow{SOCl_2}$

$\underset{(B)}{C_6H_5COCl} \xrightarrow[-NaCl]{NaN_3} \underset{(C)}{C_6H_5CON_3}$

$\xrightarrow[\text{(Curtius rearrangement)}]{\Delta(-N_2)} \underset{\text{Phenylisocyanate }(D)}{C_6H_5-N=C=O}$

22. (a) : α-D-Glucopyranose $\underset{+111°}{\rightleftharpoons}$ Equilibrium mixture $\underset{+52.5°}{}$

$\underset{+19.2°}{\rightleftharpoons} \beta\text{-}D\text{-Glucopyranose}$

Ratio of $\alpha : \beta$-form = (52.5 – 19.2) : (111 – 52.5)

$= 33.3 : 58.5$

∴ % of α-D-glucopyranose

$= \dfrac{33.3}{(33.3+58.5)} \times 100 = 36.27\%$

23. (d): $R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow RNH_2$
$+ 2NaBr + Na_2CO_3 + 2H_2O$
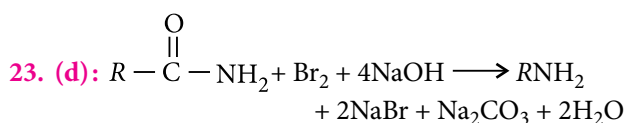
24. (b): Vitamins C and B-complex are water soluble while A, D, E and K are fat soluble.

25. (b):

$$\underset{CH_3}{\overset{CH_3}{>}}\underset{(A)}{CH-NH_2} \xrightarrow{HNO_2} \underset{CH_3}{\overset{CH_3}{>}}CH-OH + N_2$$

↓ CHCl₃/KOH/Δ

$$\underset{CH_3}{\overset{CH_3}{>}}\underset{(B)}{CH-N\overset{+}{\equiv}C} \xrightarrow{Reduction} \underset{CH_3}{\overset{CH_3}{>}}\underset{\textit{iso}\text{-propyl methyl amine}}{CH-NH-CH_3}$$
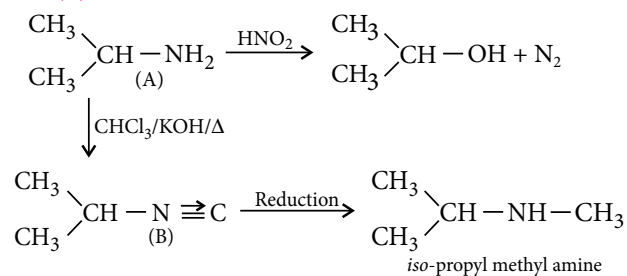
Therefore 'A' is *iso*-propyl amine.

26. (a) :

D-(+)-glucose   Mirror (Enantiomers) L-(−)-glucose

27. (d):

syn and *anti*-ketoximes

III(from I)
(In I anti C_6H_{11}– group migrates)

IV(from II)
(In II anti CH_3CH_2– group migrates)

$\xrightarrow{H^+} \underset{\text{(from III)}}{C_6H_{11}NH_2 + HOOCCH_2CH_3 +}$

$\underset{\text{(from IV)}}{C_6H_{11}COOH + H_2NCH_2CH_3}$

$\underbrace{}_{Z}$
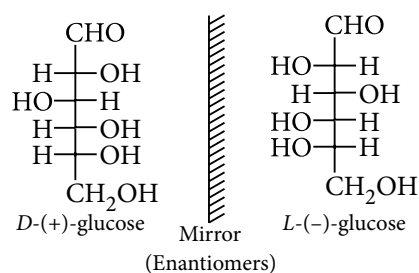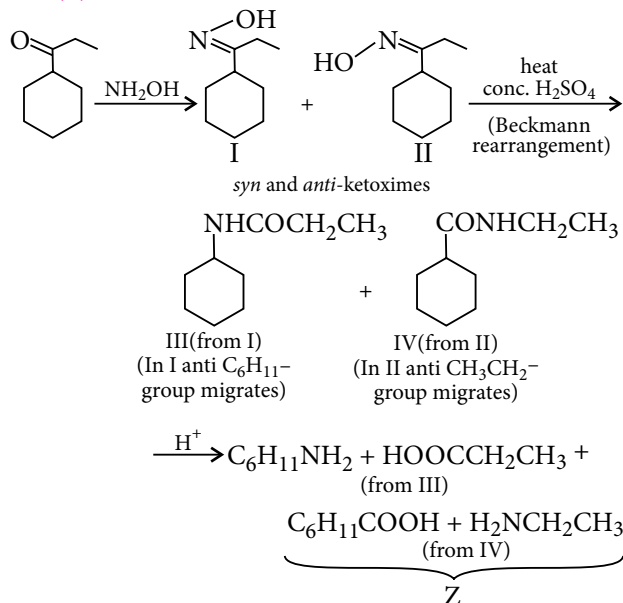
28. (c) : Carbon adjacent to oxygen atom in the cyclic structure of glucose or fructose is known as anomeric carbon. As shown in the structure 'a' and 'b' are present at the position adjacent to oxygen atom. Both carbons differ in configurations.

29. (c) : In arylamines, lone pair of electrons on nitrogen atom is delocalised over the benzene ring, thus, not available for donation. So, arylamines (Ar—NH₂) are less basic than alkylamines ($R-\ddot{N}H_2$).

30. (c) : In order to prepare 1° amine from an alkyl halide with simultaneous addition of one CH₂ group in the carbon chain, the reagent used as a source of nitrogen is KCN. Chemical transformation can be shown as

$\diamond\!\diamond$
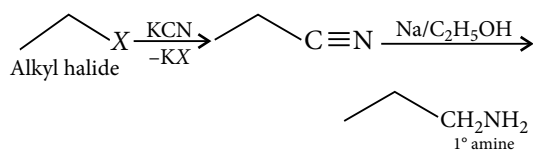
ACE YOUR WAY CBSE

Practice Paper 2017

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 tables if necessary, use of calculators is not allowed.

1. "Crystalline solids are anisotropic in nature." What does this statement mean?

2. NF_3 is an exothermic compound but NCl_3 is an endothermic compound. Explain.

3. Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?

4. What is collodion?

5. Why is aniline converted into acetanilide before nitration?

6. (i) Co^{2+} is easily oxidised to Co^{3+} in presence of a strong field ligand. Give reason.
   (ii) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.

7. The specific conductance of a saturated solution of AgCl at 298 K is found to be 1.386×10^{-6} S cm^{-1}. Calculate its solubility. ($\lambda^\circ_{Ag^+} = 62.0$ S cm^{2}mol^{-1} and $\lambda^\circ_{Cl^-} = 76.3$ S cm^2 mol^{-1})

8. An aqueous blue coloured solution of transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate 'A' which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium turns yellow and produces a white precipitate 'B'. Identify the transition metal ion. Write the chemical reactions involved in the formation of 'A' and 'B'.

OR

Account for the following :

(i)   The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic.

(ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised.

9. When *tert*-butanol and *n*-butanol are separately treated with a few drops of *dil*. KMnO$_4$ in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

10. For a certain chemical reaction, variation in the concentration, ln[R] *vs* time (min) plot is shown below:

For this reaction

(i) What is the order of the reaction?

(ii) What are the units of rate constant, k for this reaction?

(graph of $\ln[R]$ vs t (min), decreasing straight line)

(iii) Give the relationship between k and $t_{1/2}$ of this reaction.

(iv) If initial concentration for this reaction becomes half, how will $t_{1/2}$ vary?
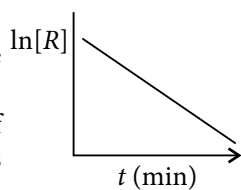
11. A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 240°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed to products? What is the half life period of this reaction?

12. Explain the following observations :
  (i) Lyophilic colloid is more stable than lyophobic colloid.
  (ii) Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.
  (iii) Sky appears blue in colour.

13. Give reasons for the following :
  (i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.
  (ii) ($\pm$)-2-butanol is optically inactive.
  (iii) C—X bond length in halobenzene is smaller than C—X bond length in CH_3—X.

14. Aluminium crystallises in a cubic close packed structure. Radius of atom in the metal is 125 pm.
  (i) What is the length of the side of the unit cell?
  (ii) How many unit cells are there in 1 cm^3 of aluminium?

15. Give reasons for the following :
  (i) Mn^{3+} is a good oxidising agent.
  (ii) $E^{\circ}_{M^{2+}/M}$ values are not regular for first row transition metals (3d-series).
  (iii) Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF_4, whereas the highest oxide is Mn_2O_7.

16. Write structures of the products of the following reactions :
  (i) $CH_3—CH=CH_2 \xrightarrow{H_2O/H^+}$
  (ii) (cyclohexanone with $CH_2-\underset{\underset{O}{\|}}{C}-OCH_3$ group) $\xrightarrow{NaBH_4}$

(iii) $CH_3—CH_2—\underset{\underset{CH_3}{|}}{CH}—CHO \xrightarrow{NaBH_4}$
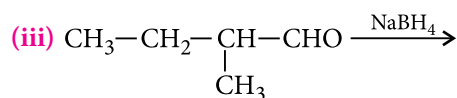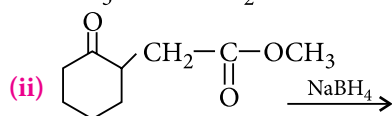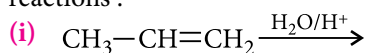
17. (i) Which solution is used for the leaching of silver metal in the presence of air in the metallurgy of silver?
  (ii) What types of metals are usually purified by the method of zone refining? Give an example.
  (iii) Why is electrolytic reduction preferred over chemical reduction for the isolation of certain metals?

18. Calculate the standard cell potential of a galvanic cell in which the following reaction takes place :
$$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$$
Calculate $\Delta_r G^{\circ}$ and equilibrium constant, K of the above reaction at 25°C.
[Given : $E^{\circ}_{Cr^{3+}/Cr} = -0.74$ V, $E^{\circ}_{Cd^{2+}/Cd} = -0.40$ V, $F = 96{,}500$ C mol^{-1}]

19. An optically active compound having molecular formula, $C_6H_{12}O_6$ is found in two isomeric forms (A) and (B) in nature. When (A) and (B) are dissolved in water they show the following equilibrium :
$$(A) \rightleftharpoons \text{Equilibrium mixture} \rightleftharpoons (B)$$
$[\alpha]_D 111°$ 52.2°   19.2°
  (i) What are such isomers called?
  (ii) Can they be called enantiomers? Justify your answer.
  (iii) Draw the cyclic structure of isomer (A).

20. Give the oxidation state, d-orbital occupation and coordination number of the central metal ion in the following complexes :
  (i) $K_3[Co(C_2O_4)_3]$ **(ii)** cis-$[Cr(en)_2Cl_2]Cl$
  (iii) $(NH_4)_2[CoF_4]$

21. Give the structures of A, B and C in the following reactions :
  (i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\,K]{HNO_2} C$
  (ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2 + KOH} B \xrightarrow{CHCl_3 + NaOH} C$

22. Draw the structures of given polymers and their monomers. Also write their uses :
  (i) Teflon   **(ii)** PMMA
  (iii) Buna-S

OR

  (i) Differentiate between copolymerisation and homopolymerisation. Give one example of each.

(ii) What is the role of benzoyl peroxide in preparation of polythene?

23. On the occasion of World Health Day, Dr. Satpal organized a 'health camp' for the poor farmers living in a nearby village. After check-up, he was shocked to see that most of the farmers suffered from cancer due to regular exposure to pesticides and many were diabetic. He distributed free medicines to them. Dr. Satpal immediately reported the matter to the National Human Rights Commission (NHRC). On the suggestions of NHRC, the government decided to provide medical care, financial assistance, setting up of super-speciality hospitals for treatment and prevention of the deadly disease in the affected villages all over India.

(i) Write the values shown by
(a) Dr. Satpal
(b) NHRC.

(ii) What type of analgesics are chiefly used for the relief of pains of terminal cancer?

(iii) Give an example of artificial sweetener that could have been recommended to diabetic patients.

24. (i) An aromatic compound 'A' (C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollens' or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' ($C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B, C and write all the reactions involved.

(ii) Give chemical tests to distinguish between
(a) Propanal and propanone
(b) Benzaldehyde and acetophenone

OR

An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidified conditions gives (B) and (D). Oxidation of (D) with $KMnO_4$ also gives (B). (B) on heating with $Ca(OH)_2$ gives (E) having molecular formula C_3H_6O. (E) does not give Tollens' test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Identify (A), (B), (C), (D) and (E).

25. (i) A solution is prepared by dissolving 1.08 g of human serum albumin (a protein obtained from blood plasma) in 50 cm^3 of aqueous solution. The solution has an osmotic pressure of 5.85 mm of Hg at 298 K. Calculate
(a) molar mass of albumin.
(b) the height of water column placed in solution. [Given, $d_{(H_2O)} = 1$ g cm^{-3}]

(ii) A complex is represented as $CoCl_3 \cdot XNH_3$. Its 0.1 m solution in aqueous medium shows $\Delta T_f = 0.558°$ C, $K_f(H_2O) = 1.86$ kg/mol/K and assume 100% ionisation and coordination number of Co(III) is 6. What is the complex?
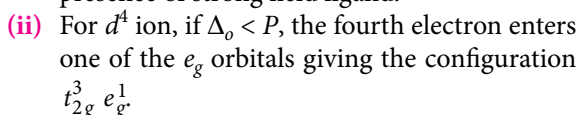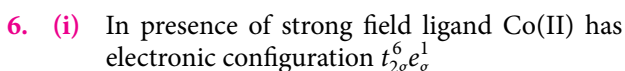
OR

(i) Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing
(a) 1.2% sodium chloride solution?
(b) 0.4% sodium chloride solution?

(ii) A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is added to this solution. The new vapour pressure becomes 2.9 kPa at 298 K. Calculate
(a) the molecular mass of solute and
(b) vapour pressure of water at 298 K.

26. (i) An amorphous solid 'A' burns in air to form a gas 'B' which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aqueous $KMnO_4$ solution and reduces Fe^{3+} to Fe^{2+}. Identify the solid 'A' and the gas 'B' and write the reactions involved.

(ii) H_2S acts only as a reducing agent but SO_2 acts as a reducing as well as oxidising agent. Why?

OR

(i) Draw the structure of
(a) H_2SO_3
(b) H_2SO_4
(c) $H_2S_2O_7$

(ii) Account for the following :
(a) H_2S has lower boiling point than H_2O.
(b) Reducing character decreases from SO_2 to TeO_2.

SOLUTIONS

1. Crystalline solids are anisotropic in nature because of different arrangements of particles in different directions. Their physical properties shows different values along different directions in the same crystals.

2. N—F bond strength is greater than F—F bond strength therefore, formation of NF_3 is spontaneous. In case of NCl_3, N—Cl bond strength is lesser than Cl—Cl bond strength. Thus, energy has to be supplied during the formation of NCl_3.

3. Grignard reagent $\overset{\delta-}{R}$—$\overset{\delta+}{Mg}X$ is a polar molecule. So, Grignard reagents are highly reactive and react with water (a good source of proton) to give hydrocarbons.
$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

4. 4% solution of cellulose nitrate in a mixture of ethyl alcohol and ether is called collodion.

5. During direct nitration of aniline, it is converted into anilinium ion which is ring deactivating and meta directing group. Hence, in order to retain its *ortho/para* directing tendency –NH_2 group is converted into —$NHCOCH_3$.

6. **(i)** In presence of strong field ligand Co(II) has electronic configuration $t_{2g}^6 e_g^1$

   It can easily lose one electron present in e_g orbital to give stable t_{2g}^6 configuration. That is why Co^{2+} is easily oxidised to Co^{3+} in the presence of strong field ligand.

   (ii) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.

7. $\Lambda^\circ_{m(AgCl)} = \lambda^\circ_{(Ag^+)} + \lambda^\circ_{(Cl^-)} = 62.0 + 76.3$
   $$= 138.3 \text{ S cm}^2 \text{ mol}^{-1}$$
   $\kappa = 1.386 \times 10^{-6} \text{ S cm}^{-1}$
   $$\Lambda^\circ_m = \frac{\kappa \times 1000}{M} = \frac{\kappa \times 1000}{\text{Solubility}}$$
   $$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda^\circ_m} = \frac{1.386 \times 10^{-6} \times 1000}{138.3}$$
   $$= 1.0 \times 10^{-5} \text{ mol L}^{-1}$$
   $$= 1.0 \times 10^{-5} \times 143.5 \text{ g L}^{-1}$$
   $$= 1.435 \times 10^{-3} \text{ g L}^{-1}$$

8. 'A' can be the black precipitate of CuS. 'B' can be cuprous iodide which could have formed after the decomposition of cupric iodide.

$$CuSO_4 + H_2S \xrightarrow[\text{medium}]{\text{Acidic}} \underset{\text{Black }(A)}{CuS\downarrow} + H_2SO_4$$
$$\underset{\text{Blue}}{CuSO_4} + 2KI \xrightarrow[\text{acidic}]{\text{Weakly}} \underset{\text{Yellow}}{CuI_2} + K_2SO_4$$
$$2CuI_2 \longrightarrow \underset{\text{White }(B)}{Cu_2I_2\downarrow} + I_2$$

OR

(i) Oxides of transition metals containing lowest oxidation states are basic due to their ability to get oxidised to higher oxidation states whereas the higher oxidation state of metals and compounds get reduced to lower ones and hence, acts as acidic in nature *e.g.*, MnO is basic whereas Mn_2O_7 is acidic.

(ii) The tendency to form complexes is high for Co(III) as compared to Co(II) because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than that for Co(II) with a $d^7(t_{2g}^6 e_g^1)$ arrangement.

9. $$\underset{n\text{-Butanol}}{\wedge\wedge OH} \xrightarrow{KMnO_4(dil.)} \wedge CHO + \underset{\text{Brown precipitate}}{MnO_2\downarrow}$$

$$\underset{tert\text{-Butanol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH} \xrightarrow{KMnO_4(dil.)} \text{No reaction}$$

This is because 3° alcohols do not undergo oxidation reaction.

10. **(i)** Reaction is of first order.
    (ii) Units of rate constant is min^{-1}.
    (iii) For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$
    (iv) No change in $t_{1/2}$ because half life period is independent of initial concentration for first order reaction.

11. For the first order reaction:
    $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$
    Let the initial concentration is 1 mol litre^{-1} and x moles of the reactants have changed to products so that $[A]_0 = 1$ and $[A] = 1 – x$
    $k = 1.5 \times 10^{-6}$, $t = 10$ hrs $= 10 \times 60 \times 60 = 36000$ s
    Substituting the values
    $$1.5 \times 10^{-6} = \frac{2.303}{36000} \log \frac{1}{1-x}$$
    or $$\log \frac{1}{1-x} = \frac{1.5 \times 10^{-6} \times 36000}{2.303}$$

or $\log \dfrac{1}{1-x} = 0.0234$

Taking antilogarithm, $\dfrac{1}{1-x} = 1.055$

$1.055 - 1.055\, x = 1$

or $x = \dfrac{1.055 - 1}{1.055} = 0.052$

Thus, 5.2% of the initial concentration has changed to products.

Calculation of half life period.

$t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{1.5 \times 10^{-6}} = 4.62 \times 10^{5}$ second
$= 128.3$ hrs.
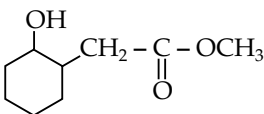
12. (i) A lyophilic solution is stable due to the charge as well as solvation of the sol particles. Such a solution can only be coagulated by removing these factors which is done by adding electrolyte and by adding a suitable solvent.
On the other hand, a lyophobic sol is stable due to charge only and hence, can be easily coagulated by adding small amount of an electrolyte.

(ii) Ferric hydroxide solution adsorbs Cl^- ions of NaCl and get neutralised. Thus, the colloidal particles get precipitated *i.e.*, ferric hydroxide is precipitated when NaCl solution is added.

(iii) The atmospheric particles of colloidal range scatter blue component of the white sunlight preferentially. That is why sky appears blue.

13. (i) Iodide is a better leaving group because of its larger size than bromide, therefore, ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(ii) (±), 2-butanol is a racemic mixture. It is a mixture which contains two enantiomers in equal proportion and thus, have zero optical rotation due to internal compensation. Therefore, it is optically inactive.

(iii) In halobenzenes (like chlorobenzene), the lone pair of electrons on halogen atom is delocalised on the benzene ring. As a result, C—X bond (C—Cl bond in case of chlorobenzene) acquires some double bond character while in CH_3—X, C—X bond is a pure single bond. Therefore, C—X bond in halobenzene is shorter than that in CH_3—X.

14. (i) For *fcc* (or *ccp*), $a = 2\sqrt{2}r = 2 \times 1.414 \times 125$ pm
$= 353.5$ pm

(ii) $a = 353.5$ pm $= 3.535 \times 10^{-8}$ cm
Volume of one unit cell $= a^3 = (3.55 \times 10^{-8}$ cm$)^3$
$= 4.417 \times 10^{-23}$ cm^3
Number of unit cells
$= \dfrac{\text{Total volume}}{\text{Volume of one unit cell}}$
$= \dfrac{1\ \text{cm}^3}{4.417 \times 10^{-23}\ \text{cm}^3} = 2.26 \times 10^{22}$

15. (i) Mn^{2+} is more stable due to half filled d^5 configuration and Mn^{3+} easily changes to Mn^{2+} by gaining an electron hence, Mn^{3+} acts as a good oxidising agent.

(ii) The $E^{\circ}_{M^{2+}/M}$ values are not regular which can be explained from the irregular variation of ionisation enthalpies (*i.e.*, $IE_1 + IE_2$) and the sublimation enthalpies which are relatively much less for manganese and vanadium.

(iii) Manganese can form $p\pi$-$d\pi$ bond with oxygen by utilising 2p-orbital of oxygen and 3d-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$-$d\pi$ bond thus, it can show a maximum of +4 oxidation state.

16. (i) $CH_3 - \underset{\underset{\text{OH}}{|}}{CH} - CH_3$

(ii)

(iii) $CH_3 - CH_2 - \underset{\underset{\text{CH}_3}{|}}{CH} - CH_2OH$

17. (i) Dilute solution of NaCN or KCN in the presence of air (*i.e.*, O_2).

(ii) The metals such as germanium, silicon, gallium, etc. which are used as semiconductors are purified by zone refining which is based upon the principle that impurities are more soluble in the molten state (melt) than in the solid state of metals.

(iii) Electropositive metals (like Na, K, Ca, Mg, Al, etc.) which cannot be reduced by chemical reduction are easily reduced electrolytically.

18. $T = 273 + 25°C = 298$ K and $n = 6$
$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.40$ V $-(-0.74)$ V $= 0.34$ V
$\Delta_r G^{\circ} = -nFE^{\circ}_{\text{cell}} = -6 \times 96500 \times 0.34$
$= -196860$ J mol^{-1}

Again $\Delta_r G° = -2.303\ RT \log K$

$\Rightarrow -196860 = -2.303 \times 8.314 \times 298 \times \log K$

$\Rightarrow \log K = 34.5014$

$\therefore\quad K = $ antilog $34.5014 = 3.172 \times 10^{34}$

19. (i) These are called anomers.

(ii) No, they are not enantiomers because this pair of stereoisomers are superimposable to each other except at C_1. Configuration of these isomers differ at C_1 hence they are anomer to each other.

(iii)

α-D(+)-Glucopyranose
(A)
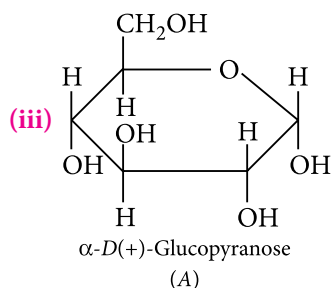
20. (i)

Complex	$K_3[Co(C_2O_4)_3]$
Oxidation state of metal atom	+3
Coordination number of central metal atom	6
d-orbital occupation	$Co^{3+} = 3d^6;\ (t_{2g})^6(e_g)^0$

(ii)

Complex	cis - $[Cr(en)_2Cl_2]Cl$
Oxidation state of metal atom	+3
Coordination number of central metal atom	6
d-orbital occupation	$Cr^{3+} = 3d^3;(t_{2g})^3$

(iii)

Complex	$(NH_4)_2[CoF_4]$
Oxidation state of metal atom	+2
Coordination number of central metal atom	4
d-orbital occupation	$Co^{2+} = 3d^7;\ (e)^4(t_2)^3$

21. (i) $CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$
(A) (B)

$\underset{273\ K}{\xrightarrow{HNO_2}}$

CH_3CH_2OH
(C)

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2 + KOH}$

$\underset{(C)}{CH_3NC} \xleftarrow{CHCl_3 + NaOH} \underset{(B)}{CH_3NH_2}$
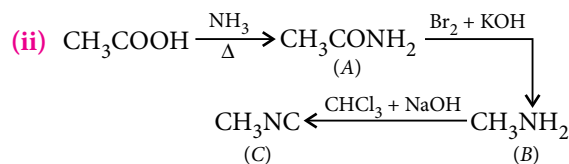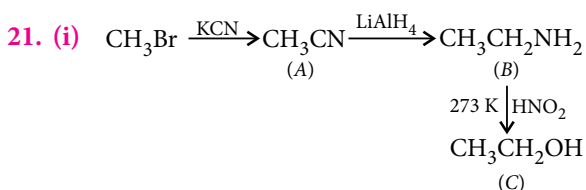
22. (i) Teflon : (Polytetrafluoroethene)
Monomer : Tetrafluoroethene.

$\underset{F}{\overset{F}{>}}C=C\underset{F}{\overset{F}{<}}$
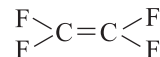
Structure of polymer : $+CF_2-CF_2 \xrightarrow{}_n$

Uses : It is used as lubricant, insulator and making cooking wares.

(ii) PMMA (Polymethylmethacrylate or plexiglass).
Monomer : Methyl methacrylate.
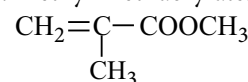
$CH_2=\underset{CH_3}{\overset{|}{C}}-COOCH_3$

Structure of polymer : $+CH_2-\underset{COOCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} \xrightarrow{}_n$

Uses : It is used as substitute of glass and making decorative materials.

(iii) Buna-S (Butadiene-Styrene rubber)
Monomer : $\underset{1,3\text{-Butadiene}}{CH_2=CH-CH=CH_2}$

and $CH=CH_2$

Styrene

Polymer :

$+CH_2-CH=CH-CH_2-\underset{C_6H_5}{\overset{|}{CH}}-CH_2 \xrightarrow{}_n$
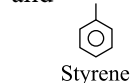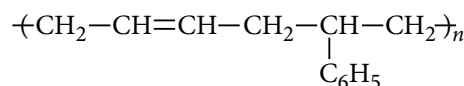
Uses : It is used in making automobile tyres and footwear.

OR

(i) Homopolymer : A polymer obtained by polymerisation of a single monomer is known as homopolymer and the process is called homopolymerisation.
e.g., Polythene made by ethene molecules.

$n CH_2=CH_2 \rightarrow +CH_2-CH_2 \xrightarrow{}_n$
Ethene   Polythene (homopolymer)
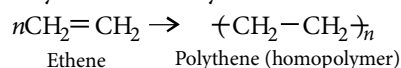
Copolymer : A polymer obtained by polymerisation of two or more different monomers is called copolymer and the reaction is called copolymerisation. When styrene and butadiene are polymerised together, a polymer called butadiene-styrene rubber is formed.

$$n CH_2=CH-CH=CH_2 + \text{(Styrene)}$$

1,3-Butadiene

Styrene

$$+CH_2-CH=CH-CH_2-CH-CH_2+_n$$

Butadiene-styrene Rubber
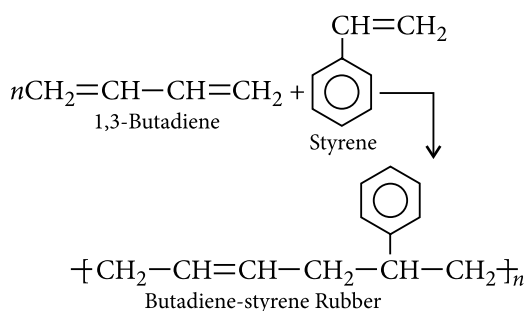
(ii) In the preparation of polythene from ethene, benzoyl peroxide acts as an initiator or free radical generator.

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \longrightarrow$$

Benzoyl peroxide

$$2C_6H_5-\overset{\overset{O}{\|}}{C}-O \xrightarrow{-2CO_2}$$

$$2C_6H_5^{\cdot}$$

Phenyl radical
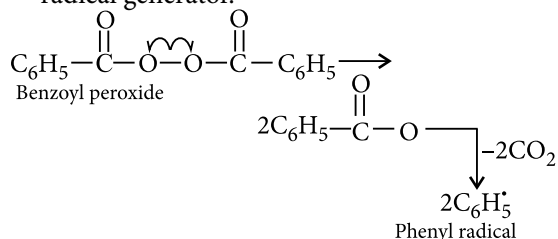
23. (i) (a) Dr. Satpal showed that a doctor should be sympathetic to the health needs of the society.

(b) NHRC showed that government should provide medical care and financial assistance to rural population of India.

(ii) Narcotic analgesics are chiefly used for the relief of pains of terminal cancer.

(iii) Saccharin is an artificial sweetener which could be recommended to diabetic patients.

24. (i) Molecular formula of compound is C_8H_8O. As 'A' does not give Tollens' or Fehling's test, it must be a ketone. It gives positive test with 2, 4 - DNP and iodoform test. It means it is methyl ketone.

$$A \xrightarrow{2,4\text{-DNP}}$$

$$A \xrightarrow{KMnO_4/H^+} C$$

$$A \xrightarrow[H^+]{I_2/NaOH} CHI_3 + C$$
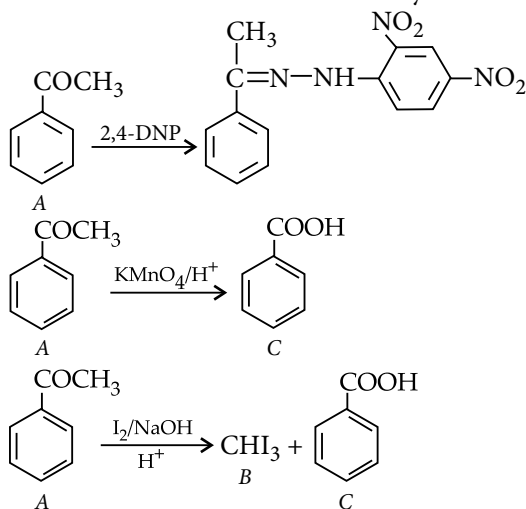
(ii) (a) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

Propanal will form the silver mirror, but propanone does not react.

(b) Benzaldehyde and acetophenone can be distinguished by Tollens' test.

Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' test.

OR

$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!\!>\!\!O + C_2H_5OH \longrightarrow CH_3COOC_2H_5$$

A, Ethanol, Ethyl ethanoate (C)

$$+ CH_3COOH$$

Ethanoic acid (B)

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3CH_2OH$$

(B) (D)

$$CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH$$

(D) (B)

$$\downarrow Ca(OH)_2 \text{ Dry distillation}$$

$$CH_3COCH_3 + CaCO_3$$

E
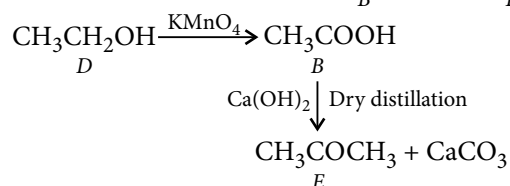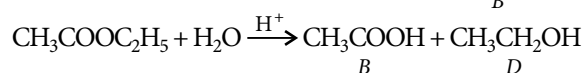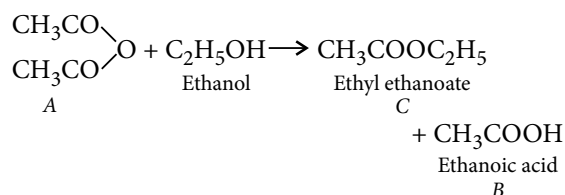
E does not give Tollens' reagent test and does not reduce Fehling's solution as it is ketone.

25. (i) (a) The molar mass can be calculated using the following relation.

$$M_{\text{albumin}} = \frac{W_{\text{albumin}} \times R \times T}{V \times \pi} \qquad ...(i)$$

Given, W_{albumin} = 1.08 g

R (gas constant) = 0.0821 L atm K^{-1} mol^{-1},

T = 298 K

π (osmotic pressure) = $\dfrac{5.85}{760}$ atm

V (volume) = $\dfrac{50}{1000}$ = 0.05 L

Substituting all these values in Eq. (i), we get

$$M_{\text{albumin}} = \frac{1.08 \times 0.0821 \times 298}{\left(\dfrac{5.85}{760}\right) \times 0.05}$$

$$= 68655 \text{ g mol}^{-1}$$

Hence, the molar mass of albumin is 68655 g mol^{-1}.

(b) The height of water column can be calculated by using the following formula :

$\pi = hdg$

$\dfrac{5.85}{760} \times 101325 = h \times 1 \times 10^3 \times 9.80$

$$(1 \text{ atm} = 101325 \text{ Pa})$$

Hence, $h = 7.958 \times 10^{-2}$ m = 7.958 cm

(ii) Molality of solution (m) = 0.1

Depression in freezing point = $\Delta T_f = 0.558°C$

$K_f(H_2O) = 1.86$ kg/mol/K

As, $\Delta T_f = K_f \times i \times m$ (i = van't Hoff factor)

$0.558 = 1.86 \times 0.1 \times i$

$\therefore\ i = \dfrac{0.558}{0.186} \approx 3$

or, $i \approx 3$ indicates the complex ionises to form 3 ions, since coordination number is 6 hence, $X = 5$.

i.e., $CoCl_3 \cdot 5NH_3 \longrightarrow \underset{\text{1 cation}}{[Co(NH_3)_5Cl]^{2+}} + \underset{\text{2 anions}}{2Cl^-}$
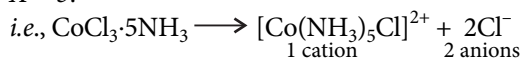
So, the complex is $[Co(NH_3)_5Cl]Cl_2$.

OR

(i) (a) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution exosmosis takes place that results in shrinking of cells.

(b) 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution endosmosis takes place that results in swelling of cells.

(ii) The relative lowering of vapour pressure is given by the following expression,

$(p°_{solvent} - p_{solution})/p°_{solvent} = n_2/(n_1 + n_2)$

for dilute solutions, $n_2 << n_1$, therefore

$(p°_{solvent} - p_{solution})/p°_{solvent} = n_2/n_1$

$\qquad\qquad = (W_2 \times M_1)/(M_2 \times W_1)$

$(p°_{solvent} - 2.8)/p°_{solvent} = (30 \times 18)/(M_2 \times 90)$

$(p°_{solvent} - 2.8)/p°_{solvent} = 6/M_2 \qquad …(1)$

Similarly for second case we get,

$(p°_{solvent} - 2.9)/p°_{solvent} = (30 \times 18)/(M_2 \times 108)$

$(p°_{solvent} - 2.9)/p°_{solvent} = 5/M_2 \qquad …(2)$

On solving eq. (1) and (2), we get

$(p°_{solvent} - 2.8)/(p°_{solvent} - 2.9) = 6/5$

$\therefore\ p°_{solvent} = 3.4$ kPa

i.e., vapour pressure of water at 298 K is 3.4 kPa

Substituting the value of $p°_{solvent}$ in (1) we get,

$(3.4 - 2.8)/3.4 = 6/M_2$ or $0.6/3.4 = 6/M_2$

$\therefore\ M_2 = 34$ g

26. (i) 'A' is S_8 and 'B' gas formed is SO_2.

In air, $\underset{(A)}{S_8} + 8O_2 \xrightarrow{\Delta} \underset{(B)}{8SO_2}$

$SO_2 + \underset{\text{Lime water}}{Ca(OH)_2} \rightarrow \underset{\text{Milky}}{CaSO_3\downarrow} + H_2O$

$\underset{\text{Violet}}{2MnO_4^-} + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + \underset{\text{Colourless}}{2Mn^{2+}}$

$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
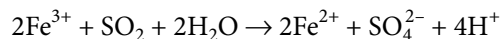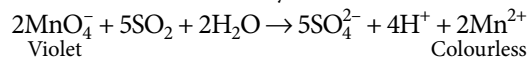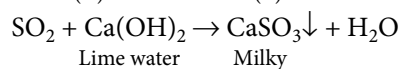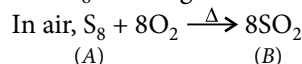
(ii) Sulphur shows oxidation states – 2, + 2, + 4, + 6. The oxidation number of S in H_2S is – 2 while in SO_2 is + 4. In H_2S, it can only increase oxidation number by losing electrons and hence, acts as a reducing agent.

On the other hand, in SO_2, it can increase or decrease its oxidation number by losing or gaining electrons. So, it acts both as reducing as well as oxidising agent.

OR

(i) (a)

Sulphurous acid (H_2SO_3)

(b)

Sulphuric acid (H_2SO_4)

(c)
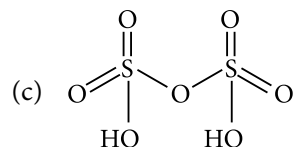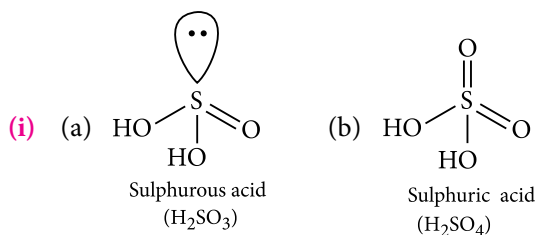
Pyrosulphuric acid (oleum) ($H_2S_2O_7$)

(ii) (a)

	H_2O		H_2S
Boiling point :	373 K	>	213 K

The abnormally high boiling point of H_2O is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not form H-bonding.

(ii) The +6 oxidation state of S is more stable than +4 therefore, SO_2 acts as a reducing agent. Further, since the stability of +6 oxidation state decreases from S to Te therefore, the reducing character of the dioxides decreases while their oxidising character increases.

Thus, TeO_2 acts as an oxidising agent.

◈ ◈

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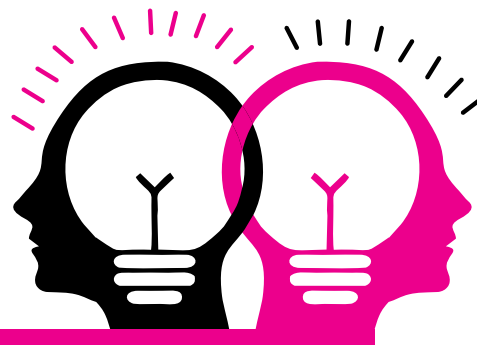
The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

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. Which one of the following is not a property of hydrophilic sols?
   (a) High concentration of dispersed phase can be easily attained.
   (b) Coagulation is reversible.
   (c) Viscosity and surface tension are about the same as for water.
   (d) None of these.

2. Ferric chloride is applied to stop bleeding because
   (a) Fe^{3+} ions coagulate negatively charged blood solution
   (b) Fe^{3+} ions coagulate positively charged blood solution
   (c) Cl^- ions coagulate positively charged blood solution
   (d) Cl^- ions coagulate negatively charged blood solution.

3. Potassium stearate is obtained by saponification of an oil or fat. It has the formula, $CH_3(CH_2)_{16}COO^-K^+$. The molecule has a hydrophobic end $(CH_3(CH_2)_{16}-)$ and a hydrophilic end (COO^-K^+). Potassium stearate is an example of :
   (a) lyophobic colloid
   (b) multimolecular colloid
   (c) macromolecular colloid
   (d) associated colloid or micelle.

4. Shape selective catalysts are so called because of
   (a) the shape of the catalyst
   (b) the specificity of the catalyst
   (c) the size of the pores of catalyst which can trap selective molecules only
   (d) their use for some selected reactions only.

5. Select the correct statement.
   (a) Surface active agents like soaps and synthetic detergents are micelles.
   (b) Soaps are emulsifying agents.
   (c) Both $C_{17}H_{35}-$ (hydrocarbon part) and $-COO^-$ (carboxylate part) of stearate ion $(C_{17}H_{35}COO^-)$ are hydrophobic.
   (d) Both (a) and (b).

6. Coagulation or demulsification can be done by some of the methods given below :
   I. By addition of a substance which would destroy the emulsifier.
   II. By addition of an electrolyte which would destroy the charge.
   III. By heating, freezing and centrifuging.
   Select the correct methods.
   (a) Only I and II   (b) I, II and III
   (c) Only II   (d) Only III

7. Which of the following graphs represents the variation of amount of chemisorption of a gas by a solid adsorbent with temperature under constant pressure condition?

   (a) $\frac{x}{m}$ vs T (b) $\frac{x}{m}$ vs T

   (c) $\frac{x}{m}$ vs T (d) $\frac{x}{m}$ vs T
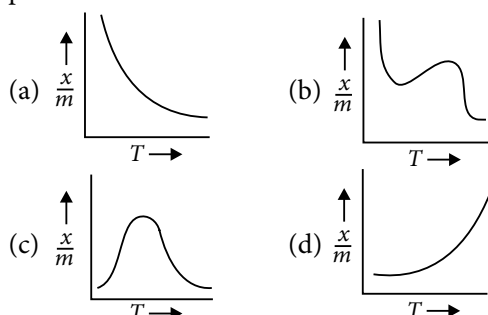
8. Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl, Na_2SO_4 and Na_3PO_4 solutions. Their coagulation values will be in the order :
   (a) $NaCl > Na_2SO_4 > Na_3PO_4$
   (b) $Na_2SO_4 > Na_3PO_4 > NaCl$
   (c) $Na_3PO_4 > Na_2SO_4 > NaCl$
   (d) $Na_2SO_4 > NaCl > Na_3PO_4$

9. Gold numbers of protective colloids *A*, *B*, *C* and *D* are 0.50, 0.01, 0.10 and 0.005 respectively. The correct order of their protective powers is
   (a) $A < C < B < D$ (b) $B < D < A < C$
   (c) $D < A < C < B$ (d) $C < B < D < A$

10. In which of the following manner the adsorption of a gas on a solid surface varies with pressure of the gas?
    (a) Fast → slow → independent of the pressure
    (b) Slow → fast → independent of the pressure
    (c) Independent of the pressure → fast → slow
    (d) Independent of the pressure → slow → fast

SECTION - II
More than One Options Correct Type

11. The correct features of the enzymes are
    (a) they are globular proteins
    (b) they show maximum activity at 37°C
    (c) each enzyme can catalyse a large number of biological reactions
    (d) the enzymes present in yeast are invertase and zymase only.

12. At critical micelle concentration (CMC)
    (a) the ions of surfactant molecules undergo association to form clusters
    (b) the turbidity of solution increases abruptly
    (c) substances like grease, fats, etc. dissolve colloidally
    (d) colligative properties increase suddenly.

13. The correct statements about adsorption are
    (a) the chemisorption of H_2 as H atoms on the surface of glass is endothermic
    (b) physical adsorption does not require activation energy
    (c) chemisorption is always unimolecular
    (d) in adsorption, only solute from the solution is adsorbed on the surface of the solid adsorbent.

SECTION - III
Paragraph Type

Paragraph for Questions 14 and 15

Emulsions are also the colloidal systems in which both the dispersed phase as well as the dispersion medium are liquids. It may be oil-in-water type or water-in-oil type. Bancroft proposed that the phase in which the emulsifier is more soluble constitutes the continuous phase of the emulsion. Emulsifiers can be used to stabilise the emulsion. Soaps, detergents, proteins, gum, etc are used as emulsifiers.

14. Which of the following is homogeneous?
    (a) Milk   (b) Paint
    (c) Shampoo   (d) None of these

15. Milk is an emulsion in which
    (a) a gas is dispersed in water
    (b) a solid is dispersed in water
    (c) fat is dispersed in water
    (d) lactose is dispersed in water.

Paragraph for Questions 16 and 17

A graph between x/m and the pressure '*P*' of the gas at a constant temperature is called adsorption isotherm, where x is the number of moles of the adsorbate and m is the mass of the adsorbent. Adsorption isotherms of different shapes have been experimentally observed. According to Freundlich adsorption isotherm, $\frac{x}{m} = kP^{1/n}$

where, k and n are constant parameters depending upon the nature of the adsorbent and adsorbate.

16. In the given isotherm, select the incorrect statement.

(a) $\frac{x}{m} \propto P$ along OA.

(b) $\frac{x}{m} \propto P^0$ when point B reached.

(c) $\frac{x}{m}$ does not increase rapidly with pressure along BC due to less surface area available for adsorption.

(d) Nature of isotherm is different for two gases for same adsorbent.
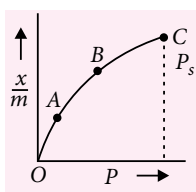
17. When a graph is plotted between log x/m and log P, it is a straight line with an angle 45° and intercept 0.3010 on y-axis. If initial pressure is 0.3 atm, what will be the amount of gas adsorbed per gram of adsorbent?

(a) 0.4   (b) 0.6   (c) 0.8   (d) 0.1

Matching List Type

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

	List I		List II
P.	Adsorption involving van der Waals' forces	1.	Specific and increases with temperature initially
Q.	Adsorption involving chemical forces	2.	Non-specific and decreases with temperature
R.	Positive adsorption of a solute on liquid surface	3.	Leads to decrease in surface tension of liquid
S.	Negative adsorption of a solute on liquid surface	4.	Leads to increase in surface tension of liquid

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

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

	List I		List II
P.	Enzymes	1.	Multimolecular colloid
Q.	Gold sol	2.	Macromolecular colloid
R.	Cellulose nitrate shaken with ethanol	3.	Associated colloid
S.	Detergent dissolved in water	4.	Collodion

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

Assertion Reason Type

20. **Assertion :** A gas with higher critical temperature is adsorbed more than a gas with lower critical temperature on the same adsorbent.
Reason : Higher critical temperature implies that the gas is more easily liquefiable.

21. **Assertion :** A colloidal sol of As_2S_3 is coagulated faster by 0.1 M $BaCl_2$ than by 0.1 M NaCl.
Reason : $BaCl_2$ gives double the number of Cl^- ions than NaCl.

22. **Assertion :** Lyophilic sols are more stable than lyophobic sols.
Reason : Lyophilic sols are highly hydrated in the solution.

Integer Value Correct Type

23. Among the following the number of colloidal systems having solid dispersed in liquid is :
Fog, clouds, butter, cell fluids, milk, paint, muddy water

24. Number of aerosols among the following is :
Paints, milk, smoke, dust, foam rubber, cheese, fog, clouds, insecticide sprays, mist

25. 50 mL of 1 M oxalic acid (molecular mass = 126) is shaken with 0.525 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. The amount of oxalic acid (in grams) adsorbed per gram of charcoal is

SECTION - I

Only One Option Correct Type

1. Which of the following polymers is an example of fibre?
    (a) Orlon   (b) Dacron
    (c) Nylon-6, 6   (d) All of these

2. Ibuprofen tablets sold in the market contain
    (a) only S-enantiomer
    (b) only R-enantiomer
    (c) racemic mixture of both R- and S-enantiomers
    (d) both R and S enantiomers are active pain hypnotic.

3. Salts of sorbic acid and propionic acid are used as
    (a) antioxidants
    (b) flavouring agents
    (c) food preservatives
    (d) nutritional supplements.

4. Drug which can possibly be used as analgesic without causing addiction and any modification is
    (a) morphine
    (b) N-acetyl-para-aminophenol
    (c) diazepam
    (d) tetra hydrocatenol.

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

6. The polymer containing strong intermolecular forces of attraction *e.g.*, hydrogen bonding is
    (a) polystyrene   (b) natural rubber
    (c) teflon   (d) nylon-6, 6.

7. Which one of the following can be used as monomer in a polymerisation reaction?
    (a) CH_3CH_2Cl (b) CH_3CH_2OH
    (c) C_6H_6 (d) C_3H_6

8. Which of the following statements is not correct regarding vinylic polymerisation?
    (a) It involves free radical polymerisation.
    (b) The presence of carbon tetrachloride in styrene polymerisation results in lowering of average molecular mass of the polymer.
    (c) The presence of benzoquinone increases the polymerisation process.
    (d) The presence of CCl_4 acts as inhibitor.

9. Equanil is
    (a) artificial sweetener (b) tranquilizer
    (c) antihistamine   (d) antifertility drug.

10. The monomeric units of terylene are ethylene glycol and
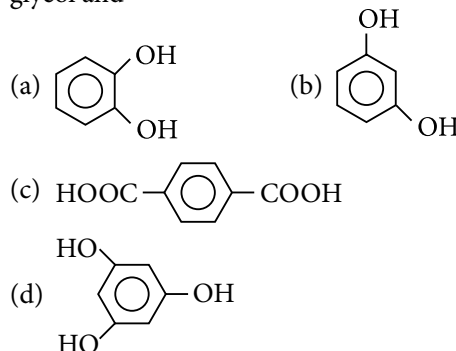
(a) benzene-1,2-diol (OH, OH)
(b) benzene-1,3-diol (OH, OH)
(c) $HOOC-C_6H_4-COOH$
(d) benzene ring with HO, HO and OH

SECTION - II

More than One Options Correct Type

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

12. Which of the following polymers exist in geometrical isomeric forms?
    (a) Polypropylene   (b) Polyacetylene
    (c) Polybutadiene   (d) Polyisoprene

13. Amongst the following drugs act as antihistamines are :
    (a) dimethindene   (b) pheniramine
    (c) diphenylhydramine (d) luminal.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

All polymers have a repeating structural unit. Depending upon whether the repeating structural unit is derived from one type of monomer molecules, or from more than one type of monomer molecules, the polymers are classified as homopolymers and copolymers respectively. These are further classified as addition and condensation polymers.

14. Which of the following sets contain only addition homopolymers?
(a) Nylon-6, natural rubber, cellulose
(b) Starch, nylon-6, 6, polyester
(c) Teflon, bakelite, orlon
(d) Neoprene, PVC, polythene

15. Which of the following is a condensation homopolymer?
(a) Cellulose   (b) Nylon-6, 6
(c) Dacron   (d) Glyptal

Paragraph for Questions 16 and 17

Drugs designed to cure some ailment in one organ in the body, do not affect the other because they work on different receptors. For example, secretion of histamine causes allergy. It also causes acidity due to release of hydrochloric acid in the stomach. Since, anti-allergic and antacids drugs work on different receptors therefore, anti-allergic drugs remove allergy while antacids remove acidity.

16. Which of the following antacids prevent the release of hydrochloric acid from the stomach wall?
(a) Ranitidine   (b) Cimetidine
(c) Omeprazole   (d) All of these

17. The release of which of the following in the body causes allergy?
(a) Hydrochloric acid (b) Prostaglandins
(c) Noradrenaline   (d) Histamine

SECTION - IV
Matching List Type

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

List I (Polymer)	List II (Uses)
P. Bakelite	1. Unbreakable crockery
Q. Low density polythene	2. Electrical switches
R. Melamine-formaldehyde resin	3. Squeeze bottles
S. Polystyrene	4. Packaging material

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

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

List I	List II
P. Sodium perborates	1. Disinfectant
Q. Chlorine	2. Antiseptic
R. Bithional	3. Laundry bleaching agent
S. Potassium stearate	4. Soap

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

SECTION - V
Assertion Reason Type

20. **Assertion :** Rayon is a semi-synthetic polymer and is taken as a better choice than cotton fabric.
Reason : Mechanical and aesthetic properties of cellulose can be improved by acetylation.

21. **Assertion :** Antiseptics are applied to living tissues.
Reason : Iodine is a powerful antiseptic.

22. **Assertion :** Glyptal is obtained by condensation polymerisation of ethylene glycol and terephthalic acid.
Reason : Glyptal is used in the manufacture of fabrics.

Integer Value Correct Type

23. The number of artificial food sweeteners among the following is :
Alitame, butylated hydroxytoluene, sucralose, terfenadine, dulcin, cimetidine, saccharin, aspartame, sulphadiazine

24. Number of lone pairs present in monomer melamine is :

25. Number of monomers of polymer ABS is

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

SURFACE CHEMISTRY

1. **(c):** The viscosity of hydrophilic sols is higher and surface tension is lower than that of water (dispersion medium).

2. **(a):** Blood consists of negatively charged colloidal particles (albuminoid substances). Hence, Fe^{3+} ions of ferric chloride cause coagulation of blood by forming a clot which stops bleeding.

3. **(d):** Potassium stearate, having both hydrophilic and hydrophobic ends, forms associated colloid or micelle.

4. **(c)**   5. **(d)**   6. **(b)**   7. **(c)**

8. **(a):** Since the sol particles migrate towards cathode, they are positively charged. Hence, anions would be effective in coagulation. Greater the valency of effective ion, smaller will be its coagulation value.

9. **(a):** Smaller the value of gold number, greater is its protective power. Thus, protective powers of A, B, C and D are in the order :
D (0.005) > B (0.01) > C (0.10) > A (0.50)

10. **(a):** Initially the adsorption of a gas increases very rapidly as the pressure is increased. After some time it does not increase much on increasing pressure due to less availability of surface. At the equilibrium pressure, adsorption reaches its maximum value and then it remains constant even though pressure is increased.

11. **(a,b):** Each enzyme catalyses a particular reaction. Yeast also contains other enzymes like maltase.

12. **(a,b,c)**

13. **(a,b,c):** Solvent from the solution may be adsorbed on the adsorbent (negative adsorption).

14. **(d):** Milk, paint and shampoo are examples of colloidal systems. A colloidal solution is always a heterogeneous system instead of homogeneous system.

15. **(c):** In milk, liquid fat (dispersed phase) is dispersed in water (dispersion medium).

16. **(b):** Along A to C in the graph x/m will depend on P raised to the power $1/n$, where $1/n$ has the value between 0 to 1, $i.e.$, fractions.

17. **(b):** $\log \dfrac{x}{m} = \log k + \dfrac{1}{n} \log P$

$\dfrac{1}{n} = \tan 45°$; $\log k = 0.3010$

$\therefore$ $n = 1$; $\therefore$ $k = 2$

$\dfrac{x}{m} = kp^{\frac{1}{n}} \Rightarrow \dfrac{x}{m} = 2 \times (0.3)^1$

$x = 0.6$ g per gram of adsorbent
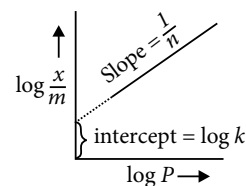
18. **(b)**   19. **(c)**

20. **(b):** Higher critical temperature implies that the intermolecular forces of attraction are strong and hence the adsorption is more.

21. **(b):** As_2S_3 being negatively charged, is coagulated faster by Ba^{2+} ions than by Na^+ ions.

22. **(a)**   23. **(3)**

24. **(6):** Aerosols are those in which gas is the dispersion medium. Smoke, dust, fog, clouds, insecticide sprays and mist are aerosols.

25. **(6):** 1 M oxalic acid solution contains 1 mole (126 g) of oxalic acid in 1000 mL of the solution.
$\therefore$ 50 mL of 1 M solution contains oxalic acid

$= \dfrac{126}{1000} \times 50 = 6.3\,g$

After adsorption, concentration of oxalic acid solution = 0.5 M
$i.e.$, 1000 mL of the solution contains oxalic acid
$= 0.5$ mole = 63 g
$\therefore$ 50 mL of the solution contains oxalic acid

$= \dfrac{63}{1000} \times 50 = 3.15\,g$

$\therefore$ Amount of oxalic acid adsorbed by 0.525 g of charcoal = 6.30 – 3.15 = 3.15 g

$\therefore$ Oxalic acid adsorbed per gram $\left(\dfrac{x}{m}\right)$

$= \dfrac{3.15}{0.525} = 6$
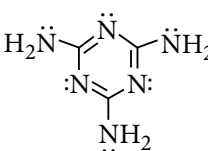
POLYMERS AND CHEMISTRY IN EVERYDAY LIFE

1. **(d):** Polymers having strongest intermolecular forces of attraction are called fibres. In case of nylon-6, 6 (polyamide) intermolecular forces of attraction are H-bonding while in dacron (polyester) and orlon (polyacrylonitrile) it is dipole-dipole interaction.

2. **(c):** Ibuprofen tablets contain both the *R*- and *S*-enantiomers, although only the *S*-enantiomer is effective. The *R*-enantiomer has no anti-inflammatory action but is slowly converted into *S*-enantiomer in the body.

3. **(c)**

4. **(b):** *N*-acetyl-para-aminophenol (paracetamol) can be used as analgesic without causing addiction and any modification.

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

6. **(d):** Nylon-6, 6 has strong intermolecular forces. It has amide linkages and therefore, has strong hydrogen bonding between two polyamides chains.

7. **(d):** $n\text{CH}_3{-}\text{CH}{=}\text{CH}_2 \longrightarrow \left(\!\!\begin{array}{c}\text{CH}_2{-}\text{CH}\\ |\\ \text{CH}_3\end{array}\!\!\right)_n$

   Propene → Polypropene

8. **(c)**   9. **(b)**
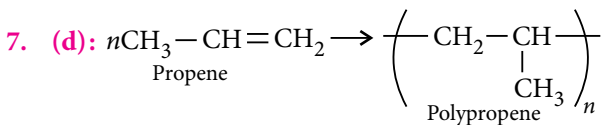
10. **(c):** Terylene is made from condensation polymerisation of ethylene glycol and terephthalic acid.

    $\text{HO}{-}\text{CH}_2{-}\text{CH}_2{-}\text{OH}$ and
    (Ethylene glycol)

    $\text{HOOC}{-}\langle\bigcirc\rangle{-}\text{COOH}$
    (Terephthalic acid)

11. **(a,b):** Barbiturates are hypnotics as well as tranquilizers.

12. **(b,c,d):** Polyisoprene, polyacetylene, and polybutadiene contain a double bond hence, show *cis-trans* isomerism.

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

14. **(d):** Neoprene, PVC and polythene are all addition homopolymers.

15. **(a):** Only cellulose is a condensation homopolymer while all others are condensation copolymers.

16. **(d)**   17. **(d)**

18. **(d)**   19. **(c)**

20. **(a)**

21. **(b):** Antiseptics are those chemicals which kill or prevent the growth of microorganisms. Antiseptics do not harm the living tissues and can be applied on cuts and wounds. They help to reduce odours resulting from the bacterial decomposition in the mouth and on the body.

22. **(d):** Glyptal is obtained by condensation polymerisation of ethylene glycol and phthalic acid and is used in manufacture of paints and lacquers.

23. **(5):** Alitame, sucralose, dulcin, saccharin and aspartame.

24. **(6):**

$$\text{H}_2\ddot{\text{N}}{-}\langle \overset{\displaystyle \ddot{\text{N}}}{\underset{\displaystyle :\text{N}{\diagdown}\text{N}:}{}}\rangle{-}\ddot{\text{N}}\text{H}_2$$
$$\underset{\ddot{\text{N}}\text{H}_2}{}$$

25. **(3):** Monomers of polymer ABS are acrylonitrile, butadiene and styrene.

⬦⬦

SOLUTIONS OF DECEMBER 2016 CROSSWORD

	¹B			²O						³K									⁶K			
	R			X			⁴A	⁵A	C	T	I	V	I	T	Y				E			
	I			I		⁷H	U	M	U	S		N							T			
	N		⁸D		R			⁹P	H	O	S	G	E	N	E				E			
¹¹G	E	M	I	N	A	L			H			¹⁰A	N	T	I	N	E	U	T	R	I	N	O
			F		N				O		¹²A	X	I	A	¹³L	A	T	T	I	C	E	
¹⁴B	U	F	F	E	R		¹⁵C		L		¹⁶D			C								
	U		I				H		Y		E			S			¹⁸C		¹⁹F			
	²⁰I	S	O	P	I	E	S	T	I	C	²¹C	¹⁷S	I	L	I	C	O	N	E	S		
			N				L		E		R	U					O		S			
²²A	E	R	O	S	O	L	A				C	Y	L		²³A	N	O	M	E	R	S	
²⁵F	R	E	O	N	S		T				T	O					P		A	²⁴H	E	L	I	U	M
	²⁶G	L	Y	C	O	G	E	N			I	S			H		B			O		
		Y									O	C		²⁸A	E	R	A	T	I	O	N	
		M									N	O		M			R			S		
		²⁹A	M	I	N	E	S	³⁰F	L	A	S	H	P	O	I	N	T					
		N										Y		C								

This specially designed column enables students to self analyse their extent of understanding of specified chapters. 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.

Aldehydes, Ketones and Carboxylic acids
Organic Compounds Containing Nitrogen

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

NEET / AIIMS
Only One Option Correct Type

1. Identify the final product B in the reaction :

$$\text{(structure)} \xrightarrow[\text{Zn, H}_2\text{O}]{\text{O}_3} A \xrightarrow[\text{Aldol, }\Delta]{\text{OH}^-} B$$

(a)

(b)

(c)

(d)
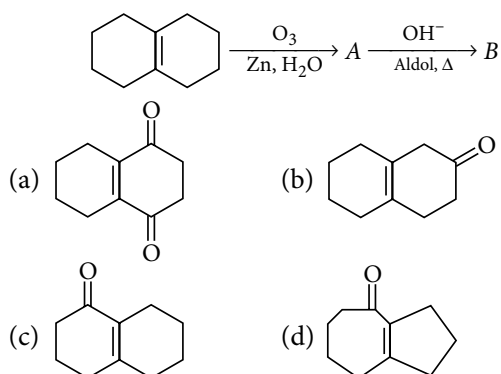
2. In the given reaction sequence

Phthalic acid $\xrightarrow{\Delta} A$

$A \xrightarrow{\text{NH}_3} B \xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} C \xrightarrow{\text{Br}_2/\text{KOH}} D \xrightarrow{\text{HCl}} E$
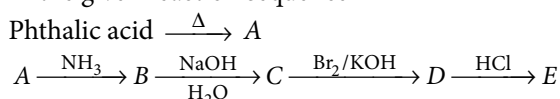
the product E is

(a) o-nitrobenzoic acid　(b) salicylic acid

(c) anthranilic acid　　　(d) crotonic acid.

3. $\text{F}-\text{C}_6\text{H}_4-\text{NO}_2 \xrightarrow[\text{(CH}_3)_2\text{NH}]{\text{DMF}} A \xrightarrow{\text{Sn/HCl}} B$

In the above sequence, B is

(a) $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{N(CH}_3)_2$

(b) $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$

(c) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{N(CH}_3)(\text{NH}_2)$

(d) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$
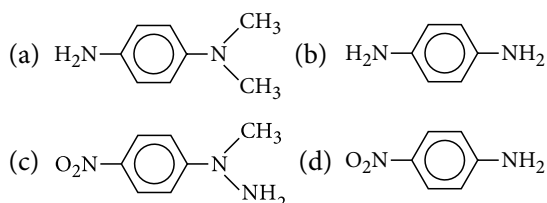
4. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute HCl. The compound so formed is treated with tetrafluoroborate which is subsequently heated dry. The final product is

(a) p-bromofluorobenzene

(b) p-bromoaniline

(c) 2, 4, 6-tribromofluorobenzene

(d) 1, 3, 5-tribromobenzene.

5. $\underset{\underset{\text{O}}{\|}}{\text{CH}_3-\text{C}-\text{CH}_3} \xrightarrow{\text{SeO}_2} X + \text{Se} + \text{H}_2\text{O}$, here X is

(a) $\text{CH}_3-\underset{\underset{\text{O}}{\|}}{\text{C}}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{H}$　(b) $\text{CH}_3-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{OCH}_3$

(c) $\text{CH}_3-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{CH}_2\text{OH}$　(d) None of these.
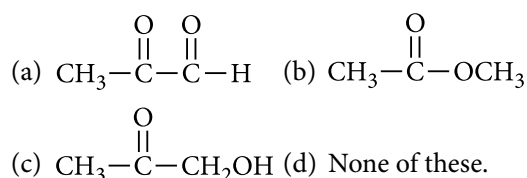
6. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is

(a) $B > A > D > C$　　　(b) $B > D > C > A$

(c) $A > B > C > D$　　　(d) $A > C > B > D$

7. Which of the following reactions does not yield an amine.
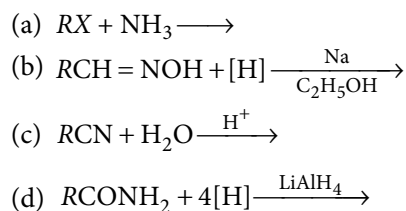
(a) $RX + \text{NH}_3 \longrightarrow$

(b) $R\text{CH} = \text{NOH} + [\text{H}] \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Na}}$

(c) $R\text{CN} + \text{H}_2\text{O} \xrightarrow{\text{H}^+}$

(d) $R\text{CONH}_2 + 4[\text{H}] \xrightarrow{\text{LiAlH}_4}$

8. In the given reaction,

$$CH_3 - \underset{\underset{O}{\parallel}}{C} - CH_2CH_2CH_2Cl \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} A,$$

A is

(a)
$$CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2CH_2CH_2Cl$$

(b)
$$CH_3 - \underset{\underset{O}{\parallel}}{C} - CH_2CH_2CH_2CH_3$$

(c) [structure: tetrahydrofuran ring with CH₃, CH₃ and O]

(d) [structure: oxetane ring with H₃C, CH₃, H₃C and O]
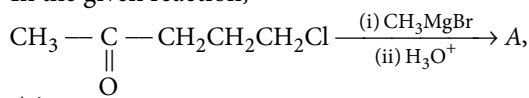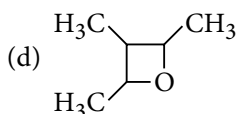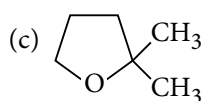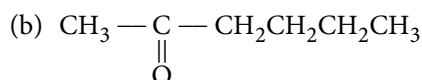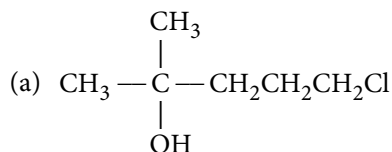
9. An organic compound, C_3H_9N (A) when treated with nitrous acid, gave an alcohol (B) and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (C) which on reduction gave isopropyl methyl amine. The structure of (A) is

(a) $\underset{CH_3}{\overset{CH_3}{>}}CH-NH_2$

(b) $CH_3CH_2-NH-CH_3$

(c) $CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$

(d) $CH_3CH_2CH_2-NH_2$
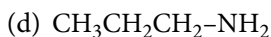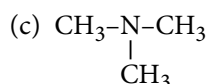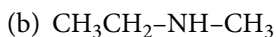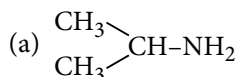
10. The correct set of reagents for the following conversion is

$$(CH_3)_2CHCOOH \longrightarrow$$ [cyclic anhydride structure with O, O, O]
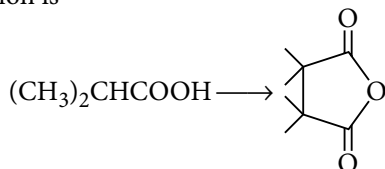
(a) P_4/Cl_2, Na, conc. H_2SO_4
(b) P_2O_5, $LiAlH_4$
(c) P_2O_5/Δ, H_2O, P_4/Cl_2, Na
(d) P_4/Cl_2, Na, P_2O_5/Δ

11. Cope elimination is an intramolecular E2 reaction because
(a) it is given by tertiary amine
(b) it is given by tertiary amine oxide containing β-hydrogen
(c) the nucleophile and leaving group are in the same molecule
(d) the less substituted alkene is the major product.

12. Amongst the acids,
(i) $CH \equiv CCOOH$ (ii) $CH_2 = CHCOOH$ and
(iii) CH_3CH_2COOH, the acidic strength follows the sequence
(a) (i) < (ii) > (iii)
(b) (i) > (ii) > (iii)
(c) (i) = (ii) = (iii)
(d) (i) = (ii) > (iii)

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 :** p-Methoxybenzaldehyde undergoes nucleophilic addition more readily than p-nitrobenzaldehyde.

Reason : The carbon atom of the aldehyde group is less electrophilic in p-nitrobenzaldehyde than in p-methoxybenzaldehyde.

14. **Assertion :** Aniline on reaction with $NaNO_2/HCl$ at 0°C followed by coupling with β-naphthol gives a dark blue precipitate.
Reason : The colour of the compound formed in the reaction of aniline with $NaNO_2/HCl$ at 0°C followed by coupling with β-naphthol is due to the extended conjugation.

15. **Assertion :** Oxidation of 1-nitronaphthalene gives 3-nitrophthalic acid while 1-aminonaphthalene on oxidation gives naphthalic acid.
Reason : An amino group attached to the benzene ring makes it resistant to oxidation whereas nitro group makes the benzene ring susceptible to oxidation.

JEE MAIN / JEE ADVANCED / PETs
Only One Option Correct Type

16. An ester 'A' with molecular formula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin 'B'. Ozonolysis of 'B' gave a ketone with molecular formula, C_8H_8O which shows positive iodoform test. The structure of 'A' is
(a) $C_6H_5COOC_2H_5$
(b) $CH_3COCH_2COC_6H_5$
(c) p-$CH_3O-C_6H_4-COCH_3$
(d) $C_6H_5COOC_6H_5$

17. Which pair of reactants would give the following amine by reductive amination?

$$X + Y \xrightarrow{H_2/pd.}$$ [structure with NH]
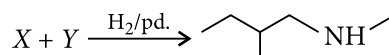
(a) Methyl amine and 2-methylbutanoic acid
(b) Ammonia and 3-methyl-2-pentanone
(c) Methyl amine and 2-methylbutanal
(d) Dimethyl amine and 2-butanone

18. Consider the following compounds,

I   II   III
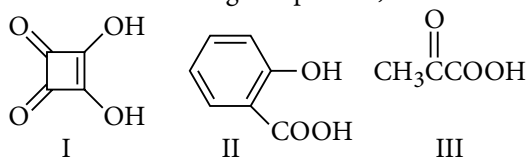
Which of the above compounds react with $NaHCO_3$ and give CO_2?
(a) I, II and III   (b) I and III
(c) II and III   (d) I and II

19. Which of the following compounds would have the smallest value for pK_a?
(a) $CHF_2CH_2CH_2COOH$
(b) $CH_3CH_2CF_2COOH$
(c) $CH_2FCHFCH_2COOH$
(d) $CH_3CF_2CH_2COOH$

More than One Options Correct Type

20. Which of the following conversions can be carried out by Clemmensen reduction?
(a) Benzaldehyde into benzyl alcohol
(b) Cyclohexanone into cyclohexane
(c) Benzoyl chloride into benzaldehyde
(d) Benzophenone into diphenylmethane

21. Reaction of $R-\overset{O}{\overset{||}{C}}-NH_2$ with a mixture of Br_2 and KOH gives $R-NH_2$ as the main product. The intermediates involved in this reaction are

(a) $R-\overset{O}{\overset{||}{C}}-NHBr$ (b) $R-NHBr$

(c) $R-N=C=O$ (d) $R-\overset{O}{\overset{||}{C}}-N\overset{Br}{\underset{Br}{}}$
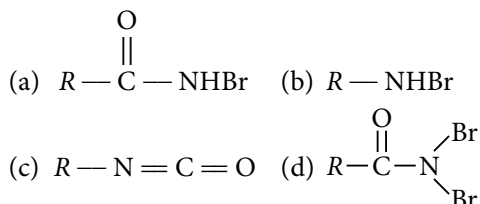
22. Arenium ion involved in the bromination of aniline is
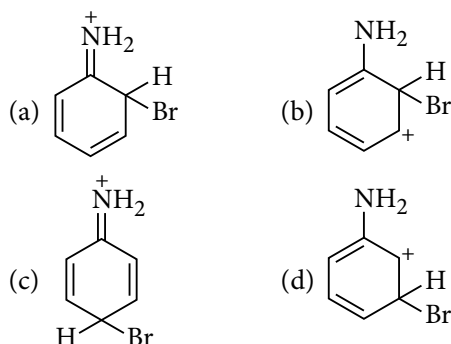
23. Which of the following compounds do not undergo aldol condensation?

(a) CH_3-CHO (b) —CHO

(c) $CH_3-\overset{O}{\overset{||}{C}}-CH_3$ (d) $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CHO$
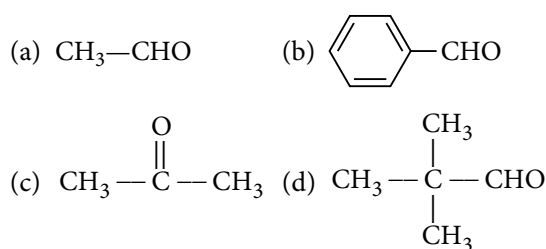
Integer Answer Type

24. How many of the following amines will undergo diazotisation?
tert-butyl amine, ethanamine, aniline, *N*-methylaniline, *p*-toluidine, *m*-chloroaniline, 2-phenylethanamine, *o*-anisidine, 2, 4, 6-tribromoaniline

25. Among the following, how many reagents can be used to reduce a $\rangle C=O$ group to a $-CH_2$ group? $LiAlH_4$, $NaBH_4$, H_2/Pd-C, Zn-Hg/HCl, NH_2NH_2/OH^-, HI/red P, Sn/HCl, $[(CH_3)_3CO]_3Al$, Mg-Hg/H_2O

26. How many of the following amines are more basic than aniline?
o-toluidine, *m*-toluidine, *p*-toluidine, *p*-anisidine, *m*-anisidine, *o*-anisidine, *p*-aminophenol, *m*-aminophenol, *o*-aminophenol

Comprehension Type

A carbonyl compound '*P*', which gives possible iodoform test undergoes reaction with MeMgBr followed by dehydration to give an olefin '*Q*'. Ozonolysis of '*Q*' leads to a dicarbonyl compound '*R*', which undergoes intramolecular aldol reaction to give predominantly '*S*'.

$$P \xrightarrow[\text{2. H}_2\text{SO}_4, \Delta]{\text{1. MeMgBr}} Q \xrightarrow[\text{2. Zn, H}_2\text{O}]{\text{1. O}_3} R \xrightarrow[\text{2. }\Delta]{\text{1. OH}^-} S$$
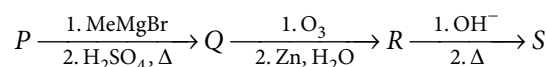
27. The structure of the carbonyl compound '*P*' is
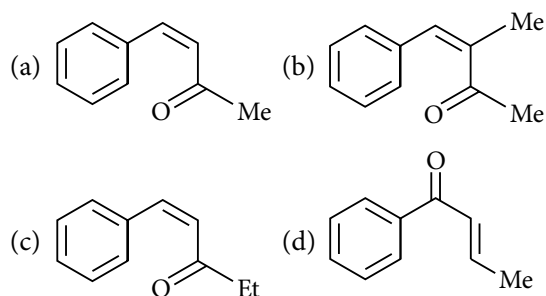
28. The structure of the product 'S' is

(a)

(b)

(c)

(d)

	A	B	C	D
(a)	P	P, Q, S	P, Q, S	Q, S, T
(b)	P, Q, S	P, Q, S	P	P, Q, S
(c)	P, Q, S	P	P, Q, S	P, Q, S
(d)	Q, S, T	P, Q, S	P, Q, S	P

30. Match each of the compounds in Column I with its characteristic reaction(s) in Column II.

Column I

(A) $CH_3CH_2CH_2CN$

(B) $CH_3CH_2OCOCH_3$

(C) $CH_3CH=CHCH_2OH$

(D) $CH_3CH_2CH_2CH_2NH_2$

Column II

(P) Reduction with Pd-C/H$_2$

(Q) Reduction with SnCl$_2$/HCl

(R) Development of foul smell on treatment with chloroform and alcoholic KOH

(S) Reduction with diisobutyl aluminium hydride (DIBAL–H)

(T) Alkaline hydrolysis

	A	B	C	D
(a)	P, Q, S, T	P	P, S, T	R
(b)	P	R	P, Q, S, T	P, S, T
(c)	R	P	P, S, T	P, Q, S, T
(d)	P, Q, S, T	P, S, T	P	R

Keys are published in this issue. Search now! ☺

Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I

(A)

(B)

(C) $CH_3CO(CH_2)_3CHO \xrightarrow[\Delta]{OH^-}$ Product

(D)

Column II

(P) Formation of six membered ring takes place.

(Q) Final product is ketone.

(R) Final product formed will give positive Tollens' test.

(S) Final product will react with 2, 4-DNP

(T) Final product have five membered ring.

CHEMISTRY MUSING

hemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / PMTs 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.

PROBLEM Set 42

JEE MAIN/NEET

1. 'X' is a colourless salt giving following reactions:

$$Y \xleftarrow{\text{NaOH}} X \xrightarrow{\text{AgNO}_3/\text{HNO}_3} \text{White ppt. soluble in } aq. \text{ NH}_3$$

Y = White ppt. which dissolves in excess of NaOH

$X \xrightarrow{\text{NH}_4\text{OH or H}_2\text{S}}$ White ppt.
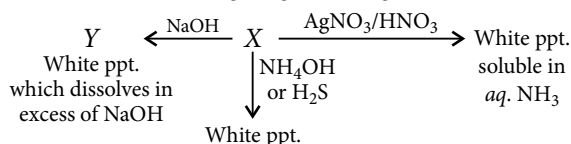
X can be
(a) $AlCl_3$
(b) $ZnCl_2$
(c) $(CH_3COO)_2Zn$
(d) $ZnBr_2$

2. Select the appropriate reagent for the following conversion.

   ⬡—CH=CH$_2$ ⟶ ⬡—CHCH$_3$ | OCH$_3$
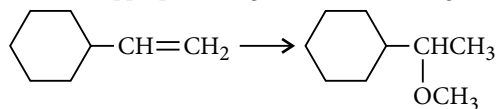
(a) H_3O^+/CH_3OH
(b) B_2H_6/H_2O_2, OH^-/CH_3OH
(c) $Hg(OAc)_2$, $CH_3OH/NaBH_4$, OH^-
(d) All of the above.

3. An electric current is passed through silver nitrate solution using silver electrodes. 10.79 g of silver was found to be deposited on the cathode. If the same amount of electricity is passed through copper sulphate solution using copper electrodes, the weight of copper deposited on the cathode is
(a) 1.6 g (b) 2.3 g (c) 3.2 g (d) 6.4 g

4. A dark brown solid (X) reacts with NH_3 to form a mild explosive which decomposes to give a violet coloured gas. (X) also reacts with H_2 to give an acid (Y). (Y) can also be prepared by heating its salt with H_3PO_4. X and Y are
(a) Cl_2, HCl
(b) SO_2, H_2SO_4
(c) Br_2, HBr
(d) I_2, HI

5. End product in the following sequence of reaction is

   ⬡—I $\xrightarrow{O_3/H_2O_2}$ $\xrightarrow{Ca(OH)_2}$ $\xrightarrow{\Delta}$ $\xrightarrow[OH^-/glycol]{NH_2-NH_2}$

(a) ▢ (b) ⬠ (c) cyclohexanone (d) ⬡
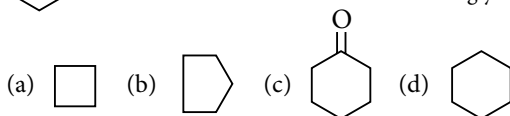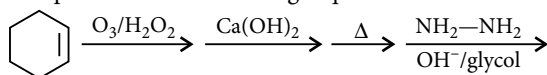
JEE ADVANCED

6. A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to take place for 10 hours, what percentage of the initial concentration would have changed into product?
(a) 5.26% (b) 6.26% (c) 7.26% (d) 8.26%

COMPREHENSION

The emission of an α or a β-particle by a radioactive element gives rise to a new element. However, successive emission of some α or β-particles may give rise to an isotope or an isobar of the original element. In a number of cases, positron emission or K-electron capture takes place, leading again to the formation of new elements, along with the emission of neutrinos or antineutrinos. These emissions also change the neutron/proton (n/p) ratio such that they give rise to stable isotopes which lie in the stability belt. However, in any disintegration reaction, the law of conservation of atomic number and mass number is always obeyed and this helps us to calculate the number of α and β-particles emitted in the reaction.

7. In nature a decay chain series starts with $_{90}Th^{232}$ and finally terminates at $_{82}Pb^{208}$. A thorium ore sample was found to contain 8×10^{-5} mL of He at STP and 5×10^{-7} g of Th^{232}. Find the age of ore sample assuming that source of He to be only due to decay of Th^{232}. Also assume complete retention of He within the ore. ($t_{1/2}Th^{232} = 1.39 \times 10^{10}$ year)
(a) 2.89×10^9 year
(b) 3.89×10^9 year
(c) 4.89×10^9 year
(d) 5.89×10^9 year

8. A positron and an electron collide and annihilated to emit two gamma photons of same energy. Calculate the wavelength corresponding to this gamma emmission.
(a) 2.425 nm
(b) 2.425 pm
(c) 3.425 nm
(d) 3.425 pm

INTEGER VALUE

9. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. The value of $\dfrac{[t_{1/8}]}{[t_{1/10}]} \times 10$ is

10. A mixture of N_2 and H_2 in the molar ratio 1 : 3 attains equilibrium when 50% of mixture has reacted. If P is the total pressure of the mixture, the partial pressure of NH_3 formed is P/y. The value of y is

◈ ◈

2 **CHEMISTRY TODAY** | JANUARY '17

Hi all!! Now the time has come when we have to practice a lot. Probably all are done with the theory part. What we have to do now is to maintain the proper timing while solving a question. This article is for that help only. Ideal time to solve the whole paper (taking care of the difficulty level) is 50 minutes. Happy practicing, thank you!

*Arunava Sarkar

TYPE-1 : SINGLE OPTION CORRECT

1. Identify the product in the following reaction.

aq. NaOH →

(a) 3 (phenol)

(b) $Ph_2C(OH)F$

(c) (triphenylmethanol structure) C—OH

(d) None of these

2. Identify the product.

$(CH_3)_4\overset{+}{N}\overset{-}{O}\overset{O}{\overset{\|}{C}}CH_3$ → ?

(a) $(CH_3)_3N$ + (structure) + $\bar{O}Bs$

(b) (cyclobutane structure with OCOCH₃ and t-C₄H₉)

(c) (cyclobutane structure with C₄H₉)

(d) (cyclobutane structure with OCOCH₃ and t-C₄H₉)

3.
$$\begin{array}{c} Br \\ H \longrightarrow Ph \\ EtO \longrightarrow H \\ Ph \end{array} \xrightarrow[acetone]{NaI} ?\ (Major\ product)$$

(a)
$$\begin{array}{c} I \\ Ph \longrightarrow H \\ EtO \longrightarrow H \\ Ph \end{array}$$

(b)
$$\begin{array}{c} I \\ H \longrightarrow Ph \\ EtO \longrightarrow H \\ Ph \end{array}$$

(c)
$$\begin{array}{c} I \\ H \longrightarrow Ph \\ H \longrightarrow OEt \\ Ph \end{array}$$
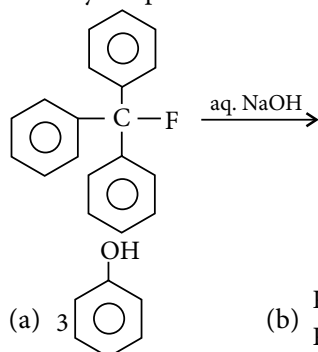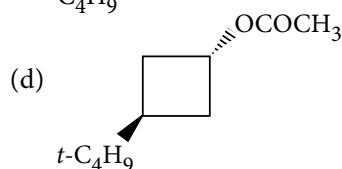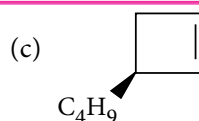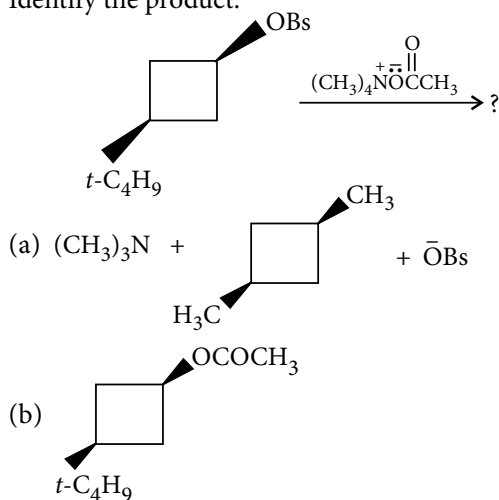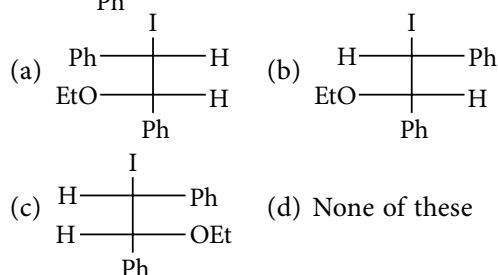
(d) None of these

4. Arrange the following according to the increasing order of reactivity in S_N2 reaction :
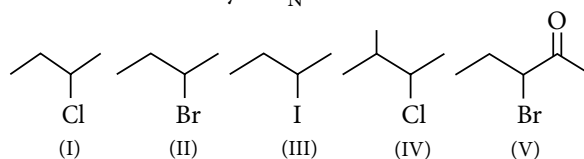
(a) I < II < III < IV < V
(b) II < III < I < IV < V
(c) III < I < II < IV < V
(d) None of these

5. The following compound on hydrolysis in aqueous acetone will give

$P = H_3CO$ —[benzene ring]— $C(Me)(H)-C(OH)(Me)-C(Me)(Me)$ —[benzene ring]— NO_2

(structures P, Q, R with Me, OH, H substituents)

$P = H_3CO$—⟨ring⟩— $\overset{Me}{\underset{H}{C}}$ $\overset{Me}{\underset{OH}{C}}$ $\overset{Me}{\underset{Me}{C}}$ —⟨ring⟩—NO_2

$Q = H_3CO$—⟨ring⟩— $\overset{Me}{\underset{OH}{C}}$ $\overset{Me}{\underset{H}{C}}$ $\overset{Me}{\underset{Me}{C}}$ —⟨ring⟩—NO_2

$R = H_3CO$—⟨ring⟩— $\overset{Me}{\underset{H}{C}}$ $\overset{Me}{\underset{Me}{C}}$ $\overset{Me}{\underset{OH}{C}}$ —⟨ring⟩—NO_2
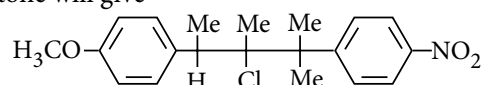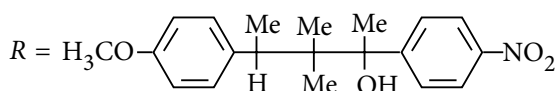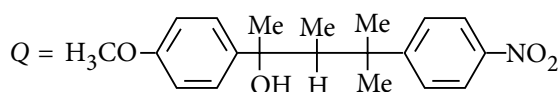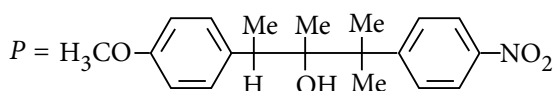
(a) a mixture of *P* and *Q*
(b) a mixture of *P* and *R*
(c) a mixture of *Q* and *R*
(d) only *R*.

6. In the following compounds, nucleophile and the leaving groups are in the same molecule :

TsO〜〜$\overset{..}{O}{}^{..}$ (I)   TfO〜〜〜$\overset{..}{O}{}^{..}$ (II)
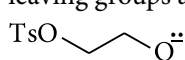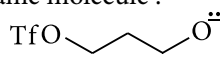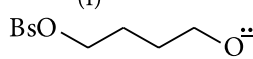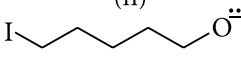
BsO〜〜〜〜$\overset{..}{O}{}^{..}$ (III)   I〜〜〜〜〜$\overset{..}{O}{}^{..}$ (IV)

All the species here show dual nature *i.e.*, they can undergo both inter and intramolecular substitution reactions. For which of the given species intramolecular substitution is most feasible?
(a) I, II   (b) II, III   (c) III, IV   (d) IV

7. In the following reaction,

$\overset{Me}{\underset{Ph}{\underset{|}{\overset{|}{D-\overset{|}{C}-Cl}}}}$
$H-\overset{|}{C}-Br$ $\xrightarrow[\text{DMSO}]{\text{NaSH (1 eq.)}}$ Major product
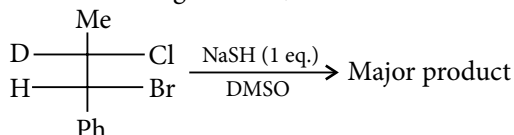
Which of the following options has the correct features for reaction mechanism, leaving group and stereochemistry?
(a) S_N2/Cl^-/inversion   (b) S_N2/Br^-/inversion
(c) S_N1/Br^-/racemisation
(d) $E2/Br^-$/anti-elimination

8. Which of the following compounds is most rapidly hydrolysed by S_N1 mechanism?
(a) C_6H_5Cl (b) $Cl-CH_2-CH=CH_2$
(c) $(C_6H_5)_3CCl$ (d) $C_6H_5CH_2Cl$

9. Consider the following compounds :
I = Acetanilide ($PhNHCOCH_3$)
II = Aniline ($PhNH_2$)
III = Benzene (C_6H_6)

IV = Acetophenone $\left(Ph-\overset{\overset{O}{\|}}{C}-CH_3 \right)$

The correct order of increasing reactivity towards electrophile (E^+) is

(a) IV < III < II < I   (b) II < III < IV < I
(c) I < II < III < IV   (d) none of these.

10. Isomeric isobutanes are :
(P) $(CH_3)_3CI$ (Q) $CH_3CH_2\overset{|}{\underset{CH_3}{C}}HI$

(R) $(CH_3)_2CHCH_2I$ (S) $CH_3CH_2CH_2CH_2I$
Arrange these according to the increasing order of reactivity in S_N2 reaction.
(a) P < Q < R < S   (b) P < R < Q < S
(c) S < R < P < Q   (d) None of these

11. Identify the product in the following reaction.

$\overset{HO-CEt_2}{\underset{Me}{\underset{(R \text{ isomer})}{}}}CH-Cl \xrightarrow{\overset{..}{\underset{..}{O}}H}$

(a) $HO-C\overset{Et}{\underset{CHMe}{\diagdown}}$ (b) $HO-CEt_2$ $\overset{}{\underset{Me}{}}CH-OH$ (R)
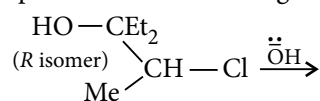
(c) $\overset{HO-CEt_2}{\underset{Me}{}}CHOH$ (S) (d) Both (b) and (c)

12. $R-X + KCN \longrightarrow RCN + KX$
Which of the following solvents will favour this reaction?
(a) Ethanol   (b) Ethyl acetoacetate
(c) DMSO   (d) None of these

13. In which of the following cases S_N1 and S_N2 products will be same? (Excluding stereoisomers)
(a) $Ph-CH_2-\overset{|}{\underset{Br}{C}}H-CH_3$

(b) [cyclohexane ring with two Br substituents]

(c) [cyclohexane ring with Me and Br substituents]
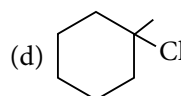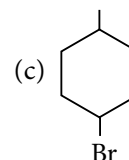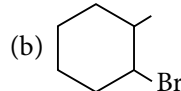
(d) [cyclohexane ring with Cl substituent]

1. Which of the following statements is(are) correct?

(a) MeO—⟨ring⟩—CH_2Cl prefers to undergo S_N1 reaction mechanism.

(b) O_2N—⟨ring⟩—CH_2Cl prefers to undergo S_N2 reaction mechanism.

(c) $MeO-CH_2Cl$ prefers to undergo S_N1 mechanism.

(d) NaCl will provide better nucleophile than NaBr in DMSO.

2. MeO-...-$\underset{Br}{\overset{Me}{|}}$ $\xrightarrow{AcOH}$ Products 1, Reaction 1

MeO-...-$\underset{Br}{}$ $\xrightarrow{AcOH}$ Products 2, Reaction 2

(R)-Pentan-2-ol $\xrightarrow[\text{(ii) } CH_3CH_2I]{\text{(i) } NaH}$ Product 3, Reaction 3

(R)-Pentan-2-ol $\xrightarrow[\text{pyridine}]{TsCl}$ $\xrightarrow[\text{EtOH}]{NaOEt}$ Product 4, Reaction 4
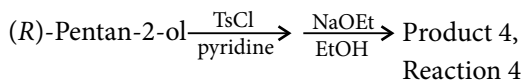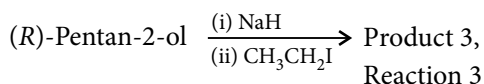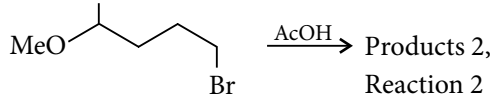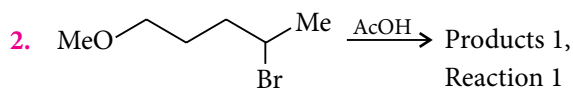
Which of the following statement(s) is(are) correct?
(a) Products 1 and products 2 are same.
(b) Products 1 and products 2 are different.
(c) Product 3 will have R and product 4 will have S-configuration.
(d) Product 3 will have S and product 4 will have R-configuration.

3. Which of the following statements is(are) correct?

(a) [structure with H, H, H, I^{127}] will undergo faster S_N2

reaction than [structure with I^{127}, H, H, H]

(b) [cyclopentane structure with OBs and NMe₂] $\xrightarrow[CH_3COOH]{CH_3COONa}$ Product(s)

[cyclopentane structure with OBs and NMe₂] $\xrightarrow[CH_3COOH]{CH_3COONa}$ Product(s)
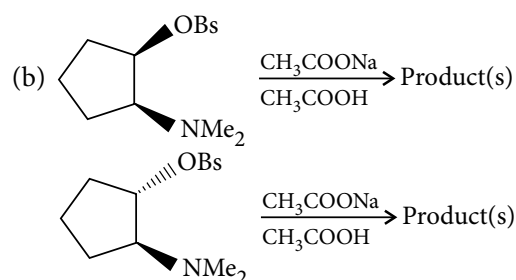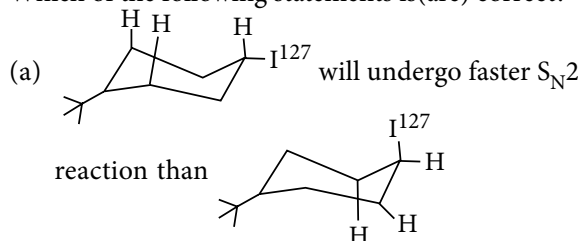
In both the cases, same product(s) will be obtained.

(c) $Et\ddot{\overset{..}{O}} > Ph\ddot{\overset{..}{O}} > CH_3C\ddot{\overset{..}{O}}O$, correct order of nucleophilicity is shown here.

(d) $(CH_3)_3CI < (CH_3)_2CHCH_2I < CH_3CH_2\underset{\overset{|}{CH_3}}{CHI}$

$< CH_3CH_2CH_2CH_2I$

Correct order of reactivity in S_N2 reaction is shown here.

TYPE-3 : INTEGER TYPE QUESTIONS

1. The number of fractions obtained after the reaction completion is

[structure: Me, Me, Ph, Ph, Br, Et] $\xrightarrow{CH_3OH}$
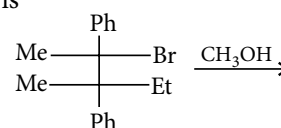
2. $CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3 \xrightarrow{Cl_2, h\upsilon} X$ (total no. of isomeric products)

$X = ?$

Detailed solutions will be published in next issue.

■■

ADVANCED CHEMISTRY BLOC

(THERMODYNAMICS)

Mukul C. Ray, Odisha

Cyclic rule in thermodynamics has its own importance. Hardly, we see books showing its applications. This small article will show you the need of applications of cyclic rule. Also read this small article to discover the existence of two inversion temperatures for gases; which we generally ignore.

CYCLIC RULE

⭕ **Applications of cyclic rule in thermodynamics and joule-thomson coefficient**

The cyclic rule in thermodynamics says

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1 \ \text{for} f(x, y, z) = 0$$

The applications of cyclic rule :

Irrespective of physics or chemistry, if we have to find out $\left(\frac{\partial P}{\partial T}\right)_V$ for a real gas.

We know that, for a real gas,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

or, $\left(P + \frac{an^2}{V^2}\right) = nRT(V - nb)^{-1}$

or, $P = nRT(V - nb)^{-1} - an^2V^{-2}$

Thus, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb}$

Now, Let's find out $\left(\frac{\partial P}{\partial V}\right)_T$ for the same real gas,

$$\left(\frac{\partial P}{\partial V}\right)_T = nRT(-1)(V - nb)^{-2} - an^2(-2)V^{-3}$$

or, $\left(\frac{\partial P}{\partial V}\right)_T = \frac{-nRT}{(V - nb)^2} + \frac{2an^2}{V^3}$

Now, if we have to find $\left(\frac{\partial V}{\partial P}\right)_T$ for the real gas.

First we have to derive using $V = f(T, P)$ and then find $\left(\frac{\partial V}{\partial P}\right)_T$, surely will be difficult to find.

Now, by applying cyclic rule

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\left(\frac{\partial P}{\partial V}\right)_T}$$

Thus, $\left(\frac{\partial V}{\partial P}\right)_T = \frac{(V - nb)^2 V^3}{-nRTV^3 + 2an^2(V - nb)^2}$

[Using the expression of $\left(\frac{\partial P}{\partial V}\right)_T$ as shown above]

Similarly, if we have to find $\left(\frac{\partial V}{\partial T}\right)_P$ for the real gas. Again the same difficult situation. First find $V = f(T, P)$ and then $\left(\frac{\partial V}{\partial T}\right)_P$

Alternatively, using cyclic rule

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V (-1) = \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial P}\right)_T}$$

⭕ **Thermal expansion coefficient and isothermal compressibility**

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

β is the volumetric thermal expansion coefficient.

β has the unit K^{-1} and usually $\beta > 0$.

Similarly, $\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

'α' has the unit bar^{-1} and $\alpha > 0$.

α is the isothermal compressibility. Questions on α and β are frequently observed in both physics and chemistry.

Before moving ahead, just imagine why volume has been divided into both α and β expressions. The reason is to make α and β extensive properties. Clearly, with dimension of K^{-1} for β and bar^{-1} for α, they are now extensive properties.

Now, another application of thermodynamics is :

For an ideal gas, $V = \dfrac{nRT}{P}$

$$\therefore \quad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \cdot \frac{P}{nRT} = \frac{1}{T}$$

$$\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -(-)\frac{nRT}{P^2} \cdot \frac{P}{nRT} = \frac{1}{P}$$

Suppose if we have to measure $\left(\dfrac{\partial P}{\partial T}\right)_V$, it will be difficult to measure. Rather, it is obtained by applying the cyclic rule.

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = -\left(-\frac{1}{\alpha V}\right)\times \beta V = \frac{\beta}{\alpha}$$

Thus, $\left(\dfrac{\partial P}{\partial T}\right)_V$ is obtained as $\dfrac{\beta}{\alpha}$.

JOULE-THOMSON EXPERIMENT

cotton plug
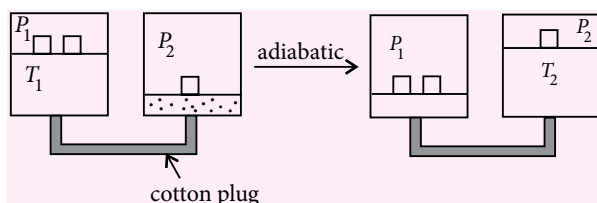
A gas (may be ideal or real though ideal gases have $\mu_{J.T.} = 0$) is allowed to undergo adiabatic expansion through a porous plug from a region of high pressure to low pressure. A change in temperature is noted.

Joule-Thomson coefficient $(\mu_{J.T.}) = \left(\dfrac{\partial T}{\partial P}\right)_H$

T and P both are intensive property. So the ratio $\mu_{J.T.}$ is also an intensive property. Like any other intensive property, it is a function of T and P and also depends on nature of the gas.

Assume that P_1 and T_1 are the initial pressure and temperature of the gas on the left hand side. Pressure on the right hand side is maintained at P_2. The temperature measured is T_2.

Note that $P_2 < P_1$. The two points (T_1, P_1) and

(T_2, P_2) are shown by 1 and 2 in a T-P curve. The two states 1 and 2 have the same enthalpy H. The same experiment is now repeated with the same initial P_1, T_1 but different new values P_3, P_4 etc. maintained on the right hand side. The corresponding temperatures measured are T_3, T_4 etc. These points are shown as 3, 4 etc. in the diagram.

Initially, while moving from P_1 to P_2, you are moving in the direction of low pressure (as $P_2 < P_1$). So ΔP is −ve. If temperature increases then ΔT is +ve and $\mu_{J.T}$ is negative. As it can be seen from the isenthalpic curve, $\mu_{J.T}$ value changes sign from point G. This curve is called isenthalpic curve. Slope of this curve at any point gives $\mu_{J.T}$, as the slope of the line is $\left(\dfrac{\partial T}{\partial P}\right)_H$.
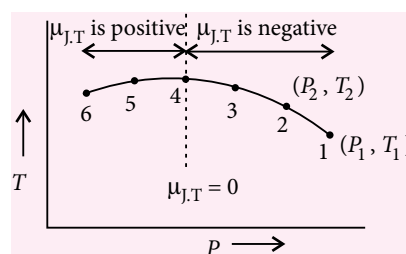
The temperature at which $\mu_{J.T}$ changes sign is called inversion temperature.

If different isenthalpic curves are drawn starting with different initial pressure.
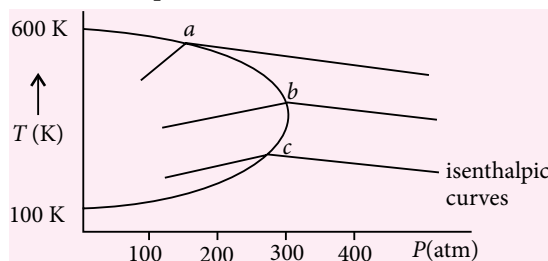
For each curve there is a T_i (where $\mu_{J.T.} = 0$). The different T_i are noted as a, b and c. On joining these points, an inversion curve for N_2 obtained. Thus, a gas typically have different inversion temperatures. For N_2, the maximum inversion temperature is 600 K and the minimum inversion temperature is 100 K (when $P \to 0$). For H_2 and He, the maximum upper T_i values are 204 K and 43 K respectively. Hydrogen and helium thus show heating effect in Joule-Thomson expansion when carried out at room temperature while other gases show cooling effect.
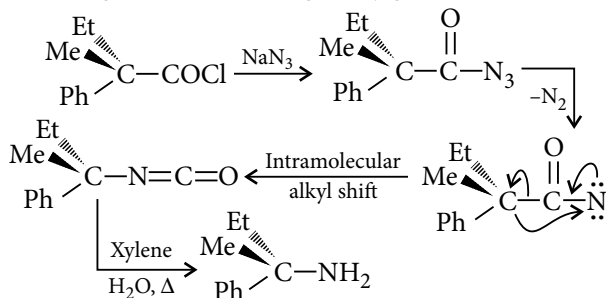
◈ ◈

CHEMISTRY MUSING

SOLUTION SET 41

1. (b) :
$$2H_5IO_6 \xrightarrow[-4H_2O]{100°C} 2HIO_4 \xrightarrow{200°C} I_2O_5 + O_2$$
Orthoperiodic acid · · · Metaperiodic acid · · · Iodine pentoxide
$$+ H_2O$$
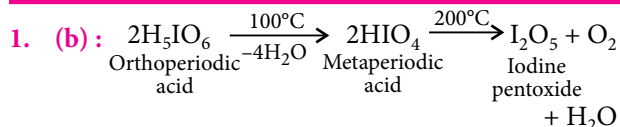
2. (a) : Curtius rearrangement involves retention of configuration of the migratory group. Thus,

3. (a) : $\frac{1}{2}mu^2 = 0.0327 \times 1.6 \times 10^{-19}$ J

$\therefore \quad u^2 = \frac{2 \times 0.0327 \times 1.6 \times 10^{-19}}{1.675 \times 10^{-27}} = 625 \times 10^4$

$\therefore \quad u = 2500$ m/s

Time taken to travel 100 metre $= \frac{100}{2500} = 0.04$ sec

Thus, $\frac{dN}{N} = \lambda . dt$

$\therefore \quad \frac{dN}{N} = \frac{0.693}{700} \times 0.04 = 3.96 \times 10^{-5}$

4. (b): Product (b) is obtained due to the strong electron withdrawing effect of the —CN group, rendering the secondary carbocation less stable than the primary carbocation.

5. (c) :

p-Toluidine ... ... *p*-Toluic acid
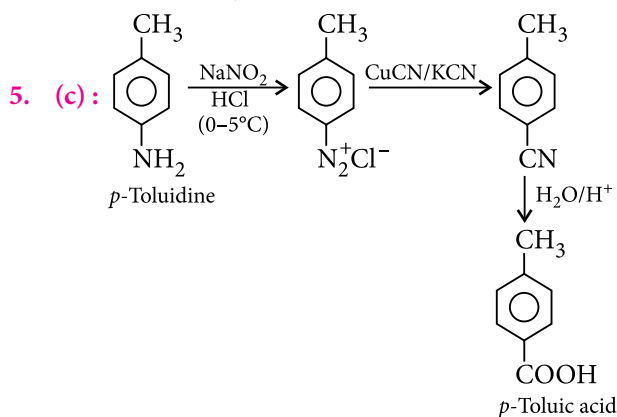
6. (a) : Milliequivalents of alkali (meq.)
$$= \frac{1}{10} \times 15.1 = 1.51$$

meq. of the acid = 1.51

$\therefore$ eq. of acid $= \frac{1.51}{1000} = 0.00151$

Now, equivalent of acid

$= \frac{\text{weight in grams}}{\text{equivalent weight}} = \frac{0.2}{\text{eq. wt.}} = \frac{0.2}{M}$

[for monobasic acid, eq. wt. = mol. wt. (M)]

$\therefore \quad \frac{0.2}{M} = 0.00151 ; M = 132.45$

$\therefore$ Molality of the acid (m)

$= \frac{\text{moles of solute}}{\text{wt. of solvent in grams}} \times 1000$

$= \frac{1}{132.45} \times \frac{1000}{100} = .076$

We have, (ΔT_f) normal $= K_f . m = 1.86 \times 0.076 = 0.141$

$\therefore \quad i = \frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{normal}}} = \frac{0.168}{0.141} = 1.19$

The monobasic acid (say AH) ionises as
$$AH \rightarrow A^- + H^+$$
moles before diss. : · · 1 mole · · 0 · · 0
moles after diss. : · · $(1 - x)$ · · x · · x
$(x = $ degree of dissociation$)$
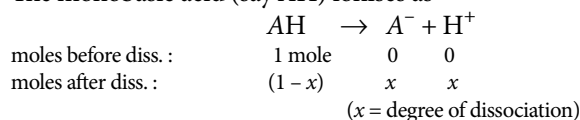
$i = \frac{1 - x + x + x}{1} = 1.19$

$\therefore \quad x = 0.19$

7. (c) · · · · · · · · **8. (b)**

9. (3) : Since, water vapour condenses to practically zero volume of water, the decrease in volume on cooling is the volume of water vapour. CO_2 is absorbed by KOH and so volume of CO_2 is equal to 48 mL.

Thus,
$$C_xH_y \text{ (say)} + O_2 \longrightarrow CO_2 + H_2O$$
· · · · 16 mL · · · · · · · · · 48 mL · · 48mL
or · · 16 moles · · · · · · · · 48 moles · 48 moles
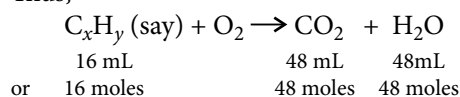
Since, C and H are completely converted to CO_2 and H_2O respectively, applying POAC for C and H atoms we get respectively,

$x \times$ moles of $C_xH_y = 1 \times$ moles of CO_2

· · 16x = 48 · · · · · · · · $\therefore \quad x = 3$

$y \times$ moles of $C_xH_y = 2 \times$ moles of H_2O

· · 16y = 2 × 48 · · · · · · · $\therefore \quad y = 6$

Hence, the formula of the hydrocarbon is C_3H_6.
Thus, there are 3 carbon atoms in the hydrocarbon.

10. (0) : In given complex, Cr is in + 1 oxidation state

$Cr^+ = d^5$ · · (because $\mu = \sqrt{3}$ B.M.)

◈ ◈
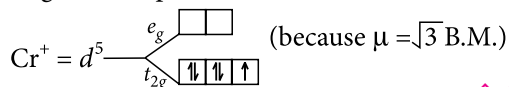
CROSSWORD

Readers can send their responses at editor@mtg.in or post us with complete address by 25th of every month to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.

ACROSS

1. The distance between two successive crests of a wave, especially points in a sound wave or an electromagnetic wave. (10)

3. Another name for 2-ethoxyethan-1-ol which is used as a solvent in the plastic industries. (10)

6. A colourless mineral consisting of magnesium oxide, occurring chiefly in marble and limestone. (9)

7. A colourless crystalline compound which is the basis of a number of white or yellow plant pigments. (7)

11. An orbital can have maximum two electrons and the electrons must have_____spins. (8)

14. A carbohydrate with seven carbon atoms. (7)

15. The amount of matter that a body contains is called _____. (4)

16. Apparatus used for the preparation of ozone by passing oxygen through an electrical discharge. (8)

18. A vitamin neither soluble in water nor in fat. (6)

20. Solvents which have the tendency to produce protons. (10)

23. Substances with different chemical composition but the same crystalline structure. (7)

26. A biological molecule that catalyses reactions in living things. (6)

28. A substance which possesses identical physical properties in all directions in its crystal form. (9)

29. A glassy lustre or sheen on a mineral surface. (8)

30. The spectroscopic notation used to denote an electronic state is called _____ symbol. (4)

DOWN

2. Process by which acetaldehyde is manufactured from ethylene. (6)

4. An organic compound whose molecule contains a three membered ring involving an oxygen atom and two carbon atoms. (7)

5. A highly flammable sticky jelly used in incendiary bombs and flame-throwers consisting of petrol thickened with special soaps. (6)

8. A French chemist who originated the sodium fusion test. (9)

9. Features that include the colour, mass, volume, density, etc. are called _____ properties. (8)
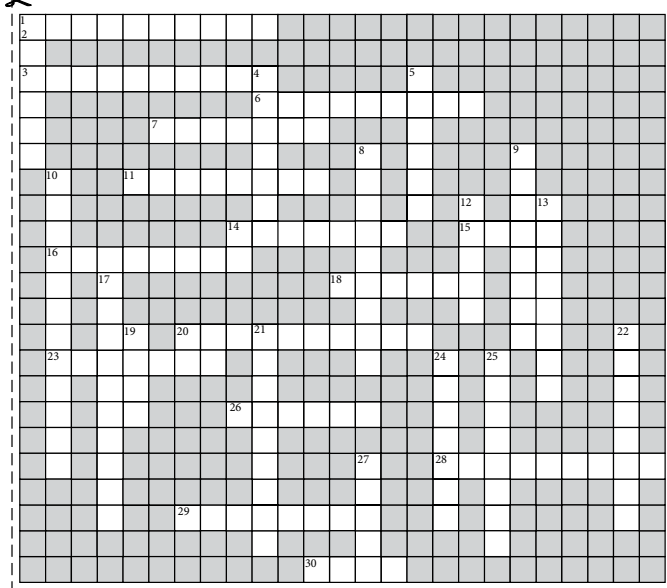
10. A rare pale greenish-yellow mineral which is used as a source of Sr compounds. (12)

12. A compound which contains nitrogen, can be synthesised by refluxing a halogenalkane with ammonia in alcohol. (5)

13. They have different number of protons but same number of neutrons. (8)

17. A tetragonal fluoride and chloride of lead PbFCl, usually occurring as transparent, colourless to yellow or yellowish brown tabular crystals. (10)

19. The attraction and repulsion between atoms and molecules which is a cornerstone of chemistry. (4)

21. The fraction of the total current carried by a particular ion during electrolysis is _____ number. (9)

22. A thermodynamic property of a real gas which if substituted for the pressure or partial pressure in the equations for an ideal gas gives equations applicable to the real gas. (8)

24. An igneous rock extensively used as a building stone. (7)

25. An element which is most abundant in the universe. (8)

27. A device that produces highly intense electromagnetic waves in the microwave region. (5)