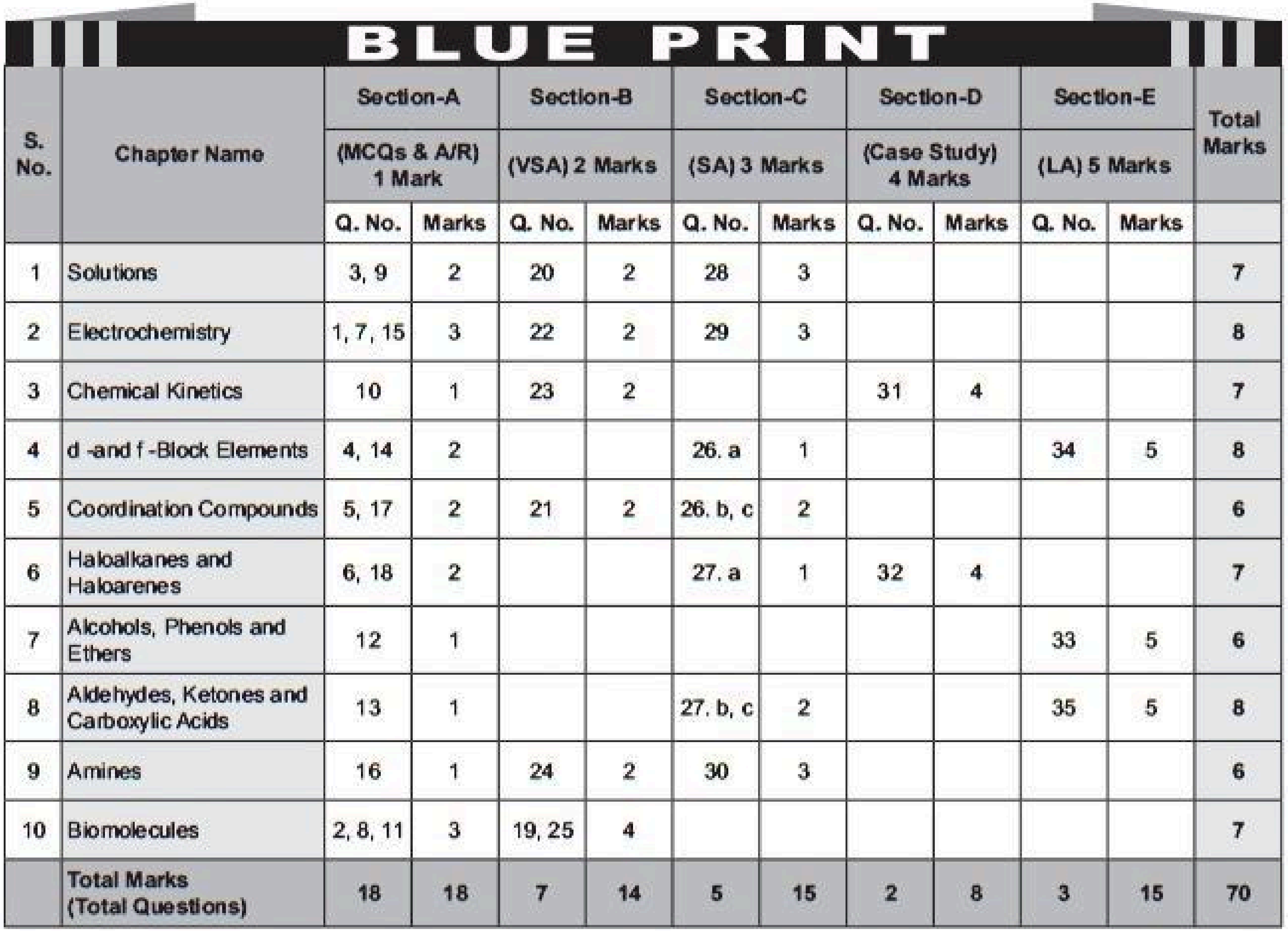
Class-XII Session 2022-23
Subject - Chemistry
Sample Question Paper - 18
With Solution



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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	
1	Solutions	3, 9	2	20	2	28	3					7
2	Electrochemistry	1, 7, 15	3	22	2	29	3					8
3	Chemical Kinetics	10	1	23	2			31	4			7
4	d -and f -Block Elements	4, 14	2			26. a	1			34	5	8
5	Coordination Compounds	5, 17	2	21	2	26. b, c	2					6
6	Haloalkanes and Haloarenes	6, 18	2			27. a	1	32	4			7
7	Alcohols, Phenols and Ethers	12	1							33	5	6
8	Aldehydes, Ketones and Carboxylic Acids	13	1			27. b, c	2			35	5	8
9	Amines	16	1	24	2	30	3					6
10	Biomolecules	2, 8, 11	3	19, 25	4							7
	Total Marks (Total Questions)	18	18	7	14	5	15	2	8	3	15	70

Time : 3 Hours **Max. Marks : 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.

1. Effect of dilution on conductivity of solution:

(a) Increases (b) Decreases (c) Unchanged (d) None of these

2. Primary structure of a protein is

(a) sequence in which α-amino acids are linked to one another

(b) sequence in which amino acids of one polypeptide chain are joined to other chain

(c) the folding patterns of polypeptide chains

(d) the pattern in which the polypeptide chains are arranged

3. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be

(K_f for water = 1.86 K kg mol^{-1}).

(a) – 0.372°C (b) – 0.520°C (d) + 0.372°C (d) – 0.570°C

4. Out of the following transition elements, the maximum number of oxidation states are shown by

(a) Sc(Z = 21) (b) Cr(Z = 24) (c) Mn(Z = 25) (d) Fe(Z = 26)

5. Which of the following will give a white precipitate upon reacting with $AgNO_3$?

(a) $K_2[Pt(en)_2Cl_2]$ (b) $[Co[Pt(NH_3)Cl_3]$ (c) $[Cr[Pt(H_2OH)_6]Cl_3$ (d) $[Fe(H_2O_3)Cl_3]$

6. Aryl halides can not be prepared by the reaction of aryl alcohols with PCl_3, PCl_5 or $SOCl_2$ because

(a) phenols are highly stable compounds.

(b) carbon-oxygen bond in phenols has a partial double bond character.

(c) carbon-oxygen bond is highly polar

(d) all of these

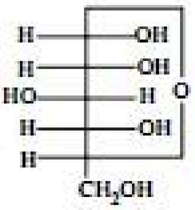
7. Kohlrausch gave the following relation for strong electrolytes:

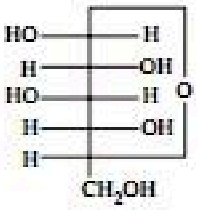
$$\wedge = \wedge_0 - A\sqrt{C}$$

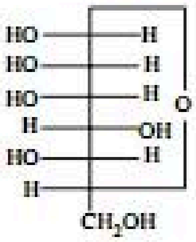
Which of the following equality holds?

(a) $\wedge = \wedge_0$ as $C \to \sqrt{A}$ (b) $\wedge = \wedge_0$ as $C \to \infty$ (c) $\wedge = \wedge_0$ as $C \to 0$ (d) $\wedge = \wedge_0$ as $C \to 1$

8. Three cyclic structures of monosaccharides are given below which of these are anomers.


(I)


(II)


(III)

(a) I and II (b) II and III (c) I and III (d) III is anomer of I and II

***FOR VISUALLY CHALLANGED LEARNERS**

***8.** The two forms of D–glucopyranose obtained from the solution of D-glucose are better called

(a) isomers (b) anomers (c) epimers (d) enantiomers

9. Molarity of H_2SO_4 is 18 M. Its density is 1.8 g/mL. Hence molality is

(a) 36 (b) 200 (c) 500 (d) 18

10. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become :

(a) 256 times (b) 512 times (c) 64 times (d) 128 times

11. DNA and RNA contain four bases each. Which of the following bases is not present in RNA?

(a) Adenine (b) Uracil (c) Thymine (d) Cytosine

12. An aromatic ether is not cleaved by HI even at 525 K. The compound is

(a) $C_6H_5OCH_3$ (b) $C_6H_5OC_6H_5$ (c) $C_6H_5OC_3H_7$ (d) Tetrahydrofuran

13. 

The product obtained is/are

(a) *o*-product (b) *m*-product (c) *o*- and *p*-products (d) *o*-, *m*- and *p*-products

***FOR VISUALLY CHALLANGED LEARNERS.**

***13.** Benzoic acid is treated with lithium aluminium hydride. The compound obtained is

(a) benzaldehyde (b) benzyl alcohol (c) toluene (d) benzene

14. Which of the following ions has the maximum magnetic moment?

(a) Mn^{2+} (b) Fe^{2+} (c) Ti^{2+} (d) Cr^{2+}

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 :** Conductivity of an electrolyte increases with decrease in concentration.

Reason : Number of ions per unit volume decreases on dilution.

16. **Assertion:** Aniline is better nucleophile than anilium ion.

Reason: Anilium ion have positive charge.

17. **Assertion:** The $[Ni(en)_3]Cl_2$ (en = ethylenediamine) has lower stability than $[Ni(NH_3)_6]Cl_2$.

Reason: In $[Ni(en)_3]Cl_2$, the geometry of Ni is trigonal bipyramidal.

18. **Assertion:** Aryl halides undergo nucleophilic substitution with ease.

Reason: Carbon-halogen bond in aryl halides have partial double bond character.

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. Write down the structures and names of the products obtained when D–glucose is treated with

(i) acetic anhydride (ii) hydrocyanic acid

20. An aqueous solution freezes at 272.07 K while pure water freezes at 273 K. Determine the molality and boiling point of the solution. Given $K_f = 1.86$ K/m; $K_b = 0.512$ K/m.

OR

What is molarity of the resulting solution obtained by mixing 2.5 L of 0.5 M urea solution and 500 mL of 2M urea solution ?

21. Square planar complexes with coordination number of four exhibit geometrical isomerism whereas tetrahedral complexes do not why?

OR

Arrange the following complexes in order of increasing electrical conductivity:

$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$.

22. Why is there a steep rise in the molar conductivity of a weak electrolyte when its concentration becomes very low?

23. Following reaction takes place in one step :

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

How will be the rate of the above reaction change if the volume of the reaction vessel is diminished to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume?

24. Describe the following giving the relevant chemical equation in each case.

(i) Carbylamine reaction

(ii) Hoffmann's bromamide reaction

25. Why does glucose reacts with Fehling's solution and phenyl hydrazine, but not with $NaHSO_3$?

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) For some of first row transition elements, the E° values are for (M^{2+}/M)

V	Cr	Mn	Fe	Co	Ni	Cu
–1·18 V	–0·91V	–1·18V	0·44V	–0·28V	–0·25V	+0·34V

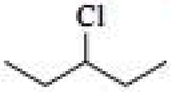
Give suitable explanation for the irregular trend in these values.

Give suitable reasons for following statements:

(b) Two complexes of nickel $\left[Ni(CN)_4\right]^{2-}$ and $\left[Ni(CO)_4\right]$ have different structures but do not differ in magnetic behaviour.

(c) Square planar complexes of MX_2L_2 type with co-ordination number of 4 exhibit geometrical isomerism while tetrahedral complexes with similar composition do not.

27. (a) Which compound in the following pair will react fast with regard to S_N2 reaction and why?



or

You are provided with four reagents:

Fehling solution$_4$, I_2/NaOH, $NaHSO_3$ and Schiff's reagent. Write which two reagents can be used to distinguish between the compounds in each of the following pairs:

(b) CH_3CHO and C_6H_5CHO

(c) $C_6H_5COCH_3$ and $C_6H_5COC_6H_5$

28. A 0.01 m aqueous solution of $AlCl_3$ freezes at -0.068 °C. Calculate the percentage of dissociation.

[Given: K_f for water = 1.86 K kg mol^{-1}]

29. (a) Calculate the *e.m.f.* of the cell in which the reaction is ;

$$Mg(s) + 2Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2Ag(s)$$

when $[Mg^{2+}] = 0.130$ M and $[Ag^+] = 1.0 \times 10^{-4}$ M. Given $E^\circ_{Mg^{2+}/Mg} = -2.37$ V and $E^\circ_{Ag^+/Ag} = +0.80$ V

(b) Calculate cell potential at 25°C.

[Given: $E^\circ_{Zn^{2+}|Zn} = -0.76$ V; $E^\circ_{Cu^{2+}|Cu} = +0.34$ V]

OR

For the cell: $Zn(s) \,|\, Zn^{2+}$ (2 M) $||\, Cu^{2+}$ (0.5 M) $|\, Cu(s)$

(a) Write equation for each half-reaction

(b) Calculate cell potential at 25°C.

[Given: $E^\circ_{Zn^{2+}|Zn} = -0.76$ V; $E^\circ_{Cu^{2+}|Cu} = +0.34$ V]

30. Give reasons: **(Any 3)**:

(a) Aniline does not undergo Friedal-Craft's reaction.

(b) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

(c) Aliphatic amines are stronger bases than ammonia.

(d) Aqueous solution of diazonium salts are good conductors.

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. Several techniques have been developed to determine the order of reaction. The rate of a reaction cannot be predicted on the basis of the overall equation, but it can be predicted on the basis of the rate-determining step. For instance, the following reaction can be broken down into three steps.

$A + D \xrightarrow{k} F + G$ (Reaction - 1)

Step - 1: $A \xrightarrow{k_1} B + C$ (slow)

Step - 2: $B + D \xrightarrow{k_2} E + F$ (fast)

Step - 3: $E + C \xrightarrow{k_3} G$ (fast)

In this case, the first step in the reaction pathway is the rate-determining step. Therefore, the overall rate of the reaction must be equal to the rate of the first step, $k_1[A]$ where k's are the rate constants of different steps.

In some cases, it is desirable to measure the rate of a reaction in relation to only one species. In a second-order reaction involving two reacting substances for instance, a large excess of one substance is included in the reaction vessel. Since a relatively small amount of this large concentration is reacted, we assume that the concentration or this substance essentially remains unchanged. Such a reaction is called a pseudo first-order reaction. A new rate constant, K', is established, equal to the product of the rate constant of the original reaction, k, and the concentration of the species in excess.

Answer the following questions :

(a) What is the molecularity of the Reaction - 1?

(b) What is the differential rate law of reaction - 1?

(c) Which is the rate determining step of the reaction-1?

(d) What is the molecularity of a pseudo first order reaction?

OR

For the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ What is the differential rate laws with respect to all the species imvohed in the reaction?

32. The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions are governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

Answer the following questions :

(a) Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.

(b) Name the instrument used for measuring the angle by which the plane polarised light is rotated.

(c) Give one use of CHI_3.

(d) Predict the major product formed when 2-bromopentane reacts with alcoholic KOH.

OR

Write the structures of the products formed when anisole is treated with HI.

SECTION-E

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

33. (a) How do you convert the following:

(i) Phenol to Anisole

(ii) Ethanol to Propan-2-ol

(b) Write mechanism of the following reaction:

$$C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2+H_2O$$

(c) Why phenol undergoes electrophilic substitution more easily than benzene?

OR

(a) Account for the following:

(i) o-nitrophenol is more steam volatile than p-nitrophenol.

(ii) t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of t-butylmethylether.

(b) Write the reaction involved in the following:

(i) Reimer-Tiemann reaction

(ii) Friedal-Crafts Alkylation of Phenol

(c) Give simple chemical test to distinguish between Ethanol and Phenol.

34. Explain the following:

(a) Why are Zn, Cd and Hg not considered transition metals?

(b) Why are the compounds of transition metals generally coloured?

(c) Why do Zr and Hf exhibit almost similar properties?

(d) What is the basic difference in electronic configuration of lanthanides and those of actinides?

(e) The first ionisation energies of elements of first transition series do not vary much with increasing atomic number.

OR

(a) Ce (III) can be easily oxidised to Ce (IV). Explain, why.

(b) What is meant by lanthanoid contraction? What effect does it have on the chemistry of the elements which follow lanthanoids?

35. How will you prepare :

(a) Propiophenone from propanenitrile

(b) 4-Chlorobenzaldehyde from 4-chlorotoluene

(c) Cyclohexanecarbaldehyde from cyclohexylmethanol

(d) 4-Methoxyacetophenone from anisole

(e) 4-Methylbenzaldehyde from toluene

Solutions

SAMPLE PAPER-5

1. (a) With increase in dilution, the conductivity of a weak electrolyte increases due to increase in ionisation. The conductivity of strong electrolytes remain constant at all dilution because they are completely ionised under all dilutions.

2. (a) The sequence in which the α-amino acids are linked to one another in a protein molecule is called its primary structure.

3. (a) $\Delta T_f = K_f \frac{1000\ W_2}{M_2 W_1} = \frac{1.86 \times 1000 \times 68.5}{342 \times 1000}$

$= 0.372$

$T_f = T°\Delta_f - \Delta T_f \Rightarrow T_f = -0.372°C$

4. (c) $Mn(25) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Mn has maximum number of oxidation states from +1 to +7 due to $3d^5 4s^2$.

5. (c) $[Cr(H_2O)_6]Cl_3$
This compound dissociates to $[Cr(H_2O)_6]^{3+}$ and $3Cl^-$ ions. Thus, it will give white precipitate of AgCl on reacting with $AgNO_3$.

6. (b) This method is not applicable for the preparation of aryl halides because the C–O bond in phenol has a partial double bond character and is difficult to break being stronger than a single bond.

7. (c) $\wedge = \wedge_0$ as $C \to 0$
$\wedge = \wedge_0 - A\sqrt{C}$
when $C = 0$, $\wedge = \wedge_0$

8. (a) Cyclic structures of monosaccharides which differ in structure at carbon -1 are known as anomers.
Here, I and II are anomer because they differ from each other at carbon-1 only.

*8. (b) The two isomeric forms (α – and β –) of D–glucopyranose differ in configuration only at C-1. Hence these are called anomers.

9. (c) Molality (m)

$$= \frac{\text{Molarity}}{\text{Density} - \frac{\text{Molarity} \times \text{Molecular mass}}{1000}}$$

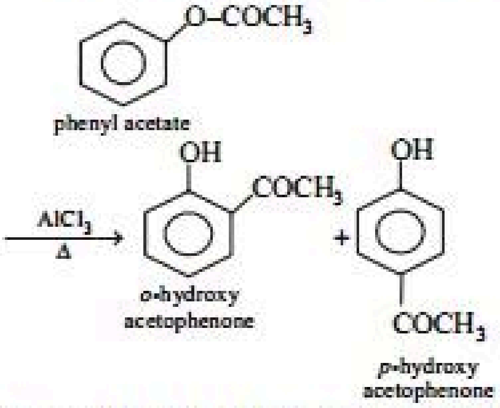
$$= \frac{18}{1.8 - \frac{18 \times 98}{1000}} = 500 \text{ mol kg}^{-1}$$

10. $\frac{r_{100°C}}{r_{10°C}} = 2^{\left(\frac{T_2 - T_1}{10}\right)} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512$ (where 2 is temperature coefficient of reaction)

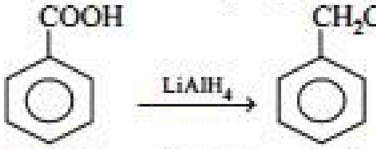
11. (c) RNA does not contain thymine.

12. (b) Due to greater electronegativity of sp^2-hybridized carbon atoms of the benzene ring, diaryl ethers are not attacked by nucleophiles like I^-.

13. (c) The phenyl esters on treatment with on anhydrous $AlCl_3$ undergoes rearrangement to give o– and p–hydroxyketones (Fries rearrangement).



*13. (b) $LiAlH_4$ reacts with the benzoic acid and reduces the – COOH group to – CH_2OH group.



+ H_2O (1 mark)

14. (a) Mn^{2+} –5 unpaired electrons; Fe^{2+} – 4 unpaired electrons
Ti^{2+} – 2 unpaired electrons; Cr^{2+} – 4 unpaired electrons
Hence, maximum no. of unpaired electron is present in Mn^{2+}.
Magnetic moment ∝ number of unpaired electrons

15. (d) Conductivity of an electrolyte decreases with decrease in concentration because number of ions per unit volume decreases on dilution.

16. (a) Aniline is a better nucleophile than anilium ion. Anilium ion contain positive charge, which reduces its tendency to donate lone pair of electrons of nitrogen $C_6H_5NH_3^+$ (anilium ion).

17. (d) $[Ni(en)_3]Cl_2$ is more stable than $[Ni(NH_3)_6]Cl_2$ because ethylenediamine is a bidentate ligand, hence it forms chelating ring with Ni^{2+} ion. In $[Ni(en)_3]Cl_2$, the geometry of Ni is octahedral.

18. (d) Aryl halides do not undergo nucleophilic substitution reaction under ordinary conditions.

19. (i) $\underset{\text{D-glucose}}{OHC-(CHOH)_4-CH_2OH} \xrightarrow{(CH_3CO)_2O}$

$\underset{\text{Glucose pentaacetate}}{OHC-(CHOCOCH_3)_4-CH_2OCOCH_3}$ (1 mark)

(ii)

$$\underset{\text{D-glucose}}{HOH_2C—(CHOH)_4—CHO} \xrightarrow{HCN}$$

$$\underset{\text{Glucose cyanohydrin}}{HOH_2C—(CHOH)_4—CH(OH)CN}$$ (1 mark)

20. Calculation of molality of solution

$\Delta T_f = K_f \times m$ or $m = \Delta T_f / K_f$ (½ mark)

$\Delta T_f = 273 - 272.07 = 0.93\ K; K_f = 1.86\ K\ kg\ mol^{-1}$. (½ mark)

$$m = \frac{(0.93K)}{(1.86K\ kg\ mol^{-1})} = 0.5\ mol\ kg^{-1} = 0.5\ m$$ (½ mark)

Calculation of boiling point of solution

$\Delta T_b = K_b \times m$
$= 0.512\ K/m \times 0.5\ m$
$= 0.256\ K$

Boiling point of solution = (373 K + 0.256 K) = 373.256 K (½ mark)

OR

Molarity of solution on mixing :

$$M_3 = \frac{M_1V_1 + M_2V_2}{(V_1 + V_2)}$$ (½ mark)

According to available data :

$M_1 = 0.5\ M,\ V_1 = 2.5\ L;\ M_2 = 2M,\ V_2 = 500\ mL = 0.5\ L$ (½ mark)

$\therefore M_3 =$

$$\frac{(0.5M \times 2.5L) + (2\ M \times 0.5\ L)}{(2.5\ L + 0.5\ L)} = \frac{(2.25\ ML)}{(3.0\ L)} = 0.75\ M$$

(1 mark)

21. Tetrahedral complexes do not show geometrical isomerism because the relative position of the ligands attached to the central metal atom are same with respect to each other. (2 marks)

OR

$[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$ (2 marks)

22. When the concentration of a weak electrolyte becomes very low, its degree of ionisation rises sharply. This results in a sharp increase in the number of ions in solution. Thus, the molar conductivity of a weak electrolyte rises steeply at low concentrations. (2 marks)

23. (a) Rate = $k[NO]^2[O_2]$ (½ mark)

Suppose initially, moles of NO = a, moles of O_2 = b, volume of the vessel = V L. Then

$$[NO] = a/V\ M,\ [O_2] = b/V\ M$$

$$\therefore \quad \text{Rate}\ (r_1) = k\left(\frac{a}{V}\right)^2\left(\frac{b}{V}\right) = k\frac{a^2b}{V^3}$$ ....(i) (½ mark)

New volume = V/3.

$$\therefore \quad \text{New concentrations :} \quad [NO] = \frac{a}{V/3} = \frac{3a}{V}$$

$$[O_2] = \frac{b}{V/3} = \frac{3b}{V}$$

$\therefore$ New rate

$$(r_2) = k\left(\frac{3a}{V}\right)^2\left(\frac{3b}{V}\right) = \frac{27\,k\,a^2b}{V^3}$$ ...(ii) (½ mark)

$\therefore \quad \frac{r_2}{r_1} = 27$ or $r_2 = 27\,r_1$, i.e., rate becomes 27 times

There is no effect on the order of reaction. (½ mark)

24. (i) Carbylamine reaction: Both aliphatic and aromatic primary amines when warmed with chloroform and an alcoholic solution of KOH, produces isocyanides or carbylamines which have very unpleasant odours. This reaction is called carbylamine reaction.

$R—NH_2 + CHCl_3 + 3KOH\ (alc) \longrightarrow$

$R—N \equiv C + 3KCl + 3H_2O$ (1 mark)

(ii) Hoffmann's bromamide reaction: When an amide is treated with bromine in alkali solution, it is converted to a primary amine that has one carbon atom less than the starting amide. This reaction is known as Hoffmann's bromamide degradation reaction.

$C_6H_5CONH_2 \xrightarrow{Br_2 + NaOH} C_6H_5NH_2$ (1 mark)

25. 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. (2 marks)

26. (a) Electrode potential value, E° depend upon following factors:

(a) Energy of sublimation of metal, ΔH_{sub},

(b) Ionisation energy $(IE_1 + IE_2)$, and

(c) Hydration energy, ΔH_{hyd}.

There is no regular trend in values of E° for transition elements because there is no definite value of above mentioned three factors. These factors are irregular due to variation in atomic size, ionic size, etc of transition metals. (1 mark)

(b) The complex $\left[Ni(CN)_4\right]^{2-}$ is square planar while $\left[Ni(CO)_4\right]$ is tetrahedral in nature. But since all the electrons in the orbitals of the central metal atom/ion in these complexes are paired, both are therefore, diamagnetic in nature. (1 mark)

(c) In square planar complexes MX_2L_2, the two identical ligands (X or L) can occupy either adjacent positions or opposite positions in the co-ordination polyhedron representing square plane. Therefore, *cis* and *trans* isomers are possible. In tetrahedral complexes, all the four positions are identical and no spatial isomerism can be shown.

(1 mark)

27. (a) In S_N2 reaction, transition state is formed, so alkyl halide whose halogen is less sterically hindered and also a better leaving group will follow preferably S_N2 path.

2° alkyl halide is less sterically 

(1 mark)

(b) I_2/NaOH or Fehling solution CH_3CHO will give positive test with these reagents (1 mark)

(c) I_2/NaOH $C_6H_5COCH_3$ will give positive iodoform test. (1 mark)

28. $m = 0.01$; $\Delta T_f = 0.068°C$; $K_f = 1.86 \text{ K kg mol}^{-1}$

If i is the van't Hoff factor for the aqueous solution of $AlCl_3$, then

$$\Delta T_f = i.K_f.m \qquad \text{(½ mark)}$$

$$\Rightarrow \quad i = \frac{\Delta T_f}{K_f.m}$$

$$\Rightarrow \quad i = \frac{0.068}{1.86 \times 0.01} \qquad \text{(½ mark)}$$

$$\Rightarrow \quad i = 3.66 \qquad \text{(½ mark)}$$

$$\begin{array}{lcccl} AlCl_3 & \rightleftharpoons & Al^{3+} & + & Cl^- \qquad \text{(½ mark)} \\ 1 & & 0 & & 0 \quad \text{initial} \\ 1-x & & x & & 3x \quad \text{at equilibrium} \end{array}$$

$$i = \frac{(1-x)+x+3x}{1} \qquad \text{(½ mark)}$$

$$\Rightarrow \quad 3.66 = 1 + 3x$$

$$\Rightarrow \quad x = 0.89$$

x is degree of dissociation.

∴ Percentage of dissociation = 89%. (½ mark)

29. (a) The given cell reaction is the net result of the following half cell reactions.

$$\begin{array}{r} Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^- \\ 2Ag^+(aq) + 2e^- \longrightarrow 2Ag\,(s) \\ \hline Mg\,(s) + 2Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2Ag\,(s) \end{array}$$

The cell may be represented as:

$$\underset{\text{Anode}}{Mg \mid Mg^{2+}(0.130\text{ M})} \;||\; \underset{\text{Cathode}}{Ag^+(1.0 \times 10^{-4}\text{ M}) \mid Ag}$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Ag^+/Ag} - E^\circ_{Mg^{2+}/Mg}$$

(½ mark)

$$= +0.80\text{ V} - (-2.37\text{ V}) = 0.80\text{ V} + 2.37\text{ V} = +3.17\text{ V}$$

(½ mark)

(b) Applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591\text{ V}}{2}\log\frac{[Mg^{2+}(aq)]}{[Ag^+(aq)]^2} \qquad [\because [Mg\,(s)] = [Ag\,(s)] = 1 \text{ and } T = 298\text{ K}] \qquad \text{(½ mark)}$$

$$\text{Or,} \quad E_{cell} = +3.17 - \frac{0.0591}{2}\log\frac{0.130}{[1.0 \times 10^{-4}]^2} \qquad \text{(½ mark)}$$

$$= +3.17 - \frac{0.0591}{2}\log 0.130 \times 10^8$$

$$= +3.17 - 0.02955 \times (8 - 0.886) \qquad \text{(½ mark)}$$

$$= +3.17 - 0.02955 \times 7.114$$

$$= +3.17 - 0.21\text{ V} = 2.96\text{ V} \qquad \text{(½ mark)}$$

OR

(a) The cell reactions are

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-(\text{anode})$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)\,(\text{cathode}) \qquad \text{(1 mark)}$$

(b)

$$E^\circ_{cell} = E_{cathode} - E_{anode} = 0.34 - (-0.76)$$

$$= 0.34 + 0.76 = 1.10\text{ V} \qquad \text{(½ mark)}$$

from Nernst equation

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad \text{(½ mark)}$$

$$E_{cell} = 1.1 - \frac{0.059}{2}\log\frac{[2]}{[0.5]} \qquad \text{(½ mark)}$$

$$= 1.1 - \frac{0.059}{2}(\log 20 - \log 5)$$

$$= 1.1 - \frac{0.059}{2} \times 0.6021$$

$$= 1.1 - 0.0177 = 1.09\text{ V} \qquad \text{(1 mark)}$$

30. (a) Aniline is basic in nature. It does not undergo Friedal-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Anilinium ion is formed in which nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction. (1 mark)

(b) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide. (1 mark)

(c) Aliphatic amines are stronger bases than ammonia due to + I effect of alkyl groups leading to high electron density on the nitrogen atom. (1 mark)

(d) Diazonium salts are present in ionic form in their aqueous solution, e.g. $RN_2^+HSO_4^-$, $RN_2^+BFO_4^-$etc. Ionic solutions are good conductors of electricity.

31. (a) One (1 mark)

(b) Rate = $k_1[A]$ (1 mark)

(c) Slowest step (step-1) of the reaction. (1 mark)

(d) Two (1 mark)

OR

For the given reaction, the rate of reaction is

$$= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} \qquad \text{(1 mark)}$$

$$= \frac{d[O_2]}{dt}$$

32. (a) Inversion occurs more than retention, leading to partial racemization. (1 mark)

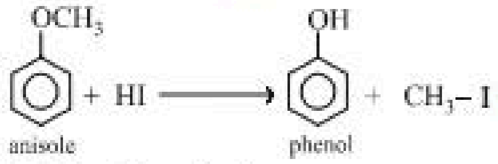
(b) Polarimeter (½ mark)

(c) Iodoform (CHI_3) is used as a disinfectant. (½ mark)

(d) (2 marks)

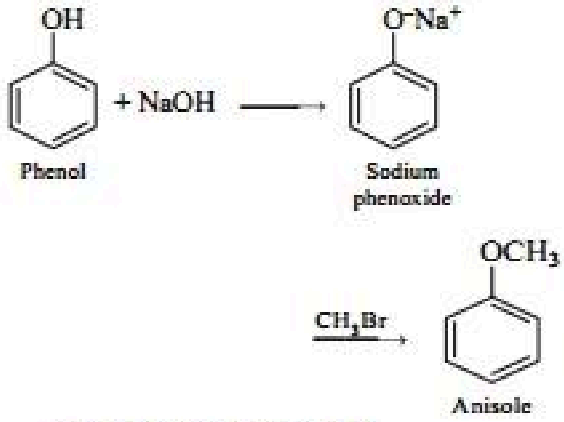
2-bromopentane pent-2-ene (major product)

OR



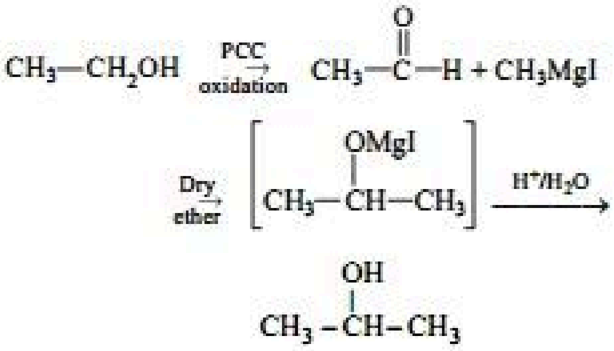
(2 marks)

33. (a) (i) Phenol to anisole



(1 mark)

(ii) Ethanol to propan-2-ol

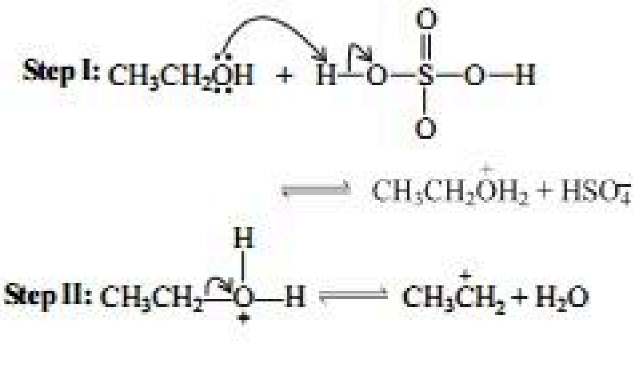


$$CH_3-CH_2OH \xrightarrow[\text{oxidation}]{PCC} CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3MgI \xrightarrow{\text{Dry ether}} \left[CH_3-\overset{OMgI}{\overset{|}{C}H}-CH_3\right] \xrightarrow{H^+/H_2O} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$$

(1 mark)

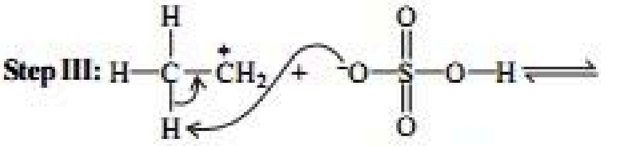
(b) $C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2+H_2O$

Mechanism is as follows:



Step I: $CH_3CH_2\ddot{O}H + H-O-\overset{O}{\underset{O}{S}}-O-H \rightleftharpoons CH_3CH_2\overset{+}{O}H_2 + HSO_4^-$

Step II: $CH_3CH_2-\overset{H}{\underset{+}{O}}-H \rightleftharpoons CH_3\overset{+}{C}H_2 + H_2O$



Step III: $H-\overset{H}{\underset{H}{C}}-\overset{+}{C}H_2 + {}^-O-\overset{O}{\underset{O}{S}}-O-H \rightleftharpoons$

$CH_2=CH_2 + H_2SO_4$

(2 marks)

(c) The rate of any electrophilic substitution reaction depends upon the electron density in the aromatic ring. Higher the electron density in the aromatic ring, higher is the rate of electrophilic substitution reaction. The presence of OH group in phenol, increases the electron density at ortho and para position by +R effect. Since the electron density is more in phenol than in benzene. Therefore phenol undergoes electrophilic substitution more easily than benzene. (1 mark)

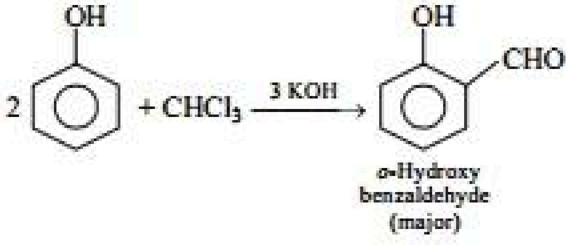
OR

(a) (i) Ortho nitrophenol is more steam volatile than para nitrophenol because o-Nitrophenol has intra molecular hydrogen bonding where as para nitrophenol has intermolecular H-bonding. Energy is required to overcome attractive forces in the molecules of *p*-nitrophenol. This means that boiling point of *o*-nitrophenol is less and is steam volatile while that of *p*-nitrophenol is more, and is non-volatile. (1 mark)

(ii) Sodium methoxides is a strong nucleophile and a strong base. Thus elimination predominates substitution. In this reaction E_1 favored over S_N1. So t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of t-butyl methyl ether. (1 mark)

Elimination reaction is favored under strong base condition while substitution reaction is favored under weak nucleophile condition.

(b) (i)

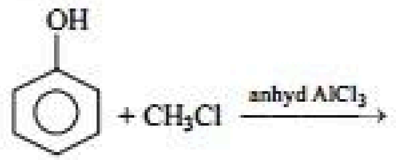


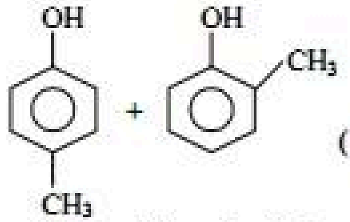
$+3KCl+2H_2O$

(1 mark)

(ii) Friedel Craft alkylation of phenol

In this reaction phenol react with alkyl halide in the presence of anhydrous $AlCl_3$ & forms *o*-methyl phenol, *p*-methyl phenol.





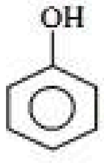
(1 mark)

Phenols undergoes Friedel craft alkylation with very low yield due to the formation of complex with $AlCl_3$.

(c) Ethanol and phenol can be distinguished by idoform test.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \rightarrow$$

$$\underset{\substack{\text{Iodoform}\\ \text{(yellow)}}}{CH\,I_3\downarrow} + HCOONa + 5H_2O$$



$+ I_2 + NaOH \rightarrow$ No reaction

(1 mark)

34. (a) These elements do not fulfill the condition or definition of a transition element . It is because neither, these elements nor their ions have incompletely filled *d*-orbitals. (1 mark)

(b) Transition metal atoms or their ions have generally partially filled *d*-orbitals and thus can undergo $d-d$ transitions by absorbing light from visible region and radiate complimentary colour. (1 mark)

(c) Zr and Hf exhibit almost similar properties because their atomic and ionic sizes are almost equal due to lanthanide contraction. (1 mark)

(d) 4 *f*-orbitals are progressively filled in lanthanides whereas in actinides 5 *f*-orbitals are progressively filled up. (1 mark)

(e) Atomic size does not vary much due to poor shielding effect of $(n-1)$ *d*-electrons on nucleus. Thus, effective nuclear charge does not vary much. Hence first ionisation energy also do not vary much.

(1 mark)

OR

(a) Ce (III) is easily oxidised to Ce (IV) because Ce (IV) has more stable electronic configuration.

$$\underset{(Z=58)}{Ce} \longrightarrow [Xe]_{54}\, 4f^1\, 5d^1\, 6s^2$$

$$Ce(III) \longrightarrow [Xe]_{54}\, 4f^1\, 5d^0\, 6s^0$$

Ce (III) can further loose one $4f^1$ electron easily to acquire stable Ce(IV). (2 marks)

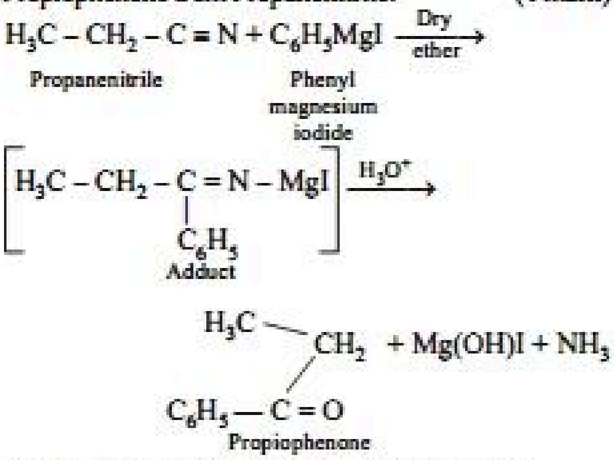
(b) The decrease in atomic and ionic size with the increase in atomic number in lanthanoids is called lanthanoid contraction. (1 mark)

It has the following effects:

(i) The ionisation energy in 5*d* series is more than that in 3*d* and 4*d* series. (1 mark)

(ii) There is resemblance between properties of elements of 4*d* and 5*d* transition series. (1 mark)

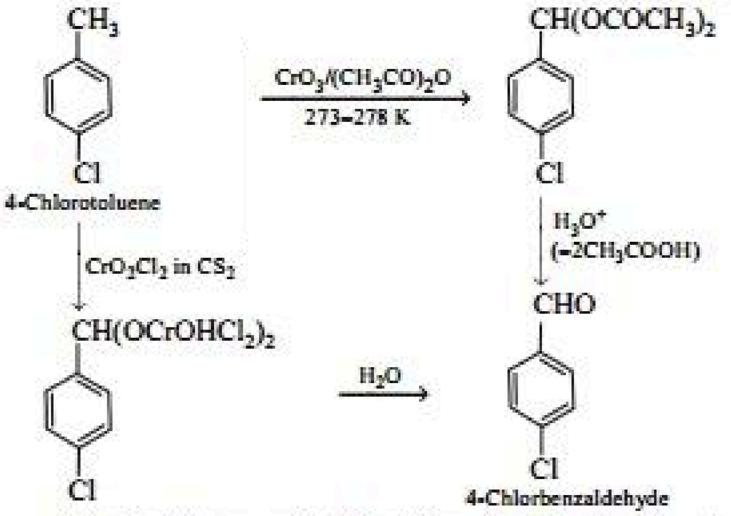
35. (a) Propiophenone from Propanenitrile: (1 mark)



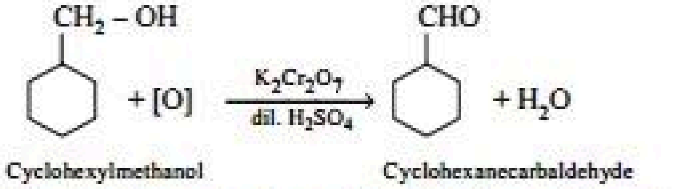
$$\underset{\text{Propanenitrile}}{H_3C-CH_2-C\equiv N} + \underset{\substack{\text{Phenyl}\\ \text{magnesium}\\ \text{iodide}}}{C_6H_5MgI} \xrightarrow[\text{ether}]{\text{Dry}}$$

$$\underset{\text{Adduct}}{\left[H_3C-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{C}}=N-MgI\right]} \xrightarrow{H_3O^+}$$

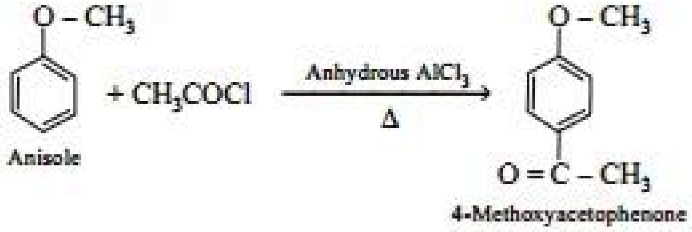
(b) 4-Chlorobenzaldehyde from 4-Chlorotoluene: (1 mark)



(c) Cyclohexanecarbaldehyde from Cyclohexylmethanol: (1 mark)



(d) 4-Methoxyacetophenone from Anisole: (1 mark)



(e) 4-Methylbenzaldehyde from Toluene: (1 mark)