

Class-XII Session 2022-23
Subject - Chemistry
Sample Question Paper - 24
With Solution

BLUE PRINT

S. No.	Chapter Name	Section-A		Section-B		Section-C		Section-D		Section-E		Total Marks	
		(MCQs & A/R) 1 Mark		(VSA) 2 Marks		(SA) 3 Marks		(Case Study) 4 Marks		(LA) 5 Marks			
		Q. No.	Marks	Q. No.	Marks	Q. No.	Marks	Q. No.	Marks	Q. No.	Marks	Q. No.	Marks
1	Solutions	5, 8	2							33	5	7	
2	Electrochemistry	2, 13, 16	3	20	2	27	3					8	
3	Chemical Kinetics	6, 17	2	24	2	30	3					7	
4	d -and f -Block Elements	10	1	19	2					35	5	8	
5	Coordination Compounds			25	2			32	4			6	
6	Haloalkanes and Haloarenes	3, 9	2			26. a	1	31	4			7	
7	Alcohols, Phenols and Ethers	4, 11	2	21	2	26. b, c	2					6	
8	Aldehydes, Ketones and Carboxylic Acids	1, 15, 18	3							34	5	8	
9	Amines	14	1	22	2	28	3					6	
10	Biomolecules	7, 12	2	23	2	29	3					7	
	Total Marks (Total Questions)	18	18	7	14	5	15	2	8	3	15	70	

General Instructions

Read the following instructions carefully

- (a) There are 35 questions in this question paper with internal choice.
- (b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
- (c) SECTION B consists of 7 very short answer questions carrying 2 marks each.
- (d) SECTION C consists of 5 short answer questions carrying 3 marks each.
- (e) SECTION D consists of 2 case-based questions carrying 4 marks each.
- (f) SECTION E consists of 3 long answer questions carrying 5 marks each.
- (g) All questions are compulsory.
- (h) Use of log tables and calculator are not allowed.

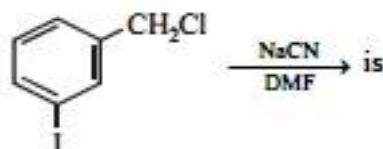
SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

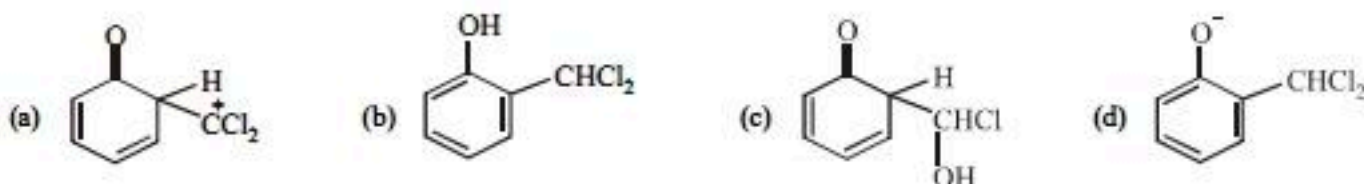
- Acetaldehyde does not respond to
 - (a) Tollen's test
 - (b) Benedict's test
 - (c) Lucas test
 - (d) Iodoform test
- The chemical reaction,

$$2\text{AgCl(s)} + \text{H}_2\text{(g)} \longrightarrow 2\text{HCl(aq)} + 2\text{Ag(s)}$$
 taking place in a galvanic cell is represented by the notation
 - (a) $\text{Pt(s)} | \text{H}_2\text{(g), 1 bar} | 1\text{M KCl(aq)} | \text{AgCl(s)} | \text{Ag(s)}$
 - (b) $\text{Pt(s)} | \text{H}_2\text{(g), 1 bar} | 1\text{M HCl(aq)} | 1\text{M Ag}^+\text{(aq)} | \text{Ag(s)}$
 - (c) $\text{Pt(s)} | \text{H}_2\text{(g), 1 bar} | 1\text{M HCl(aq)} | \text{AgCl(s)} | \text{Ag(s)}$
 - (d) $\text{Pt(s)} | \text{H}_2\text{(g), 1 bar} | 1\text{M HCl(aq)} | \text{Ag(s)} | \text{AgCl(s)}$

- The structure of the major product formed in the following reaction



- (a)
 - (b)
 - (c)
 - (d)
- When phenol is reacted with CHCl_3 and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate?

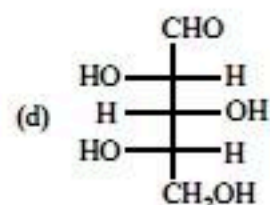
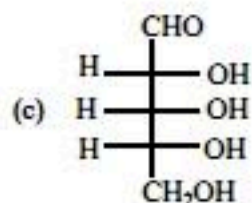
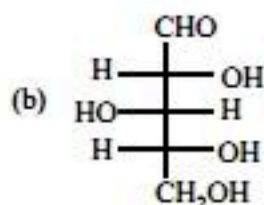
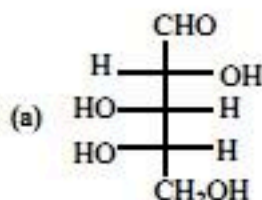


- On the basis of information given below mark the correct option.

Information

- (i) In bromoethane and chloroethane mixture intermolecular interactions of A — A and B — B type are nearly same as A — B type interactions.
- (ii) In ethanol and acetone mixture A — A or B — B type intermolecular interactions are stronger than A — B type interactions.

- (iii) In chloroform and acetone mixture A — A or B — B type intermolecular interactions are weaker than A — B type interactions.
- (a) Solution (ii) and (iii) will follow Raoult's law
 (b) Solution (i) will follow Raoult's law
 (c) Solution (ii) will show negative deviation from Raoult's law
 (d) Solution (iii) will show positive deviation from Raoult's law
6. The plot of concentration of the reactant vs time for a reaction is a straight line with a negative slope. The reaction follows a rate equation
 (a) zero order (b) first order (c) second order (d) third order
7. Which of the following statements is incorrect?
 (a) In α -helix structure a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw.
 (b) In β -structure of proteins all peptide chains are stretched out to nearly maximum extension.
 (c) During denaturation 1° and 2° structures are destroyed but 3° structure remains intact.
 (d) All the above statements are incorrect.
8. The solubility of N_2 in water at 300 K and 500 torr partial pressure is 0.01 g L^{-1} . The solubility (in g L^{-1}) at 750 torr partial pressure is :
 (a) 0.0075 (b) 0.005 (c) 0.02 (d) 0.015
9. Which one is the most reactive towards S_N1 reaction?
 (a) $C_6H_5CH(C_6H_5)Br$ (b) $C_6H_5CH(CH_3)Br$ (c) $C_6H_5C(CH_3)(C_6H_5)Br$ (d) $C_6H_5CH_2Br$
10. Which of the following pairs has the same size?
 (a) Fe^{2+}, Ni^{2+} (b) Zr^{4+}, Ti^{4+} (c) Zr^{4+}, Hf^{4+} (d) Zn^{2+}, Hf^{4+}
11. Which of the following reactions will not result in the formation of anisole?
 (a) Phenol + dimethyl sulphate in presence of a base (b) Sodium phenoxide is treated with methyl iodide
 (c) Reaction of diazomethane with phenol (d) Reaction of methylmagnesium iodide with phenol
12. Which L-sugar on oxidation gives an optically active dibasic acid (2COOH groups)?



OR

***FOR VISUALLY CHALLENGED LEARNER**

- *12. Rapid interconversion of α -D-glucose and β -D-glucose to solution is known as:
 (a) racemization (b) asymmetric induction
 (c) fluxional isomerization (d) mutarotation
13. The unit of specific conductivity is
 (a) ohm cm^{-1} (b) ohm cm^{-2} (c) $\text{ohm}^{-1} \text{ cm}$ (d) $\text{ohm}^{-1} \text{ cm}^{-1}$
14. Which of the following reactions will not give a primary amine?
- (a) $\text{CH}_3\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{KOH}}$ (b) $\text{CH}_3\text{CN} \xrightarrow{\text{LiAlH}_4}$
 (c) $\text{CH}_3\text{NC} \xrightarrow{\text{LiAlH}_4}$ (d) $\text{CH}_3\text{CONH}_2 \xrightarrow{\text{LiAlH}_4}$

In the following questions (15-18) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
 (b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
 (c) Assertion is correct, but reason is wrong statement.
 (d) Assertion is wrong, but reason is correct statement.
15. **Assertion:** Nitration of benzoic acid gives *m*-nitrobenzoic acid.
Reason : Carboxyl group increases the electron-density at *meta*-position.
16. **Assertion :** Specific conductance decreases with dilution whereas equivalent conductance increases.
Reason : On dilution, number of ions per millilitre decreases but total number of ions increases considerably.
17. **Assertion :** The order of a reaction can have fractional value.
Reason : The order of a reaction cannot be written from balanced equation of a reaction.
18. **Assertion :** Acetaldehyde on treatment with alkali gives aldol.
Reason : Acetaldehyde molecule contains α -hydrogen atom.

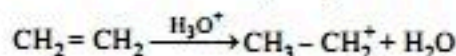
SECTION-B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

19. Use the data to answer the following and also justify giving reason:

	Cr	Mn	Fe	Co
$E^0_{M^{2+}/M}$	-0.91	-1.18	-0.44	-0.28
$E^0_{M^{3+}/M^{2+}}$	-0.41	+1.57	+0.77	+1.97

- (a) Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?
 (b) Which is the most stable ion in +2 oxidation state and why?
20. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell.
21. (a) Arrange the following compounds in the increasing order of their acid strength:
p-cresol, *p*-nitrophenol, phenol
 (b) Write the mechanism (using curved arrow notation) of the following reaction:



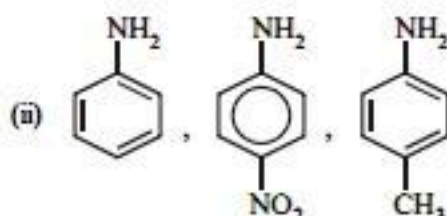
OR

Write the structures of the products when Butan-2-ol reacts with the following

- (a) CrO_3 (b) $SOCl_2$

22. Arrange the following in increasing order of their basic strength.

- (i) $C_6H_5-NH_2$, $C_6H_5-CH_2-NH_2$, $C_6H_5-NH-CH_3$



23. Why on electrolysis in acidic solution amino acids migrate towards cathode while in alkaline solution these migrate towards anode?

24. In the reaction $A + 2B \longrightarrow 3C + 2D$, the rate of disappearance of B is $1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$. What will be the rate of the reaction and rate of disappearance of A and appearance of C?
25. Write IUPAC name of the complex $[\text{Pt}(\text{en})_2\text{Cl}_2]$. Draw structures of geometrical isomers for this complex.

OR

Using IUPAC norms write the formulae for the following:

- Hexaamminecobalt(III) sulphate
- Potassium trioxalatochromate(III)

SECTION-C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

26. (a) Why haloarenes undergo electrophilic substitution reaction?
Write the chemical equations involved in the below reactions.

- Phenol reacts with conc. HNO_3 ?
- Ethyl chloride reacts with NaOC_2H_5 ?

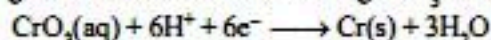
27. Calculate $\Delta_r G^\circ$ and $\log K_c$ for the following reaction:



Given: $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.403 \text{ V}$; $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763 \text{ V}$

OR

Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation:



Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?

[Atomic mass of Cr = 52 g mol^{-1} , $1 \text{ F} = 96500 \text{ C mol}^{-1}$]

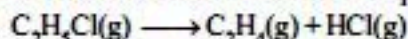
28. An aromatic compound 'A' on heating with Br_2 and KOH forms a compound 'B' of molecular formula $\text{C}_6\text{H}_7\text{N}$ which on reacting with CHCl_3 and alcoholic KOH produces a foul smelling compound 'C'. Write the structures and IUPAC names of compounds A, B and C.
29. Why does glucose reacts with Fehling's solution and phenyl hydrazine, but not with NaHSO_3 ?
30. Following data are obtained for the reaction :
- $$\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$$

t/s	0	300	600
$[\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

- Show that it follows first order reaction.
- Calculate the half-life.
(Given $\log 2 = 0.3010$ $\log 4 = 0.6021$)

OR

For the first order thermal decomposition reaction, the following data were obtained :



Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant.

(Given : $\log 2 = 0.301$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

SECTION-D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31. The reactions of haloalkanes may be divided into the following categories: (i) Nucleophilic substitution (ii) Elimination reactions (iii) Reaction with metals. (i) Nucleophilic substitution reactions in this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction. It is one of the most useful classes of organic reactions of alkyl halides in which halogen is bonded to sp^3 hybridised carbon. This reaction has been found to proceed by two different mechanisms substitution nucleophilic bimolecular (S_N2) The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants. Substitution nucleophilic unimolecular (S_N1) S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). The reaction between *tert*-butyl bromide and hydroxide ion yields *tert*-butyl alcohol and follows the first order kinetics.

Answer the following questions :

- (a) Write reaction of 1-Chlorobutane on heating with alcoholic KOH.
- (b) Write treatment of 1, 3-dichloropropane on reaction with alc. KOH.
- (c) Why Alkyl halides give elimination reaction with alcoholic KOH, but nucleophilic substitution with aqueous KOH?

OR

Why S_N2 reactions always proceed with inversion of configuration?

32. Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions on magnetic and optical properties of coordination compounds. Many approaches have been put forth to explain the nature of bonding in coordination compounds. It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory. The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. According to the theory, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting.

Answer the following questions :

- (a) Why NF_3 is a weaker ligand than $N(CH_3)_3$?
- (b) $[FeF_6]^{3-}$ is a low spin complex, Justify.
- (c) Potassium ferrocyanide is diamagnetic, whereas potassium ferricyanide is paramagnetic, Explain.

OR

$[Cr(H_2O)_6]^{2+} \rightarrow [Cr(H_2O)_6]^{3+}$ while converting, colour continuously changes, why?

SECTION-E

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

33. (a) The vapour pressures of pure liquids A and B are 70 mm and 90mm Hg respectively at 25 °C. The mole fraction of 'A' in a solution of two is 0.3. Assuming that A and B form an ideal solution, calculate the partial pressure of each component is equilibrium with the solution.
- (b) (i) Two liquids A and B boil at 145 °C and 190 °C respectively. Which of them has a higher vapour pressure at 80 °C?
- (ii) Why is the vapour pressure of a solution of glucose in water lower than that of water?

OR

- (a) Vapour pressure of pure water at 35°C is 31.82 mm Hg. When 27.0 g of solute is dissolved in 100 g of water (at the same temperature) vapour pressure of the solution, thus formed is 30.95 mm Hg. Calculate the molecular mass of solute.
- (b) (i) What are non-ideal solutions ?
- (ii) What role does the molecular interaction play in deciding the vapour pressure of following solutions?
- (1) Alcohol and acetone
 - (2) Chloroform and acetone

34. An organic compound [A] with molecular formula $C_9H_{10}O$ forms an orange-red precipitate [B] with 2, 4 - DNP reagent. Compound [A] gives yellow precipitate [C] on heating with iodine in the presence of sodium hydroxide along with a colourless compound [D]. The compound [A] does not reduce Tollen's reagent or Fehling's solution nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, compound [A] gives a carboxylic acid [E] having molecular formula $C_7H_6O_2$. Deduce the structure of the organic compounds [A] to [E].

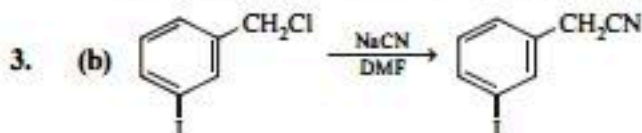
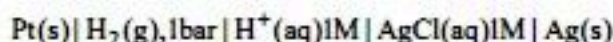
OR

- (a) You are provided with four reagents: Fehling's solution, $I_2/NaOH$, $NaHSO_3$ and Schiff's reagent. Which reagents can be used to distinguish between the compounds in each of the following pairs:
- (i) CH_3CHO and CH_3COCH_3 (ii) CH_3CHO and C_6H_5CHO
(iii) $C_6H_5COCH_3$ and $C_6H_5COC_6H_5$
- (b) How will you convert :
- (i) Formaldehyde to acetaldehyde (ii) Acetaldehyde to methyl alcohol.
35. (a) Size of trivalent lanthanoid cations decreases with increase in the atomic number.
(b) Transition metal fluorides are ionic in nature, whereas, bromides and chlorides are usually covalent in nature.
(c) Which oxidation state of Mn is most stable and why?
(d) Which transition element show highest oxidation state and in which compound?
(e) Which is the densest transition element?

Solutions

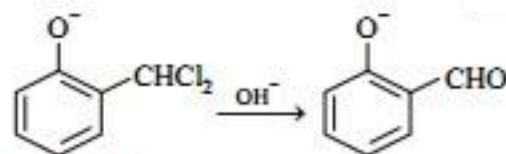
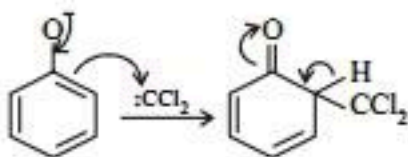
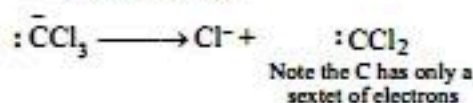
SAMPLE PAPER-7

- (c) Lucas test is used to detect alcohols.
- (a) $2\text{AgCl(s)} + \text{H}_2(\text{g}) \rightarrow 2\text{HCl(aq)} + 2\text{Ag(s)}$
The activities of solids and liquids are taken as unity and at low concentrations, the activity of a solute is approximated to its molarity.
The cell reaction will be



Nuclear substitution will not take place.

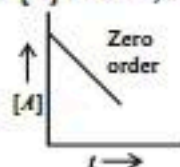
- (d) Reimer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring.



A benzal chloride

- (b) A mixture of bromoethane and chloroethane is an example of ideal solution. For an ideal solution, the A—A or B—B type intermolecular interaction is nearly equal to A—B type interaction.
Chloroform and acetone mixture is an example of non-ideal solution having negative deviation while ethanol-acetone mixture shows positive deviation.

- (a) Plots of conc. [A] Vs time, t



- (c) During denaturation 2° and 3° structures are destroyed but 1° structure remains intact.

- (d) According to Henry's law

$$\frac{P_1}{P_2} = \frac{S_1}{S_2} \Rightarrow \frac{500}{750} = \frac{0.01}{S_2}$$

$$\therefore S_2 = \frac{750 \times 0.01}{500} = 0.015 \text{ g/L}$$

- (c) $\text{S}_{\text{N}}1$ reactions involve the formation of carbocations, hence higher the stability of carbocation, more will be reactivity of the parent alkyl halide. Thus tertiary carbocation formed from (c) is stabilized by two phenyl groups and one methyl group, hence most stable.
- (c) Due to lanthanide contraction, the size of Zr and Hf (atom and ions) become nearly similar.
- (d) Phenol has active (acidic) hydrogen so it reacts with CH_3MgI to give CH_4 , and not anisole
 $\text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{MgI} \longrightarrow \text{CH}_4 + \text{C}_6\text{H}_5\text{OMgI}$
- (a) (a) and (d) are L^- sugar but (a) gives an optically active dibasic acid.

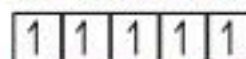
OR

- (d)
- (d) $\text{ohm}^{-1} \text{cm}^{-1}$
- (c) CH_3NC (methyl isocyanide) on reduction with LiAlH_4 gives secondary amine.
- (c) Carboxyl group decreases the electron density at m -position relative to o - and p -positions.
- (d) Daniell cell is a type of galvanic cell.
- (b) The order of a reaction can have fractional value.
The order of a reaction cannot be written from balanced equation of a reaction because its value changes with pressure, temperature and concentration. It can only be determined experimentally. (1 mark)
- (a) Acetaldehyde gives aldol condensation reaction because it contains α -hydrogen. (1 mark)
- (a) Cr^{2+} is a stronger reducing agent because the more negative the electrode potential, greater is the reducing power of the electrode.

$$E_{\text{Cr}^{2+}/\text{Cr}}^0 = -0.91 > E_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.44$$

($\frac{1}{2} + \frac{1}{2} = 1$ Mark)

- (b) Mn^{2+} is the most stable ion because it ($\text{Mn}^{2+} - d^5$)



has half filled electronic configuration and it has most negative reduction potential

$$E_{\text{Mn}^{2+}/\text{Mn}}^0 = -1.18\text{V}$$

($\frac{1}{2} + \frac{1}{2} = 1$ Mark)

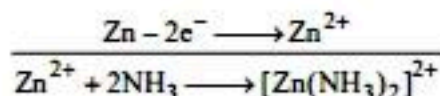
20. The dry cell also known as Leclanche cell is used in transistors.

The reactions taking place at the anode and cathode are given below.

Cathode Reaction :



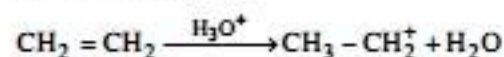
Anode Reaction:



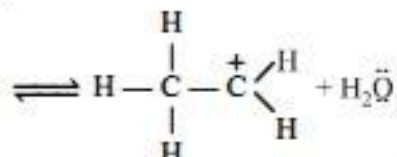
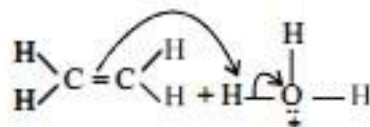
(1 + 1 = 2 Marks)

21. (a) Increasing order of acid strength is p -cresol < phenol < p -nitrophenol (1 Mark)

(b) Reaction :



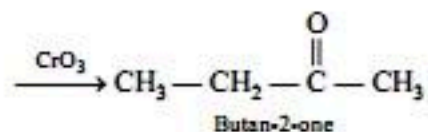
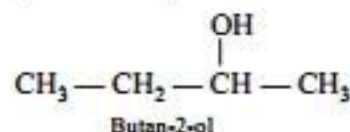
Mechanism :



(1 Mark)

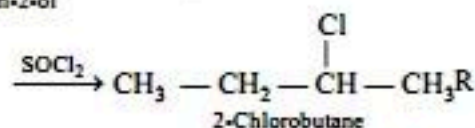
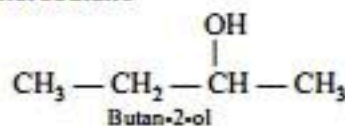
OR

- (a) Secondary alcohol (butan-2-ol) on reaction with chromic anhydride (CrO_3) oxidises to ketone (butan-2-one).



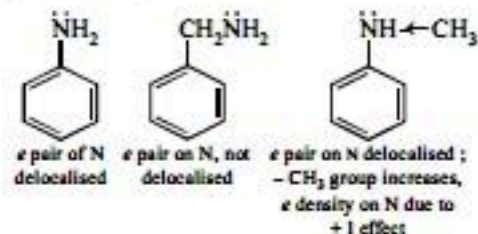
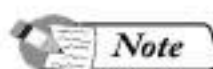
(1 Mark)

- (b) Butan-2-ol on treating with SOCl_2 forms 2-chlorobutane

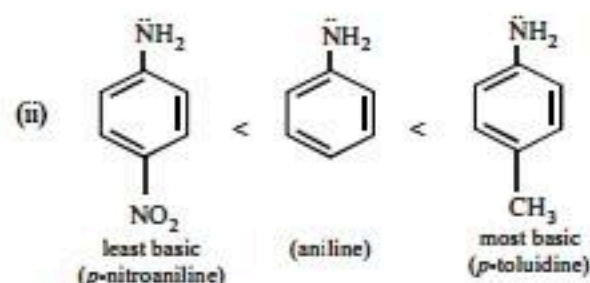


(1 Mark)

9. (i) The order of increasing basic strength is
 $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
 least basic most basic (1 Mark)



A pair of electron of nitrogen in $C_6H_5CH_2.NH_2$ is available for donation.



(1 Mark)



Nitro group is electron withdrawing hence reduces basic character, while methyl group is electron repelling hence increases basic character of aniline.

23. In acidic solution, an amino acid exists as a positive ion, $R-CH(\overset{+}{N}H_3)-COOH$. Therefore, when an electric field is applied, the amino acid migrates towards the cathode.

In alkaline solution, an amino acid exists as a negative ion, $R-CH(NH_2)-COO^-$. Therefore, when an electric field is applied, it migrates towards the anode. (2 marks)

24. Given reaction is $A + 2B \longrightarrow 3C + 2D$, thus rate of this reaction

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{1}{2} \frac{d[D]}{dt}$$

$$\frac{-d[B]}{dt} = 1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1} \text{ (given)}$$

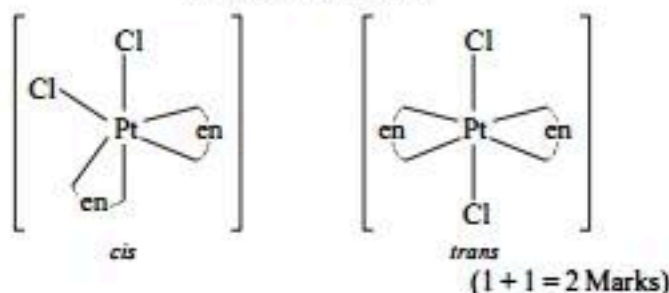
$$\text{Rate} = \frac{-1}{2} \frac{d[B]}{dt} = \frac{1}{2} \times 1 \times 10^{-2} = 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

(1 mark)

$$\frac{-d[A]}{dt} = \frac{-1}{2} \frac{d[B]}{dt} = \frac{1}{2} \times (1 \times 10^{-2}) = 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{d[C]}{dt} = \frac{-3}{2} \frac{d[B]}{dt} = \frac{3}{2} \times (1 \times 10^{-2}) = 1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

25. Bis(ethylene diamine) dichloro platinum (II)
Geometrical isomers

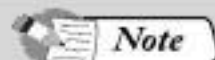
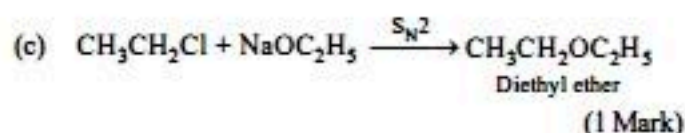
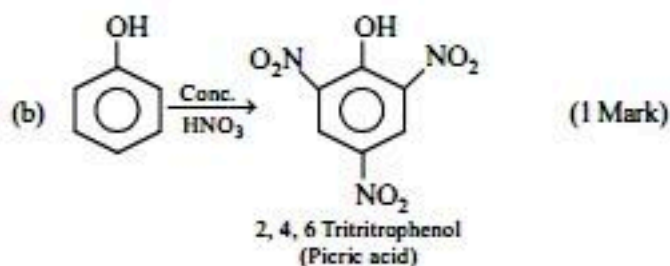
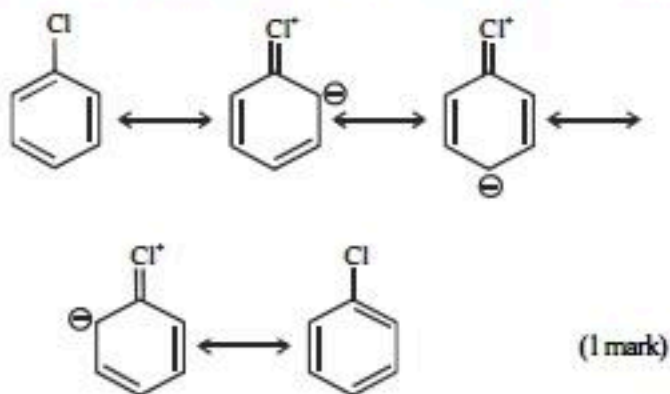


*cis-isomer of $[\text{Pt}(\text{en})_2\text{Cl}_2]$ has enantiomer pair i.e., *d* and *l* form while *trans-isomer* is optically inactive due to plane of symmetry in the molecule.*

OR

- (i) Hexaamminecobalt (III) sulphate (1 Mark)
 $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$
- (ii) Potassium trioxalatochromate (III) (1 Mark)
 $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$

26. (a) The C – X bond in haloarenes is quite strong due to partial double bond character and delocalisation of electrons in benzene ring. The negative charge centres get developed at ortho and para positions, and thus electrophile (positively charged species) can attack the benzene ring and then H^+ is removed to acquire stability.



When picric acid is hydrated then it is safe to handle, but it becomes a powerful explosive when dry (less than 10% H_2O). Dry picric acid is highly sensitive to heat, shock and friction. The moistened solid is classified as a flammable solid.

27. $\text{Cd}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+} + \text{Cd}(\text{s})$

$$E_{\text{cell}}^0 = E_{\text{Cd}^{2+}/\text{Cd}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \quad (\frac{1}{2} \text{ Mark})$$

$$= -0.403 - (-0.763) = 0.36\text{V} \quad (\frac{1}{2} \text{ Mark})$$

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

$$n = 2$$

$$\Delta G^0 = -2 \times 96500 \times 0.36 = -69480 \text{ J mol}^{-1}$$

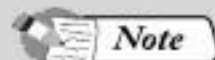
$$= -69.480 \text{ kJ mol}^{-1} \quad (1 \text{ Mark})$$

$$\Delta G^0 = -2.303 RT \log K_c \quad (\frac{1}{2} \text{ Mark})$$

$$\frac{\Delta G^0}{-2.303 RT} = \log K_c$$

$$\frac{-69480}{-2.303 \times 8.314 \times 298} = \log K_c$$

$$12.17 = \log K_c \quad (\frac{1}{2} \text{ Mark})$$



Relation between E_{cell}^0 and K_c might be calculated as given below which can be used to determine the value of K_c directly from given value of E_{cell}^0 .

$$\therefore \Delta G = -nFE_{\text{cell}}^0$$

$$\therefore \Delta G = -2.303 RT \log K_c$$

Now, $nFE_{\text{cell}}^0 = 2.303 RT \log K_c$

$$nE_{\text{cell}}^0 = \frac{2.303 RT}{F} \log K_c$$

$$= \frac{2.303 \times 8.314 \times 298}{96500} \log K_c$$

$$= 0.059 \log K_c$$

$$nE_{\text{cell}}^0 = 0.059 \log K_c$$

OR

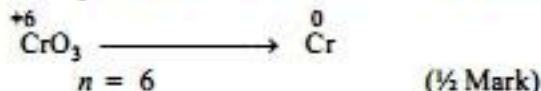
$$m = \frac{\text{Atomic mass}}{n \times F} \times Q \quad (\frac{1}{2} \text{ Mark})$$

where

m = mass deposited

t = time

Atomic mass = 52 g mol⁻¹; Q = 24000 C; F = 96500 C mol⁻¹



$$m = \frac{52 \times 24000}{6 \times 96500} = \frac{12480}{5790} = 2.15 \text{ g}$$

(½ Mark)

2.15 g of Cr will be electroplated by 24000 C

$$Q = i \times t \quad \left(\frac{1}{2} \text{ Mark}\right)$$

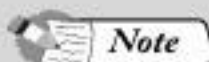
$$m = \frac{\text{Atomic mass}}{n \times F} \times i \times t$$

$$m = 1.5 \text{ g}; i = 12.5 \text{ A}, t = ?$$

$$1.5 = \frac{52}{6 \times 96500} \times 12.5 \times t$$

$$t = \frac{1.5 \times 6 \times 96500}{52 \times 12.5} \quad \left(\frac{1}{2} \text{ Mark}\right)$$

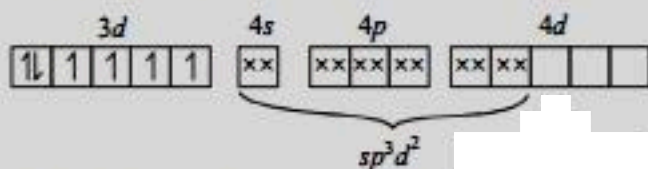
$$= 1336.15 \text{ sec} \quad \left(\frac{1}{2} \text{ Mark}\right)$$



Note

[Fe(H₂O)₆]²⁺ complex.

Fe²⁺ - 3d⁶



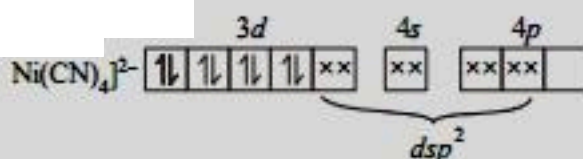
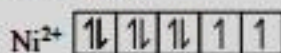
(H₂O is a weak ligand does not lead to pairing of electrons). It will be a outer orbital complex.

Magnetic character

n = 4 (4 unpaired e⁻s), paramagnetic due to unpaired e⁻s

[Ni(CN)₄]²⁻ complex.

Ni²⁺ - 3d⁸

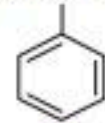
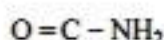


Pairing of electrons occurs due to strong CN⁻ ligand.

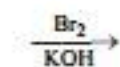
Magnetic nature

n = 0 (no. unpaired electron). Diamagnetic

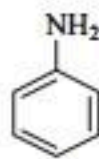
28.



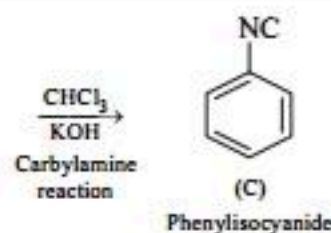
(A)
Benzamide



Hoffman
bromamide
degradation

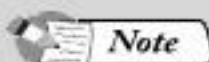


(B)
Aniline
or
Phenylamine



CHCl₃
KOH
Carbylamine
reaction

(1 + 1 + 1 = 3 Marks)



Note

Carbylamine reaction is given by aliphatic and aromatic primary amine only.

29. The reactions of glucose with Fehling's solution and phenyl hydrazine are characteristic of a -CHO group. In aqueous solution open chain, aldehyde form is in equilibrium with the cyclic hemiacetal form. Since these reactions are irreversible, the equilibrium shifts towards the open chain and eventually all the glucose reacts.

The addition reaction of an aldehyde with bisulphite is reversible reaction. It means that enough aldehyde should remain in equilibrium with the bisulphite adduct to satisfy the equilibrium with the cyclic form. At equilibrium the concentration of open chain form is very low. Consequently, there is no reaction. (3 marks)

30. (a) At 300 s

For the first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}, \quad \left(\frac{1}{2} \text{ Mark}\right)$$

where [A]₀ is initial concentration & [A] is final concentration

$$= \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = \frac{2.303}{300} \log 2$$

$$= 2.31 \times 10^{-3} \text{ sec}^{-1} \quad \left(\frac{1}{2} \text{ Mark}\right)$$

At 600 s

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}}$$

$$= \frac{2.303}{600} \log 4 = \frac{2.303}{600} \times 0.6021$$

$$= 2.31 \times 10^{-3} \text{ sec}^{-1} \quad (1 \text{ Mark})$$

In equal time interval, k is constant when using first order reaction, therefore it follows first order kinetics.

$$(b) \quad t_{1/2} = \frac{0.693}{k}, k = 2.31 \times 10^{-3}$$

$$= \frac{0.693}{2.31 \times 10^{-3}} = 300 \text{ sec} \quad (1 \text{ Mark})$$

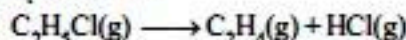
Half life is 300 sec.

OR

Given :

$$P_1 = 0.30 \text{ atm}$$

$$P_2 = 0.50 \text{ atm}$$



$$P_1 \quad \quad \quad 0 \quad \quad \quad 0 \quad \quad \quad (\text{At } t = 0 \text{ s})$$

$$P_1 - x \quad \quad \quad x \quad \quad \quad x \quad \quad \quad (\text{At } t = 300 \text{ s})$$

$$\therefore P_1 - x + x + x = P_2$$

$$0.30 + x = 0.50$$

$$x = 0.20; P_1 - x = 0.30 - 0.20$$

$$= 0.10 \text{ atm}$$

(1 Mark)

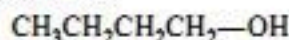
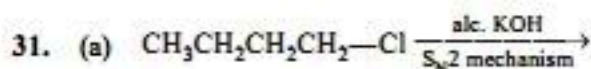
For a first-order decomposition reaction, we know that

$$k = \frac{2.303}{t} \log \left(\frac{P_1}{P_1 - x} \right) \quad \left(\frac{1}{2} \text{ Mark} \right)$$

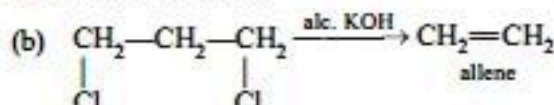
$$= \frac{2.303}{300} \log \left(\frac{0.30}{0.10} \right) \quad \left(\frac{1}{2} \text{ Mark} \right)$$

$$= \frac{2.303 \times \log 3}{300} = \frac{2.303 \times 0.4771}{300}$$

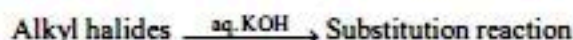
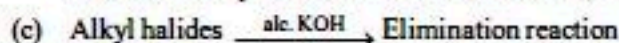
$$k = 0.0037 \text{ s}^{-1} \quad (1 \text{ Mark})$$



This reaction occurs through concerted mechanism ($\text{S}_\text{N}2$), not through the carbocation intermediate as the substrate is primary alkyl halide. (1 Mark)

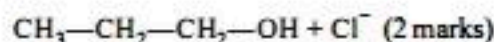
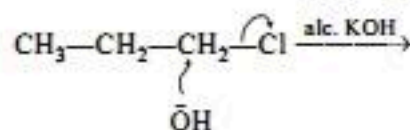
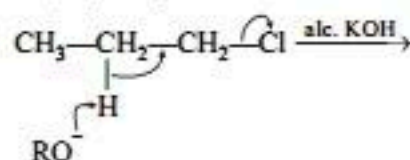


It is the nucleophilic elimination reaction. (1 mark)



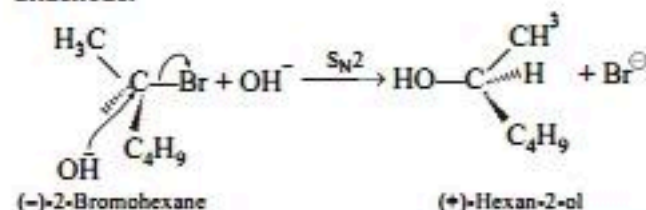
In case of alcoholic KOH, the attacking reagent is RO^- whereas in aqueous KOH solution, it is OH^- . RO^- is stronger base than OH^- because OH^- is highly hydrated in aqueous medium, so it attacks the α -carbon of the alkyl halide directly.

In alcoholic medium RO^- being a stronger base takes up the β -hydrogen atom and results in the formation of alkene.



OR

Inversion of configuration in the product occurs because the nucleophile attacks the α -carbon atom of alkyl halide on the side opposite to the one where the halogen atom is attached.



(-)-2-Bromohexane

(+)-Hexan-2-ol

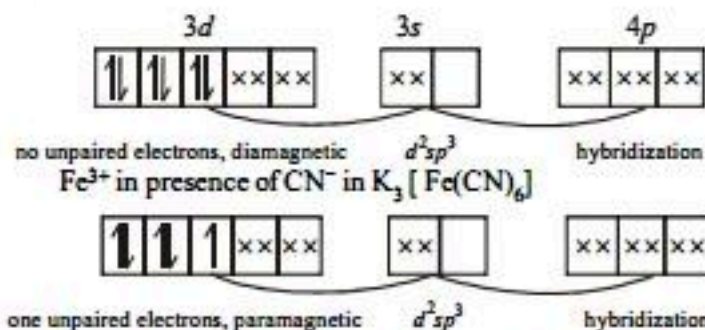
(2 marks)

32. (a) NF_3 is a weaker ligand due to high electronegativity of fluorine which withdraws electrons from N due to which the lone pair of electrons on N atom can't be ligated. $\text{N}(\text{CH}_3)_3$ is a strong ligand because CH_3 groups are electron releasing and thus increase electron availability on N atom. (1 Mark)

- (b) $[\text{FeF}_6]^{3-}$ is a high spin complex as F^- is a weak ligand. (1 Mark)

- (c) In potassium ferrocyanide, Fe is in the form Fe^{2+} and in potassium ferricyanide, Fe is in the form Fe^{3+} . CN^- is a strong field ligand. So, it will pair up all the $3d^6$ electrons of Fe^{2+} and make it diamagnetic. In Fe^{2+} , all the $3d^5$ electrons are not paired up. One electron remains unpaired. So, it is paramagnetic.

Fe^{2+} in presence of CN^- in $\text{K}_4[\text{Fe}(\text{CN})_6]$



Crystal field splitting in ferrocyanide is less than in ferricyanide ion as higher the oxidation state of the metal, greater will be the crystal field splitting. (2 Marks)

OR

- (c) Oxidation state of Cr in $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is +2.

Electronic configuration of Cr = $[\text{Ar}]_{18} 4s^1 3d^5$

Electronic configuration of Cr^{2+} = $[\text{Ar}]_{16} 3d^4$

H_2O is a weak field ligand.

CFSE value $[-0.4n_{t_2g} + 0.6n_{e_g}] \Delta_0 + nP$

$$= [-0.4 \times 3 + 0.6 \times 1] \Delta_0 + 0 = -0.6 \Delta_0$$

Oxidation state of Cr in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is +3

Electronic configuration of Cr^{3+} = $[\text{Ar}]_{16} 3d^3$

CFSE value of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

$$= [-0.4n_{t_2g} + 0.6n_{e_g}] \Delta_0 + nP$$

$$= [-0.4 \times 3 + 0] \Delta_0 + 0 = -1.2 \Delta_0 \quad (2 \text{ Marks})$$

33. (a) Here $P_A^0 = 70 \text{ mm Hg}$. $P_B^0 = 90 \text{ mm Hg}$.

$$X_A = 0.3$$

$$\therefore X_B = 1 - X_A = 1 - 0.3 = 0.7 \quad (1/2 \text{ mark})$$

$$\text{According to Raoult's Law, } P_A = P_A^0 X_A \quad (1/2 \text{ mark})$$

$$= 70 \times 0.3 = 21 \text{ mm Hg.}$$

$$P_B = P_B^0 X_B = 90 \times 0.7 = 63 \text{ mm Hg.} \quad (1 \text{ mark})$$

- (b) (i) Liquid A will have higher vapour pressure at 80°C . (1 mark)

(ii) When any solute, *i.e.*, glucose is dissolved in water, the surface of the solution is occupied of (non-volatile) molecules. Whereas in case of pure water whole surface is occupied by solvent molecules. Therefore, the number of solvent molecules escaping from the surface is correspondingly reduced as compared to the pure solvent and thus results in the decrease of vapour pressure. (2 marks)

OR

- (a) Using Raoult's law equation of lowering of vapour pressure :

$$\frac{P_A^0 - P_A}{P_A^0} = x_B \quad (1/2 \text{ mark})$$

$$\text{or } \frac{31.82 - 30.95}{31.82} = \frac{27/M_B}{100/18} \quad (1/2 \text{ mark})$$

$$\text{or } \frac{0.87}{31.82} = \frac{27}{M_B} \times \frac{18}{100}$$

$$\text{or } M_B = \frac{27 \times 18 \times 31.82}{0.87 \times 100} \text{ or } 177.75 \text{ g mol}^{-1}$$

Hence, molecular mass of the solute = $177.75 \text{ g mol}^{-1}$.

(1 mark)

- (b) (i) Non-ideal solutions are those solutions which do not follow Raoult's Law.

$$\text{Also } \Delta H_{\text{mix}} \neq 0 \text{ and } \Delta V_{\text{mix}} \neq 0. \quad (1 \text{ mark})$$

The force of attraction between A-A and B-B is not equal to that between A-B.

(ii) (1) In alcohol and acetone solution, force of attraction is less between alcohol and acetone molecules than in pure alcohol molecules as well as in pure acetone molecules, therefore, vapour pressure increases. (1 mark)

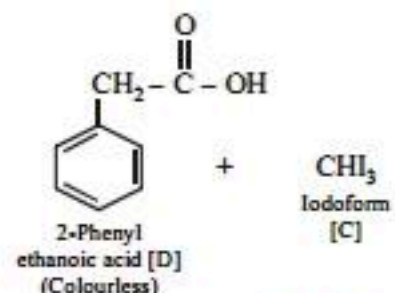
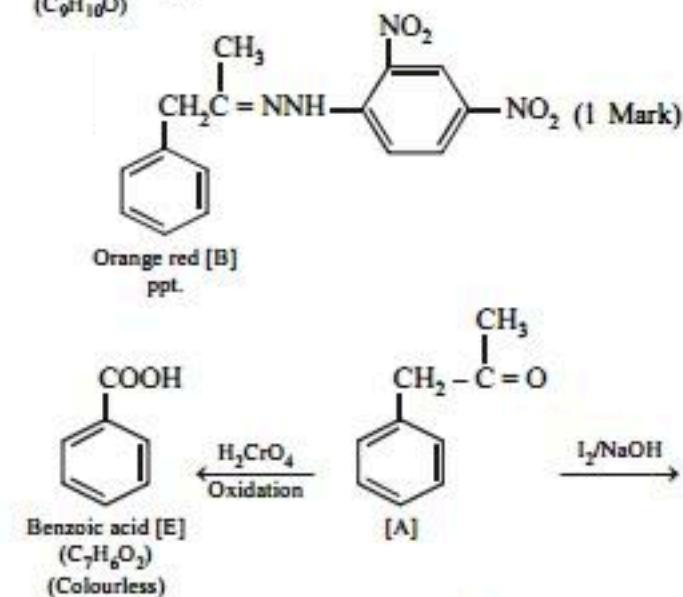
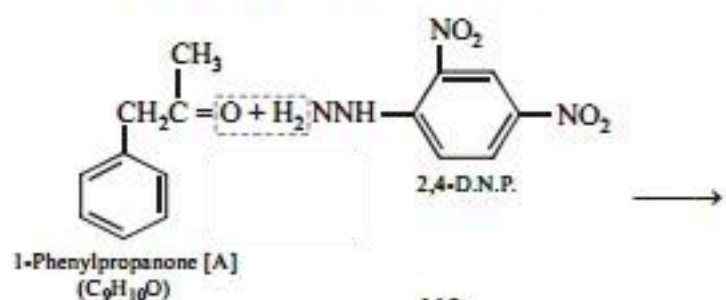
(2) In chloroform and acetone, force of attraction increases due to intermolecular H-bonding therefore, vapour pressure decreases. (1 mark)

34. (i) Positive test with 2, 4-DNP and negative tests with Tollen's reagent and Fehling's solution suggest that the compound [A] is a ketone. Since it responds to iodoform test (I_2/NaOH), it must be a methyl ketone (CH_3COR). (1 Mark)

- (ii) The molecular formula suggests a high degree of unsaturation which is ruled out because it does not decolourise either bromine water or Baeyer's reagent. Thus, we may conclude that it is an aromatic compound and the side chain has $-\text{COCH}_3$ group. (1 Mark)

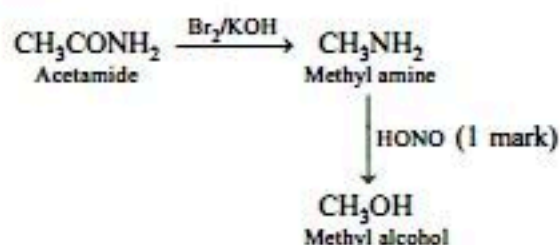
- (iii) Thus, the compound [A] is $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_3$ (1-phenylpropanone).

The reactions involved are as follows :



(1 mark)

(a) (i) Schiff's reagent or Fehling's solution. (1 mark)
(ii) $I_2/NaOH$ or Fehling's solution (1 mark)
(iii) $I_2/NaOH$. (1 mark)
(b) (i) Formaldehyde to acetaldehyde



35. (a) Size of trivalent lanthanoid cations decreases with increase in the atomic number. It is due to poor shielding effect of $4f$ -electrons. As effective nuclear charge increases, ionic size decreases. (1 mark)
- (b) Ionic character of metal halide depends upon the electronegativity difference between the metal and halogen. F is more electronegative than Cl and Br, therefore, fluorides of transition metals are ionic whereas chlorides and bromides are covalent in nature. (1 mark)
- (c) + 2 oxidation state of Mn is most stable. In this oxidation state, it has exactly half-filled d -orbitals. (1 mark)
- (d) Osmium, (Os) shows highest oxidation state in osmium tetroxide (OsO_4). (1 mark)
- (e) Osmium (Os) is the densest transition element. (1 mark)