

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. Write the IUPAC name of the following compounds (*any two*) :
 - (a) $(H_3CCH_2)_2NCH_3$

(b) $H_3CNHCH(CH_3)_2$

- (c) $(H_3C)_2N-CH_2CH_3$
- 2. Limiting molar conductivity of an electrolyte cannot be determined experimentally. Why?
- 3. Arrange the following compounds in increasing order of their basic strength:
 (a) Aniline, *p*-nitroaniline and *p*-toluidine
 (b) C₆H₅NH₂, C₆H₅NHCH₃, C₆H₅CH₂NH₂

SECTION - B

4. Out of hexacyanomanganese(III) and hexachloridomanganese(III) which has maximum number of unpaired electrons. Why?

OR

Explain the bonding in coordination compounds in terms of Werner's postulates.

- 5. Explain, cyclohexylamine is a stronger base than aniline. Draw resonating structures of aniline.
- 6. For Freundlich adsorption isotherm, a plot of $\log (x/m) (y$ -axis) and $\log p (x$ -axis) gives a straight line. The intercept and slope for the line is 0.4771 and 2, respectively. What is the mass of gas, absorbed per gram of adsorbent if the initial pressure is 0.04 atm. (log 3 = 0.4771)

OR

- (a) Why does physisorption decrease with the increase of temperature?
- (b) Explain how the phenomenon of adsorption find application in the production of vaccum.
- (c) Write one difference between solution and colloid.
- 7. What is meant by the following terms? Give an example of the reaction for their formation in each case.
 - (a) Cyanohydrin (b) Acetal
 - (c) Semicarbazone

Maximum marks : 35

OR

How will you convert ethanal into the following compounds?

- (a) Butane-1,3-diol
- (b) But-2-enal
- (c) But-2-enoic acid

8.
$$\operatorname{Fe}^{3+} \xrightarrow{\operatorname{SCN}^{-}} (A) \xrightarrow{F^{-}} (B)$$

Blood red colouration $\xrightarrow{F^{-}} (B)$

What are (*A*) and (*B*)? Give IUPAC name of (*A*). Find the spin only magnetic moment of (*B*).

9. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm⁻¹. Calculate its molar conductivity.

OR

The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω . What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm⁻¹?

- **10.** (a) What is lanthanoid contraction?
 - (b) Explain the following:
 - (i) Why is europium(II) more stable than cerium(II)?
 - (ii) Why is +3 oxidation state of gadolinium (Z = 64) and lutetium (Z = 71) especially stable?
- 11. Give plausible explanation for each of the following :
 - (a) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
 - (b) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
 - (c) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

SECTION - C

- 12. Read the passage given below and answer the questions that follow.
 - In a reaction, the rates of disappearance of different reactants or rates of formation of different products may not be equal but rate of reaction at any instant of time has the same value expressed in terms of any reactant or product. Further, the rate of reaction may not depend upon the stoichiometric coefficients of the balanced chemical equation. The exact powers of molar concentrations of reactants on which rate depends are found experimentally and expressed in terms of 'order of reaction.' Each reaction has a characteristic rate constant depends upon temperature. The units of the rate constant depend upon the order of reaction. The following questions are multiple choice questions. Choose the most appropriate answer :
 - (a) The rate constant of a reaction is found to be 3×10^{-3} mol⁻² L² sec⁻¹. What is the order of the reaction ?

 - (b) In the reaction, $A + 3B \rightarrow 2C$, what is the rate of formation of *C*?
 - (c) Rate of a reaction can be expressed by following rate expression, Rate = $k[A]^2[B]$, if concentration of A is increased by 3 times and concentration of B is increased by 2 times, how many times rate of reaction increases?
 - (d) The rate of a certain reaction is given by, rate = $k[H^+]^n$. The rate increases 100 times when the pH changes from 3 to 1. What is the order (n) of the reaction ?

OR

In a chemical reaction $A + 2B \rightarrow$ products, when concentration of A is doubled, rate of the reaction increases 4 times and when concentration of B alone is doubled rate continues to be the same. What is the order of the reaction?

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Class 12 - Chemistry

1. (a)
$$\frac{H_3CH_2C}{H_3CH_2C}$$
N-CH₃

IUPAC name : N-Ethyl-N-methylethanamine

(b)
$$H_3C - N - C \xrightarrow{CH_3}_{H H H}$$

N-Methylpropan-2-amine (2° amine)

2. In weak electrolyte, the conductivity of the solution increases very slowly with dilution of solution and goes on increasing up to infinity. Therefore, it cannot be measured experimentally.



3. (a) *p*-Nitroaniline < Aniline < *p*-Toluidine

$$O_2N \longrightarrow NH_2 < O \longrightarrow NH_2 < H_2N \longrightarrow CH$$

The availability of *l.p.* on N of *p*-nitroaniline is drastically reduced by presence of electron withdrawing $-NO_2$ group on it.

In contrast, presence of electron releasing $-CH_3$ group increases the electron density on N atom and improves basicity in *p*-toluidine.

(b) $C_6H_5NH_2(I) < C_6H_5NHCH_3(II) < C_6H_5CH_2NH_2(III)$ Involvement of *l.p.* of N in resonance causes aniline to have low basicity. In II, the –Me group through its +*I* effect improves the electron density on N and therefore its basic strength increases. In III, the –NH₂ is farther off from benzene ring and hence *l.p.* is localized on it and hence the basic strength is highest.

4. In $[Mn(CN)_6]^{3-}$, Mn is in +3 state so, it has configuration of $3d^4$.

Since CN^- is a strong field ligand hence pairing of electrons in 3*d*-orbital takes place.



So, $[Mn(CN)_6]^{3-}$ has two unpaired electrons. But in $[MnCl_6]^{3-}$, Cl^- is a weak field ligand, so no pairing takes place and it has four unpaired electrons.

OR

The main postulates are :

(i) In coordination compounds metals show two types of linkages (valencies)-primary and secondary.

(ii) The primary valencies are normally ionisable and are satisfied by negative ions.

(iii)The secondary valencies are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valency is equal to the coordination number and is fixed for a metal.

(iv) The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

5. Aniline is a weaker base than cyclohexylamine because of resonance.

Resonance structures of aniline are :

$$\stackrel{:\mathrm{NH}_2}{\longmapsto} \stackrel{\oplus \mathrm{NH}_2}{\longleftrightarrow} \stackrel{\oplus \mathrm{NH}_2}{\longleftrightarrow} \stackrel{\oplus \mathrm{NH}_2}{\bigoplus} \stackrel{\oplus \mathrm{NH}_2}{\longleftrightarrow} \stackrel{\otimes \mathrm{H}_2}{\longleftrightarrow} \stackrel{:\mathrm{NH}_2}{\longleftrightarrow} \stackrel{\mathrm{NH}_2}{\longleftrightarrow} \stackrel{\mathrm$$

In case of cyclohexylamine there is no resonance.

6. According to Freundlich adsorption isotherm,

$$\left(\frac{x}{m}\right) = K(p)^{1/n}$$
$$\log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log p$$

On comparing this with equation of straight line, we get,

Slope =
$$\frac{1}{2} = 2$$

Intercept = log K = 0.4771
K = antilog (0.4771) = 3

$$\therefore \quad \frac{x}{m} = (3.04)^2 = 3(4 \times 10^{-2})^2 = 48 \times 10^{-4} \text{ g}$$
OR

(a) Physical adsorption of a gas by a solid is generally reversible. Thus,

 $Solid + Gas \rightleftharpoons Gas/Solid + Heat$

Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le Chatelier's principle).

(b) Production of vacuum : Adsorption can be applied to create condition of high vacuum. Vessel which has already been exhausted by vacuum pump is connected to a bulb containing charcoal. The remaining traces of air inspite of low pressure are adsorbed by the charcoal almost completely.

(c) Solution : In true solution, the size of the particles is about 10^{-10} m.

Colloid : In a colloid, the size of the particles is in between 10^{-7} to 10^{-9} m.

7. (a) Cyanohydrin : Compounds formed when aldehydes or ketones react with hydrogen cyanide are called cyanohydrins.



(b) Acetal : Acetals are the diethers which are formed by the addition of two molecules of alcohols to aldehydes in the presence of dry hydrogen chloride.

$$R - C - H + 2R' - OH \xrightarrow{HCl gas} R - C - OR'$$
Aldehyde
$$R - C - H + 2R' - OH \xrightarrow{HCl gas} R - C - OR'$$

(c) Semicarbazone : Compounds formed when aldehydes or ketones react with semicarbazide are called semicarbazones.

$$R \xrightarrow{C=O} H_2N \xrightarrow{NH-C-NH_2} \xrightarrow{O} \\ Semicarbazide O \\ R \xrightarrow{C=N-NH-C-NH_2} \\ R \xrightarrow{C=N-NH-C-NH_2} \\ OR \\ OR \\ (a) 2CH_3 \xrightarrow{-C-H} \xrightarrow{aq. NaOH} \\ Ethanal \\ OH \\ CH_3 \xrightarrow{-CH-CH_2-C-H} \xrightarrow{LiAlH_4} \\ OH \\ CH_3 \xrightarrow{OH} -CH-CH_2-CH_2 \xrightarrow{OH} \\ OH \\ CH_3 \xrightarrow{OH} -CH-CH_2 \xrightarrow{OH} \xrightarrow{OH} \\ OH \\ CH_3 \xrightarrow{OH} -CH-CH_2 \xrightarrow{OH} \xrightarrow{OH} \\ OH \\ CH_3 \xrightarrow{OH} -CH-CH_2 \xrightarrow{OH} \xrightarrow{OH} \xrightarrow{OH} \\ OH \\ CH_3 \xrightarrow{OH} \xrightarrow{OH}$$



8. $(A) = [Fe(SCN)(H_2O)_5]^{2+}; (B) = [FeF_6]^{3-}$ IUPAC name of A is : pentaaquathiocyanatoferrate (III) ion

Spin magnetic moment of (B) = $\sqrt{n(n+2)} = \sqrt{5(5+2)}$ = $\sqrt{5 \times 7}$ or 5.92 BM. [:: n = 5 in Fe³⁺]

9. Given, Conductivity, $\kappa = 0.0248$ S cm⁻¹ Molarity, $C_m = 0.20$ M = 0.20 mol L⁻¹

Using formula
$$\Lambda_m = \frac{1000 \times \kappa}{C}$$

$$\Lambda_m = \frac{(1000 \,\mathrm{cm}^3 \,\mathrm{L}^{-1}) \times (0.0248 \,\mathrm{S} \,\mathrm{cm}^{-1})}{(0.20 \,\mathrm{mol} \,\mathrm{L}^{-1})} = 124 \,\mathrm{S} \,\mathrm{cm}^2 \,\mathrm{mol}^{-1}$$

OR

Given, $C_m = 0.001$ M, $R = 1500 \Omega$, $\kappa = 0.146 \times 10^{-3}$ S cm⁻¹, $G^* = ?$ Cell constant $= \frac{\text{Conductivity}}{\text{Conductance}} = \text{Conductivity} \times \text{Resistance}$

= $(0.146 \times 10^{-3} \text{ S cm}^{-1}) \times (1500 \Omega) = 0.219 \text{ cm}^{-1}$

10. (a) A unique feature of lanthanoids is the decrease in atomic and ionic radii from lanthanum to lutetium. The gradual and steady decrease across the period is called lanthanoid contraction .

(b) (i) Europium (II) has electronic configuration $[Xe]4f^75d^0$ while cerium (II) has electronic configuration $[Xe]4f^{1}5d^1$. In Eu²⁺, 4*f* subshell is half-filled and 5*d*-subshell is empty. Since half-filled and

completely-filled electronic configurations are more stable, hence Eu^{2+} ions is more stable than Ce^{2+} .

(ii) This is because gadolinium in +3 state has half-filled 4f-subshell ($4f^7$) and lutetium in +3 state has completely filled 4f-subshell which are very stable configurations.

11. (a) Formation of cyanohydrin involves the nucleophilic attack of cyanide ions (CN⁻) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,2,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.



(b) Although semicarbazide has to $-NH_2$ groups but one of them which is directly attached to carbonyl group, is involved in resonance. So, this nitrogen is not able to act as an effective nucleophile.

$$H_2 \overset{O}{\longrightarrow} C \overset{O}{\longrightarrow} H_2 \overset{$$

So, it is the other $-NH_2$ group which acts as nucleophile and is involved in condensation with aldehydes and ketones to give semicarbazone derivatives.

(c) During the preparation of ester from alcohol and carboxylic acid in presence of acid, the water or ester should be removed as fast as it is formed because it is a reversible reaction. If they are not removed, then the reverse reaction also starts and an equilibrium is established, so the overall yield of the ester will be low.

$$R - C - OH + R' - OH = R - C - O - R' + H_2O$$

12. (a) Unit of *k* for *n*th order = $(\text{mol } \text{L}^{-1})^{1-n} \sec^{-1}...(i)$ Here, $k = 3 \times 10^{-3} \text{ mol}^{-2} \text{L}^{2} \sec^{-1}$ Unit of $k = \text{mol}^{-2} \text{L}^{2} \sec^{-1} \Rightarrow (\text{mol } \text{L}^{-1})^{-2} \sec^{-1} ...(ii)$ Comparing (i) and (ii) we get, $1 - n = -2 \Rightarrow n = 3$ (b) Rate $= -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt}$

(c) Given, $R_1 = k[A]^2 [B]$ According to question, $R_2 = k[3A]^2 [2B]$ $= k \times 9 [A]^2 \times 2 [B] = 18 \times k [A]^2 [B] = 18 R_1$ (d) Rate $(r) = k[H^+]^n$ When pH = 3; $[H^+] = 10^{-3}$ and when pH = 1; $[H^+] = 10^{-1}$

$$\therefore \quad \frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n} \implies \frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n \quad (\because r_2 = 100 r_1)$$
$$\implies (10^{-2})^1 = (10^{-2})^n \implies n = 1$$

Let the order of reaction w.r.t. A is x and w.r.t. B is y.

$$r_1 = k[A]^x [B]^y$$
 ...(i)
 $r_2 = k[2A]^x [B]^y$...(ii)

$$r_3 = k[A]^x [2B]^y$$
 ...(iii)

$$\frac{r_1}{r_2} = \frac{k[A]^x[B]^y}{k[2A]^x[B]^y}$$
$$\Rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^x \Rightarrow x = 2$$

Similarly,
$$\frac{r_1}{r_3} = \frac{k[A]^x[B]^y}{k[A]^x[2B]^y}$$

$$\Rightarrow 1 = \left(\frac{1}{2}\right)^{y} \Rightarrow \left(\frac{1}{2}\right)^{0} = \left(\frac{1}{2}\right)^{y} \Rightarrow y = 0$$

Hence the rate law equation is Rate = $k[A]^2[B]^0 \Rightarrow$ Order of reaction = 2