MARKING SCHEME PRACTICE PAPER - 07

 (i) (b) In haloalkanes, C-atom with which halogen is attached is sp³-hybridised but in haloarene is sp²-hybridised.

Or

(b) Benzyl halogen compound is the one in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to an aromatic ring, e.g.



(ii) (c) The IUPAC name of the compound is 4-bromopent-2-ene.

(1)

(1)

(1)

(1)

- (iii) (b) For dihalogen derivatives, the prefixes o, m, p are used in common system but in IUPAC system, the numerals 1, 2; 1, 3 and 1, 4 are used.
- (iv) (b)



Common name sym-tribromobenzene IUPAC name 1, 3,5-tribromobenzene

2. (i) (b) Amorphous solids soften over a range of temperature due to their short range order of arrangement of constituents. These can be moulded and blown into various shapes. Both assertion and reason are correct but reason is not the correct explanation of assertion.

Or

(d) Crystalline solids are anisotropic as these have different arrangement of particles along different directions. Hence, assertion is incorrect whereas reason is correct.

- (ii) (a) In covalent solids, atoms are held very strongly due to strong and directional nature of covalent bonds. Both assertion and reason are correct and reason is the correct explanation of assertion.
- (iii) (c) Although HCl and SO2 are polar molecular solids but they have neither free electrons nor free ions. Due to the absence of free electrons or ions these are non-conductors of electricity. Hence, assertion is correct and reason is incorrect.
- (iv) (b) Ionic solids have strong intermolecular forces of attraction which make them hard and brittle. Because of the presence of free ions, these can conduct electricity in molten state or in aqueous solution.

3. (c) Unit of rate constant =
$$\frac{\text{time}^{-1}}{\text{concentration}^{(n-1)}}$$

where, n = order of reaction

Given, unit of rate constant = L mol⁻¹ s⁻¹

$$\therefore \text{ L mol}^{-1} \text{ s}^{-1} = \frac{(\text{s})^{-1}}{(\text{L mol}^{-1})^{n-1}} = \frac{(\text{s})^{-1}}{(\text{L mol}^{-1})^{n-1}} = \text{s}^{-1} (\text{L mol}^{-1})^{n-1} \text{or} \qquad 1 = n - 1 \Rightarrow n = 2 \text{Order of reaction} = 2$$
(1)

.: Order of reaction = 2

4. (a) Formula of tetramminedichloroplatinum (IV) chloride is [Pt(NH₃)₄Cl₂]Cl₂. In aqueous solution, the above compound ionises as:

$$[Pt(NH_3)_4Cl_2]Cl_2 \xleftarrow{} [Pt(NH_3)_4Cl_2]^{2+} + 2Cl_2^{-}$$

So, the number of chloride ion is 2. (1)

5. (a) Catalyst used is V_2O_5

2

(C)

$$SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

(b) On moving down the group H---X bond length increases so correct increasing order of their acidic strength is HF < HCl < HBr < HI (1)

6. (c) In the Hofmann bromamide degradation, amine is formed with side products Na₂CO₃, NaBr and H₂O $RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + Na_2O_3$

$$+ 2NaBr + 2H_2O$$
 (1)

(c)
$$(CH_3)_3N < (CH_3)_2NH < CH_3NH_2$$
, because the order of boiling points is 1° > 2° > 3°. (1)

7. (a) Proline has an imino (>NH) group



8. (a) Melting point of group 15 elements increases upto arsenic and then decreases upto bismuth.

So, the correct order is N < P < As > Sb > Bi

(d) N₂ molecule, N \equiv N, has one σ -bond and two (1)π-bonds.

- **9.** (b) $CH_3CH = CH CH_3 + CHCl_3$ Chloroform But-2-ene C(OH)₃ NaOH hydrolysis CH-CH2CH3 COOH CH3-CH-CH2CH3 2- methylbutanoic acid
- 10. (d) Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with Nal in dry acetone. This reaction is known as Finkelstein reaction.

 $RX + Nal \longrightarrow RI + NaX$

NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le-Chatelier's principle.

Or

(c) The given reaction follows S_N^2 mechanism and S_N2 reactions are favoured in polar aprotic medium like DMSO, DMF... etc.

 $CH_3CH_2CH_2Br + NaCN \xrightarrow{DMF} CH_3CH_2CH_2CN + NaBr$

 (b) Phenols are much more acidic than alcohols due to stabilisation of phenoxide ion by resonance.



(1/2)

12. (c) Assertion is correct but Reason incorrect.

Correct Reason The total number of ions in solution increases on dilution but the number of ions per unit volume that carry current in solution decreases on dilution. (1)

(b) Both Assertion and Reason are correct statements but Reason is not the correct explanation of Assertion. (1)

Or

(a) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

14. (c) Assertion is correct but Reason is incorrect.

Correct Assertion For d^4 configuration, high spin complex with configuration $t_{2g}^3 e_g^1$ is formed. (1)

- 15. (a) Both Assertion and Reason are correct statements and Reason is correct explanation of Assertion. (1)
- (b) Both Assertion and Reason are correct statements but Reason is not the correct explanation of Assertion.
 (1)
- 17. The depression in freezing point are in order:

 $CH_3COOH < CI_3CCOOH < F_3CCOOH$ Fluorine, being the most electronegative, has the highest negative inductive effect. As a result of this, F_3C COOH is the strongest acid while CH_3COOH is the weakest acid. Hence, CF_3 —COOH ionises to the largest while CH_3COOH ionises to the minimum extent to give ions in their solutions in water. Greater the ions produced, greater is the depression in freezing point. Hence, the depression in freezing point is the maximum for the trifluroacetic acid and minimum for acetic acid. (2)

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

 \therefore 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)

(ii) Rate $= -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt}$ Rate of change in concentration of A $= -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = 0.5 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ Rate of change in concentration of C

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

19. The solution Sb_2S_3 is a negatively charged solution. Greater the valency of the flocculating ion, greater is the coagulation. This is known as Hardy-Schulze rule. For a negatively charged solution,

$$AI^{3+} > Ca^{2+} > Na^+ \simeq NH_4^+$$

(2)

Hence, the most effective coagulating agent for Sb_2S_3 solution is $Al_2(SO_4)_3$.

20. When SO₂ gas is passed through lime water first slowly, milky appearance arises due to formation of insoluble CaSO₄. On passing excess SO₂ through this solution, milky appearance disappears because of formation of soluble Ca(HSO₃)₂.

$$Ca(OH)_{2} + SO_{2} \longrightarrow CaSO_{4} \downarrow + H_{2}O$$

$$CaSO_{3} + H_{2}O + SO_{2} \longrightarrow Ca(HSO_{3})_{2}$$
(2)

- 21. (i) The oxide of a transition metal in low oxidation state is basic, e.g. TiO, VO, MnO, FeO, Cu₂O, NiO. The oxides of transition elements in higher oxidation states are acidic. e.g. V₂O₅, CrO₃. (1)
 - (ii) This is because oxygen and fluorine are highly electronegative elements. (1)



Due to resonance in phenol, C—O bond of phenol has some partial double bond character. Partial double bond character strengthen the bond. So, it is difficult to break this C—O bond of phenol while the C—O bond of alcohol is purely single bond and comparatively weaker bond. So alkyl halides can be prepared by the reaction of alcohols with HCl in the presence of ZnCl₂ while aryl halides can not be prepared by reaction of phenol with HCl in the presence of ZnCl₂. (1)

$$\begin{array}{c} C_{0}H_{5}OH \xrightarrow{HCI} No \text{ reaction} \\ Phenol & ZnCl_{2} \end{array} \xrightarrow{RCH_{2}OH} RCH_{2}OH \xrightarrow{HCI} RCH_{2}Cl + H_{2}O \\ Alcohol & ZnCl_{2} \xrightarrow{RCH_{2}Cl} Alkyl \text{ chloride} \end{array}$$
(1)

23. (i) The structures of *m*-aminophenol and *o*-amino phenol are as follows :



The $--NH_2$ group is an electron releasing group. Thus, the presence of $--NH_2$ group on the ring decreases the acid strength of phenol. The effect of any substituent is more significant when it is in *ortho* or *para* position than in *meta* position. Thus, *m*-amino phenol is stronger than o-aminophenol. (1)

(ii) In alcohols, the alkyl group is an electron releasing group. As a result, the electron density on oxygen increases. This effect along with the presence of two lone pairs of electrons on O-atom makes alcohols weakly basic. (1)



24. For NaCl, Z = 4, Molar mass, $M = 58.5 \text{ g mol}^{-1}$

Density, $d = 2.165 \, \text{g cm}^{-3}$

Density,
$$d' = \frac{Z \times M}{a^3 \times N_A}$$

= $\left(\frac{4 \times 58.5 \text{ g mol}^{-1}}{2.165 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{ mol}^{-1}}\right)^{1/3}$
 $a = (179.54)^{1/3} \times 10^{-8} \text{ cm} = 5.64 \times 10^{-8} \text{ cm}$ (3)

Distance between Na⁺ and Cl⁻ ions = a/2

$$=\frac{5.64 \times 10^{-8} \text{ cm}}{2}$$
$$= 2.82 \times 10^{-8} \text{ cm}$$

- (i) Due to inert-pair effect Bi(V) has a strong tendency to accept two electrons from any other species, thus acting as an oxidising agent. (1)
 - (ii) H₃PO₃ has two oxygenated H-atoms. Since, P—OH hydrogen is ionisable, hence H₃PO₃ is a diprotic acid.
 (1)

Or

(i) The structural formula of Al2Cl6 is shown below ;



(ii) The structural formula of $SF_4(g)$ is shown below. (1)



(1)
 (26. (i) The noble gas species which is isostructural with ICl₄ is XeF₄ and BrO₃ is isostructural with XeO₃.
 Structures of XeF₄ and XeO₃ are as follows:



(ii) (a) $\underset{\text{(Cold,dilute)}}{2\text{NaCH}} + \text{Cl}_2(g) \longrightarrow \text{NaCl}(aq) +$

2

30.

(1)

(b) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$ (1)

(b) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$ (1) **27.** (i) The outer electronic configuration of the given ions are:

V ³⁺	Cu ⁺	Sc ³⁺
3d ²	3ď ¹⁰	3ď ⁰
Coloured	Nod-d transition	
Fe ³⁺	Co ²⁺	MnO ₄
3d ⁵	3d ⁷	3d ⁰
Coloured	Coloured	Coloured
	3d ² Coloured Fe ³⁺ 3d ⁵	3d ² 3d ¹⁰ Coloured Nod-d t Fe ³⁺ Co ²⁺ 3d ⁵ 3d ⁷

- (ii) (a) Due to lanthanoid contraction, the ionic size decreases on moving from La³⁺ to Lu³⁺. As a result, the covalent character in bonding increases in the direction La³⁺ → Lu³⁺. La₂O₃ is more ionic and Lu₂O₃ is more covalent.
 - (b) Radii of 4d and 5d-block elements are almost equal.
 (1)
- 28. (i) Amino acids may be acidic, basic or neutral depending upon the relative number of amino and carboxyl groups present in the molecule. Equal number of amino carboxyl groups makes it neutral, more number of amino than carboxyl groups makes it basic and more carboxylic groups as compared to amino groups makes it acidic. (11/2)
 - (ii) The amino acids exist as Zwitter ions
 (H₃N—CHR—COO⁻) in aqueous solution. Due to this, dipolar salt like structure amino acids have strong dipole-dipole attractions.

Thus, their melting points are higher than corresponding halo acids which do not have salt like character. Secondly, they interact strongly with H2O due to their salt like character.

As a result, polar amino acids dissolve in polar solvents like H2O. Hence, the solubility of amino acids in water is higher than that of corresponding halo acids, which do not have any salt like character (11/2)

Or

Following are the two reactions for the identification of glucose



Reaction with acetyl chloride Reaction of glucose with acetyl chloride or acetic anhydride, gives glucose



29. (i) HNO₂ reacts with $C_5H_{13}N$ to give an alcohol, means the compound is primary amine. $C_5H_{13}N$ means $C_5H_{11}NH_2$ (11/2)(primary amine). Optically active alcohol means C₅H₁₁OH segment contain a chiral carbon.



(ii) The entire reaction sequence can be written as:



30. (i) In aryl alkyl ethers, +*R*-effect of the alkoxy group (—OR) increases the electron density in the benzene ring, $(1\frac{1}{2})$ thereby activating the benzene ring towards electrophilic substitution reactions.



(ii) Electron density is more at o-and p-positions so, o-and p-products are mainly formed during electrophilic $(1\frac{1}{2})$ substitution reactions.



(11/2)

Or

(i) (a) Propene -----> Propan-2-ol

$$CH_{3} - CH = CH_{2} \xrightarrow{H^{*}/H_{2}O} CH_{3} - CH - CH_{3}$$
Propene
$$OH$$
Propan-2:ol
(1/2)

(b) Benzyl chloride ------ Benzyl alcohol



(c) Ethyl magnesium chloride ----> Propan-1-ol

$$\begin{array}{c} H \\ & & & \\ & & \\ H \\ & & \\$$

(d) Methyl magnesium bromide ------> 2-methylpropan-2-ol



(ii) The — OH group in alcohols is involved in intermolecular hydrogen bonding or H-bonding due to which they exist as associated molecules and hence, have higher boiling and melting points in comparison at hydrocarbons.

31. (i)
$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 3Cd(s) + 3Cr^{3+}(aq)$$

Thus, $Cr(s)|Cr^{3+}(aq)|$ is anode and $Cd^{2+}(aq)Cd(s)|$ is cathode.

Then,
$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = E_{(Cd^{2+}/Cd)}^{\circ} - E_{Cr/Cr^{3+}}^{\circ}$$

Taking the values of the standard electrode potentials,

$$E_{cell}^{\circ} = -0.40 \text{ V} - (0.74 \text{ V}) = +0.34 \text{ V}$$

$$\Delta_r G^{\circ} = -nF E_{cell}^{\circ} = -6 \times 96500 \times 0.34 \text{ J} \text{ mol}^{-1} - 196860 \text{ J} \text{ mol}^{-1}$$

$$\Delta_r G^{\circ} = -196.86 \text{ kg mol}^{-1}$$

The equilibrium constant of the cell reaction is obtained from equation, $\Delta_r G^\circ = -2.303 RT \log K - 196860 \text{ J mol}^{-1} = -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log \text{ K}$

$$\log K = \frac{-196860 \text{ J mol}^{-1}}{-2.303 \times 8.314 \text{ JK}^{-1} \text{mol}^{-1} \times 298 \text{ K}} = 34.5 \implies K = 3.17 \times 10^{34}$$

(ii) $Fe^{2+}(aq) + Ag^{+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Thus, Pt / Fe^{2+} , Fe^{3+} electrode is anode and Ag^+ / Ag is cathode in this cell.

Then,
$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = E_{Ag^+/Ag}^{\circ} - E_{Fe^{3+}/Fe^{2+}}^{\circ}$$

Substituting E° values,

$$E_{cell}^{\circ} = 0.80 V - 0.77 V = 0.03 V$$

$$\Delta_r G^{\circ} = -nF E_{cell}^{\circ}$$

$$= -1 \times 96500 \times 0.03 \text{ J mol}^{-1} = -2895 \text{ J mol}^{-1} - 2.895 \text{ kJ mol}^{-1}$$

(21/2)

(1)

(1/2)

$$\log K = \frac{\Delta_{l} G_{cell}^{*}}{-2.303 \text{ RT}}$$
$$= \frac{-2895 \text{ J mol}^{-1}}{-2.303 \times 8.314 \text{ JK}^{-1} \text{mol}^{-1} \times 298 \text{ K}}$$
$$\log K = 0.507 \implies K = 3.2$$
(21/2)

Given data is as follows:

C (mol L ⁻¹)	0.001	0.01	0.02	0.05	
VC	0.032		0.02		
$10^2 \times \kappa (\mathrm{Sm}^{-1})$			0.14	0.22	0.32
	1.23/	11.85	23.15	55.53	106.74
$10^4 \times \kappa (\text{Sm}^{-1})$	1.237	11.85	23.15	55 53	106.74
Å	123 7	118 5	145 -	00.00	100.74
		110.0	115.7	111.1	106.74

$$\hat{\Lambda} = \frac{1000 \times \kappa (\text{Sm}^{-1})}{C (\text{mol}/1)}$$

The Λ - \sqrt{C} plot is shown in the following plot :



- 32. (i) (a) When one mole of CoCl₃.6 NH₃ is mixed with AgNO₃, three moles of AgCl are precipitated which indicates that three ionisable chloride ions in the complex are present. Hence, its structural formula is [Co(NH₃)₆]Cl₃. (1)
 - (b) In both the complexes, Fe is in +2 state with the configuration $3d^6$, i.e. it has four unpaired electrons. As the ligands H₂Oand CN^- possess different crystal field splitting energy (Δ_0) they absorb different components of visible light (VIBGYOR) for *d*-*d* transition. Hence, the transmitted colours are different.
 - (c) According to VBT, $sp^{3}d^{2}$ -hybridisation is found in $[Co[H_2O]^{2+}$ and its structure is octahedral. It is an outer orbital complex because in this complex two outer *d*-orbitals (*nd*) participate in hybridisation, and it has three unpaired electrons. It has a weak ligand (H₂O). Its nature is paramagnetic. (1)

(ii)
$$\ln [Co(NH_3)_6]^{3+}$$
, Co is present as Co³⁺ and has 3d⁶ configuration. In the presence of NH₃, the 3d-electrons pair up leaving two d-orbitals empty to be involved in d^2sp^3 -hybridisation forming inner orbital complex in the case of $[Co(NH_3)_6]^{3+}$.



Since, (n - 1) d-orbitals are not available but the nd-orbitals are used in bond formation, i.e in hybridisation, the complex is called outer orbital complex.

Or

(2)

(i) Mn (II) ion has $3d^{5}$ configuration. In the presence of H₂O molecules (acting as weak field ligands), the distribution of these five electrons is $t_{2g}^{3}e_{g}^{2}$, i.e. all the electrons remain unpaired to form a high spin complex.



However, in the presence of CN^- (acting as strong field ligands), the distribution of these electrons is $t_{2g}^5 e_g^0$, i.e. two t_{2g} orbitals contains paired electrons while the third t_{2g} orbital contains one unpaired electron. The complex formed is a low spin complex.



(CN⁻ being strong field ligand paired up the d-electron of metal atom.)



Hydrolysis

Butanoic acid [B]

> + CH3CH2CH2CH2OH Butan-1-ol [C]

 $CH_3CH_2CH_2CH_2OH \xrightarrow{[0]} CH_3CH_2CH_2COOH$ Butanoic acid (oxidation) Butan-1-ol [C] $\xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CH}_3 \xrightarrow{\text{CH}_2} \text{CH}_2 \xrightarrow{\text{CH}_2} \text{CH}_2$ Dehydration (-H₂O) But -1-ene Conc. H₂SO₄ (3) Or



(a) Cross-aldol condensation If different (ii) carbonyl compounds having acidic hydrogen at a-position are condensed to give a. B-unsaturated compounds. Then, reaction is called cross-aldol condensaton.



(b) Cannizzaro's reaction Those aldehydes or ketones which do not have α-hydrogen atom reacts with conc. NaOH or KOH to form carboxylic acid salt and alcohol. This reaction is known as Cannizzaro's reaction.

e.g.

2HCHO + NaOH ----> HCOONa + CH₂OH Formaldehyde Sodium Methyl formate alcohol (1)

(c) HVZ (Hell-Volhard-Zelinsky reaction) a-hydrogen atom containing carboxylic acid in presence of red phosphorus reacts with chlorine or bromine to form a-halo substituted carboxylic acid. This reaction is known as HVZ reaction.

