

MARKING SCHEME

PRACTICE PAPER - 05

1. (i) (a) For a hypothetical reaction, $R \rightarrow$ products; rate $= -k[R]$. The negative sign used in the rate expression indicates decrease in the concentration of reactants with time. (1)

(ii) (a) The curve P tells, that the gradual increase in concentration with the passage of time and concentration of product increases in the course of reaction. (1)

(iii) (d) Rate of reaction $= -\frac{\Delta[\text{Hg}]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$ (1)

(iv) (a) Complete expression for in spontaneous rate of reaction is as follows :

$$-\frac{d[X]}{2dt} = \frac{-d}{dt}[Y] = +\frac{d[X_2Y]}{dt} \quad (1)$$

Or

$$(a) \frac{-\Delta[\text{SO}_2]}{\Delta t} = 2 \left(-\frac{\Delta[\text{O}_2]}{\Delta t} \right)$$

$$\therefore \frac{-\Delta[\text{SO}_2]}{\Delta t} = 2 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$= 5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$= 50.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} \quad (1)$$

2. (i) (b) Bond cleavage in haloarene is difficult than haloalkane due to partial double bond. Character in $\text{C}-\text{Cl}$ bond because of resonance, so it is less reactive towards nucleophilic substitution reaction. (1)

Phenyl carbocation is very unstable. (1)

(ii) (a) Nitro group present at *ortho* or *para*-position withdraws the electron density from benzene ring and thus, facilitates the attack of nucleophile on haloarene. (1)

(iii) (a) Halogen atom due to $-I$ -effect has some tendency to withdraw electron from benzene ring. So, the ring gets deactivated as compared to benzene. Hence, electrophilic substitution reactions in haloarene occur slowly and require more drastic conditions as compared to those in benzene. (1)

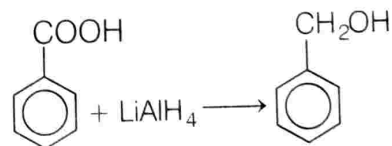
(iv) (c) Presence of $-\text{Cl}$ in chlorobenzene activates the ring at *ortho* and *para*-positions. $-\text{NO}_2$ group is a *meta*-directing group. Hence, Assertion is correct but Reason is incorrect. (1)

Or

(b) Chlorine is an electron withdrawing group, yet it acts as *ortho*, *para*-directing group in electrophilic aromatic substitution reaction due to its $+R$ -effect. (1)

3. (c) Electronic configuration of Ti^{3+} is $3d^1$. Thus, Ti^{3+} contains an unpaired electron, so it will exhibit colour in aqueous solution due to $d-d$ transition. (1)

4. (d) Benzoic acid reacts with LiAlH_4 to give benzyl alcohol.



(1)

5. (a) **Williamson's synthesis** is used for the preparation of symmetrical as well as unsymmetrical ethers. (1)



Or

(a) Alkyl aryl ethers are cleaved at the alkyl oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.

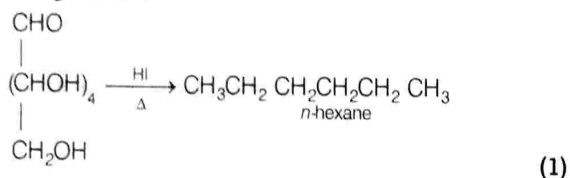
6. (a) 1° amines have the highest boiling points due to the presence of two H-atoms that would undergo hydrogen bonding to a greater extent as compared to 2° and 3° amines. (1)

7. (a) Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and thus, are not regarded as transition metals. However, being the end members of the three transition series, their chemistry is studied along with the chemistry of the transition metals. (1)

Or

(b) The stability of +2 oxidation state in different ions can be determined on the basis of electrode potential data. On the basis of electrode potentials, the correct order is $Mn > Fe > Cr > Co$. The more stability of Mn^{2+} stable d^5 configuration. (1)

8. (d) On prolonged heating with HI, glucose forms hexane, suggesting that all 6 C-atoms are linked in straight chain.



9. (c) For a zero order reactions, a graph of concentration and time is linear with a non-zero intercept, $[R_0]$ and negative slope, $-k$.

Or

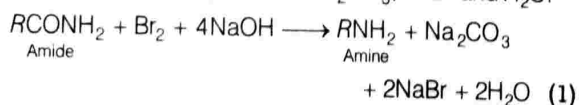
(c) Order of reaction = 2 + 1 = 3

So, units of rate constant

$$= \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1} = \text{mol}^{1-3} \text{L}^{3-1} \text{s}^{-1}$$

$$= \text{mol}^{-2} \text{L}^2 \text{s}^{-1} \quad (1)$$

10. (c) In the Hoffmann bromamide degradation, amine is formed with side products Na_2CO_3 , NaBr and H_2O .



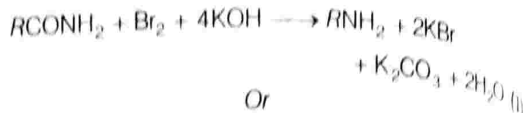
11. (a) Sodium stearate is a major component of many bar soap chemical formula of sodium stearate is



Or

(d) For positive sol, the flocculating power of anions are in the order $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$ more the charge of anion, more is the flocculating power. (1)

12. (d) Assertion is incorrect but Reason is correct. Hofmann bromamide reaction is used for converting an amide into primary amine containing one carbon less than the parent amide.



Or

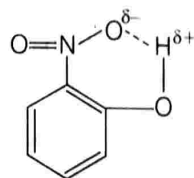
(d) Reduction of nitro compounds with Fe scrap and HCl is preferred because FeCl_2 formed gets hydrolysed to release HCl during the reaction.

Thus, only a small amount of HCl is required to initiate the reaction.

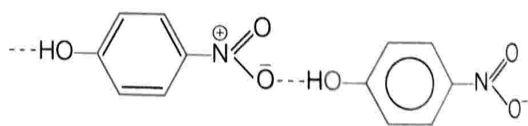
13. (a) Half and completely filled set of orbitals are relatively more stable. Thus, electronic configuration of Cr is $3d^5 4s^1$ instead of $3d^4 4s^2$. The energy gap between the two sets ($3d$ and $4s$) of orbitals is small enough to prevent electron entering the $3d$ -orbitals. Similarly, in the case of Cu, the configuration is $3d^{10} 4s^1$ and not $3d^9 4s^2$.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion. (1)

14. (d) *o*-nitrophenol is more volatile due to intramolecular hydrogen bonding, while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



o-nitrophenol (intramolecular H-bonding)



p-nitrophenol (intermolecular H-bonding) (1)

15. (a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion.

The C—O bond is carbonyl group composed of one sigma and one pi bond. The carbon in carbonyl group is sp^2 -hybridised. Therefore, three bonds in the carbonyl carbon are planar. (1)

16. (c) Carbocation intermediate obtained from $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more stable than that obtained from $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ because it is stabilised by two phenyl groups due to resonance. Therefore, the former bromide is reactive than the latter in $\text{S}_{\text{N}}1$ reactions. Thus, Assertion is correct but Reason is incorrect. (1)

17. (i) Given that, Rate = $k [\text{CH}_3\text{OCH}_3]^{3/2}$
 In this problem, pressure is in bar and time is in minutes. So, the unit of rate = bar min^{-1}
 Also, unit of k = Unit of rate/unit of $[\text{CH}_3\text{OCH}_3]^{3/2}$
 \therefore Unit of k = $\text{bar min}^{-1} / \text{bar}^{3/2} = \text{bar}^{-1/2} \text{min}^{-1}$. (1)

(ii) It is a first order reaction because for 75% completion of reaction two half-lives are required (as, $t_{1/2} = 2 \text{ h}$), which suggests that $t_{1/2}$ is independent of initial concentration. (1)

Or

Let the order of A and B be a and b respectively.

Thus, rate = $k[A]^a[B]^b$

$$r_2 = k[0.3]^a[0.2]^b \quad \dots(i)$$

$$r_3 = k[0.3]^a[0.4]^b \quad \dots(ii)$$

Divide (i) by (ii) to get,

$$\frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{[0.2]^b [0.3]^a}{[0.4]^b [0.3]^a}$$

$$\therefore \frac{1}{4} = \frac{1}{2^b} \Rightarrow 2^2 = 2^b \Rightarrow b = 2$$

$$\text{Similarly, } r_1 = k[0.1]^a [0.1]^b \quad \dots(iii)$$

$$r_4 = k[0.4]^a [0.1]^b \quad \dots(iv)$$

Divide (iii) by (iv) to get,

$$\Rightarrow \frac{6 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{[0.1]^a [0.1]^b}{[0.4]^a [0.1]^b} \Rightarrow \frac{1}{4} = \frac{1}{4^a} \Rightarrow 4^1 = 4^a$$

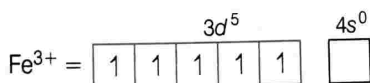
$$\therefore a = 1$$

$$\text{Thus, rate} = k[A][B]^2 \quad (2)$$

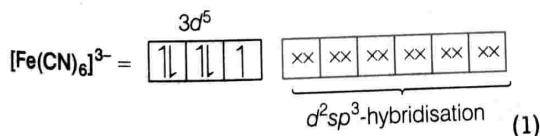
18 $[\text{Fe}(\text{CN})_6]^{3-}$ In this complex, Fe is present as Fe^{3+} .

The electronic configuration of $\text{Fe} = [\text{Ar}] 3d^6 4s^2$

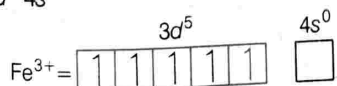
Outer electronic configuration of $\text{Fe}^{3+} = 3d^5 4s^0$



CN^- being a strong field ligand, pairs up the unpaired d -electrons. Thus, low spin complex is formed.



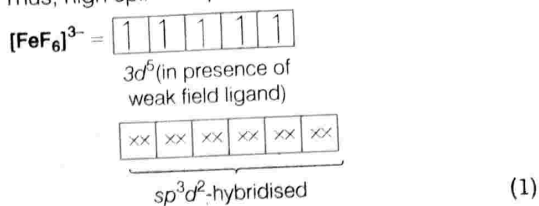
$[\text{FeF}_6]^{3-}$ In this complex, the oxidation state of Fe is +3. Outer electronic configuration of $\text{Fe}^{3+} = 3d^5 4s^0$



F^- is a weak field ligand, so no pairing occurs.

Thus, $3d$ -orbitals are not available to take part in bonding.

Thus, high spin complex is formed.



19. The resistance (R) of a conductor varies directly with length (l) and inversely with area of cross-section (A).

$$\text{i.e. } R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A}$$

$$\text{where, } \rho = \text{resistivity or } \rho = \frac{RA}{l}$$

Conductivity (κ) is the reciprocal of resistivity (ρ).

$$\text{So, } \kappa = \frac{1}{\rho} = \frac{1}{RA/l} = \frac{l}{RA} = \frac{1}{R} \left[\frac{l}{A} \right] \quad (1)$$

$$\kappa = \frac{1}{R} \left[\frac{l}{A} \right] = \frac{1}{R} \cdot G^*$$

$$\text{Here, } G^* = \frac{l}{A} = \text{cell constant}$$

The molar conductivity of a solution is related to its conductivity by the following relation.

$$\Lambda_m = \frac{\kappa \times 1000}{M} \text{ S cm}^2 \text{ mol}^{-1}$$

where, M = molarity

Thus, the cell constant, resistance of the solution in the cell and conductivity of the solution are related by the following expression :

$$\Lambda_m = \frac{\frac{G^*}{R} \times 1000}{M} \quad (1)$$

Or

$$\text{Given, } \Lambda_m = 138.9 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Molarity, } M = 1.5 \text{ M} = 1.5 \text{ mol L}^{-1} \Rightarrow \kappa = ?$$

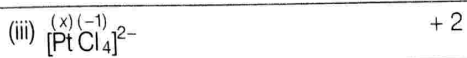
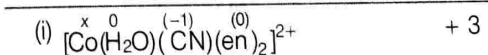
$$\text{We know that, } \Lambda_m = \frac{\kappa \times 1000}{M}$$

$$138.9 \text{ S cm}^2 \text{ mol}^{-1} = \frac{\kappa \times 1000}{1.5 \text{ mol cm}^{-3}}$$

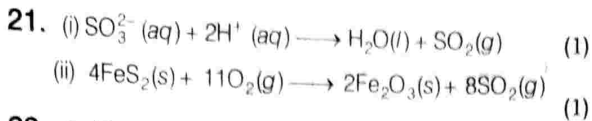
$$\kappa = \frac{138.9 \text{ S cm}^2 \text{ mol}^{-1} \times 1.5 \text{ mol cm}^{-3}}{1000}$$

$$= 0.208 \text{ S cm}^{-1} \quad (2)$$

20. Coordination entities Oxidation state of metal

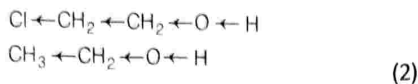


[4 × 1/2 = 2]



22. 2-chloroethanol is more acidic than ethanol. Due to $-I$ -effect (electron withdrawing group) of the Cl-atom, electron density in O—H bond decreases. So, O—H bond of 2-chloroethanol becomes weaker than O—H bond of ethanol.

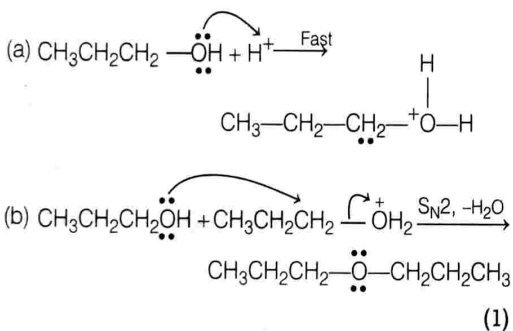
Thus, 2-chloroethanol is more acidic than ethanol.



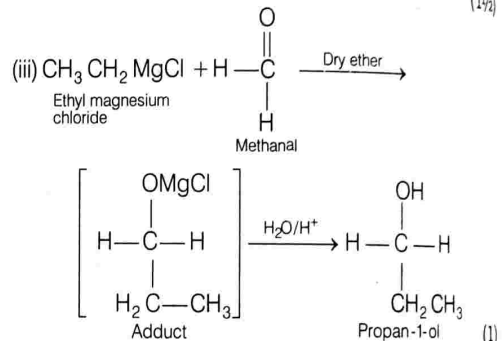
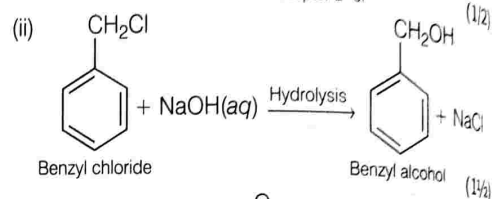
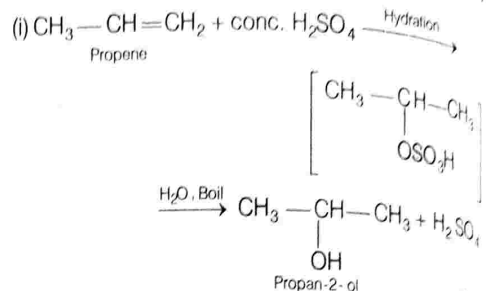
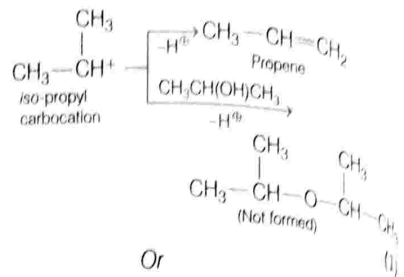
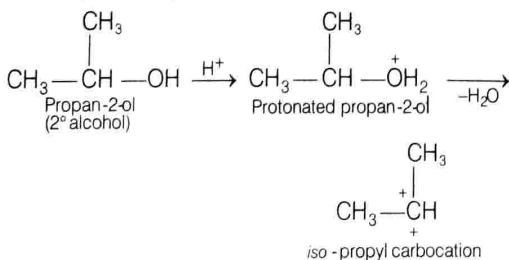
23. (i) Due to lanthanoid contraction, the atomic radii of the second and third rows of transition elements is almost same. So, they resemble each other much more as compared to first row elements and show similar characteristics. (1)

(ii) It is because of the presence of unpaired electrons in chromium which allows d - d overlap in addition to metallic bonding. Zinc does not have any unpaired electron in it. (1)

24. (i) Acid catalysed dehydration of 1° alcohols to ethers occur by $\text{S}_{\text{N}}2$ reaction involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule.



Under these conditions, 2° and 3° alcohols, however give alkenes rather than ethers. The reason is that, due to steric hindrance, nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur. Instead protonated 2° and 3° alcohols lose a water molecule to form stable 2° and 3° carbocations. These carbocations prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.



25. (i) When electric current is passed through a sol, its particles migrate towards either of the electrodes depending upon the nature of charge on the colloidal particles. This phenomenon is called electrophoresis. (1)

(ii) When a beam of light is passed through a sol, the colloidal particles scatter light in all directions making its path visible. This scattering of light by the colloidal particles is known as Tyndall effect. (1)

26. (i) In o - or p -amino benzoic acids, the lone pair of electrons on the NH_2 group is donated towards the benzene ring. As a result, acidic character of $-\text{COOH}$ group and basic character of $-\text{NH}_2$ group decreases. Therefore, the weakly acidic $-\text{COOH}$ group cannot transfer H^+ ion to the weakly basic $-\text{NH}_2$ group. Thus, o - or p -amino benzoic acids do not exist as Zwitter ions.

29. 0.15 M solution means 0.15 mole of benzoic acid are present in 1 L or 1000 mL of solution.

Molar mass of benzoic acid (C_6H_5COOH)

$$= 6 \times 12 + 5 \times 1 + 1 \times 12 + 2 \times 16 + 1 = 122 \text{ g mol}^{-1}$$

$$\therefore 1 \text{ mole of benzoic acid} = 122 \text{ g}$$

$$\therefore 0.15 \text{ mole of benzoic acid} = 0.15 \times 122 = 18.3 \text{ g}$$

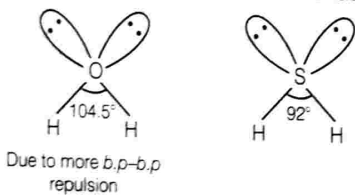
$$\therefore 0.15 \text{ mole are present in } 1000 \text{ mL of solution.}$$

$$\text{So, } 1000 \text{ mL of solution contains benzoic acid} = 18.3 \text{ g}$$

$$\therefore 250 \text{ mL of solution contains benzoic acid}$$

$$= \frac{18.3 \times 250}{1000} = 4.575 \text{ g} \quad (3)$$

30. (i) Existence of ClF_3 and $ClCl_3$ can be explained on the basis of size of central atom. As fluorine is more electronegative as compared to chlorine and has smaller size, thus, one large Cl-atom can accommodate three smaller F atoms but reverse is not true. (1)
- (ii) Bond angle of H_2O ($H-O-H = 104.5^\circ$) is larger than that of H_2S ($H-S-H = 92^\circ$). Oxygen is more electronegative than sulphur, therefore bond pair electrons of $O-H$ bond will be closer to oxygen and there will be more bond pair-bond pair repulsion between bond pairs of two $O-H$ bonds.



- (iii) Fluorine atom is smaller in size, so six F^- ions can surround a sulphur atom. The case is not so with chlorine atom due to its large size. So, SF_6 is known but SCl_6 is not known due to interionic repulsion between large Cl^- ions. (1)

31. Degree of unsaturation also known as double bond equivalent is calculated by using the formula.

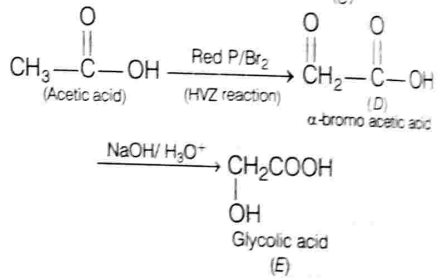
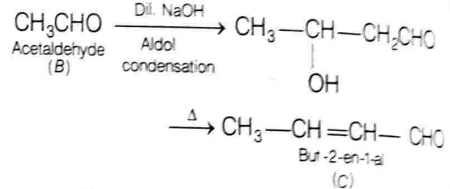
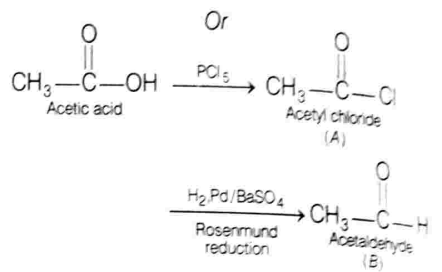
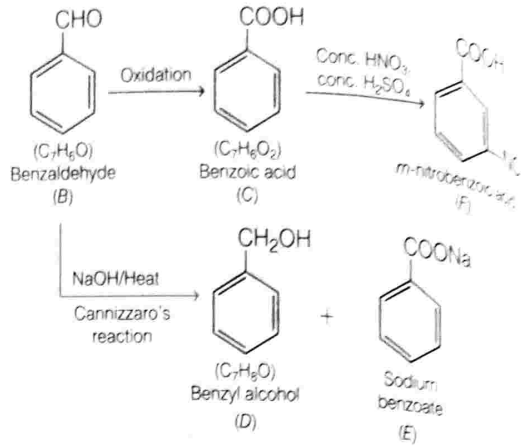
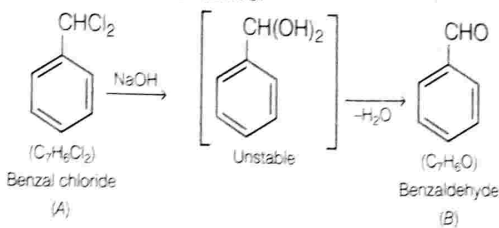
$$\Delta BE = C - \frac{H}{2} - \frac{X}{2} + \frac{N}{2} + 1$$

where, X is number of halogens.

The molecular formula of the compound given is $C_7H_6Cl_2$.

Thus, the degree of unsaturation is 4 (i.e. one ring and 3 double bonds are present). Two Cl atoms are replaced by OH on hydrolysis. Thus, both Cl atom are at same positions. (2)

The reactions are as follows:



Thus, A = Acetyl chloride ; B = Acetaldehyde
C = But-2-en-1-al
D = α -bromoacetic acid
E = Glycolic acid

32. (i) Cell constant, $G^* = \text{conductivity} \times \text{resistance}$

$$G^* = \kappa \times R = 1.29 \text{ Sm}^{-1} \times 100.0$$

$$= 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1} \quad (1)$$

Conductivity (κ) of 0.02 M KCl solution

$$= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520 \Omega} = 0.248 \text{ Sm}^{-1} \quad (1)$$

Concentration = 0.02 M

$$= 1000 \times 0.02 \text{ mol m}^{-3} = 20 \text{ mol m}^{-3}$$

Molar conductivity, (Λ_m)

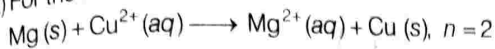
$$= \frac{\kappa}{C} = \frac{0.248 \text{ S m}^{-1}}{20 \text{ mol m}^{-3}} = 124 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1} \quad (1)$$

(ii) From Kohlrausch's law,

$$\begin{aligned}\lambda_{(\text{NH}_4\text{OH})} &= \lambda_{\text{NH}_4\text{Cl}} + (\lambda_{\text{NaOH}} - \lambda_{\text{NaCl}}) \\ &= 129.8 + (217.4 - 108.45) \\ &= 238.75 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}\quad (1)$$

Or

(i) (a) For the reaction,



$$E_{\text{cell}}^{\circ} = +2.71 \text{ V}, 1F = 96500 \text{ C mol}^{-1} \quad (\text{given})$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \quad (1)$$

$$= -2 \times 96500 \times 2.71 = -523030 \text{ J mol}^{-1}$$

$$= -523.030 \text{ kJ mol}^{-1} \quad (1)$$

(b) The standard electrode potential of hydrogen electrode is zero. (1)

(ii) The order in which the metals displace each other from their salts is Mg, Al, Zn, Fe, and Cu. (2)

33. (i) Separation of Zr and Hf are quite difficult because of lanthanoid contraction. Due to lanthanoid contraction, they have almost same size and thus, similar chemical properties. That's why, it is very difficult to separate them by chemical methods. (1)

(ii) The electronic configuration of given ion are :
 $\text{Ti}^{3+} = 3d^1$, $\text{V}^{3+} = 3d^2$, $\text{Fe}^{2+} = 3d^6$, $\text{Zn}^{2+} = 3d^{10}$

$\therefore \text{Fe}^{2+}$ has maximum number of unpaired electrons. (1)

(iii) The two consequences of lanthanoid contraction are:

(a) **Basic character of oxides and hydroxides**

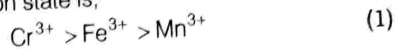
Due to the lanthanoid contraction, the covalent nature of Ln—OH bond increases. So, the basic character of oxides and hydroxides decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. (1)

(b) **Similarity in the size or radii of elements of second and third transition series**

Because of lanthanoid contraction, elements which follow the third transition series are considerably smaller than that would otherwise be expected. The normal size increases from $\text{Sc} \rightarrow \text{Y} \rightarrow \text{La}$ but their trend disappears after lanthanoids. Thus, pairs of elements such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size. Due to almost similar size, such pairs have very similar properties which make their separation difficult and, hence they are also called chemical twin. (1)

(iv) $E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^{\circ}$ is negative (-0.4 V). It shows the stability of Cr^{3+} ions, i.e. Cr^{3+} in solution cannot be reduced to Cr^{2+} ions. Further, Mn^{3+} has higher positive value of E° . So, it is easily converted to Mn^{2+} as compared to the conversion of Fe^{3+} to Fe^{2+} . Hence, Cr^{3+} is the most stable, Mn^{3+} is least stable, while Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+} .

Thus, the correct increasing order of stability of +3 oxidation state is,



Or

(i) +4 oxidation state exists in $_{58}\text{Ce}$, $_{59}\text{Pr}$, $_{60}\text{Nd}$, $_{65}\text{Tb}$ and $_{66}\text{Dy}$. (1/2)

+2 oxidation state exists in $_{60}\text{Nd}$, $_{62}\text{Sm}$, $_{63}\text{Eu}$, $_{69}\text{Tm}$ and $_{70}\text{Yb}$. (1/2)

Generally, +2 oxidation state is exhibited by the elements with configuration $5d^0 6s^2$, so that two electrons may be easily lost. Similarly, +4 oxidation state is shown by the element which after losing four electrons acquire configuration either close to $4f^0$ or $4f^7$. (1)

(ii) (a) As oxidation number (or oxidation state) of an element increases, the acidic character of oxide increases. In general, the oxides in lower oxidation states of metals are basic and in their higher oxidation states they are acidic, whereas in the intermediate oxidation state, the oxides are amphoteric.

In lower oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. In higher oxidation state, valence electrons are involved in bonding and, hence not available for donation. Instead, their effective nuclear charge is high and, hence they behave as acids. (1)

(b) Oxygen and fluorine both have small size and high value of electronegativity. So, they can oxidise the metal to their highest oxidation state. (1)

(c) Due to the high electronegativity and multiple bond formation of oxygen atom, metal atom exhibits highest oxidation state in oxoanions, e.g. Cr in $\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-} has an oxidation state of +6. (1)