12th Std.

MARCH - 2017

[Time : 3 hours] **Chemistry** (With Answers) [Maximum Marks : 150]

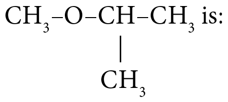
Part - I

Note : (i) Answer **all** the questions. **[30×1=30]**

(ii) Choose the most suitable answer from the given **four** alternatives and write the option code and the corresponding answer.

1. The half life period of a first order reaction is 10 minutes. Then its rate constant is :
   - (*a*) 6.93×10^{2} min^{-1}
   - (*b*) 0.693×10^{-2} min^{-1}
   - (*c*) 6.93×10^{-2} min^{-1}
   - (*d*) 69.3×10^{-1} min^{-1}
2. The Tyndall's effect associated with colloidal particles is due to :
   - (*a*) absorption of light
   - (*b*) reflection of light
   - (*c*) scattering of light
   - (*d*) presence of charge
3. The intramolecular hydrogen bonding is present in:
   - (*a*) o-nitrophenol
   - (*b*) m-nitrophenol
   - (*c*) p-nitrophenol
   - (*d*) phenol
4. Name the compound employed to arrest bleeding.
   - (*a*) $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$
   - (*b*) $K_2SO_4.Al_2(SO_4)_3.24Al(OH)_3$
   - (*c*) $K_2SO_4.Al_2(SO_4)_3.4H_2O$
   - (*d*) $K_2SO_4.Al_2(SO_4)_3.24H_2O$
5. In the equilibrium $N_2+3H_2 \rightleftharpoons 2NH_3$, the maximum yield of NH_3 will be obtained with the process having:
   - (*a*) low pressure and high temperature
   - (*b*) low pressure and low temperature
   - (*c*) high pressure and low temperature
   - (*d*) high pressure and high temperature
6. The IUPAC name of dimethyl sec. butylamine is:
   - (*a*) 2-amino-3-methyl butane
   - (*b*) 2-(N-methyl amino) butane
   - (*c*) 2-(N, N-demethyl amino) butane
   - (*d*) 2-(N, N-dimethyl amino) propane
7. The transition element used for making calorimeters is :
   - (*a*) Cr
   - (*b*) Ni
   - (*c*) Zn
   - (*d*) Cu
8. $2H_2O_{(g)} + 2Cl_{2(g)} \rightleftharpoons 4HCl_{(g)} + O_{2(g)}$ for this equilibrium :
   - (*a*) $K_p = K_c$
   - (*b*) $K_p > K_c$
   - (*c*) $K_p < K_c$
   - (*d*) $K_p = \frac{1}{K_c}$
9. An example for lyophilic colloid is:
   - (*a*) colloidal solutions of metal
   - (*b*) sulphur in water
   - (*c*) gelatin
   - (*d*) $Fe(OH)_3$ colloid
10. Which of the following compound is optically active ?
    - (*a*) CH_3CH_2COOH
    - (*b*) $HOOC–CH_2–COOH$
    - (*c*) $CH_3CH(OH)COOH$
    - (*d*) $Cl_2CHCOOH$
11. With a mixture of Conc. HNO_3 and Conc. H_2SO_4 Anisole gives:
    - (*a*) ortho nitro anisole
    - (*b*) para nitro anisole
    - (*c*) ortho and para nitro anisole
    - (*d*) meta nitro anisole
12. The number of chloride ions that surrounds the central NA^+ ion in NaCl crystal is :
    - (*a*) 6
    - (*b*) 8
    - (*c*) 4
    - (*d*) 12
13. Which compound is formed when excess of KCN is added to an aqueous solution of copper sulphate ?
    - (*a*) $Cu_2(CN)_2$
    - (*b*) $K_2[Cu(CN)_6]$
    - (*c*) $K[Cu(CN)_2]$
    - (*d*) $Cu_2(CN)_2 + (CN)_2$
14. The building block of proteins are :
    - (*a*) α - hydroxy acid
    - (*b*) α - amino acid
    - (*c*) β- hydroxy acid
    - (*d*) β - amino acid

15. The isomerism exhibited by $C_2H_5OC_2H_5$ and



$CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ is:

(*a*) functional (*b*) metamerism
(*c*) position (*d*) chain

16. Formaldehyde polymerises to give :
(*a*) paraformaldehyde (*b*) paraldehyde
(*c*) formalin (*d*) formic acid

17. The basic character of amines is due to :
(*a*) tetrahedral structure
(*b*) presence of nitrogen atom
(*c*) lone pair of electrons on nitrogen atom
(*d*) high electronegativity of nitrogen

18. Effective nuclear charge can be calculated by using the formula :
(*a*) $Z^* = S - Z$ (*b*) $Z^* = Z + S$
(*c*) $Z = Z^* - S$ (*d*) $Z^* = Z - S$

19. Which one of the following processes does not involve coagulation ?
(*a*) Peptisation
(*b*) Formation of delta
(*c*) Purification of drinking water using alum
(*d*) Tanning of leather using tannin

20. $_{92}U^{235}$ nucleus absorbs a neutron and disintegrates into $_{54}Xe^{139}$, $_{38}Sr^{94}$ and x. What will be the product x ?
(*a*) 2 neutrons (*b*) 3 neutrons
(*c*) α - particle (*d*) β - particle

21. When nitromethane is reduced with Zn/NH_4Cl, we get :
(*a*) CH_3NH_2 (*b*) $C_2H_5NH_2$
(*c*) CH_3NHOH (*d*) C_2H_5COOH

22. Raffinose on hydrolysis gives :
(*a*) two monosaccharides
(*b*) three monosaccharides
(*c*) one disaccharide and one monosaccharide
(*d*) two monosaccharides and one disaccharide

23. An example of a complex compound having coordination number 4 :
(*a*) $K_4[Fe(CN)_6]$ (*b*) $[Co(en)_3]Cl_3$
(*c*) $[Fe(H_2O)_6]Cl_3$ (*d*) $[Cu(NH_3)_4]Cl_2$

24. The liquid that deviates from Trouton's rule is :
(*a*) Hydrochloric acid (*b*) Sulphuric acid
(*c*) Phosphoric acid (*d*) Acetic acid

25. sp^2 hybridisation is not present in _________ ion.
(*a*) CO_3^{2-} (*b*) SO_4^{2-}
(*c*) NO_3^- (*d*) NO_2^-

26. Which of the following does not result in an increase in entropy?
(*a*) crystallisation of sucrose from solution
(*b*) rusting of iron
(*c*) conversion of ice to water
(*d*) vapourisation of camphor

27. Which Mg alloy is used in making parts of jet engines ?
(*a*) 3 % Mish metal and 0.1 % Zr.
(*b*) 30% Mish metal and 1% Zr.
(*c*) 30% Mish metal and 0.1 % Zr.
(*d*) 3% Mish metal and 1% Zr.

28. Oxocations are formed by:
(*a*) Lanthanides (*b*) Actinides
(*c*) Noble gases (*d*) Alkali metals

29. For the titration between hydrochloric acid and sodium carbonate, the indicator used is :
(*a*) potassium permanganate
(*b*) phenolphthalein
(*c*) phenol red
(*d*) methyl orange

30. The reaction of ethylene glycol with PI_3 gives:
(*a*) ICH_2-CH_2I (*b*) $CH_2=CH_2$
(*c*) $CH_2=CHI$ (*d*) $ICH=CHI$

PART - II

[15 × 3 = 45]

Note : (i) Answer **any fifteen** questions.
(ii) Each answer should be in **one** or **two** sentences.

31. State Heisenberg's uncertainty principle.

32. Ionisation energy of Carbon is more than that of Boron. Why?

33. Write a note on plumbo solvency.

34. Draw the electron dot formula of $H_4P_2O_7$.

35. Why do transition elements form alloys?
36. Write short note on chrome plating.
37. Calculate Q value of the following nuclear reaction

$$_{13}Al^{27} + {}_{2}He^{4} \rightarrow {}_{14}Si^{30} + {}_{1}H^{1} + Q$$

The exact mass of $_{13}Al^{27}$ is 26.9815 amu, $_{14}Si^{30}$ is 29.9738 amu, $_{2}He^{4}$ is 4.0026 amu and $_{1}H^{1}$ is 1.0078 amu.

38. Write any three applications of superconductors.
39. What is entropy ? What are its units .
40. State Le Chatelier's principle.
41. What is a pseudo first order reaction ? Give an example.
42. Write the Arrhenius equation and explain the terms.
43. What is peptisation ? Give an example.
44. Write three significances of Henderson equation.
45. Write any three differences between enantiomers and diastereomers.
46. Alcohols cannot be used as a solvent for Grignard reagent. Give reason.
47. How will you prepare benzyl alcohol from toluene?
48. What is Rosenmund's reduction ? What is the purpose of adding $BaSO_4$ in this reaction?
49. How is methyl cyanide obtained from acetamide?
50. Write about Gabriel phthalimide synthesis.
51. Give any three characteristics of dyes.

PART - III

Note : Answer **any seven** questions choosing at least **two** questions from each section.

[7 × 5 = 35]

SECTION - A

52. Describe the Davisson and Germer experiment.
53. How is silver extracted from Argentite ore ?
54. Write the consequences of lanthanide contraction.
55. Explain coordination and ionisation isomerism with suitable examples.

SECTION - B

56. What are the characteristics of free energy, G ?
57. Derive the expressions for K_p and K_c for decomposition of PCl_5.
58. What are the characteristics of order of a reaction?
59. The e.m.f of the half cell $Cu^{2+}_{(aq)}/Cu_{(s)}$ containing 0.01 M Cu^{2+} solution is +0.301 V. Calculate the standard e.m.f. of the half cell.

SECTION - C

60. Give any five differences between aromatic and aliphatic ethers.
61. Write the following reactions:
    (i) Clemmensen reduction
    (ii) Perkins reaction
62. Write the mechanism involved in the esterification of a carboxylic acid with alcohol.
63. Write short notes on anaesthetics.

PART - IV **[4 × 10 = 40]**

Note : (i) Answer **four** questions in **all**.
(ii) Questions number **70** is **compulsory** and answer **any three** from the remaining questions.

64. a) Explain Pauling method to determine ionic radii.
    b) Describe how noble gases are isolated from air by Ramsey-Raleigh method.
65. a) Using Valence Bond theory prove that $[Ni(CN)_4]^{2-}$ is diamagnetic, whereas $[Ni(NH_3)_4]^{2+}$ is paramagnetic.
    b) Explain Radiocarbon dating.
66. a) Describe the nature of glass.
    b) What are the differences between physical adsorption and chemical adsorption.
67. a) Explain Oatwald's dilution law.
    b) Mention the IUPAC conventions for writing cell diagram.
68. a) Describe the conformations of cyclohexanol. Comment on their stability.
    b) How are the following conversions carried out?
       i) Salicylic acid → aspirin
       ii) Salicyclic acid → methyl salicylate
       iii) Formic acid → formamide
69. a) How do primary, secondary and tertiary amines react with nitrous acid?
    b) Elucidate the structure of glucose.
70. a) An organic compound (A) of molecular formula C_6H_6O, gives violet colour with neutral ferric chloride. Compound (A) when refluxed with $CHCl_3$ and NaOH gives two isomers (B) and (C). Compound (A) when added to diazomethane in alkaline medium gives an ether (D). Identify (A), (B), (C) and (D). Explain the reactions.
    b) Compound (A) is an orange red crystal and also a powerful oxidising agent. Compound

(A) when treated with potassium chloride and concentrated sulphuric acid evolves coloured gas (B). When KOH reacts with (A) an yellow solution of (C) is obtained. Identify (A), (B) and (C). Explain the reactions.

(OR)

c) An organic compound (A) of molecular formula C_2H_4O is prepared by the reduction of compound (B) of molecular formula C_2H_3N dissolved in ether, with $SnCl_2$ and HCl. Compound (A) reduces Tollen's reagent. When a drop of conc. H_2SO_4 is added to compound (A), it polymerises to give a cyclic compound (C). Identify (A), (B) and (C). Explain the reactions.

d) Ionic conductance at infinite dilution of Al^{3+} and SO_4^{2-} are 189 ohm^{-1} cm^2 $gm.equiv.^{-1}$ and 160 ohm^{-1} cm^2 $gm.equiv.^{-1}$. Calculate equivalent and molar conductance of the electrolytes at infinite dilution.

❖❖❖❖❖

ANSWERS

PART - I

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

PART - II

31. Heisenberg's uncertainity principle: It is impossible to measure simultaneously both the position and velocity of a microscopic particle with absolute accuracy or certainty mathematically.

$$\Delta x.\Delta p \geq \frac{h}{4\pi}$$

Δx = Uncertainty in the position of the particle

Δp = Uncertainty in the momentum of the particle.

32. Carbon (Z = 6) and Boron (Z = 5)

The I.E. of carbon (At. No.6) is more than that ofboron (At. No.5)

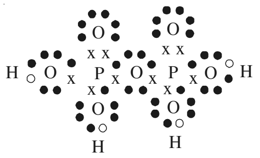
Reason: Carbon (Z = 6; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1 2p_z^0$) is having more nuclear charge than boron (Z = 5; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^0\ 2p_z^0$). In both the cases, one has to remove electron from same 2p-subshell. Carbon is having more nuclear charge than boron. Therefore the nucleus of carbon, attracts the outer 2p-electron more firmly than does boron. Thus, first I.E. of carbon would be more than that of boron.

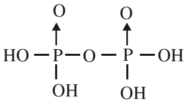
33. Lead is not attacked by pure water in the absence of air, but water containing dissolved air has a solvent action on lead due to the formation of lead hydroxide, a poisonous compound. This phenomenon is called **Plumbo solvency.**

$$2Pb + O_2 + 2H_2O \longrightarrow 2Pb(OH)_2$$

Lead hydroxide

34. The Structure of pyrophosphoric acid is represented as :





$$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH$$

35. Transition metals form alloys with each other. This is because they have almost similar size and the atoms of one metal can easily take up positions in the crystal lattice of the other.

(e.g) Alloys of Cr-Ni, Cr-Ni-Fe, Cr-V-Fe, Mn-Fe......etc.

36. The articles to be plated with chromium are made the cathode in an electrolytic bath consisting of chromic acid and sulphuric acid while the anode is made of a plate of lead.

During electrolysis chromium deposits on the article (cathode). Generally the articles are first plated with nickel and then subjected to chromium plating.

37. $\Delta m = (29.9738 + 1.0078) - (26.9815 + 4.0026)$

$= -0.0025$ amu

$Q = 0.0025 \times 931$ MeV

$= 2.328$ MeV

38. (i) Super conductivity is the basis of new generation of energy saving power systems. Super conducting generators are smaller in size and weight when we compare with conventional generators. These generators consume very low energy and so we can save more energy.

(ii) High efficiency ore separating machines are built by using super conducting magnets.

(iii) Super conducting solenoids are used in Nuclear Magnetic Resonanance Imaging equipment which is a whole body scan equipment.

39. **Entropy** is a measure of randomness or disorder of the molecules of a system and it is a thermodynamics state function. The entropy function 'S' represents the ratio of heat involved (q) to the temperature (T) of the process.

$$S = \frac{q}{T}$$

Units of entropy :

i.e., (i) calories per degree per mole.

(ii) eu per mole.

(iii) cgs unit of entropy = cal K^{-1} (or) eu.

(iv) SI unit is JK^{-1} (or) Eu.

40. According to **Le Chatelier's principle**, "if a system at equilibrium is subjected to a disturbance or stress, then the equilibrium shifts in the direction that tends to nullify the effect of the disturbance or stress".

41. In a second order reaction, when one of the reactant's concentration is in excess (10 to 100 times) of the other reactant then the reaction follows a first order kinetics and such a reaction is called **pseudo first order reaction**.

E.g. Hydrolysis of ester in the presence of acid.

E.g. Acid catalysed hydrolysis of ester

$$\underset{\text{methyl acetate}}{CH_3COOCH_3} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{methyl alcohol}}{CH_3OH}$$

42. Arrhenius equation,

$k = Ae^{-Ea/RT}$

k = Rate constant; A = Frequency factor;

Ea = Activation energy; R = Gas constant;

T = Temperature in Kelvin

43. **Peptisation :**

The dispersion of a precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptisation. The electrolyte used is called a peptizing agent.

Example :

Silver chloride can be converted into a sol by adding hydrochloric acid

44. 1. The pH of a buffer solution can be calculated from the initial concentrations of the weak acid and the salt provided K_a is given.

2. The dissociation constant of a weak acid (or weak base) can be determined by measuring the pH of a buffer solution containing equimolar concentrations of the acid (or base) and the salt.

3. A buffer solution of desired pH can be prepared by adjusting the concentrations of the salt and the acid added for the buffer.

45.

Enantiomer	Diastereomer
1. Optical isomers having the same magnitude but different sign of optical rotation.	Differ in the magnitude of optical rotation.
2. They have configuration with non-super impossible object mirror image relationship.	They are never mirror images
3. Enantiomers are identical in all properties except the sign of optical rotation.	Diastereomers differ in all physical propeties.
4. Separation of enantiomers is a tedious process.	Separation from the other pairs of enantiomers is easy.

46. Strongly basic substances like organo metallic compounds (RMgX-Grignard reagent) are decomposed by alcohol.

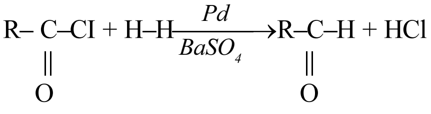
$R{-}OH + CH_3MgBr \longrightarrow R{-}O{-}Mg{-}Br + CH_4$

Hence, alcohols cannot be used as a solvent for Grignard reagent.

47. Benzyl alcohol is obtainted by the chlorination of toulene followed by hydrolysis with aqueous NaOH.

$$\underset{\text{Tolune}}{C_6H_5CH_3} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + NaCl$$

48. **Rosenmund's reduction:** Acid chlorides are reducted to aldehydes by hydrogen in the presence of palladium suspended in barium sulphate ($BaSO_4$) as catalyst.



$$R{-}\underset{\underset{O}{\|}}{C}{-}Cl + H{-}H \xrightarrow[BaSO_4]{Pd} R{-}\underset{\underset{O}{\|}}{C}{-}H + HCl$$

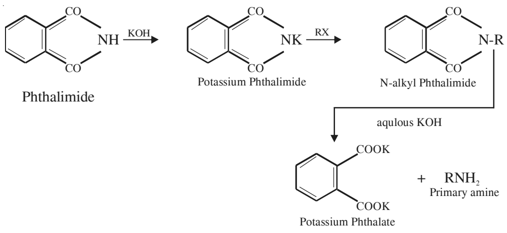
Acid chloride Aldehyde

$BaSO_4$ is used as a catalytic poison to stop the reduction at the stage of aldehyde. Otherwise, the aldehyde formed willbe further reduced to primary alcohol.

49. By heating with P_2O_5 it forms methylcyaniole

$$CH_3CONH_2 \xrightarrow[-H_2O]{P_2O_5} CH_3C \equiv N$$

50. Gabriel phthalimide synthesis. This involves the treatment of phthalimide with potassium hydroxide to form potassium salt. The salt is then heated with an alkyl halide to give N-alkyl phtalimide which in turn reacts with potassium hydroxide to form patassium phthalate salt and a pure primary amine.



51. Characteristics of dye.

(i) A dye should have a suitable colour

(ii) It should be able to fix itself or be capable of being fixed to the fabric.

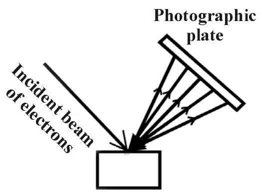
(iii) It should be fast to light.

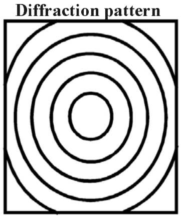
(iv) It should be resistant to the action of water, dilute acids and alkalies.

52. Davisson and Germer observed that, a beam of electrons obtained from a heated tungsten filament is accelerated by using a high positive potential. When this fine beam of accelerated electrons is allowed to fall on a large single crstal of Nickel, the electrons are scattered in different directions. The diffraction pattern so obtained is similar to the diffraction pattern obtained by

Bragg's experiment on diffraction of X-rays from a target in the same way. Since X-rays have wave character, the electrons must also have wave character associated with them. Moreover, the wavelength of the electrons as determined by the diffraction experiments were found to be in agreement with the values calculated from de Broglie equation.

So, it is clear that an electron behaves as a wave





53. The important ores of silver are :

(a) Argentite Ag_2S
(b) Horn silver AgCl
(c) Ruby silver $Ag_2 S.Sb_2S_3$

Extraction of silver from argentite (Ag_2S)

Mac Arthur Forrest cyanide process

(i) **Concentration :** The crushed ore is concentrated by froth floatation process.

(ii) **Treatment with NaCN:** The concentrated ore is treated with a solution of 0.4–0.6% sodium cyanide for several hours. The mixture is continuously agitated by a cur\rent of air so that Ag present in the ore is converted into soluble sodium argento cyanide complex.

$$Ag_2S + 4NaCN \rightleftharpoons \underset{\text{Sod.argentocyanide}}{2Na[Ag(CN)_2]} + Na_2S$$

(iii) **Precipitation of silver :** The solution containing sodium argento cyanide is filtered to remove insoluble impurities and the filtrate is treated with zinc dust, so that silver gets precipitated.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2 [Zn(CN)_4] + 2Ag\downarrow$$

(iv) **Electrolytic refining :** The impure silver is further purified by electrolytic refining. In electrolytic refining.
Anode is impure silver
Cathode is a thin sheet of pure silver
Electrolyte is Silver nitrate solution + 1% nitric acid.
On passing electric current, pure silver gets deposited at the cathode.

54. Consequences of lanthanide contraction :

(i) **Basicity of ions :** Due to lanthanide contraction, the size of Ln^{3+} ions decrease regularly with decrease in atomic number. According to Fajan's rule, decrease in size of Ln^{3+} ions increase the covalent character and decreases the basic character between Ln^{3+} and OH – ion in $Ln(OH)_3$. Since the order of size of Ln^{3+} ion are
$La^{3+} > Ce^{3+} ... > Lu^{3+}$

(ii) There is regular decrease in their ionic radii.

(iii) Regular decrease in their tendency to act as reducing agent, with increase in atomic number.

(iv) Due to lanthanide contraction, second and third rows of *d*-block elements (transition elements) are quite close in their properties.

(v) Due to lanthanide contraction, these elements occur together in natural minerals and are difficult to separate.

55. ***(i) Coordination isomerism.*** In a bimetallic complex, the distribution of ligands between the two coordination spheres can vary, giveing rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism.

This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centres :

1. $[Co^{III}(NH_3)_6]\,[Cr^{III}(CN)_6]$ and $[Cr^{III}(NH_3)_6]\,[Co^{III}(CN)_6]$
Hexammine Hexacyano Hexammine Hexaacyano
Cobalt (III) Chromate (III) Chromium (III) Cobaltate(III)

2. $[Pt^{II}(NH_3)_4]\,[Cu^{II}Cl_4]$ and $[Cu^{II}(NH_3)_4]\,[Pt^{II}Cl_4]$
Tetraammine Tetrachloro Tetraammine Tetrachloro
Platinum (II) Cuprate (II) Copper (II) Platinate (II)

In the above isomers, the intercharge of ligands in the coordination sphere of cationic and anionic part take place and leads to coordination isomerism.

(ii) Ionisation isomerism. Coordination compounds having the same molecular formula but forming different ions in solution are called ionisation isomers. This property is known as ionisation isomerism.

In this thype of isomerism is furnished by the red-violet.

$[Co(NH_3)_5Br]SO_4$	$[Co(NH_3)_5SO_4]Br$
Penta ammine bromo	Penta ammine sulphato
cobalt (III) sulphate	cobalt (III) bromide
Red violet isomer	Red isomer

Red violet isomer yields sulphate ion and red isomer furnishes bromide ion in solution.

SECTION - B

56. Characteristics of Free energy 'G' :

i) G is defined as (H-TS) where H and S are the enthalpy and entropy of the system respectively. T = temperature. Since H and S are state functions, G is the state function.

ii) G is an extensive property while $\Delta G = (G_2 - G_1)$ which is the free energy change between the initial (1) and final (2) states of the system becomes the intensive property when mass remains constant between initial and final states (or) when the system is a closed system.

iii) G has a single value for the thermodynamic state of the system.

iv) G and ΔG values correspond to the system only. There are three cases of ΔG in predicting the nature of the process. When, $\Delta G < 0$ (negative), the process is spontaneous and feasible; $\Delta G = 0$. The process is in equilibrium and $\Delta G > 0$ (positive), the process is nonspontaneous and not feasible.

v) $\Delta G = \Delta H - T\Delta S$. But according to I law of thermodynamics, $\Delta H = \Delta E + P\Delta V$ and $\Delta E = q - w$.

$\therefore \Delta G = q - w + P\Delta V - T\Delta S$

But $\Delta S = \dfrac{q}{T}$ and $T\Delta S = q$ = heat involved in the process.

$\therefore \Delta G = q - w + P\Delta V - q = -w + P\Delta V$

(or) $-\Delta G = w - P\Delta V$ = network.

The decrease in free energy $-\Delta G$, accompanying a process taking place at constant temperature and pressure is equal to the maximum obtainable work from the system other than work of expansion.

This qunatity is called as the "net work" of the system and it is equal to $(w - P\Delta V)$

$\therefore$ Network $= -\Delta G = w - P\Delta V$.

$-\Delta G$ represents all other forms of work obtainable from the system such as electrical, chemical or surface work etc other than P-V work.

57. The dissociation equilibrium of PCl_5 in gaseous state is written as

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Let 'a' moles of PCl_5 vapour be present inV litres initially. If x moles of PCl_5 dissociate to PCl_3 andCl_2 gases at equilibrium will be $\dfrac{a-x}{V}, \dfrac{x}{V}$ and $\dfrac{x}{V}$ respectively.

$$\therefore K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{a-x}{V}}$$

$$= \frac{x^2}{V^2} \times \frac{V}{a-x} \qquad \boxed{K_c = \frac{x^2}{(a-x)V}}$$

x = degree of dissociation

$$x = \frac{\text{Number of moles dissociated}}{\text{Total number of moles present initially}}$$

$$K_c = \frac{x^2}{(1-x)V}$$

[∵ Initially the no. of PCl_5 present = 1 mole]

$$= \frac{x^2P}{(1-x)RT} \qquad [\because PV=RT]$$

In terms of partial pressure of PCl_5, PCl_3, and Cl_2, then

$$K_c = \frac{pPCl_3.pCl_2}{pPCl_5}\text{atm} \quad \boxed{K_p = \frac{x^2P}{1-x^2}} \text{ atm.}$$

58. (i) The magnitude of order of a reaction may be zero or fractional or integral values. For an elementary reaction, its order is never fractional since it is a one step process.

(ii) It should be determined only by experiments. It cannot be predicted in terms of stoichiometry of reactants and products.

(iii) Simple reactions possess low values of order like n = 0, 1, 2 reactions with order greater than or equal to 3.0 are called complex reactions. Higher order reactions are rare.

(iv) Some reactions show fractional order depending on rate.

(v) Higher order reactions may be experimentally converted into simpler order reactions by using excess concentrations of one or more reactants.

59.
$$E^0_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu} + \frac{2.303RT}{nF}\log\frac{[Cu^{2+}]}{[Cu]}$$

$$= +0.301 + \frac{0.0591}{2}\log\frac{0.01}{1}$$

$$E^0 = 0.301 + \frac{0.059}{2} \times 2 = 0.3591V$$

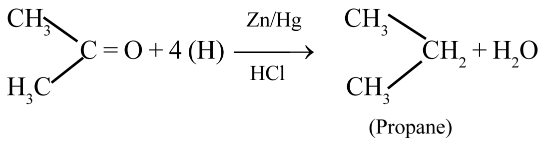
$$E^0 = 0.36V$$

SECTION - C

60.

Aromatic ether (Anisole)	**Aliphatic ethers (Diethyl ether)**
1. Comparatively high boiling liquid.	Volatile liquid
2. Used in perfumery.	Used as anaesthetic
3. Not used as solvent.	Used as a solvent
4. Cannot be used as a substitute for petrol.	Mixed with alcohol, used as a substitute for petrol.
5. On heating with HI forms phenol and CH_3I only.	It forms C_2H_5OH and C_2H_5I
6. With nitrating mixture forms nitro anisoles.	Nitration does not take place.
7. Does not form peroxide easily.	Forms peroxide in air.

61. (i) Aldehydes and ketones can be reduced to hydrocarbons by zinc amalgam and con.HCl.



(ii) **Perkin's reaction :** When benzaldehyde is heated with acetic anhydride in the presence of sodium acetate, it forms cinnamic acid.

$$C_6H_5CH{=}O{+}CH_3{-}CO{-}O{-}COCH_3 \xrightarrow[\Delta]{CH-CHO} C_6H_5CH{=}CH{-}COOH{+}CH_3COOH$$

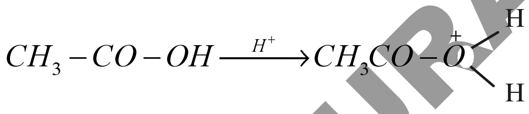
62. Carboxylic acid reacts with alcohols in the presence of mineral acid as catalyst and forms esters. This reaction is called esterification.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{H^+} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

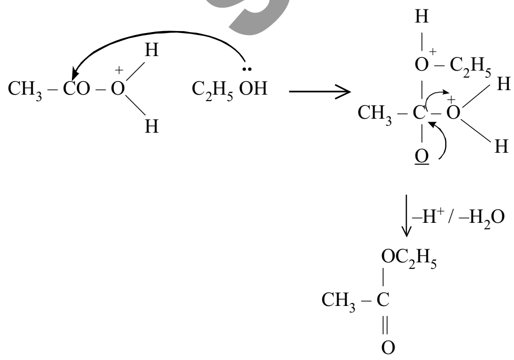
Mechanism of esterification.

Protonation of the -OH group of the acid, enhances the nucleophilic attack by alcohol to give the ester.

Step 1: Protonation of carboxylic acid.



Step 2: Attack by nucleophile.



63. Anaesthetics

The drugs which produce loss of sensation are called anaesthetics. They are classified into two types.

(i) **General anaesthetics** are the agent, which bring about loss of all modalities of sensation, particularly pain along with 'reversible' loss of conciousness.

(ii) **Local anaesthetics** prevent the pain sensation in localised areas without affecting the degree of conciousness.

(i) Nitrous oxide N_2O : It is a colourless, inoragnic non-irritating gas. It is the safest of the anaesthetic agents. This is used after mixing general anaesthetics like ether.

PART - IV

64.a) Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr and CsCl.

(i) In each ionic crystal, the cations and anions are isoelectronic with inert gas configuration.

$$\left.\begin{array}{ll} K^+ & 2,8,8 \\ Cl^- & 2,8,8 \end{array}\right\} \text{Ar type configuration}$$

(ii) The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the internuclear distance between them.

$$r(C^+) + r(A^-) = d(C^+{-}A^-) \quad \text{...........(1)}$$

where $r(C^+)$ = radius of cation

$r(A^-)$ = radius of anion A^-

$d(C^+{-}A^-)$ = internuclear distance between C^+ and A^-

(iii) For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge.

$$r(C^+) \propto \frac{1}{Z^*(C^+)} \quad \text{.........(2)}$$

$$r(A^-) \propto \frac{1}{Z^*(A^-)} \quad \text{...........(3)}$$

where $Z^*(C^+)$ and $Z^*(A^-)$ are the effective nuclear charges of C^+ and A^- respectively.

On combining (2) and (3),

$$\frac{r(C^+)}{r(A^-)} = \frac{Z^*(A^-)}{Z^*(C^+)} \quad ....(4)$$

The two equations (1) and (4) can be used to evaluate the values of $r(C^+)$ and $r(A^-)$ provided the values of $d(C^+–A^-)$, $Z^*(C^+)$ and $Z^*(A^-)$ are known.

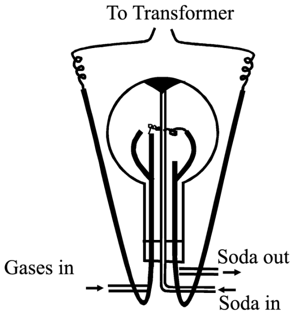
(iv) The value of screening constant S and effective nuclear charge (Z^*) can be calculated by using **Slater rules**.

b) **Isolation of noble gases from air :** The noble gases are isolated from air by removing oxygen and nitrogen from air free from CO_2, water vapour, dust particles etc. This can be done by either chemical method or physical method.

Step 1. Chemical method :

Removal of oxygen and nitrogen of the atmoshphere as Nitrogen dioxide.

Ramsay-Raleigh's method : A mixture of air and oxygen is constantly admitted into a glass globe of about 50 litres capacity. Two platinum electrodes are introduced and a discharge from a transformer of about 6000-8000 volts is passed by the action of which nitrogen and oxygen rapidly combine to form oxides of nitrogen. The oxides are dissolved out in a solution of sodium hydroxide are continuously circulated through the flask.



Chemical Method for isolation of Noble Gases

$$N_2 + O_2 \longrightarrow 2NO$$

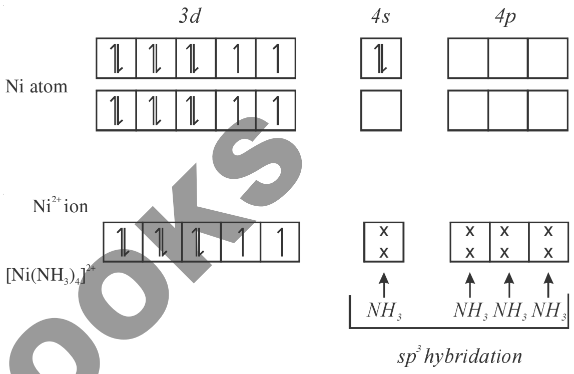
$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + 2NaOH \longrightarrow NaNO_3 + NaNO_2 + H_2O$$

Oxygen if any, is removed by introducing alkaline pyrogallol in the globe. The supply of air and electric discharge is shut after some time and the remaining mixture of noble gases is pumped out.

65. a) $[Ni(CN)_4]^{2-}$ is diamagnetic whereas $[Ni(NH_3)_4]^{2+}$ is paramagnetic. This fact is explained with the help of VB theory.

$[Ni(NH_3)_4]^{2+}$: Nickel atom Ni (Z = 28)



The number of unpaired electrons are two so it is paramagnetic in nature.

65. b) This method was developed by Willard and Libby to determine the age of wood or animal fossils. This method is based on the fact that ${}_6C^{14}$, radioactive isotope of carbon is formed in the upper atmosphere by reaction with neutrons (from cosmic rays)

$${}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1H^1$$

The C^{14} atoms thus produced are rapidly oxidised to ${}^{14}CO_2$ which in turn is incorporated in plants as result of photosynthesis. Animals too consume C^{14} by eating plants. On death, organisms cease to take in fresh carbonations. Carbon-14 begins to decay

$${}_6C^{14} \longrightarrow {}_7N^{14} + {}_{-1}e^0$$

5700 years a fossil will lose half the amount of carbon-14 present in its living state. Therefore by knowing either the amount of C^{14} or the number of particles emitted per minute per gram of carbon at the initial and final stages, the age of carbon material can be determined by the following equation

$$t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{\text{Amount of } C^{14} \text{ in fresh wood}}{\text{Amount of } C^{14} \text{ in dead wood}}$$

Uses: (1) Carbon dating has proved to be a great tool for correlating facts of historical importance.

(2) It is very useful in understanding the evolution of life and rise and fall of civilizations.

66. a) Ordinary glass is a transparent amorphus substance. It is not a true solid. It is essentially a solution of silica in a mixture of other silicates which has not crystallized on cooling.

Glass has no definite melting point. It softens when heated at a certain temperature, with the further rise in temperature, blown in a mould into desired shape which it retains on cooling.

The chief characteristics of glass are hardness, rigidity and ability to withstand shearing stresses which are all properties of the solid state. Glasses are optically isotropic and on heating without any sharp transition passes into a mobile liquid. At high temperature glasses undergo phase transition when crystals separate first as they do form super cooled liquid. Therefore glasses are considered as amorphous solids (or) super cooled liquids. Glassy or vitreous state is a condition in which certain substances can exist lying between solid and liquid state.

66. b)

Physical adsorption	Chemical adsorption
(i) It is due to intermolecular Vander Waal's force	i) It is due to chemical bond formation.
(ii) It depends on the nature of gas. Easily liquefiable gases are absorbed easily.	ii) It is more specific than physical adsorption
(iii) Heat of adsorption is small.	iii) Heat of adsorption is large
(iv) Reversible.	iv) Irreversible.
(v) It occurs rapidly at low temperature and decreases with increase of temperature.	v) It icreases with increase of temperature.
(vi) Increase of pressure favours physical adsorption	vi) Change of pressure has no effect on chemical adsorption.
(vii) If forms multimolecular layers on adsorbent surface	vii) It forms unimolecular layer

67. a) Ostwald's dilution law relates the dissociation constant of the weak electrolyte with the degree of dissociation and the concentration of the weak electrolyte. Consider the dissociation equilibrium of CH_3COOH which is a weak electrolyte in water.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

α = degree of dissociation of acetic acid.	CH_3COOH	CH_3COO^-	$H+$
Initially	1mole	–	–
After sometime degree of dissciation	α	α	α
At equilibrium the remaining is	$1-\alpha$	α	α
concentration at equilibrium	$(1-\alpha)$C	αC	αC

$$\therefore K_a = \frac{\alpha C \times \alpha C}{(1-\alpha)C}$$

$$\boxed{K_a = \frac{\alpha^2 C}{1-\alpha}}$$ Ostwald's dilution law

If α is too small, $K_a = \alpha^2 C$

$$\alpha^2 C = K_a$$

$$\alpha^2 = \frac{K_a}{C}$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$[H^+] = C\alpha$$

$$= \text{C}\sqrt{\frac{K_a}{C}}$$

$$= \sqrt{\frac{K_a C^2}{C}} = \sqrt{K_a C}$$

$$\therefore [H^+] = \sqrt{K_a C}$$

$K_a = \alpha^2 C$ – Ostwald's dilution law for weak acid.

$K_b = \alpha^2 C$ – Ostwald's dilution law for weak base.

67. b) IUPAC Conventions: In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a single vertical line (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

Phase Boundary
$Zn \mid Zn^{2+}$ $Cu^{2+} \mid Cu$
ANODE HALF-CELL CATHODE HALF-CELL

It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half-cell it is on the right of the metal ion.

(2) A double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

(3) Anode half-cell is written on the left and cathode half-cell on the right.

(4) In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as

Salt Bridge
$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$
ANODE HALF-CELL CATHODE HALF-CELL

(5) The symbol for an inert electrode, like the platinum electrode is often enclosed in a bracket. For **example**,

Inert Electrode
$Mg \mid Mg^{2+} \parallel H^+ \mid H_2(Pt)$
ANODE HALF-CELL CATHODE HALF-CELL

(6) The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1 V and is represented as

$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu \quad E = +1.1\ V$
← Direction of electron flow

If the emf acts in the opposite direction through the cell circuit it is denoted as a negative value.

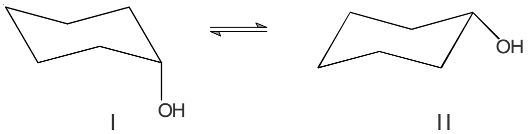
$Cu \mid CuSO_4 \parallel ZnSO_4 \mid Zn \quad E = -1.1\ V$
→ Direction of electron flow

The negative sign also indicates that the cell is not feasible in the given direction and the reaction will take place in the reverse direction only. The overall cell reaction for E = –1.1 V of the daniel cell is

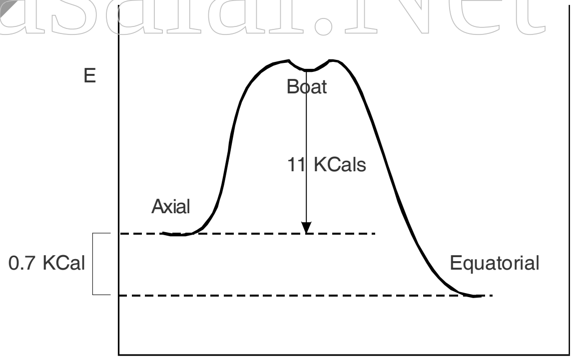
$$Cu_{(s)} + Zn_{(aq)}^{2+} \rightarrow Cu_{(aq)}^{2+} + Zn_{(s)}$$

68. (a)

Cyclohexanol exists in two chair forms. These two forms are interconvetible and exist in equilibrium.

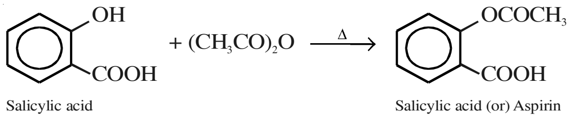


In one form (I) the –OH group is axially oriented. In the other form (II) the –OH group is equatorially oriented. The energy of the axial conformer is little higher than that of the equatorial conformer. Because the axial substituent experiences steric interaction with the axial H-atoms present at the third carbon atoms. This decreases the stability of the axial conformer. This is called 1 : 3-diaxial interaction. This interaction is absent in the equatorial conformer. Hence equatorial cyclohexanol is present to an extent of about 90% in the equilibrium mixture. The axial isomer is present only to 10%.

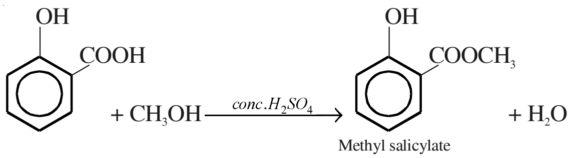


68. (*b*)

(i) Salicylic acid undergoes acetylation by heating with acetic anhydride to form aspirin.



(ii) Salicylic acid on the heating with methyl alcohol in the presence of conc. H_2SO_4, a pleasant. Smelling liquid methyl salicylate is formed.



(iii) $HCOOH + NH_3 \longrightarrow HCOONH_4 \xrightarrow[-H_2O]{\Delta} HCONH_2$

Ammonium formate formanide

69. (*a*)

(a) $CH_3NH_2 + O=N-OH \longrightarrow [CH_3-N=N-OH] \longrightarrow CH_3OH + N_2$

Methyl amine Methanol

(*b*) Secondary amines react with nitrous acid to form N–Nitroso amines which are water insoluble yellow oils.

$(CH_3)_2NH + HO-N=O \longrightarrow (CH_3)_2N-N=O$

Dimethylamine N-nitroso dimethylamine (yellow oil)

(*c*) Tertiary amines react with nitrous acid to form trialkyl ammonium nitrite salts which are soluble in water.

$(CH_3)_3N + HONO \longrightarrow (CH_3)_3NH^+NO_2^-$

Trimethyl ammonium nitrite (Salt soluble in water)

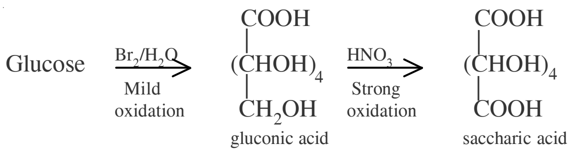
69. (*b*)

The structure of glucose has been derived from the following facts.

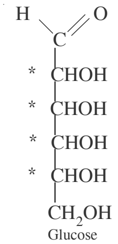
1. Elemental analysis and molecular weight determination show that the molecular formula of glucose is $C_6H_{12}O_6$.
2. Complete reduction of glucose with concentrated hydriodic acid in the presence of red phosphorous produces n-hexane as the major product. This indicates that the six carbon atoms in the glucose molecule form an unbranched chain of six carbon atoms.

$$\text{Glucose} \xrightarrow[\text{Reduction}]{\text{HI/P}} \underset{\text{n-hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

3. Glucose readily dissolves in water to give a neutral solution. This indicates that the glucose molecule does not contain a carboxyl ($-\overset{\overset{\displaystyle O}{\|}}{C}-OH$) group
4. Glucose reacts with hydroxylamine to form a monoxime or adds only one mole of HCN to give a cyanohydrin. This reaction indicates the presence of either an aldehyde ($-\overset{\overset{\displaystyle O}{\|}}{C}-OH$) or a ketone ($-\overset{\overset{\displaystyle O}{\|}}{C}-$) group.
5. Mild oxidation of glucose with bromine water gives gluconic acid. This indicates the **presence of an aldehyde group** since only the aldehyde group can be oxidised to an acid, containing same number of carbon atoms. Since the six carbon atoms in glucose form a consecutive unbranched chain, the aldehyde group, must occupy one end of this chain.
6. Further oxidation of gluconic acid with nitric acid gives saccharic acid. This indicates the **presence of a primary alcoholic group.**



7. Glucose **reduces** an ammoniacal solution of silver nitrate (Tollen's reagent) to metallic silver or a basic solution of cupric ion (Fehling's solution) to red cuprous oxide. These reactions further confirm the **presence** of a **aldehyde group.**
8. Glucose reacts with acetic anhydride in the presence of pyridine to form a penta acetate. This reaction indicates the **presence of five hydroxyl groups** in a glucose molecule. From the above evidences we conclude that glucose is a penta hydroxy hexanal (an aldohexose) and can be represented by the following structure.



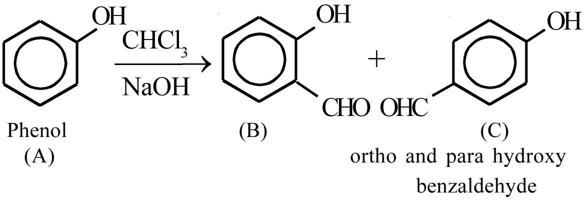
* C = asymmetric carbon atom

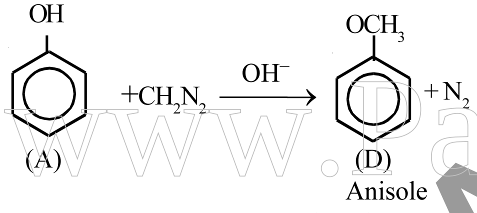
Glucose

(2,3,4,5,6 penta hydroxy hexanal)

70. ***(a)***

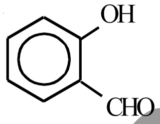
$C_6H_5OH \longrightarrow$ Phenol





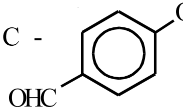
A - C_6H_5OH - Phenol

B -



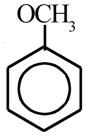
- orthohydroxy benzaldehyde

C -



- para hydroxy benzaldehyde

D -



- Anisole

70. ***(b)***

(i) Compound (A) is a powerful oxidising agent and it is a red orange crystal means it must be **Potassium dichromate** $K_2Cr_2O_7$. Its melting point is 396°C.

(ii) Potassium dichromate reacts with a chloride salt and conc. H_2SO_4 to give **Chromyl chloride** gas CrO_2Cl_2 (B) and it is reddish brown in colour.

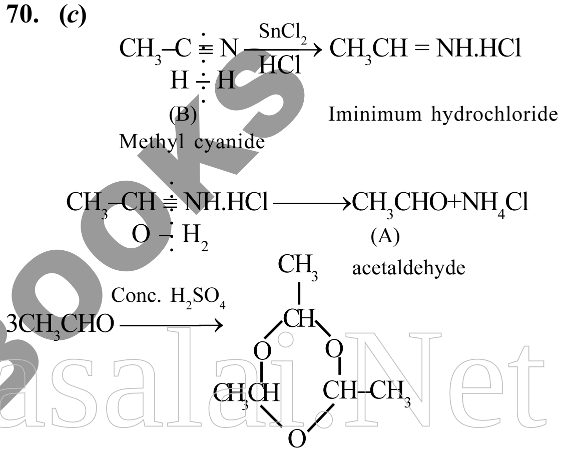
$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2\uparrow + 6KHSO_4 + 3H_2O$$

(iii) **Potassium dichromate** reacts with an alkali KOH to give potassium chromate K_2CrO_4 (C) which is yellow in colour.

$$K_2Cr_2O_7 + 2KOH \longrightarrow \underset{\substack{\text{Potassium chromate}\\ \text{(C)}\\ \text{Yellow}}}{2K_2CrO_4} + H_2O$$

A	$K_2Cr_2O_7$	Potassium dichromate
B	CrO_2Cl_2	Chromyl chloride
C	K_2CrO_4	Potassium chromate

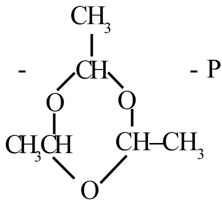
70. ***(c)***



A - CH_3CHO - paraldehyde

B - CH_3CN - Methyl cyanide

C -



- Paraldehyde

70. ***(d)***

The electrolyte

$$Al_2(SO_4)_3 \quad \lambda_\infty Al_2(SO_4)_3 = \frac{1}{3}\lambda_\infty Al^{3+} + \frac{1}{2}\lambda_\infty SO_4^{2-}$$

equivalent conductance at infinite dilution

$$\lambda_\infty Al_2(SO_4)_3 = \frac{189}{3} + \frac{160}{2} = 63 + 80 = 143\ mho\ cm^2 gm.equiv^{-1}$$

molar conductance at infinite dilution

$$\mu_\infty Al_2(SO_4)_3 = 2\times189 + 3\times160 = 858\ \text{mho cm}^2\text{mol}^{-1}$$

❖❖❖❖❖