

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  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NO}_2^-$  and  $\text{Cl}^-$  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  $\text{K}_2\text{PtCl}_4$ .

(b) Show d orbital splitting pattern of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$ .
- (a) In an octahedral  $\text{Ni}^{2+}$  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?  
 $\text{Cds}$ ,  $\text{HgI}_2$ ,  $[\text{Fe}(\text{Phenanthroline})_3]^{2+}$ , 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 :  
 $\text{CoCl}_4^{2-}$ ,  $\text{CoBr}_4^{2-}$ ,  $\text{CoI}_4^{2-}$ .
- (a)  $\text{Co}^{2+}$  can form several tetrahedral complexes but  $\text{Ni}^{2+}$  forms only limited number of tetrahedral complexes. Justify the statement.

(b) What type of spinel structure has been observed in  $\text{Mn}_3\text{O}_4$ ?
- (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 :  $\text{Eu}^{2+}$  and  $\text{Tb}^{4+}$  are stable in addition to their common oxidation state.
7. (a)  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$  ions can function as oxidising agent like  $\text{MnO}_4^-$  in acidic-aqueous medium. Write half-cell reactions for the reductions and comment on their oxidizing ability with respect to  $\text{MnO}_4^-$  .  
 (b) Complexes of  $\text{Cu}^{2+}$  are quite common but those of  $\text{Au}^{2+}$  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  $\text{Ln}^{3+}$  ions give rise to multiple sharp peaks. Comment.

## (CHT - 31b)

## Unit - I

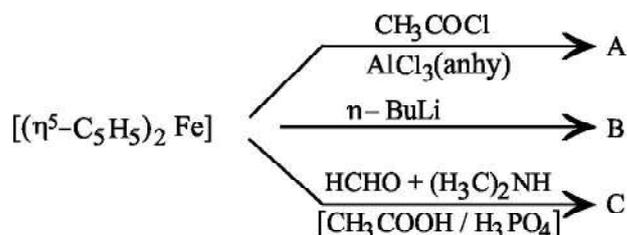
9. (a) What are the different modes of binding of CO in polynuclear carbonyls? How these are differentiated experimentally?  
 (b) Explain the carbonyl stretching frequencies  $\left[ \bar{\nu}(\text{CO}), \text{cm}^{-1} \right]$  in the following compounds :
- |                                                       |                            |                           |
|-------------------------------------------------------|----------------------------|---------------------------|
|                                                       | $[\text{Mo}(\text{CO})_6]$ | $[\text{W}(\text{CO})_6]$ |
| $\left[ \bar{\nu}(\text{CO}), \text{cm}^{-1} \right]$ | 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  $1652 \text{ cm}^{-1}$ .  
 But in the complex  $\text{K}[\text{PtCl}_3\text{CH}_3\text{CH}=\text{CH}_2]$ ,  $\nu_{\text{C}=\text{C}}$  is  $1504 \text{ cm}^{-1}$ . — 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)  $\text{Fe}^{2+}$  and 0.20 (M)  $\text{Ce}^{4+}$  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  $\text{CH}_3\text{COOH}$  and  $\text{HCl}$  by  $\text{NaOH}$ .
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  $\text{NO}_3^-$  and  $\text{NO}_2^-$  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  $\text{NH}_4^+$  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)  $\text{NaOH}$  and  
(ii) 1.0 (M)  $\text{KMnO}_4$  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  $\text{Fe}^{2+}$ . The reduced solution requires 37.20 mL of 0.02 (N)  $\text{KMnO}_4$  solution for titration of  $\text{Fe}^{2+}$ . Calculate the percentage of iron in the ore.  
(b) What is Reinhardt solution? State its role in the estimation of  $\text{FeCl}_3$  permanganometrically.

27. (a) Explain the role of pH and stability constant in the complexometric estimation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in aqueous solution.  
(b) With suitable example, discuss the role of an adsorption indicator in precipitation reaction.
28. (a) How can  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  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  $\text{KBrO}_3$  (Mol. wt = M) during iodometric titration.

### Unit - II

30. (a) What happens when  $\text{H}_2\text{S}$  is passed through  
(i)  $\text{CuSO}_4$   
(ii)  $\text{K}_2\text{Cr}_2\text{O}_7$   
(iii)  $\text{SbCl}_3$  solution in acid medium?  
(b) Explain solubility of  $\text{MSO}_4$  in aqueous medium. (M = Mg, Ca, Sr, Ba).
31. (a) (i) Atomic radii of  $\text{Na}^+$  and  $\text{Ag}^+$  are almost same, but their acidic nature are different. Explain and identify the more acidic one.  
(ii) Which one of  $\text{NH}_3$ ,  $\text{NF}_3$  and  $\text{N}(\text{CH}_3)_3$  will be more basic?  
(b) Precipitate of  $\text{Mg}(\text{OH})_2$  is soluble in  $\text{NH}_4\text{Cl}$  but not in  $\text{NaCl}$  – Explain.
32. (a) Thermodynamically interpret that “all nitrates are soluble in water.”  
(b) Arrange the following complexes in order of their increasing acidity :  
 $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Na}(\text{H}_2\text{O})_6]^+$ ,  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
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