Sample Question Paper - 16
Chemistry (043)
Class- XII, Session: 2021-22
TERM II

Time allowed : 2 hours *Maximum marks : 35*

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. In a pseudo first order reaction in water, the following results were obtained :

t/s	0	30	60	90
A/mol L^{-1}	0.55	0.31	0.17	0.085

Calculate the average rate of reaction between the time interval 30 to 60 seconds.

2. Write the reaction of the alkylation of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

3. Ammonolysis of alkyl halides does not give a corresponding amine in pure state. Why?

SECTION - B

4. (i) Account for the following by giving reaction :

Oxidation of toluene to benzaldehyde with CrO_3 is carried out in presence of acetic anhydride.

(ii) Ethanoic acid is miscible in water but benzoic acid is insoluble in water. Why?

5. (a) Use the data to answer the following and also justify giving reasons :

	Cr	Mn	Fe	Co
$E^\circ_{M^{2+}/M}$	–0.91	–1.18	–0.44	–0.28
$E^\circ_{M^{3+}/M^{2+}}$	–0.41	+1.57	+0.77	+1.97

(i) Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?

(ii) Which is the most stable ion in +2 oxidation state and why?

(b) Zn, Cd, Hg are considered as *d*-block elements but not as transition elements. Why?

OR

(a) How would you account for the following : Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.

(b) What is meant by 'lanthanoid contraction'?

6. Depict the galvanic cell in which the reaction $Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ takes place. Further show :

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

OR

For the cell reaction,

$Ni_{(s)} | Ni^{2+}_{(aq)} || Ag^+_{(aq)} | Ag_{(s)}$

Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by operation of this cell?

$E^\circ_{Ni^{2+}/Ni} = -0.25$ V and $E^\circ_{Ag^+/Ag} = 0.80$ V

7. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

OR

The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$

Experiment	**Time/s^{-1}**	**Total pressure/atm**
1	0	0.5
2	100	0.6

What is the rate of reaction when total pressure is 0.65 atm?

8. Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, select the complex which

(i) is repelled by applied magnetic field.

(ii) is less reactive

(iii) uses outer *d*-orbitals for bonding with ligands

(iv) have $\Delta_o > p$

(Atomic no. of Co = 27)

OR

Explain the following terms giving a suitable example in each case :

(i) Ambidentate ligand

(ii) Denticity of a ligand

(iii) Crystal field splitting in an octahedral field.

9. How would you bring about the following conversion?

(i) Propanal to butanone

(ii) Benzaldehyde to benzophenone

(iii) Benzoyl chloride to benzonitrile

Give complete equation and reaction conditions in each case.

10. Assign suitable reasons for the following :

(i) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.

(ii) In the 3*d* series from Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomization of Zn is the lowest.

(iii) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured.

11. State one chemical method each to distinguish between the following pairs of organic compounds.

(i) Acetaldehyde and acetone

(ii) Phenol and benzoic acid

(iii) Propanone and ethanol

SECTION - C

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

Colloidal particles carry either positive or negative charge. The nature of this charge is the same on all the dispersed particles in a given colloidal solution and may be either positive or negative. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particles usually takes place. When KI solution is added to the $AgNO_3$ solution till KI is in excess, the precipitated silver iodide adsorbs iodide ions from the dispersion medium, and negatively charged colloidal solution results. If the colloidal sol of AgI is prepared by adding $AgNO_3$ solution to KI solution till $AgNO_3$ is in slight excess, Ag^+ ions will be adsorbed giving positive charge to the colloidal particles. The combination of the two layers of opposite charges around the colloidal particles is called Helmholtz electrical double layer. The presence of equal and similar charges on colloidal particles is largely responsible for providing stability to the colloidal solution.

(a) Why does the presence of equal and similar charges on colloidal particles provide stability?

(b) Why is a negatively charged sol obtained on adding $AgNO_3$ solution to KI solution?

(c) Out of KI or K_2SO_4, which electrolyte is better in the coagulation of positive sol?

(d) Write the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$.

OR

What is the reason for the charge on sol particles?

Solution

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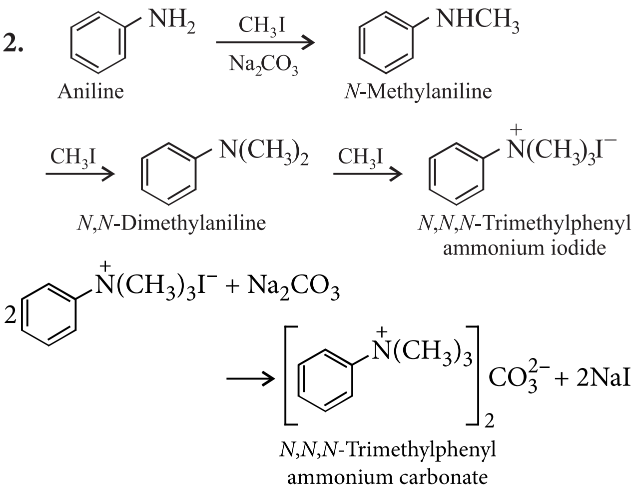
1. (i) Average rate $= -\dfrac{C_2 - C_1}{t_2 - t_1}$

From the data when $t = t_1 = 30$ s, $C_1 = 0.31$ mol L^{-1} and when $t = t_2 = 60$ s ; $C_2 = 0.17$ mol L^{-1}

$$\therefore \text{ Average rate} = -\frac{(0.17 - 0.31)\text{ mol L}^{-1}}{(60 - 30)\text{ s}}$$

$$= \frac{0.14\text{ mol L}^{-1}}{30\text{ s}} = 4.67 \times 10^{-3}\text{ mol L}^{-1}\text{ s}^{-1}$$

2.

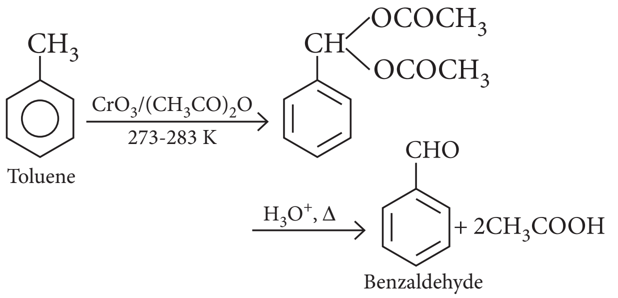


3. If alkyl halide is in excess, the hydrogen atoms of ammonia are successively replaced by alkyl group to form primary, secondary and tertiary amines which further react with alkyl halide to form quaternary ammonium salt as follows :

$$\text{NH}_3\text{(alc.)} \xrightarrow[-HX]{+RX} \underset{1^\circ\text{ Amine}}{RNH_2} \xrightarrow[-HX]{+RX} \underset{2^\circ\text{ Amine}}{R_2NH}$$

$$\xrightarrow{+RX} \underset{3^\circ\text{ Amine}}{R_3N} \xrightarrow{+RX} \underset{\text{Tetra alkyl ammonium halide}}{R_4N^+X^-}$$

4. (i) Oxidation of toluene to benzaldehyde is carried out with CrO$_3$ in presence of acetic anhydride because it traps aldehyde as *gem* diacetate and further oxidation does not take place to give carboxylic acid.



(ii) Ethanoic acid is miscible in water due to the formation of H–bonding with water but as the size of hydrophobic part increases its solubility decreases so, benzoic acid is insoluble.

5. (a) (i) Cr^{2+} is a stronger reducing agent than Fe^{2+}. $E^\circ_{Cr^{3+}/Cr^{2+}}$ is negative (–0.41 V) whereas $E^\circ_{Fe^{3+}/Fe^{2+}}$ is positive (+ 0.77 V). Thus Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+}. Hence, Cr^{2+} is stronger reducing agent than Fe^{2+}.

(ii) More positive is the value of E°, reaction will be more feasible.

As $E^\circ_{Co^{3+}/Co^{2+}}$ is maximum, thus Co^{2+} ion is most stable.

(b) Zn, Cd, Hg are considered as *d*-block elements but not as transition elements because they do not have partly filled *d*-orbitals in their atomic state or their common oxidation states (*i.e.*, Zn^{2+}, Cd^{2+}, Hg^{2+}).

OR

(a) Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.

e.g., $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$
$Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

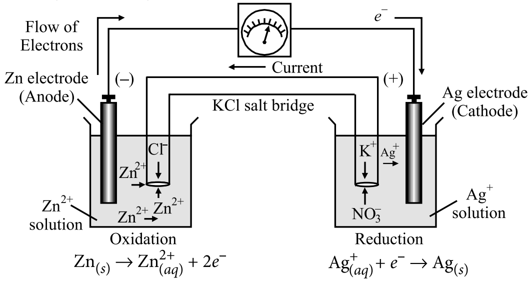
(b) The steady decrease in the atomic and ionic radii (having the same charge) with increase in atomic number across the series from lanthanum to lutetium is known as lanthanoid contraction.

6. The reaction is

$$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

Cell can be represented as

$$Zn|Zn^{2+}_{(aq)}||Ag^+_{(aq)}|Ag$$



(i) The zinc electrode is negatively charged (anode) as it pushes the electrons into the external circuit.

(ii) Ions are the current carriers within the cell.

(iii) The reactions occurring at two electrodes are :

At zinc electrode (anode) : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

At silver electrode (cathode) : $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

OR

At anode : $Ni \longrightarrow Ni^{2+} + 2e^-$

At cathode : $[Ag^+ + e^- \longrightarrow Ag] \times 2$

Cell reaction : $Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ_{Ag^+/Ag} - E^\circ_{Ni^{2+}/Ni} = 0.80\text{ V} - (-0.25)\text{ V}$$

$$E^\circ_{cell} = 1.05\text{ V}$$

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_c$$

$$\log K_c = \frac{E^\circ_{cell} \times n}{0.0591} = \frac{1.05 \times 2}{0.0591}$$

$\log K_c = 35.53$

$K_c = \text{antilog } 35.53 = 3.38 \times 10^{35}$

7. Given $t_{1/2} = 5730$ years

$$\therefore \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\text{ years}} = 1.209 \times 10^{-4}\text{ years}^{-1}$$

Let the initial concentration of ^{14}C (concentration in living tree) be 100. The concentration observed in the artifact = 80.

From the integrated rate law of first order reaction

$$t = \frac{2.303}{k}\log\frac{R_0}{R_t} = \frac{2.303 \times 5730}{0.693}\log\frac{100}{80}$$

$$= \frac{2.303 \times 5730}{0.693}\log 1.25$$

$$= \frac{2.303 \times 5730}{0.693} \times 0.09691 = 1845\text{ years}$$

OR

	$SO_2Cl_2 \rightarrow$	SO_2 +	Cl_2
Initial pressure	p_0	0	0
Pressure at time t	$p_0 - p$	p	p

Let initial pressure, $p_0 \propto R_0$

Total Pressure at time t, $P_t = p_0 - p + p + p = p_0 + p$

Pressure of reactants at time t, $p_0 - p = 2p_0 - P_t \propto R$

$$k = \frac{2.303}{t}\log\frac{p_0}{2p_0 - P_t}$$

$$= \frac{2.303}{100}\log\frac{0.5}{2 \times 0.5 - 0.6} = \frac{2.303}{100}\log 1.25 = 2.2318 \times 10^{-3}\text{ s}^{-1}$$

Pressure of SO_2Cl_2 at time t $(p_{SO_2Cl_2})$

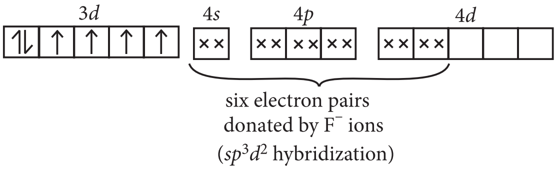
$= 2p_0 - P_t = (2 \times 0.50 - 0.65)$ atm $= 0.35$ atm

Rate at that time $= k \times p_{SO_2Cl_2}$

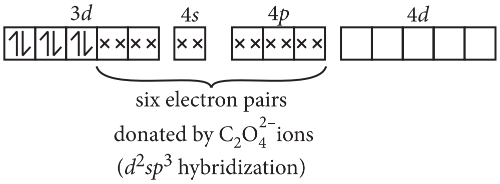
$= (2.2318 \times 10^{-3}) \times (0.35) = 7.8 \times 10^{-4}$ atm s^{-1}

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

$[CoF_6]^{3-}$:



$[Co(C_2O_4)_3]^{3-}$:



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

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

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

(iv) $[Co(C_2O_4)_3]^{3-}$ is low spin complex due to absence of any unpaired electron.

OR

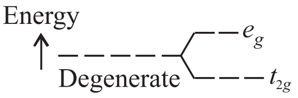
(i) **Ambidentate ligand :** A unidentate ligand which can coordinate to central metal atom through two different atoms is called ambidentate ligand. For example, NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.

(ii) **Denticity :** The number of coordinating groups present in ligand is called the denticity of ligand. For example, bidentate ligand ethane-1, 2-diamine has two donor nitrogen atoms which can link to central metal atom.

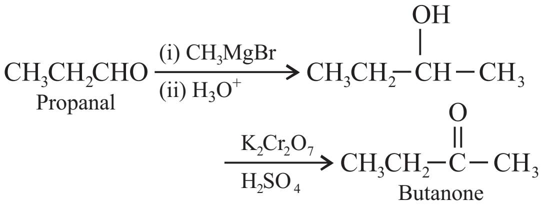
$$H_2\ddot{N}—CH_2—CH_2—\ddot{N}H_2$$

Ethane-1, 2-diammine

(iii) **Crystal field splitting in octahedral field :** The splitting of the degenerate d-orbitals into three orbitals of lower energy, t_{2g} set and two orbitals of higher energy e_g set due to the interaction of ligand in an octahedral crystal field is known as crystal field splitting in an octahedral field.



9. (i)



$$\underset{\text{Propanal}}{CH_3CH_2CHO} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} CH_3CH_2-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Butanone}}{CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_3}$$

(ii)
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_6H_5COOH \xrightarrow{CaCO_3}$$
$$\underset{\text{Cal. benzoate}}{(C_6H_5COO)_2Ca} \xrightarrow[-CaCO_3]{\text{Dry distil.}} \underset{\text{Benzophenone}}{C_6H_5-CO-C_6H_5}$$

(iii)
$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow[-NH_4Cl]{2NH_3}$$
$$C_6H_5CONH_2 \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Benzonitrile}}{C_6H_5-C\equiv N}$$

10. (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(ii) Zinc ($Z = 30$) has completely filled *d*-orbital ($3d^{10}$), so *d*-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

(iii) Only those ions are coloured which have partially filled *d*-orbitals facilitating *d*-*d* transitions.

Sc^{3+} with $3d^0$ configuration is colourless while Ti^{3+} ($3d^1$) is coloured.

11. (i) Acetaldehyde reduces Tollens' reagent to silver mirror but acetone does not.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + 2H_2O + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3$$

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{\text{Tollens' reagent}} \text{No reaction}$$

(ii) Benzoic acid being a stronger acid than phenol, decomposes $NaHCO_3$ to evolve CO_2 but phenol does not.

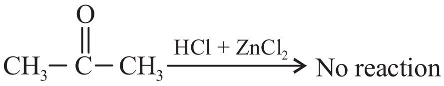
$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2\uparrow$$

$$C_6H_5OH \xrightarrow{NaHCO_3} \text{No evolution of } CO_2$$

(iii) When treated with Lucas reagent (conc. HCl + anhyd. $ZnCl_2$) ethanol gives cloudiness on heating.

$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$

Propanone does not give Lucas test.



$$CH_3-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{HCl + ZnCl_2} \text{No reaction}$$

12. (a) The main reason for the stability of colloids is the electrostatic stabilisation *i.e.*, equal and same type of charge on the colloidal particles which causes repulsion between them and prevents the coagulation of the sol.

(b) When $AgNO_3$ solution is added to aqueous KI solution, a negatively charged sol of AgI is formed. This is due to selective adsorption of I^- ions from the dispersion medium.

$$AgI + \underset{\text{Dispersion medium}}{I^-} \longrightarrow \underset{\text{Negative sol}}{[AgI]I^-}$$

(c) K_2SO_4 is more effective in causing coagulation of positively charged colloidal sol. because greater the valency of the coagulating ion, greater is its power to bring about coagulation.

(d) Hydrolysis is the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_{3(sol)} + 3HCl$$

OR

The charge on sol particles is due to preferential adsorption of ions from solution.