MM: 70

Time: 3 hours

### **General Instructions:**

## Read the following instructions carefully.

- a) There are 35 questions in this question paper with internal choice.
- b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
- c) SECTION B consists of 7 very short answer questions carrying 2 marks each.
- d) SECTION C consists of 5 short answer questions carrying 3 marks each.
- e) SECTION D consists of 2 case-based questions carrying 4 marks each.
- f) SECTION E consists of 3 long answer questions carrying 5 marks each.
- g) All questions are compulsory.
- h) Use of log tables and calculators is not allowed

#### Section A

1.  $(y)H_3\overset{\oplus}{N} \overset{\oplus}{N}H_3(z)$   $COOH \overset{(x)}{(x)}$ 

[1]

The order of decreasing acidity of these acidic sites is:

a) 
$$z > x > y$$

b) 
$$x > y > z$$

c) 
$$x > z > y$$

d) 
$$y > x > z$$

- 2. In context with the transition elements, which of the following statements is **incorrect**?
- [1]

- a) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.
- b) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
- c) Once the d<sup>5</sup> configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
- d) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.
- 3. When ethylene glycol is heated with oxalic acid in the presence of cone. H<sub>2</sub>SO<sub>4</sub>, the [1] product formed is:

- Which of the following expressions is correct for the rate of reaction given below? 4. [1]  $5Br^{-}(aq) + BrO^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_{2}(aq) + 3H_{2}O(1)$ 
  - a)  $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[H^+]}{\Delta t}$

b)  $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$ 

c)  $\frac{\Delta[Br^-]}{\Delta t} = 5 \frac{\Delta[H^*]}{\Delta t}$ 

- d)  $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5} \frac{\Delta[H']}{\Delta t}$
- Give the products of the reaction 5.

[1]

$$PhC \equiv CMe \xrightarrow{H_3O^+, Hg^{2+}} ?$$

a) PhCH2CH2CHO

b) PhCOCH2CH3

c) PhCOCOMe

- d) PhCH2COCH3
- 6. Standard reduction electrode potentials of three metals A, B and C are +0.5 V, -3.0 [1] V and -1.2 V respectively. The reducing power of these metals are:
  - a) C > B > A

b) B > C > A

c) A > B > C

- d) A > C > B
- 7. In which of the following compounds transition metal has zero oxidation state?
- [1]

a) NH2 · NH2

b) NOClO<sub>4</sub>

c) [Fe(CO)5]

- d) CrO5
- 8. The decreasing order of basicity of following aniline derivatives is

[1]

(P)

(Q)

(R)



a) S > R > P > Q

b) Q > S > R > P

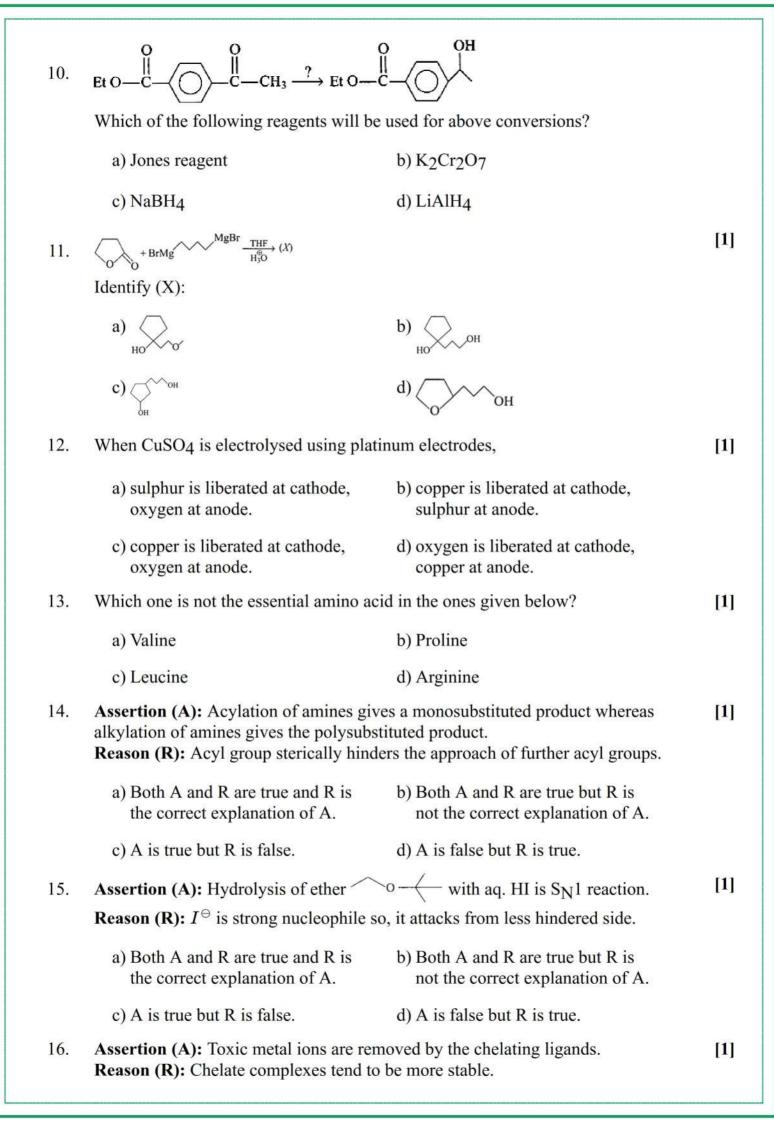
c) P > Q > R > S

- d) S > R > O > P
- The rate expression for a reaction is  $-\frac{dc}{dt} = \frac{\alpha c}{1+\beta c}$  ( $\alpha$  and  $\beta > 0$ ). The half life of the 9. [1] reaction can be given by:
  - a)  $\frac{1}{\alpha}$  In 2 +  $\beta c_0$

b) In 2 +  $\frac{\beta c_0}{2}$ 

c)  $\frac{1}{\alpha} \ln 2 + \frac{\beta c_0}{2\alpha}$ 

d) In 2 +  $\frac{\beta c_0}{2\alpha}$ 



	<ul><li>a) Both A and R are true and R is the correct explanation of A.</li></ul>	b) Both A and R are true but R is not the correct explanation of A.	
	c) A is true but R is false.	d) A is false but R is true.	
17.	The compound which forms acetaldehyde when heated with dilute NaOH is:		
	a) 1, 2 dichloroethane	b) 1, 1, 1 trichloroethane	
	c) 1 chloroethane	d) 1, 1 dichloroethane	
18.	Assertion (A): FeCl <sub>3</sub> reacts with KCNS to give blood red colouration.  Reason (R): FeCl <sub>3</sub> reacts with KCNS to form potassium ferro-ferricyanide.		
	a) Both A and R are true and R is the correct explanation of A.	b) Both A and R are true but R is not the correct explanation of A.	
	c) A is true but R is false.	d) A is false but R is true.	
	Sec	tion B	
19.	With the help of provided energy profile diagram, explain the physical significance of energy of activation $(E_a)$ in chemical reactions.		
20.	Name a ligand which is bidentate and give an example of the complex formed by this ligand.		
		OR	
	CuSO <sub>4</sub> .5H <sub>2</sub> O is blue in colour while CuSO <sub>4</sub> is colourless. Why?		
21.	Conductivity of $2.5 \times 10^{-4}$ M methanoic acid is $5.25 \times 10^{-5}$ S cm <sup>-1</sup> , Calculate its molar conductivity and degree of dissociation. Given: $\lambda^{\circ}$ (H <sup>+</sup> ) = 349.5 S cm <sup>2</sup> mol <sup>-1</sup> and $\lambda^{\circ}$ (HCOO <sup>-</sup> ) = 50.5 S cm <sup>2</sup> mol <sup>-1</sup> .		
		OR	
	Three electrolytic cells A, B, C containing solutions of ZnSO <sub>4</sub> , AgNO <sub>3</sub> and Cult respectively are connected in series. A steady current of 1.5 amperes was passed them until 1.45 g of silver deposited at the cathode of cell B. How long did the of flow? What mass of copper and zinc were deposited?		
22.	How many moles of mercury will be produced by electrolysing 10 M $Hg(NO_3)_2$ solution with a current of 2.00 A for three hours? [ $Hg(NO_3)_2 = 200.6gmol^{-1}$ ]		[2]
23.	What happens when pressure greater that solution separated by a semi permeable in		[2]
24.	Write the products of the following react	tions:	[2]
	H peroxide		

	ii. $CH_3 - CH_2 - CH = CH_2 + HC1$				
25.	Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis i. 1-propoxypropane ii. Ethoxybenzene iii. 2-Methoxy-20methylpropane iv. 1-Methoxyethane	[2]			
	Section C				
26.	Complete the following equations and mention the name of the reactions: a. RNH <sub>2</sub> + CHCl <sub>3</sub> +3KOH → b. RCONH <sub>2</sub> + Br <sub>2</sub> +4NaOH →	[3]			
27.	Formulate the galvanic cell in which the following reaction takes place. $Zn(s) + 2Ag^{+}$ (aq) $\rightarrow Zn^{2}$ +(aq) + $2Ag(s)$ ; $E^{0}(Zn^{2+} Zn) = -0.76V$ and $E^{0}(Ag^{+} Ag) = 0.80 \text{ V}$	[3]			
	<ul><li>i. Which one of its electrodes is negatively charged?</li><li>ii. The reaction taking place at each of its electrode.</li><li>iii. The carriers of current within this cell.</li></ul>				
28.	<ul><li>a. Write the steps in valued in the preparation of</li><li>i. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> from Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub></li></ul>	[3]			
	ii. KMnO <sub>4</sub> from MnO <sub>2</sub>				
	<ul> <li>b. What is meant by actinoid contraction? .Why chemistry of actinoids are difficult to study.</li> </ul>				
29.	A hydrocarbon C <sub>5</sub> H <sub>10</sub> does not react with chlorine in dark but gives a single monochloro compound C <sub>5</sub> H <sub>9</sub> Cl in bright sunlight. Identify the hydrocarbon.	[3]			
	OR				
	How can you convert the following:				
	i. Sodium phenoxide to o-hydroxybenzoic acid				
	ii. Acetone to propene				
	iii. Phenol to chlorobenzene				
30.	For a reaction: $H_2 + Cl_2 \xrightarrow{hv} 2HCl$ Rate = k	[3]			
	<ul><li>i. Write the order and molecularity of this reaction.</li><li>ii. Write the unit of k.</li></ul>				
	Section D				
31.	Read the text carefully and answer the questions:	[4]			
	When a solution of an $\alpha$ -amino acid is placed in an electric field depending on the pH of the medium, the following three cases may happen.				

$$H_2NCHRCOO^- \underset{II}{\overset{H^+}{\longleftrightarrow}} H_3 \overset{+}{\overset{+}{N}} CHRCOO^- \underset{OH^-}{\overset{H^+}{\longleftrightarrow}} H_3 \overset{+}{\overset{+}{N}} CHRCOOH$$

- i. In alkaline solution,  $\alpha$ -amino acids exist as anion II, and there is a net migration of amino acids towards the anode.
- ii. In acidic solution,  $\alpha$ -amino acids exist as cation III, and there is a net migration of amino acid towards the cathode.
- iii. If II and III are exactly balanced there is no net migration; under such conditions, anyone molecule exists as a positive ion and as a negative ion for exactly the same amount of time, and any small movement in the direction of one electrode is subsequently canceled by an equal movement back toward the other electrode. The pH of the solution in which particular amino acid does not migrate under the influence of an electric field is called the isoelectric point of that amino acid.
- (i) In aqueous solutions, amino acids mostly exist as
- (ii) Amino acids are least soluble
- (iii) The p $K_{a_1}$  and p $K_{a_2}$  of an amino acid are 2.3 and 9.7 respectively. The isoelectric point of the amino acid.

OR

Arrange in order of increasing acid strengths.

# 32. Read the text carefully and answer the questions:

[4]

Valence Bond Theory (VBT) According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar. the geometry of a complex is predicted from the knowledge of its magnetic behaviour on the basis of the valence bond theory. The magnetic moment of coordination compounds can be measured by magnetic susceptibility experiments. The results can be used to obtain information about the number of unpaired electrons and hence structures adopted by metal complexes. VB theory suffers from the shortcomings, It involves a number of assumptions, It does not give a quantitative interpretation of magnetic data, It does not explain the colour exhibited by coordination compounds, It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

- (i) CO is a stronger complexing reagent than NH3.
- (ii) The molecular shape of Ni(CO)4 is not the same as that of [Ni(CN)4]<sup>2-</sup>. Give reason.
- (iii) Write the hybridization and magnetic behaviour of the complex [Ni(CO)4]. (At.no. of Ni = 28)

In the diamagnetic octahedral complex,  $[Co(NH_3)_6]^{3+}$ , the oxidation state of cobalt ion?

#### Section E

- Arrange the following compounds in increasing order of their property as indicated: [5] 33.
  - i. Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)
  - ii. CH3CH2CH(Br)COOH, CH3CH(Br)CH2COOH, CH3CH2CH2COOH (acid strength)
  - iii. Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

OR

Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

- i. CH<sub>3</sub>CO(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>
- ii. CH3CH2CHBrCH2(CH3)CHO
- iii. CH3(CH2)5CHO
- iv. Ph CH = CH CHO

vi. PhCOPh

- i. A solution contains 5.85 g NaCl (Molar mass = 58.5 g mol<sup>-1</sup>) per litre of 34. solution. It has an osmotic pressure of 4.75 atm at 27°C. Calculate the degree of dissociation of NaCl in this solution (Given:  $R = 0.082 L atm K^{-1} mol^{-1}$ )
  - ii. State Henry's law. Why is air diluted with helium in the tanks used by scuba divers?

OR

What is the advantage of osmotic pressure method over the elevation of boiling point method for determining molecular mass of solute?

35. Answer the following questions:

[5]

[5]

- Account for the following: There are irregularities in the electronic configuration of (i) actinoids.
- (ii) Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does the preparation of aryl iodides requires the presence of an oxidising agent?
- (iii) Give the IUPAC name of the given ether.

$$C_2H_5OCH_2 - \underset{CH_3}{CH_5OCH_2} - CH - CH_3$$

- (iv) Why Amines are basic substances while amides are neutral?
- (v) Write the products obtained after hydrolysis of lactose.

## SOLUTION

#### Section A

1. **(b)** 
$$x > y > z$$

**Explanation:** 

2. (b) In the highest oxidation states, the transition metal show basic character and form cationic complexes.

**Explanation:** In the highest oxidation states, the transition metal show basic character and form cationic complexes.

Explanation: 
$$\begin{array}{c|c}
OH & HO \\
OH & HO
\end{array}$$

4. (a) 
$$\frac{\Delta[\mathrm{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\mathrm{H}^+]}{\Delta t}$$

Explanation: For the equation

$$5Br^{-}(aq) + BrO^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_{2}(aq) + 3H_{2}O(1)$$

Rate law expression can be written as

Rate law expression can be written as
$$\frac{-1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{-1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{+1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{-5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

(b) PhCOCH<sub>2</sub>CH<sub>3</sub>

**Explanation:** Hydration of given alkyne will occur according to Markovnikoff's rule leading to the formation of enol which will tautomerise to give keto form.

The general reaction of alkyne hydrations shown below:

$$R-C \equiv CH \xrightarrow{\begin{array}{c} H_2O, \ H_2SO_4 \\ HgSO_4 \end{array}} R-C = CH \xrightarrow{\begin{array}{c} OH \ H \\ I = I \\ Enol \end{array}} R-C - CH \xrightarrow{\begin{array}{c} O \ H \\ I = I \\ Ketone \end{array}} R$$

Same reaction will occur with

$$PhC \equiv CMe \xrightarrow{H_3O^+, Hg^{2+}} ? PhC(OH) = CHCH_3 \Leftrightarrow PhCOCH_2CH_3$$
 .

6. **(b)** B > C > A

**Explanation:** More is  $E_{RP}^{\circ}$  more is oxidising power or lesser is reducing power.

7. (c) [Fe(CO)<sub>5</sub>]

**Explanation:** In iron carbonyl, the oxidation number of 'Fe' is zero.

$$[Fe(CO)_5] \longrightarrow x + 5 \times 0 = 0 \Rightarrow x = 0$$

8. (a) S > R > P > Q

**Explanation:** The para-substituted anilines are more basic than ortho-substituted aniline because of the para effect.

Aniline is more basic than ortho-substituted aniline. Between ortho and meta basicity can be compared by +M, -M, +I and -I. +M and -M will not operate at the meta position.

9. (c)  $\frac{1}{\alpha} \ln 2 + \frac{\beta c_0}{2\alpha}$ 

**Explanation:**  $\frac{1}{\alpha} \ln 2 + \frac{\beta c_0}{2\alpha}$ 

10. (c) NaBH4

Explanation: NaBH<sub>4</sub> is a selective reducing agent for carbonyl compounds.

12. (c) copper is liberated at cathode, oxygen at anode.

**Explanation:** 
$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : 
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

At anode: 
$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

13. **(b)** Proline

**Explanation:** Those amino acids which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids. Proline is not an essential amino acid.

14. (c) A is true but R is false.

**Explanation:** Amines on acetylation give monosubstituted product, while on alkylation gives polysubstituted product as well.

15. **(b)** Both A and R are true but R is not the correct explanation of A.

Explanation: Both A and R are true but R is not the correct explanation of A.

16. (a) Both A and R are true and R is the correct explanation of A.

**Explanation:** When a solution of the chelating ligand is added to a solution containing toxic metals ligands chelates the metal ions by the formation of a stable complex.

17. (d) 1, 1 dichloroethane

**Explanation:**  $CH_3CHCl_2 + OH^- \rightarrow CH_3CH(OH)_2 \rightarrow CH_3CHO + H_2O$ 

Gem diols like (CH<sub>3</sub>CH(OH)<sub>2</sub>) are generally not stable. The 2 -OH group attached to the same C removes H<sub>2</sub>O and forms carbonyl compounds.

18. (c) A is true but R is false.

Explanation: A is true but R is false.

#### Section B

19. The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold value is called as an activation energy.

Activation energy  $(E_a)$  = Threshold energy  $(E_t)$  - Average K.E. of the reactants  $(E_R)$ 

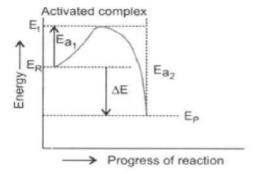
Activation energy of a chemical reaction can be illustrated by a potential energy diagram.

Here,  $E_R$  = energy of reactant.

 $E_p$  = energy of product.

 $E_{a1}$  = activation energy for forward reaction

 $E_{a2}$  = activation energy for backward reaction.



E, Threshold energy

$$\Delta E$$
 = Heat of reaction=  $E_P$  -  $E_R$ 

Each reaction has a specific value of activation energy. If the value of activation energy is less for a particular reaction, large number of molecules can attain this energy and, therefore, fraction of effective collisions will be large and the rate of reaction will be high. On the other hand, if activation energy is high, lesser number of molecules will be able to attain the same, thereby decreasing the fraction of effective collisions and, therefore, rate of reaction will be slow. It is the existence of activation energy barrier that accounts for kinetic stability of fuel. Such energy barriers are blissful for existence of life on earth otherwise fuels or explosives might have burst under ordinary conditions. The substance called as catalyst can be used to alter the activation energy of the reaction.

20. Ethylene diamine (en) is bidentate ligand [Co(en)<sub>3</sub>]<sup>3+</sup>. Its IUPAC name is tris (ethylene diamine) cobalt (III) ion.

OR

In CuSO<sub>4.5</sub>H<sub>2</sub>O, water acts as a ligand. As a result, it causes crystal field splitting. Hence, the d-d transition of the electron is possible in CuSO<sub>4.5</sub>H<sub>2</sub>O and shows blue colour. In the anhydrous CuSO<sub>4</sub> due to the absence of water (ligand), crystal field splitting is not possible and hence no d-d transitions of electron and no colour imparted.

21. Molar conductivity of  $2.5 \times 10^{-4}$  M solution is

$$\begin{split} &\Lambda_{\rm m}^C = \frac{\kappa \times 1000}{M} = \frac{5.25 \times 10^{-5} \times 1000}{2.5 \times 10^{-4}} \\ &\Lambda_{\rm m}^C = 210 {\rm Scm}^2 {\rm mol}^{-1} \\ &\lambda_{\rm m}^{\infty} ({\rm HCOOH}) = \lambda_{\rm (HCOO^-)}^0 + \lambda_{\rm (H^+)}^0 \\ &\lambda_{\rm m}^{\infty} = 50.0 + 349.5 \\ &\lambda_{\rm m}^{\infty} = 399.5 \\ &\lambda_{\rm m}^{\infty} \approx 400 \ {\rm cm}^2 \ {\rm mol}^{-1} \\ &\alpha = = \frac{\Lambda_{\rm m}^c}{\Lambda_{\rm m}^{\infty}} = \frac{210}{400} \\ &\alpha = 0.525 \end{split}$$

OR

$$Ag^+ + e^- \rightarrow Ag$$
  
i.e. 108 g of Ag are deposited by 1 F = 96500 C  
1.45 g of Ag will be deposited by =  $\frac{96500}{108} \times 1.45C$   
= 1295.6  
 $Q = I \times t$   
 $t = \frac{Q}{I}$   
=  $\frac{1295.6}{1.50} = 863.7S = 14$  min, 24 sec  
 $Cu^{2+} + 2e^- \rightarrow Cu$   
i.e. 2 × 96500  $C$  deposit Cu = 63.5 g  
∴ 1295.6 C will deposit  $Cu = \frac{63.5}{2 \times 96500} \times 1295.6$ 

= 0.426 g 
$$Zn^{2+} + 2e^- \rightarrow Zn$$
 Zn deposited =  $\frac{65.3}{2 \times 96500} \times 1295.6 = 0.438$  g

22. Given, current = 2A,

Time = 
$$3h = 3 \times 60 \times 60s$$

$$m = Zlt = \frac{E}{96500}It$$

$$= \frac{200.6 \times 2 \times 3 \times 60 \times 60}{2 \times 96500}$$

= 22.45 g

Number of moles =  $\frac{22.45}{200.6}$  = 0.112 mol

23. Reverse osmosis occurs i.e. net flow of the solvent is from solution to solvent. Here the solvent molecules from the solution side would move into pure solvent through semipermeable membrane.

24. i. 
$$\stackrel{\text{H}}{\longrightarrow}$$
  $\stackrel{\text{peroxide}}{\longrightarrow}$   $C_6H_5$  -  $CH_2$  -  $CH_2Br$ 

ii. CH<sub>3</sub> - CH<sub>2</sub> - CH = CH<sub>2</sub> + HCl  $\rightarrow$  CH<sub>3</sub> - CH<sub>2</sub> - CHCl-CH<sub>3</sub>

25. i.  $CH_3-CH_2-CH_2-ONa+CH_3CH_2CH_2I \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3+NaI_{1-Propoxypropane}$ 

ii. 
$$ONa \rightarrow C_2H_5$$
 +  $C_2H_5I \rightarrow OC_2H_5$  + NaI

iii. 
$$CH_3-igcup_{CH_3}^{CH_3}-ONa+CH_3I o CH_3-igcup_{CH_3}^{CH_3}-OCH_3+NaI$$

iv. 
$$CH_3CH_2ONa + CH_3I \rightarrow CH_3XH_2OCH_3 + NaI$$

#### **Section C**

26. i. Carbylamine reaction

$$RNH_2 + CHCL_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$$

ii. Hoffmann bromamide degradation reaction

$$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

27. The cell reaction is  $Zn(s) + 2Ag^{+}(aq) \rightleftharpoons Zn^{2+}(aq) + 2Ag(s)$ .

The cell is represented as  $Zn(s)\left|Zn^{2+}(aq)\right|Ag^{+}(aq)\left|Ag(s)\right|$ ;  $E^{O}\left(Zn^{2+}|Zn\right)$  = -0.76V and  $E^{O}\left(Ag^{+}|Ag\right)$  = 0.80 V.

- i. Since zinc (Zn) is more reactive than silver (Ag). So, Zn electrode is negatively charged.
- ii. At anode : Oxidation will takes place;  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$  (oxidation)

At cathode: Reduction will takes place;  $Ag^+(aq) + e^- \rightarrow Ag(s)$  (reduction)

- iii. Ions are the carriers of current within the cell.
- 28. a. i. Sodium dichromate is more soluble than potassium dichromate. The latter is, therefore, prepared by treating the solution of sodium dichromate with potassium chloride. Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2KCl → K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2NaCl
  - ii. Commercially it is prepared by the alkaline oxidative fusion of MnO<sub>2</sub> followed by the electrolytic oxidation of manganate (VI).

electrolytic oxidation of manganate (VI).

$$MnO_2 \xrightarrow{fused \ with \ KOH \ and \ oxidised \ by \ KnO_3} MnO_4^{2-}$$
 $MnO_4^{2-} \xrightarrow{electrolytic \ oxidation} MnO_4^{-}$ 

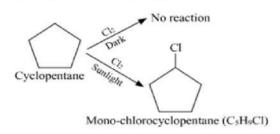
b. The decrease in atomic and ionic size with the increase in atomic number in Actinoids is called actinoid contraction. The actinoids are radioactive elements and the earlier members

have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z = 103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

29. A hydrocarbon with the molecular formula, C<sub>5</sub>H<sub>10</sub> belongs to the group with a general molecular formula C<sub>n</sub>H<sub>2n</sub>. Therefore, it may either be an alkene or a cycloalkane. Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane. Further, the hydrocarbon gives a single monochloro compound, C<sub>5</sub>H<sub>9</sub>Cl by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H-atoms that are all equivalent. Also, as all H-atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.



Cyclopentane (C<sub>5</sub>H<sub>10</sub>) The reactions involved in the question are:



OR

i. Conversion of Sodium phenoxide to o-hydroxybenzoic acid involve following step:

ii. Conversion of Acetone to propene involve following step:

$$CH_3$$
  $C = O$   $(H)$   $CH_3$   $CHOH$   $CH_3$   $CHOH$   $CH_3$   $CHOH$   $CH_3$   $CHOH$   $CH_3$   $CH_3$   $CH_4$   $CH_5$   $CH_5$   $CH_5$   $CH_5$   $CH_7$   $CH_8$   $CH_8$   $CH_8$   $CH_8$   $CH_9$   $CH_9$ 

iii. Conversion of Phenol to chlorobenzene involve following steps:

30. i. For a reaction,  $H_2 + Cl_2 \xrightarrow{hv} 2HCl$ 

Rate= k, suggests that the reaction is of zero order. Further, the molecularity of a given reaction is 2 as two molecules are participating in the reaction.

Hence, order = zero and molecularity = two.

ii. The unit of k for zero order reaction is equal to the rate of a reaction which is mol  $L^{-1}s^{-1}$ . Hence, the unit of k for the given reaction is mol  $L^{-1}s^{-1}$ .

#### Section D

31. Read the text carefully and answer the questions:

When a solution of an  $\alpha$ -amino acid is placed in an electric field depending on the pH of the medium, the following three cases may happen.

$$H_2NCHRCOO^- \stackrel{H^+}{\longleftrightarrow} H_3 \stackrel{+}{N}CHRCOO^- \stackrel{H^+}{\longleftrightarrow} H_3 \stackrel{+}{N}CHRCOOH$$

i. In alkaline solution,  $\alpha$ -amino acids exist as anion II, and there is a net migration of amino acids towards the anode.

- ii. In acidic solution,  $\alpha$ -amino acids exist as cation III, and there is a net migration of amino acid towards the cathode.
- iii. If II and III are exactly balanced there is no net migration; under such conditions, anyone molecule exists as a positive ion and as a negative ion for exactly the same amount of time, and any small movement in the direction of one electrode is subsequently canceled by an equal movement back toward the other electrode. The pH of the solution in which particular amino acid does not migrate under the influence of an electric field is called the isoelectric point of that amino acid.
- $\stackrel{\text{(i)}}{}{H_3}\stackrel{+}{N}CHRCOO^-$

In aqueous solutions, amino acids mostly exist as zwitterion or dipolar ions.

- (ii) Amino acids are least soluble at their isoelectric points. At a specific pH, called isoelectric point, the positive and negative charges balance each other and the net charge becomes zero. If there is a charge, the amino acid prefers to interact with water, rather than other amino acid molecules, this charge makes it more soluble.
- (iii) Isoelectric point =  $\frac{2.3+9.7}{2}$  = 6

OR

Carboxylic acids are stronger acids than -  $NH_3$ , therefore X is the strongest acid. Since - COOH has -I effect which decreases with distance therefore, effect is more pronounced on Z than on Y. As a result Z is more acidic than Y, therefore, the overall order of increasing acid strength is X > Z > Y.

# 32. Read the text carefully and answer the questions:

Valence Bond Theory (VBT) According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar. the geometry of a complex is predicted from the knowledge of its magnetic behaviour on the basis of the valence bond theory. The magnetic moment of coordination compounds can be measured by magnetic susceptibility experiments. The results can be used to obtain information about the number of unpaired electrons and hence structures adopted by metal complexes. VB theory suffers from the shortcomings, It involves a number of assumptions, It does not give a quantitative interpretation of magnetic data, It does not explain the colour exhibited by coordination compounds, It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

- (i) CO is a stronger complexing ligand than NH3 because it contains both  $\sigma$  and  $\pi$  character and can form a back bond (M  $\rightarrow$  CO) also. Therefore, CO forms a stronger bond with the metal. It is also called a strong field ligand.
- (ii) The molecular shape of [Ni(CO)4] is tetrahedral because this complex nickel involves sp<sup>3</sup> hybridisation. In [Ni(CN)4]<sup>2-</sup>, nickel involves dsp<sup>2</sup> and its shape is square planer.
- (iii)[Ni(CO)] involves sp<sup>3</sup> hybridization of nickel and the complex is tetrahedral. Magnetic behaviour: Diamagnetic.

#### Section E

33. i. When HCN reacts with a compound, the attacking species is a nucleophile, **CN**<sup>-</sup>. Therefore, as the negative charge on the compound increases, its reactivity with HCN decreases. In the given compounds, the +I effect increases as shown below. It can be observed that steric hindrance also increases in the same manner (no of alkyl groups).

$$\begin{array}{c} \text{CH}_{3} \\ \text{H} \\ \text{C} = 0 \end{array} > \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \end{array} = 0 \\ \text{CH}_{3} \\ \text{Acetone} \end{array} > \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \end{array} = \begin{array}{c} \text{CH}$$

Hence, the given compounds can be arranged according to their increasing reactivities toward HCN as: Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetaldehyde

ii. After losing a proton, carboxylic acids gain a negative charge as shown:  $R = COOH \rightarrow R = COO^- + H^+$  Now any group that will belo stabilise

 $R-COOH \rightarrow R-COO^- + H^+$  Now, any group that will help stabilise the negative charge will increase the stability of the carboxylate ion and as a result, will increase the strength of the acid. Thus, groups having +I effect will decrease the strength of the acids and groups having - I effect will increase the strength of the acids. In the given compounds,

-CH3 group has +I effect and Br - group has - I effect. Thus, acids containing **Br** - are stronger. Now, the +I effect of isopropyl group is more than that of n-propyl group. Hence, (CH3)2CHCOOH is a weaker acid than CH3CH2CH2COOH. Also, the -I effect grows weaker as distance increases. Hence, CH3CH(Br)CH2COOH is a weaker acid than CH3CH2CH(Br)COOH. Hence, the strengths of the given acids increase as:

(CH<sub>3</sub>)<sub>2</sub>CHCOOH < CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH < CH<sub>3</sub>CH(Br)CH<sub>2</sub>COOH < CH<sub>3</sub>CH<sub>2</sub>CH(Br)COOH.

iii. As we have seen in the previous case, electron-donating groups decrease the strengths of acids, while electron-withdrawing groups increase the strengths of acids. As methoxy group is an electron-donating group, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Nitro group is an electron-withdrawing group and will increase the strengths of acids. As 3,4-dinitrobenzoic acid contains two nitro groups, it is a slightly stronger acid than 4-nitrobenzoic acid. Hence, the strengths of the given acids increase as: 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

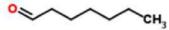
OR

i. CH<sub>3</sub>CO(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>

IUPAC name of compound: Heptan-2-one Common name: Methyl n-propyl ketone ii. CH<sub>3</sub>CH<sub>2</sub>CHBrCH<sub>2</sub>(CH<sub>3</sub>)CHO

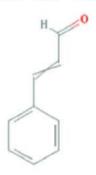
IUPAC name of compound: 4-Bromo-2-methylhaxanal Common name:  $(\gamma$ -Bromo- $\alpha$ -methyl-caproaldehyde)

## iii. CH3(CH2)5CHO



IUPAC name of compound: Heptanal

iv. 
$$Ph - CH = CH - CHO$$

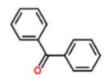


IUPAC name of compound: 3-phenylprop-2-enal

Common name:  $\beta$ -Pheynolacrolein

IUPAC name: Cyclopentanecarbaldehyde

### vi. PhCOPh



IUPAC name: Diphenylmethanone

Common name: Benzophenone

34. i. Given: Weight of NaCl given = 5.85g molecular mass of NaCl = 58.5g/mol

Osmatic pressure = 4.75 atm

Temperature T = 27 C

$$=(27+273) \text{ K}$$

$$= 300 K$$

degree of dissociation of NaCl = ?

We know that,

$$\pi = iCRT, C = \frac{5.85}{58.5 \times 1} M$$

$$4.75 = \frac{i \times 5.85}{58.5/1} \times 0.082 \times 300$$

$$i = \frac{4.75 \times 58.5}{5.85 \times 0.082 \times 300}$$

$$i = 1.93$$

For dissociation, Here n 2

$$i = 1 + \alpha(n - 1)$$

$$1.93 = 1 + (2 - 1)\alpha$$

$$1 + \alpha = 1.93$$

$$\alpha = 1.93 - 1$$

Hence, degree of dissociation of NaCl = 0.93 or 93%

ii. **Henry's law:** At a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

Air diluted with the helium (11% helium, 56.2% nitrogen, and 32.1% oxygen) in the tanks used by scuba divers to avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood because of an increase in pressure underwater and decreasing pressure towards the water surface.

OR

We know that

$$\pi = CRT$$

Where  $\pi$  is the osmotic pressure and R is the gas constant

$$\pi = \frac{n_2}{V}RT$$

Where V is volume of solution 1 litre and containing n<sub>2</sub> moles of solute.

$$\pi V = rac{W_2}{M_2} RT$$

$$M_2 = rac{W_2RT}{\pi V}$$

By the above relation molar mass of solute can be calculated. The osmotic pressure method has the advantage over other method, as pressure measurement is done at room temperature and molarity of the solution is used instead of molality. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecular as they are generally not stable at higher temperatures and polymers have poor solubility.

- 35. Answer the following questions:
  - (i) The irregularities in the electronic configuration of the actinoids is due to extra stability of the f<sup>0</sup>, f<sup>7</sup> and f<sup>14</sup> occupancies of the 5f-orbitals.
  - (ii) Iodination of arenes is reversible in nature due to the formation of HI. To move the reaction forward, an oxidizing agent like HNO3 or HIO4 oxidises HI, thus stabilizing the product formed.

- (iii)The IUPAC name of  $C_2H_5OCH_2-CH-CH_3$  is 1-Ethoxy-2-methylpropane.
- (iv)In amines, alkyl group is electron releasing which increases electron density on nitrogen and making them basic whereas in amides carbonyl group is electron withdrawing, therefore they are neutral.
- (v) Hydrolysis of Lactose gives D-galactose and D-glucose.

Lactose

D-galactose D-glucose