

*Time allowed : 2 hours* 

## General Instructions :

### Read the following instructions carefully.

- 1. There are 12 questions in this question paper with internal choice.
- 2. SECTION A Q. No. 1 to 3 are very short answer questions carrying 2 marks each.
- 3. SECTION B Q. No. 4 to 11 are short answer questions carrying 3 marks each.
- 4. SECTION C Q. No. 12 is case based question carrying 5 marks.
- 5. All questions are compulsory.
- 6. Use of log tables and calculators is not allowed.

# **SECTION - A**

- 1. How are the following conversions carried out? (*any two*) :
  - (i) Ethyl cyanide to ethanoic acid.
  - (ii) Butan-1-ol to butanoic acid.
  - (iii) Benzoic acid to *m*-bromobenzoic acid.
- 2. Two half-reactions of an electrochemical cell are given below :

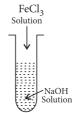
 $\begin{array}{l} {\rm MnO}^-_{4(aq)} + 8{\rm H}^+_{(aq)} + 5e^- \rightarrow {\rm Mn}^{2+}_{(aq)} + 4{\rm H}_2{\rm O}_{(l)}, E^\circ = + \ 1.51{\rm V} \\ {\rm Sn}^{2+}_{(aq)} \rightarrow {\rm Sn}^{4+}_{(aq)} + 2e^-, \ E^\circ = + \ 0.15 {\rm V} \end{array}$ 

Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured.

- 3. Arrange the following compounds as directed :
  - (i) In increasing order of solubility in water :  $(CH_3)_2NH$ ,  $CH_3NH_2$ ,  $C_6H_5NH_2$
  - (ii) In increasing order of boiling point :  $(C_2H_5)_2NH$ ,  $(C_2H_5)_3N$ ,  $C_2H_5NH_2$

# **SECTION - B**

**4.** (i) A colloidal sol is prepared by the given method in figure. What is the charge on hydrated ferric oxide colloidal particles formed in the test tube? How is the sol represented?



- (ii) Give reasons for the following observations :
  - (a) Leather gets hardened after tanning.
  - (b) Lyophilic sol is more stable than lyophobic sol.

Maximum marks: 35

OR

Explain what is observed when :

- (i) A beam of light is passed through a colloidal solution.
- (ii) KCl solution is added to hydrated ferric oxide sol.
- (iii) Electric current is passed through a sol.
- 5. Write the name, the structure and the magnetic behaviour of each one of the following complexes :
  - (i)  $[Pt(NH_3)_2Cl(NO_2)]$
  - (ii)  $[Co(NH_3)_4Cl_2]Cl$
  - (iii) Ni(CO)<sub>4</sub>
  - (At. nos. Co = 27, Ni = 28, Pt = 78)
- 6. (i)  $CH_3CHO + HCHO \xrightarrow{dil. NaOH}_{Heat} A \xrightarrow{HCN}_{H_3O^+} B$ Write the structure of compound *B*.
  - (ii) What is the product of the following reaction?

$$(i)$$
 LiAlH<sub>4</sub>  
 $(ii)$  H<sub>2</sub>O

- 7. (a) Electrolysis of aqueous  $CuCl_2$  solution liberates  $Cl_2$  at anode not  $O_2$ . Why?
  - (b) Suggest a method for the determination of limiting molar conductivity of weak electrolytes.

## OR

When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.

[Specific conductance of 0.1 M KCl =  $1.29 \times 10^{-2}$  ohm<sup>-1</sup> cm<sup>-1</sup>]

8. An organic compound with molecular formula  $C_5H_{10}O$  does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acid. Identify the compound and write all chemical equations for the reactions.

## OR

Arrange the following compounds in an increasing order of their property as indicated :

- (i) Benzoic acid, 3,4-dinitrobenzoic acid, 4-methoxybenzoic acid (acid strength)
- (ii) CH<sub>3</sub>CH<sub>2</sub>CH(Br)COOH, CH<sub>3</sub>CH(Br)CH<sub>2</sub>COOH, (CH<sub>3</sub>)<sub>2</sub>CHCOOH(acid strength)
- **9.** Explain the following :
  - (i) Copper (I) ion is not stable in an aqueous solution.
  - (ii) With same  $(d^4)$  configuration Cr (II) is reducing whereas Mn (III) is oxidising.
  - (iii) Transition metals in general act as good catalysts.
- **10.** (a) Write the chemical reaction of methyl amine with benzoyl chloride and write the IUPAC name of the product obtained.
  - (b) Arrange the following in the increasing order of their  $pK_b$  values :  $C_6H_5NH_2$ ,  $NH_3$ ,  $C_2H_5NH_2$ ,  $(C_2H_5)_2NH$

- **11.** (i)  $Co^{2+}$  is easily oxidised to  $Co^{3+}$  in presence of a strong ligand. Why?
  - (ii) Write the coordination number and oxidation state of platinum in the complex  $[Pt(en)_2Cl_2]$ .

#### OR

- (i) Write the IUPAC name of  $[Cr(NH_3)_6][Co(CN)_6]$ .
- (ii) Give the formula of each of the following coordination entities :
  - (a)  $Co^{3+}$  ion is bound to one  $Cl^{-}$ , one  $NH_3$  molecule and two bidentate ethylene diamine (*en*) molecules.
  - (b)  $Ni^{2+}$  ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behaviour of each of the above coordination entities.

# **SECTION - C**

**12.** Read the passage given below and answer the following questions : The half-life of a reaction is the time required for the concentration of reactant to decrease by half, *i.e.*,

$$[A]_t = \frac{1}{2}[A]$$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k}$$

this means  $t_{1/2}$  is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first order kinetics may be over in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time.

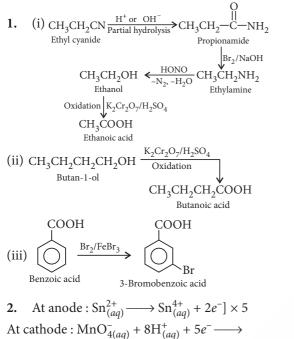
- (a) A first order reaction has a rate constant  $k = 3.01 \times 10^{-3} \text{ s}^{-1}$ . How long will it take to decompose half of the reactant?
- (b) The rate constant for a first order reaction is  $7.0 \times 10^{-4}$  s<sup>-1</sup>. If initial concentration of reactant is 0.080 M, what is the half life of reaction?
- (c) Draw the plot of  $t_{1/2}$  vs initial concentration  $[A]_0$  for a first order reaction.
- (d) Is the half life period of a first oder reactions dependent on temperature?

OR

The rate of a first order reaction is 0.04 mol  $L^{-1}s^{-1}$  after 10 minutes and 0.03 mol  $L^{-1}s^{-1}$  after 20 minutes of initiation. What is the half-life of reaction?

#### **CHEMISTRY - 043**

### **Class 12 - Chemistry**



 $Mn^{2+}_{(aa)} + 4H_2O_{(l)}] \times 2$ 

Net cell reaction :

$$2\mathrm{MnO}_{4(aq)}^{-} + 5\mathrm{Sn}_{(aq)}^{2+} + 16\mathrm{H}_{(aq)}^{+} \longrightarrow 2\mathrm{Mn}_{(aq)}^{2+} + 5\mathrm{Sn}_{(aq)}^{4+} + 8\mathrm{H}_{2}\mathrm{O}_{(l)}$$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.51 \text{ V} - 0.15 \text{ V} = 1.36 \text{ V}$$
Since call potential is positive therefore the reaction is

Since, cell potential is positive therefore the reaction is product favoured.

3. (i)  $C_6H_5NH_2 < (CH_3)_2NH < CH_3NH_2$ 

1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

(ii) 1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen. The degree of association due to hydrogen bonding and hence the boiling point increase as  $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$ 

4. (i)  $\operatorname{FeCl}_3 + \operatorname{NaOH} \longrightarrow \operatorname{Fe}_2\operatorname{O}_3 \cdot x\operatorname{H}_2\operatorname{O} \stackrel{:}{:} \operatorname{OH}^-$ Negatively charged sol

(ii) (a) Animal hides are colloidal in nature. When a hide, which has positively charged particles is soaked in tannin, containing negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather.

(b) Lyophilic sol is more stable than lyophobic sol because it is highly hydrated in the solution.

OR

(i) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

(ii) The positively charged colloidal particles of ferric hydroxide sol get coagulated by the oppositely charged Cl<sup>-</sup> ions provided by KCl.

(iii) On passing electric current through a sol, colloidal particles start moving towards oppositely charged electrodes where they lose their charge and get coagulated (electrophoresis).

5. (i)  $[Pt(NH_3)_2Cl(NO_2)]$ :

Diamminechloridonitrito-N-platinum(II) It is square planar and diamagnetic. (ii)  $[Co(NH_3)_4Cl_2]Cl$ : Tetraamminedichloridocobalt (III) chloride It is octahedral and diamagnetic. (iii)Ni(CO)<sub>4</sub>: Tetracarbonylnickel(0) It is tetrahedral and diamagnetic.

5. (i)  

$$HCHO + H_3CCHO \xrightarrow{\text{NaOH}} HOCH_2 - CH_2CHO \xrightarrow{\Delta}$$
  
 $CH_2 = CH - CH - OH \xleftarrow{\text{HCN}} CH_2 = CH - CHO$   
 $\downarrow H_3O^+$   
 $CH_2 = CH - CH - OH$   
 $(B)$   
 $COH$ 

(ii) LiAlH<sub>4</sub> reduces 
$$C = O \longrightarrow CHOH$$
 group

without affecting the double bond.

$$\xrightarrow[(i) LiAlH]{(i) H_2O} \xrightarrow[(i) HO H]{HO H}$$

7. (a) During electrolysis of a queous  ${\rm CuCl}_2$  following reactions take place

CuCl<sub>2</sub>  $\longrightarrow$  Cu<sup>2+</sup> + 2Cl<sup>-</sup> At cathode Cu<sup>2+</sup> + 2e<sup>-</sup>  $\longrightarrow$  Cu<sub>(s)</sub> At anode two reactions are possible 2Cl<sup>-</sup>  $\longrightarrow$  Cl<sub>2(g)</sub> + 2e<sup>-</sup>; E<sup>o</sup> = 1.36 V H<sub>2</sub>O  $\rightarrow$  2H<sup>+</sup> +  $\frac{1}{2}$ O<sub>2</sub> + 2e<sup>-</sup>; E<sup>o</sup> = 1.23 V

At anode the reaction with lower value of  $E^{\circ}$  should take place and thus water should get oxidised to give

O<sub>2</sub>. But on account of overpotential of oxygen, chlorine is produced at anode.

(b) By using Kohlrausch's law, we can easily calculate the limiting molar conductivity of weak electrolyte.

e.g., 
$$\Lambda_{mCH_{3}COOH}^{\circ} = \lambda_{CH_{3}COO}^{\circ} + \lambda_{H^{+}}^{\circ}$$
  
=  $[\lambda_{CH_{3}COO^{-}}^{\circ} + \lambda_{Na}^{\circ}] + [\lambda_{H^{+}}^{\circ} + \lambda_{Cl^{-}}^{\circ}] - [\lambda_{Na}^{\circ} + \lambda_{Cl^{-}}^{\circ}]$   
=  $\Lambda_{m(CH3COONa)}^{\circ} + \Lambda_{m(HCI)}^{\circ} - \Lambda_{m(NaCI)}^{\circ}$   
 $\mathbf{OR}$   
 $\kappa = 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$   
 $\kappa = \frac{1}{R} \times \text{Cell constant}$   
 $\Rightarrow \text{ Cell constant} = \kappa \times R$   
 $= 1.29 \,\Omega^{-1} \text{ m}^{-1} \times 85 \,\Omega = 109.65 \text{ m}^{-1}$   
For second solution,

$$\kappa = \frac{1}{R} \times \text{Cell constant} = \frac{1}{96 \ \Omega} \times 109.65 \ \text{m}^{-1}$$
$$= 1.142 \ \Omega^{-1} \text{m}^{-1}$$
$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142 \ \Omega^{-1} \text{m}^{-1} \times 1000 \ \text{cm}^3}{0.052 \ \text{mol}}$$
$$\Lambda_m = \frac{1.142 \ \Omega^{-1} \text{cm}^{-1} \times 10^{-2} \times 1000 \ \text{cm}^3}{0.052 \ \text{mol}}$$
$$= 219.61 \ \text{S} \ \text{cm}^2 \ \text{mol}^{-1}$$

8. The given compound does not reduce Tollens' reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen sulphite indicates it to be a carbonyl compound. Since this compound gives positive iodoform test, so it should

contain 
$$-C - CH_3$$
 group.

On the basis of this information, two possible structures are written as under :

$$CH_3 - C - CH_2 - CH_2 - CH_3 \text{ and } CH_3 - C - CH - CH_3$$
  
I

On oxidation, this compound gives ethanoic and propanoic acids which confirm its structure to be I.

$$CH_{3}-C-CH_{2}-CH_{2}-CH_{3}\xrightarrow{[O]}_{Vigorous}$$
  

$$CH_{3}COOH + CH_{3}CH_{2}COOH$$

$$OR$$

(i) The overall acid strength increases in the order.4-Methoxybenzoic acid < benzoic acid <</li>

3,4-dinitrobenzoic acid.

(ii) We know that + *I*-effect decreases while –*I*-effect increases the acid strength of carboxylic acids. The overall acid strength increases in the order :

$$\label{eq:ch3} \begin{split} (\mathrm{CH}_3)_2\mathrm{CHCOOH} < \mathrm{CH}_3\mathrm{CH}(\mathrm{Br})\mathrm{CH}_2\mathrm{COOH} < \\ \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}(\mathrm{Br})\mathrm{COOH}. \end{split}$$

**9.** (i) In aqueous solutions,  $Cu^+$  undergoes disproportionation to form a more stable  $Cu^{2+}$  ion.

 $2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$ Cu<sup>2+</sup> in aqueous solutions is more stable than Cu<sup>+</sup>

ion because hydration enthalpy of  $Cu^{2+}$  is higher than that of  $Cu^{+}$ . It compensates the second ionisation enthalpy of Cu involved in the formation of  $Cu^{2+}$  ions. (ii)  $E^{\circ}$  values for the  $Cr^{3+}/Cr^{2+}$  and  $Mn^{3+}/Mn^{2+}$  couples are

$$\operatorname{Cr}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Cr}_{(aq)}^{2+}; E^{\circ} = -0.41 \text{ V}$$
  
 $\operatorname{Mn}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Mn}_{(aq)}^{2+}; E^{\circ} = +1.551 \text{ V}$ 

These  $E^{\circ}$  values indicate that  $Cr^{2+}$  is strongly reducing while  $Mn^{3+}$  is strongly oxidising agent.

(iii) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

10. (a) 
$$CH_3NH_2 + C_6H_5COCl \longrightarrow O_{II} CH_2NH - C - C_6H_5 CH_2N$$

(b) Stronger the base, lower will be its  $pK_b$  value. Hence increasing order of  $pK_b$  values is:

$$(C_2H_5)_2NH < C_2H_5NH_2 < NH_3 < C_6H_5NH_2$$

11. (i) In presence of strong field ligand, Co(II) has electronic configuration  $t_{2g}^6 e_g^1$ 

$$---- \underbrace{\bigwedge^{\uparrow} - e_g}_{\underline{1} \underline{1} \underline{1} \underline{1} \underline{1} \underline{1}_{2g}} \Delta_o > P$$

It can easily lose one electron present in  $e_g$  orbital to give stable  $t_{2g}^6$  configuration. This is why Co<sup>2+</sup> is easily oxidised to Co<sup>3+</sup> in the presence of strong field ligand. (ii) Coordination number and oxidation state of Pt in the complex [Pt(*en*)<sub>2</sub>Cl<sub>2</sub>] are 6 and +2 because *en* is a bidentate and neutral ligand.

## OR

(i) Hexaamminechromium(III)hexacyanidocobaltate(III).

(ii)  $[Co(en)_2 Cl(NH_3)]^{2+}$ 

Amminechlorido*bis*(ethane-1,2-diamine)cobalt(III) ion In presence of strong NH<sub>3</sub> and *en* ligand,  $Co^{3+}$  (3*d*<sup>6</sup>)

forms low spin complex. Hence, complex is diamagnetic. (b)  $[Ni(C_2O_4)_2(H_2O)_2]^{2-}$ :

Diaquadioxalatonickelate(II) ion

In the presence of weak  $H_2O$  and *ox* ligand, Ni(II) forms high spin complex ( $sp^3d^2$  hybridisation). It is paramagnetic.

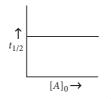
**12.** (a) For a first order reaction :

$$t_{1/2} = \frac{0.693}{k}, \ k = 3.01 \times 10^{-3} \text{ s}^{-1}$$
  
 $\therefore \quad t_{1/2} = \frac{0.693}{3.01 \times 10^{-3}} = 230.3 \text{ s}$ 

(b) Half life  $(t_{1/2})$  of a first order reaction is given as :

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7.0 \times 10^{-4}} = 990 \text{ s}$$

(c) For a first order reactions,  $t_{1/2} = k[A]_0^0 = k$ . Thus  $t_{1/2}$  is independent of initial concentration. Hence plot of  $t_{1/2} vs [A]_0$  will be a horizontal line.



(d) Yes, for a first order reaction  $t_{1/2} = \frac{0.693}{k}$ 

therefore  $t_{1/2}$  depends upon k and hence depends on temperature because rate constant k is a function of temperature.

#### OR

Let the concentrations of the reactant after 10 min and 20 min be  $C_1$  and  $C_2$  respectively.

$$\therefore \text{ Rate after 10 min} = k.C_1$$
  
= 0.04 × 60 mol L<sup>-1</sup>min<sup>-1</sup>  
andrate after 20 min = k.C\_2

 $= 0.03 \times 60 \text{ mol } \text{L}^{-1} \text{min}^{-1}$ 

 $\therefore \quad \frac{C_1}{C_2} = \frac{4}{3}$ 

Let the reaction starts after 10 minutes.

$$k = \frac{2.303}{10} \log \frac{C_1}{C_2} = \frac{2.303}{10} \log \frac{4}{3} = 0.02878$$
  
$$\therefore \quad t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{0.02878} = 24.086 \text{ min}$$