

2020

CHEMISTRY — HONOURS

Fifth Paper

Full Marks : 100

*Candidates are required to give their answers in their own words
as far as practicable.*

Answer **any eight** questions, taking **one** from each **Unit**.

All questions carry equal marks.

(CHT - 31a)

Unit - I

- (a) Arrange the ligands H_2O , NH_3 , NO_2^- and Cl^- in order of increasing trans-effect and hence design two step syntheses of the cis- and trans-isomers of $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ starting from K_2PtCl_4 .

(b) Show d orbital splitting pattern of $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$.
- (a) In an octahedral Ni^{2+} complex the absorption bands arising from d – d transitions occur at $10,750 \text{ cm}^{-1}$, $17,500 \text{ cm}^{-1}$ and $28,200 \text{ cm}^{-1}$. Assign the bands from the Orgel diagram.

(b) What type of CT has been observed in the following compounds?
 Cds , HgI_2 , $[\text{Fe}(\text{Phenanthroline})_3]^{2+}$, Prussian blue.
- (a) What is tetragonal distortion? Which d^n configurations would lead to weak and strong Jahn-Teller distortion in octahedral complexes?

(b) Arrange in the increasing order of the magnetic moment of the following species :
 CoCl_4^{2-} , CoBr_4^{2-} , CoI_4^{2-} .
- (a) Co^{2+} can form several tetrahedral complexes but Ni^{2+} forms only limited number of tetrahedral complexes. Justify the statement.

(b) What type of spinel structure has been observed in Mn_3O_4 ?
- (a) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic and of orange yellow coloured while $[\text{CoF}_6]^{3-}$ is paramagnetic and blue. Explain the difference qualitatively.

(b) Draw the structures of all possible isomers of the complex $\text{Ma}_2\text{b}_2\text{c}_2$, where a, b and c are monodentate ligands.

Please Turn Over

Unit - II

6. (a) Explain briefly the principle of separation of lanthanides by ion exchange process.
 (b) Comment on the statement : Eu^{2+} and Tb^{4+} are stable in addition to their common oxidation state.
7. (a) TcO_4^- and ReO_4^- ions can function as oxidising agent like MnO_4^- in acidic-aqueous medium. Write half-cell reactions for the reductions and comment on their oxidizing ability with respect to MnO_4^- .
 (b) Complexes of Cu^{2+} are quite common but those of Au^{2+} are unstable — explain.
8. (a) Describe the method of preparation of $\text{K}_2\text{Cr}_2\text{O}_7$. Discuss its use as an analytical reagent.
 (b) Electronic spectra of Ln^{3+} ions give rise to multiple sharp peaks. Comment.

(CHT - 31b)

Unit - I

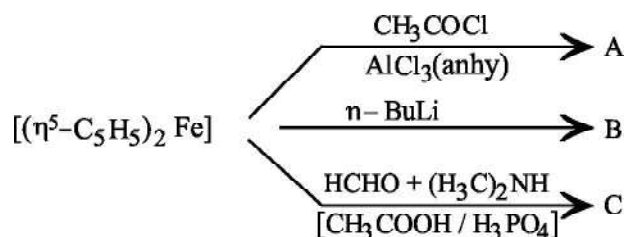
9. (a) What are the different modes of binding of CO in polynuclear carbonyls? How these are differentiated experimentally?
 (b) Explain the carbonyl stretching frequencies $\left[\bar{\nu}(\text{CO}), \text{cm}^{-1} \right]$ in the following compounds :
- | | | |
|---|----------------------------|---------------------------|
| | $[\text{Mo}(\text{CO})_6]$ | $[\text{W}(\text{CO})_6]$ |
| $\left[\bar{\nu}(\text{CO}), \text{cm}^{-1} \right]$ | 1984 | 1960 |
10. (a) Explain the mechanism of the following reaction –
 $\text{CH}_3\text{Mn}(\text{CO})_5 + \text{CO} \rightarrow \text{Mn}(\text{COCH}_3)(\text{CO})_5$.
 (b) Compare the redox activities of $[\text{Fe}(\text{Cp})_2]$ and $[\text{Co}(\text{Cp})_2]$ complexes (Cp = Cyclopentadienyl anion).
11. (a) In free $\text{CH}_3\text{CH}=\text{CH}_2$ compound, $\nu_{\text{C}=\text{C}}$ is 1652 cm^{-1} .
 But in the complex $\text{K}[\text{PtCl}_3\text{CH}_3\text{CH}=\text{CH}_2]$, $\nu_{\text{C}=\text{C}}$ is 1504 cm^{-1} . — Explain.
 (b) Find out X and Y in the following compounds :
 (i) $\text{Mn}(\text{CO})_x(\text{NO})_y$
 (ii) $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_x(\text{NO})_y$.
12. (a) Find out the number of metal-metal bonds in the following compounds.
 (i) $\text{Rh}_6(\text{CO})_{16}$
 (ii) $\text{Os}_4(\text{CO})_{14}$
 (iii) $[\text{Fe}_5(\text{CO})_{15}]^{2-}$

(b) Cite example of compounds where the oxidation state of –

(i) Mn is – 3

(ii) Cr is – 1.

13. (a) Identify the following A, B and C :



(b) Describe the electronic structure of $\text{IrCl}_2(\text{NO})(\text{PPh}_3)_2$.

Unit - II

14. (a) Name the metal ion(s) present in the active site of the following biomolecules :

(i) Nitrogenase

(ii) Cytochrome – C – Oxidase

(iii) Myoglobin.

(b) Describe the biological function of carbonic anhydrase.

15. (a) Mention main reactions involved in Photosystem I and Photosystem II in photosynthesis.

(b) Name two gold drugs and indicate their function.

16. (a) Explain cooperative effects in haemoglobin and indicate the role of haemoglobin in maintaining the body pH.

(b) Write antidotes of Lewisite gas poisoning and Wilson's disease.

(CHT - 31c)

Unit - I

17. (a) Calculate potential of a solution obtained by reacting 10 mL each of 0.20 (M) Fe^{2+} and 0.20 (M) Ce^{4+} in acid medium. Given $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ}$ is 0.77V and $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ}$ is 1.44V.

(b) Give a scheme for spectro-photometric estimation of iron.

Please Turn Over

18. (a) R_f values of three amino acids A_1 , A_2 and A_3 are 0.15, 0.34 and 0.67 respectively. Discuss the position of these amino acids during TLC separation.
(b) State limitations of Beer's law.
19. (a) State the principle of estimation of K in water by atomic emission spectrometry.
(b) Show and explain the nature of the curve found during conductometric titration of a mixture of CH_3COOH and HCl by NaOH .
20. (a) Depict the principle of pH-metric titration with a suitable example.
(b) Discuss any two factors that affect the selectivity of ion exchange resins.
21. (a) What do you understand by 'equivalent conductance' and 'cell constant'? Point out their SI unit.
(b) Why is atomic absorption spectroscopy preferable to atomic emission spectroscopy?

Unit - II

22. (a) State the principle for the estimation of NO_3^- and NO_2^- in water sample.
(b) What do you mean by TDS and COD of a sample of water?
23. (a) Calculate the standard deviation for the set of data 0.754, 0.758, 0.756 and 0.760 obtained during repeated estimation of a metal in a blood sample.
(b) State detection principle of small amount of NH_4^+ in water.
24. (a) Consider the following set of replicate measurements :
9.5, 8.5, 9.1, 9.3, 9.1. Calculate (i) Mean (ii) Median (iii) Spread or range.
(b) How are systematic method errors detected?

(CHT - 31d)

Unit - I

25. (a) Oxalic acid can function both as an acid and as a reductant. For 500 mg $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, how many millilitres of
(i) 0.1 (M) NaOH and
(ii) 1.0 (M) KMnO_4 are required separately for complete reaction?
(b) Give the name and chemical formula of the constituents of Portland cement and basic slag.
26. (a) A 0.7150 g specimen of iron ore is brought into solution and all iron content is reduced to Fe^{2+} . The reduced solution requires 37.20 mL of 0.02 (N) KMnO_4 solution for titration of Fe^{2+} . Calculate the percentage of iron in the ore.
(b) What is Reinhardt solution? State its role in the estimation of FeCl_3 permanganometrically.

27. (a) Explain the role of pH and stability constant in the complexometric estimation of Ca^{2+} and Mg^{2+} in aqueous solution.
(b) With suitable example, discuss the role of an adsorption indicator in precipitation reaction.
28. (a) How can Cu^{2+} , Zn^{2+} and Mg^{2+} in a mixture be estimated complexometrically using EDTA? State the principle involved.
(b) Why starch indicator is added near the end point in an iodometric titration?
29. (a) How will you dissolve steel and estimate Mn in it permanganometrically?
(b) Showing ionic equation calculate the equivalent weight of KBrO_3 (Mol. wt = M) during iodometric titration.

Unit - II

30. (a) What happens when H_2S is passed through
(i) CuSO_4
(ii) $\text{K}_2\text{Cr}_2\text{O}_7$
(iii) SbCl_3 solution in acid medium?
(b) Explain solubility of MSO_4 in aqueous medium. (M = Mg, Ca, Sr, Ba).
31. (a) (i) Atomic radii of Na^+ and Ag^+ are almost same, but their acidic nature are different. Explain and identify the more acidic one.
(ii) Which one of NH_3 , NF_3 and $\text{N}(\text{CH}_3)_3$ will be more basic?
(b) Precipitate of $\text{Mg}(\text{OH})_2$ is soluble in NH_4Cl but not in NaCl – Explain.
32. (a) Thermodynamically interpret that “all nitrates are soluble in water.”
(b) Arrange the following complexes in order of their increasing acidity :
 $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Na}(\text{H}_2\text{O})_6]^+$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
-