

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. The complexation of  $Fe^{2+}$  and chelating agent dipyridyl has been studied kinetically in both forward and reverse directions.

 $Fe^{2+} + 3(dipy) \longrightarrow [Fe(dipy)_3]^{2+}$ 

Rate of forward reaction =  $(1.45 \times 10^{13})$  [Fe<sup>2+</sup>][dipy]<sup>3</sup> and rate of reverse reaction =  $(1.22 \times 10^{-4})$  [Fe (dipy)<sub>3</sub>]<sup>2+</sup> Find the rate constant for the complex.

- **2.** Account for the following :
  - (a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.
  - (b)  $pK_a$  value of 4-nitrobenzoic acid is lower than that of benzoic acid.
- 3. What do the following reactions produce? (any two).
  - (a) Reaction of benzaldehyde with methyl amine.
  - (b) Reaction of propanal with dilute NaOH.
  - (c) Reaction of cyclohexanone in presence of  $H_2/Ni$ .

# **SECTION - B**

- 4. Classify the following as primary, secondary or tertiary amine :
  - (a) Allylamine
  - (b) Aniline
  - (c) Trimethylamine

#### OR

 $\operatorname{CH}_{3}\operatorname{Cl} \xrightarrow{\operatorname{KCN}} A \xrightarrow{\operatorname{LiAlH}_{4}} B \xrightarrow{\operatorname{CHCl}_{3} + \operatorname{KOH} (\operatorname{alc.})} C$ 

- (a) Identify product *A*.
- (b) Identify product *B*.
- (c) Identify product C.

Maximum marks : 35

- 5. (a) Is  $[Zn(NH_3)_6]^{2+}$  outer orbital complex or inner orbital complex?
  - (b) Is  $[Ni(H_2O)_6]^{2+}$  paramagnetic or diamagnetic?

## OR

Arrange the following in increasing order according to the properties indicated :

- (a)  $[Fe(H_2O)_6]^{2+}$ ,  $[Fe(CN)_2(H_2O)_4]$ ,  $[Fe(CN)_4(H_2O)_2]^{2-}$ (Order of  $\Delta_o$ )
- (b)  $[Cu(H_2O)_4]^+$ ,  $[Cu(NH_3)_4]^{2+}$ ,  $[CoF_6]^{3-}$ (Number of unpaired electrons)
- 6. How does amount of gas absorbed by solid depend upon nature of gas? Why is adsorption of  $CO_2$  on tungsten higher in comparison to  $O_2$ ?
- 7. The half life for the reaction,  $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + O_{2(g)}$  is 2.4 hr at 30°C.
  - (a) Starting with 10 g, what is the mass of  $N_2O_5$  left after 9.6 hr?
  - (b) How much time is required to reduce  $5.0 \times 10^{10}$  molecules of N<sub>2</sub>O<sub>5</sub> to  $1.0 \times 10^8$  molecules?
- 8. How are the following conversions carried out?
  - (a) Ethyl cyanide to ethanoic acid.
  - (b) Butan-1-ol to butanoic acid.
  - (c) Benzoic acid to *m*-bromobenzoic acid.
- 9. Give the structures of products *A*, *B* and *C* in the following reactions :

(a) 
$$CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$$

(b) 
$$CH_3COOH \xrightarrow{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow{CHCl_3 + Alc. NaO} B$$

In the following reaction, identify *X*, *Y* and *Z*.

$$X \xrightarrow{\text{Bromination}} Y \xrightarrow{\text{NaNO}_2/\text{HCl}} Z \xrightarrow{\text{Boiling}}_{C_2\text{H}_5\text{OH}}$$

$$sym\text{-Tribromobenzene}$$

 Following ions are given : Cr<sup>2+</sup>, Cu<sup>2+</sup>, Cu<sup>+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup> Identify the ion which is

- (a) a strong reducing agent.
- (b) unstable in aqueous solution.
- (c) a strong oxidising agent.

Give suitable reason in each.

11. Explain the hybridisation in following complexes :

- (a)  $[Mn(CN)_6]^{4-}$
- (b)  $[Cr(NH_3)_6]^{3+}$
- (c)  $[Co(NH_3)_6]^{3+}$

Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities :

- (a)  $[Cr(NH_3)_4Cl_2]Cl_3$
- (b)  $[Co(en)_3]Cl_3$
- (c)  $K_2[Ni(CN)_4]$

# **SECTION - C**

12. Read the passage given below and answer the following questions.

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal *M* is

 $M_{(s)} \mid M^+(aq.; 0.05 \text{ molar}) \mid M^+(aq.; 1 \text{ molar}) \mid M_{(s)}$ 

- (a) What is value of  $\Delta E$  for the cell?
- (b) What will be the magnitude of cell potential if 0.05 M solution of  $M^+$  is replaced by 0.0025 M solution?
- (c) What are the conditions for a reaction to be feasible in term of electrochemistry?
- (d) What is the emf of the cell when the cell reaction attains equilibrium?

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### OR

Does the potential of cell change with concentration of ions in solution or voltage of cell?

### Solution

### **CHEMISTRY - 043**

#### Class 12 - Chemistry

1. At dynamic equilibrium,

Rate of formation of complex = Rate of disappearance of complex

$$(1.45 \times 10^{13})$$
[Fe<sup>2+</sup>][dipy]<sup>3</sup> =  $(1.22 \times 10^{-4})$ [Fe(dipy)<sub>3</sub>]<sup>2-</sup>

$$\therefore \quad k = \frac{[\text{Fe}(\text{dipy})_3]^{2+}}{[\text{Fe}^{2+}][\text{dipy}]^3} = \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}$$

2. (a) Due to presence of electron withdrawing group (-COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

(b) Due to presence of strong electron withdrawing group (-NO<sub>2</sub>), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore,  $pK_a$  value is lower.

3. (a) 
$$\langle \bigcirc \rangle$$
 - CHO + NH<sub>2</sub>CH<sub>3</sub>  $\rightarrow$   
Benzaldehyde  $\langle \bigcirc \rangle$  - CH = NCH<sub>3</sub> + H<sub>2</sub>O  
(b) CH<sub>3</sub>CH<sub>2</sub>CHO + CH<sub>2</sub> - CHO  $\frac{\text{NaOH}}{\text{Aldol condensation}}$   
CH<sub>3</sub>  $OH$   
CH<sub>3</sub> - CH<sub>2</sub>CH - CHCHO  
CH<sub>3</sub>

(c) 
$$H_{2/Pt}$$
  $H_{OH}$ 

- **4.** (a) Primary amine
- (b) Primary amine
- (c) Tertiary amine

(a)  $CH_3Cl \xrightarrow{KCN} CH_3CN$ 

2.

(b) 
$$CH_3CN \xrightarrow{\text{LiAlH}_4} CH_3CH_2NH_2$$
  
(B)

(c) 
$$CH_3CH_2NH_2 \xrightarrow{CHCl_3 + alc. KOH} CH_3CH_2NC \xrightarrow{(C)}$$

Δ

OR

5. (a) 
$$\mathbb{Z}n^{2+} \rightarrow 3d^{10} 4s^0$$
  
 $\mathbb{Z}n^{2+} : \boxed{1 1 1 1 1}$   
 $[\mathbb{Z}n(\mathrm{NH}_3)_6]^{2+} : \underbrace{4s}_{\mathrm{XX}} \underbrace{4p}_{\mathrm{XX}} \underbrace{4d}_{\mathrm{XX}} \underbrace{4s}_{\mathrm{XX}} \underbrace{4d}_{\mathrm{XX}} \underbrace{4d}_{$ 

In other cases NH<sub>3</sub> being strong field ligand causes pairing of electrons and the resulting complexes will be inner orbital. But in case of Zn, their is no availability of inner *d*-orbital due to fully filled *d*-orbital.

(b) Oxidation state of Ni in 
$$[Ni(H_2O)_6]^{2+} = +2$$

$$Ni^{2+}(Z=28) \rightarrow 3d^8$$

Since, H<sub>2</sub>O is a weak field ligand, electrons remain unpaired hence, the compound is paramagnetic.

OR

(a) 
$$[Fe(H_2O)_6]^{2+} < [Fe(CN)_2(H_2O)_4] < [Fe(CN)_4(H_2O)_2]^{2-}$$

The value of  $\Delta_{0}$  for mixed ligands depends on the additive contributions of the ligand strength. Since CN<sup>-</sup> has greater ligand strength than H<sub>2</sub>O, the strength increases as the number of CN<sup>-</sup> ions increases.

(b) 
$$[Cu(H_2O)_4]^+ < [Cu(NH_3)_4]^{2+} < [CoF_6]^{3-1}$$
  
(n = 0) (n = 1) (n = 3)

The amount of gas adsorbed by a solid depends 6. on the nature of gas. In general, more easily liquefiable gases (i.e., higher critical temperature) are readily adsorbed as van der Waals' forces are stronger near the critical temperature.

More easily liquefiable gases, (e.g.,  $NH_3$ ,  $CO_2$ ) are readily adsorbed, as van der Waals forces are stronger near the critical temperatures. So, adsorption of CO<sub>2</sub> will be highest.

7. For a first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.4 \times 60 \times 60} = 8.02 \times 10^{-5} \,\mathrm{s}^{-1}$$

(a) Now using the expression

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$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$a = 10 \text{ g; } t = 9.6 \text{ hr} = 9.6 \times 60 \times 60 \text{ s; } k = 8.02 \times 10^{-5} \text{ s}^{-1}$$

$$8.02 \times 10^{-5} = \frac{2.303}{9.6 \times 60 \times 60} \log \frac{10}{a-x}$$

$$\log \frac{10}{a-x} = \frac{8.02 \times 10^{-5} \times 9.6 \times 60 \times 60}{2.303}$$

$$\log \frac{10}{a-x} = \frac{2.77171}{2.303} \implies \frac{10}{a-x} = 15.9$$

$$a-x \atop (\text{amount left)} = \frac{10}{15.9} = 0.628 \text{ g}$$
(b)  $t = \frac{2.303}{k} \log \frac{a}{a-x}$ 

$$t = \frac{2.303}{8.02 \times 10^{-5}} \log \left( \frac{5.0 \times 10^{10}}{1.0 \times 10^8} \right) = \frac{2.303 \times 2.698}{8.02 \times 10^{-5}}$$
  
= 77503 s = 21.52 hr



**10.** (a)  $Cr^{2+}$  is reducing since its configuration is converted to  $d^3$  from  $d^4$ .  $d^3$  has half filled  $t_{2g}$  configuration with higher stability.

(b)  $Cu^+$  is unstable in aqueous solution. In aqueous solutions,  $Cu^+$  undergoes disproportionation to form a more stable  $Cu^{2+}$  ion.

$$2\mathrm{Cu}^+_{(aq)} \to \mathrm{Cu}^{2+}_{(aq)} + \mathrm{Cu}_{(s)}$$

(c)  $Mn^{3+}$  is a strong oxidising agent because electronic configuration of  $Mn^{2+}$  is  $3d^5$  which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*,  $3^{rd}$  electron cannot be lost easily.

11. (a) 
$$[Mn(CN)_{6}]^{4}$$
:  $\boxed{11}$   $\boxed{11}$   $\boxed{1}$   $\boxed{12}$   $\underbrace{13}$   $\underbrace{4s}$   $\underbrace{4p}$   $\underbrace{12}$   $\underbrace$ 

For feasible cell,  $E^{\circ}$  is positive, hence from the above equation, K > 1 for a feasible cell reaction.

(d) The emf of the cell is 0 at equilibrium.

### OR

Yes, the potential of electrode changes with change in concentration of ions in solution.