

Time allowed : 2 hours

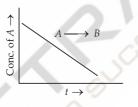
General Instructions :

Read the following instructions carefully.

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

SECTION - A

For a general reaction $A \longrightarrow B$, plot of concentration of A vs time is given in Figure. 1.



Answer the following question on the basis of this graph (any two).

- (a) What is the order of the reaction?
- (b) What will be the new $t_{1/2}$ if concentration of A is doubled?
- (c) What are the units of rate constant?
- 2. Illustrate the following name reactions giving a chemical equations in each case :
 - (a) Clemmensen reaction
 - (b) Cannizzaro reaction
- 3. Depict the electrochemical cell and calculate the E° for each cell.
 - (a) $2Ag^+ + Cd \longrightarrow Ag + Cd^{2+}$

(b)
$$\operatorname{Cl}_{2(g)} + 2I^{-} \longrightarrow 2CI^{-} + I_{2(g)}$$

(b) $CI_{2(g)} + 2I \longrightarrow 2CI + I_{2(s)}$ (Given : $E^{\circ}_{Ag^+/Ag} = 0.80$ V, $E^{\circ}_{Cd^{2+}/Cd} = -0.40$ V, $E^{\circ}_{Cl_2/Cl^-} = 1.36$ V, $E^{\circ}_{I_2/I^-} = 0.54$ V)

SECTION - B

- 4. Give one chemical test to distinguish between the compounds of the following pairs:
 - (a) CH_3NH_2 and $(CH_3)_2NH$
 - (b) Aniline and ethanamine
 - (c) $(CH_3)_2NH$ and $(CH_3)_3N$

Maximum marks : 35

OR

Account for the following :

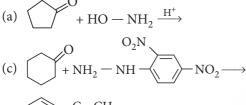
- (a) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (b) Gabriel phthalimide synthesis is preferred for synthesising primary amines.
- (c) Aniline is a weaker base than cyclohexylamine.

5. Answer the following questions :

- (a) Write the IUPAC name of $[Pt(NH_3)BrCl(NO_2)]^-$
- (b) Compare the magnetic behaviour of the complex entities $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{3+}$.

OR

- (a) Co^{2+} is easily oxidised to Co^{3+} in presence of a strong field ligand. Give reason.
- (b) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.
- 6. Predict the products of the following reactions :



(b)
$$\begin{array}{|c|} C - CH_3 \\ \parallel \\ O \end{array} + CH_3CH_2NH_2 - H^+ \end{array}$$

- 7. Explain what is observed when :
 - (a) NaCl solution is added to hydrated ferric oxide sol.
 - (b) Electric current is passed through a colloidal solution.
 - (c) a freshly prepared precipitate of Fe(OH)₃ is shaken with a small amount of FeCl₃ solution.
- 8. How would you account for the following :
 - (a) Metal-metal bonding is more extensive in the 4*d* and 5*d* series of transition elements than the 3*d* series.
 - (b) Mn(III) undergoes disproportionation reaction easily.
 - (c) Most of the transition metal ions exhibit characteristic colours in aqueous solutions.
- 9. Using valence bond theory explain out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which complex is
 - (a) diamagnetic
 - (b) more stable
 - (c) outer orbital complex

OR

Explain the following :

- (a) Low spin octahedral complexes of nickel are not known.
- (b) CO is a stronger ligand than NH_3 for many metals.
- (c) $[Ni(H_2O)_6]^{2+}$ is green and becomes violet when ethane 1, 2-diamine is added to it.
- **10.** For the cell,

 $Zn_{(s)} | Zn^{2+} (2 M) || Cu^{2+} (0.5 M) | Cu_{(s)}$

- (a) Write the oxidation and reduction half-reactions.
- (b) Calculate the cell potential at 25°C.

(Given : $E_{Zn^{2+}/Zn}^{\circ} = -0.76 \text{ V}; E_{Cu^{2+}/Cu}^{\circ} = +0.34 \text{ V}$)

11. The following initial rate data were obtained at 300 K for the reaction : $2A + B \rightarrow C + D$.

| | $[A]/mol L^{-1}$ | [<i>B</i>]/mol L ⁻¹ | Rate/mol L ⁻¹ s ⁻¹ |
|------|------------------|----------------------------------|--|
| I. | 0.2 | 0.1 | $6.0 	imes 10^{-2}$ |
| II. | 0.4 | 0.1 | $2.4 	imes 10^{-1}$ |
| III. | 0.2 | 0.2 | $1.2 	imes 10^{-1}$ |

(a) Deduce the rate law.

(b) If half-life of reaction is independent of initial concentration of the reactant, what is the order of the reaction?

OR

During nuclear explosion, one of the products is 90 Sr with half-life of 28.1 years. If 1 µg of 90 Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years if it is not lost metabolically?

SECTION - C

12. Read the passage given below and answer the questions that follow.

Aldehydes and ketones having acetyl group $\begin{pmatrix} O \\ CH_3 - C \end{pmatrix}$ are oxidised by sodium hypohalate (NaOX) or

halogen and alkali (X_2 + OH⁻) to corresponding sodium salt having one carbon atoms less than the carbonyl compound and give a haloform.

$$R \longrightarrow C \longrightarrow CH_3 \xrightarrow{\text{NaOX}} r \longrightarrow R \longrightarrow C \longrightarrow O$$

Sodium hypoiodite (NaOI) when treated with compounds containing CH_3CO- group gives yellow precipitate of iodoform. Haloform reaction does not affect a carbon-carbon double bond present in the compound.

- (a) Amongst propionaldehyde and isopropyl alcohol which will give positive iodoform test.
- (b) Write the iodoform reaction of acetone.
- (c) For the given reaction,

Identify the starting compound *A*.

(d) An organic compound 'A' has the molecular formula C_3H_6O . It undergoes iodoform test. Give the IUPAC name of A.

OR

In the following reaction sequence,

$$Ph \xrightarrow{Heat} OH \xrightarrow{Heat} [E] \xrightarrow{I_2} [F] + [G]$$

(* implies ¹³C labelled carbon)

What are the structures of *E*, *F* and *G*?

Solution

CHEMISTRY - 043

Class 12 - Chemistry

1. (a) Zero order reaction

(b) $t_{1/2}$ doubles since for zero order reaction,

 $t_{1/2} \propto$ initial concentration.

(c) mol $L^{-1} s^{-1}$

For a zero order reaction

 $[R] = -kt + [R]_0$ hence plot of [R], (conc. of A) vs t is a straight line with slope = -k.

$$\frac{dx}{dt} = k [A]^0 = \frac{\text{mol } L^{-1}}{s} \times \frac{1}{(\text{mol } L^{-1})^0} = \text{mol } L^{-1} s^{-1}$$

2. (a) Clemmensen reduction : The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} C = O \xrightarrow{Zn - Hg}{HCl} \xrightarrow{CH_{3}} CH_{2} + H_{2}O \\ CH_{3} \\ Propanone \\ Propane \end{array}$$

(b) **Cannizzaro reaction :** Aldehydes which do not contain α -H atom undergo disproportionation when heated with concentrated alkali.

HCHO + HCHO <u>conc. NaOH</u> → HCOONa + CH₃OH Methanal Sodium formate Methanol

3. (a)
$$Cd|Cd^{2+}||Ag^{+}|Ag$$

 $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = (0.80) - (-0.40) = 1.20 V$
(b) Pt, $I_{(aq)}^{-}|I_{2(s)}||Cl_{2(g)}|Cl_{(aq)}^{-}$,Pt
 $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = (1.36) - (0.54) = 0.82 V$

4. (a) Methylamine gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test.

(b) Aniline being an aromatic primary amine on treatment with $HNO_2[NaNO_2 + HCl (dil.)]$ at 273–278 K followed by treatment with an alkaline solution of β -naphthol gives an orange coloured azo dye. Ethylamine does not give this test.

(c) Tertiary amines do not react with benzene sulphonyl chloride while secondary amines react and give a product insoluble in alkali.

OR

(a) The formation of hydrated ferric oxide may be understood by taking into consideration the basic strength of CH_3NH_2 . In presence of CH_3NH_2 , water hydrolyses as

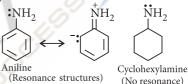
$$CH_3 - \ddot{N}H_2 + H H \rightarrow CH_3 - \dot{N}H_3 + \bar{O}H$$

These OH ions react with FeCl_3 as:

 $2\text{FeCl}_3 + 6\overline{OH} \longrightarrow 2\text{Fe}(OH)_3 \text{ or } \text{Fe}_2O_3.3H_2O$ hydrated ferric oxide

(b) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

(c) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $-\dot{N}H_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH₂ group. So, cyclohexylamine is a stronger base.



5. (a) Amminebromidochloridonitrito-N-platinate(II)
(b) (i) [Fe(CN)₆]⁴⁻ ion :

$$Fe^{2+} \text{ ion } \underbrace{3d^6}_{11, 1, 1, 1, 1} \underbrace{4s^0}_{11, 1, 1, 1, 1} \underbrace{4p^0}_{11, 1, 1, 1, 1}$$

 Fe^{2+} ion hybridised (under the influence of strong field ligand).

 $[Fe(CN)_6]^{4-}$ ion formation :

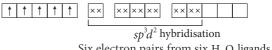
 d^2sp^3 hybridisation

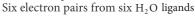
Six pairs of electrons from six CN⁻ ions Since the complex ion does not contain any unpaired electron, so it is diamagnetic.

(ii)
$$[Fe(H_2O)_6]^{3+}$$
 ion :
 $3d^5 \qquad 4s^0 \qquad 4p^0 \qquad 4d^0$
 Fe^{3+} ion $[\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow]$

Fe³⁺ ion is hybridised (under the influence of weak field ligand)

 $[Fe(H_2O)_6]^{3+}$ ion formation :

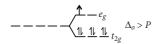




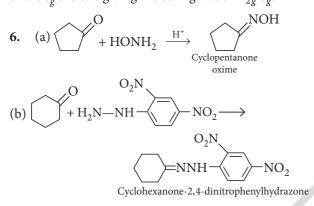
As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

OR

(a) In presence of strong field ligand Co(II) has electronic configuration $t_{2\rho}^6 e_{\sigma}^1$



It can easily lose one electron present in e_g orbital to give stable t_{2g}^6 configuration. That is why Co²⁺ is easily oxidised to Co³⁺ in the presence of strong field ligand. (b) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.



7. (a) The positively charged colloidal particles of ferric hydroxide sol get coagulated by the oppositely charged Cl^- ions provided by NaCl.

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

(c) On treating a precipitate of iron (III) oxide with a small amount of FeCl_3 solution, a reddish brown coloured colloidal solution is formed. In this case, Fe^{3+} ions from ferric chloride are adsorbed by $\text{Fe}(\text{OH})_3$ precipitate.

 $\begin{array}{c} \operatorname{Fe(OH)}_3 + \operatorname{Fe}^{3+} \longrightarrow & \operatorname{Fe(OH)}_3 \text{. Fe}^{3+} \\ \operatorname{ppt.} & \operatorname{Electrolyte} & \operatorname{Colloidal sol} \end{array}$

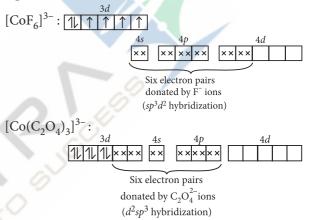
8. (a) The metals of 4d and 5d-series have more frequent metal bonding in their compounds than the 3d-metals because 4d and 5d-orbitals are more exposed in space than the 3d-orbitals. So the valence

electrons are less tightly held and form metal-metal bonding more frequently.

(b) Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half-filled *d*-orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

(c) Since, transition elements contain partially filled d-subshells, therefore, electrons in these subshells go from lower d-subshells to higher d-subshells. This is called d-d transition. This transition takes place by absorbing energy from the visible light. The mixture of the wavelength which is not absorbed is transmitted out. This accounts for the colour of transition elements..

9. Formation of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ can be represented as :



(a) $[Co(C_2O_4)_3]^{3-}$ is diamagnetic as all the electrons are paired.

(b) $[Co(C_2O_4)_3]^{3-}$ is more stable as $C_2O_4^{2-}$ is a chelating ligand and forms chelate rings.

(c) $[CoF_6]^{3-}$ is outer orbital complex as it undergoes sp^3d^2 hybridization using the outer 4*d*-orbital.

OR

(a) Nickel forms octahedral complexes mainly in +2 oxidation state which has $3d^8$ configuration. In presence of strong field ligand also, it has two unpaired electrons in e_{σ} orbital.

Hence, it does not form low spin octahedral complexes. (b) CO is stronger ligand than NH_3 because CO has vacant molecular orbitals with which it can form π -bond with metal through back donation.

(c) Ethane-1,2-diamine is stronger ligand than H_2O . When H_2O molecule is replaced by ethane-1,2-diamine (*en*) the crystal field splitting energy (Δ_o) increases. Complex absorbs light of higher frequency for *d*-*d* transition. This is why colour of complex changes from green to violet.

10. (a) Oxidation half reaction :

$$Zn_{(s)} \longrightarrow Zn_{(aq)}^{2+} + 2e^{-}$$

Reduction half reaction :
 $Cu_{(aq)}^{2+} + 2e^{-} \longrightarrow Cu_{(s)}$
(b) $E_{cell}^{o} = 0.34 - (-0.76) = 1.10 \text{ V}$
 $E_{cell} = E_{cell}^{o} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$
 $\Rightarrow E_{cell} = 1.10 - \frac{0.0591}{2} \log \frac{2}{0.5}$
 $= 1.10 - \frac{0.0591}{2} \log \frac{2}{0.5}$
 $= 1.10 - \frac{0.059}{2} \times 0.6021$
 $= 1.10 - 0.0177 = 1.0823 \text{ V}$

11. (a) Let the rate law for the given reaction be Rate = $k[A]^x[B]^y$

Then,
$$\frac{r_{\text{II}}}{r_{\text{I}}} = \frac{2.4 \times 10^{-1}}{6.0 \times 10^{-2}} = \frac{k(0.4)^{x} \times (0.1)^{y}}{k(0.2)^{x} \times (0.1)^{y}}$$

 $4 = 2^{x} \implies x = 2$
Again, $\frac{r_{\text{III}}}{r_{\text{I}}} = \frac{1.2 \times 10^{-1}}{6.0 \times 10^{-2}} = \frac{k(0.2)^{x} \times (0.2)^{y}}{k(0.2)^{x} \times (0.1)^{y}}$
or, $2 = 2^{y} \implies y = 1$

Hence, the rate law = $k[A]^2[B]^1$

(b) If half life is independent of the initial concentration, then the order of the reaction is 2.

OR

Radioactive disintegration follows first order kinetics. Hence,

Decay constant of ⁹⁰Sr, (λ) = $\frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$ $= 2.466 \times 10^{-2} \text{ yr}^{-1}$

To calculate the amount left after 10 years, Given, $[R_0] = 1 \mu g$, t = 10 years, $\lambda = 2.466 \times 10^{-2} \text{ yr}^{-1}, [R] = ?$

Using formula, $\lambda = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$ or $2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$ or, $\log [R] = -0.1071$ or, $[R] = \text{Antilog}(-0.1071) = 0.7814 \,\mu\text{g}$ 12. (a) Iodoform test is given by the organic Ο OH compounds having CH_3 —CH— or CH_3 —CH— group. CH₃-CH-OH : Isopropyl alcohol CH₃

CH₃CH₂CHO : Propionaldehyde

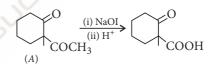
Ο

Therefore, isopropyl alcohol will give positive iodoform test.

(b) Iodoform reaction of acetone occurs in following steps :

$$CH_3 - C - CH_3 + NaOI \longrightarrow CH_3COONa + CHI_3$$

(c) Given reagents indicate the presence of $-COCH_3$ group in the starting compound A.



(d) Since compound $A(C_3H_6O)$ undergoes iodoform test, it must be CH₃COCH₃ *i.e.*, propan-2-one.

OR

