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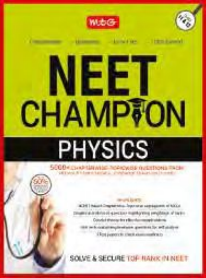
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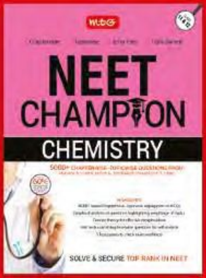
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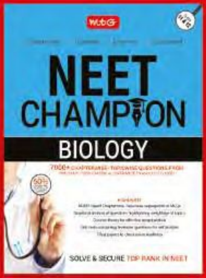
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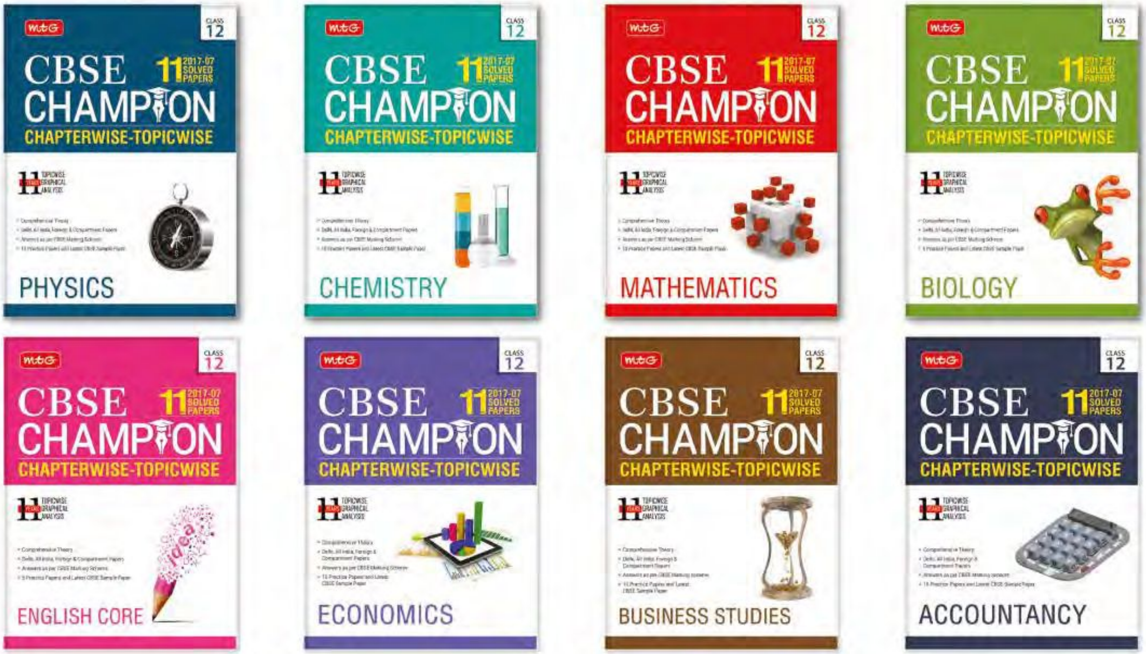

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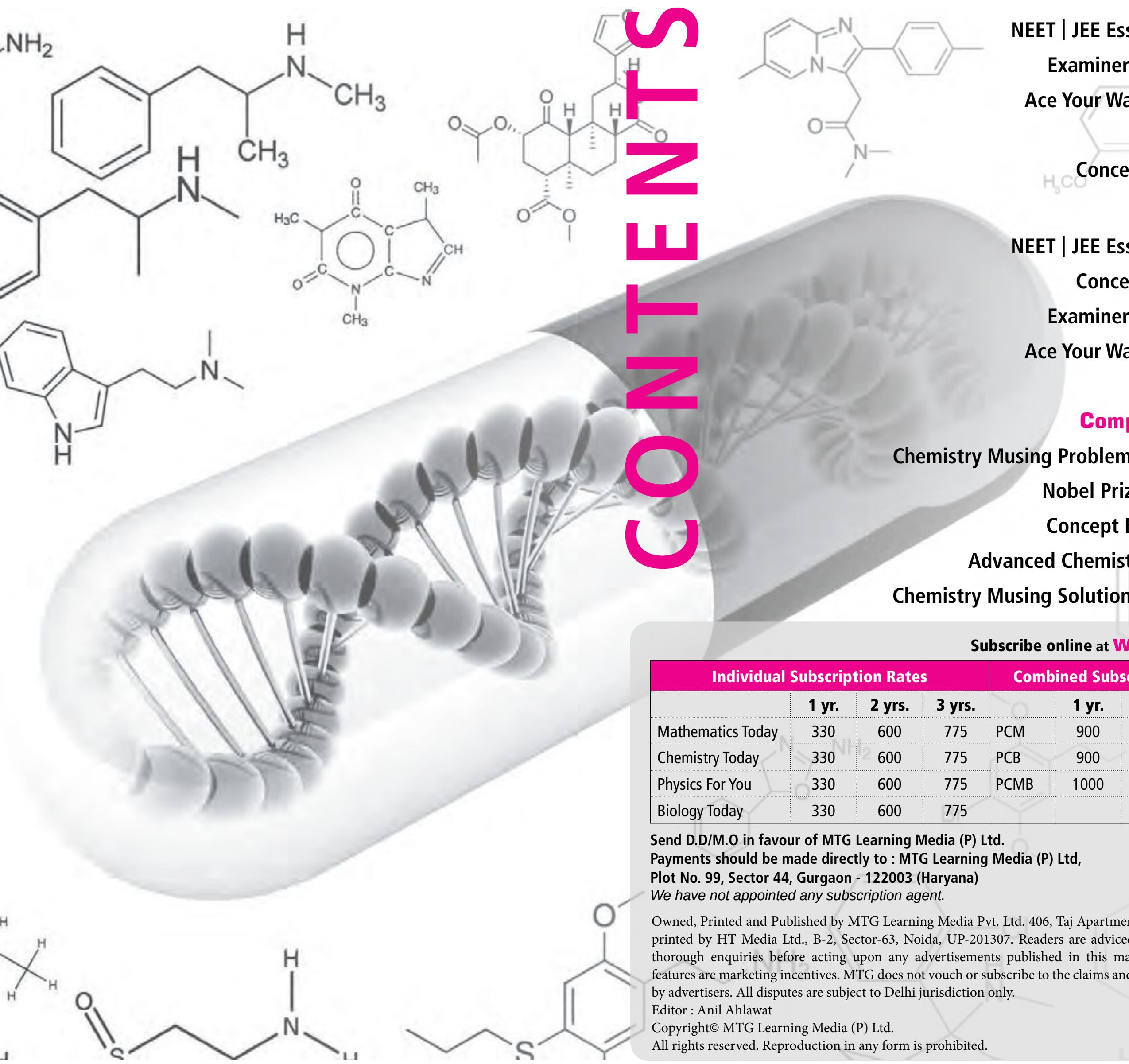

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NEET | JEE ESSENTIALS

Class
XI

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Unit 5

Hydrogen | The *s*-Block Elements

HYDROGEN

INTRODUCTION

Hydrogen is the first and lightest element in the periodic table. It was discovered by Henry Cavendish in 1766. He prepared the gas by treating iron with dil. H_2SO_4. Name 'hydrogen' was proposed by Lavoisier because it produces water on burning with oxygen (in Greek : hydra means water, gene means producing).

H Hydrogen

Symbol : H

Atomic Number : 1

Electronic configuration : $1s^1$

Molecular forms : H_2, D_2, T_2, HD

Isotopes : Protium, ${}^1_1H$; Deuterium, ${}^2_1H$ or D; Tritium, ${}^3_1H$ or T

Ionic forms : H^-, H^+, H_2^+, H_3^+

Position of Hydrogen in Periodic Table

Resemblance with alkali metals due to

1. Electronic configuration (ns^1): $1s^1$
2. Electropositive character, (M^+) : H^+
3. Oxidation state (+1) : $\overset{+1}{H}\overset{-1}{Cl}$, $\overset{+1}{Na}\overset{-1}{Cl}$

Resemblance with halogens due to

1. Electronic configuration : One e^- less than the nearest inert gas configuration.
2. Electronegative character : Both have tendency to accept one e^- to form anions.
3. Ionisation energy : Comparable with halogens.

Differences from alkali metals and halogens

1. Less electropositive than alkali metals and less electronegative than halogens.
2. Nature of oxides : Oxide of hydrogen is neutral *i.e.* H_2O while alkali metals form basic and halogens form acidic oxides.
3. Size of ions : H^+ is much smaller than alkali metal ions and H^- is much larger than halide ions.


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DIHYDROGEN

Preparation

- **Laboratory Method :** In laboratory, hydrogen is prepared by the action of dilute suphuric acid on granular zinc in the Woulfe bottle.
  $Zn + H_2SO_{4(dil.)} \longrightarrow ZnSO_4 + H_2$
- **Commercial methods :**

(i) By electrolysis of water

$$2H_2O_{(l)} \xrightleftharpoons{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$$

(ii) From syngas (Bosch process)

$$C_{(s)} + H_2O_{(g)} \xrightarrow[\text{Ni}]{1270\text{ K}} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}} - 121.3\text{ kJ}$$

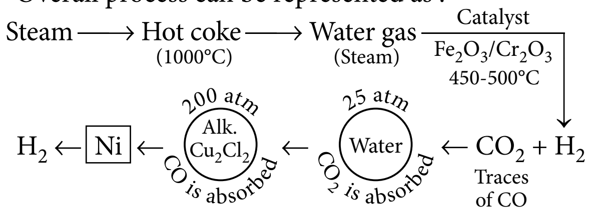
This process is called coal gasification.

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$$\underbrace{CO_{(g)} + H_2O_{(g)}}_{\text{Syngas}} + \underset{\text{Steam}}{H_2O_{(g)}} \xrightarrow[\text{catalyst}]{673\text{ K}} CO_{2(g)} + 2H_{2(g)}$$

This is called water-gas shift reaction.

Overall process can be represented as :



- **Lane's Process**

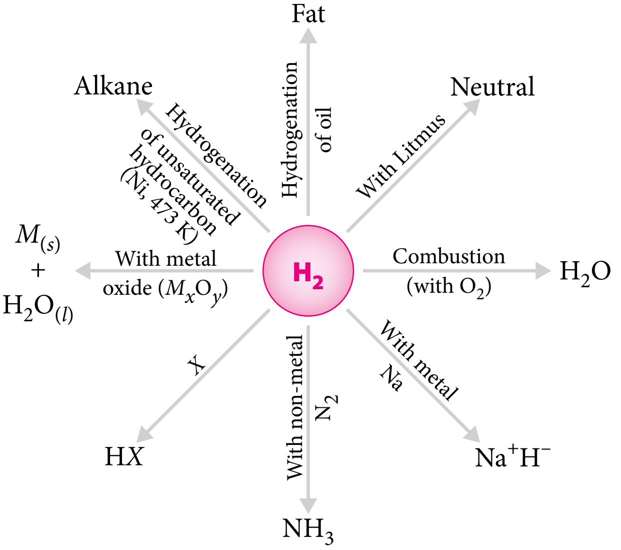
$$3Fe + 4H_2O_{(g)} \xrightarrow{1023\text{-}1073\text{ K}} Fe_3O_4 + 4H_2 + 160.7\text{ kJ}$$

- **As a byproduct :** In the manufacture of NaOH and Cl_2 by electrolysis of brine solution, hydrogen is produced as a byproduct.

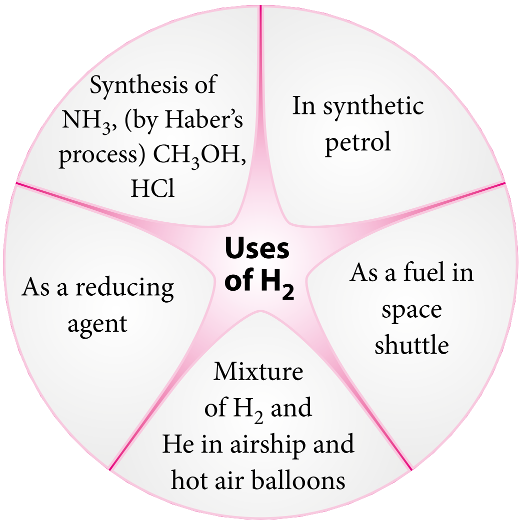
$$2Na^+_{(aq)} + 2Cl^-_{(aq)} + 2H_2O_{(l)} \longrightarrow Cl_{2(g)} + H_{2(g)} + 2Na^+_{(aq)} + 2OH^-_{(aq)}$$

Properties

- **Physical Properties :**
  - Colourless, odourless and tasteless gas.
  - Non-polar in nature and slightly soluble in water.
  - Liquefied under low temperature and high pressure.
- **Chemical Properties :**



- **Uses of hydrogen :**



INFO SHOTS

A new photocatalyst for extraction of hydrogen from seawater !

Hydrogen can be produced to power fuel cells by extracting the gas from seawater, but the electricity required to do it makes the process costly. Recently, UCF researchers has come up with a new hybrid nanomaterial that harnesses solar energy and uses it to generate hydrogen from seawater more cheaply and efficiently than current materials. This catalyst not only harvest a much broader spectrum of light than other materials, but also stand up to the harsh conditions found in seawater.

Hydrides

Hydrogen form binary hydrides with elements of *s*, *p*, (except noble gases), *d* and *f*-block.

Ionic or Saline Hydrides

- Group-1,2 elements form ionic hydrides, *e.g.*, NaH, CaH_2, CsH, SrH_2 etc.
- BeH_2, MgH_2 have slightly covalent character.
- Used in synthesis of other useful hydrides.

  $8LiH + Al_2Cl_6 \xrightarrow[\text{Ether}]{\text{Dry}} 2LiAlH_4 + 6LiCl$

Metallic or Interstitial Hydrides

- *d* and *f*-block elements form metallic hydrides. These are non-stoichiometric, being deficient in hydrogen, *e.g.*, $LaH_{2.87}$, $YbH_{2.55}$, etc.
- Metals of group-7, 8, 9 do not form hydrides and this region of periodic table is referred as hydride gap.
- Metallic hydrides can be used as hydrogen storage media.

Covalent or Molecular Hydrides

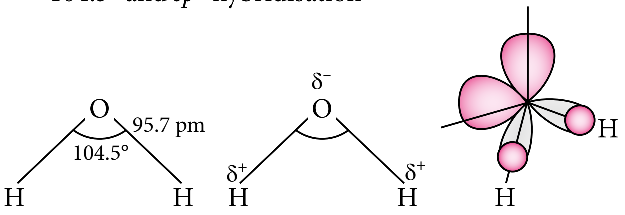
- *p*-Block elements form molecular or covalent hydrides. These are usually volatile compounds with low m.pt. and b.pt. These are of three types :
  - **Electron-deficient hydrides :** Formed by group-13 elements, *e.g.* B_2H_6, $(AlH_3)_n$, etc.
  - **Electron-precise hydrides :** Formed by group-14 elements, *e.g.*, CH_4, SiH_4, etc.
  - **Electron-rich hydrides :** Formed by group-15, 16 and 17 elements, *e.g.*, NH_3, H_2O, HCl, etc.

WATER

It is a crucial compound for the survival of all life forms. Human body has about 65% water and some plants have as much as 95% of water. It is a solvent of great importance.

Properties

- **Structure of water :** Bent structure with bond angle 104.5° and sp^3 hybridisation



(a) (b) (c)

H_2O molecule

- **Physical Properties :**
  - Pure water is colourless, odourless and tasteless.
  - It freezes at 0 °C and boils at 100 °C.
  - It has maximum density 1 g cm^{-3} at 4 °C.
- **Chemical Properties :**
  - Amphoteric nature

    $$\underset{\text{Acid 1}}{H_2O_{(l)}} + \underset{\text{Base 2}}{H_2O_{(l)}} \longrightarrow \underset{\text{Acid 2}}{H_3\overset{+}{O}_{(aq)}} + \underset{\text{Base 1}}{OH^-_{(aq)}}$$

    This self-ionisation of water is also called auto-protolysis.
  - Hydrolytic reaction

    $CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$
  - As reducing agent

    $xCO_2 + yH_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_x(H_2O)_y + xO_2$
  - Hydrate formation : Water combine with ionic salts is called water of crystallisation and such crystals are called hydrated salts.
    - Coordinated water : $[Ni(H_2O)_6]^{2+}$
    - Hydrogen bonded water : $CuSO_4{\cdot}5H_2O$
    - Interstitial water : $BaCl_2{\cdot}2H_2O$

Hard and Soft Water

- Water free from soluble salts of Ca and Mg, and which forms lather with soap readily is called soft water.
- Hard water does not form lather with soap.

Hardness of Water and Methods for Removal

Temporary Hardness

Due to presence of bicarbonates of Ca and Mg.

Boiling

$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + CO_2\uparrow + H_2O$

$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2CO_2$

Clark's process

$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$

$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$

Synthetic resins method

Cation exchange :

$2Resin-H^+ + 2M^+_{(aq)} \longrightarrow M(Resin)_2 + 2H^+$

(in hard water) (Exhausted resin)

Anion exchange :

$Resin-NH_3^+OH^- + Cl^- \rightarrow Resin\ NH_3^+Cl^- + OH^-$

(in hard water) (Exhausted resin)

$[M = Ca^{2+}, Mg^{2+}]$

Permanent Hardness

Due to presence of chlorides and sulphates of Ca and Mg.

Calgon's method

$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$

Sod. hexameta-phosphate

$M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$

$(M = Mg, Ca)$

Washing soda

$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2NaCl$

$MSO_4 + Na_2CO_3 \longrightarrow MCO_3\downarrow + Na_2SO_4$

$(M = Mg, Ca)$

Permutit Process

$Na_2Z + MCl_2 \longrightarrow MZ + 2NaCl$

(Sod. zeolite) (From hard water) (Settle down at bottom)

$M = Mg, Ca\ ;\ Z = Al_2Si_2O_8 \cdot xH_2O$

HYDROGEN PEROXIDE

Hydrogen peroxide was discovered by the French chemist J.L. Thenard in 1818. Its molecular formulas is H_2O_2.

Laboratory method **Preparation** **Industrial method**

By electrolysis of 50% H_2SO_4

$2SO_4^{2-} \xrightarrow{electrolysis} S_2O_8^{2-} + 2e^-$

$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$

Peroxodisulphuric acid Peroxomonosulphuric acid

$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$

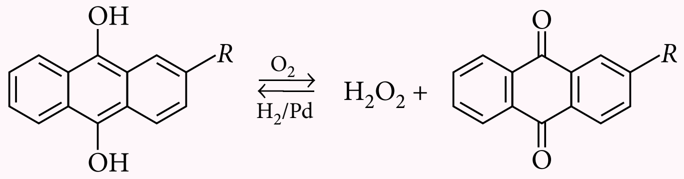
Merck's Method

$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$

By Barium Peroxide

$BaO_2 \cdot 8H_2O_{(s)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + H_2O_{2(aq)} + 8H_2O_{(l)}$

By auto-oxidation of 2-alkylanthraquinol



2-Alkylanthraquinol 2-Alkylanthraquinone

Physical Properties

- Very pale blue liquid, soluble in water, alcohol and ether.
- It boils at 152 °C and freezes at –0.89 °C.

Strength of H_2O_2

- Volume strength means volume of O_2 liberated at N.T.P. by the decomposition of 1 mL of H_2O_2. 30 volume H_2O_2 means 30 mL of O_2 liberated at NTP from 1 mL H_2O_2.
  Volume strength = $5.6 \times N = 11.2 \times M$

Chemical Properties

- Decomposition
  $2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)} : \Delta H_{(g)} = -196.0$ kJ
  This is an example of auto-oxidation and auto-reduction.
- Acidic nature
  $2NaOH + H_2O_2 \longrightarrow Na_2O_2 + 2H_2O$
- Oxidising character

In acidic medium	In basic medium
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$H_2O_2 + OH^- + 2e^- \rightarrow 3OH^-$

- Reducing character

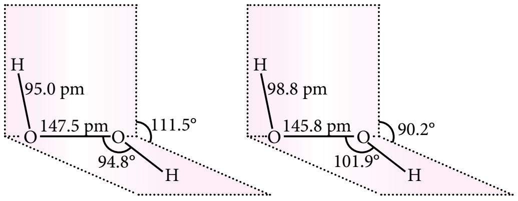
In acidic medium	In basic medium
$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$	$H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + 2e^-$

- Bleaching action (due to nascent O)
  $H_2O_2 \longrightarrow H_2O + [O]$
  Colouring matter + [O] $\longrightarrow$ Colourless matter
- Addition reaction
  $\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O_2 \longrightarrow \underset{\text{Ethylene glycol}}{(CH_2OH)_2}$

Uses

- As bleaching agent and disinfectant.
- Mixture of H_2O_2 and hydrazine hydrate used as rocket propellent.
- For restoring the colour of old painting.
- As an antiseptic under the name perhydrol.

Structure



(Gas Phase) (Solid Phase)

Heavy Water (D_2O)

- Prepared by prolonged electrolysis of ordinary water.
- Used to prepare deuterium compounds like
  $CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$
  $SO_3 + D_2O \longrightarrow D_2SO_4$
- Used as a moderator in nuclear reactor and in reaction mechanism.

Dihydrogen as a fuel

- Hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen.
- Pollutants in combustion of dihydrogen will be less than petrol.

THE *s*-BLOCK ELEMENTS

INTRODUCTION

Elements of periodic table in which the last electron enters the outermost *s*-orbital, are called *s*-block elements. They are classified in two groups :

Group	1 (alkali metals)	2 (alkaline earth metals)
Electronic configuration	ns^1	ns^2

ELECTRONIC CONFIGURATIONS OF *s*-BLOCK ELEMENTS

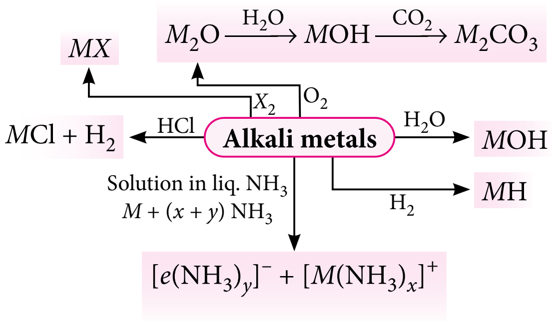
Alkali metals			Alkaline earth metals		
Elements	Atomic Number	Electronic configuration	Elements	Atomic Number	Electronic configuration
Lithium (Li)	3	[He] $2s^1$	Beryllium (Be)	4	[He] $2s^2$
Sodium (Na)	11	[Ne] $3s^1$	Magnesium (Mg)	12	[Ne] $3s^2$
Potassium (K)	19	[Ar] $4s^1$	Calcium (Ca)	20	[Ar] $4s^2$

Rubidium (Rb)	37	[Kr] $5s^1$	Strontium (Sr)	38	[Kr] $5s^2$
Caesium (Cs)	55	[Xe] $6s^1$	Barium (Ba)	56	[Xe] $6s^2$
Francium (Fr)	87	[Rn] $7s^1$	Radium (Ra)	88	[Rn] $7s^2$

GENERAL PROPERTIES OF *s*-BLOCK ELEMENTS

Alkali metals	Alkaline earth metals
Atomic/ionic radii	
• Increase on moving down from Li to Cs.	• Smaller than group-1 elements and increase from Be to Ra.
Ionization enthalpy	
• Decreases down the group as the size increases.	• 1^{st} *I.E.* of group-2 is higher than group-1 due to small size. In general, on moving down the group *I.E.* decreases.
Hydration enthalpy	
• Decreases with increase in size. $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	• Decreases with increase in size. $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
Physical appearance	
• Silvery white due to presence of mobile electron.	• Silver white lustre but harder than alkali metals.
Melting and boiling point	
• Decreases with increase in atomic number.	• Higher than group-1 and there is no regular trend in their m.pt. and b.pt.

CHEMICAL PROPERTIES OF ALKALI METALS



TRENDS IN ALKALI METALS

- **Strength of hydroxide (basicity) :** CsOH > RbOH > KOH > NaOH > LiOH
- **Stability of carbonates :** $Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$
- **Reactivity towards H_2/X :** Li > Na > K > Rb > Cs
- **M.pt. and b.pt. of halides :** $MF > MCl > MBr > MI$

Uses of Alkali Metals

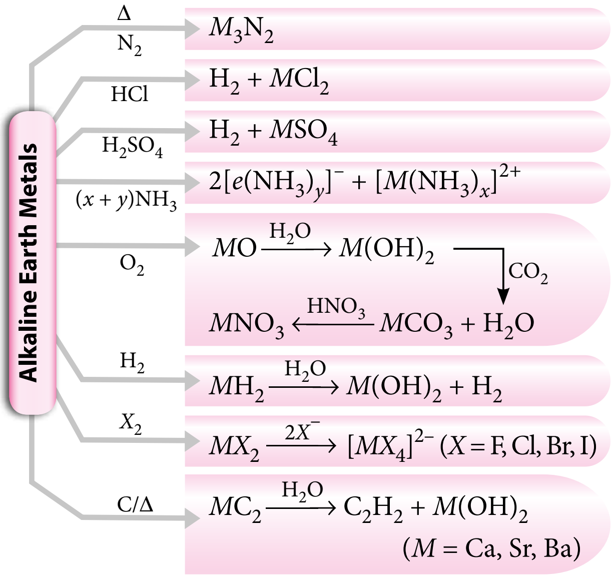
Li
- In alloy formation.
- Used in armour plate and aircraft parts.
- In refining of Cu and Ni to treat rheumatism.

Na
- Used for making antiknocking compounds.
- In sodium vapour lamps.
- Used in many organic compounds formation.
- As a liquid coolant in nuclear powder stations.

K
- As a fertilizer.
- In biological systems.
- In manufacturing of soap.
- As an excellent adsorbent of CO_2.

Cs
- In devising photoelectric cells (solar cells).

CHEMICAL PROPERTIES OF ALKALINE EARTH METALS



TRENDS IN ALKALINE EARTH METALS

- **Basic character/solubility :** $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- **Lattice enthalpy :** $Be(OH)_2 > Mg(OH)_2 > Ca(OH)_2 > Sr(OH)_2 > Ba(OH)_2$
- **Thermal stability :** $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
- **Hydration enthalpy :** $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
- **Basicity of oxides :** $\underset{\text{Amphoteric}}{BeO} < \underset{\text{Weakly basic}}{MgO} < \underset{\text{Basic}}{CaO} < \underbrace{SrO < BaO}_{\text{Strongly basic}}$
- **Solubility of halides :** $BeX_2 < MgX_2 < CaX_2 < SrX_2 < BaX_2$
- **Reducing nature :** Be < Mg < Ca < Sr < Ba

Uses of Alkaline Earth Metals

Be

- In alloy formation.
- In windows of *X*-ray tubes.
- In high strength spring.

Mg

- Its alloy used in aircraft construction.
- In toothpaste.
- In aluminothermy.
- In Grignard reagent.

Ca

- In the extractions of metals.
- In casting and forging.
- In cement and mortar.

ANOMALOUS BEHAVIOUR

Anomalous behaviours of the first element of a group is due to

- small atomic and ionic radii
- high electronegativity and ionization enthalpy
- high polarising power
- absence of *d*-electrons in its valence shell.

Diagonal Relationship

Diagonal similarity is known as diagonal relationship, is due to similarity in ionic sizes and/or charge/radius ratio of the elements.

	Group 1	Group 2	Group 3	Group 4
2nd period	Li ↘	Be ↘	B ↘	C
3rd period	Na	Mg	Al	Si

Points of Difference

Li with other alkali metals	Be with other alkaline earth metals
• Much harder • Higher m.pt. and b.pt. • Li forms monoxide while others form peroxides (M_2O_2) and superoxides (MO_2). • Ability to form nitrides. • LiOH is weak base while others are strong. • Ability to form hydrates $LiCl\cdot 2H_2O$ • $LiNO_3$ forms the oxide on gentle heating while others form nitrites. $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$ $2NaNO_3 \rightarrow 2NaNO_2 + O_2$	• Harder than magnesium. • Higher m.pt. and b.pt. • Does not react with cold water while other metals (except Mg) do, *e.g.*, $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$ • Be forms covalent compound while others form ionic. • Does not exhibit coordination number more than four. • Oxide and hydroxide of Be are amphoteric in nature. • Be_2C reacts with water, forming methane while others give alkyne. $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + \underset{\text{Methane}}{CH_4}$ $Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + \underset{\text{Propyne}}{C_3H_4}$

Compounds of Sodium

Sodium Carbonate (Washing soda, $Na_2CO_3 \cdot 10H_2O$)

Preparation :

- By solvay process.

  $2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$

  $(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$

  $NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3$

  $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

Properties :

- White crystalline solid, exist as $Na_2CO_3 \cdot 3H_2O$.
- Its anhydrous form is known as soda ash.

Uses :

- For softening of hard water.
- In washing.
- In textile industry.
- Metal refining.
- As a laboratory reagent.

Sodium Chloride (NaCl)

Preparation :

- Sea water is the major source. Concentrated solution of sea water is saturated with HCl gas.

Properties :

- White crystalline solid, soluble in water.
- Density of pure NaCl is 2.17 g/mL.
- Pure NaCl is non-hygroscopic.
- It has high m.pt. and b.pt.
- It is insoluble in alcohol.

Uses :

- As a table salt.
- As a freezing mixture.
- In manufacturing of Na_2CO_3, NaOH, etc.
- In textile industries.
- Impure salt (rock salt) is used to de-ice roads.
- As a preservative of food articles like fish, meat, etc.

Sodium Hydroxide (Caustic soda, NaOH)

Preparation :

- By electrolysis of NaCl in Castner-Kellner cell.

  Cathode : $Na^+ + e^- \xrightarrow{Hg}$ Na-amalgam

  Anode : $Cl^- \longrightarrow 1/2Cl_2 + e^-$

  2Na-amalgam $+ 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$

Properties :

- White, transluscent and deliquescent solid, soluble in water.
- Its aqueous solution is soapy to touch and corrosive.

Uses :

- In manufacturing of soap, paper and artificial silk.
- In petroleum refining.
- In purification of bauxite.
- In textile industries for mercerising cotton fabrics.

Sodium Hydrogen Carbonate (Baking powder, $NaHCO_3$)

Preparation :

$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$

Properties :

- White crystalline solid, sparingly soluble in water.
- Aqueous solution is alkaline in nature.
- Aqueous solution is weakly basic.

  $NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$
- The solution gives yellow colour with methyl orange but no colour with phenolphthalein.

Uses :

- In fire extinguishers.
- In preparation of baking powder.
- As an antiseptic and antacid.
- In manufacturing of soda.

COMPOUNDS OF CALCIUM

Calcium Hydroxide (Slaked Lime) ; $Ca(OH)_2$

Preparation :

- $CaO + H_2O \longrightarrow Ca(OH)_2$
- $CaCl_2 + 2NaOH \longrightarrow Ca(OH)_2 + 2NaCl$

Properties :

- White amorphous powder, spraringly soluble in water.
- Its aqueous solution is known as lime water and suspension of it in water is known as milk of lime.
- $Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{(Milkiness)}}{CaCO_3} + H_2O$
- $2Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}_{\text{Bleaching Powder}} + 2H_2O$
- $CaCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$

Uses :

- In the manufacture of bleaching powder.
- For absorbing acidic gases.
- For detection of CO_2.
- As a disinfectant.

Calcium Oxide (Quick Lime) ; CaO

Preparation :

- $CaCO_3 \overset{\Delta}{\rightleftharpoons} CaO + CO_2$

Properties :

- It is a white amorphous solid.
- On heating in oxyhydrogen flame, emits brilliant white light (known as limelight).
- When exposed to atmosphere,
  $CaO + \underset{\text{(Moisture)}}{H_2O} \longrightarrow \underset{\text{(Slaked Lime)}}{Ca(OH)_2}$
  $CaO + CO_2 \longrightarrow \underset{\text{(Limestone)}}{CaCO_3}$
- Being a basic oxide, can combine with acidic impurities.
  $CaO + SiO_2 \xrightarrow{\Delta} CaSiO_3$

Uses :

- Purification of sugar.
- Important constituent of cement, mortar, caustic soda lime (CaO + NaOH) etc.

Calcium Carbonate (Limestone) ; $CaCO_3$

Preparation :

- From slaked lime :
  $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$
- From calcium chloride :
  $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

Properties :

- White fluffy solid and insoluble in water.
- $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
- Liberates CO_2
  $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2\uparrow + H_2O$
  $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2\uparrow + H_2O$

Uses :

- In building material, in the manufacturing of quick lime, Na_2CO_3.
- In the extraction of metals.
- As an antacid, abrasive in toothpaste, filler in cosmetics.

Calcium Sulphate (Plaster of Paris) ; $(CaSO_4)_2 \cdot H_2O$

Plaster of Paris is calcium sulphate hemihydrate $CaSO_4 \cdot \frac{1}{2} H_2O$.

Preparation :

- $\underset{\text{Gypsum}}{2(CaSO_4 \cdot 2H_2O)} \xrightarrow[393\text{ K}]{\Delta} \underset{\text{Plaster of Paris}}{2(CaSO_4) \cdot H_2O} + 3H_2O$
  $2(CaSO_4).H_2O \xrightarrow{473\text{ K}} \underset{\text{(Dead burnt plaster)}}{2CaSO_4 + H_2O}$

Properties :

- It is white powder.
- On mixing with water, it sets into hard mass after sometime.
  $(CaSO_4)_2 \cdot H_2O + 3H_2O \longrightarrow \underset{\text{Gypsum}}{2(CaSO_4 \cdot 2H_2O)}$

Uses :

- For producing moulds for pottery, ceramic etc.
- For making statues, models and other decorative materials.
- In surgical bandages.
- In dentistry.

Cement

It was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the famous building store found near Portland in England. It is a finely ground mixture of calcium silicates and aluminates which set to a hard mass when treated with water.

Composition of Cement

CaO = 50-60%
SiO_2 = 20-25%
Al_2O_3 = 5-10%
MgO = 2-3%
Fe_2O_3 = 1-2%
SO_3 = 1-2%

INFO SHOTS

Sodium is associated with an increased risk of type 2 diabetes!

According to a latest research, sodium intake may be linked to an increased risk of developing both type 2 diabetes (T2D) and Latent Autoimmune Diabetes in Adults (LADA).

The main source of sodium in the diet is through salt. Salt (sodium chloride) contains 40% sodium, thus for every 2.5 g of salt consumed, 1 g is sodium. Research has suggested that excessive salt consumption may increase the risk of developing T2D, possibly through a direct effect on insulin resistance, and/or by promoting high blood pressure and weight gain.

Biological Importance

Sodium and Potassium

Na^+ :

- Major component of blood plasma.
- Helps in nerve signal transmission and function of heart.
- It maintains the electrolyte balance in the body.
- In transport of sugar and amino acids into cell.

K^+ :

- Activating some enzymes.
- Produces energy rich ATP molecules.
- Protein synthesis.
- For transmission of nerve signals.

Calcium and Magnesium

Ca^{2+} :

- In stabilisation of protein.
- As a messenger for harmonal action.
- As a triger for the contraction of muscles.
- In maintenance of rhythm of heart.

Mg^{2+} :

- Catalyses enzymatic reactions.
- In photosynthesis.
- With ATP forms complex, which release energy.

SPEED PRACTICE

1. In the absence of hydrogen bonding, the boiling point of water would have been
(a) 100° C (b) 0° C (c) −80° C (d) 373° C

2. When sodium reacts with sufficient amount of air, the product obtained is
(a) Na_2O (b) Na_2O_2 (c) NaO_2 (d) NaO

3. Identify the incorrect statement about heavy water.
(a) It reacts with SO_3 to form deuterated sulphuric acid (D_2SO_4).
(b) It is used as a coolant in nuclear reactors.
(c) It reacts with CaC_2 to produce C_2D_2 and $Ca(OD)_2$.
(d) It reacts with Al_4C_3 to produce CD_4 and $Al(OD)_3$.
(JEE Main Online 2016)

4. Which of the following complex is the most stable?
(a) $[Be(H_2O)_4]^{2+}$ (b) $[Mg(H_2O)_4]^{2+}$
(c) $[Ca(H_2O)_4]^{2+}$ (d) $[Sr(H_2O)_4]^{2+}$

5. K_2CO_3 cannot be prepared by Solvay process because
(a) K_2CO_3 decomposes in the process
(b) $KHCO_3$ is soluble in water
(c) $KHCO_3$ is insoluble in water
(d) $KHCO_3$ is thermally stable.

6. A metal *M* readily forms a water-soluble sulphate MSO_4, a water-insoluble hydroxide $M(OH)_2$ and an oxide *MO* which becomes inert on heating. The hydroxide is soluble in NaOH. The metal *M* is
(a) Be (b) Mg (c) Ca (d) Sr

7. Ionic metal hydrides react with water to give hydrogen gas. Which of the following hydrides will produce maximum amount of H_2 if equal mass of each hydride is taken?
(a) LiH (b) CaH_2 (c) NaH (d) MgH_2

8. Both lithium and magnesium display several similar properties due to the diagonal relationship, however, the one which is incorrect, is
(a) both form nitrides
(b) nitrates of both Li and Mg yield NO_2 and O_2 on heating
(c) both form basic carbonates
(d) both form soluble bicarbonates.
(JEE Main 2017)

9. The hydride ion, H^- is a stronger base than hydroxide ion, OH^-. Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water?
(a) $H^-_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^-_{(aq)}$
(b) $H^-_{(aq)} + H_2O_{(l)} \longrightarrow OH^-_{(aq)} + H_{2(g)}$
(c) $H^-_{(aq)} + H_2O_{(l)} \longrightarrow$ No reaction
(d) $H^-_{(aq)} + 2H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + H_{2(g)}$

10. What is the product obtained when $MgCl_2.6H_2O$ is strongly heated?
(a) $MgCl_2$ (b) MgO
(c) $MgCl_2.2H_2O$ (d) $MgCl_2.4H_2O$

11. Which of the following hydrides is not ionic?
(a) CaH_2 (b) BaH_2 (c) SrH_2 (d) BeH_2

12. The compound formed when gypsum is dissolved in aqueous ammonium sulphate solution is
(a) $CaSO_4 \cdot NH_4Cl \cdot H_2O$
(b) $CaCl_2(NH_4)_2SO_4 \cdot H_2O$
(c) $CaSO_4(NH_4)_2SO_4 \cdot 2H_2O$
(d) $CaCl_2 \cdot NH_4Cl \cdot 2H_2O$

13. Which of the following statements about hydrogen is incorrect?
(a) Hydronium ion, H_3O^+ exists freely in solution.
(b) Dihydrogen does not act as a reducing agent.
(c) Hydrogen has three isotopes of which tritium is the most common.
(d) Hydrogen never acts as cation in ionic salts.
(NEET Phase-I 2016)

14. The solubility of hydroxides, fluorides or oxalates of the metals of group II
(a) increases down the group
(b) decreases down the group
(c) varies randomly
(d) is same.

15. Polyphosphates are used as water softening agents because they
(a) form soluble complexes with anionic species
(b) form soluble complexes with cationic species
(c) precipitate cationic species
(d) precipitate anionic species.

16. The correct sequence of increasing covalent character is represented by
(a) $LiCl < NaCl < BeCl_2$ (b) $BeCl_2 < LiCl < NaCl$
(c) $NaCl < LiCl < BeCl_2$ (d) $BeCl_2 < NaCl < LiCl$

17. A 'hair-bleach' solution contains H_2O_2. The amount of H_2O_2 in a 12.5 g sample was determined by titration with $KMnO_4$ in acidic medium. 39.3 mL of 0.5045 N $KMnO_4$ was required by the sample. What is the mass percentage of H_2O_2 in the bleach solution?
(a) 2.69 (b) 3.15 (c) 3.37 (d) 2.12

18. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field?
(a) K (b) Rb
(c) Li (d) Na **(NEET 2017)**

19. When a substance (*A*) reacts with water it produces a combustible gas (*B*) and a solution of substance (*C*) in water. When another substance (*D*) reacts with this solution of (*C*) it produces the same gas (*B*) on warming. (*D*) may also produce the gas (*B*) on reaction with dilute sulphuric acid at room temperature. (*A*) imparts a deep golden yellow colour to a smokeless flame of Bunsen burner. *A*, *B*, *C* and *D* are respectively

(a) Na, H_2, NaOH, Zn
(b) K, H_2, KOH, Al
(c) Ca, H_2, $Ca(OH)_2$, Sn
(d) CaC_2, C_2H_2, $Ca(OH)_2$, Fe

20. The decomposition temperature is maximum for
(a) $MgCO_3$ (b) $CaCO_3$
(c) $BaCO_3$ (d) $SrCO_3$

21. The hardness of water sample containing 0.002 mol of magnesium sulphate dissolved in a litre of water is expressed as
(a) 20 ppm (b) 200 ppm
(c) 2000 ppm (d) 120 ppm.

22. Flame test is not given by
(a) Be (b) K (c) Sr (d) Ca

23. The label on a bottle of H_2O_2 solution reads as '10 volume'. The concentration of H_2O_2 in percentage by volume is
(a) 4.05% (b) 3.03% (c) 6.06% (d) 2.03%

24. In context with beryllium, which one of the following statements is incorrect?
(a) It is rendered passive by nitric acid.
(b) It forms Be_2C.
(c) Its salts rarely hydrolyse.
(d) Its hydride is electron-deficient and polymeric.
(NEET Phase-II 2016)

25. The maximum possible number of hydrogen bonds a water molecule can form, is
(a) 2 (b) 4 (c) 3 (d) 1

26. Cement does not contain
(a) calcium (b) aluminium
(c) sulphur (d) iron.

27. Which one of the following processes will produce hard water?
(a) Saturation of water with $CaCO_3$
(b) Saturation of water with $MgCO_3$
(c) Saturation of water with $CaSO_4$
(d) Addition of Na_2SO_4 to water

28. Which one out of the NaOH and KOH, is a better absorber of CO_2?
(a) NaOH (b) KOH
(c) Both absorb CO_2 equally
(d) Cannot be predicted

29. Which of the following is not correct?
(a) $2Li_2O \xrightarrow[673\text{ K}]{\text{heat}} Li_2O_2 + 2Li$
(b) $2K_2O \xrightarrow[673\text{ K}]{\text{heat}} K_2O_2 + 2K$
(c) $2Na_2O \xrightarrow[673\text{ K}]{\text{heat}} Na_2O_2 + 2Na$
(d) $2Rb_2O \xrightarrow[673\text{ K}]{\text{heat}} Rb_2O_2 + 2Rb$

30. Bleaching Powder slowly loses its activity when it stands in air. This is due to
(a) loss of $CaCl_2$
(b) formation of $Ca(OH)_2$
(c) reaction with CO_2 to evolve Cl_2
(d) reaction with water to evolve O_2.

SOLUTIONS

1. **(c) :** Forces of attraction are minimum at – 80° C, thus water is most volatile at this temperature.

2. **(b):** $2Na + O_2 \xrightarrow{575\text{ K}} \underset{\text{Sodium peroxide}}{Na_2O_2}$

3. **(b):** Heavy water is used as a moderator in nuclear reactors to control the speed of neutrons.

4. **(a)**

5. **(b):** $KHCO_3$ is highly soluble in water thus, it cannot be precipitated.

6. **(a)**

7. **(a) :** Suppose 1 g of each hydride is taken.

$LiH + H_2O \longrightarrow LiOH + H_2$
8 g 2 g
1 g 2/8 g

$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$
42g 4 g
1 g 4/42 g or 2/21 g

$NaH + H_2O \longrightarrow NaOH + H_2$
24 g 2 g
1 g 2/24 g

$MgH_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2H_2$
26 g 4 g
1 g 4/26 = 2/13 g

Thus, LiH will produce maximum amount of H_2.

8. **(c) :** Due to the diagonal relationship, both Li and Mg display some similar properties, but in case of carbonates, Mg can form basic carbonate such as $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. In contrast, Li only forms typical carbonate Li_2CO_3 as other alkali metals. It does not form any basic carbonate having both carbonate and hydroxide ions.

9. **(b):** The stronger base H^- will displace OH^- from water as shown in the reaction :
$H^-_{(aq)} + H_2O_{(l)} \longrightarrow OH^-_{(aq)} + H_{2(g)}$

10. **(b):** $MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$

11. **(d):** Among all alkaline earth metal hydrides, except BeH_2 and MgH_2, all hydrides CaH_2, SrH_2 and BaH_2 are ionic.

12. (c) : $CaSO_4{\cdot}2H_2O + (NH_4)_2SO_4 \longrightarrow CaSO_4{\cdot}(NH_4)_2SO_4{\cdot}2H_2O$

13. (b, c) : Dihydrogen acts as a powerful reducing agent and reduces metal oxides such as CuO, ZnO, PbO and Fe_3O_4 to their respective metals.

$CuO + H_2 \longrightarrow Cu + H_2O$

$ZnO + H_2 \longrightarrow Zn + H_2O$

$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$

Hydrogen has three isotopes of which protium is the most common and tritium is radioactive.

14. (a) : Both lattice energy and hydration energy decrease down the group due to gradual increase in size of M^{2+} ion. Lattice energy tends to increase the solubility while hydration energy tends to decrease the solubility. However, lattice energy predominates hydration energy. Therefore, solubility increases down the group.

15. (b) : Polyphosphates, *e.g.,* calgon are used as water softening agents because they form soluble complexes with cations, Ca^{2+} and Mg^{2+}.

16. (c) : LiCl and $BeCl_2$ are predominantly covalent compounds but NaCl is an ionic compound. The covalent character of LiCl and $BeCl_2$ is due to polarisation of Cl^- ion by Li^+ and Be^{2+}ions. As the polarisation is more due to Be^{2+}ions as it has smaller size and greater charge, $BeCl_2$ is more covalent than LiCl.

17. (a) : $2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

1000 mL of 1N $MnO_4^- \equiv$ 1000 mL of 1N H_2O_2

Equivalent of H_2O_2 = equivalent of MnO_4^-

$$= \frac{39.3 \times 0.5045}{1000} = 0.0198$$

$\therefore$ Amount of pure $H_2O_2 = 0.0198 \times 17 = 0.337$ g

$$\% \text{ of } H_2O_2 \text{ in bleach solution} = \frac{0.337}{12.5} \times 100 = 2.69\ \%$$

18. (c) : The hydration enthalpy of alkali metal ions decreases with increase in ionic sizes *i.e.,*

$Li^+ > Na^+ > K^+ > Rb^+$

Hence, lithium having maximum degree of hydration, will be least mobile. Thus, the order of ionic mobility is :

$[Li_{(aq)}]^+ < [Na_{(aq)}]^+ < [K_{(aq)}]^+ < [Rb_{(aq)}]^+$

19. (a) : $\underset{(A)}{2Na} + 2H_2O \longrightarrow \underset{(C)}{2NaOH} + \underset{(B)}{H_2}$

$\underset{(D)}{Zn} + \underset{(C)}{2NaOH} \xrightarrow{\Delta} Na_2ZnO_2 + \underset{(B)}{H_2}$

$\underset{(D)}{Zn} + H_2SO_{4(dil.)} \longrightarrow ZnSO_4 + \underset{(B)}{H_2}$

20. (c) : Thermal stability of carbonates of alkaline earth metals increases with increase in atomic mass down the group or with increasing cationic size :

$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

21. (b) : Amount of $MgSO_4 = 0.002 \times 120$

$= 0.24$ g of $MgSO_4$

Also, 120 g of $MgSO_4 \equiv 100$ g of $CaCO_3$

$$\therefore\ 0.24 \text{ g of } MgSO_4 \equiv \frac{100 \times 0.24}{120} = 0.2 \text{ g of } CaCO_3$$

1 L of water = 10^3 mL = 1000 g ($\because \rho\ H_2O = 1$ g/cc)

Thus, 10^3 g of water contains = 0.2 g of $CaCO_3$

Hence, 10^6 g of water shall contain

$$= \frac{0.2 \times 10^6}{10^3} = 200 \text{ g}$$

Therefore, hardness of water is 200 ppm.

22. (a) : All elements of *s*-block (group I and group II) except Be and Mg give characteristic colour to the flame.

23. (b) : $\underset{68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22400\text{ mL}}{O_2}$

22400 mL of O_2 is formed from 68 g of H_2O_2.

$$\therefore\ 10 \text{ mL of } O_2 \text{ is formed by } \frac{68}{22400} \times 10 \text{ g of } H_2O_2$$

$= 0.0303$ g H_2O_2

1 mL of H_2O_2 solution contains 0.0303 g H_2O_2

$\therefore$ 100 mL of H_2O_2 solution contains

$= 0.0303 \times 100 = 3.035$ g $= 3.035\%$ of H_2O_2

24. (c) : Beryllium salts are readily hydrolysed.

25. (b) : Water molecule can form two hydrogen bonds through its two hydrogen atoms and another two hydrogen bond with two lone pairs of electrons of O-atom.

26. (c)

27. (c) : Permanent hardness of water is due to the presence of chlorides and sulphates of calcium and magnesium.

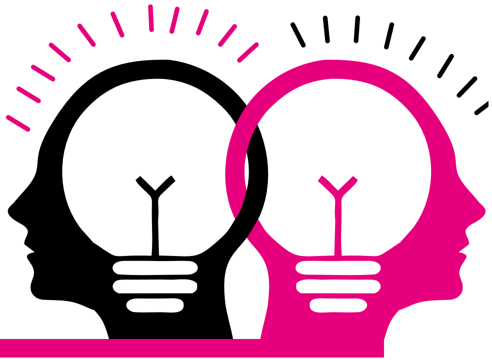
28. (b) : KOH is better absorber of CO_2 because K_2CO_3 formed is more soluble and does not separate out.

29. (a) : Lithium does not form peroxide.

30. (c) : $CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$

◆◆

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.

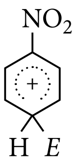
Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 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).

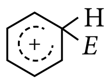
HYDROCARBONS

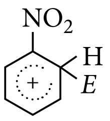
SECTION - I

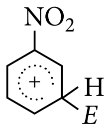
Only One Option Correct Type

1. The electrophile, E^+ attacks the benzene ring to generate the intermediate σ-complex. Which of the following, σ-complex is of the lowest energy?

(a) 

(b) 

(c) 

(d) 

2. 3-Octyne is synthesized by adding a bromoalkane in a mixture of sodium amide and an alkyne. The bromoalkane and alkyne are respectively

(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C{\equiv}CH$

(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C{\equiv}CH$

(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

3. *trans*-2-Phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces

(a) 4-phenylcyclopentene

(b) 2-phenylcyclopentene

(c) 1-phenylcyclopentene

(d) 3-phenylcyclopentene.

4. When cyclohexane is poured on water, it floats, because

(a) cyclohexane is in 'boat' form

(b) cyclohexane in 'chair' form is heavier than water

(c) cyclohexane is more dense than water

(d) cyclohexane is less dense than water.

5. Which of the compound with molecular formula C_5H_{10} yields acetone on ozonolysis?

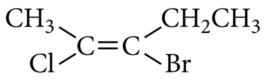
(a) 3-Methyl-1-butene

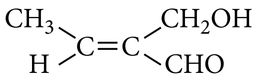
(b) Cyclopentane

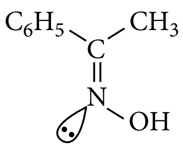
(c) 2-Methyl-1-butene

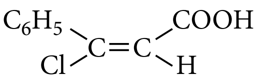
(d) 2-Methyl-2-butene

6. The *Z*-isomer among the following is

(a) 

(b) 

(c) 

(d) 

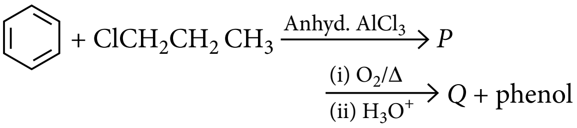
7. Which of the given reaction conditions will give maximum yields of C_2H_5Cl?

(a) $C_2H_6 \text{ (excess)} + Cl_2 \xrightarrow{\text{UV light}}$

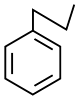
(b) $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{dark}}$

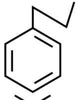
(c) $C_2H_6 + Cl_2 \text{ (excess)} \xrightarrow{\text{UV light}}$

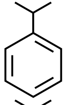
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

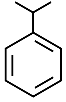
8. 

The major products P and Q are

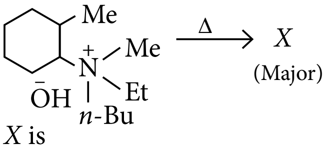
(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

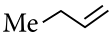
(c)  and CH_3COCH_3

(d)  and CH_3CH_2CHO

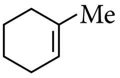
9. In the following reaction,

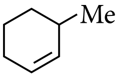


X is

(a) 

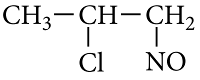
(b) $CH_2=CH_2$

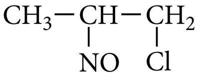
(c) 

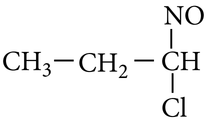
(d) 

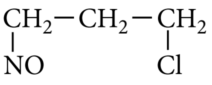
10. $CH_3-CH=CH_2 + NOCl \longrightarrow P$

Identify product P.

(a) 
$CH_3-\underset{Cl}{CH}-\underset{NO}{CH_2}$

(b) 
$CH_3-\underset{NO}{CH}-\underset{Cl}{CH_2}$

(c) 
$CH_3-CH_2-\overset{NO}{\underset{Cl}{CH}}$

(d) 
$\underset{NO}{CH_2}-CH_2-\underset{Cl}{CH_2}$

SECTION - II

More than One Options Correct Type

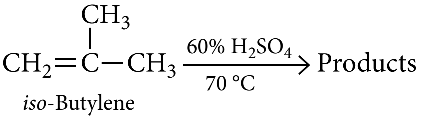
11. Which of the following are cumulative dienes?

(a) $CH_3-CH=C=CH-CH_3$

(b) $CH_2=CH-CH=CH_2$

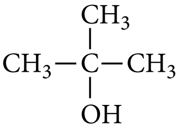
(c) $CH_2=CH-CH_2CH=CH_2$

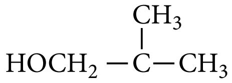
(d) $CH_3CH_2CH=C=CH-CH_3$

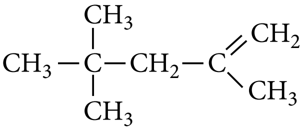
12. 
$CH_2=\overset{CH_3}{C}-CH_3 \xrightarrow[70\,°C]{60\%\ H_2SO_4}$ Products

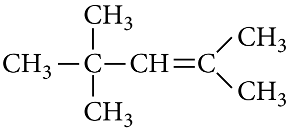
iso-Butylene

Products of the given reaction are

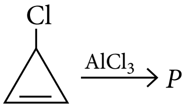
(a) 

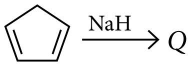
(b) 

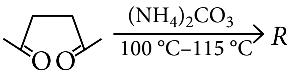
(c) 

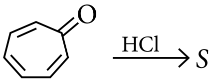
(d) 

13. Among P, Q, R and S the aromatic compounds are









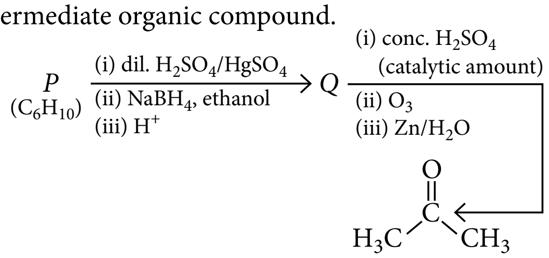
(a) P (b) Q (c) R (d) S

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

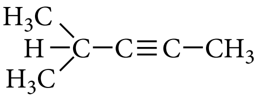
An acyclic hydrocarbon P, having molecular formula C_6H_{10} gave acetone as the only organic product through the following sequence of reactions in which Q is an intermediate organic compound.

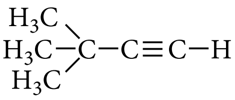


14. The structure of the compound P is

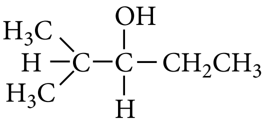
(a) $CH_3CH_2CH_2CH_2C{\equiv}CH$

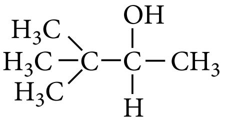
(b) $CH_3CH_2C{\equiv}CCH_2CH_3$

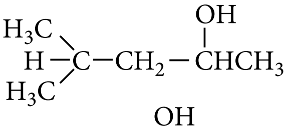
(c) 

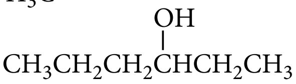
(d) 

15. The structure of the compound Q is

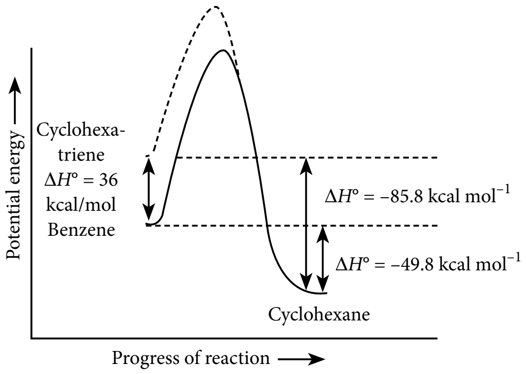
(a) 

(b) 

(c) 

(d) 
$CH_3CH_2CH_2\overset{OH}{C}HCH_2CH_3$

Paragraph for Questions 16 and 17



To evaluate resonance energy of benzene, we can compare heat of hydrogenation of cyclohexane and benzene (or its derivative).

16. Heat of hydrogenation of cyclohexene is

(a) -85.8 kcal mol^{-1}

(b) -49.8 kcal mol^{-1}

(c) -36.0 kcal mol^{-1}

(d) -28.6 kcal mol^{-1}.

17. Resonance energy of benzene is

(a) -49.8 kcal mol^{-1}

(b) -36 kcal mol^{-1}

(c) $+36.0$ kcal mol^{-1}

(d) -28.6 kcal mol^{-1}.

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)	Benzene	(i)	Phosgene
(Q)	Ethylene	(ii)	Silver mirror test
(R)	Acetaldehyde	(iii)	Mustard gas
(S)	Chloroform	(iv)	$(4n+2)\pi$ electrons
		(v)	Carbylamine

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

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

	List I		**List II**
(P)	Alkyl halide + Sodium in presence of dry ether	(i)	Sulphonation
(Q)	Arene + Acid halide in presence of anhyd. $AlCl_3$	(ii)	Wurtz reaction
(R)	Arene + Fuming sulphuric acid	(iii)	Catalytic hydrogenation
(S)	Arene + Hydrogen in presence of Ni	(iv)	Friedel–Crafts reaction

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

SECTION - V

Assertion Reason Type

20. **Assertion :** 1-butene on reaction with HBr in presence of peroxide produces 1-bromobutane.
Reason : It involves the formation of a primary radical.

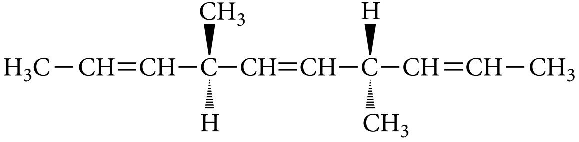
21. **Assertion :** Benzene on heating with conc. H_2SO_4 gives benzenesulphonic acid which when heated with superheated steam under pressure gives benzene.
Reason : Sulphonation is a reversible process.

22. **Assertion :** The gauche conformation of ethylene glycol is more stable than its anti-conformation.
Reason : The gauche conformation is stabilized by H-bonding.

SECTION - VI

Integer Value Correct Type

23. The number of optically active products obtained from the complete ozonolysis of the given compound is



$H_3C-CH=CH-\overset{CH_3}{\underset{H}{C}}-CH=CH-\overset{H}{\underset{CH_3}{C}}-CH=CH-CH_3$

24. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is

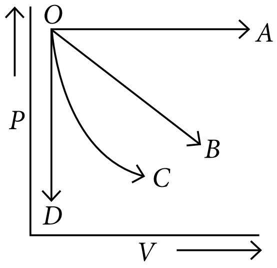
25. Which of the following molecules have zero dipole moment?
cis-1, 2-Dichloroethene, *trans*-1, 2-dichloroethene, 1, 1-dichloroethene, *trans*-2-pentene, *cis*-2-pentene, 1-butyne, 2-butyne, *trans*-2-butene, *cis*-2-butene

THERMODYNAMICS

SECTION - I

Only One Option Correct Type

1. For which of the following process, $q = \Delta U$?



(a) $O \rightarrow A$ (b) $O \rightarrow D$
(c) $O \rightarrow B$ (d) $O \rightarrow C$

2. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 J K^{-1} mol^{-1} respectively. For the reaction,
$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$, $\Delta H° = -30$ kJ mol^{-1}, to be at equilibrium, the temperature will be
(a) 500 K (b) 750 K (c) 1000 K (d) 1250 K

3. Internal energy and pressure for one mole of a gas of unit volume are related as
(a) $p = \frac{2}{3}E$ (b) $p = \frac{E}{2}$ (c) $p = \frac{3}{2}E$ (d) $p = 2E$

4. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) ⟶ (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU = 30.0 L atm. The change in enthalpy (ΔH) of the process in L atm is
(a) 40.0 (b) 42.3
(c) 44.0
(d) not defined, because pressure is not constant.

5. The direct conversion of A to B is difficult, hence it is carried out by the following path :

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

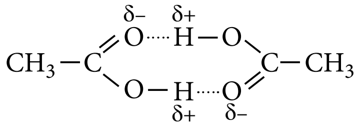
Entropy change (ΔS) for the process,
$A \rightarrow C$ = 50 e.u. ; $C \rightarrow D$ = 30 e.u. ; $B \rightarrow D$ = 20 e.u.
(where e.u. is unit of entropy), then $\Delta S(A \rightarrow B)$ is
(a) +100 e.u. (b) +60 e.u.
(c) –100 e.u. (d) –60 e.u.

6. Which of the algebric relationships on the basis of given thermochemical equations is correct?
(i) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H = x$ kJ mol^{-1}
(ii) $C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$; $\Delta_r H = y$ kJ mol^{-1}
(iii) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H = z$ kJ mol^{-1}
(a) $z = x + y$ (b) $x = y - z$
(c) $x = y + z$ (d) $y = 2z - x$

7. An athlete has taken 100 g glucose of energy equivalent to 1560 kJ. He utilizes 50% of this gained energy in an event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. (Enthalpy of H_2O for evaporation = 44 kJ mol^{-1})
(a) 346 g (b) 316 g (c) 323 g (d) 319 g

8. The volume of a gas is reduced to half from its original volume. Its specific heat will be
(a) reduced to half (b) doubled
(c) remain constant (d) increased four times.

9. Acetic acid, CH_3COOH can form a dimer $(CH_3COOH)_2$ in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5 kJ per mol of dimer.



If at 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 then $\Delta S°$ for the reaction is
(a) 0.163 kJ (b) 0.2010 kJ
(c) 0.1251 kJ (d) 0.091 kJ.

10. Standard enthalpies of formation of O_3, CO_2, NH_3 and HI are +142.2, −393.2, −46.2 and +25.9 kJ mol^{-1} respectively. The order of their increasing stabilities will be

(a) O_3, CO_2, NH_3, HI (b) CO_2, NH_3, HI, O_3
(c) O_3, HI, NH_3, CO_2 (d) NH_3, HI, CO_2, O_3

SECTION - II

More than One Options Correct Type

11. Select the correct option for the equilibrium under standard conditions as given :

$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}\ ;\ \Delta S_1^\circ$
$H_2O_{(l)} \rightleftharpoons H_2O_{(v)}\ ;\ \Delta S_2^\circ$
$H_2O_{(s)} \rightleftharpoons H_2O_{(v)}\ ;\ \Delta S_3^\circ$

(a) $\Delta S_1^\circ > \Delta S_2^\circ$ (b) $\Delta S_2^\circ >>> \Delta S_1^\circ$
(c) $\Delta S_3^\circ > \Delta S_2^\circ$ (d) $\Delta S_3^\circ > \Delta S_1^\circ$

12. Which of the following statements are not correct?

(a) The presence of reacting species in a covered beaker is an example of open system.
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

13. Which of the following expressions regarding entropy are correct?

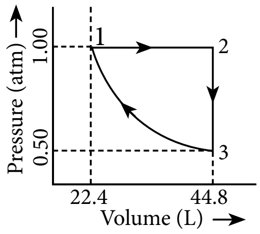
(a) $\Delta S_{\text{system}} = \dfrac{q}{T}$
(b) $\Delta S_{\text{system}} = \Delta S_{\text{total}} + \Delta S_{\text{surrounding}}$
(c) $\Delta S = S_{\text{final}} - S_{\text{initial}}$
(d) $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

A sample containing 1 mole of a monoatomic ideal gas $\left(C_v = \frac{3}{2}R\right)$ is taken through the cycle as shown :



14. Temperature at points 1, 2 and 3 are, respectively

(a) 273 K, 546 K, 273 K (b) 546 K, 273 K, 273 K
(c) 273 K, 273 K, 273 K (d) 546 K, 546 K, 273 K.

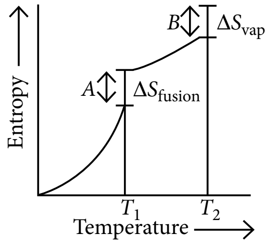
15. ΔE for the process $(1 \rightarrow 2)$ is

(a) 3.4 J (b) 3.4×10^3 J
(c) −3.4 J (d) -3.4×10^3 J.

Paragraph for Questions 16 and 17

Entropy is a measure of degree of randomness. Entropy is directly proportional to temperature. Every system tries to acquire state of maximum randomness or disorder. Entropy is a measure of unavailable energy.
Unavailable energy = Entropy × Temperature
The ratio of entropy of vapourisation and boiling point of a substance remains almost constant.

16. Observe the graph and identify the correct statement.



(a) T_1 is melting point and T_2 is boiling point.
(b) T_1 is boiling point and T_2 is melting point.
(c) ΔS_{fusion} is more than ΔS_{vap}.
(d) T_2 is lower than T_1.

17. The law of thermodynamics formulated by Nernst, which helps to determine absolute entropy is

(a) zeroth law (b) first law
(c) second law (d) third law.

SECTION - IV

Matching List Type

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

List I		**List II**
(P) $H_2 \rightarrow 2H$	1.	$\Delta H = B.E.\ (C\equiv C) + 2B.E.\ (H-H) - B.E.\ (C-C) - 4B.E.\ (C-H)$
(Q) $CH_4 \rightarrow C + 4H$	2.	$\Delta H = \Delta_f H$ of H × 2
(R) $C_2H_2 + 2H_2 \rightarrow C_2H_6$	3.	ΔH = Average bond energy × 4
(S) $C_2H_4 + H_2 \rightarrow C_2H_6$	4.	$\Delta H = B.E.(C=C) + B.E.\ (H-H) - B.E.\ (C-C) - 2B.E.\ (C-H)$

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

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

List I	**List II**
(P) $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$	1. $\Delta H = \Delta U - 2RT$
(Q) $PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$	2. $\Delta H = \Delta U + 3RT$
(R) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$	3. $\Delta H = \Delta U$
(S) $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$	4. $\Delta H = \Delta U + RT$

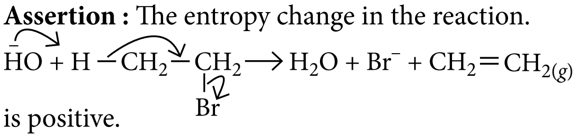
	P	Q	R	S
(a)	3	1	2	4
(b)	3	4	1	2
(c)	2	1	4	3
(d)	4	2	1	3

SECTION - V

Assertion Reason Type

20. Assertion : The isothermal reversible work of expansion is always greater than that of irreversible expansion of an ideal gas.
Reason : Work is a path dependent function.

21. Assertion : The entropy change in the reaction.



$$HO^- + H-CH_2-CH_2(Br) \longrightarrow H_2O + Br^- + CH_2{=}CH_{2(g)}$$

is positive.

Reason : Entropy increases when number of gaseous particles (*i.e.,* molecules or ions) of the product increases.

22. Assertion : If both ΔH° and ΔS° are positive then reaction will be spontaneous at high temperature.
Reason : All processes with positive entropy change are spontaneous.

SECTION - VI

Integer Value Correct Type

23. The freezing point of *iso*-butane is −160 °C. $\Delta H_{(\text{solid} \rightarrow \text{liquid})}$ is +4520 J mol^{-1}. For this fusion process, entropy change in J mol^{-1} is 10 y. The value of y is

24. At dynamic equilibrium, the reaction on both sides occur at the same rate and the mass on both sides of the equilibrium does not undergo any change. This condition can be achieved only when the value of ΔG is

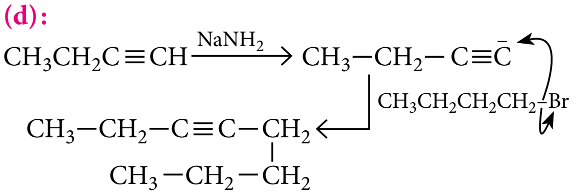
25. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28, was burnt in excess of oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that, heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

SOLUTIONS

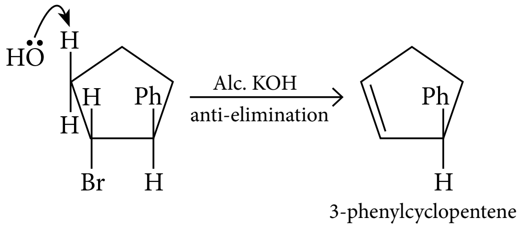
HYDROCARBONS

1. (b) : —NO_2 is an electron-withdrawing group and hence, will destabilise σ-complex thus, others are of higher energy.

2. (d) :



3. (d) :

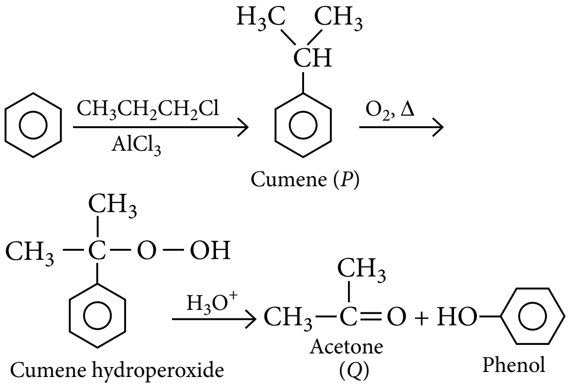


3-phenylcyclopentene

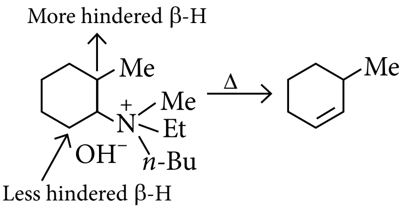
4. (d) **5. (d)** **6. (a)**

7. (a) : C_2H_6 must be in excess for the best yield of C_2H_5Cl.

8. (c) : It is cumene hydroperoxide rearrangement reaction.

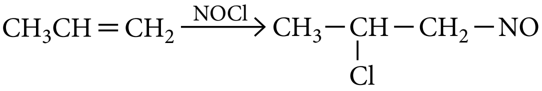


9. (d):



In Hofmann elimination reaction, less sterically hindered β-hydrogen is removed and less substituted alkene is the major product.

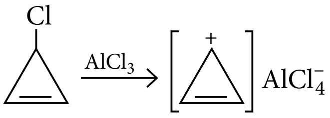
10. (a): $NOCl \longrightarrow NO^+ + Cl^-$



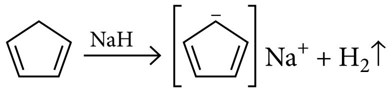
$$CH_3CH{=}CH_2 \xrightarrow{NOCl} CH_3{-}\underset{\displaystyle Cl}{\underset{|}{C}H}{-}CH_2{-}NO$$

11. (a, d) **12. (c, d)**

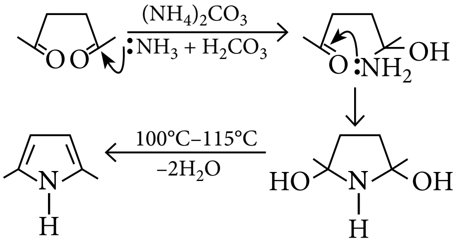
13. (a, b, c, d) :



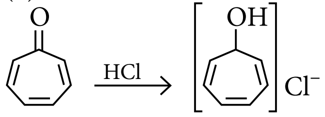
(*P*) Aromatic



(*Q*) Aromatic

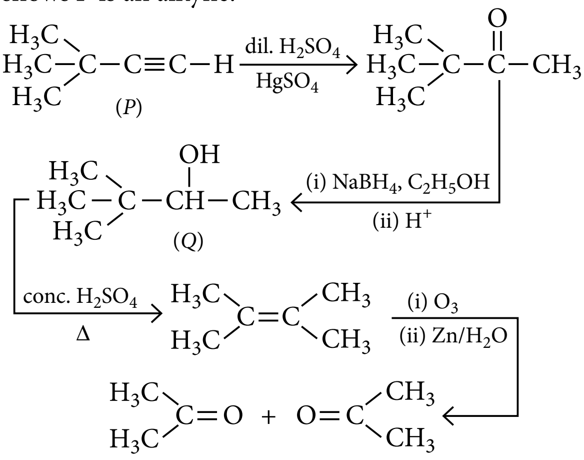


(*R*) Aromatic



(*S*) Aromatic

14. (d): The formula, C_6H_{10} resemble C_nH_{2n-2} which shows *P* is an alkyne.



15. (b)

16. (d): Cyclohexene has one C = C bond.

ΔH of cyclohexene = –85.8/3 = –28.6 kcal mol^{-1}

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

20. (c): Formation of 1-bromobutane from 1-butene involves secondary free radical as intermediate.

(i) $(C_6H_5CO)_2O_2 \longrightarrow 2C_6H_5COO^\bullet$

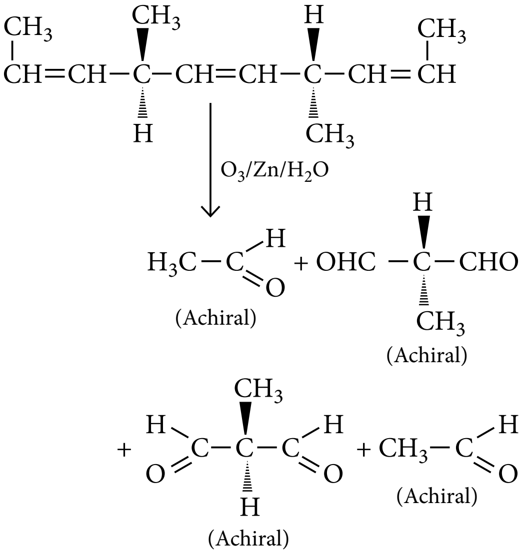
$C_6H_5COO^\bullet + HBr \longrightarrow C_6H_5COOH + Br^\bullet$

(ii) $CH_3CH_2CH{=}CH_2 + Br^\bullet \longrightarrow CH_3CH_2\dot{C}HCH_2Br$

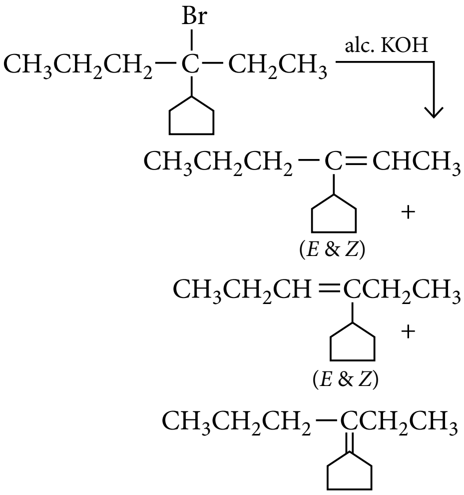
(iii) $CH_3CH_2\dot{C}HCH_2Br + HBr \longrightarrow CH_3CH_2CH_2CH_2Br + Br^\bullet$

21. (a) **22. (a)**

23. (0):



24. (5):



25. (3): *trans*-1,2-Dichloroethene, *trans*-2-butene, 2-butyne have zero dipole moment.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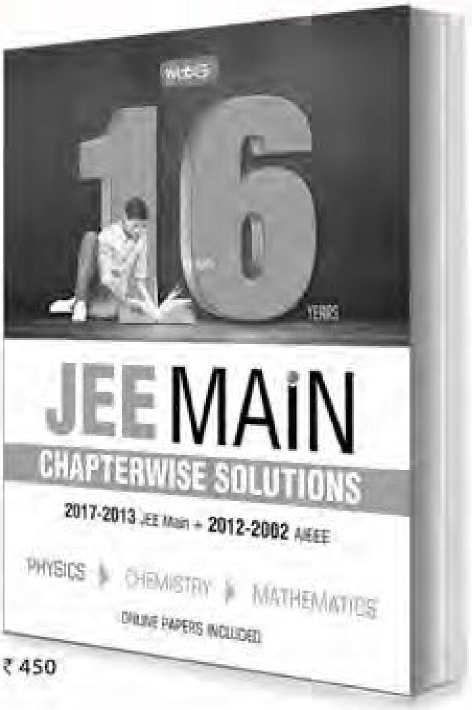
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THERMODYNAMICS

1. **(b):** $w = -P\Delta V$
During process $O \to D$, no change in volume *i.e.*, $\Delta V = 0$
$\therefore \quad w = -P\Delta V = O\,;\, \Delta U = q - w \Rightarrow \Delta U = q$

2. **(b):** For the reaction,
$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$$
$$\Delta S^\circ = \Sigma S^\circ_{(\text{products})} - \Sigma S^\circ_{(\text{reactants})}$$
$$\Delta S^\circ = 50 - [40 \times \frac{3}{2} + 60 \times \frac{1}{2}] = -40\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$\because \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
At equilibrium, $\Delta G^\circ = 0$
$\therefore \quad \Delta H^\circ = T\Delta S^\circ$
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-30\times10^3}{-40} = 750\ \text{K}$$

3. **(a):** $\because \quad PV = RT$ (For one mole)
At unit volume ; $\quad p \times 1 = RT$
Internal energy, $E = \frac{3}{2}RT \Rightarrow \frac{3}{2}p$
$\therefore \quad p = \frac{2}{3}E$

4. **(c):** $\Delta H = H_2 - H_1 = (E_2 + P_2V_2) - (E_1 + P_1V_1)$
$= (E_2 - E_1) + (P_2V_2 - P_1V_1)$
$= 30 + (4 \times 5 - 2 \times 3) = 44$ L atm

5. **(b)** : $\Delta S(A \to B) = \Delta S(A \to C) + \Delta S(C \to D) - \Delta S(B \to D)$
$= 50 + 30 - 20 = +60$ e.u.

6. **(c)**

7. **(d):** Energy left unutilized $= \frac{1560}{2} = 780$ kJ
Amount of water perspired
$$= \frac{\text{Energy left unutilized}}{\text{Enthalpy of evaporation of water}} = \frac{780}{44}\ \text{mol}$$
$$\text{Amount of water(in g)} = \frac{780\times18}{44} = 319\ \text{g}$$

8. **(c):** The specific heat is an intensive property which does not depend on the quantity and size of matter.

9. **(a):** $\Delta G^\circ = -2.303\ RT \log K$
$= -\ 2.303 \times 8.314 \times 298 \log (1.3 \times 10^3)$
$= -17767.688\ \text{J} = -17.767$ kJ
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$-17.767 = -66.5 - 298 \times \Delta S^\circ$
$$\Delta S^\circ = \frac{-66.5+17.767}{298} = -0.163\ \text{kJ}$$

10. **(c):** Exothermic compounds are more stable than endothermic compounds. Greater is the amount of heat evolved in the formation of a compound, more will be its stability.

11. **(b, c, d)** 12. **(a, b, d)**

13. **(a, c, d):** $\Delta S_{\text{system}} = \Delta S_{\text{total}} - \Delta S_{\text{surrounding}}$

14. **(a):** At point (1), pressure is 1 atm and volume is 22.4 L for one mole of gas which indicates NTP state. Thus, temperature is 273 K. At point (2), pressure is again 1 atm but volume is doubled, so temperature is also doubled *i.e.*, 546 K. At point (3), pressure is halved but volume is doubled, so temperature is 273 K.

15. **(b):** $\Delta E = nC_v\Delta T = 1 \times 3/2 \times 8.314 \times 273 = 3.4 \times 10^3$ J

16. **(a)** 17. **(d)** 18. **(b)**

19 **(b):** (P) : $\Delta n_g = 2 - 2 = 0$; hence, $\Delta H = \Delta U$
(Q) : $\Delta n_g = 2 - 1 = 1$; hence, $\Delta H = \Delta U + RT$
(R) : $\Delta n_g = 2 - 4 = -2$; hence, $\Delta H = \Delta U - 2RT$
(S) : $\Delta n_g = 5 - 2 = 3$; hence, $\Delta H = \Delta U + 3RT$

20. **(b)** 21. **(a)**

22. **(c):** Spontaneity of a process depends upon ΔG° which combines with both factors, ΔH° and ΔS°.
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
For the spontaneity, ΔG° should be negative. If ΔH° is +ve, ΔS° is +ve then, ΔG° will be −ve only when $T\Delta S > \Delta H$ which is possible at high temperature.

23. **(4):** $\Delta S = \frac{q_{\text{rev}}}{T} = \frac{4520}{(-160+273)} = \frac{4520}{113} = 40\ \text{J mol}^{-1}$
$\Delta S = 10y = 40 \;\Rightarrow\; y = 4$

24. **(0):** At equilibrium, $\Delta G = 0$

25. **(9):** $C_v = 2.5\ \text{kJ K}^{-1} = 2500\ \text{J K}^{-1}$
$\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45$ K
ΔH, due to combustion of 3.5 g gas
$= C_v \times \Delta T = 2500 \times 0.45 = 1125$ J
Given, molecular weight of gas = 28 = 1 mol
Hence, ΔH due to combustion of 1 mole of gas
$$= \frac{1125}{3.5} \times 28 = 9000\ \text{J mol}^{-1} = 9\ \text{kJ mol}^{-1}$$

◆

ACE YOUR WAY CBSE XI

Series 5

CHAPTERWISE PRACTICE PAPER : HYDROGEN | THE *s*-BLOCK ELEMENTS

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 are metallic hydrides also called interstitial hydrides?

2. Why is Li_2CO_3 decomposed at a lower temperature?

3. What is meant by 15 volume of H_2O_2 solution?

4. Why crystalline salts of alkaline earth metals contain more number of water of crystallisation than that of corresponding alkali metals?

5. Why H_2O_2 cannot be stored for prolonged period?

6. Among LiI or KI, which one is more soluble in ethanol and why?

7. Answer the following questions :

(i) How would you prepare very pure dihydrogen in the laboratory?

(ii) How would you prepare heavy hydrogen in the laboratory?

8. Why is the temperature maintained around 393 K during the preparation of plaster of Paris?

OR

On exposure to air, sodium hydroxide becomes liquid and after sometimes it changes to white powder. Explain why?

9. Calculate the volume strength of a solution containing 30·36 g/lit of H_2O_2.

10. A compound *X* shows the following reactions :

(i) Zinc powder when boiled with a concentrated solution of *X*, it gets dissolved and hydrogen is evolved.

(ii) When an aqueous solution of *X* is added to an aqueous solution of stannous chloride, a white precipitate is obtained first which dissolves in excess of solution *X*.

Identify the compound *X* and write down the reactions involved.

11. Arrange the following :

(i) CaH_2, BeH_2 and TiH_2 in order of increasing electrical conductance.

(ii) LiH, NaH and CsH in order of increasing ionic character.

(iii) H – H, D – D and F – F in order of increasing bond dissociation enthalpy.

12. What happens when

(i) Magnesium is burnt in air

(ii) Quicklime is heated with silica

(iii) Calcium nitrate is heated?

13. Comment on the reactions of dihydrogen with

(i) Chlorine **(ii)** Sodium

(iii) Copper (II) oxide.

14. List three properties which illustrate the diagonal relationship between lithium and magnesium and three properties which illustrate the difference of lithium with other alkali metals.

15. How is hydrogen peroxide obtained in the laboratory? Write any two methods.

16. Explain the following :

(i) NaCl is not hygroscopic but table salt on exposure to air damps up.

(ii) Unlike Na_2CO_3, K_2CO_3 cannot be prepared by Solvay process.

(iii) It is necessary to add gypsum in the final stages of preparation of cement.

OR

(i) Write down the reaction sequence to obtains :

- **(a)** Bleaching powder from $CaCO_3$.
- **(b)** Anhydrous $MgCl_2$ from hydrated magnesium chloride.

(ii) Complete the following reaction :

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow$$

17. What is meant by water gas shift reaction? Discuss its use for the preparation of hydrogen.

18. Starting with sodium chloride how would you proceed to prepare (state the steps only)

(i) Sodium metal **(ii)** Sodium hydroxide

(iii) Sodium peroxide?

19. What do you understand by

(i) electron-deficient **(ii)** electron-precise and

(iii) electron-rich hydrides?

Provide justification with suitable examples.

20. Answer the following questions :

(i) Why can caesium be used in photoelectric cell while lithium cannot?

(ii) Lithium has highest ionization enthalpy in group I elements, yet it is the strongest reducing agent, why?

(iii) Why is calcium preferred over sodium to remove last traces of moisture from alcohol?

21. Calculate the normality of 20 volume solution of H_2O_2.

22. Compare the thermal stability of the following compounds of the alkali metals with those of alkaline earth metals.

(i) Nitrates **(ii)** Carbonates

23. Teacher told the students that water should be softened before using in boilers. Karina one of the students, asked the reason. The teacher explained the reason in detail to her and then Karina got satisfied.

(i) What explanation should be given by teacher?

(ii) What is temporary hardness?

(iii) Temporary hard water becomes soft on boiling. Why?

(iv) What values are shown by Karina?

24. Give the names and formula of the compounds indicated in the following statements:

(i) A compound of Ca used in setting fractured bones.

(ii) A compound of Mg, S, O and H used as a purgative in medicine.

(iii) A compound of Ca and C used for the production of acetylene (Give reaction also).

(iv) A compound of Ca, C and N used as a fertilizer.

(v) A triatomic compound of calcium which on treatment with water gives H_2 (Give reaction also).

OR

Aqueous solution of an inorganic compound (*X*) shows the following reactions :

(i) It decolourises an acidified $KMnO_4$ solution accompanied by the evolution of oxygen.

(ii) It liberates iodine from an acidified KI solution.

(iii) It gives a brown precipitate with alkaline $KMnO_4$ solution with evolution of oxygen.

(iv) It removes black stains from old oil paintings.

Identify (*X*) and give chemical equation for the reactions involved.

25. Complete the following chemical reactions.

(i) $Na_{(s)} + H_{2(g)} \rightarrow$ **(ii)** $MnO^-_{4(aq)} + H_2O_{2(aq)} \rightarrow$

(iii) $CaO_{(s)} + H_2O_{(g)} \rightarrow$ **(iv)** $AlCl_{3(g)} + H_2O_{(l)} \rightarrow$

(v) $Ca_3N_{2(s)} + H_2O_{(l)} \rightarrow$

Classify the above reactions into (*a*) hydrolysis (*b*) redox and (*c*) hydration.

OR

What do you understand by the terms :

(i) hydrogen economy **(ii)** hydrogenation

(iii) syngas **(iv)** water-gas shift reaction

(v) hard water?

26. Explain the following :

(i) A sodium fire in laboratory is not extinguished by water.

(ii) Sodium and potassium do not form complex ions.

(iii) Alkali metals are paramagnetic but their salts are diamagnetic.

(iv) The softness of group IA metals increases down the group with increasing atomic number.

(v) Alkali metals are obtained by the electrolysis of the molten salts and not by the electrolysis of their aqueous solutions.

OR

Explain the following :

(i) Alkaline earth metals are weaker reducing agents than alkali metals.

(ii) Beryllium shows covalency whereas other alkaline earth metals show electrovalency.

(iii) Alkaline earth metals prefer to form M^{2+} ions.

(iv) Be and Mg do not give colour to the flame whereas other alkaline earth metals do so.

(v) The atomic radius of Mg is smaller than sodium.

SOLUTIONS

1. In metallic hydrides, hydrogen is present in the interstices (holes or voids) existing in between the atoms in the lattice without changing the original crystal structure of the metal. That is why, these hydrides are called interstitial hydrides.

2. The Li^+ ion exerts a strong polarising action and distorts the electron cloud of the nearby oxygen atom of the large CO_3^{2-} ion. This results in the weakening of the C—O bond and strengthening of the Li—O bond. Hence, it is less stable and decompose at lower temperature.

3. 15 volume H_2O_2 solution means that 1 litre of this solution gives 15 litre of oxygen at S.T.P.

4. This is because of higher tendency of alkaline earth metal ions towards hydration as they have smaller ionic size and higher charge than alkali metals.

5. H_2O_2 is an unstable compound which decomposes on standing to give water and oxygen, thus cannot be stored for a long period of time.

6. LiI is more soluble than KI in ethanol. Due to its small size, the lithium ion has a higher polarising power than potassium ion. It polarises the electron cloud of the iodide ion to a much greater extent than potassium ion. This causes a greater covalent character in LiI than KI. Hence, LiI is more soluble than KI in ethanol.

7. (i) Fairly pure hydrogen can be obtained by treating pure magnesium or pure aluminium with chemically pure H_2SO_4 or HCl diluted with distilled water. The gas is passed over P_2O_5 and is collected by the displacement of mercury.

$$Mg_{(s)} + H_2SO_{4(aq)} \longrightarrow MgSO_{4(aq)} + H_{2(g)}$$

(ii) Heavy hydrogen can be produced by the action of sodium metal on heavy water.

$$\underset{\text{Heavy water}}{2D_2O_{(l)}} + \underset{\text{Sodium}}{2Na_{(s)}} \rightleftharpoons \underset{\text{Sodium deuteroxide}}{2NaOD_{(aq)}} + \underset{\text{(Deuterium) Heavy hydrogen}}{D_{2(g)}}$$

8. Plaster of Paris is prepared by heating gypsum to 393 K.

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O} \xrightarrow{393\ K} \underset{\text{Plaster of Paris}}{CaSO_4.1/2\ H_2O} + \frac{3}{2} H_2O$$

If the temperature is raised above 393 K, plaster of Paris is further dehydrated to form anhydrous calcium sulphate which is known as dead burnt plaster since it loses the property of setting with water.

OR

On exposure to air, sodium hydroxide continuously absorbs CO_2 from atmosphere and converted into sodium carbonate. A stage reaches when the solution becomes saturated and crystals are formed. After some time, these Na_2CO_3 crystals lose water of crystallisation (efflorescence) on standing in air and crumble in to white powder.

9. Volume strength of 30.36 g/lit H_2O_2 means the volume of O_2 (in L) that is librated from 30.36 g of H_2O_2.

$$\underset{68\ g}{2H_2O_2} \xrightarrow{\text{Decomposition}} 2H_2O + \underset{22{\cdot}4\ L\ \text{at S.T.P.}}{O_2}$$

68 g of H_2O_2 produce O_2 at S.T.P. = 22.4 L

30·36 g of H_2O_2 will produce O_2 at S.T.P.

$$= \frac{30{\cdot}36 \times 22{\cdot}4}{68} = 10\ L$$

∴ Volume strength of H_2O_2 = 10 L.

10. The compound X is NaOH and the reactions involved are

$$Zn + \underset{(X)}{2NaOH} \rightarrow Na_2ZnO_2 + H_2\uparrow$$

$$SnCl_2 + \underset{(X)}{2NaOH} \rightarrow \underset{\text{white ppt.}}{Sn(OH)_2} + 2NaCl$$

$$Sn(OH)_2 + \underset{(X)}{2NaOH} \rightarrow \underset{\text{soluble}}{Na_2SnO_2} + 2H_2O$$

11. (i) BeH_2 is significantly covalent, CaH_2 is ionic and TiH_2 is metallic hydride. Hence, increasing electrical conductance :

$BeH_2 < CaH_2 < TiH_2$

(ii) Electronegativity decreases as Li > Na > Cs.
Thus, increasing ionic character :
LiH < NaH < CsH

(iii) Due to lone pairs of F, bond pairs experience repulsion, hence, F–F has low bond dissociation energy. In D–D, due to higher nuclear attraction bond dissociation energy is greater than H–H. Increasing bond dissociation enthalpy :
F–F < H–H < D–D

12. **(i)** When magnesium is burnt in air it forms magnesium oxide and magnesium nitride with dazzling brilliance.

$2Mg + O_2 \longrightarrow 2MgO$

$3Mg + N_2 \longrightarrow Mg_3N_2$

(ii) When quicklime is heated with silica, it gives calcium silicate.

$$CaO + SiO_2 \xrightarrow{\text{Above 1273 K}} \underset{\text{Calcium silicate}}{CaSiO_3}$$

(iii) When calcium nitrate is heated, it gives CaO, NO_2 and O_2.

$2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$

13. **(i)** Dihydrogen reduces chlorine to chloride ion (Cl^-) and itself gets oxidised to H^+ ion in HCl. An electron pair is shared between H and Cl to form a covalent molecule of hydrogen chloride.

$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$

(ii) Sodium reduces dihydrogen to form hydride (H^-) ion and itself gets oxidised to sodium (Na^+) ion. During this reaction, an electron is transferred from Na to H leading to the formation of an ionic compound of sodium hydride (NaH).

$2Na_{(s)} + H_{2(g)} \xrightarrow{\Delta} 2NaH_{(s)}$

(iii) Hydrogen reduces copper (II) oxide to copper metal (in zero oxidation state) and itself gets oxidised to H_2O, which is a covalent molecule.

$$\overset{+2\ -2}{CuO_{(s)}} + \overset{0}{H_{2(g)}} \longrightarrow \overset{0}{Cu_{(s)}} + \overset{+1\ -2}{H_2O_{(l)}}$$

14. Properties which illustrate the diagonal relationship between Li and Mg :

(i) Both Li and Mg are harder and have higher melting points than other elements in their respective groups.

(ii) Lithium and magnesium both form only monoxides when heated in oxygen.

$4Li + O_2 \rightarrow 2Li_2O$

$2Mg + O_2 \rightarrow 2MgO$

(iii) Chlorides of both Li and Mg are deliquescent and soluble in alcohol and pyridine.

Properties which illustrate the point of difference of Li to other alkali metals :

(i) Li is much harder. Its m.pt. and b.pt. are higher than the other alkali metals.

(ii) Li is least reactive but the strongest reducing agent among all the other alkali metals.

(iii) $LiNO_3$, on heating gives a mixture of NO_2 and O_2 while nitrates of rest of alkali metals gives only oxygen.

$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

15. In laboratory, hydrogen peroxide may be prepared from sodium peroxide and barium peroxide.

(i) Sodium peroxide is added in small amount to an ice cold dilute solution (20 per cent) of sulphuric acid.

$$Na_2O_2 + \underset{\text{Ice cold}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O_2$$

Sodium sulphate formed is removed by crystallisation, and a dilute solution of H_2O_2 is obtained.

(ii) Paste of $BaO_2.8H_2O$ is prepared and added gradually to an ice cold dilute sulphuric acid. The solution is kept well-stirred throughout.

$BaO_2 + H_2SO_4$ (ice cold) $\longrightarrow BaSO_4 + H_2O_2$

Barium sulphate precipitates out leaving behind a dilute solution of hydrogen peroxide.

16. **(i)** Pure NaCl is not hygroscopic. The commercial common salt or table salt consists of small amount of $MgCl_2$ and $CaCl_2$ which absorb moisture from atmosphere making it damp.

(ii) In Solvay process, $NaHCO_3$ is prepared first which becomes sparingly soluble and on heating, Na_2CO_3 is obtained.

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

$KHCO_3$ is soluble in water and can not be obtained in solid state that is why K_2CO_3 is not formed by this method.

(iii) When cement is mixed with water, it becomes hard over a period of time. This is called setting of cement. Gypsum is often added to portland cement to prevent early hardening or flash setting allowing a longer working time. Gypsum slows down the setting of cement so that cement is adequately hardened.

OR

(i) (a) Getting bleaching powder from $CaCO_3$.

$$\begin{tikzcd}[column sep=large] CaCO_3 \arrow[r, "\Delta"] & \begin{matrix} CaO \\ + \\ CO_2 \end{matrix} \arrow[r, "H_2O"] & Ca(OH)_2 \arrow[d, "Cl_2", "40°C"'] \\ & & \underset{\text{(Bleaching powder)}}{CaOCl_2 + H_2O} \end{tikzcd}$$

(b) Anhydrous $MgCl_2$ from hydrated $MgCl_2$: To make hydrated $MgCl_2$ anhydrous, it is first heated in air and then in a current of HCl gas.

$$MgCl_2.6H_2O \xrightarrow[\text{HCl gas}]{\text{Heated in presence of}} MgCl_2 + 6H_2O$$

(ii) $Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3 + CaCO_3 + 2H_2O$

17. Water gas shift reaction involves a selective oxidation of CO to CO_2 by passing a mixture of water gas and steam (excess) over a catalyst containing ferric oxide and chromium oxide at 773 K. Water gas is obtained by passing steam over red hot coke.

$$\underset{\text{Red hot}}{C_{(s)}} + H_2O_{(g)} \xrightarrow{1270\text{ K}} \underbrace{CO_{(g)} + H_{2(g)}}_{\left[\begin{matrix}\text{Water gas}\\ \text{(Syngas)}\end{matrix}\right]}$$

$$\underbrace{H_{2(g)} + CO_{(g)}}_{\text{Water gas}} + H_2O_{(g)} \xrightarrow[773\text{ K}]{Fe_2O_3/Cr_2O_3} CO_{2(g)} + 2H_{2(g)}$$

$CO_{2(g)}$ is removed by passing the mixture through water under high pressure. Thus, water gas shift reaction generates more hydrogen.

18. (i) $NaCl_{(s)} \xrightarrow{\text{heat}} \underset{\text{(Molten)}}{NaCl} \xrightarrow{\text{electrolysis}} \underset{\text{at cathode}}{Na_{(s)}} + \underset{\text{at anode}}{½Cl_2}$

(ii)

$$\begin{tikzcd}[column sep=large] NaCl_{(aq)} \arrow[r, "\text{electrolysis}", "\text{Hg-cathode}"'] & \underset{\text{at cathode}}{Na-Hg} + \underset{\text{at anode}}{½\, Cl_{2(g)}} \arrow[d, "H_2O"'] \\ & NaOH_{(aq)} + ½\, H_{2(g)} + Hg \end{tikzcd}$$

(iii) $NaCl_{(s)} \xrightarrow{\text{heat}} \underset{\text{(molten)}}{NaCl} \xrightarrow{\text{electrolysis}} \underset{\text{at cathode}}{Na_{(s)}} + \underset{\text{at anode}}{½Cl_{2(g)}}$

This sodium is then heated on aluminium trays in air (free of CO_2) to form its peroxide.

$$2Na_{(s)} + \underset{\text{in air}}{O_{2(g)}} \longrightarrow Na_2O_{2(s)}$$

19. (i) Electron-deficient hydrides are those which do not have sufficient number of electrons to form normal covalent bonds. For example, hydrides of group 13 (BH_3, AlH_3, etc). To make up their deficiency they generally exist in polymeric forms such as B_2H_6, Al_2H_6, etc.

(ii) Electron-precise hydrides are those which have sufficient number of electrons required for forming covalent bonds. For example, hydrides of group 14 (CH_4, SiH_4, GeH_4, SnH_4, PbH_4 etc).

(iii) Electron-rich hydrides are those which have excess electrons required to form normal covalent bonds. For example, hydride of group 15 or 17 (*i.e.*, NH_3, PH_3, H_2O, H_2S, H_2Se, H_2Te, etc). The excess electrons in these hydrides are present as lone pairs.

20. (i) Caesium has the lowest while lithium has the highest ionization enthalpy. Hence, Cs can lose electrons very easily while lithium cannot and hence can not be used in photoelectric cell.

(ii) In aqueous solutions, the tendency of an element to lose electrons does not entirely depend upon its ionization enthalpy. It also depends upon its enthalpy of sublimation and the enthalpy of hydration of the ion left after the loss of an electron. The combined effect of these factors is measured in terms of electrode potential. Since lithium has the most negative electrode potential in group I elements, therefore, lithium is the strongest reducing agent.

(iii) Both Na and Ca react with water to form their respective hydroxides. On the other hand, Na readily reacts with alcohol to form sodium ethoxide but Ca reacts very slowly. Thus, when Ca is used, it will react more readily with water than with alcohol.

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$$

Therefore, Ca is preferred over Na to remove the last traces of moisture from alcohol.

21. H_2O_2 decomposes as follows :

$$\underset{2\text{ mol}}{2H_2O_2} \longrightarrow 2H_2O + \underset{1\text{ mol} = 22.4\text{ L (at STP)}}{O_2}$$

Let us take 1 L of 20 volume H_2O_2. Then,

1 L of $H_2O_2 \equiv 20$ L of oxygen

From the stoichiometry,

22.4 L of oxygen is given by 4 equiv. of H_2O_2

$$1\text{ L of oxygen is given by } \frac{4\text{ equiv.}}{22.4} \text{ of } H_2O_2$$

$$20\text{ L of oxygen is given by } \frac{4\text{ equiv.}}{22.4} \times 20 = 3.57\text{ equiv.}$$

Thus, 1 L of H_2O_2 contains 3.57 equivalents of H_2O_2 in it.

∴ Normality of H_2O_2 sample = 3.57

22. **(i)** Thermal stability of nitrates : Nitrates of both alkali and alkaline earth metals decompose on heating. All alkaline earth metal nitrates decompose to form metal oxide, NO_2 and O_2.

$$2M(NO_3)_2 \xrightarrow{\Delta} 2MO + 4NO_2 + O_2$$

(M = Be, Mg, Ca, Sr or Ba)

The nitrates of Na, K, Rb and Cs decompose to form metal nitrites and O_2.

$$2MNO_3 \xrightarrow{\Delta} 2MNO_2 + O_2 \; (M = \text{Na, K Rb, Cs})$$

However, due to diagonal relationship between Li and Mg, lithium nitrate decomposes like $Mg(NO_3)_2$ to form metal oxide, NO_2 and O_2.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

(ii) Thermal stability of carbonates : Carbonates of alkaline earth metals decompose on heating to form metal oxide and CO_2.

$$MCO_3 \xrightarrow{\Delta} MO + CO_2 \; (M = \text{Be, Mg, Ca, Sr, Ba})$$

Further as the electropositive character of the metal increases down the group, the stability of these metal carbonates increases or the temperature of their decomposition increases as shown below :

$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
373 K	813 K	1173 K	1563 K	1633 K

Due to diagonal relationship between Li and Mg, Li_2CO_3 decomposes in the same way as $MgCO_3$.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

All other alkali metal carbonates are stable and do not decompose even at high temperature.

23. **(i)** Water should be softened before using in boilers otherwise it may cause various boiler problems like

(a) Scale and sludge formation

(b) Priming and foaming

(c) Boiler corrosion.

(ii) Temporary hardness of water is the hardness caused by the presence of dissolved calcium and magnesium bicarbonates.

(iii) On boiling the calcium/magnesium bicarbonate decomposes to give calcium/magnesium carbonate, which is insoluble in water. Therefore, it precipitates out.

$$Ca(HCO_3)_2 \xrightarrow{\text{boiling}} \underset{\text{Insoluble}}{CaCO_3\downarrow} + CO_2 + H_2O$$

$$Mg(HCO_3)_2 \xrightarrow{\text{boiling}} \underset{\text{Insoluble}}{MgCO_3} + H_2O + CO_2$$

(iv) Curiosity, Knowledge and self awareness.

24. **(i)** Plaster of Paris, $2CaSO_4 \cdot H_2O$

(ii) Magnesium sulphate, $MgSO_4 \cdot 7H_2O$

(iii) Calcium carbide, CaC_2

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

(iv) Calcium cyanamide (Nitrolim), $CaCN_2 + C$

(v) Calcium hydride (hydrolith), (CaH_2)

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

OR

(i) $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(ii) $2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + 2H_2O$

(iii) $2KMnO_4 + 3H_2O_2 \longrightarrow 2KOH + \underset{\text{Brown}}{2MnO_2} + 2H_2O + 3O_2$

(iv) $\underset{\text{Black}}{PbS} + 4H_2O_2 \longrightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$

Therefore, compound (X) is H_2O_2.

25. **(i)** $2Na + H_2 \rightarrow 2NaH$ (Redox reaction)

(ii) $2MnO_4^- + 5H_2O_2 \xrightarrow{6H^+} 2Mn^{2+} + 8H_2O + 5O_2$ (Redox reaction)

(iii) $CaO + H_2O \rightarrow Ca(OH)_2$ (Hydrolysis reaction)

(iv) $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$ (Hydration reaction)

(v) $Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3$ (Hydrolysis reaction)

OR

(i) Hydrogen economy : The energy is transported and stored in the form of liquid or gaseous hydrogen which is considered to be a possible source of clean energy. This proposal to use hydrogen as fuel is called hydrogen economy.

(ii) Hydrogenation : The process of addition of hydrogen to unsaturated hydrocarbons is known as hydrogenation.

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + H_2 \xrightarrow[\text{473 K}]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{H_3C{-}CH_3}$$

$$\underset{\text{Ethyne}}{H{-}C{\equiv}C{-}H} + 2H_2 \xrightarrow[\text{473 K}]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{H_3C{-}CH_3}$$

(iii) Syngas : The mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or syngas. Nowadays, syngas is produced from sewage, saw dust, scrap wood, newspapers, etc.

(iv) Water-gas shift reaction : Commercial dihydrogen is obtained by mixing water gas with steam and passed over a mixture of ferric oxide and chromium oxide heated at 500 °C.

$$CO_{(g)} + H_2O_{(g)} \xrightarrow[\text{catalyst}]{773\text{ K}} CO_{2(g)} + H_{2(g)}$$

This is called water-gas shift reaction.

(v) Hard water : The water containing calcium and magnesium salts in the form of hydrogen carbonate, chloride and sulphate is known as hard water.

26. (i) Since sodium reacts vigorously with water, sodium fire should not be extinguished with water, but carbon tetrachloride (pyrene) should be used to extinguish sodium fire in laboratory.

(ii) In order to form complex compounds, a metal should have the vacant *d*-orbitals which Na or K or other alkali metals do not have so cannot form complex ions.

(iii) The alkali metals have one unpaired electron in their outermost shell, thus these are paramagnetic. While in their salts, alkali metals are present as cations which have inert gas configuration thus their salt are diamagnetic.

(iv) The softness of group IA metals increases down the group because there is continuous decrease of metallic bond strength on account of an increase in atomic size. Bigger is the atomic size of metal, its metallic bond strength is weak and metal becomes soft.

(v) The aqueous solution of alkali metal salt contains metal cation, H^+, OH^- and anion. In that condition the discharge potential of H^+ ions is lower than the metal cations and on electrolysis of solutions of alkali metal salts, hydrogen is discharged at cathode rather than the metal.

OR

(i) Since the oxidation potential of alkaline earth metals is lower than that of alkali metals, thus alkaline earth metals are weaker reducing agents than alkali metals.

(ii) The polarising power of Be^{2+} ion is high, due to its high charge density. The large distortion of electron cloud of the anion brings covalent character. Be has high value of electronegativity and when it reacts with another element, the electronegativity difference is not much and the bond formed is therefore covalent.

(iii) The existence of divalent ions in solid state is due to greater lattice energy released in the formation of compounds of divalent cations than to those of monovalent cations. High value of hydration energy of divalent cations counter balances the higher value to ionisation energy. Thus, alkaline earth metals prefer to form M^{2+} ions.

(iv) In case of Ca, Sr, Ba, Ra, the electron can be excited by the supply of energy. When excited electron comes in its original position it releases energy in the form of light. But Be and Mg have small size, thus their electrons are tightly held and thus excitation of electron is difficult. Hence, they do not show flame colouration.

(v) Shell number of both Na and Mg is same. But number of electrons in Mg is more, thus attractive force in Mg is greater than that in Na and thus Mg has smaller size than Na.

……

MPP-7 MONTHLY Practice Problems

Class XI

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

The *s*-Block Elements

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

NEET / AIIMS

Only One Option Correct Type

1. When $NaNO_2$ is treated with Na
(a) $NaNO_3$ is formed
(b) Na_2O and N_2 are formed
(c) Na_2O_2 and N_2 are formed
(d) Na_2O and Na_3N are formed.

2. Sodium metal reacts with Al_2O_3 at high temperature to give a sodium compound *X*. *X* reacts with carbon dioxide in water to form *Y*. *Y* is
(a) Na_2CO_3 (b) Na_2O_2
(c) $NaAlO_2$ (d) Na_2O

3. In Solvay process, NaCl combines with NH_4HCO_3 to give
(a) precipitate of $NaHCO_3$
(b) precipitate of Na_2CO_3
(c) solution of $NaHCO_3$
(d) solution of Na_2CO_3.

4. Elements of group I give colour to the Bunsen burner flame due to
(a) softness
(b) low melting point
(c) low ionisation enthalpy
(d) single electron in the outermost orbit.

5. Stability of nitrides of IIA group elements is in order
(a) $Ca_3N_2 < Mg_3N_2 < Be_3N_2$
(b) $Be_3N_2 < Mg_3N_2 < Ca_3N_2$
(c) $Ca_3N_2 < Be_3N_2 < Mg_3N_2$
(d) $Mg_3N_2 < Be_3N_2 < Ca_3N_2$

6. Consider the following abbreviations for hydrated alkali ions
$X = [Li(H_2O)_n]^+$ $Y = [K(H_2O)_n]^+$
$Z = [Cs(H_2O)_n]^+$

Which of the following is the correct order of size of these hydrated alkali ions?
(a) $Z > X > Y$ (b) $X = Y = Z$
(c) $X > Y > Z$ (d) $Z > Y > X$

7. Calcium is obtained by
(a) electrolysis of molten $CaCl_2$
(b) electrolysis of solution of $CaCl_2$ in water
(c) reduction of $CaCl_2$ with carbon
(d) roasting of limestone.

8. Which of the following is not correct about the solution when moderate amount of sodium metal is dissolved in liquid ammonia at low temperature?
(a) Na^+ ions are produced in solution.
(b) A blue coloured solution is obtained.
(c) The solution acts as a good conductor of electricity.
(d) Liquid ammonia remains diamagnetic.

9. What happens when quick lime is exposed to air?
(a) It produces $CaCO_3$ and H_2O.
(b) It produces $Ca(OH)_2$ and H_2O.
(c) It produces $Ca(OH)_2$ and $CaCO_3$.
(d) It produces CaH_2 and H_2O.

10. By adding gypsum to cement
(a) setting time of cement becomes less
(b) setting time of cement increases
(c) colour of cement becomes light
(d) shining surface is obtained.

11. Comparing calcium oxide and magnesium oxide, which of the two would be more stable?
    (a) Magnesium oxide would be more stable because the magnesium cation is smaller than the calcium cation.
    (b) Magnesium oxide would be more stable because magnesium has lower atomic mass than calcium.
    (c) Calcium oxide would be more stable because the calcium cation is smaller than the magnesium cation.
    (d) Calcium oxide would be more stable because calcium has greater atomic mass than magnesium.

12. The pair of compounds which cannot exist together in solution is
    (a) $NaHCO_3$ and NaOH
    (b) Na_2CO_3 and $NaHCO_3$
    (c) Na_2CO_3 and NaOH
    (d) $NaHCO_3$ and NaCl.

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 :** Among the alkali metals, lithium salts exhibit the least electrical conductance in aqueous solutions.
    Reason : Smaller the radius of the hydrated cation, lower is the electrical conductance in aqueous solutions.

14. **Assertion :** Na_2SO_4 is soluble in water but $BaSO_4$ is insoluble in water.
    Reason : In case of $BaSO_4$, its lattice energy is more than its hydration energy.

15. **Assertion :** Barium is not required for normal biological functions in human.
    Reason : Barium does not show variable oxidation states.

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. Na_2O_2
    (a) is diamagnetic in nature
    (b) is a salt of dibasic acid H_2O_2
    (c) oxidises Cr^{3+} (green) to CrO_4^{2-} (yellow)
    (d) all of these.

17. All the products are same when *X* and *Y* react with water. *X* and *Y* are respectively :
    (a) Ca, CaO
    (b) Na, NaH
    (c) NaOH, Na_2CO_3
    (d) Na, K

18. A metal *M* readily forms water soluble sulphate MSO_4, water insoluble hydroxide $M(OH)_2$ and oxide *M*O which becomes inert on heating. The hydroxide is soluble in NaOH. Thus, *M* is
    (a) Mg
    (b) Sr
    (c) Be
    (d) Ca

19. The alkali metals form hydrides by direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following order?
    (a) CsH > RbH > KH > NaH > LiH
    (b) KH > NaH > LiH > CsH > RbH
    (c) NaH > LiH > KH > RbH > CsH
    (d) LiH > NaH > KH > RbH > CsH

More than One Options Correct Type

20. Select the correct statements.
    (a) Alkali metals form alloys amongst themselves.
    (b) Alkali metals dissolve readily in mercury.
    (c) The process of formation of amalgams by alkali metals is highly exothermic.
    (d) The process of formation of amalgam by alkali metals is highly endothermic.

21. Which of the following compounds are used for textile industry?
    (a) Na_2CO_3
    (b) $NaHCO_3$
    (c) NaOH
    (d) NaCl

22. The compounds formed upon combustion of sodium metal in excess air are
    (a) Na_2O_2
    (b) Na_2O
    (c) NaO_2
    (d) NaOH

23. In the diaphragm cell used for the electrolysis of brine, the reactions that occur are
    (a) $2Na + 2H_2O \rightarrow 2NaOH + H_2$
    (b) $2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
    (c) $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$
    (d) $2Cl^- \longrightarrow Cl_2 + 2e^-$

Integer Answer Type

24. Out of Be, Mg, Ca, Sr and Ba, total number of metals whose nitrates are decomposed according to following reaction :

$$2M(NO_3)_2 \xrightarrow{\Delta} \text{"Residue"} + 4NO_2 + O_2$$

25. Total number of alkali metals (non-radioactive) which produce stable superoxide when burn with excess of O_2 is

26. Total number of moles of water in 1 mole of epsom salt is

Comprehension Type

On treatment with cold water, element (*A*) reacted quietly, liberating colourless gas (*B*) and solution (*C*). Lithium reacted with gas (*B*) giving a solid product (*D*) which gave effervesence with water to give basic solution (*F*). When CO_2 was passed through solution (*C*), initially white ppt. (*E*) was formed but this redissolved forming solution (*G*) when more CO_2 was passed. Ppt. (*E*) effervescenced when moistened with conc. HCl and gave a deep red colouration to Bunsen flame. (*E*) on heating with excess of carbon at 2000 °C gave (*H*).

27. Consider the following statements about a salt solution (*G*).

(I) It causes permanent hardness of water.
(II) It cannot be obtained in solid state.
(III) It causes temporary hardness to water.
(IV) It can be obtained in solid state.

Correct statements are

(a) I and II only
(b) I and IV only
(c) II and III only
(d) II and IV only

28. Solid (*H*) on hydrolysis gives a gas, which on passing through ammonical $AgNO_3$, gives

(a) white ppt.
(b) red ppt.
(c) no ppt.
(d) brown ppt.

Matrix Match Type

29. Match the Column I with Column II and choose the correct option using the codes given below.

Column I (Compound)	**Column II (Use)**
(A) $CaCO_3$	(p) Used in gun powder
(B) $Na_2S_2O_3 \cdot 5H_2O$	(q) Used in fire extinguishers
(C) $NaNO_3$	(r) Used as a flux in metallurgy
(D) $NaHCO_3$	(s) Used in black and white photography

	A	B	C	D
(a)	r	s	p	q
(b)	p	s	q	r
(c)	r	q	p	s
(d)	r	s	q	p

30. Match the Column I with Column II and choose the correct option using the codes given below.

Column I	**Column II**
(A) Complex formation	(p) Be
(B) Formation of covalent compounds	(q) Mg
(C) High solubility of salts	(r) Ca
(D) Explosive reaction with acids	(s) Sr

	A	B	C	D
(a)	q	p	p, q	q, s
(b)	p	p	p, q	r, s
(c)	p, s	q	r	s
(d)	p	q	r, s	p, q

◆◆

Keys are published in this issue. Search now! ☺

SELF CHECK

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

Check your score! If your score is

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

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Class XII

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Unit 5

Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers

HALOALKANES AND HALOARENES

HALOALKANES

INTRODUCTION

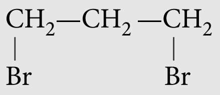
- Compounds derived from alkanes by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are termed as halogen derivatives of alkanes or haloalkanes.

HALOALKANES

Monohalogen derivatives : $C_nH_{2n+2} \xrightarrow[+X]{-H} C_nH_{2n+1}X$

CH_3Cl	C_2H_5Br
Methyl chloride	Ethyl bromide

Di-halogen derivatives : $C_nH_{2n+2} \xrightarrow[+2X]{-2H} C_nH_{2n}X_2$

Gem-dihalide	**Vic-dihalide**	**α–ω halides**
Both halogen atoms are attached to same carbon atom.	The halogen atoms are attached to adjacent carbon atom, known as alkylene halides.	The halogen atoms are attached to terminal carbon atoms.
e.g., $CH_3CH_2CHCl_2$ 1, 1-dichloropropane	*e.g.*, $ClCH_2—CH_2Cl$ 1, 2-dichloroethane	 $CH_2(Br)—CH_2—CH_2(Br)$ 1, 3-dibromopropane

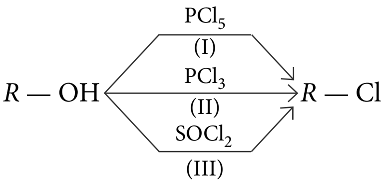
Tri-halogen derivatives : $C_nH_{2n+2} \xrightarrow[+3X]{-3H} C_nH_{2n-1}X_3$

$CHCl_3$	$CHBr_3$	CHI_3
Chloroform	Bromoform	Iodoform

Tetrahalogen derivatives : Four hydrogen atoms are replaced by four halogen atoms. *e.g.*, CCl_4, CBr_4, $Cl_2HC—CHCl_2$, etc.

PREPARATION

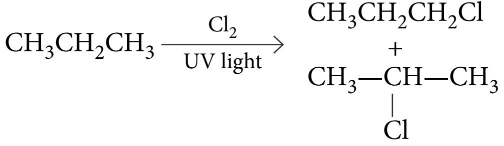
- **From alcohols :**



$$R-OH \xrightarrow[\text{(I)}]{PCl_5} R-Cl \qquad R-OH \xrightarrow[\text{(II)}]{PCl_3} R-Cl \qquad R-OH \xrightarrow[\text{(III)}]{SOCl_2} R-Cl$$

Most preferred method is (III) because other products of this reaction (SO_2 and HCl) are gaseous and can easily escape.

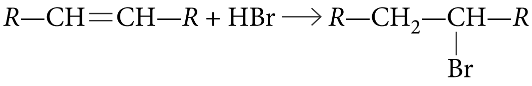
- **From hydrocarbons :**



$$CH_3CH_2CH_3 \xrightarrow[\text{UV light}]{Cl_2} CH_3CH_2CH_2Cl + CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3$$

  - Free radical mechanism is followed.
  - Order of ease of substitution : 3° > 2° > 1° (alkyl)
    Benzylic ≈ allylic > alkyl > vinylic ≃ arylic

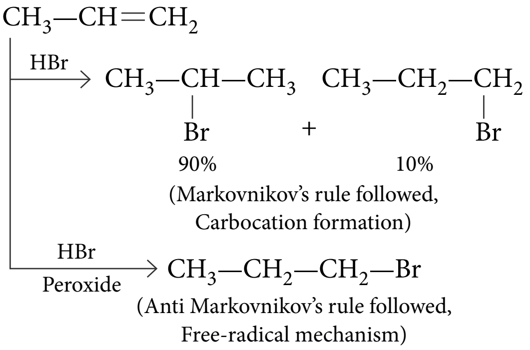
- **From alkene (by *HX* addition) :**
  - **From symmetrical alkenes :**



$$R-CH=CH-R + HBr \longrightarrow R-CH_2-\underset{\underset{\displaystyle Br}{|}}{CH}-R$$

(Single product obtained)

  - **From unsymmetrical alkenes :**



$$CH_3-CH=CH_2 \xrightarrow{HBr} \underset{90\%}{CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3} + \underset{10\%}{CH_3-CH_2-\underset{\underset{\displaystyle Br}{|}}{CH_2}}$$

(Markovnikov's rule followed, Carbocation formation)

$$CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-CH_2-CH_2-Br$$

(Anti Markovnikov's rule followed, Free-radical mechanism)

  - **Markovnikov's rule :** During the addition across unsymmetrical double bond, the negative part of the attacking reagent goes to the carbon atom carrying lesser number of hydrogen atoms while the positive part goes to the carbon atom with more number of hydrogen atoms.
  - **Anti-Markovnikov's rule :** When HBr is added to unsymmetrical double bond in presence of peroxide, the reaction takes place contrary to the Markovnikov's rule. This is known as anti–Markovnikov's rule, peroxide effect or Kharasch effect. This law is applicable for the addition of HBr only.

- **From silver salts of acids :**
  - **Borodine Hunsdiecker reaction :**

    $CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + CO_2 + AgBr$

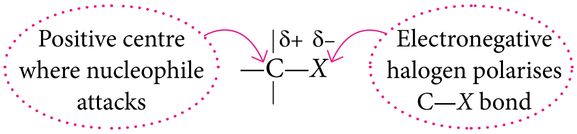
- **By halogen exchange method :**
  - **Finkelstein reaction**
    $R-X + NaI \longrightarrow R-I + NaX \qquad (X = Cl, Br)$
  - **Swartz reaction (For alkyl fluoride)**
    $H_3C-Br + AgF \longrightarrow H_3C-F + AgBr$

PHYSICAL PROPERTIES

- Alkyl halides are very slightly soluble in water but soluble in organic solvents.
- Alkyl bromides and iodides are heavier than water whereas alkyl chlorides and fluorides are lighter than water.
- The boiling points of alkyl halides are in the order *RI* > *RBr* > *RCl* > *RF* and the boiling points of alkyl halides increases with increase in size of the alkyl group.
- Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amount.

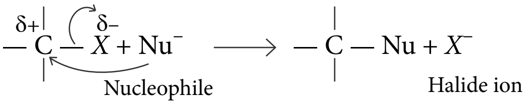
NATURE OF C—*X* BOND

- In haloalkanes, the carbon is bonded to a halogen atom (*X* = F, Cl, Br, I) which is more electronegative than carbon. Consequently, the C—*X* bond is polar in nature and its bond length increases from C—F to C—I.



CHEMICAL PROPERTIES

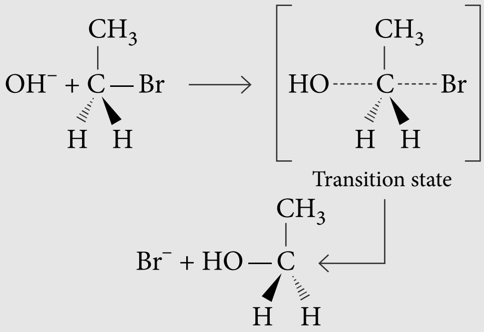
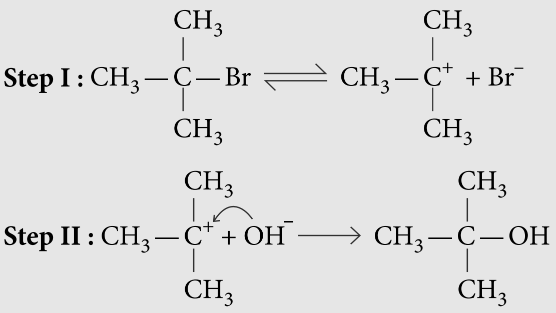
- **Nucleophilic substitution reactions :** The reactions in which a stronger nucleophile displaces a weaker nucleophile (leaving group) are called nucleophilic substitution reactions.



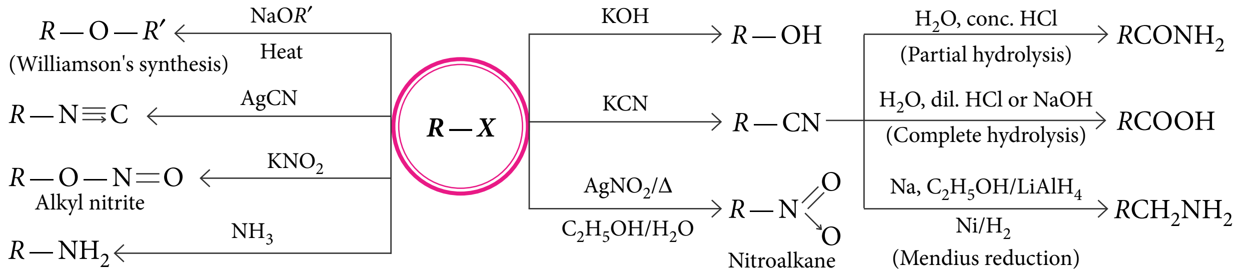
$$-\overset{\delta+}{\underset{|}{\overset{|}{C}}}-\overset{\delta-}{X} + \underset{\text{Nucleophile}}{Nu^-} \longrightarrow -\underset{|}{\overset{|}{C}}-Nu + \underset{\text{Halide ion}}{X^-}$$

  - **Leaving group ability :** $I^- > Br^- > Cl^- > F^-$
  - **Order of reactivity :** $R-I > R-Br > R-Cl > R-F$

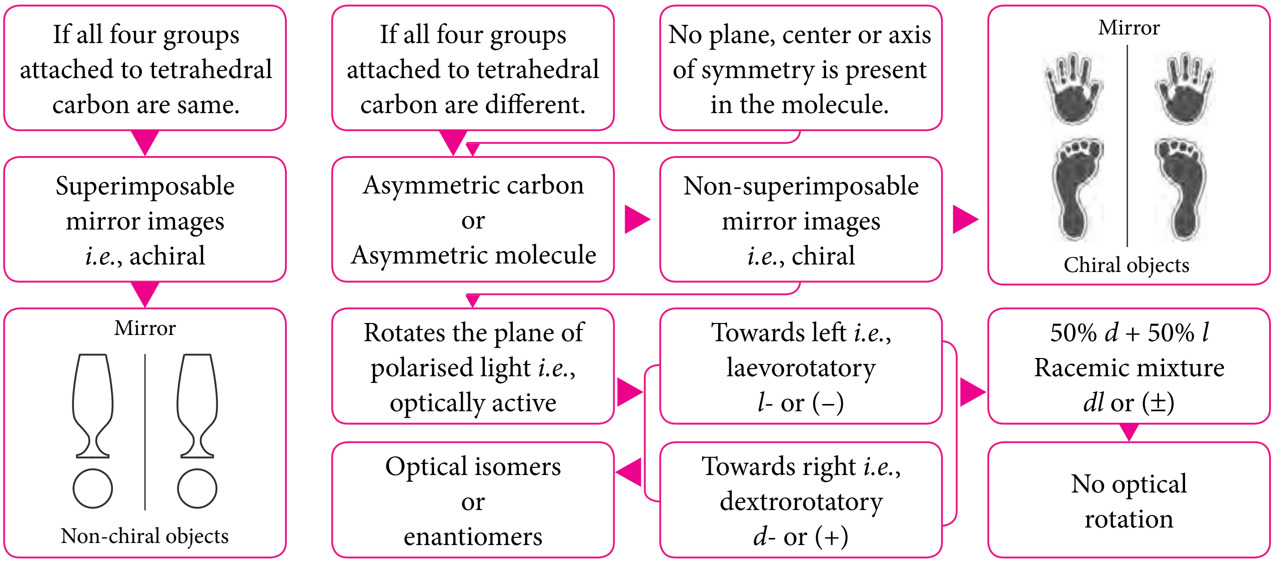
Types of Nucleophilic Substitution Reactions

S_N2 (Biomolecular)	S_N1 (Unimolecular)
Mechanism : 	**Mechanism :** 
Rate = $k[RX][OH^-]$	Rate = $k[RX]$
Single step reaction.	Two step reaction.
Inversion of configuration takes place.	Carbocation rearrangement may take place.
Reactivity order of alkyl halides : $CH_3X > 1° > 2° > 3°$	Reactivity order of alkyl halides : $3° > 2° > 1° > CH_3X$

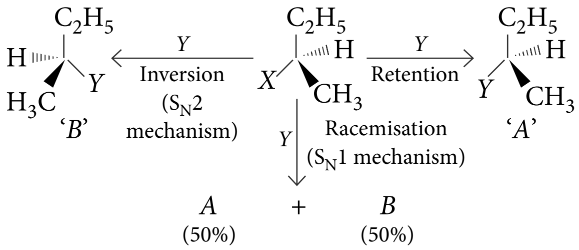
- **Examples of substitution reactions :**



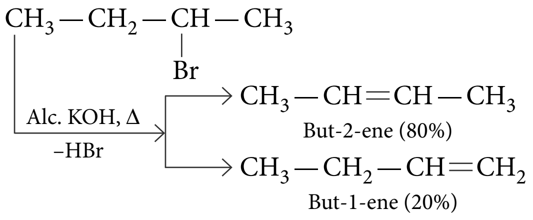
- **Optical Activity :** Compounds which rotate the plane of polarised light when they pass through the prism, are called optically active compounds and the phenomenon is known as optical activity.



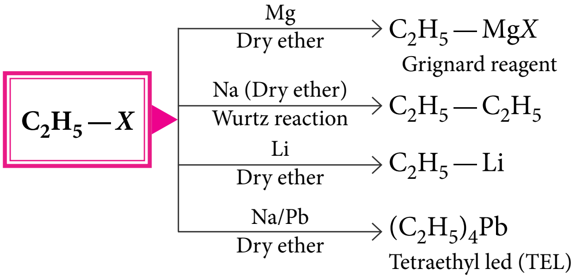
- **Inversion, retention and racemisation :** When a reaction takes place at an asymmetric carbon atom following reactions are possible :



- **Elimination reactions :**
  - **Dehydrohalogenation :** These reactions are called β-elimination reactions which follow Saytzeff's rule.

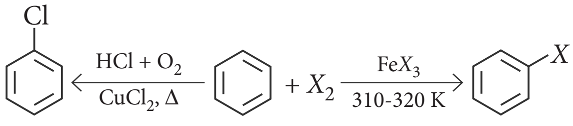


  - **Saytzeff rule :** In haloalkane, when elimination of hydrogen halide in two different ways occur, then that alkene will be preferred, in which carbon atoms joined by the double bond are maximum alkylated *i.e.*, contain largest number of alkyl groups.
  - **Ease of formation of alkene :**
    $R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > RCH=CH_2 > H_2C=CH_2$
  - **Ease of dehydrohalogenation :**
    3° alkyl halide > 2° alkyl halide > 1° alkyl halide
- **Reactions with metals :**

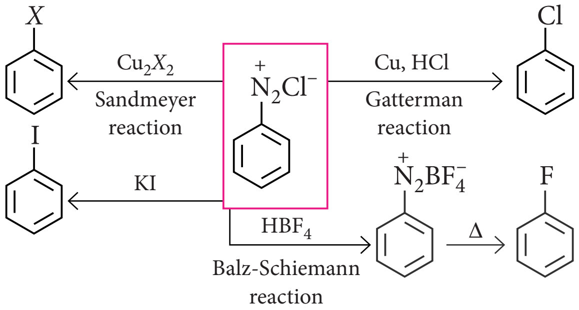


HALOARENES

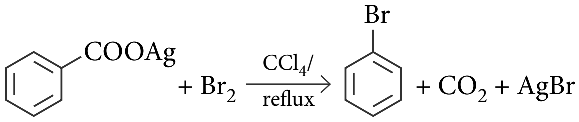
PREPARATION

- 

(Raschig process)

- 

- **Hunsdiecker reaction :**

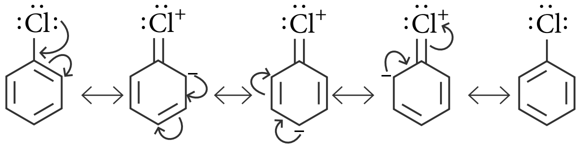


PHYSICAL PROPERTIES

- Aryl halides are colourless stable liquids with pleasant odour, insoluble in water but readily miscible with organic solvents.
- Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from fluoro to iodo compounds.

CHEMICAL PROPERTIES

- **Nucleophilic substitution reactions :** Haloarenes are less reactive towards nucleophilic substitution reactions:
  - Due to resonance effect :

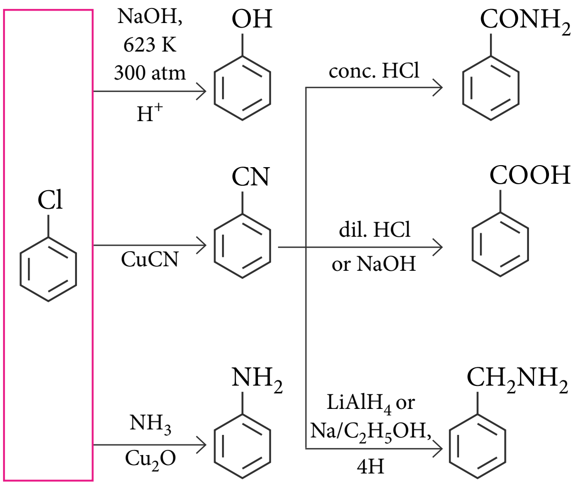


Thus, C—Cl bond acquires double bond character and difficult to break.

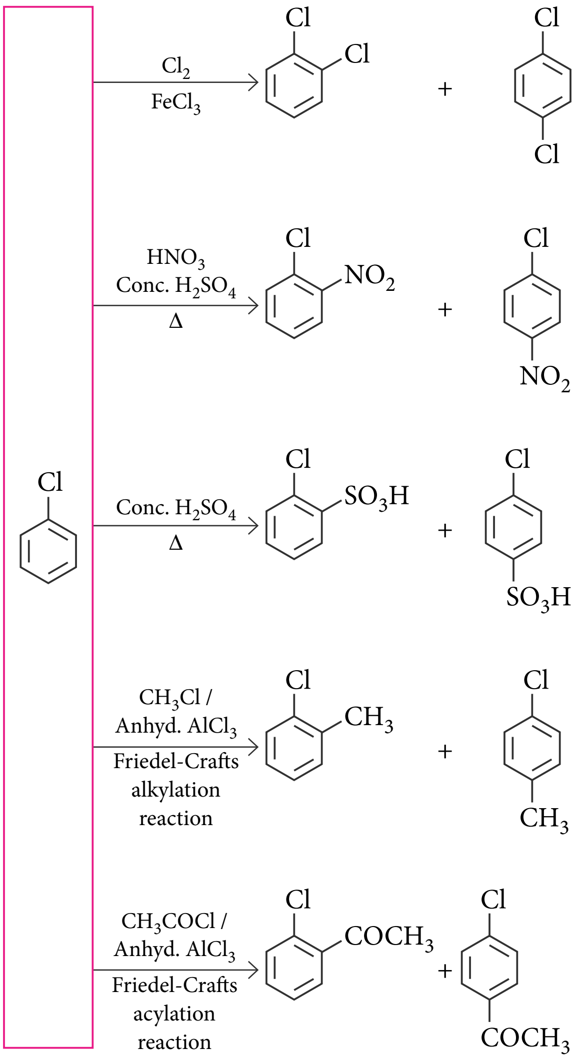
  - C atom in haloarenes is sp^2 hybridised, thus has greater *s*-character, so difficult to break.
  - Instability of phenyl cation : Phenyl cation formed by self-ionisation will not be stabilised hence, S_N1 mechanism ruled out.

MPP-7 CLASS XI ANSWER KEY

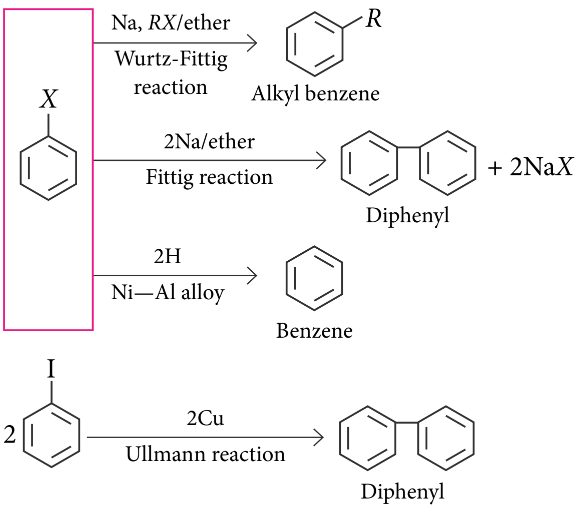
1. (b)	**2.** (a)	**3.** (a)	**4.** (d)	**5.** (a)
6. (c)	**7.** (a)	**8.** (d)	**9.** (c)	**10.** (b)
11. (a)	**12.** (a)	**13.** (c)	**14.** (a)	**15.** (b)
16. (d)	**17.** (b)	**18.** (c)	**19.** (d)	**20.** (a,b,c)
21. (a,c)	**22.** (a,b)	**23.** (a,b,c,d)		**24.** (5)
25. (3)	**26.** (7)	**27.**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



- **Electrophilic substitution reactions :** As electron density increases at *o*, *p*-positions, electrophilic substitution reactions occur at *o*, *p*-positions.



- **Other reactions :**



INFOSHOTS

Halogen derivative of 1, 3-disubstituted thiourea!

1, 3-disubstituted thiourea derivatives have attracted an increasing attention due to their potential in medicinal chemistry. Among them, the broad spectrum of biological activities of fluorinated thiourea derivatives has been investigated and various bioactivities, such as antimicrobial, antiviral and anticancer have been reported. In recent years, several chlorophenyl, fluorophenyl and (trifluoromethyl) phenyl thiourea compounds have been described as potent antistaphylococcal and antifungal agents.

CONCEPT
MAP
CLASS XI

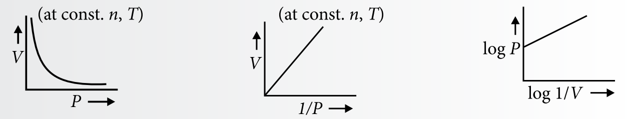
Gaseous State

A gas occupies a volume about 1600 times greater than that of an equal weight of liquid. If gas is compressed to 1/1600th of its volume above critical temperature (which is different for each gas) no phase change occurs and the resulting substance is a gas that is just as dense as a liquid.

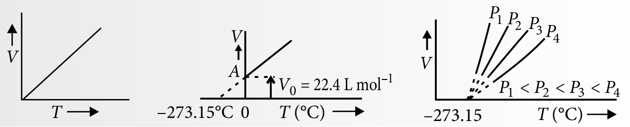
Gas Laws

- **Boyle's law :** It states that at a constant temperature (T), $P \propto (1/V)$ or $PV = \text{constant} \Rightarrow P_1V_1 = P_2V_2$
- **Charles' law :** It states that at constant pressure (P), $V \propto T$ or $(V/T) = \text{constant} \Rightarrow V_1/T_1 = V_2/T_2$
- **Avogadro law :** It states that at constant temperature (T) and pressure (P), $V \propto n$ or $(V/n) = \text{constant}$
- **Gay Lussac's law :** It states that at constant volume (V), $P \propto T$ or $(P/T) = \text{constant}$.

Boyle's Law



Charles' Law



Ideal Gas Equation

$PV = nRT$ [R = gas constant]

$0.0821 \text{ L atm K}^{-1}\text{ mol}^{-1}$ — **R** (gas constant) — $0.083 \text{ L bar K}^{-1}\text{ mol}^{-1}$

$8.314 \text{ J K}^{-1}\text{ mol}^{-1}$ — **R** (gas constant) — $1.99 \text{ cal K}^{-1}\text{ mol}^{-1}$

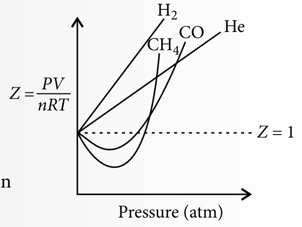
Deviation from Ideal Gas Behaviour (Real Gas)

- Real gas follows gas laws only at high temperature and low pressure.
- It follows van der Waals' equation; $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

Compressibility Factor

$Z = 1$ refers to ideal behaviour
$Z > 1$ shows positive deviation
$Z < 1$ shows negative deviation

where, Z is compressibility factor which measures the deviation from ideal behaviour.



- **Relation between critical constants and van der Waals' constants :** $V_c = 3b,\ P_c = \frac{a}{27b^2},\ T_c = \frac{8a}{27Rb}$
- As the value of a increases, the critical temperature (T_c) also increases. Higher the critical temperature of the gas, more easily it liquefies.

The ease of liquefaction order : $Cl_2 > CO_2 > CH_4 > H_2 > He$

Graham's Law of Diffusion

$$\frac{r_1}{r_2} = \frac{v_1/t_1}{v_2/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Dalton's Law of Partial Pressure

It states that "at a given temperature, the total pressure (P_{total}) exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of partial pressures of the component gases".

$P_{total} = p_1 + p_2 + p_3 + ...$ (where p_1, p_2, p_3 are partial pressures of component gases)

Kinetic Molecular Theory of Gases

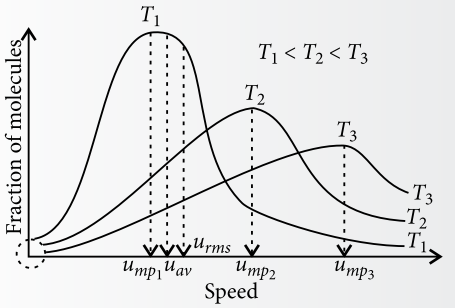
- All gases are made up of a very large number of minute particles like atoms or molecules.
- The molecules are in continuous random motion in all directions.
- Molecular collisions are perfectly elastic.
- The intermolecular forces of attraction are negligible.
- The average kinetic energy of a gas molecule is directly proportional to the absolute temperature.
- Kinetic gas equation : $PV = 1/3\, mnu^2$

Molecular Speed

- Root mean square velocity : $u_{rms} = \sqrt{\frac{3RT}{M}}$
- Average velocity : $u_{av} = \sqrt{\frac{8RT}{\pi M}}$
- Most probable speed : $u_{mp} = \sqrt{\frac{2RT}{M}}$

$u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224$

Maxwell–Boltzmann Distribution Curve



◌ Signifies that speed is never zero but it tends towards zero.

Diazonium Salt

General formula : $ArN_2^+X^-$

X^- may be Cl^-, Br^-, HSO_4^-, BF_4^-, etc.

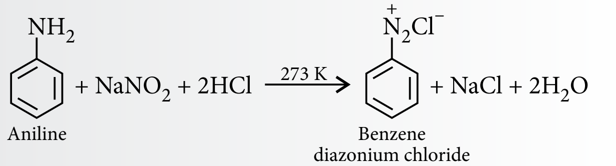
Azo dyes can be prepared using diazonium salts, these contain a highly delocalised system of electrons which delocalise in both benzene rings and the two nitrogen atoms bridging the rings. This extended delocalisation give colours to these azo compounds. Modifying the group present in molecule can give rise to different colours.

CONCEPT MAP

CLASS XII

Preparation

The reaction of converting aromatic primary amine to diazonium salt is called diazotisation.

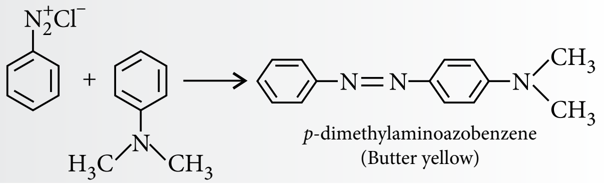


Physical Properties

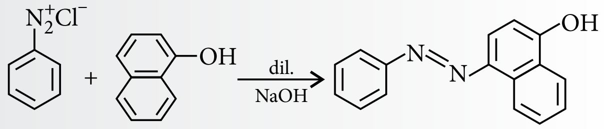
- Colourless crystalline solids.
- Readily soluble in water, less soluble in alcohol.
- These are unstable and explode in dry state.
- Their aqueous solutions are neutral to litmus.

Applications

- To produce water-fast dyed fabrics by immersing the fabric in an aqueous solution of the diazonium compound, followed by immersion in a solution of the coupler.
- Synthesis of organic compounds.
- Diazonium salts are light sensitive and break down near UV or violet light. This property has led to their use in document reproduction.

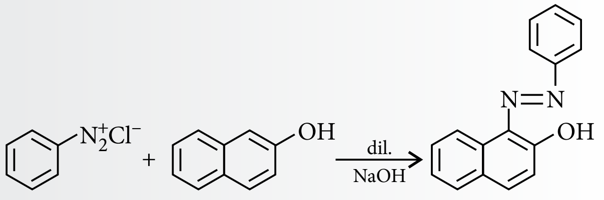


p-dimethylaminoazobenzene
(Butter yellow)



α-Naphthol

1-Phenylazo-4-naphthol

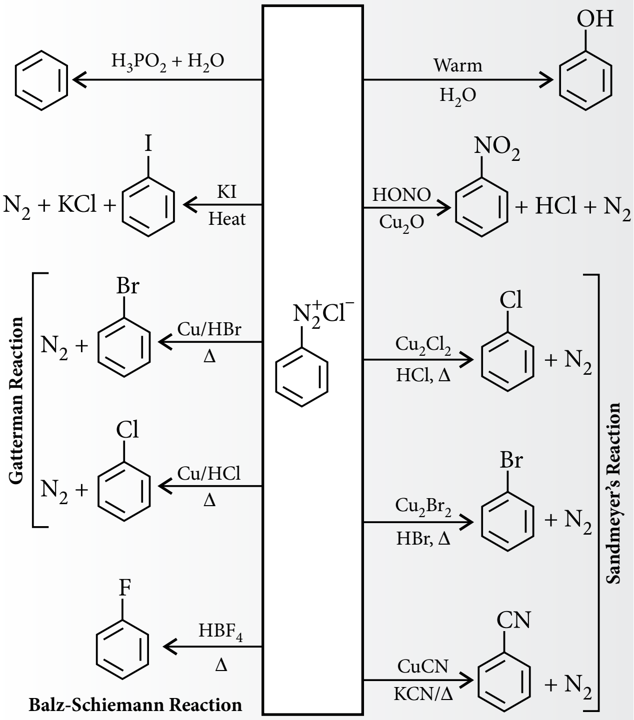


β-Naphthol

1-Phenylazo-2-naphthol
(Orange dye)

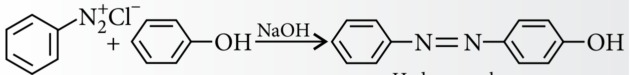
Chemical Properties

Reactions Involving Displacement of Diazo Group

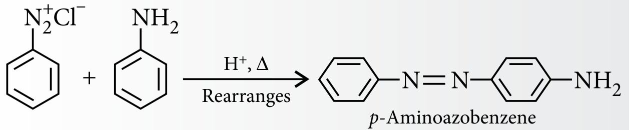


Reactions Involving Retention of Diazo group

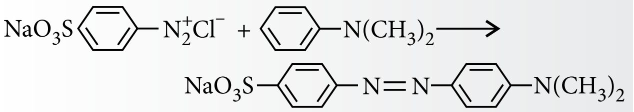
- The azo products obtained have an extended conjugate system having both aromatic rings joined through —N=N— bond.
- These compounds are often coloured and are used as a dye.



p-Hydroxyazobenzene
(Orange dye)



p-Aminoazobenzene
(Yellow dye)



Methyl orange

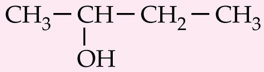
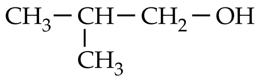
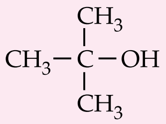
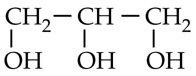
ALCOHOLS, PHENOLS AND ETHERS

ALCOHOLS

- Alcohols are the hydroxyl derivatives of alkanes having general formula, $C_nH_{2n+1}OH$.

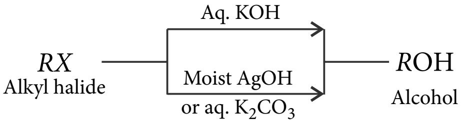
NOMENCLATURE

- In common system, alcohols are named as alkyl alcohol.
- According to IUPAC system, alcohols are called '*alkanols*', by replacing '*-e*' of alkane by '*-ol*'.

Compound	Common name	IUPAC name
$CH_3-CH_2-CH_2-CH_2-OH$	*n*-Butyl alcohol	Butan-1-ol
 $CH_3-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_2-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-OH$	*Iso*-butyl alcohol	2-Methylpropan-1-ol
 $CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
 $\underset{\displaystyle OH}{\underset{\vert}{CH_2}}-\underset{\displaystyle OH}{\underset{\vert}{CH}}-\underset{\displaystyle OH}{\underset{\vert}{CH_2}}$	Glycerol	Propane -1, 2, 3-triol

PREPARATION

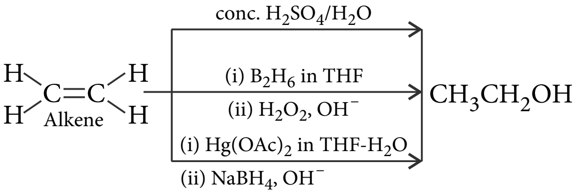
- **From alkyl halides :**



$$\underset{\text{Alkyl halide}}{RX} \xrightarrow{\text{Aq. KOH}} \underset{\text{Alcohol}}{ROH}$$

$$\underset{\text{Alkyl halide}}{RX} \xrightarrow[\text{or aq. } K_2CO_3]{\text{Moist AgOH}} \underset{\text{Alcohol}}{ROH}$$

- **From alkenes :**



$$\underset{\text{Alkene}}{H_2C=CH_2} \xrightarrow{\text{conc. } H_2SO_4/H_2O} CH_3CH_2OH$$

$$\underset{\text{Alkene}}{H_2C=CH_2} \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } B_2H_6 \text{ in THF}} CH_3CH_2OH$$

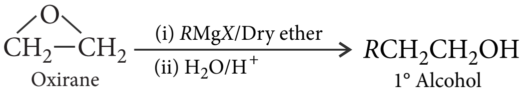
$$\underset{\text{Alkene}}{H_2C=CH_2} \xrightarrow[\text{(ii) } NaBH_4,\ OH^-]{\text{(i) } Hg(OAc)_2 \text{ in THF-}H_2O} CH_3CH_2OH$$

- **From amines :**

$$\underset{1^\circ\text{ Amine}}{RNH_2} \xrightarrow{NaNO_2/\text{dil. } HCl} ROH + N_2 + H_2O$$

- **From ethers :**

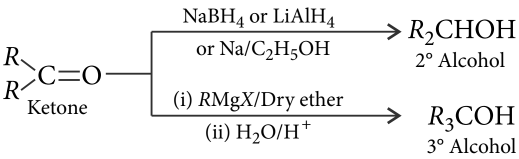
$$\underset{\text{Ether}}{ROR} \xrightarrow[\Delta]{H_2O/\text{dil. } H_2SO_4} 2ROH$$



$$\underset{\text{Oxirane}}{CH_2-CH_2 \ (\text{-O-})} \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } RMgX/\text{Dry ether}} \underset{1^\circ\text{ Alcohol}}{RCH_2CH_2OH}$$

- **From carbonyl compounds :**

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[NaBH_4 \text{ or } LiAlH_4]{H_2/Pt \text{ or } Pd \text{ or } Ni} \underset{1^\circ\text{ Alcohol}}{RCH_2OH}$$

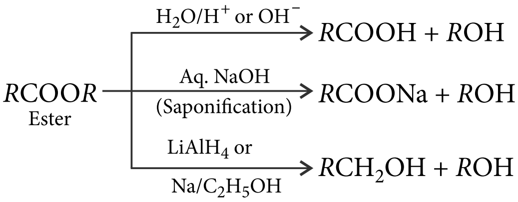


$$\underset{\text{Ketone}}{R_2C=O} \xrightarrow[\text{or } Na/C_2H_5OH]{NaBH_4 \text{ or } LiAlH_4} \underset{2^\circ\text{ Alcohol}}{R_2CHOH}$$

$$\underset{\text{Ketone}}{R_2C=O} \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } RMgX/\text{Dry ether}} \underset{3^\circ\text{ Alcohol}}{R_3COH}$$

- **From acids and their derivatives :**

$$\underset{\text{Carboxylic acid}}{RCOOH} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4 \text{ or } B_2H_6/\text{ether}} RCH_2OH$$



$$\underset{\text{Ester}}{RCOOR} \xrightarrow{H_2O/H^+ \text{ or } OH^-} RCOOH + ROH$$

$$\underset{\text{Ester}}{RCOOR} \xrightarrow[\text{(Saponification)}]{\text{Aq. NaOH}} RCOONa + ROH$$

$$\underset{\text{Ester}}{RCOOR} \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} RCH_2OH + ROH$$

$$\underset{\text{Acid anhydride}}{(RCO)_2O} \xrightarrow[\text{ether}]{LiAlH_4} 2RCH_2OH$$

$$\underset{\text{Acid chloride}}{RCOCl} \xrightarrow{LiAlH_4} RCH_2OH + HCl$$

PHYSICAL PROPERTIES

- Lower alcohols are liquid at room temperature while higher ones are solid.
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.
- Alcohols have high boiling points. Order of boiling point : 1° alcohols > 2° alcohols > 3° alcohols

CHEMICAL PROPERTIES

- The hydroxyl group present in alcohols is a very reactive group. The reactions of the hydroxyl group consists of either cleavage of C — O bond or the cleavage of O — H bond as both are highly polarised with negative end of the dipoles at oxygen.
- In O — H cleavage, the order of reactivity :
  Primary > Secondary > Tertiary
- In C — O cleavage, the order of reactivity :
  Tertiary > Secondary > Primary

ALCOHOLS

$\xrightarrow{\text{Na}} \text{RONa} + \text{H}_2$

$\xrightarrow[\text{Conc. H}_2\text{SO}_4]{\text{RCOOH}} \text{RCOOR} + \text{H}_2\text{O}$

$\xrightarrow[\text{Base}]{\text{RCOCl}} \text{RCOOR} + \text{HCl}$

$\xrightarrow[\text{Base}]{(\text{RCO})_2\text{O}} \text{RCOOR} + \text{RCOOH}$

$\xrightarrow{R'\text{MgX}} R'\text{H} + \text{Mg}(OR)X$

$\xrightarrow{HX} RX + \text{H}_2\text{O}$

$\xrightarrow{PX_3} RX + \text{H}_3\text{PO}_3$

$\xrightarrow{\text{PCl}_5} R\text{Cl} + \text{POCl}_3 + \text{HCl}$

$\xrightarrow{\text{SOCl}_2} R\text{Cl} + \text{SO}_2\uparrow + \text{HCl}\uparrow$

$\xrightarrow[443\text{ K}]{\text{Conc. H}_2\text{SO}_4} \text{RCH}{=}\text{CH}_2 + \text{H}_2\text{O}$

$\xrightarrow[413\text{ K}]{\text{Conc. H}_2\text{SO}_4} ROR + \text{H}_2\text{O}$

$\xrightarrow[\text{or KMnO}_4/\text{OH}^-]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} R\text{—COOH}$

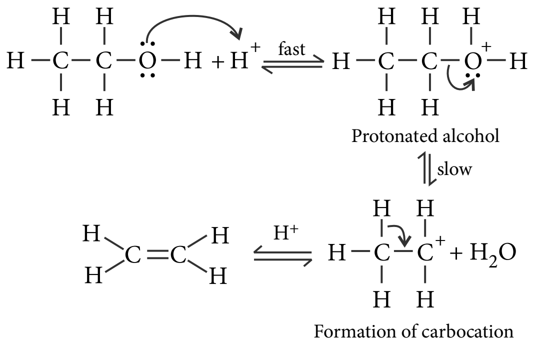
$\xrightarrow[-\text{H}_2]{\text{Cu}/573\text{ K}} \text{RCHO or } R\text{COR or alkene}$
(from 1° alcohol) (from 2° alcohol) (from 3° alcohol)

$\xrightarrow[\text{or CrO}_3\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}]{\text{PCC}} \text{RCHO}$

- **Dehydration of alcohols :**

$$\text{C}_2\text{H}_5\text{OH} \xrightarrow[443\text{ K}]{\text{Conc. H}_2\text{SO}_4} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}$$

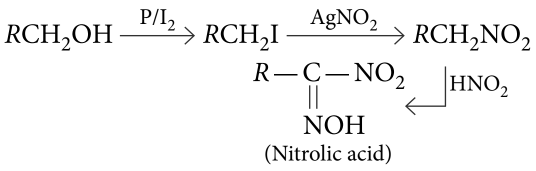
  - **Mechanism :**



  - The order of stability of carbocations :
    3° > 2° > 1°
  - It always occurs in accordance with the Saytzeff rule *i.e.*, the more substituted alkene is the major product.

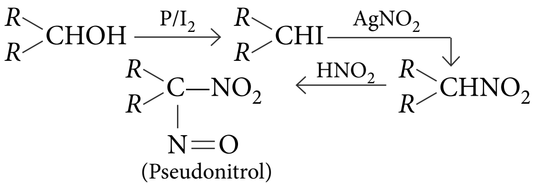
Distinction between 1°, 2° and 3° Alcohols

- **Lucas test :** Alcohols + ZnCl_2 + HCl
  - **1° Alcohol :** $R\text{CH}_2\text{OH} + \text{ZnCl}_2 + \text{HCl} \longrightarrow$ No reaction at room temperature
  - **2° Alcohol :** $R_2\text{CHOH} + \text{ZnCl}_2 \longrightarrow R_2\text{CHCl};$ White turbidity appeared after 5-10 min.
  - **3° Alcohol :** $R_3\text{COH} + \text{ZnCl}_2 + \text{HCl} \longrightarrow R_3\text{CCl};$ White turbidity appeared immediately.
- **Victor Meyer test :**
  - **1° Alcohol :**



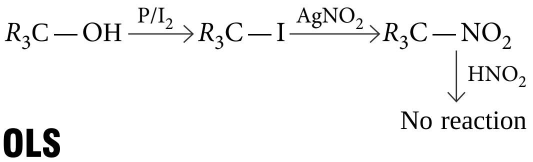
Nitrolic acid on treatment with alkali gives blood red colouration.

  - **2° Alcohol :**



Pseudonitrol on treatment with alkali gives blue colouration.

- **3° Alcohol :**



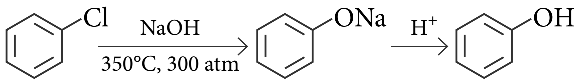
$$R_3C-OH \xrightarrow{P/I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2} \text{No reaction}$$

PHENOLS

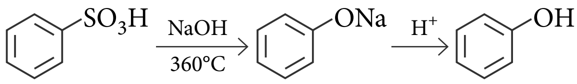
- Phenols are derivatives of benzene in which a ring hydrogen is replaced by —OH group.

PREPARATION

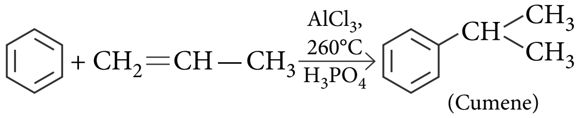
- **Hydrolysis of chlorobenzene (Dow's process) :**

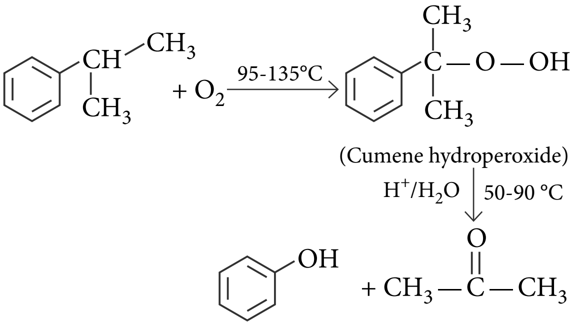


- **From benzene sulphonic acid (alkali fusion of sodium benzene sulfonate) :**



- **From cumene hydroperoxide :**

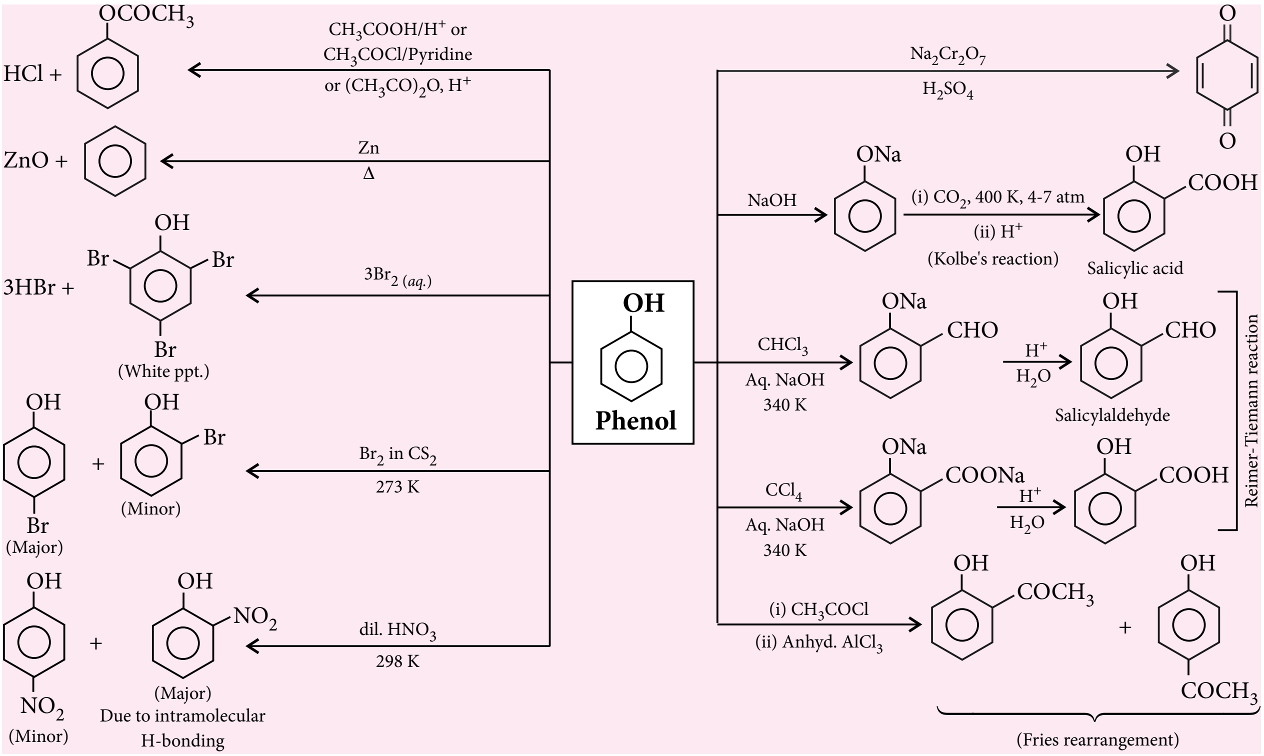




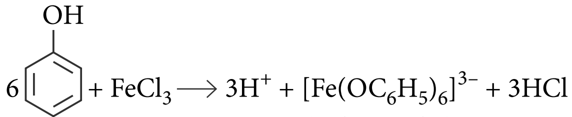
PHYSICAL PROPERTIES

- Phenol is a colourless, crystalline, deliquescent solid, attains pink colour on exposure to air and light.
- Its melting point is 315 K and boiling point 455 K. The boiling point of phenol is much higher than the corresponding aromatic hydrocarbons and the haloarenes.
- It is soluble in water due to inter-molecular H-bonding among themselves and with water.
- It is poisonous in nature but acts as antiseptic and disinfectant.

CHEMICAL PROPERTIES

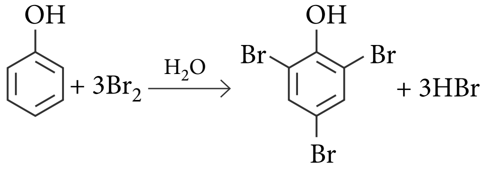


- **Test for phenols :**
  - **Ferric chloride test :** Phenol gives violet colour with neutral $FeCl_3$ solution.



(violet complex)

  - **Bromine water test :** Phenol gives white ppt. with Br_2-water due to the formation of 2, 4, 6-tribromophenol.



(white ppt.)

- **Acidity of phenol :** Phenols are much more acidic than alcohols but less than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants (K_a) or pK_a. Smaller the pK_a value, stronger the acid. The relative acidity follows the following order:

Acidic strength decreases

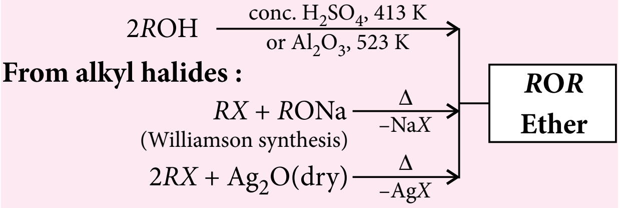
K_a (approx.)	pK_a value
(10^{-5}) RCOOH Carboxylic acid	5
(10^{-7}) H_2CO_3 Carbonic acid	7
(10^{-10}) C_6H_5OH Phenol	8-10
(10^{-14}) HOH Water	14
(10^{-18}) ROH Alcohols	16-18

ETHERS

- **General formula :** $C_nH_{2n+2}O$ ($R—O—R'$)
- **Symmetrical ether :** When R and R' are same groups. *e.g.*, $CH_3—O—CH_3$, $C_2H_5—O—C_2H_5$
- **Unsymmetrical ether :** When R and R' are different groups. *e.g.*, $CH_3—O—C_6H_5$, $CH_3—O—C_2H_5$

PREPARATION

From alcohols by dehydration :



$$2ROH \xrightarrow[\text{or } Al_2O_3,\ 523\ K]{\text{conc. } H_2SO_4,\ 413\ K}$$

From alkyl halides :

$$RX + RONa \xrightarrow[-NaX]{\Delta}$$

(Williamson synthesis)

$$2RX + Ag_2O(\text{dry}) \xrightarrow[-AgX]{\Delta}$$

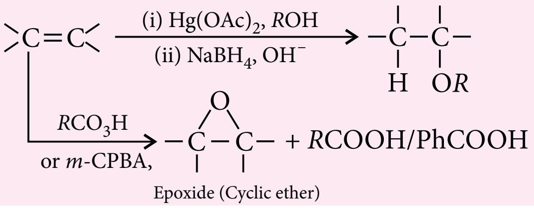
From Grignard reagent :

$$ROCH_2X + R'MgX \xrightarrow[-MgX_2]{\text{Dry ether}} ROCH_2R'$$

From diazomethane :

$$ROH + CH_2N_2 \xrightarrow[-N_2]{HBF_4,\ \Delta} ROCH_3$$

From alkenes :

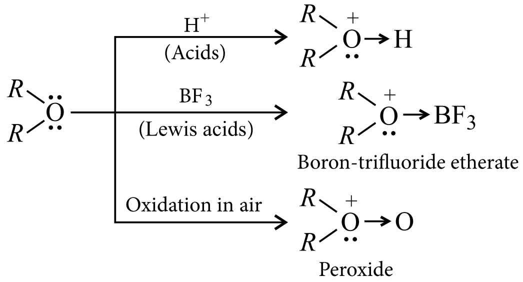


PHYSICAL PROPERTIES

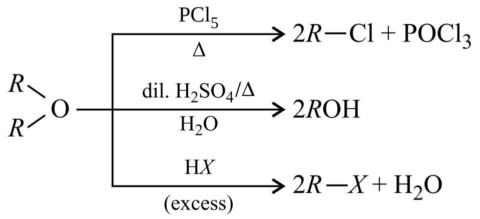
- Ethers have a bent structure and are dipolar in nature.
- Boiling points of ethers show a gradual increase with increase in molecular mass.
- They are lighter than water. Lower ethers are highly volatile and very inflammable.
- They are sparingly soluble in water but readily soluble in organic solvents.
- Dimethyl ether and ethyl methyl ether are gases. All ethers are colourless liquids with characteristic ether smell.

CHEMICAL PROPERTIES

- **Reactions of lone pair of oxygen :**



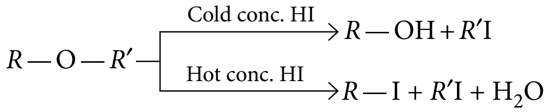
- **Cleavage of $R-O-R$ bond :**



$$R-O-R \xrightarrow[\Delta]{PCl_5} 2R-Cl + POCl_3$$

$$R-O-R \xrightarrow[H_2O]{\text{dil. } H_2SO_4/\Delta} 2ROH$$

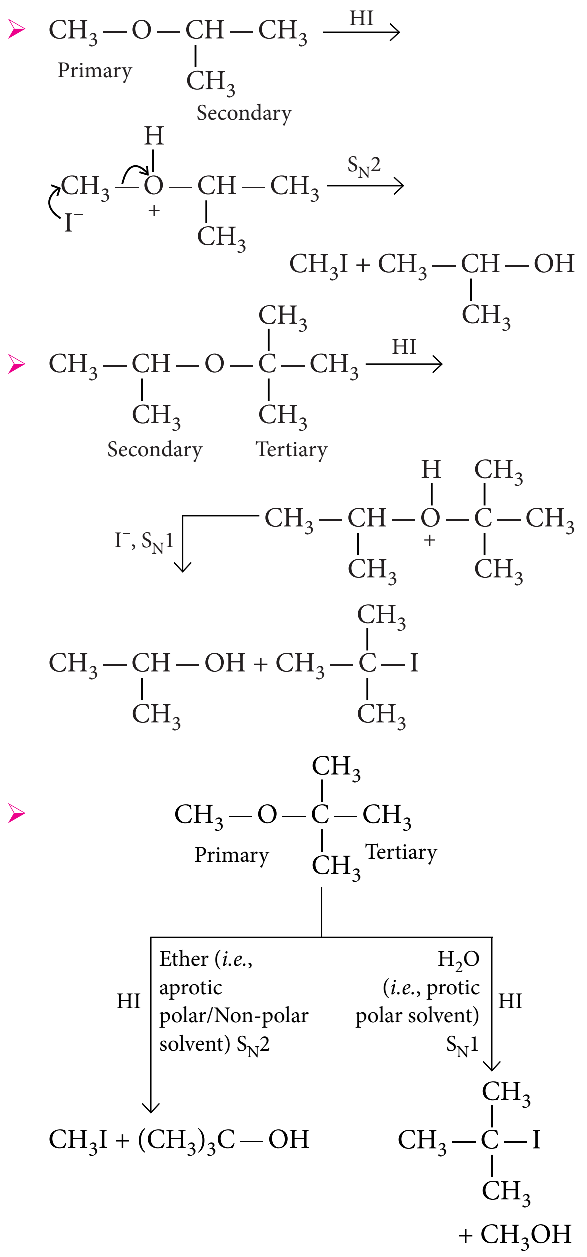
$$R-O-R \xrightarrow[\text{(excess)}]{HX} 2R-X + H_2O$$



$$R-O-R' \xrightarrow{\text{Cold conc. HI}} R-OH + R'I$$

$$R-O-R' \xrightarrow{\text{Hot conc. HI}} R-I + R'I + H_2O$$

- **Different possibilities of reaction of ether with HI :**



➢ $\underset{\text{Primary}}{CH_3}-O-\underset{\underset{\text{Secondary}}{CH_3}}{\underset{|}{CH}}-CH_3 \xrightarrow{HI}$

$\underset{I^-}{CH_3}-\overset{\overset{H}{|}}{\underset{+}{O}}-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{S_N2} CH_3I + CH_3-\underset{\underset{CH_3}{|}}{CH}-OH$

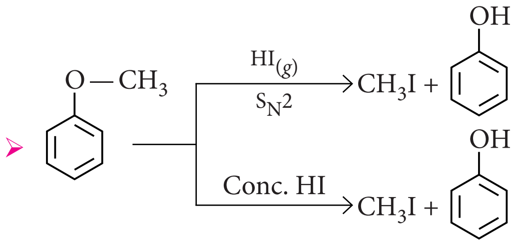
➢ $\underset{\text{Secondary}}{CH_3-\underset{\underset{CH_3}{|}}{CH}}-O-\underset{\text{Tertiary}}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3} \xrightarrow{HI}$

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{H}{|}}{\underset{+}{O}}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{I^-,\ S_N1} CH_3-\underset{\underset{CH_3}{|}}{CH}-OH + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I$

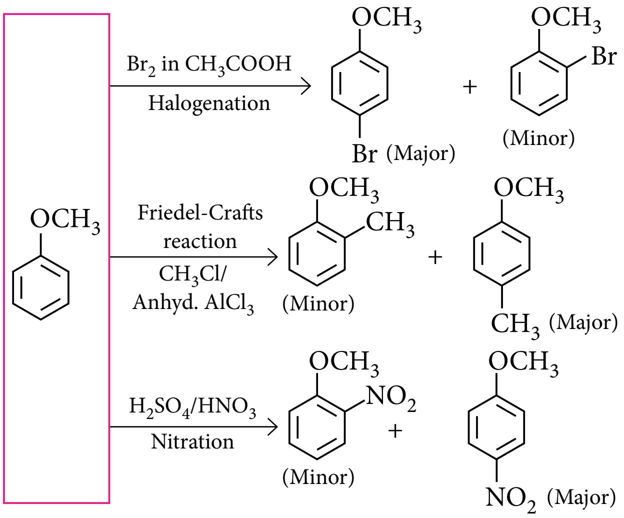
➢ $\underset{\text{Primary}}{CH_3-O}-\underset{\text{Tertiary}}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$

$\xrightarrow[\text{Ether (i.e., aprotic polar/Non-polar solvent) } S_N2]{HI} CH_3I + (CH_3)_3C-OH$

$\xrightarrow[\text{(i.e., protic polar solvent) } S_N1]{HI,\ H_2O} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I + CH_3OH$

➢ 

- **Electrophilic substitution reactions of aromatic ethers :**



USES

- Diethyl ether is used as solvent for oils, fats, waxes, plastics and lacquers.
- Provide inert medium for reactions.
- Used in surgery as an anaesthetic.
- Used in perfumery and in the manufacture of smokeless powder.

INFOSHOTS

A bioinspired *ortho*-sulfiliminyl phenol synthesis!

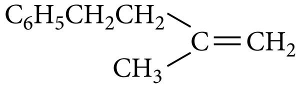
A variety of synthetic methods have been developed to construct the *ortho*-functionalized phenols which are highly useful in chemical industry, functional materials and medicines. These methods mainly include three kind of strategies (*a*) rearrangement of aromatic O—*X* bonds (*b*) directing group-assisted *ortho* C—H hydroxylation of arenes and (*c*) *ortho* C—H functionalization of phenols.

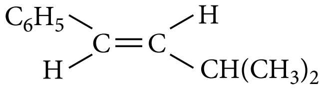
SPEED PRACTICE

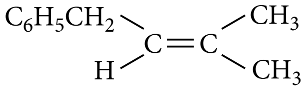
1. Which one of the following properties is exhibited by phenol?
   (a) It is soluble in aq. NaOH and evolves CO_2 with aq. $NaHCO_3$.
   (b) It is soluble in aq. NaOH and does not evolve CO_2 with aq. $NaHCO_3$.
   (c) It is not soluble in aq. NaOH but evolves CO_2 with aq. $NaHCO_3$.
   (d) It is insoluble in aq. NaOH and does not evolve CO_2 with aq. $NaHCO_3$.

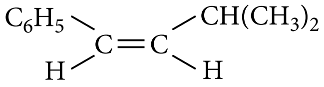
2. The major product of the following reaction is

$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc. } H_2SO_4}$$

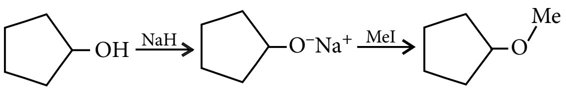
(a)


(b)


(c)


(d)


3. The reaction

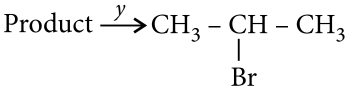


can be classified as
   (a) dehydration reaction
   (b) Williamson alcohol synthesis reaction
   (c) Williamson ether synthesis reaction
   (d) alcohol formation reaction.

(NEET Phase-I 2016)

4. Identify the set of reagents/reaction conditions, (x and y) in the following set of transformation.

$$CH_3-CH_2-CH_2Br \xrightarrow{x}$$



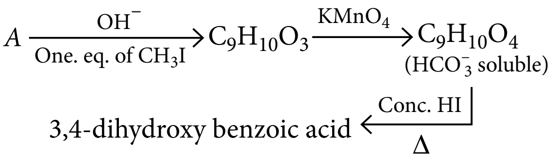
$$\text{Product} \xrightarrow{y} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

   (a) x = dilute aqueous NaOH, 20 °C; y = HBr/acetic acid, 20 °C
   (b) x = conc. alcoholic NaOH, 80 °C; y = HBr/acetic acid, 20 °C
   (c) x = dilute aqueous NaOH, 20 °C; y = $Br_2/CHCl_3$, 0 °C
   (d) x = conc. alcoholic NaOH, 80 °C; y = $Br_2/CHCl_3$, 0 °C

5. $CH_3Br + Nu^- \longrightarrow CH_3 — Nu + Br^-$
   The decreasing order of the rate of the above reaction with the given nucleophiles is
   [Nu^- = (*A*) PhO^-, (*B*) AcO^-, (*C*) HO^-, (*D*) CH_3O^-]
   (a) $D > C > A > B$ (b) $D > C > B > A$
   (c) $A > B > C > D$ (d) $B > D > C > A$

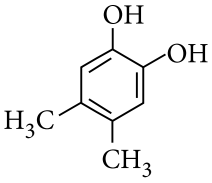
6. Etherates are
   (a) ethers
   (b) solution in ether
   (c) complexes of ethers with Lewis acids
   (d) complexes of ethers with Lewis bases.

7. An organic compound (X) with molecular formula C_7H_8O is insoluble in aqueous $NaHCO_3$ but dissolves in NaOH. When treated with bromine water (X) rapidly gives (Y), $C_7H_5OBr_3$. The compounds (X) and (Y) respectively are
   (a) benzyl alcohol and 2, 4, 6-tribromo-3-methoxy benzene
   (b) benzyl alcohol and 2, 4, 6-tribromo-3-methyl phenol
   (c) *o*-cresol and 3, 4, 5-tribromo-2-methyl phenol
   (d) *m*-cresol and 2, 4, 6-tribromo-3-methyl phenol.

8.


$$A \xrightarrow[\text{One eq. of } CH_3I]{OH^-} C_9H_{10}O_3 \xrightarrow{KMnO_4} \underset{(HCO_3^- \text{ soluble})}{C_9H_{10}O_4} \xrightarrow[\Delta]{\text{Conc. HI}} \text{3,4-dihydroxy benzoic acid}$$

Starting substrate 'A' (gives intense colour with $FeCl_3$ and positive Tollens' test) is

(a)


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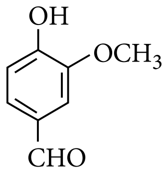
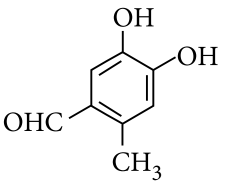
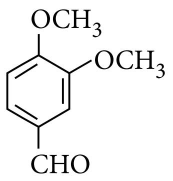
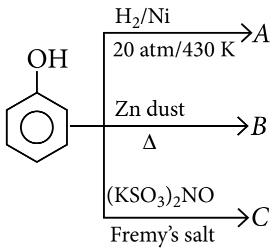
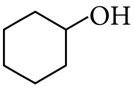
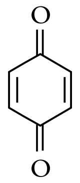
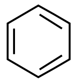
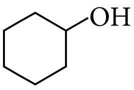
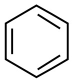
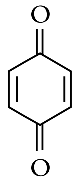
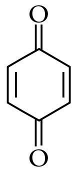
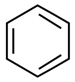
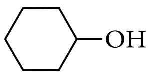
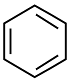
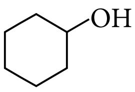
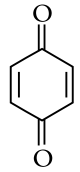


(c) 

(d) 

9. 

The compounds *A*, *B* and *C* respectively are

	A	***B***	***C***
(a)			
(b)			
(c)			
(d)			

10. S_N1 reaction undergoes through a carbocation intermediate as follows :

$$R-X_{(aq)} \underset{}{\overset{\text{Slow}}{\rightleftharpoons}} R^+_{(aq)} + X^-_{(aq)} \xrightarrow[\text{fast}]{H_2O} ROH_{(aq)} + HX_{(aq)}$$

[R = t-Bu, *iso*-Pr, Et, Me]; (X = Cl, Br, I)

Choose the correct statements for S_N1 reaction.

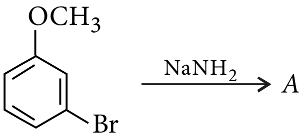
(I) The decreasing order of rate of S_N1 reaction is t-BuX > *iso*-PrX > EtX > MeX

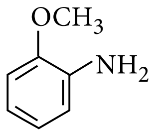
(II) The decreasing order of ionization energy is MeX > EtX > *iso*-PrX > t-BuX.

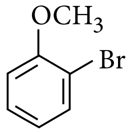
(III) The decreasing order of energy of activation is t-BuX > *iso*-PrX > EtX > MeX.

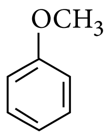
(a) Only I and II (b) Only I and III
(c) Only II and III (d) All of these.

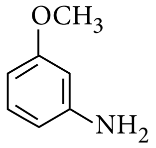
11. Identify *A* and predict the type of reaction.



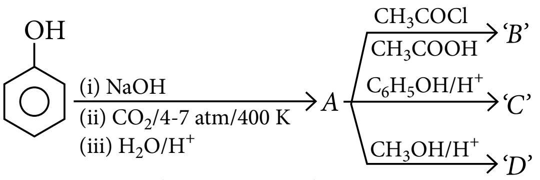
(a)  ; Elimination-addition reaction

(b)  ; Cine substitution

(c)  ; Cine substitution

(d)  ; Substitution reaction

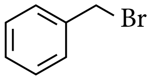
(NEET 2017)

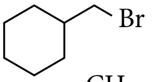
12. 

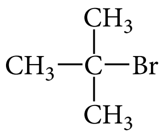
Here, *B*, *C* and *D* respectively are
(a) aspirin, salol, oil of winter green
(b) salol, aspirin, oil of winter green
(c) oil of winter green, aspirin, salol
(d) oil of winter green, salol, aspirin.

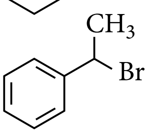
13. Chloropicrin is obtained by the reaction of
(a) chlorine on picric acid
(b) nitric acid on chloroform
(c) steam on carbon tetrachloride
(d) nitric acid on chlorobenzene.

14. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reactions is (are)

I. 

II. 

III. 
$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-Br$

IV. 

(a) I and II follow S_N2 mechanism
(b) compound IV undergoes inversion of configuration

(c) the order of reactivity for I, III, and IV is : IV > I > III
(d) I and III follow S_N1 mechanism.

[JEE Advanced 2017]

15. Consider thiolate ion (RS^-) and alkoxide ion (RO^-). Which of the following statements is correct?
(a) RS^- is more basic and less nucleophilic than RO^-.
(b) RS^- is less basic and less nucleophilic than RO^-.
(c) RS^- is less basic but more nucleophilic than RO^-.
(d) RS^- is more basic and more nucleophilic than RO^-.

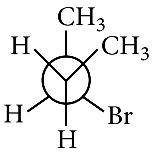
16. Diethyl ether when refluxed with excess of HI gives two molecules of _(i)_. Ethers can be most commonly prepared by reaction of _(ii)_ and _(iii)_. The method is called _(iv)_.
Here, (i), (ii), (iii) and (iv) respectively are
(a) ethyl iodide, sodium alkoxide, alkyl halide, Williamson synthesis
(b) ethanol, alcohol, alkyl halide, substitution
(c) methyl iodide, Grignard reagent, alkyl halide, Williamson synthesis
(d) ethyl iodide, phenol, alkyl iodide, esterification.

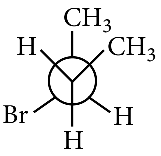
17. Phenyl methyl ether (anisole) reacts with HI to give phenol and methyl iodide but not iodobenzene and methyl alcohol because
(a) I^- attacks the methyl group as C—O bond between phenyl and oxygen is formed by sp^2 hybridised carbon, thus difficult to break
(b) I^- ion is not reactive towards benzene
(c) phenol is formed as a result of hydrolysis of iodobenzene
(d) methyl alcohol formed during reaction, reacts with I^- to form methyl iodide.

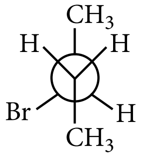
18. Consider the following reaction,
$CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$
This reaction will be the fastest in
(a) ethanol (b) methanol
(c) *N*, *N*-dimethylformamide (DMF)
(d) water.

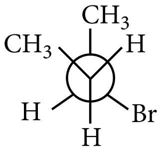
(NEET Phase-II 2016)

19. In the dehydrohalogenation of 2-bromobutane, which conformation leads to the formation of *cis*-2-butene?

(a)


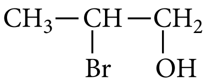
(b)


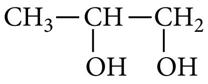
(c)


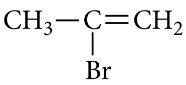
(d)


20. In the following series of chemical reactions, identify *Z* :

$C_3H_7OH \xrightarrow[160\text{-}180°C]{\text{Conc. } H_2SO_4} X \xrightarrow{Br_2} Y \xrightarrow[\text{alc. KOH}]{\text{Excess of}} Z$

(a)

$CH_3-\underset{\underset{\textstyle Br}{|}}{CH}-\underset{\underset{\textstyle OH}{|}}{CH_2}$

(b)

$CH_3-\underset{\underset{\textstyle OH}{|}}{CH}-\underset{\underset{\textstyle OH}{|}}{CH_2}$

(c)

$CH_3-\underset{\underset{\textstyle Br}{|}}{C}=CH_2$

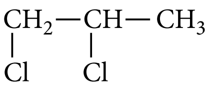
(d) $CH_3C\equiv CH$

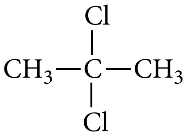
21. Glycerol forms salt with sodium metal at 110 °C. The sodium salt is
(a) monosalt (b) disalt
(c) trisalt
(d) mixture of monosalt and disalt.

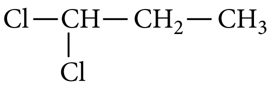
22. In the following reaction sequence :

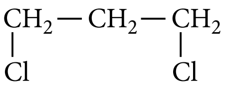
$\underset{(C_3H_6Cl_2)}{I} \xrightarrow{KOH_{(aq)}} II \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3MgBr} III \xrightarrow[\text{Conc. HCl}]{\text{Anhy. } ZnCl_2}$ gives turbidity immediately.

The compound I is

(a)

$\underset{\underset{\textstyle Cl}{|}}{CH_2}-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_3$

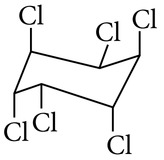
(b)

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

(c)

$Cl-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_2-CH_3$

(d)

$\underset{\underset{\textstyle Cl}{|}}{CH_2}-CH_2-\underset{\underset{\textstyle Cl}{|}}{CH_2}$

[JEE Main Online 2017]

23. Dehydrohalogenation by strong base is slowest in

(a)


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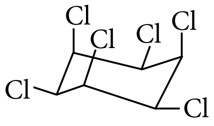

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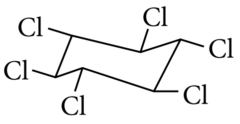
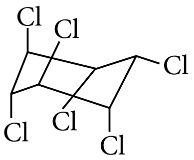
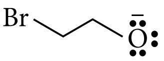
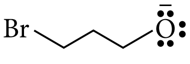
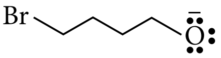


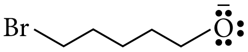
(d)


24. In the following compounds, nucleophile and the leaving groups are present in the same molecule :

I. 

II. 

III. 

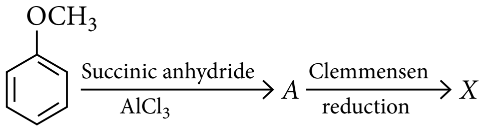
IV. 

These dual nature species can undergo intramolecular and intermolecular nucleophilic substitution reactions. Intramolecular substitution reaction is possible only in

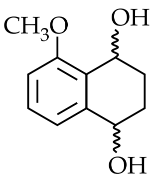
(a) I, II (b) II, III (c) III, IV (d) IV

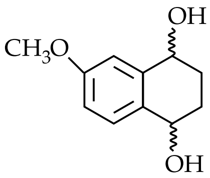
25. 0.037 g of an alcohol, *R*—OH was added to CH_3MgBr and the gas evolved measured 11.2 mL at STP. The molecular mass of *R*—OH will be

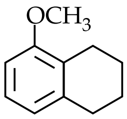
(a) 47 (b) 79 (c) 74 (d) 77

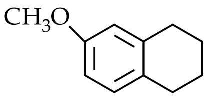
26. 

X is

(a) 

(b) 

(c) 

(d) 

[JEE Main 2016]

27. Which of the following reagents cannot be used to oxidise primary alcohols to aldehydes?

(a) CrO_3 in anhydrous medium

(b) $KMnO_4$ in acidic medium

(c) Pyridinium chlorochromate

(d) Heat in the presence of Cu at 573 K

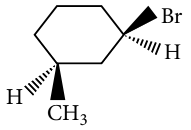
28. Chloromethane on treatment with excess of ammonia yields mainly

(a) *N*, *N*-dimethylmethanamine

(b) *N*-methylmethanamine

(c) methanamine

(d) mixture containing all these in equal proportion.

29.  + aq. KOH $\xrightarrow{\text{acetone}}$ Product

(1*R*, 3*S*)-*cis*-1-Bromo-3-methylcyclohexane

The product formed in the reaction is

(a) (1*R*, 3*S*)-*cis*-3-methylcyclohexanol

(b) (1*S*, 3*S*)-*cis*-3-methylcyclohexanol

(c) (1*S*, 3*S*)-*trans*-3-methylcyclohexanol

(d) (1*R*, 3*R*)-*trans*-3-methylcyclohexanol.

30. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled *A* and *B* for testing. *A* and *B* were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and some $AgNO_3$ solution added. Solution *B* gave yellow precipitate. Which one of the following statements is true for the experiment?

(a) Addition of HNO_3 was unnecessary.

(b) *A* was C_6H_5I.

(c) *A* was $C_6H_5CH_2I$.

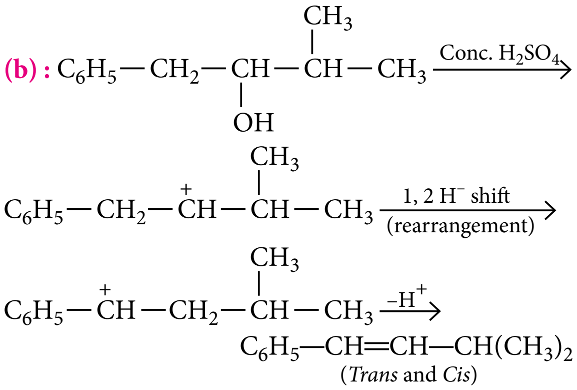
(d) *B* was C_6H_5I.

SOLUTIONS

1. **(b) :** Phenol is soluble in aq. NaOH forming sodium phenoxide.

$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$

But phenol does not evolve CO_2 with aq. $NaHCO_3$ and aq. Na_2CO_3 because phenol is weaker acid than carbonic acid.

2. **(b) :** 

$$C_6H_5-CH_2-\underset{\underset{OH}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$$

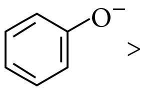
$$C_6H_5-CH_2-\overset{+}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow[\text{(rearrangement)}]{1,2\ H^-\text{ shift}}$$

$$C_6H_5-\overset{+}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow{-H^+} C_6H_5-CH{=}CH-CH(CH_3)_2$$

(*Trans* and *Cis*)

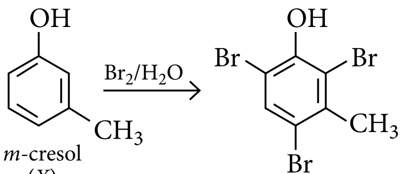
Trans is major product as it is thermodynamically more stable.

3. **(c)** **4.** **(b)**

5. **(a) :** $CH_3O^- > HO^- >$  $> CH_3COO^-$

(*D*) (*C*) (*A*) (*B*)

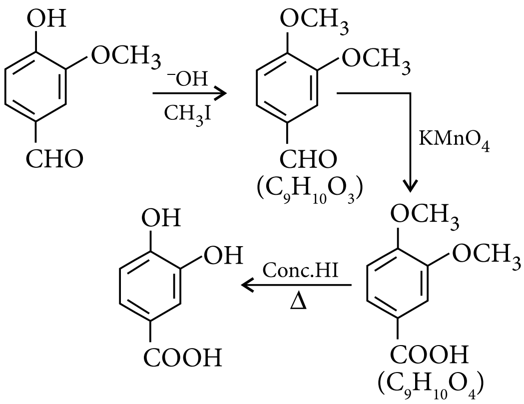
6. **(c)**

7. **(d) :** 

m-cresol (*X*)

2, 4, 6-tribromo-3-methylphenol (*Y*)

8. (b) :



9. (b)

10. (a) : For S_N1 reaction, rate depends upon the stability of carbocation formed. Thus, rate of S_N1 reaction is
$t\text{-Bu}X > iso\text{-Pr}X > \text{Et}X > \text{Me}X$
Higher rate of reaction is possible only if activation energy is low.
So, order of activation energy is
$t\text{-Bu}X < iso\text{-Pr}X < \text{Et}X < \text{Me}X$
Order of ionization energy is
$t\text{-Bu}X < iso\text{-Pr}X < \text{Et}X < \text{Me}X$

11. (d) : *m*-Bromoanisole gives only the respective *meta*-substituted product through benzyne intermediate. This is a substitution reaction which goes by an elimination-addition pathway.

12. (a)

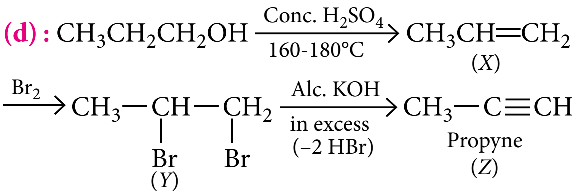
13. (b) : $Cl_3C\text{—}H + HO\text{—}NO_2 \xrightarrow{\Delta} \underset{\text{Chloropicrin}}{Cl_3C\text{—}NO_2} + H_2O$

14. (a, b, d) :
(a) Compounds I and II are 1° alkyl halides, thus they undergo S_N2 mechanism.
(b) Compound IV undergoes inversion of configuration due to intimate-ion pair formation, inversion predominates over retention.
(c) Stability of carbocations follows the order :
$\underset{\text{(IV)}}{2^\circ \text{ benzylic}} > \underset{\text{(III)}}{3^\circ \text{ alkyl}} > \underset{\text{(I)}}{1^\circ \text{ benzylic}}$
(d) I is a benzylic halide, thus, it also undergoes S_N1 reaction easily as benzylic carbocation is resonance stabilised and III also follows S_N1 mechanism as it is a 3° alkyl halide.

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

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

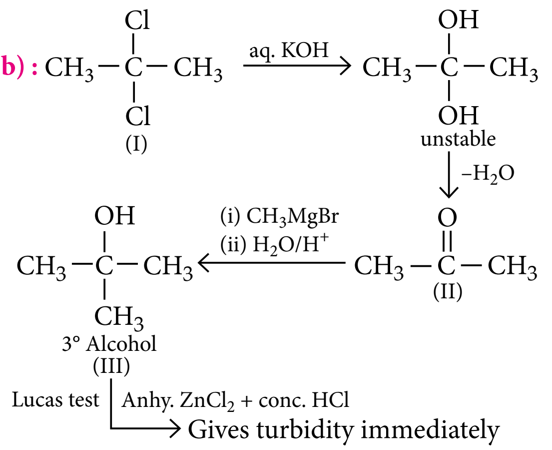
20. (d) :



$$CH_3CH_2CH_2OH \xrightarrow[160\text{-}180^\circ C]{\text{Conc. } H_2SO_4} \underset{(X)}{CH_3CH{=}CH_2}$$
$$\xrightarrow{Br_2} \underset{(Y)}{CH_3\text{—}\underset{\displaystyle Br}{\underset{|}{CH}}\text{—}\underset{\displaystyle Br}{\underset{|}{CH_2}}} \xrightarrow[\substack{\text{in excess} \\ (-2\text{ HBr})}]{\text{Alc. KOH}} \underset{\substack{\text{Propyne} \\ (Z)}}{CH_3\text{—}C{\equiv}CH}$$

21. (d)

22. (b) :



23. (c) **24. (c)**

25. (c) : $\underset{\text{1 mol}}{R\text{—OH}} + CH_3MgBr \longrightarrow \underset{\substack{\text{1 mol} \\ \text{or} \\ \text{22400 mL at STP}}}{CH_4} + Mg(Br)OR$

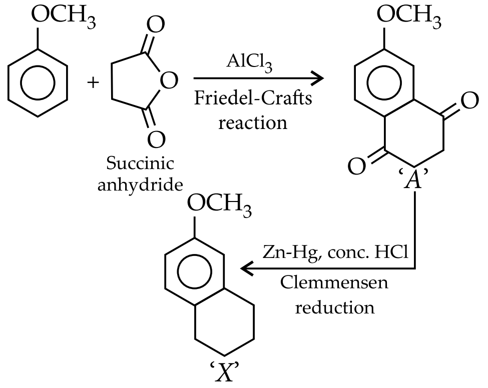
11.2 mL CH_4 at STP is formed from 0.037 g ROH.

$\therefore$ 22400 mL CH_4 at STP will be formed from

$$\frac{0.037}{11.2} \times 22400 \text{ g } ROH = 74 \text{ g } ROH$$

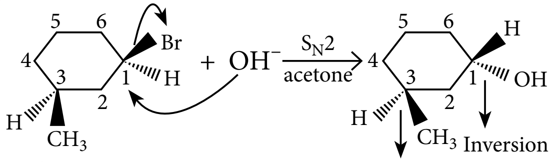
$\therefore$ Molecular mass of ROH = 74

26. (d) :



27. (b) **28. (c)**

29. (c) :



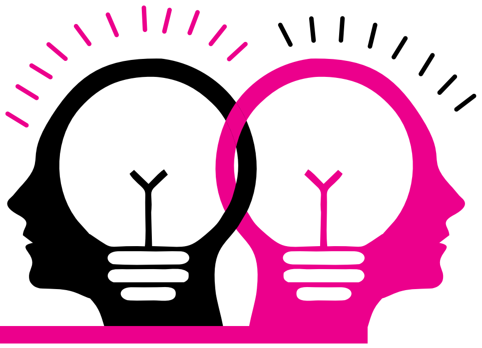
(1*R*, 3*S*)-*cis*-1-Bromo-3-methylcyclohexane

(1*S*, 3*S*)-*trans*-3-Methyl--cyclohexanol

30. (b)

◆ ◆

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).

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

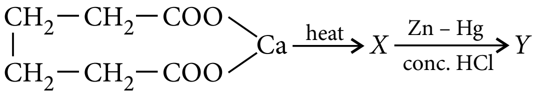
SECTION - I

Only One Option Correct Type

1. Which of the following is paraldehyde?
(a) $(HCHO)_4$ (b) $(CH_3CHO)_3$
(c) $(HCHO)_3$ (d) $(CH_3CHO)_4$

2. The carboxyl functional group is present in
(a) picric acid (b) barbituric acid
(c) ascorbic acid (d) aspirin.

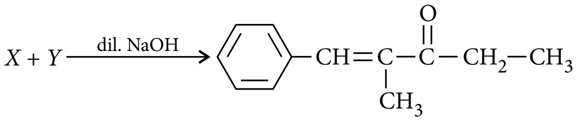
3. Identify the product Y in the following reaction sequence :



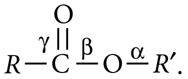
$$\left.\begin{array}{l}CH_2-CH_2-COO\\ |\\ CH_2-CH_2-COO\end{array}\right> Ca \xrightarrow{\text{heat}} X \xrightarrow[\text{conc. HCl}]{\text{Zn – Hg}} Y$$

(a) Pentane (b) Cyclobutane
(c) Cyclopentane (d) Cyclopentanone

4. Identify the starting reagents (X and Y) needed to make the following compound by crossed aldol condensation.



(a) Acetophenone and butanal
(b) Benzaldehyde and 2-pentanone
(c) Acetophenone and 2-butanone
(d) Benzaldehyde and 3-pentanone

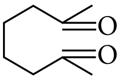
5. In an ester molecule there are three C — O bonds,  $R\overset{\gamma}{-}\overset{\overset{O}{\|}}{C}\overset{\beta}{-}O\overset{\alpha}{-}R'$. What do you expect regarding their relative bond lengths?
(a) $\alpha < \beta < \gamma$ (b) $\beta = \gamma > \alpha$
(c) $\beta > \gamma > \alpha$ (d) $\gamma < \beta < \alpha$

6. In order to prepare acetone from acetyl chloride in one step, which of the following reagents will be the best?
(a) Reduction with H_2/Pd-$BaSO_4$
(b) Reduction with HI
(c) Grignard reagent
(d) Dimethyl cadmium

7. $2CH \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} (X) \xrightarrow{LiAlH_4} (Y) \xrightarrow{P/Br_2} (Z)$

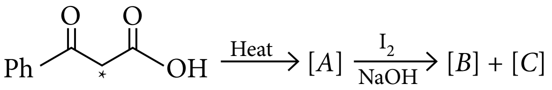
In the given sequence of reactions, (Z) is
(a) ethylene bromide (b) ethanol
(c) ethyl bromide (d) ethylidene bromide.

8. IUPAC name of the following compound is

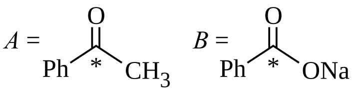


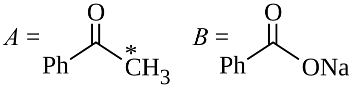
(a) heptane 2, 6-dione
(b) octan-6-one
(c) octane 2, 7-dione
(d) hexane-2, 5-dione.

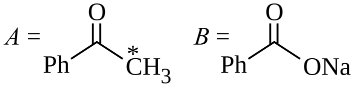
9. In the following reaction sequence, the correct structures of *A*, *B* and *C* are

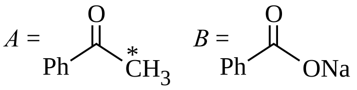


(* implies ^{13}C labelled carbon)

(a)  $C = CHI_3$

(b)  $C = CHI_3$

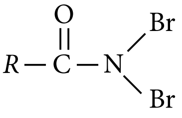
(c)  $C = \overset{*}{C}HI_3$

(d)  $C = \overset{*}{C}H_3I$

10. The correct sequence of steps involved in the mechanism of Cannizzaro reaction is
(a) nucleophilic attack, transfer of H^- and transfer of H^+
(b) transfer of H^-, transfer of H^+ and nucleophilic attack
(c) transfer of H^+, nucleophilic attack and transfer of H^-
(d) electrophilic attack by OH^-, transfer of H^+ and transfer of H^-.

SECTION - II

More than One Options Correct Type

11. Reaction of $R-\overset{O}{\overset{\parallel}{C}}-NH_2$ with a mixture of Br_2 and KOH gives $R-NH_2$ as the main product. The intermediates involved in this reaction are
(a) $R-\overset{O}{\overset{\parallel}{C}}-NHBr$
(b) $R-NHBr$
(c) $R-N=C=O$
(d) 
$R-\overset{O}{\overset{\parallel}{C}}-N\begin{smallmatrix}Br\\Br\end{smallmatrix}$

12. Which of the following reactions is used for detecting the presence of carbonyl group?
(a) Reaction with hydroxylamine
(b) Reaction with hydrazine
(c) Reaction with phenyl hydrazine
(d) Reaction with semicarbazide

13. Aqueous solution of sodium succinate on electrolysis gives
(a) CH_3-CH_3
(b) $CH_2=CH_2$
(c) $CH\equiv CH$
(d) CO_2

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

The acidic strength of saturated aliphatic carboxylic acids depends mainly upon the inductive effect of the substituent and its position with respect to the $-COOH$ group. Electron donating substituents tend to decrease, whereas electron withdrawing substituents tend to increase the acidic strength. The effect of electron donating substituents and electron withdrawing substituents is more pronounced at *p*-position than that at *m*-position. Due to *ortho* effect, *o*-substituted benzoic acids are usually stronger than benzoic acid regardless of the nature of substituent whether electron donating or electron withdrawing.

14. Which of the following is expected to be highly ionized in water?
(a) $ClCH_2CH_2CH_2COOH$
(b) $CH_3CHClCH_2COOH$
(c) $CH_3CH_2CCl_2COOH$
(d) $CH_3CH_2CHClCOOH$

15. Which of the following acids has the smallest dissociation constant?
(a) $CH_3CHFCOOH$
(b) FCH_2CH_2COOH
(c) $BrCH_2CH_2COOH$
(d) $CH_3CHBrCOOH$

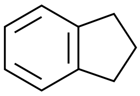
Paragraph for Questions 16 and 17

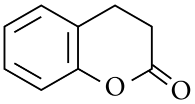
In the following reaction sequence, the compound *J* is an intermediate.

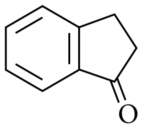
$$I \xrightarrow[CH_3COONa]{(CH_3CO)_2O} J \xrightarrow[\substack{\text{(ii) } SOCl_2 \\ \text{(iii) anhyd. } AlCl_3}]{\text{(i) } H_2\text{, Pd/C}} K$$

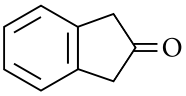
$J(C_9H_8O_2)$ gives effervescence on treatment with $NaHCO_3$ and positive Baeyer's test.

16. The compound *K* is

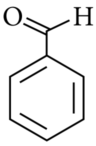
(a) 

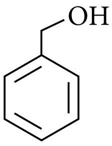
(b) 

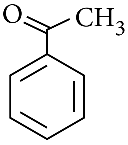
(c) 

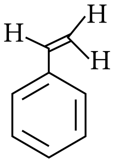
(d) 

17. The compound *I* is

(a) 

(b) 

(c) 

(d) 

SECTION - IV

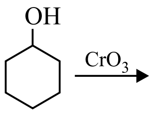
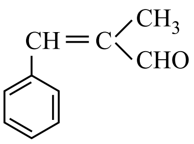
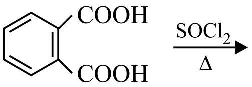
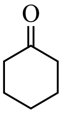
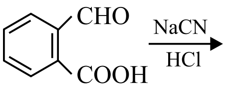
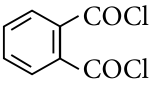
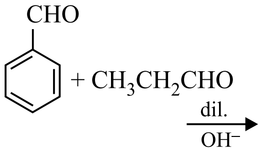
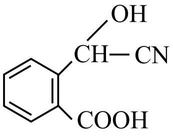
Matching List Type

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) Schiff's reagent	(i) Elimination reaction
(Q) Alcoholic KOH	(ii) Colourless solution due to SO_2
(R) Ammoniacal $AgNO_3$	(iii) Aldehydes
(S) Benedict solution	(iv) Chloroform

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

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

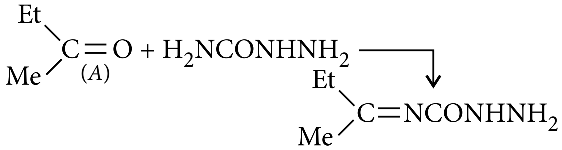
List I	**List II**
(P) 	(i) 
(Q) 	(ii) 
(R) 	(iii) 
(S) 	(iv) 

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

SECTION - V

Assertion Reason Type

20. Assertion : The following reaction occurs



Reason : The semicarbazone of (*A*) does not show geometrical isomerism.

21. Assertion : Esters which contain α-hydrogens undergo Claisen condensation reaction.

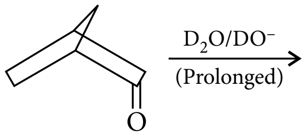
Reasons : Reduction of esters by $LiAlH_4$ gives acids.

22. Assertion : HCHO reacts with NH_3 to give urotropine.

Reason : Urotropine is a medicine for troubles in urinary track.

SECTION - VI

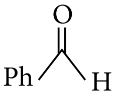
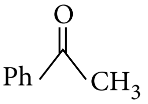
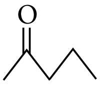
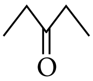
Integer Value Correct Type

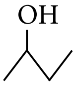
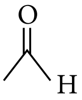
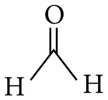
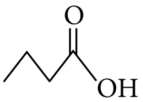
23. 

How many hydrogen atoms are replaced by *D*?

24. If formic acid, acetic acid, propanoic acid and benzoic acid are mixed with phosphorus and bromine then how many products will be formed?

25. The number of compounds among the following which give iodoform test is

, , , 

, , , , 

COORDINATION COMPOUNDS

SECTION - I

Only One Option Correct Type

1. Crystal field stabilisation energy for high spin d^4 octahedral complex is
(a) $-0.6\Delta_o$ (b) $-1.8\Delta_o$
(c) $-1.6\Delta_o + P$ (d) $-1.2\Delta_o$

2. A solution containing 2.675 g of $CoCl_3 \cdot 6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in the solution were treated with excess of $AgNO_3$ to give 4.32 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is (At. mass of Ag = 108 u)
(a) $[Co(NH_3)_6]Cl_3$
(b) $[CoCl_2(NH_3)_4]Cl \cdot 2NH_3$
(c) $[CoCl_3(NH_3)_3] \cdot 3NH_3$
(d) $[CoCl(NH_3)_5]Cl_2 \cdot NH_3$

3. According to IUPAC nomenclature, sodium nitroprusside is named as
(a) sodium nitroferricyanide
(b) sodium nitroferrocyanide
(c) sodium pentacyanonitrosylferrate (II)
(d) sodium pentacyanonitrosylferrate (III).

4. Ferrocene is an example of
(a) sandwiched complex (b) pi-bonded complex
(c) a complex in which all the five carbon atoms of cyclopentadiene anions are bonded to the metal
(d) all of the above.

5. Which kind of isomerism is exhibited by octahedral complex, $[Co(NH_3)_4Br_2]Cl$?
(a) Geometrical and ionisation
(b) Geometrical and optical
(c) Optical and ionisation
(d) Geometrical only

6. When EDTA solution is added to Mg^{2+} ion solution, then which of the following statements is not true?
(a) Four coordinate sites of Mg^{2+} are occupied by EDTA and remaining two sites are occupied by water molecules.
(b) All six coordinate sites of Mg^{2+} are occupied.
(c) pH of the solution is decreased.
(d) Colourless $[Mg - EDTA]^{2-}$ chelate is formed.

7. The oxidation number, *d*-orbital occupation and coordination number of Cr in the complex *cis*-$[Cr(en)_2Cl_2]Cl$ are respectively
(a) +3, 3*d* and 4 (b) +3, 4*d* and 6
(c) +3, 3*d* and 6 (d) +2, 3*d* and 6

8. If $P > \Delta_o$ then d^4 is represented as
(a) $t_{2g}^{211}\ e_g^0$ (b) $t_{2g}^{111}\ e_g^1$
(c) $t_{2g}^0\ e_g^{22}$ (d) $t_{2g}^1\ e_g^{21}$

9. What are the correct oxidation state, coordination number, configuration, magnetic character and magnetic moment of $K_4[Mn(CN)_6]$?

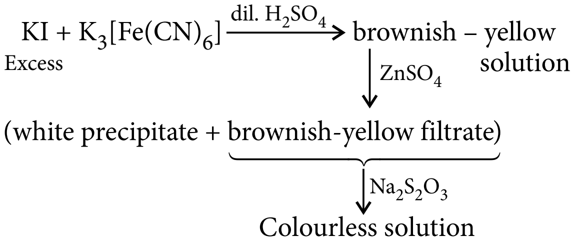
	O.S.	C.N.	Configuration	Magnetic Character	Magnetic Moment
(a)	+6	6	$t_{2g}^5\ e_g^0$	Diamagnetic	0
(b)	+2	6	$t_{2g}^4\ e_g^1$	Diamagnetic	0
(c)	+2	6	$t_{2g}^5 e_g^0$	Paramagnetic	1.732
(d)	+4	6	$t_{2g}^3\ e_g^2$	Diamagnetic	0

10. Which of the following isomers will give white precipitate with $BaCl_2$ solution?
(a) $[Co(NH_3)_5SO_4]Br$ (b) $[Co(NH_3)_5Br]SO_4$
(c) $[Co(NH_3)_4(SO_4)_2]Br$
(d) $[Co(NH_3)_4Br(SO_4)]$

SECTION - II

More than One Options Correct Type

11. For the given aqueous reactions which of the following statements are true?



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

12. The type of isomerism present in nitropentaammine chromium(II) chloride is
(a) optical (b) linkage
(c) ionisation (d) polymerisation.

13. For complex ion, $[Cu(NH_3)_4]^{2+}$
(a) stability constant is $\dfrac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$
(b) stability constant is the inverse of instability constant

(c) greater is the stability constant, stronger is the Cu—NH_3 bond

(d) the given complex is only produced when excess of NH_3 solution is added to Cu^{2+} solution.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Exp. (A) : When $Fe(CN)_2$ solution is treated with KCN solution, species formed no longer gives tests of Fe^{2+} and CN^-.

Exp. (B) : When K_2SO_4 solution is treated with $Al_2(SO_4)_3$ solution, species formed gives tests of K^+, Al^{3+} and SO_4^{2-}.

14. Species formed in experiment (A) does not give test of Fe^{2+} and CN^-. It is due to formation of

(a) $K_2[Fe(CN)_4]$ (b) $K_3[Fe(CN)_5]$

(c) $K_3[Fe(CN)_6]$ (d) $K_4[Fe(CN)_6]$

15. Species formed in experiment (B) is

(a) complex (b) double salt

(c) liquid crystal (d) none of these.

Paragraph for Questions 16 and 17

Double salts are addition compounds which lose their identity in aqueous solution whereas complexes which are also addition compounds do not lose their identity in aqueous solution. The coordination compounds show isomerism and find applications in photography, qualitative analysis, metallurgy, water purification and in the treatment of various diseases.

16. Which of the following statements is incorrect?

(a) Alum is a double salt.

(b) Calcium salt of EDTA is used in the treatment of lead poisoning.

(c) Effective atomic number of the metals in complexes $[Ni(CO)_4]$ and $[Fe(CN)_6]^{4-}$ is same.

(d) Tris(triphenylphosphine)rhodium(I) chloride is effective heterogeneous catalyst for hydrogenation of alkenes.

17. Choose the correct option for the complex $[PtCl_2(en)_2]^{2+}$.

(a) Platinum is in +2 oxidation state.

(b) Racemic mixture is obtained on mixing mirror images of its *trans*-form in 1 : 1 molar ratio.

(c) It has two five membered chelating rings.

(d) Both (b) and (c).

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 (Complex)	List II (Hybridisation)
(P) $[Ni(CO)_4]$	(i) sp^3d^2
(Q) $[Ni(CN)_4]^{2-}$	(ii) sp^3
(R) $[Fe(CN)_6]^{4-}$	(iii) d^2sp^3
(S) $[MnF_6]^{4-}$	(iv) dsp^2

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

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

List (Complex ion)	List II (Colour)
(P) $[CoF_6]^{3-}$	(i) Blue-green
(Q) $[Co(NH_3)_6]^{3+}$	(ii) Pale yellow
(R) $[Co(H_2O)_6]^{3+}$	(iii) Green
(S) $[Co(CN)_6]^{3-}$	(iv) Yellow-orange

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

SECTION - V

Assertion Reason Type

20. Assertion : The complex ion *trans*-$[Co(en)_2Cl_2]^+$ is optically active.

Reason: It is an octahedral complex.

21. Assertion : In complex $[Cr(NH_3)_4BrCl]Cl$, the 'spin only' magnetic moment is close to 1.73 B.M.

Reason: Mononuclear complexes of chromium(III) in strong field ligand have three unpaired electrons.

22. Assertion : $[Ni(en)_3]Cl_2$ has lower stability than $[Ni(NH_3)_6]Cl_2$.

Reason: In $[Ni(en)_3]Cl_2$, the geometry of Ni is trigonal bipyramidal.

SECTION - VI

Integer Value Correct Type

23. The number of possible geometrical isomers for the complex $[Pt(NO_2)(py)(NH_2OH)(NH_3)]$ is

24. What is the coordination number of the metal ion in the red complex formed in a qualitative analysis of iron(III)?

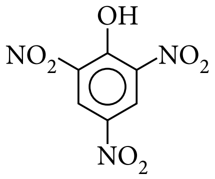
25. What is the denticity of $N(CH_2CH_2NH_2)_3$?

SOLUTIONS

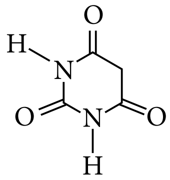
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

1. (b)

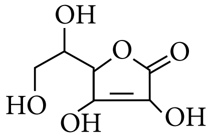
2. (d):



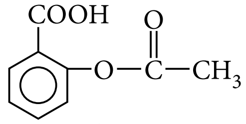
Picric acid



Barbituric acid

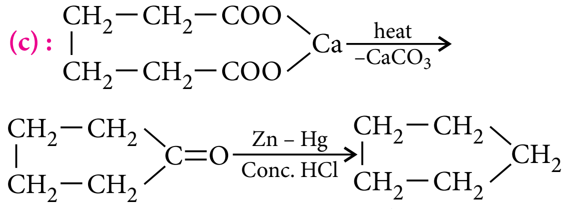


Ascorbic acid



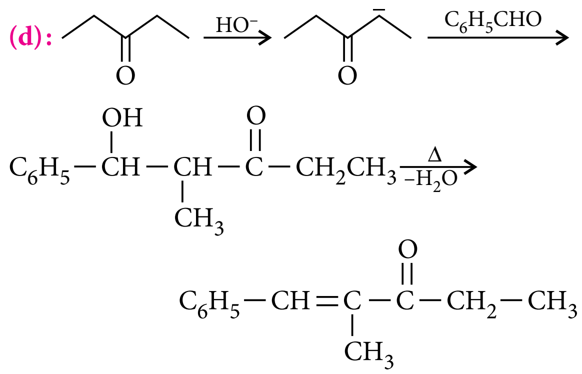
Aspirin

3. (c) :



Cyclopentane

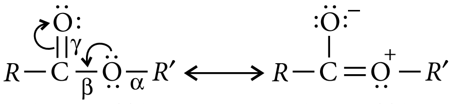
4. (d):



$$\xrightarrow{HO^-}\ \xrightarrow{C_6H_5CHO}$$

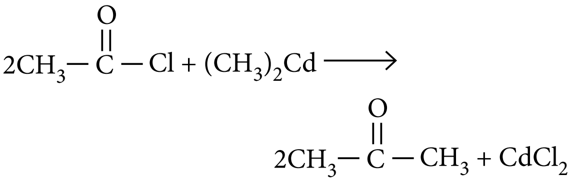
$$C_6H_5-\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-CH_2CH_3 \xrightarrow[-H_2O]{\Delta} C_6H_5-CH=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{||}}{C}-CH_2-CH_3$$

5. (d): The γ C—O bond is shortest because it has double bond character. The β C—O bond is shorter because it also has some double bond character due to resonance. The α C—O bond is longest because it is always a single bond.



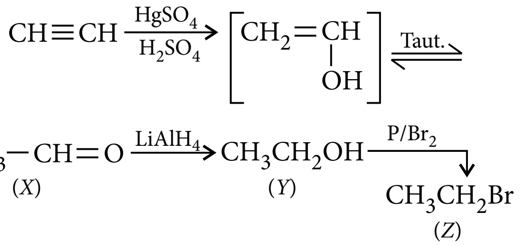
I (More stable) II (Less stable)

6. (d): With calculated amount of Grignard reagent, ketones are formed. But excess of Grignard reagent can lead to the formation of tertiary alcohol. Thus, dimethyl cadmium is the best reagent.



$$2CH_3-\overset{\overset{O}{||}}{C}-Cl + (CH_3)_2Cd \longrightarrow 2CH_3-\overset{\overset{O}{||}}{C}-CH_3 + CdCl_2$$

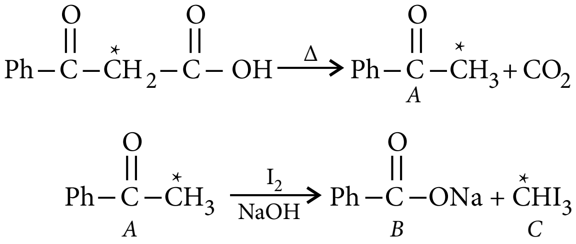
7. (c) :



$$CH\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} \left[CH_2=\underset{\underset{OH}{|}}{CH}\right] \xrightleftharpoons{Taut.} \underset{(X)}{CH_3-CH=O} \xrightarrow{LiAlH_4} \underset{(Y)}{CH_3CH_2OH} \xrightarrow{P/Br_2} \underset{(Z)}{CH_3CH_2Br}$$

8. (c)

9. (c) :



$$Ph-\overset{\overset{O}{||}}{C}-\overset{*}{C}H_2-\overset{\overset{O}{||}}{C}-OH \xrightarrow{\Delta} \underset{A}{Ph-\overset{\overset{O}{||}}{C}-\overset{*}{C}H_3} + CO_2$$

$$\underset{A}{Ph-\overset{\overset{O}{||}}{C}-\overset{*}{C}H_3} \xrightarrow[NaOH]{I_2} \underset{B}{Ph-\overset{\overset{O}{||}}{C}-ONa} + \underset{C}{\overset{*}{C}HI_3}$$

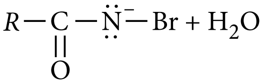
10. (a)

11. (a, c) : $RCONH_2 + Br_2 + 4KOH_{(aq)} \longrightarrow RNH_2 + 2KBr + 2H_2O + K_2CO_3$

Mechanism :

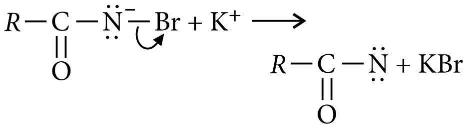
Step I : $RCONH_2 + Br_2 + KOH \longrightarrow RCONHBr + KBr + H_2O$

Step II : $RCONHBr + OH^- \longrightarrow$



$$R-\underset{\underset{O}{||}}{C}-\underset{..}{\ddot{N}}^{-}-Br + H_2O$$

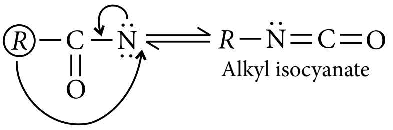
Step III :



$$R-\underset{\underset{O}{||}}{C}-\underset{..}{\ddot{N}}^{-}-Br + K^+ \longrightarrow R-\underset{\underset{O}{||}}{C}-\underset{..}{\ddot{N}} + KBr$$

Nitrene

Step IV :

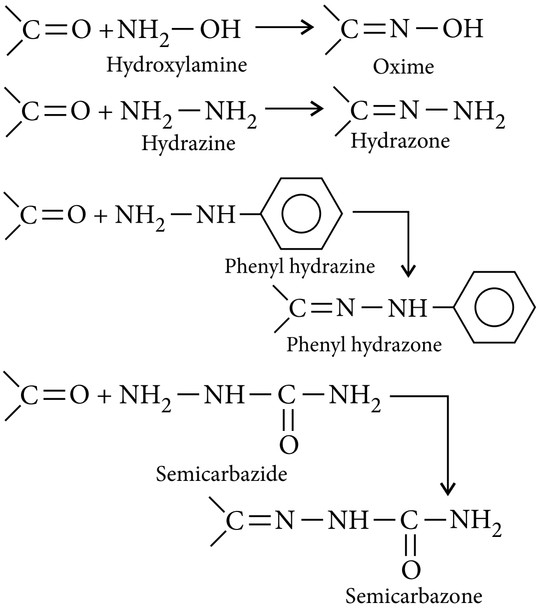


$$R-\underset{\underset{O}{||}}{C}-\underset{..}{\ddot{N}} \rightleftharpoons R-\ddot{N}=C=O$$

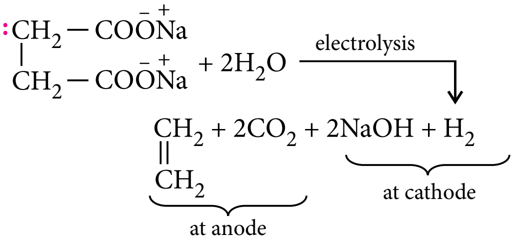
Alkyl isocyanate

Step V : $R-N=C=O + 2KOH \longrightarrow RNH_2 + K_2CO_3$

12. (a, b, c, d) : The main reaction of carbonyl compounds is nucleophilic addition reaction. Reactions with ammonia derivatives are also examples of nucleophilic addition reaction.



13. (b,d):

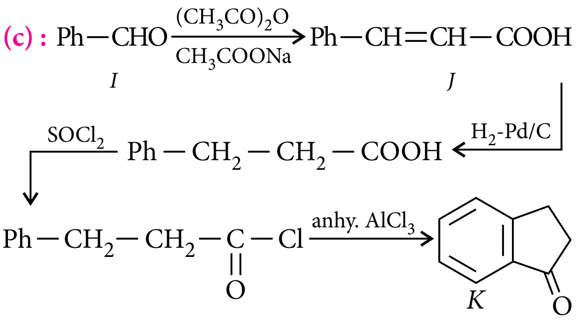


$$\begin{matrix}CH_2-CO\overset{-}{O}\overset{+}{Na}\\ |\\ CH_2-CO\overset{-}{O}\overset{+}{Na}\end{matrix} + 2H_2O \xrightarrow{\text{electrolysis}} \underbrace{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + 2CO_2}_{\text{at anode}} + \underbrace{2NaOH + H_2}_{\text{at cathode}}$$

14. (c) : Due to –*I* effect of Cl.

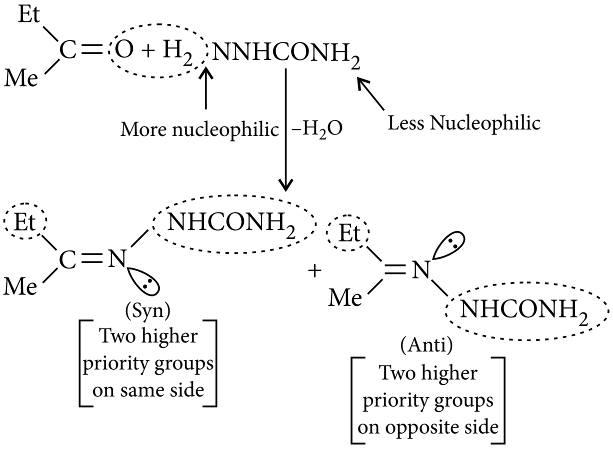
15. (c) : $BrCH_2CH_2COOH$ has the smallest dissociation constant (*i.e.*, the weakest acid) since Br has less –*I*-effect than F and is far from the —COOH group.

16. (c) :



17. (a) **18. (a)** **19. (d)**

20. (d): The semicarbazone formation occurs with more nucleophilic $(NH_2\ NHCONH_2)$ side.



More nucleophilic

–H_2O

Less Nucleophilic

(Syn)

Two higher priority groups on same side

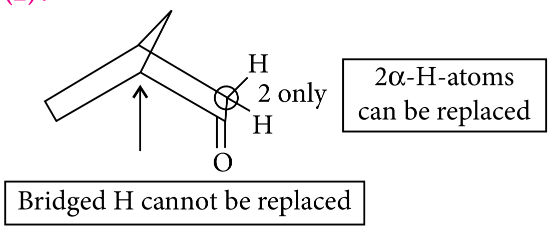
(Anti)

Two higher priority groups on opposite side

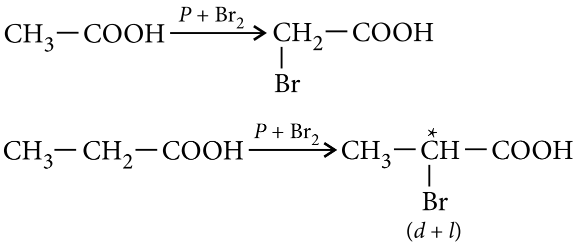
21. (c) : It is known that esters with α-hydrogen form carbanion when treated with base. It brings about nucleophilic substitution at the carbonyl group of the ester to yield β-keto ester. This is known as Claisen condensation reaction. $LiAlH_4$ reduces esters to alcohols.

22. (b): $6HCHO + 4NH_3 \longrightarrow \underset{\text{Urotropine}}{(CH_2)_6N_4} + 6H_2O$

23. (2):



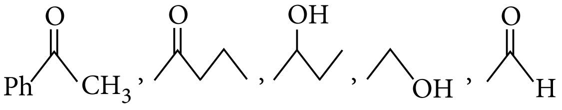
24. (3): Formic acid and benzoic acid do not contain α-H atoms so they cannot give Hell—Volhard—Zelinsky reaction.



$$CH_3-COOH \xrightarrow{P + Br_2} \underset{\substack{|\\ Br}}{CH_2}-COOH$$

$$CH_3-CH_2-COOH \xrightarrow{P + Br_2} CH_3-\underset{\substack{|\\ Br\\ (d\,+\,l)}}{\overset{*}{C}H}-COOH$$

25. (5): Compounds having $CH_3-\overset{\overset{O}{\|}}{C}-$ or $CH_3-\overset{\overset{OH}{|}}{CH}-$ groups give positive iodoform test.



COORDINATION COMPOUNDS

1. **(a) :** The configuration will be $t_{2g}^3\, e_g^1$

$\therefore$ CFSE $= 3(-0.4) + 1(0.6) = -0.6\,\Delta_o$

2. **(a) :** $CoCl_3{\cdot}6NH_3 \rightarrow xCl^- \xrightarrow{AgNO_3} xAgCl\downarrow$

$$\text{Moles of AgCl} = \frac{4.32}{143.5}$$

$$\text{and moles of } CoCl_3{\cdot}6NH_3 = \frac{2.675}{267.5}$$

$$\text{or}\quad \frac{4.32}{143.5} = x\frac{2.675}{267.5}$$

$\therefore\ x = 3$

Hence, the formula of the complex is $[Co(NH_3)_6]Cl_3$.

3. **(c) :** Sodium nitroprusside $Na_2[Fe(CN)_5NO]$ is named as sodium pentacyanonitrosylferrate (II). In this compound, NO exists in +1 and Fe exists in +2 oxidation state.

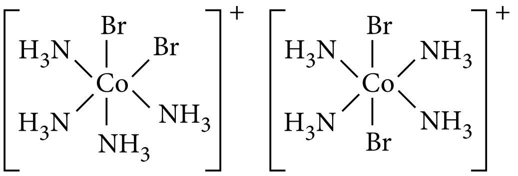
4. **(d) :** Ferrocene is a sandwich complex in which all the five carbon atoms of cyclopentadienyl anion are linked to the metal by pi-bonds.

5. **(a) :** Octahedral complex, $[Co(NH_3)_4Br_2]Cl$ shows ionisation as well as geometrical isomerism.

Ionisation isomers are :

$[Co(NH_3)_4Br_2]Cl$ and $[Co(NH_3)_4BrCl]Br$

Geometrical isomers are :



cis –form *trans* –form

6. **(a)**

7. **(c) :** Oxidation state of Cr $= x + 2(-1) = +1$

$\Rightarrow\ x = +3$

Cr^{3+} occupies $3d$ orbitals and its coordination number in the given complex is 6.

8. **(b) :** If $P > \Delta_o$, it favours the high spin complexes and there is no pairing of d-electrons taken place.

So, $3d^4$ will be $t_{2g}^3\, e_g^1$ or $t_{2g}^{111}\, e_g^1$.

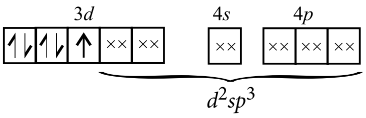
9. **(c) :** Oxidation state : $4(+1) + x + 6(-1) = 0$

$4 + x - 6 = 0 \quad\Rightarrow\quad x = +2$

C.N. = 6, configuration $= t_{2g}^5 e_g^0$

$Mn^{2+} = 3d^5 4s^0$

$[Mn(CN)_6]^{4-}$:



It has one unpaired electron and hence it is paramagnetic in nature.

$\mu = \sqrt{1(1+2)} = \sqrt{3}\ = 1.732$ B.M.

10. **(b) :** $[Co(NH_3)_5Br]SO_4 \rightleftharpoons [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$

$$SO_4^{2-} + BaCl_2 \longrightarrow \underset{\text{white ppt.}}{BaSO_4} + 2Cl^-$$

11. **(a, c, d) :** $2KI + 2K_3[Fe(CN)_6] \xrightarrow{\text{dil. } H_2SO_4}$

$2K_4[Fe(CN)_6] + I_2$ ...(i)

$$\underset{\text{(Excess)}}{I_2 + KI} \longrightarrow KI_3 \qquad \text{...(ii)}$$

$$K_4[Fe(CN)_6] + ZnSO_4 \longrightarrow \underset{\text{White ppt.}}{K_2Zn_3[Fe(CN)_6]_2}$$

$$\underset{\substack{\text{Brownish}\\ \text{yellow filtrate}}}{KI_3} + 2Na_2S_2O_3 \longrightarrow \underset{\text{Colourless solution}}{Na_2S_4O_6 + 2NaI + KI}$$

(a) is correct as in reaction (i), I^- (–1) is being oxidised to $I_2(0)$ and Fe^{3+} is being reduced to Fe^{2+}.

(b) is incorrect as white precipitate is of $K_2Zn_3[Fe(CN)_6]_2$ or $Zn_2[Fe(CN)_6]$.

(c) is correct as

$$\underset{\text{Filtrate}}{I_3^-} \rightleftharpoons I^- + I_2 \xrightarrow{\text{Starch}} \text{Blue colour}$$

(d) is correct as white precipitate of $K_2Zn_3[Fe(CN)_6]_2$ or $Zn_2[Fe(CN)_6]$ is soluble in NaOH as

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

12. **(b, c) :** $[Cr(NH_3)_5NO_2]Cl$

In, —NO_2 : N is donating site while in —ONO, O is donating site. Thus, it can behave as linkage isomer and Cl is present out of the coordination sphere thus it can behave as ionisation isomer as well.

13. **(a, b, c, d) :** $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$

$$\text{Stability constant } (\beta) = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}]\cdot[NH_3]^4}$$

$$\text{Stability constant} \propto \frac{1}{\text{Instability constant}}$$

14. (d): $4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$

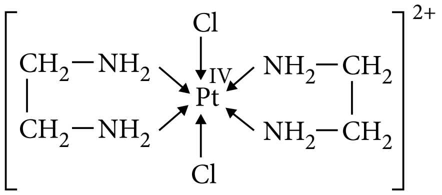
$K_4[Fe(CN)_6]$ is a complex which dissociates as $4K^+$ and $[Fe(CN)_6]^{4-}$ but not as CN^- or Fe^{2+} in aqueous solution.

15. (b): $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Potash alum
(Double salt)

16. (d): Wilkinson's catalyst is homogeneous catalyst for hydrogenation of alkenes.

17. (c) :

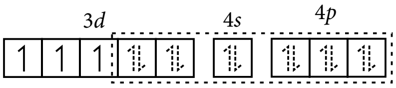


trans-form is optically inactive because it is achiral.

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

21. (d): Cr^{3+} having $3d^3$ configuration always have 3 unpaired electrons with strong field as well as weak field ligands.

Hybridisation in $[Cr(NH_3)_4BrCl]^+$ is as follows :



d^2sp^3 hybridisation

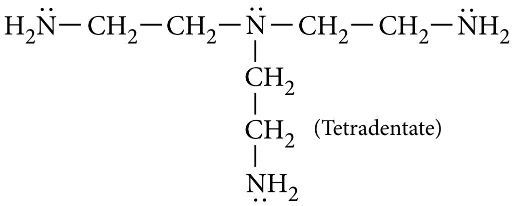
So, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

22. (d): $[Ni(en)_3]Cl_2$ is more stable than $[Ni(NH_3)_6]Cl_2$ because it is chelate compound. It has octahedral geometry.

23. (3)

24. (6): Complex ion formed is $[Fe(H_2O)_5SCN]^{2+}$. It has coordination number six.

25. (4):



$H_2\ddot{N}-CH_2-CH_2-\ddot{N}(CH_2CH_2\ddot{N}H_2)-CH_2-CH_2-\ddot{N}H_2$ (Tetradentate)

◆◆

ACE YOUR WAY CBSE XII

Series 6

CHAPTERWISE PRACTICE PAPER : ALDEHYDES, KETONES AND CARBOXYLIC ACIDS | AMINES

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 carry 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. Arrange the following in the decreasing order of ease of hydrolysis:
$CH_3COOC_2H_5, CH_3COCl, (CH_3CO)_2O, CH_3CONH_2$

2. Write down the reactions of ethyl cyanide with
(i) alk. H_2O_2 **(ii)** dil. HCl

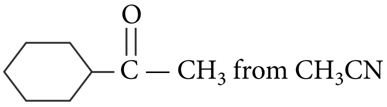
3. Name the alkene which on reductive ozonolysis gives only acetone.

4. Why does aniline dissolve in aqueous HCl?

5. Arrange the following in decreasing order of their acidic strength :
CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

6. Compare the basicity of the following compound:
(i) $H_2C{=}CHCH_2NH_2$ **(ii)** $CH_3CH_2CH_2NH_2$
(iii) $HC{\equiv}CCH_2NH_2$

7. How will you obtain the following?

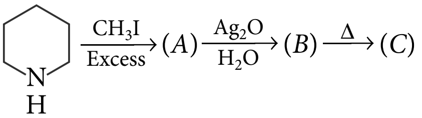
(i)  from CH_3CN

(ii)  from HCN

OR

Give a chemical test to distinguish between
(i) Formic acid and acetic acid
(ii) Oxalic acid and acetic acid.

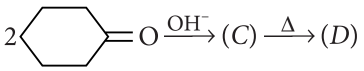
8. Complete the following reaction :



9. Write the IUPAC name of the following compounds :
(i) $(CH_3)_2CH—CO—CH(CH_3)_2$
(ii) $Ph—CH{=}CH—CHO$

10. Answer the following questions :
(i) How will you convert an alkyl halide into a primary amine having one carbon atom more than the alkyl halide?
(ii) How will you convert a carboxylic acid into an amine having one carbon atom less than the carboxylic acid?

11. Identify *A*, *B*, *C* and *D* in the reactions given below :
(i) $2CH_3CH_2CHO \xrightarrow{OH^-} (A) \xrightarrow{\Delta} (B)$

(ii) 

12. How will you convert the following :
(i) Nitrobenzene into aniline
(ii) Primary amine to secondary amine
(iii) Aniline into *N*-phenylethanamide?

13. Can Gatterman–Koch reaction be considered similar to Friedel–Crafts acylation? Discuss.

14. State the reason for the following :
(i) Acetylation of aniline reduces its activation effect.
(ii) Methyl amine is more basic than aniline.
(iii) Although —NH_2 is *o*/*p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

15. How will you obtain :
(i) Butanoic acid from 1-bromopropane
(ii) Propanoic acid from ethyne
(iii) 2-Methylbutanoic acid from butan-2-ol?

16. Give the structures of *A*, *B* and *C* in the following reactions :
(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$
(ii) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\text{-}278\text{ K}]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

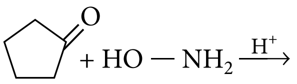
17. What happens when
(i) Acetamide is heated with bromine and caustic potash
(ii) Acetyl chloride reacts with water
(iii) Acetamide reacts with phosphorus pentoxide?

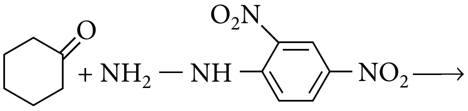
18. Answer the following questions :
(i) Why electrophilic substitution in aromatic amines takes place more readily than benzene?
(ii) Why primary amines have higher boiling point than corresponding tertiary amines?
(iii) Write two important uses of *N*, *N*-dimethyl amines (DMA).

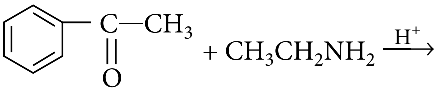
OR

(a) Arrange the following in increasing order of basic strength : Aniline, *p*-nitroaniline and *p*-toluidine.
(b) State reason for the following :
  (i) Ethylamine is soluble in water whereas aniline is not.
  (ii) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

19. Predict the products of the following reactions :

(i) 

(ii) 

(iii) 

20. Write short notes on the following :
(i) Carbylamine reaction **(ii)** Diazotisation
(iii) Gabriel phthalimide synthesis.

21. An organic compound *A* contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acids. Derive the structure of compound *A*.

22. An aromatic compound '*A*' on treatment with aqueous ammonia and on heating forms compound '*B*' which on heating with Br_2 and KOH forms a compound '*C*' of molecular formula C_6H_7N. Write the structure and IUPAC name of compounds *A*, *B* and *C*.

23. Sushil's friends want to play Holi with synthetic colours, eggs, muddy water etc. Sunil persuades his friends to play Holi with natural colours. He reminds that last time one of his friend had suffered from skin allergy after playing Holi with synthetic colours. It took long time to recover. Sushil's friends agreed and prepared natural colours using leaves and flowers.
(i) What is diazotisation reaction?
(ii) Name two dyes prepared by diazotisation.
(iii) Write equation for the preparation of any one of the above dyes.
(iv) What are the values expressed by Sushil?

24. **(i)** Identify *A*, *B* and *C* in the following sequence of the reactions :

$$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgCl} A \xrightarrow[\Delta]{\text{Conc.}H_2SO_4} B \xrightarrow{\text{HBr/Peroxide}} C$$

(ii) Predict the structure of products formed when benzaldehyde is treated with
(a) Conc.NaOH
(b) HNO_3/H_2SO_4 (at 273-383 K).

OR

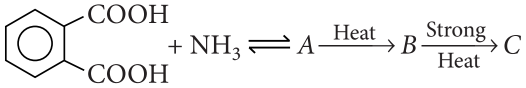
(i) Give a chemical test to distinguish between the following :

(a) Benzoic acid and ethyl benzoate

(b) Benzophenone and acetophenone.

(ii) Complete the following reaction :

(iii) Identify *A*, *B* and *C* in the following sequence:



25. How will you convert :

(i) Benzyl chloride to 2-phenylethanamine

(ii) Toluene to *o*-chlorotoluene

(iii) Toluene to *m*-chlorotoluene?

OR

$$\underset{\substack{(X)\\ \text{Optically active}}}{C_5H_{13}N} \xrightarrow{\text{aq. } NaNO_2/HCl} \underset{\substack{\text{Tertiary}\\ \text{alcohol}}}{Y}$$

(i) Identify (*X*) and (*Y*). **(ii)** Is *Y* optically active?

(iii) Give structures of intermediate(s), if any, in the formation of *Y* from *X*.

26. (i) An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

(ii) A compound (*A*) $C_5H_8O_2$ liberates CO_2 on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yields (*B*) $C_5H_{10}O_2$ on hydrogenation. Compound (*B*) can be separated into two enantiomers. Write structural formulae for (*A*) and (*B*) with reason.

OR

An organic compound (*A*) of molecular weight 140.5 has 68.32% carbon, 6.4% hydrogen and 25.26% chlorine. Hydrolysis of (*A*) with dilute acid gives compound (*B*) $C_8H_{10}O$. Compound (*B*) can be oxidised under mild conditions to form compound (*C*), C_8H_8O. Compound (*C*) forms a phenylhydrazone (*D*) with phenylhydrazine and gives positive iodoform test. Deduce the structures of (*A*) to (*D*) with proper reasoning.

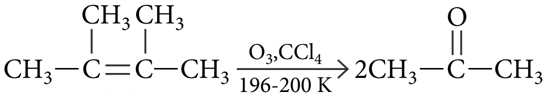
SOLUTIONS

1. $CH_3COCl > (CH_3CO)_2O > CH_3COOC_2H_5 > CH_3CONH_2$

2. (i) $C_2H_5CN + H_2O \xrightarrow[\text{conc. HCl}]{H_2O_2(\text{alk.})} \underset{\text{Propanamide}}{C_2H_5CONH_2}$

(ii) $C_2H_5CN \xrightarrow{\text{dil. HCl}} C_2H_5COOH + NH_4Cl$

3.



$$\underset{\text{2, 3-Dimethylbut-2-ene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3} \xrightarrow[196\text{-}200\text{ K}]{O_3, CCl_4} 2\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3}$$

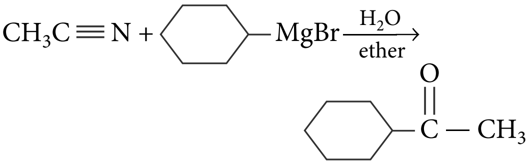
4. Aniline dissolves in aqueous HCl due to the formation of water soluble salt.

$$C_6H_5NH_2 + HCl \longrightarrow \underset{\text{Anilinium chloride}}{C_6H_5\overset{+}{N}H_3Cl^-}$$

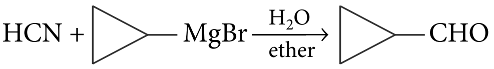
5. $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

6. The significant difference among these three bases depends on hybridisation of β-carbon atom. The compounds containing carbon with more *s*-character show more electron withdrawing nature and hence least basic. Thus, decreasing order of basicity is, (ii) > (i) > (iii).

7. (i)



(ii)



OR

(i) Formic acid produces silver mirror with ammoniacal silver nitrate solution. Acetic acid does not give this test.

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Tollens' reagent}}{2Ag(NH_3)_2\,NO_3} \longrightarrow \underset{\text{Silver mirror}}{2Ag} + CO_2 + 2NH_4NO_3 + 2NH_3$$

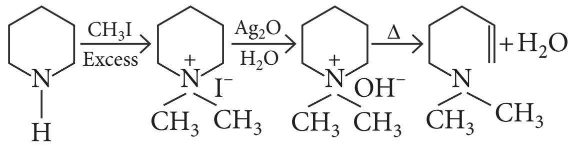
(ii) Oxalic acid on heating evolve CO_2 gas. The gas when passed through lime water forms a white precipitate.

$$\underset{\text{Oxalic acid}}{(COOH)_2} \longrightarrow \underset{\text{Formic acid}}{HCOOH} + CO_2\uparrow$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{white ppt.}}{CaCO_3} + H_2O$$

Acetic acid does not give this test.

8.



Piperidine (*A*) (*B*) (*C*)

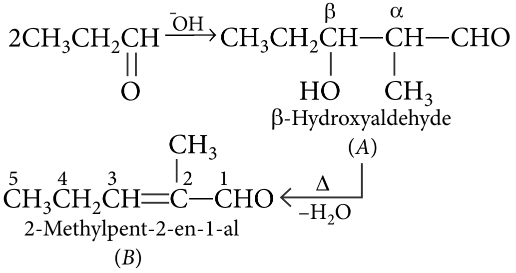
9. **(i)** 2, 4-Dimethylpent-3-one

(ii) 3-Phenylprop-2-enal

10. **(i)** $C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow[{[4H]}]{Na,\ C_2H_5OH} C_2H_5CH_2NH_2$

(ii) $CH_3COOH \xrightarrow[Heat]{NH_3} CH_3CONH_2 \xrightarrow[\Delta]{Br_2,KOH} CH_3NH_2$

11. **(i)**



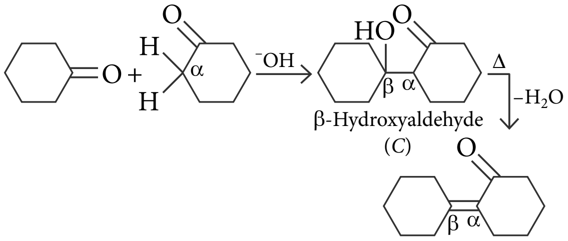
$$2CH_3CH_2\underset{\underset{O}{\|}}{C}H \xrightarrow{^-OH} CH_3CH_2\overset{\beta}{\underset{\underset{HO}{|}}{C}}H-\overset{\alpha}{\underset{\underset{CH_3}{|}}{C}}H-CHO$$

β-Hydroxyaldehyde (*A*)

$$\xrightarrow[-H_2O]{\Delta} \overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H=\overset{\overset{CH_3}{|}}{\underset{2}{C}}-\overset{1}{C}HO$$

2-Methylpent-2-en-1-al (*B*)

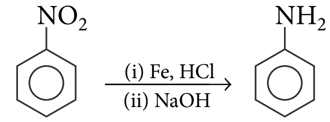
(ii)



β-Hydroxyaldehyde (*C*)

α, β-Unsaturated ketone (*D*)

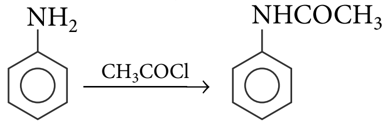
12. **(i)**



Nitrobenzene Aniline

(ii) $\underset{\text{1° Amine}}{RNH_2} \xrightarrow[\text{(Carbylamine reaction)}]{KOH/CHCl_3} RNC \xrightarrow{H_2/\,Pt} \underset{\text{2° Amine}}{RNHCH_3}$

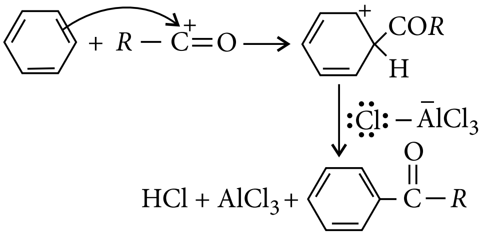
(iii)



Aniline *N*-Phenylethanamide

13. Yes, Friedel–Crafts acylation involves attack of acylium ion, ($R-\overset{+}{C}=O$) an electrophile on aromatic substrates to give rise to aromatic ketones. Gatterman–Koch reaction involves attack of $H-C\equiv\overset{+}{O}$ (an electrophile) on aromatic substrates to give rise to aromatic aldehydes.

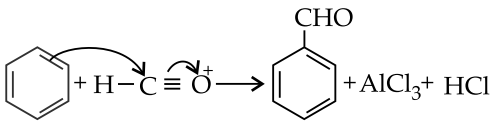
Friedel – Crafts reaction :



Gatterman–Koch reaction :

$CO + HCl + AlCl_3 \xrightleftharpoons{CuCl}$

$[H\overset{+}{C}=O \longleftrightarrow HC\equiv\overset{+}{O}] + AlCl_4^-$



Thus, Gatterman–Koch aldehyde synthesis can be considered similar to Friedel-Crafts acylation.

14. **(i)** After acetylation of aniline, acetanilide is formed in which electron density on N-atom decreases due to the presence of —$COCH_3$ group, having –*I* effect, and hence, activation effect of aniline gets reduced.

(ii) In aniline, lone pair of electrons on nitrogen atom is not free for donation because it is involved in resonance. But in case of methylamine, lone pair of electrons on nitrogen atom is free for donation. So, aniline is less basic than methylamine.

(iii) Nitration is carried out with conc. HNO_3 / H_2SO_4. In presence of acid, the —NH_2 group of aniline gets protonated and is converted into —$^+NH_3$ group. This positively charged group acts as a strong electron withdrawing and act as a *meta*-directing group. Hence, the incoming electrophile goes to *m*-position and therefore, significant amount of *m*-nitroaniline is formed.

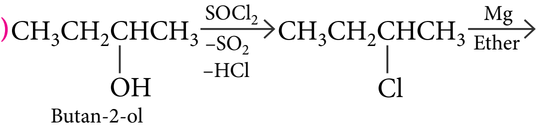
15. **(i)** $\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow{KCN} CH_3CH_2CH_2CN \xrightarrow{H_3O^+} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$

(ii) $\underset{\text{Ethyne}}{HC\equiv CH} \xrightarrow[Hg^{2+}]{HCl} H_2C=CHCl \xrightarrow[Ether]{Mg}$

$H_2C=CHMgCl \xrightarrow{CO_2} H_2C=CHCOOMgCl \xrightarrow{H^+}$

$H_2C=CHCOOH \xrightarrow{H_2/Pd} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$

(iii)



$$\underset{\text{Butan-2-ol}}{CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3} \xrightarrow[-SO_2,\ -HCl]{SOCl_2} CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3 \xrightarrow[Ether]{Mg}$$

$C_2H_5CH(CH_3)MgCl \xrightarrow{CO_2} C_2H_5CH(CH_3)COOMgCl$

$\underset{\text{2-Methylbutanoic acid}}{C_2H_5CH(CH_3)COOH} \xleftarrow[-Mg(OH)Cl]{H^+/H_2O}$

16. **(i)**

$$\begin{tikzcd}
C_6H_5N_2^+Cl^- \arrow[r, "CuCN"] & \underset{\substack{\text{Benzonitrile}\\(A)}}{C_6H_5CN} \arrow[d, "H_2O/H^+"] \\
\underset{\substack{\text{Benzamide}\\(C)}}{C_6H_5CONH_2} & \underset{\substack{\text{Benzoic acid}\\(B)}}{C_6H_5COOH} \arrow[l, "NH_3", "\Delta"']
\end{tikzcd}$$

(ii)

$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Sn + HCl"] & \underset{(A)}{C_6H_5NH_2} \arrow[d, "NaNO_2 + HCl", "273\text{-}278\ K"'] \\
\underset{(C)}{C_6H_5OH} & \underset{(B)}{C_6H_5N_2^+Cl^-} \arrow[l, "H_2O/\Delta"']
\end{tikzcd}$$

17. **(i)** $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow{\Delta} \underset{\text{Methyl amine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$

(ii) $\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + HCl$

(iii) $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\Delta]{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$

18. **(i)** $-NH_2$ group is electron releasing group, having $+R$-effect thus increases electron density in benzene ring. So, aniline is more reactive towards electrophilic substitution reaction than benzene.

(ii) Boiling point of amines is high due to presence of hydrogen bonding between amine molecules. In primary amine, large number of hydrogen atoms are available for hydrogen bonding than as compare to tertiary amines. Thus, have higher boiling point.

(iii) **(a)** It is used as an intermediate in the manufacture of dyes and other substances.

(b) It is important precursor to dyes such as crystal violet.

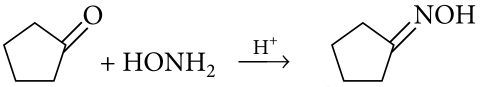
OR

(a) Electron withdrawing group ($-NO_2$) on benzene ring decreases the basicity and electron donating group ($-CH_3$) on benzene ring increases the basicity of the compound.
Increasing order of basic strength :
p-nitroaniline < aniline < *p*-toluidine

(b) **(i)** Ethylamine is soluble in water due to formation of intermolecular hydrogen bonding with water molecules. However, in aniline, due to presence of large hydrophobic aryl group, the extent of hydrogen bonding decreases considerably and hence, insoluble in water.

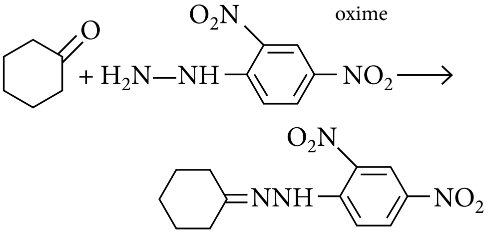
(ii) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which a mixture of products is formed and it is not possible to separate individual amines from the mixture.

19. **(i)**



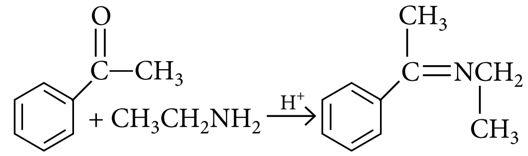
Cyclopentanone oxime

(ii)



Cyclohexanone-2,4-dinitrophenylhydrazone

(iii)



20. **(i)** **Carbylamine reaction :** Both aliphatic or aromatic 1° amines on warming with $CHCl_3$ in presence of alcoholic KOH solution produce an offensive smell of carbylamines.

(ii) **Diazotisation :** Aromatic diazonium salts are prepared by adding a cold aqueous solution of $NaNO_2$ to the solution of an aromatic 1° amine in a mineral acid (HCl, H_2SO_4, etc.) at 273-278 K. This reaction is called diazotisation.

(iii) **Gabriel phthalimide synthesis :** In this reaction, phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Further, potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylphthalimide which on alkaline hydrolysis gives phthalic acid and primary amine.

21. C = 69.77%, H = 11.63%

$\therefore$ O = 100 − (69.77 + 11.63) = 18.6%

Element	Percentage	Molar mass	Relative number ratio	Simple ratio
C	69.77	12	5.81	5
H	11.63	1	11.63	10
O	18.6	16	1.16	1

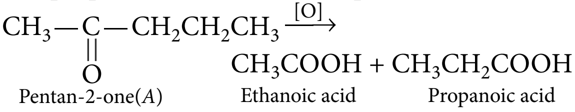
Empirical formula of given compound = $C_5H_{10}O$
Empirical formula mass = 5 × 12 + 10 × 1 + 1 × 16 = 86

$$\Rightarrow \quad n = \frac{86}{86} = 1$$

∴ Molecular formula = $(C_5H_{10}O)_1 = C_5H_{10}O$

Since, it does not give Tollens' test but gives positive iodoform test, so it is a methyl ketone derivative *i.e.*, have —$COCH_3$ group.

Since, on vigorous oxidation it gives ethanoic acid and propanoic acid, hence, it is pentan-2-one.



$$\underset{\text{Pentan-2-one}(A)}{CH_3-\underset{\underset{O}{\parallel}}{C}-CH_2CH_2CH_3} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

22. Since the compound '*C*' with molecular formula C_6H_7N is obtained from compound *B* on heating with Br_2 and KOH, the compound '*B*' must be an amide and the compound '*C*' must be an amine. Thus, aromatic amine having molecular formula C_6H_7N is $C_6H_5NH_2$, *i.e.*, aniline.

$$\underset{(B)}{C_6H_5CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2+KOH} \underset{(C)}{C_6H_5NH_2}$$

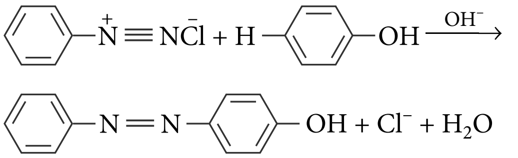
Since, the compound '*B*' is formed from compound '*A*' by treating with ammonia and then heating, the compound '*A*' must be benzoic acid.

$$\underset{(A)}{C_6H_5COOH} \xrightarrow[\text{(ii) }\Delta]{\text{(i) aq. }NH_3} \underset{(B)}{C_6H_5CONH_2}$$

23. **(i)** The nitrosylation of primary aromatic amines with nitrous acid leads to diazonium salts, this reaction is known as diazotisation.

(ii) *p*-Hydroxyazobenzene (Orange dye)
p-Aminoazobenzene (Yellow dye)

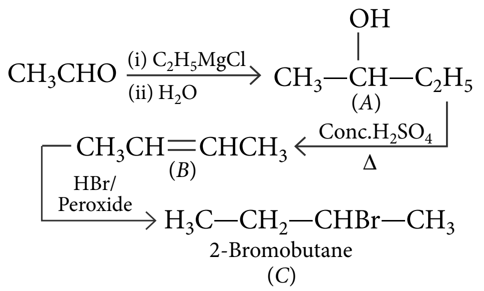
(iii)



p-Hydroxyazobenzene

(iv) Environment conservation, health concern for friend.

24. **(i)**

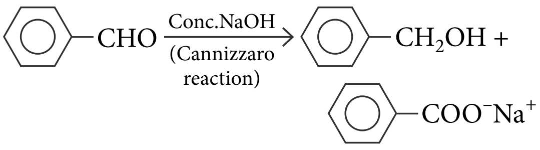


$$CH_3CHO \xrightarrow[\text{(ii) }H_2O]{\text{(i) }C_2H_5MgCl} \underset{(A)}{CH_3-\overset{\overset{OH}{|}}{CH}-C_2H_5}$$

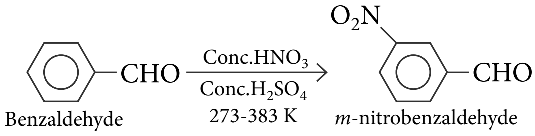
$$\underset{(A)}{CH_3-\overset{\overset{OH}{|}}{CH}-C_2H_5} \xrightarrow[\Delta]{\text{Conc.}H_2SO_4} \underset{(B)}{CH_3CH=CHCH_3}$$

$$\underset{(B)}{CH_3CH=CHCH_3} \xrightarrow{\text{HBr/Peroxide}} \underset{\underset{(C)}{\text{2-Bromobutane}}}{H_3C-CH_2-CHBr-CH_3}$$

(ii) **(a)**



(b)



OR

(i) **(a)** $C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2\uparrow$
(effervescence)

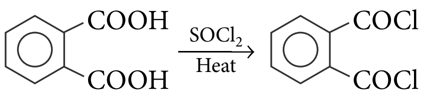
$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow$ No reaction

(b) Acetophenone with I_2/NaOH gives yellow precipitate of iodoform but benzophenone does not.

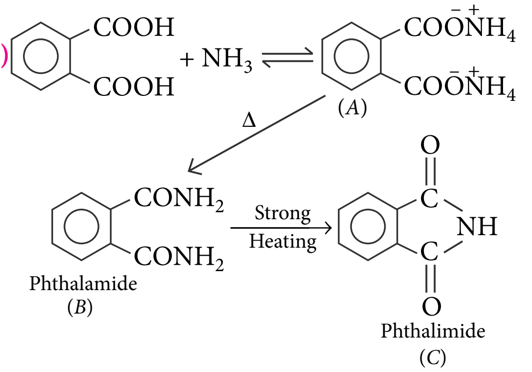
$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3 + 3NaI + 3H_2O$

$C_6H_5COC_6H_5 + I_2 + NaOH \longrightarrow$ No reaction

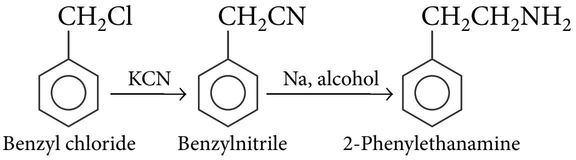
(ii)



(iii)



25. **(i)**



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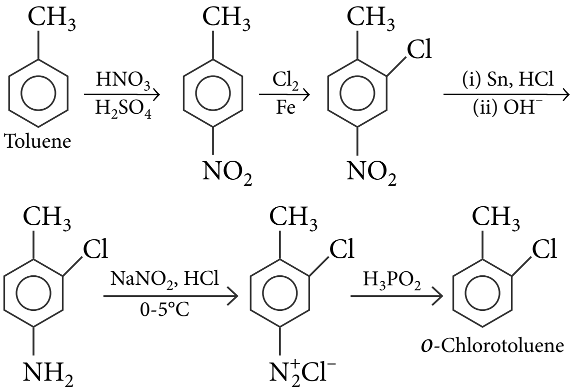
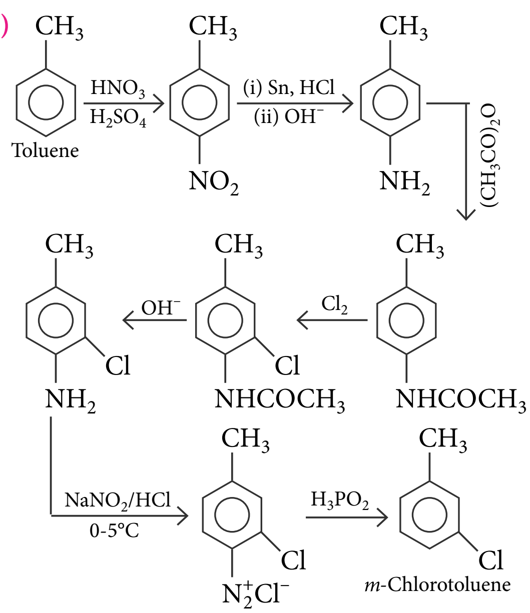
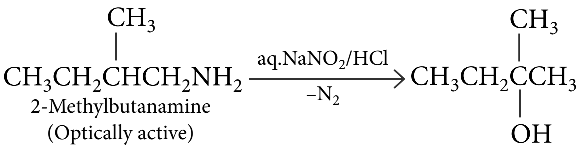


(iii)



OR

(i) As the compound (X) on treatment with HNO_2 evolves N_2 gas, therefore, (X) must be a primary amine. The compound (X) is optically active, it must contain a chiral carbon. The —NH_2 group cannot be directly attached to chiral carbon since such amines undergo racemisation due to nitrogen inversion. Therefore, the structure of the compound (X) is

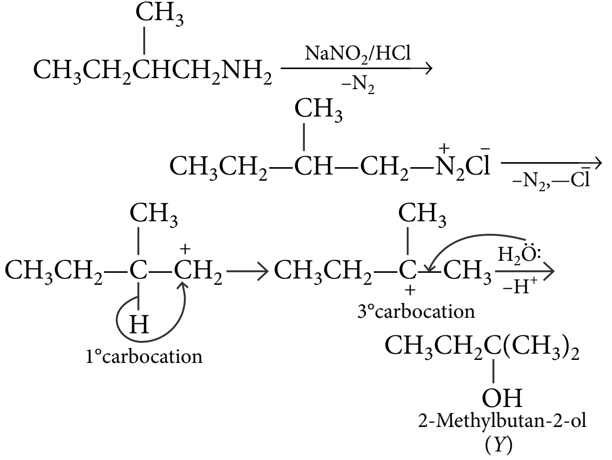


$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2NH_2 \xrightarrow[-N_2]{aq.NaNO_2/HCl} CH_3CH_2\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$$

2-Methylbutanamine (Optically active) (X) (Y)

(ii) Y is optically inactive due to absence of chiral carbon.

(iii) The formation of the compound (Y) from the compound (X) may be explained as follows :



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2NH_2 \xrightarrow[-N_2]{NaNO_2/HCl}$$

$$CH_3CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{+}{N}_2\overset{-}{Cl} \xrightarrow{-N_2,-\overset{-}{Cl}}$$

$$CH_3CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{C}H_2 \longrightarrow CH_3CH_2-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[-H^+]{H_2\ddot{O}:} CH_3CH_2\underset{\underset{OH}{|}}{C}(CH_3)_2$$

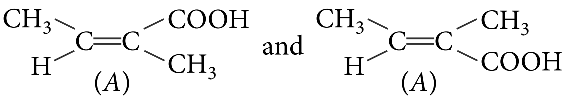
1°carbocation 3°carbocation 2-Methylbutan-2-ol (Y)

26. (i) Since the compound forms 2, 4-DNP derivative and reduces Tollens' reagent, it must be an aldehyde. Since the compound undergoes Cannizzaro reaction, *i.e.*, there is no α-hydrogen as —CHO group is directly attached to the benzene ring.

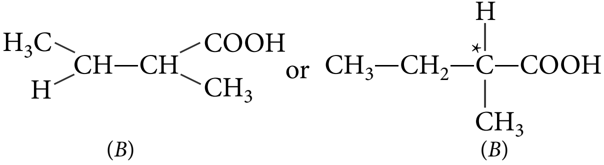
These observations suggest that the compound is *o*-ethylbenzaldehyde.

(ii) Since compound (A) liberates CO_2 on reaction with $NaHCO_3$ it is carboxylic acid.

As it undergoes hydrogenation, it should contain double bond. Therefore, A can be



On adding two H – atoms, it will form



(B) has asymmetric carbon and therefore, will exist in two enantiomeric forms.

OR

Element	Percentage of atoms	Relative number ratio	Simplest ratio
C	68.32	5.69	8
H	6.4	6.4	9
Cl	25.26	0.71	1

Therefore, empirical formula of compound (A) $= C_8H_9Cl$

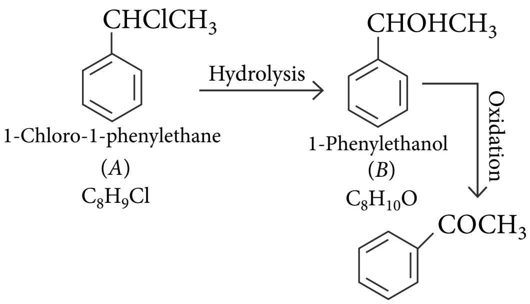
Empirical weight = 12 × 8 + 1 × 9 + 35.5 = 140.5

Molecular weight (given) = 140.5

As empirical weight and molecular weight are same,

∴ Molecular formula $= C_8H_9Cl$

Since (C) reacts with phenyl hydrazine, therefore, it is a carbonyl compound. Since (C) gives positive iodoform test, it has — $COCH_3$ group.



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MPP-7 MONTHLY Practice Problems

Class XII

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

Alcohols, Phenols and Ethers

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

NEET / AIIMS

Only One Option Correct Type

1. $CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$

In the above reaction, the leaving group is

(a) $[HOZnCl_2]^-$ (b) H_2O

(c) HO^- (d) H_3O^+

2. $C_6H_5OH \xrightarrow[NaOH]{CCl_4} X \xrightarrow[Heat]{Zn\ dust} Y \xrightarrow[(ii)\ Soda\ lime/\Delta]{(i)\ Na} Z$

In the above reaction sequence, *Z* is

(a) toluene (b) cresol

(c) benzene (d) benzol.

3. In the manufacture of ethanol from sugar the enzymes used are

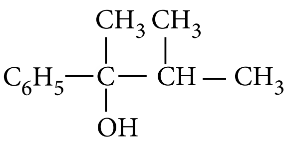
(a) diastase and zymase

(b) maltase and zymase

(c) diastase and invertase

(d) invertase and zymase.

4. Which of the following reagents will convert acetophenone to the given alcohol ?



$$C_6H_5-\underset{OH}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_3$$

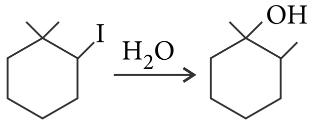
(a) $CH_3CH_2CH_2MgBr$ followed by hydrolysis

(b) $CH_3CH(Br)CH_3$, $AlCl_3$

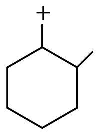
(c) $(CH_3)_2CHMgBr$ followed by acid hydrolysis

(d) $CH_3CHOHCH_3$, Zn

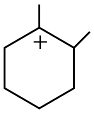
5. Which of the following is not expected to be the intermediate of the given reaction?



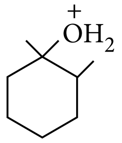
(a)



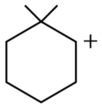
(b)



(c)



(d)



6. Between *p*-nitrophenol and *p*-cresol, solubility in base is

(a) almost nil in both the cases

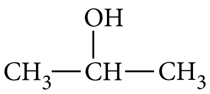
(b) higher for *p*-nitrophenol

(c) higher for *p*-cresol

(d) equal in both the cases.

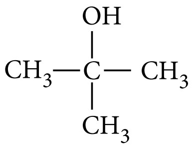
7. Which of the following sets of compounds cannot turn clear orange solution of CrO_3/dil. H_2SO_4 to greenish blue solution?

I. CH_3-CH_2-OH II.



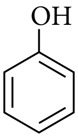
$$CH_3-\overset{OH}{CH}-CH_3$$

III.



$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

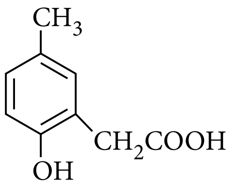
IV.

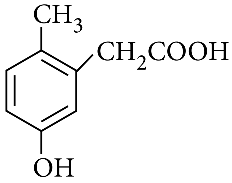


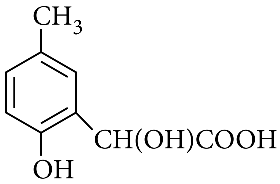
(a) I, IV (b) II, III

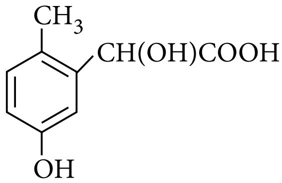
(c) I, II (d) III, IV

8. *p*–Cresol reacts with chloroform in alkaline medium to give a compound *A* which adds hydrogen cyanide to form compound *B*. The latter, on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

(a)


(b)


(c)


(d)


9. In the followng reaction,

$$C_2H_5OC_2H_5 \xrightarrow{\text{Red P + HI}} 2X + H_2O$$

X is

(a) ethane (b) ethylene
(c) butane (d) propane.

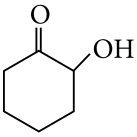
10. In Williamson's synthesis, ethoxyethane is prepared by

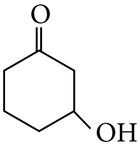
(a) passing ethanol over heated alumina
(b) heating sodium ethoxide with ethyl bromide
(c) treating ethyl alcohol with excess of H_2SO_4 at 430–440 K
(d) heating ethanol with dry Ag_2O.

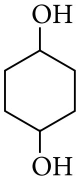
11. Aluminium *iso*-propoxide is used as a specific reagent for which of the following conversions?

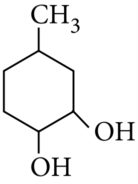
(a) $R-NO_2 \longrightarrow R-NOH$
(b) $RCOOR \longrightarrow RCH_2OH$
(c) $RCH=CHCHO \longrightarrow RCH=CH-CH_2OH$
(d) $RCH=CH-CH_2Cl \longrightarrow RCH=CHCH_3$

12. In which of the following maximum dehydration takes place?

(a)


(b)


(c)


(d)


Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. Assertion : Anisole undergoes electrophilic substitution at *o*- and *p*-positions.
Reason : Anisole is less reactive than phenol towards electrophilic substitution reactions.

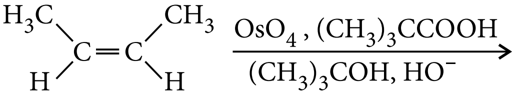
14. Assertion : Phenols and alcohols can be distinguished by NaOH.
Reason : Alcohols are very weak acids as compared to phenols.

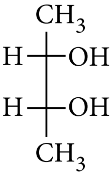
15. Assertion : Solubility of *n*-alcohols in water decreases with increase in molecular mass.
Reason : The proportion of the hydrocarbon part in alcohols increases with increase in molecular mass which permits enhanced hydrogen bonding with water.

JEE MAIN / JEE ADVANCED

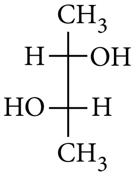
Only One Option Correct Type

16. What is/are the product(s) of the following reaction?

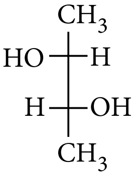




(1)



(2)

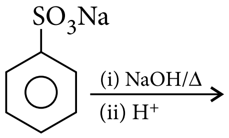


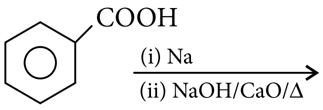
(3)

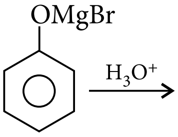
(a) Only 1
(b) 1 : 1 mixture of 2 and 3
(c) Only 2
(d) 1 : 1 : 1 mixture of 1, 2 and 3

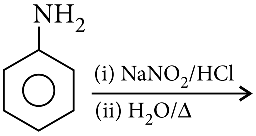
17. An organic compound *A* reacts with methyl magnesium iodide to form an addition product which on hydrolysis forms the compound *B*. Compound *B* gives blue colour salt in Victor Meyer's test. The compounds *A* and *B* are respectively
(a) acetaldehyde, tertiary butyl alcohol
(b) acetaldehyde, ethyl alcohol
(c) acetaldehyde, isopropyl alcohol
(d) acetone, isopropyl alcohol.

18. Which of the following reactions does not yield phenol?

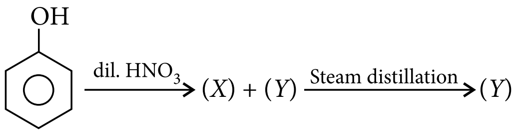
(a) 

(b) 

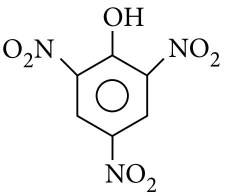
(c) 

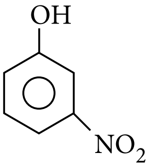
(d) 

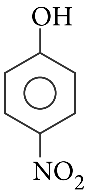
19. Consider the following reaction,

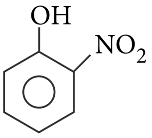


Low boiling fraction '*Y*' is

(a) 

(b) 

(c) 

(d) 

More than One Options Correct Type

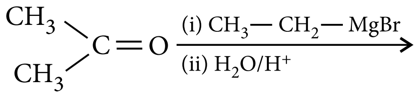
20. Which of the following statements about ethers are correct?
(a) Ethers are relatively inert compounds.
(b) Ethers are weakly acidic.
(c) Ethers form oxonium salts.
(d) Ethers form stable complexes with Lewis acids.

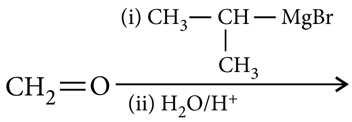
21. Propan-1-ol and propan-2-ol can be best distinguished by
(a) oxidation with alkaline $KMnO_4$ followed by reaction with H_2O
(b) oxidation with PCC followed by reaction with Tollens' reagent
(c) heating with copper followed by reaction with iodoform
(d) reaction with conc. H_2SO_4 followed by reaction with Fehling's solution.

22. Which of the following reactions give 2-butanol as a product?

(a) $CH_3-CH{=}O \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3-CH_2-MgBr}$

(b) $CH_3-CH_2-CH{=}O \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3-MgBr}$

(c) 

(d) 

$CH_2{=}O \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3-\underset{\underset{CH_3}{|}}{CH}-MgBr}$

23. Diethyl ether can be distinguished from *n*-butanol by
(a) aqueous $FeCl_3$ solution
(b) reaction with Na metal
(c) Tollens' reagent
(d) reaction with chromic anhydride (CrO_3) in dil. H_2SO_4.

Winners of September 2017 Crossword

- Devjit Acharjee, West Bengal
- Ajay Chatterji, Odisha

Solution Senders of Chemistry Musing

Set - 51

- Sukanya Sahoo, West Bengal
- Aradhana Chopra, New Delhi

Set - 50

- Anshuman Pan, West Bengal
- Kanav Kapoor, Uttar Pradesh

Integer Answer Type

24. Among the following, the number of alcohols showing iodoform test is

CH_3OH, CH_3CH_2OH, $(CH_3)_2\,CHOH$, $(CH_3)_3\,C-OH$, $CH_3CH_2CH_2CH_2OH$, $CH_3CHOHCH_2CH_3$, $CH_3CH_2CH_2OH$, $(C_2H_5)_2CHOH$, $CH_3CHOHCH(CH_3)_2$

25. How many of the following substances are less acidic than ethyl alcohol?

Water, acetylene, carbonic acid, methanol, *iso*-propyl alcohol, phenol, *tert*-butyl alcohol, *n*-propyl alcohol

26. How many ethers will be formed when a mixture of ethyl alcohol and methyl alcohol is treated with conc. H_2SO_4?

Comprehension Type

The cleavage of ethers to give the original alkyl halide and the alcohol is carried out by heating the ether with a halogen acid. Usually, HI at 373 K is used, but some ethers can be cleaved even by HBr or HCl. Depending upon the nature of the alky/aryl groups around the oxygen atom and the polarity of the solvent in which HI is dissolved, the reaction may follow either S_N2 or S_N1 mechanism.

27. Which of the following ethers is cleaved even by hydrogen chloride at room temperature?

(a) $C_6H_5-O-CH_2CH_3$

(b) $CH_3CH_2-O-CH_2CH_3$

(c) $(CH_3)_3C-O-CH_2CH_3$

(d) $(CH_3)_3C-O-C(CH_3)_3$

28. The major products formed when the following ether is heated with conc. HI

$CH_3CH_2CH_2-O-C(CH_3)_2CH_2CH_3$

are

(a) $CH_3CH_2CH_2I + HO-C(CH_3)_2CH_2CH_3$

(b) $CH_3CH_2CH_2OH + I-C(CH_3)_2CH_2CH_3$

(c) $CH_3CH_2CH_2I + I-C(CH_3)_2CH_2CH_3$

(d) $CH_3CH_2CH_2OH + (CH_3)_2C=CHCH_3$

Matrix Match Type

29. Match column I with column II and choose the correct option using the codes given below :

Column I	**Column II**
(A) Obtained by reaction between ethyl acetate and excess of CH_3MgBr followed by acidic hydrolysis	(p) CH_3CH_2OH
(B) Gets easily oxidised by $K_2Cr_2O_7/H_2SO_4$	(q) $CH_3CH_2CHOHCH_3$
(C) Produces blue colouration in Victor-Meyer's test	(r) C_6H_5OH
(D) Produces violet colouration with neutral $FeCl_3$ solution	(s) $(CH_3)_3COH$

	A	**B**	**C**	**D**
(a)	p	s	r	q
(b)	s	p	q	r
(c)	q	r	p	s
(d)	r	q	s	p

30. Match column I with column II and choose the correct option using the codes given below :

Column I	**Column II**
(A) Phenol + Neutral $FeCl_3$	(p) No reaction
(B) Phenol + $Br_{2(aq.)}$	(q) Violet colour
(C) Phenol + $NaHCO_3$	(r) White ppt.
(D) Picric acid + $NaHCO_3$	(s) CO_2 gas is evolved

	A	**B**	**C**	**D**
(a)	p	r	q	s
(b)	s	p	q	r
(c)	q	r	p	s
(d)	p	q	s	r

◆◆

Keys are published in this issue. Search now! ☺

SELF CHECK

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

Check your score! If your score is

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

CHEMISTRY MUSING

PROBLEM SET 52

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. The pyknometric density of NaCl crystal is 2.165×10^3 kg m^{-3} while its *X*-ray density is 2.178×10^3 kg m^{-3}. The fraction of unoccupied sites in NaCl crystal is

(a) 5.96 (b) 5.96×10^{-2}
(c) 5.96×10^{-1} (d) 5.96×10^{-3}

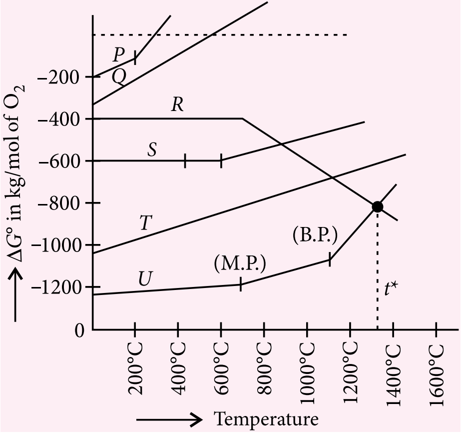
2. '*A*' on heating at higher temperature (>700 °C) in air gives a white infusible amorphous powder *B* which is decomposed when heated in the current of steam to give white powder '*C*' and a gas '*D*'. '*D*' turns red litmus blue and in aqueous solution, gives reddish brown ppt. with K_2HgI_4. Compound '*C*' on strong heating gives '*E*'. Here, *E* is

(a) B_2O_3 (b) SiO_2 (c) NH_3 (d) N_2O

3. Hexavalent uranium mineral such as carnotite is leached with soda ash, the dissolution of uranium takes place by forming uranyl tricarbonate ion. Leaching reaction of uranium is accompanied by generation of OH^-. The generation of OH^- ion makes the slurry more alkaline and uranium gets precipitated in the form of

(a) Na_2UO_4 (b) $Na_2U_3O_7$
(c) $Na_4(UO_2)(CO_3)_3$ (d) UO_2SO_4

4. Ellingham diagram for some oxides of *P*, *Q*, *R*, *S*, *T* and *U* is given.



Select the incorrect statement.

(a) Below 400 °C oxide of *P* should decompose into metal and O_2.
(b) Extraction of *A* is possible by reduction of its oxide by *T* and *U*.
(c) At 500 °C reduction of oxide of *P*, *Q* is possible by *R*.
(d) Reduction of T_2O_3 to *T* is possible by *R* below 1000 °C.

5. For the equilibrium,

$$LiCl.3NH_{3(s)} \rightleftharpoons LiCl.NH_{3(s)} + 2NH_{3(g)}$$

$K_p = 9$ atm^2, at 40 °C. A 5 litre flask contains 0.1 mole of $LiCl.NH_3$. How many moles of NH_3 should be added to the flask at this temperature to drive the backward reaction for completion?

(a) 0.58 (b) 0.2 (c) 0.78 (d) 0.4

JEE ADVANCED

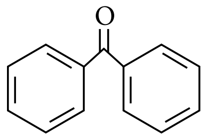
6. The number of unpaired electrons in octahedral complexes of d^9 and d^4 ions when $\Delta_o > P$ and $\Delta_o < P$.

	$d^9(\Delta_o > P)$	$d^9(\Delta_o < P)$	$d^4(\Delta_o > P)$	$d^4(\Delta_o < P)$
(a)	1	1	4	4
(b)	1	3	2	4
(c)	1	1	2	4
(d)	1	0	4	4

COMPREHENSION

The word "aromatic" though started with benzene and its derivatives only, now it signifies a large variety of organic compounds. The compound is said to be aromatic if it is cyclic planar and contain $(4n + 2)\pi$ electrons. When the closed loop contains $4n$ electrons, the system is rather less stable or anti-aromatic.

7. Which of the following has the highest value of dipole moment?

(a)


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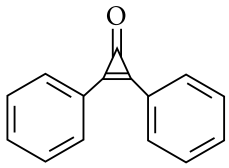
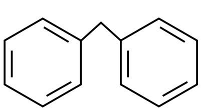
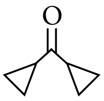
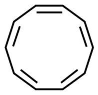
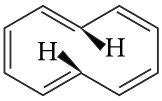
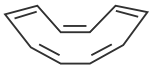


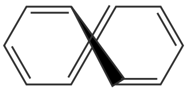
(c)  (d) 

8. Which of the following is the most stable isomer of the hydrocarbon, $C_{10}H_{10}$?

(a) 

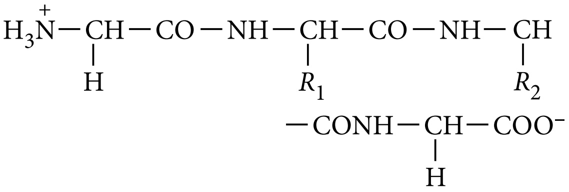
(b) 

(c) 

(d) 

INTEGER VALUE

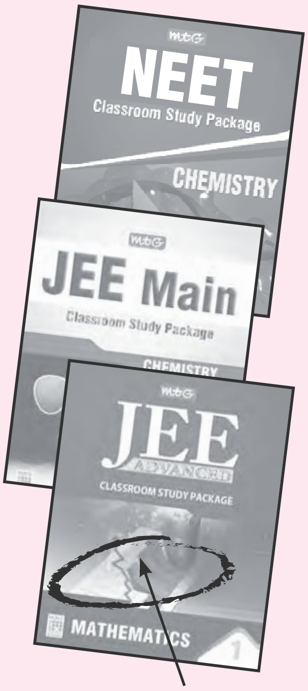
9. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH 7.0?



$$H_3\overset{+}{N}-\underset{H}{\underset{|}{CH}}-CO-NH-\underset{R_1}{\underset{|}{CH}}-CO-NH-\underset{R_2}{\underset{|}{CH}}-CONH-\underset{H}{\underset{|}{CH}}-COO^-$$

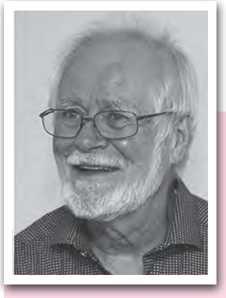
Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

10. For estimating ozone in the air, a certain volume of air is passed through an alkaline KI solution when O_2 is evolved and iodide is oxidised to iodine. When such a solution is acidified, the free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ solution. In an experiment, 9 L of air at 1 atm and 27 °C were passed through an alkaline KI solution, and at the end, the iodine was entrapped in a solution which on titration required 1.5 mL of 0.01 N $Na_2S_2O_3$ solution. If the volume percentage of ozone in the sample is $x \times 10^{-3}$ then x is



Chemistry Nobel Prize Winners 2017

The Nobel prize in Chemistry 2017 was awarded to Jacques Dubochet, Joachim Frank and Richard Henderson for the development of cryo-electron microscopy, which simplifies and improves the imaging of biomolecules. This method has moved biochemistry into a new era.



Jacques Dubochet
Born : 1942, Aigle, Switzerland
Affiliation at the time of the award : University of Lausanne, Lausanne, Switzerland

Joachim Frank
Born: 1940, Siegen, Germany
Affiliation at the time of the award : Columbia University, New York, USA

Richard Henderson
Born: 1945, Edinburgh, Scotland
Affiliation at the time of the award : MRC Laboratory of Molecular Biology, Cambridge, United Kingdom

Molecules of Life, Captured in 3D

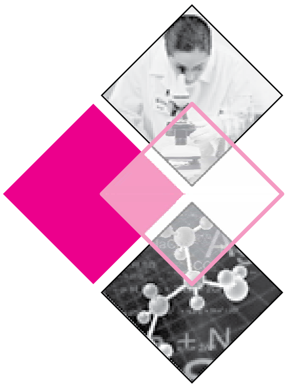
Scientific breakthroughs often build upon the successful visualisation of objects invisible to the human eye. However, biochemical maps have long been filled with blank spaces because the available technology has difficulty in generating images of life's molecular machinery. Cryo-electron microscopy changes all of this. Researchers can now freeze biomolecules mid-movement and visualise processes they have never previously seen, which is decisive for both the basic understanding of life's chemistry and for the development of pharmaceuticals.

Electron microscopes were long believed to only be suitable for imaging dead matter, because the powerful electron beam destroys biological material. But in 1990, Richard Henderson succeeded in using an electron microscope to generate a three-dimensional image of a protein at atomic resolution. This breakthrough proved the technology's potential.

Joachim Frank made the technology generally applicable. Between 1975 and 1986, he developed an image processing method in which the electron microscope's fuzzy two-dimensional images are analysed and merged to reveal a sharp three-dimensional structure.

Jacques Dubochet added water to electron microscopy. Water evaporates in the electron microscope's vacuum, which makes the biomolecules collapse. In the early 1980s, Dubochet succeeded in vitrifying water – he cooled water so rapidly that it solidified in its liquid form around a biological sample, allowing the biomolecules to retain their natural shape even in a vacuum.

Following these discoveries, the electron microscope's every nut and bolt have been optimised. The desired atomic resolution was reached in 2013, and researchers can now routinely produce three-dimensional structures of biomolecules. In the past few years, scientific literature has been filled with images of everything from proteins that cause antibiotic resistance, to the surface of the Zika virus. Biochemistry is now facing an explosive development and is all set for an exciting future.



CONCEPT BOOSTER

Hello My family!! Wish you all enjoyed a lot in the festive season and side by side definitely have studied to keep the brain engine smooth and energetic. This is the time when you need a proper planning how to proceed in the forthcoming months with your preparation. Be convinced you will get me always beside you. I will start giving study plan and sequence of study in the forthcoming issues along with some off topics which you need to study. In the beginning, in this issue I have discussed JAHN-TELLER EFFECT, a very important but less discussed topic of COORDINATION CHEMISTRY. Keep your eyes intact on CHEMISTRY TODAY CONCEPT BOOSTER always for further guidance.

*Arunava Sarkar

SPECIAL TOPIC OF COORDINATION CHEMISTRY

At the beginning, know the fact that Jahn-Teller effect or Jahn-Teller theorem give an idea about the additional stabilisation of the system.

JAHN-TELLER THEOREM

Any non-linear system in its orbitally degenerate electronic state will be unstable and therefore in order to attain stability this electronic state will undergo distortion in its geometry and thus will cause a splitting in its orbitally degenerate electronic state. This theorem was developed in the year 1937. Remember that orbitally degenerate electronic state is that state which represents more than one electronic arrangement with the same energy.

Jahn-Teller distortion is therefore that phenomena where distortion in the geometry of the non-linear system takes place in order to gain more stability.

Jahn-Teller distortion lowers the symmetry of the system in such a way that it lowers the energy of the system. It also takes place automatically.

The best example to understand Jahn-Teller distortion is Cu^{2+} :

$Cu^{2+} \rightarrow {}_{18}[Ar]3d^9$

$$\underset{3d^9}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}} \quad \underset{4s^0}{\boxed{}} \quad \underset{4p^0}{\boxed{}\boxed{}\boxed{}}$$

With a perfect octahedral geometry, this configuration can be given as :

$e_g^3 : \boxed{\uparrow\downarrow}\boxed{\uparrow}$

$t_{2g}^6 : \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

(Ground state)

Now, two options are here :

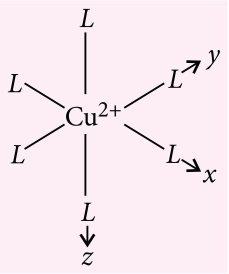
$$\left.\begin{array}{l} \text{Option-1} : t_{2g}^6\, d_{z^2}^2\, d_{x^2-y^2}^1 \\ \\ \text{Option-2} : t_{2g}^6\, d_{z^2}^1\, d_{x^2-y^2}^2 \end{array}\right\} \text{equal energy}$$

OPTION 1

The *d*-electron charge density will be higher in *z*-direction than in *x*- or *y*-direction. So, the nuclear charge of Cu^{2+} rather the positive charge of Cu^{2+} will be more in *z*-direction rather in *x*- or *y*-direction. As a result, the negative charge of the ligands along the *z*-direction will be less attractive than that of along *x*- or *y*-direction.

Now think the scenario! Due to lesser attraction, ligands along *z*-direction will move away from the metal ion whereas ligands along *x*- and *y*-directions will move nearer to the metal ion.

Obviously, now the octahedral geometry will get distorted to tetragonal geometry and it will be with the elongation along *z*-directions and compression along *x*- and *y*-directions.



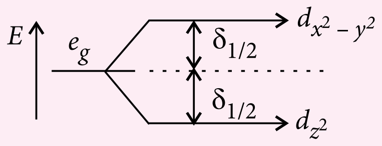
(Distortion of the octahedral geometry to tetragonal geometry due to Jahn-Teller effect)

So, what we found ultimately? There is elongation of metal-ligand bonds along *z*-direction. That is why the *d*-electrons of the metal ion experience lesser electrostatic repulsion force from the negative charge on the ligands.

---

*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

The similar repulsion force will be more felt at the x- and y-directions. So, due to all these d_{z^2} will be of lower energy and $d_{x^2-y^2}$ will be of higher energy. In this way the degeneracy gets disturbed and gets lifted.



(Lifting of degeneracy of e_g orbitals due to Jahn-Teller effect when more electrons are there in d_{z^2} than $d_{x^2-y^2}$)

Now, there is a catch here. No external energy supply is required for the splitting here. It is automatic. Hence, overall energy of the split orbitals will be equal to the energy of the unsplit orbitals. So, if we assume that before the spliting, the energy of the orbitals was E, then after the spliting total energy of d_{z^2} and $d_{x^2-y^2}$ will be E. This is commonly known as 'Centre of gravity rule' according to which the centre of gravity of the split orbitals is maintained.

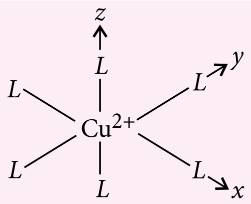
So, in a nut shell, when there are more electrons in d_{z^2} rather than in $d_{x^2-y^2}$ of an octahedral complex of any metal ion, distortion of octahedral geometry to tetragonal geometry will occur by elongation of metal-ligand bonds along z-direction.

OPTION 2

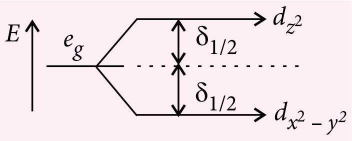
Here, $d_{x^2-y^2}$ has two electrons and d_{z^2} has one electron. This is why the negative charges on the ligands along x- and y- directions are less attracted by the nucleus or rather nuclear charge. This is of course because of the more effective screening. This screening is of course less along the z-direction as there is only one electron in d_{z^2}. As a consequence, there is elongation of metal-ligand bond along x- and y-directions whereas there is contraction of metal-ligand bond across z-direction. As a result the octahedral geometry of Cu^{2+} ion gets distorted and it takes tetragonal geometry.

MPP-7 CLASS XII ANSWER KEY

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



Also, electrostatic repulsion experienced by d-electrons of Cu^{2+} from the negative charge on ligands along x- and y-direction will be less than the similar force experienced by the d-electron(s) from the negative charge along the z-direction. This is why $d_{x^2-y^2}$ becomes of lower energy and d_{z^2} becomes of higher energy. So degeneracy of two orbitals get lifted.



Now, we will take a few aspects which must be understood properly.

First of all, remember that apart from the $t_{2g}^6\ e_g^3$ configuration (ground state) resulting into the formation of octahedral complex, other ground state configuration which show Jahn-Teller effect is $t_{2g}^6\ e_g^1$. The point to be noted here is in both of these configurations t_{2g} is uniformly filled up and the type of distortion here depends upon e_g orbital *i.e.* whether the electron occupies $d_{x^2-y^2}$ or d_{z^2} orbital

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Exam Update

JEE (Advanced) 2018

The Joint Entrance Examination (Advanced) 2018 will be conducted by the IITs . The performance of a candidate in this examination will form the basis for admission to the Bachelor's, Integrated Master's and Dual Degree programs (entry at the 10+2 level) in all the IITs. The decisions of the JAB 2018 will be final in all matters related to JEE (Advanced) 2018 and admission to IITs.

Candidates should be among the top 2,24,000 (including all categories) by scoring positive marks in Paper-1 of JEE (Main)-2018.

Examination will be held on May 20, 2018. The entire JEE (Advanced) 2018 Examination will be conducted in fully computer based test mode. The exam consists of two papers, Paper 1 and Paper 2, each of three hours' duration, and will be held in two sessions. Both the papers are compulsory.

For more information visit www.jeeadv.ac.in

ADVANCED CHEMISTRY BLOC

(RE-READING ORGANIC CHEMISTRY)

Mukul C. Ray, Odisha

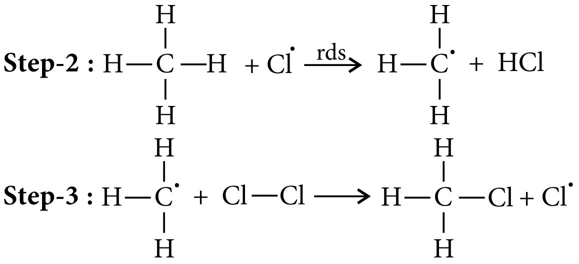
In a span of six episodes, we would be covering the indispensable points of organic chemistry, exactly what you need to understand or memorise in this column. Things are really simple in organic chemistry. You just take one step, means one concept or one reaction at a time. Rehearse and progress daily, without fail, even though for 30 minutes. Soon you will realise the things come to your mind effortlessly.

ALIPHATIC HYDROCARBONS

1. Halogenation of alkanes

Chlorination of methane

Step-1 : $Cl_2 \xrightarrow{h\nu} 2\dot{C}l$



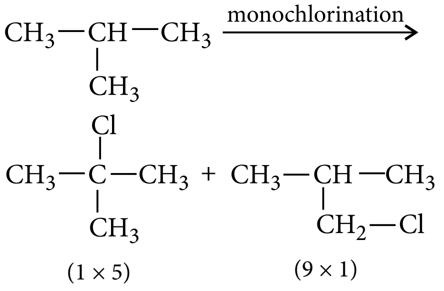
$$\textbf{Step-2 :}\ \mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H} + \mathrm{Cl}^{\bullet} \xrightarrow{\text{rds}} \mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{}^{\bullet}} + \mathrm{HCl}$$

$$\textbf{Step-3 :}\ \mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{}^{\bullet}} + \mathrm{Cl-Cl} \longrightarrow \mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-Cl} + \mathrm{Cl}^{\bullet}$$

Step-2 is endothermic but step-3 is exothermic, thus overall process is exothermic. For all other alkanes, both steps are exothermic.

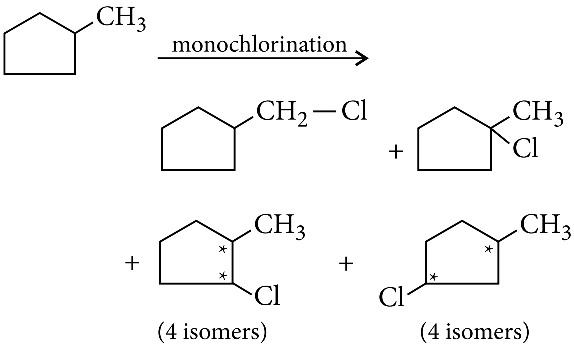
In chlorination, the selectivity of $Cl^{\bullet}$ towards primary, secondary and tertiary hydrogen is in the ratio of 1 : 3.8 : 5.

This helps us to calculate the product distribution.



$$\mathrm{CH_3-\underset{\displaystyle CH_3}{CH}-CH_3} \xrightarrow{\text{monochlorination}} \underset{(1\times 5)}{\mathrm{CH_3-\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{C}}-CH_3}} + \underset{(9\times 1)}{\mathrm{CH_3-\underset{\displaystyle CH_2-Cl}{CH}-CH_3}}$$

Relative amount of *t*-butyl chloride is 5 while for 2-methyl-1-chloropropane it is 9. No doubt, the later one is the major product.



(4 isomers) (4 isomers)

Together there will be 10 isomers of product possible from the above reaction.

For bromination of methane, step-2 is endothermic but step-3 is exothermic. The overall process is weakly exothermic.

The selectivity ratio of $Br^{\bullet}$ towards 1°, 2° and 3° is 1 : 82 : 1600. So no need to calculate, you just go for tertiary product as the major product always.

2. Nitration of alkanes

Nitration involves C—C bond cleavage along with C—H bond.

$$CH_3-CH_3 \xrightarrow[\Delta]{HNO_3} CH_3-CH_2-NO_2 + CH_3-NO_2$$

3. Physical properties of alkanes

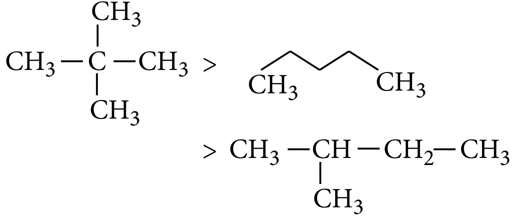
Melting point : $C_2H_6 > CH_4 > C_3H_8$

From propane onwards, melting point gradually increases though not regularly. The difference is less between odd and even as compared to that while moving from even to odd in case of *n*-alkanes. This is the "oscillation" or "alteration rule."

Check the data (No need to remember) :

Alkane	C_3H_8	$n\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$
M.P.	−189.9 °C	−135 °C	−131.5 °C	−94.3°C

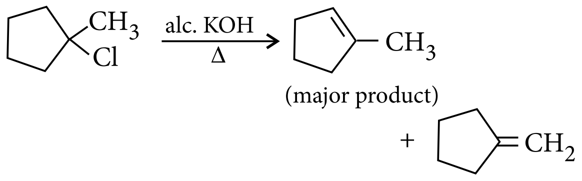
And order of melting point :

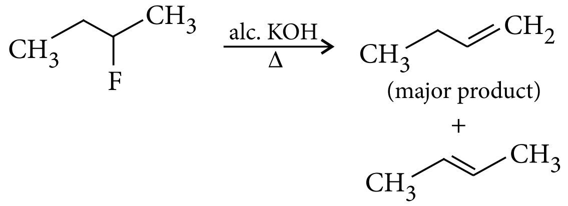


Boiling points for *n*-alkanes show a smooth increase along the series. For identical number of carbon containing compounds boiling point decreases with increase in branching.

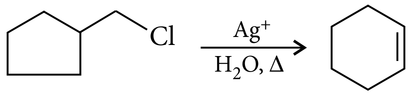
4. Preparation of alkenes

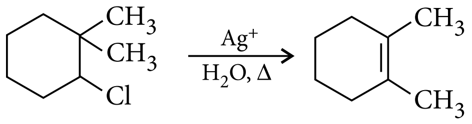
Strong base and heating condition on alkyl halides mostly certifies E_2 mechanism. Generally, it gives Saytzeff product except when –F or –$\overset{+}{N}H_3$ is the leaving group or bulky base is present where Hofmann elimination gives dominating product.





Branched alkyl halides, Ag^+ catalyst, weaker base like H_2O or CH_3OH and heating condition confirms E_1 mechanism. Saytzeff product is always the major product.

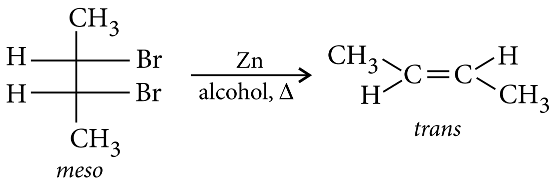


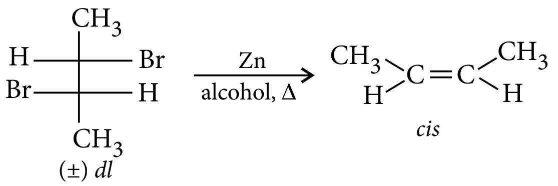


Zn is a dehalogenating agent that causes anti-elimination.

Remember the following table. Carefully check there is a symmetry.

Alkene	**Addition**	**Product**
cis	*Syn*	*Meso*
cis	*Anti*	*dl* (±)
trans	*Anti*	*Meso*
trans	*Syn*	*dl* (±)

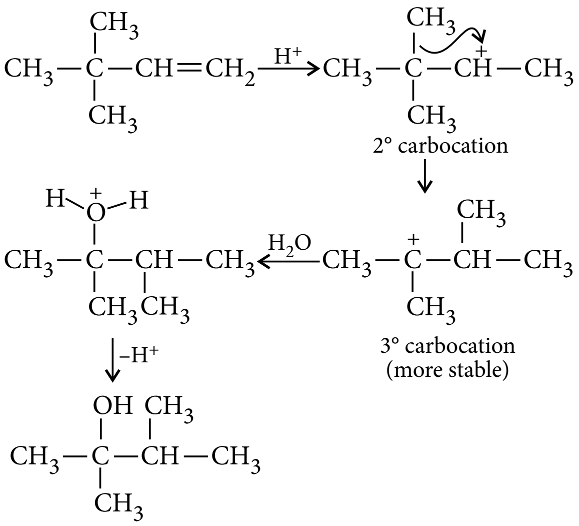




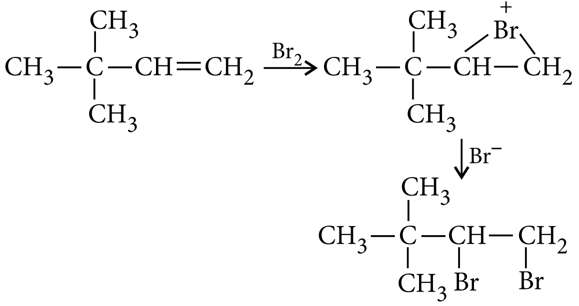
5. Addition reactions on alkenes

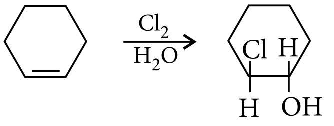
Alkenes generally follow addition electrophilic (AdE) mechanism.

Addition of HX and H_3O^+ : Alkene adds H^+ ion across double bond to give a carbocation, which rearranges and then pick the nucleophile.



But addition of Br_2, Cl_2/H_2O involve a cyclic halonium ion. Hence, no rearrangement takes place. The net result is anti-addition.





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CHEMISTRY MUSING

SOLUTION SET 51

1. (d): $$M_{\text{solute}} = \frac{K_f \times w_{\text{solute}} \times 1000}{W_{\text{solvent}} \times \Delta T_f}$$

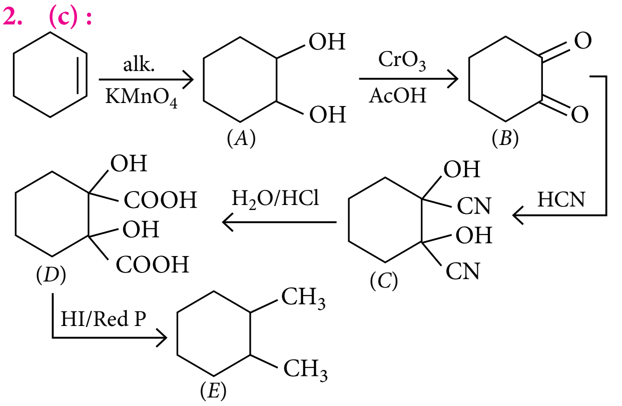
$$= \frac{4.90 \times 3.26 \times 1000}{226 \times 0.112} = 631 \text{ g mol}^{-1}$$

Now, molecular mass of $\text{Se}_x = x \times 79$

$631 = x \times 79 \Rightarrow x = 8$

$\therefore$ Molecular formula of selenium = Se_8

2. (c) :



3. (c) : Given : $T_i = 17\ °\text{C} = 290$ K ; $T_f = 57\ °\text{C} = 330$ K

$$\pi_i = 580 \text{ torr} = \frac{580}{760} \text{ atm} ; \pi_f = 165 \text{ torr} = \frac{165}{760} \text{ atm}$$

Using equation, $\pi = CRT$

$$\frac{580}{760} = C_i \times R \times 290 \qquad \text{...(i)}$$

$$\frac{165}{760} = C_f \times R \times 330 \qquad \text{...(ii)}$$

Dividing eqn (i) by (ii), we get

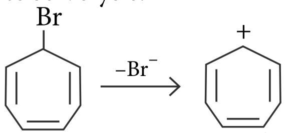
$$\frac{C_i}{C_f} = \frac{2}{1/2} = 4 \Rightarrow \text{Dilution} = 4 \text{ times}$$

4. (d): The compound combines with one mole of hydrogen to form normal hexane, hence the hydrocarbon is *n*-hexene.

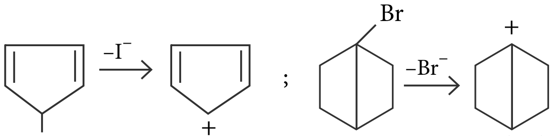
$$\underset{n\text{-Hexene}}{C_6H_{12}} + H_2 \xrightarrow{\text{Pt}} \underset{n\text{-Hexane}}{C_6H_{14}}$$

$$\underset{\text{Hex-3-ene}}{CH_3CH_2CH{=}CHCH_2CH_3} \xrightarrow[\text{KMnO}_4]{[\text{O}]} \underset{\text{Propanoic acid}}{2CH_3CH_2COOH}$$

5. (d): A compound which forms stable carbocation undergoes solvolysis.



Aromatic carbocation (stable)



Anti-aromatic carbocation (unstable)

Bridged carbocation (unstable)

Hence, compounds given in options (b) and (c) do not undergo solvolysis.

6. (c) : (a) $$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + \underset{(X)}{C_3H_{4(g)}}$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + \underset{(Y)}{CH_{4(g)}}$$

(b) $$NH_4NO_3 \xrightarrow{\Delta} \underset{(X)}{N_2O_{(g)}} + 2H_2O$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} \underset{(Y)}{N_{2(g)}} + 4H_2O + Cr_2O_3$$

(c) $$NH_4Cl + NaOH_{(aq)} \longrightarrow \underset{(X)}{NH_{3(g)}} + NaCl + H_2O$$

$$NaNO_3 + 4Al + 7NaOH \longrightarrow 4Na_2AlO_2 + \underset{(Y)}{NH_{3(g)}} + 2H_2O$$

(d) $$4Zn + 10HNO_{3(\text{dil.})} \xrightarrow{\text{Cold}} 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$3Ag + 4HNO_{3(\text{dil.})} \xrightarrow{\text{Cold}} 3AgNO_3 + \underset{(Y)}{NO_{(g)}} + 2H_2O$$

7. (c) : On increasing concentration of NH_3, the concentration of H^+ ion decreases.

$$E_{\text{red}} = E°_{\text{red}} - \frac{0.0591}{n}\log[H^+]$$

$$E_{\text{red}} = 0 - \frac{0.0591}{1}\log 10^{-11} = -0.0591 \times (-11) = 0.65$$

8. (c) : NH_3 has no effect on the standard reduction potential.

9. (3) : $$\underset{\substack{\text{Chromite ore}\\(X)}}{4FeO\cdot Cr_2O_3} + 8Na_2CO_3 + 7O_2 \longrightarrow 8CO_2 + \underset{\text{Ferric oxide}}{2Fe_2O_3} + \underset{\text{Sodium chromate}}{8Na_2CrO_4}$$

Conversion of sodium chromate into sodium dichromate.

$$\underset{\substack{\text{Sodium}\\\text{chromate }(Y)}}{2Na_2CrO_4} + \underset{(\text{Conc.})}{H_2SO_4} \longrightarrow \underset{\substack{\text{Sodium}\\\text{dichromate }(Z)}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

In $FeO\cdot Cr_2O_3(X)$; oxidation number of Cr = +3

In $Na_2Cr_2O_7(Z)$; oxidation number of Cr = +6

10. (1) : $\pi = i\text{CRT}$

For 1 M Na_2SO_4 ; $i = 3, \pi = 3RT$

For 1 M KCl ; $i = 2, \pi = 2RT$

For 1.5 M K_2SO_4 ; $i = 3, \pi = 4.5RT$

For 1.5 M NaCl ; $i = 2, \pi = 3RT$

For 2 M $Al_2(SO_4)_3$; $i = 5, \pi = 10RT$

For 0.5 M $BaSO_4$; $i = 2, \pi = 1RT$

Hence, only one compound, *i.e.*, 1.5 M NaCl has same osmotic pressure as that of 1 M Na_2SO_4 solution.

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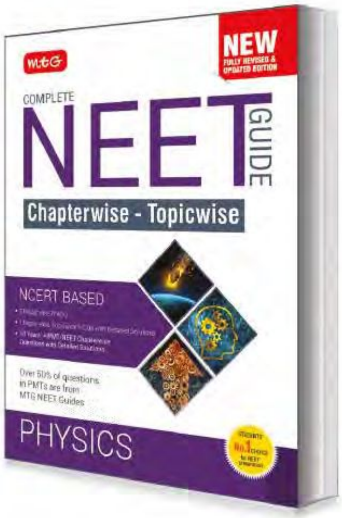
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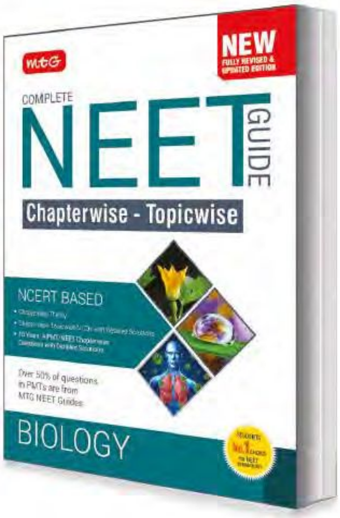
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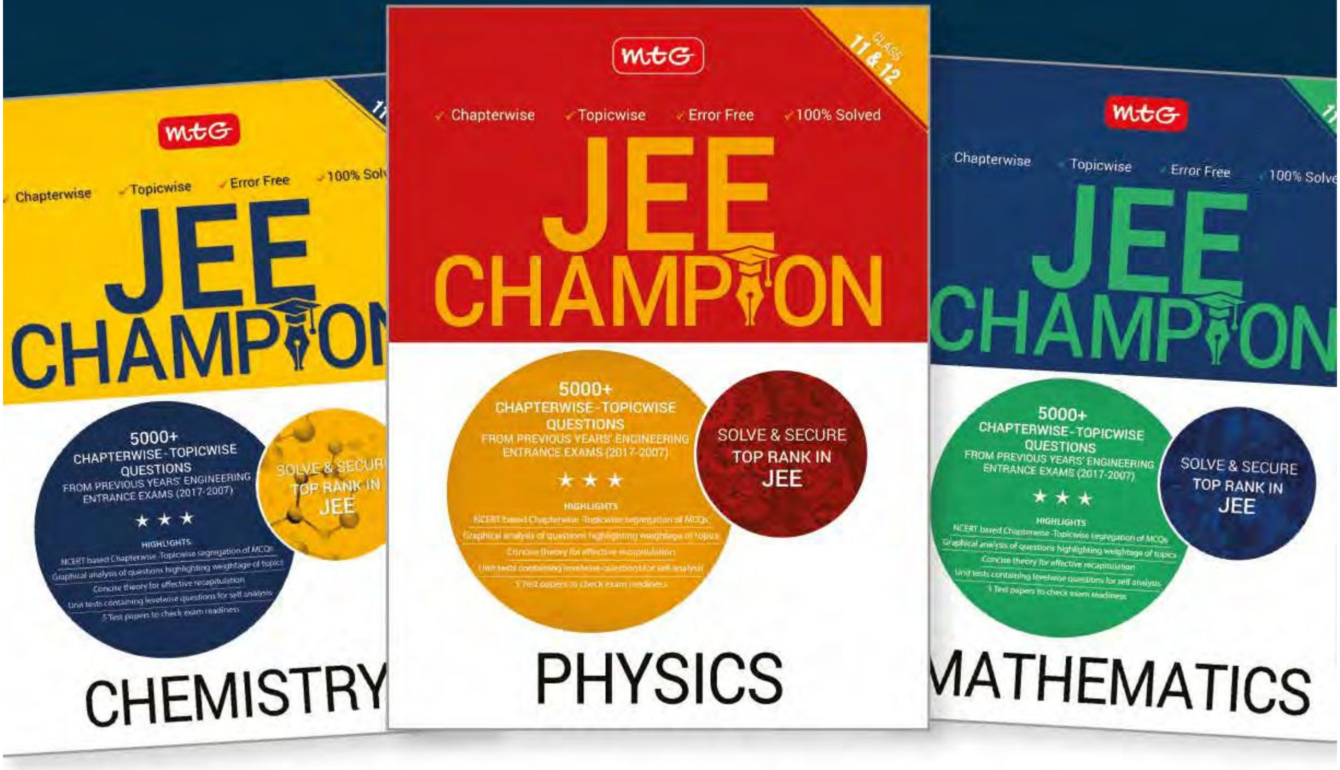
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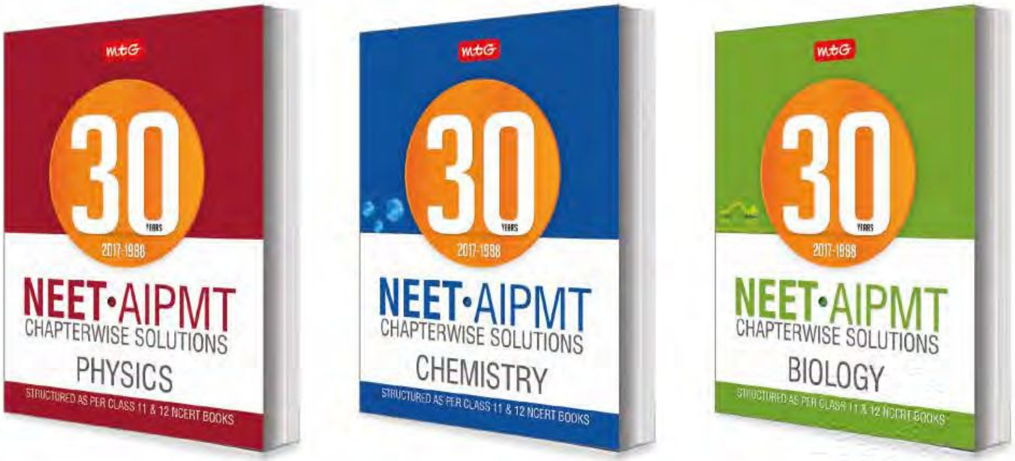
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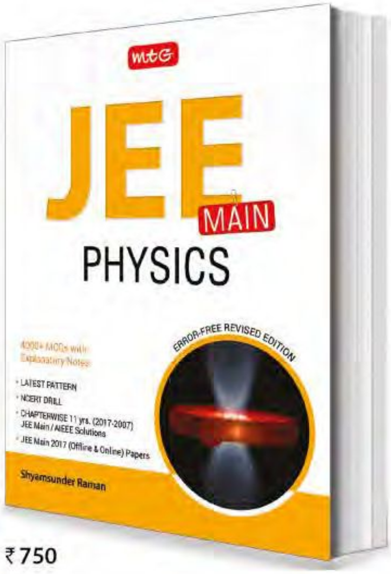

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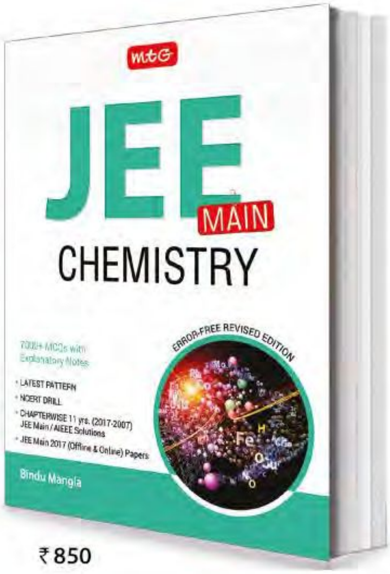

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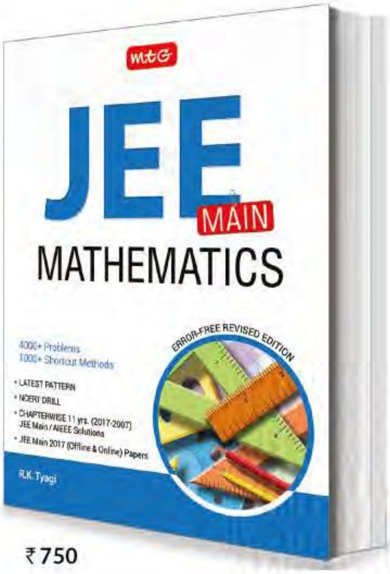

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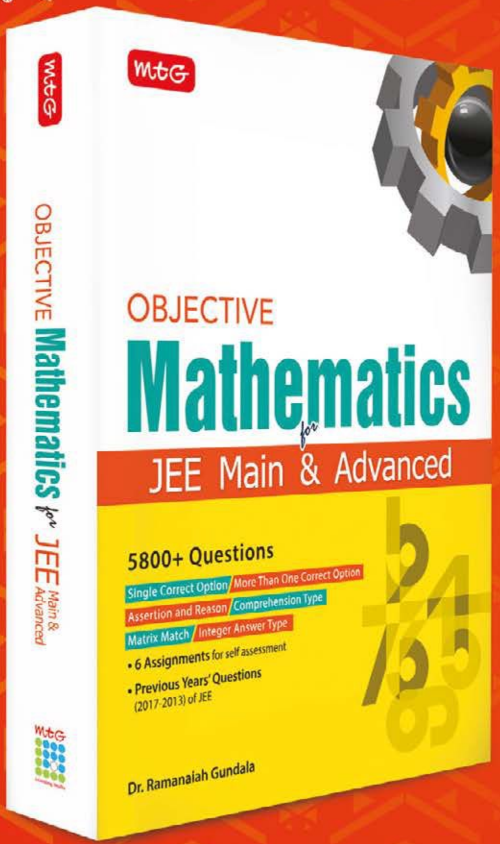


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