(c) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

- (ii) What happens when D-glucose is treated with the following reagents?
- (a) HI
- (b) Bromine water
- (c) HNO₃

<u>Solutions</u> Section A

S1. Ans. (d)

S2. Ans. (c), (d)

Sol. Statement (a) HCl cannot be used because some $KMnO_4$ is consumed in the reaction. Is Correct as it reacts with $KMnO_4$ to get oxidized and follows up with the liberation of Cl_2 gas.

Statement (b) Nitric acid is not used for the above purpose because it itself acts as a self-oxidizing agent and will react with the reducing agent. It is Correct as it is a very strong oxidizing agent which reduces the KMnO₄.

Statement (c) The equivalent weight of KMnO₄ in the basic medium is 158. This is Incorrect as the equivalent weight of KMnO₄ in the basic medium is 52.66gm/equivalent.

Statement (d) The number of electrons involved in the oxidation of KMnO₄ in an acidic medium is 3. This is Incorrect as the number of electrons involved in the oxidation of KMnO₄ in an acidic medium is 5.

S3. Ans. (a)

Sol. Alanine can be synthesised from pyruvate via transamination.



S4. Ans.(c)

Sol. All naturally occurring proteins from all living organisms consist of L amino acids. Most naturally occurring chiral amino acids are S, with the exception of cysteine.

S5. Ans. (b)

Sol. The molecules of water are held together by hydrogen bonds. As the new force of attraction between water and alkyl halides molecules are weaker than the forces of attraction already existing between alkyl halide- alkyl halide molecules and water - water molecules, they cannot form hydrogen bonds with water.

S6. Ans. (d)

Sol. p - Dichlorobenzene is more symmetrical than the o- and m- isomers. So, it fits more closely in the crystal lattice. Therefore, more energy is required to break the crystal lattice of p - dichlorobenzene. Therefore p - dichlorobenzene has highest melting point than the 0- and m- isomers. It has melting point of 53.5 degree Celsius.

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S7. Ans. (d) **Sol.** k = 10⁻² kt = R₀ - R

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 $10^{-2} \times 10 \times 60 = 10/1 - R$ $R = 6 \mod L^{-1}$ 6 moles react unreacted mole = 10-6 = 4 moles.

S8. Ans. (d)

S9. Ans. (b)

Sol. Dry cell (Leclanche cell) and Mercury cell are primary voltaic cells. They cannot be recharged. Hence, none of the given options is a secondary cell.

Lead accumulator (lead storage battery) is a secondary cell.

S10. Ans. Option (c) ΔG° is negative, K is greater than 1 Sol. $\Delta G^0 = -nFE^0$ (i) $\Delta G^0 = -2.303 \text{ RT} \log K_{ag}$...(ii) From eq. (i) if E⁰ is positive Then ΔG^0 is negative in equation (ii), ΔG^0 is negative So, log K > 0 → K > 1

S11. Ans. (c)

Sol. The formula of potassium dicyano-bis-(oxalato) nickelate(II) is $K_4[Ni(CN)_2(ox)_2]$. Nickelate (II) implies anion forms the complex part with Ni as the central atom and in +2 oxidation state. bis-oxalato implies there are 2 oxalato ligands.

S12. Ans. (a)

Sol. The correct IUPAC name is Triammine trinitro-N-cobalt(III). In this case, the alphabetical order of the groups is followed i.e. ammine group followed by the nitro- group. Co is in +3 oxidation state.

S13. Ans. (c)

Sol. Given: $X(ROH)+Cu(hot) \rightarrow alkene$

Primary alcohol passed over Cu at 300°C is dehydrogenated to aldehydes and hydrogen gas liberates secondary alcohols are dehydrogenated to ketones with liberation of hydrogen gas tertiary alcohol is dehydrated to alkene. This method can therefore be used to distinguish between primary, secondary and tertiary alcohol. Thus X should be a tertiary alcohol

S14. Ans. (b)

Sol. Picric acid is a yellow colored compound. Its chemical name is 2,4,6 -trinitrophenol.



S15. Ans. (a)

Sol. When a mixture of formaldehyde and another aldehyde without an α -hydrogen atom is treated with concentrated alkali, it oxidizes formaldehyde to carboxylic acid and reduces another aldehyde to alcohol.

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S16. Ans. (d)

Sol. Under Wolff Kishner reduction, an aldehyde or ketone is converted into the corresponding alkane.

S17. Ans. (d)

Sol. Amines are derivatives of ammonia. N atom is sp³ hybridised.

S18. Ans. (d)

Sol. Intermolecular hydrogen bonding is strongest in methylamine [CH₃-NH₂] because N has more electron affinity.

Section B

S19. Ans. The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$. Hence, the reducing power of the given metals increases in the following order: Ag < Hg < Cr < Mg < K

OR

The decomposition of NH_3 on platinum surface is represented by the following equation. $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ Therefore, Rate = $-1/2 d[NH_3]/dt = d[N_2]/dt = 1/3 d[H_2]/dt = k = 2.5 x 10^{-4} mol L^{-1} s^{-1}$ Therefore, the rate of production of N2 is $d[N_2]/dt = 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$ And, the rate of production of H₂ is $d[H_2]/dt = 3 \times 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$ $= 7.5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$

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S20. Ans. (v) Co<sup>2+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>7</sup>
Or, [Ar]<sup>18</sup> 3d<sup>7</sup>
(vi) Lu<sup>2+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>6</sup> 4f<sup>14</sup> 5d<sup>1</sup>
Or, [Xe]<sup>54</sup> 4f<sup>14</sup> 5d<sup>1</sup>
(vii) Mn<sup>2+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup>
Or, [Ar]<sup>18</sup> 3d<sup>5</sup>
(viii) Th<sup>4+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>10</sup> 4f<sup>14</sup> 5s<sup>2</sup> 5p<sup>6</sup> 5d<sup>10</sup> 6s<sup>2</sup> 6p<sup>6</sup>
Or, [Rn]<sup>86</sup>
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S21. Ans. FeSO₄ solution when mixed with (NH4)2SO4 in 1: 1 molar ratio produces a double salt $FeSO_4(NH_4)_2SO_4.6H_2O$. This salt is responsible for giving the Fe^{2+} .

CuSO₄ mixed with aqueous ammonia in the ratio of 1:4 gives a complex salt. The complex salt does not ionize to give Cu²⁺, hence failing the test.

S22. Ans. (i)



2-Bromo-3-chlorobutane (ii)

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1-Bromo-1-chloro-1,2,2-trifluoroethane (iii)

$$CI = {}^{4}CH_{2} = {}^{3}C \equiv {}^{2}C = {}^{1}CH_{2} = Br$$

1-Bromo-4-chlorobut-2-yne (iv)



2-Bromo-3, 3-bis(4 - chlorophenyl) butane

S23. Ans. (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1 – phenylethanol can be synthesized.







A cyclic product is produced in the presence of dry HCl gas, called ethylene glycol ketals, when ketones react with ethylene glycol.



General structure of an imine

The reaction of aldehydes and ketones with ammonia or 1⁰-amines forms imine derivatives



S25. Ans. Generally a primary cell known as Leclanche cell is used in the transistor. Anode Reaction: $Zn \rightarrow Zn^{2+} + 2e^{-}$ Cathode Reaction: $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

Section C

S26. Ans. 10% w/w means 10 g glucose is present in 100 g solution. Mass of water = 100 - 10 = 90 g = 0.90 kg10 g glucose = 10/180 mol = 0.0555 moles Number of moles in 90 g of $H_2O = 90/18$ mol = 5 moles Molality of the solution = 0.0555/0.090 m = 0.617 m Mole fraction of glucose = 0.0555/(5 + 0.0555) = 0.01Mole fraction of $H_2O = 1 - 0.01 = 0.99$ Volume of 100 g solution = 100/1.2 m L = 83.33 mL = 0.08333 L Molarity = 0.0555 mol/0.08333 L = 0.67 M

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OR

According to Henry's law, at a particular temperature, the solubility of a gas in given volume of a liquid is directly proportional to the pressure of the gas above the liquid.

m∝p

m = k p

Where, k = Henry's constant.

Here, m and p represent the mass of the dissolved gas and pressure respectively. Some important applications of Henry's law:

To increase the solubility of CO₂ in soft drinks, the bottle is sealed under high pressure.

Scuba divers face the problems of high concentration of dissolved gasses while breathing air at high pressure underwater. When the divers reach the surface, the pressure gradually decreases. This releases the dissolved gasses and leads to the formation of bubbles of nitrogen in blood. This blocks capillaries and creates a medical condition known bends which are painful and dangerous to life. To avoid bends, tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

The partial pressure of oxygen at high altitudes is smaller than at the sea level. This results in low concentration of oxygen in the blood and tissues. Low blood oxygen causes climbers to become weak and unable to think. Such symptoms are known as anoxia.

S27. Ans. The galvanic cell in which the given reaction takes place is depicted as:

 $Zn(s)|Zn^{2+}(aq)||Ag^{+}(aq)|Ag(s)|$

(i) Zn electrode (anode) is negatively charged.

(ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc. (iii) The reaction taking place at the anode is given by, $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ The reaction taking place at the cathode is given by,



S28. Ans.. Let the concentration of the reactant be [A] = a

Rate of reaction, $R = k [A]^2$

= ka²

(i) If the concentration of the reactant is doubled, i.e. [A] = 2a, then the rate of the reaction would be

 $R' = k(2a)^2$

= 4ka2

= 4 R

Therefore, the rate of the reaction would increase by 4 times.

(ii) If the concentration of the reactant is reduced to half, i.e. [A] = 1/2 a, then the rate of the reaction would be

$$R'' = k \left(\frac{1}{2}a\right)$$
$$= \frac{1}{4}ka$$
$$= \frac{1}{4}R$$

Therefore, the rate of the reaction would be reduced to ¼ th.

S29. Ans. The oxidation states displayed by the first half of the first row of transition metals are given in the table below.

It can be easily observed that except Sc, all others metals display +2 oxidation state. Also, on moving from Sc to Mn, the atomic number increases from 21 to 25. This means the number of electrons in the 3d-orbital also increases from 1 to 5.

Sc (+2) = d^1 Ti (+2) = d^2 V (+2) = d^3 Cr (+2) = d^4 Mn (+2) = d^4

$$\ln(+2) = d^5$$

+2 oxidation state is attained by the loss of the two 4s electrons by these metals. Since the number of d electrons in (+2) state also increases from Ti (+2) to Mn(+2), the stability of +2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has d⁵ electrons (that is half-filled d shell, which is highly stable).

S12. Ans.



CCl₄ is a symmetrical molecule. Therefore, the dipole moments of all four C− Cl bonds cancel each other. Hence, its resultant dipole moment is zero.

As shown in the above figure, in CHCl₃, the resultant of dipole moments of two C – Cl bonds is opposed by the resultant of dipole moments of one C–H bond and one C – Cl bond. Since the resultant of one C – H bond and one C–Cl bond dipole moments is smaller than two C–Cl bonds, the opposition is to a small extent. As a result, CHCl₃ has a small dipole moment of 1.08 D.

On the other hand, in case of CH_2Cl_2 , the resultant of the dipole moments of two C – Cl bonds is strengthened by the resultant of the dipole moments of two C – H bonds.

Result, CH_2Cl_2 has a higher dipole moment of 1.60 D than $CHCl_3$ i.e., CH_2Cl_2 has the highest dipole moment. Hence, the given compounds can be arranged in the increasing order of their dipole moments as: $CCl_4 < CHCl_3 < CH_2Cl_2$

OR

The hydroboration – oxidation reaction is the reaction where borane is added in order for the oxidation to take place. For example, propan – 1 – ol is formed by making propene undergo the hydroboration – oxidation reaction. In the above reaction, the reaction between propene and diborane $(BH_3)_2$ takes place in order to form trialkyl

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borane which acts an additional product. This additional product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



Section D

S31. Ans. (I) (d): DNA occurs in nucleus of the cell while RNA is found mainly in cytoplasm of the cell.



(II) (b)

Nucleosides contain only sugar and a base whereas nucleotides contain sugar, base and a phosphate group as well.

OR

(c)

Sol. The segment of DNA which ats as the instruction manual for the synthesis of protein is gene.

(iii) **Nucleotide**: The chemical composition of nucleotide consists of a phosphate group, a sugar and a nitrogenous base. They are one of the major causes of cancer-causing agents to this very day. Some of the major examples of nucleotides are adenosine, guanosine etc.

Nucleoside: A nucleoside has a chemical composition that consists of a sugar and a base without the phosphate group. They are used as agents in medicine that are primarily used against viruses and cancer-causing agents. Some of the key examples of nucleosides are the same as nucleotides only with the addition of phosphate groups.

S32. Ans. (i) (d)

(ii) (b): The correct order of acidic strength is
 (IV) > (III) > (I) > (II)
 PKa 9.2 10.0 11.0 15.9

OR

(a): Weaker acids have higher pK_a . -OCH3 at meta position exerts only –I effect, hence increases the acidity. -I effect order: -NO₂ > -OCH₃ > -CI.

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-CH₃ has +I effect. So, order is (a)

(iii) In O-nitrophenol, NO₂ is -M group, that's why it is withdrawing the electron from O⁻ ion and making it stable, hence the OH group of O-nitrophenol is more acidic than O-cresol.



Section E

S33. Ans. A homogeneous mixture of two or more non-reacting substances whose composition varies within certain fixed limits, known as a solution. Generally, the component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes.

When the solutions contain two, three or four components, it is known as binary, ternary or quaternary solutions respectively. On the basis of physical state of components, the solutions are of the following types:

1) When both solute and solvent are in solid state. Example: Alloys.

2) When solute is in solid and solvent is in liquid state.

Example: Sugar or salt solutions.

3) When solute is in solid and solvent is in gaseous state.

Example: iodine vapours in air.

4) When both solute and solvent are in liquid state.

Example: alcohol in water.

5) When solute is in liquid and solvent is in solid state. Example: Zinc amalgam.

6) When solute is in liquid and solvent is in gaseous state. Example: water vapour in air.

7) When both solute and solvent are in gaseous state. Example: air.

8) When solute is in gaseous and solvent is in liquid state. Example: aerated drinks.

9) When solute is in gaseous and solvent is in solid state. Example: dissolve gas in mineral.

OR

(i) Conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area of crosssection 1 sq. cm. The inverse of resistivity is called conductivity or specific conductance. It is represented by the symbol κ . If ρ is resistivity, then we can write:

k = 1 p

The conductivity of a solution at any given concentration is the conductance (G) of one unit volume of solution kept between two platinum electrodes with the unit area of cross-ection and at a distance of unit length. i.e., $G = k a / l = k \times 1 = k$ (Since a = 1, | = 1)

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Conductivity always decreases with a decrease in concentration, both for weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decrease with a decrease in concentration.

Molar conductivity:

Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section A and distance of unit length.

 $\Lambda m = k (a/l)$

Now, I = 1 and A = V (volume containing 1 mole of the electrolyte).

∧m = kV

Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution. The variation of Λ_m with Vc for strong and weak electrolytes is shown in the following plot:



(ii) As we move along the lanthanoid series, the atomic number increases gradually by one. This means that the number of electrons and protons present in an atom also increases by one. As electrons are being added to the same shell, the effective nuclear charge increases. This happens because the increase in nuclear attraction due to the addition of proton is more pronounced than the increase in the interelectronic repulsions due to the addition of electron. Also, with the increase in atomic number, the number of electrons in the 4f orbital also increases. The 4f electrons have poor shielding effect. Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the attraction of the nucleus for the outermost electrons increases. This results in a steady decrease in the size of lanthanoids with the increase in the atomic number. This is termed as lanthanoid contraction.

Consequences of lanthanoid contraction

(i) There is similarity in the properties of second and third transition series.

(ii) Separation of lanthanoids is possible due to lanthanide contraction.

(iii) It is due to lanthanide contraction that there is variation in the basic strength of lanthanide hydroxides. (Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.)

S34. Ans. 34. (i) A is an organic compound with a molecular formula C8H16O2. This gives a carboxylic acid (B) and alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester.

Further, oxidation of alcohol (C) with chromic acid gives acid B. Thus, B and C must contain an equal number of carbon atoms.

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A total of 8 carbon atoms are present in compound A, each of B and C contain 4 carbon atoms.

Again, alcohol C gives but-1-ene on dehydration. Therefore, C is of straight-chain and hence, it is butan-1-ol.



 N_2 + $C_6H_5CH_2$ - OH + HCI Benzyl alcohol

In another case, HNO_2 reacts with aniline at a very low temperature which in turn forms stable diazonium salt. Hence, the evolution of nitrogen gas does not happen.

$C_6H_5NH_2 \xrightarrow{NaNO_2 + HCI} C_6H_5 - N_2CI + NaCI + 2H_2O$

(b) N – methylaniline & Aniline can be made notable by using the Carbylamine test.

On heating Primary amines with ethanolic , chloroform and potassium hydroxide, foul-smelling isocyanides or carbylamines are formed. As Aniline is a primary aromatic primary, it gives a positive carbylamines test. On the other h&, as, N – methyl aniline is a secondary amine it does not give a positive carbylamines test.

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(e) Heteroleptic: they are complexes with their metal ion being bounded to more than one kind of donor group. Example – $[Co(NH_3)_4Cl_2]^+$, $[Ni(CO)_4]$

(f) **Homoleptic**: they are complexes with their metal ion being bounded to only one type of donor. **Example** – $[PtCl_4]^{2^-}$, $[Co(NH_3)_6]^{3^+}$

Ans35. (i) (a) Aniline does not take Friedel – Crafts reaction.

Friedel – Crafts reaction is performed in the presence of $AlCl_3$. But, as we know that, $AlCl_3$ has an acidic nature, whereas aniline does not. Aniline is basic in nature. Therefore, aniline is then reacted with $AlCl_3$ forming a salt (this has been shown in the equation given below). The electrophilic substitution in the benzene ring is deactivated because of the positive charge on the N – atom. Hence, aniline does not undergo the Friedel – Crafts reaction.

(b) On comparing the stabilities, we observe that the stability of Diazonium salts of aromatic amines is more than that of aliphatic amines. Resonance is undergone by the diazonium ion, which is depicted in the figure given below.

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