2021

CHEMISTRY — HONOURS

Fifth Paper

Full Marks : 100

The figures in the margin indicate full marks.

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

(CHT – 31a)

Unit – I

Answer ***any three*** questions.

1. (a) How will you chemically differentiate between *cis* and *trans* isomers of $[Pt(NH_3)_2Cl_2]$?
(b) Cite one example each for 'kinetically labile' and 'kinetically inert' complexes. 3+2

2. (a) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are octahedral complexes of Fe(II). Comment on their (i) crystal field stabilization energy and (ii) magnetic properties.
(b) Using CFSE indicate whether $MnCr_2O_4$ is a normal or inverted spinel. 3+2

3. (a) Aqueous solution of Mn^{2+} is faintly coloured whereas aqueous solution of MnO_4^- is intensely coloured. — Explain.
(b) Mn^{2+} ion generally forms tetrahedral complexes. —Justify. 3+2

4. (a) $[Ni(H_2O)_6]^{2+}$ shows transitions at 9000, 14000 and 25000 cm^{-1}. Assign the transitions with required Orgel diagram.
(b) OH^- ion is in lower position than H_2O in the spectrochemical series. — Explain. 3+2

5. (a) Calculate the spin-only magnetic moment of Co^{2+} (High Spin and Low Spin) and Ni^{2+} ions.
(b) Draw all the possible isomers of the complex Ma_3b_3, where a and b are monodentate ligands. 3+2

Unit – II

Answer ***any two*** questions.

6. (a) Draw a comparison between lanthanides and actinides in terms of similarities and differences.
(b) Complexes of Cu(II) are common but those of Au(II) are unstable. — Explain. 3+2

7. (a) What do you mean by lanthanide contraction? Why have Nb and Ta almost same ionic radii?
(b) The third ionization energy for Eu and Yb are comparatively higher than other lanthanides. — Explain. 3+2

8. (a) Explain briefly the principle of separation of lanthanides by ion-exchange method.
(b) Tb^{4+} is stable in addition to its common oxidation state. —Justify. 3+2

(CHT – 31b)

Unit – I

Answer ***any three*** questions.

9. (a) Using 18 electron rule predict the number of metal-metal bonds in $Co_4(CO)_{12}$ and $Os_3(CO)_{12}$.
(b) Give one example of each of η^3 and η^5 ligand. 3+2

10. (a) Acetylation of ferrocene may produce either one or three 1, 1′ - disubstituted isomer(s). Which one actually takes place and why?
(b) Starting from K_2PtCl_6 how would you prepare Zeise's salt? 3+2

11. (a) What is Ziegler-Natta catalyst and how does it function?
(b) State the differences between 'oxidative addition' and 'insertion reactions' with examples. 3+2

12. (a) What is 'Hydroformylation Reaction'? Discuss the role of Cobalt organometallics as catalyst in the above reaction.
(b) Comment on the CO stretching frequencies ($\bar{\nu}$ in cm^{-1}) given below:

CO	$[Ti(CO)_6]^{2-}$	$[V(CO)_6]^{-}$	$[Cr(CO)_6]$	$[Mn(CO)_6]^{+}$
2143	1750	1860	2000	2090

3+2

13. (a) Two different stretching vibrations of CO bonds are observed in $Fe_2(CO)_9$. — Explain.
(b) Compare the redox activities of $[Fe(cp)_2]^+$ and $[Co(cp)_2]$ complexes {cp = cyclopentadienyl} and explain. 3+2

Unit – II

Answer ***any two*** questions.

14. (a) Name the metal ions present in the active site of the following biomolecules (i) Nitrogenase (ii) Carbonic anhydrase (iii) Cytochrome-c-oxidase.
(b) Explain with examples the 'Essential' and 'Beneficial' elements in living system. 3+2

15. (a) Explain principle of chelation therapy with special reference to the detoxification effect of arsenic poisoning in life system.
(b) Give the light phase and dark phase reactions that occur in photosynthetic process. 3+2

16. (a) Explain the term 'Bohr Effect' in connection to release of O_2 from Haemoglobin.
(b) Name one gold drug and state its therapeutic applications. 3+2

(CHT – 31c)

Unit – I

Answer ***any three*** questions.

17. (a) How can you estimate iron spectrophotometrically?

(b) Why is atomic absorption spectroscopy preferable to atomic emission spectroscopy? 3+2

18. (a) R_f values of three amino acids A1, A2 and A3 are 0·15, 0·34 and 0·67 respectively. Discuss the position of these amino acids during TLC separation.

(b) What will be the nature of the curve during titration of a mixture of CH_3COOH and HCl with NaOH conductometrically? 3+2

19. (a) Depict the principle of pH-metric titration with a suitable example.

(b) Calculate the potential at the end point of the titration of Fe(II) with $KMnO_4$ in H_2SO_4. 3+2

Given $E^0_{Fe^{3+}/Fe^{2+}} = + 0{\cdot}77$ V

$E^0_{MnO_4^-/Mn^{2+}} = + 1{\cdot}51$ V

20. (a) The solution of a substance (M.W. = 54·95) has an absorbance of 0·350 when its concentration was $1{\cdot}52 \times 10^{-4}$ M with optical path of 1 cm. What is the molar absorptivity and concentration of the solution of the same substance with an absorbance of 0·700 under identical condition?

(b) What is reference electrode? Represent a reference electrode of your choice and express its chemical reaction. 3+2

21. (a) Discuss the principle of determination of total cations in water by ion exchange method.

(b) State the limitations of Beer's law. 3+2

Unit – II

Answer ***any two*** questions.

22. (a) How can you determine the BOD of water sample?

(b) What do you mean by accuracy and precision in quantitative chemical analysis? 3+2

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 blood sample.

(b) What do you mean by TDS and COD of a sample of water? 3+2

24. (a) How will you detect a trace amount of CO and H_2S in water sample?

(b) State the principle of estimation of NO_2^- in water sample. 3+2

(CHT – 31d)

Unit – I

Answer ***any three*** questions.

25. (a) Give the principle for the estimation of $CaCO_3$ and $MgCO_3$ in dolomite sample.
(b) Define co-precipitation and post-precipitation. 3+2

26. (a) What is Zimmermann-Reinhardt solution? State its role in the estimation of $FeCl_3$ permanganometrically.
(b) Find out the oxidimetric and acidimetric equivalent weight of $KH(IO_3)_2$. 3+2

27. (a) Discuss the principle of estimation of Fe^{3+} and Al^{3+} in a given mixture complexometrically.
(b) The permanganate end point is gradually faded out with time. —Explain. 3+2

28. (a) Discuss the role of an adsorption indicator for precipitation titration with suitable examples.
(b) What volume of $\left(\frac{M}{50}\right)$ EDTA solution is to be required to titrate a solution containing 1·0 gm $CaCO_3$?
[Molecular weight of $CaCO_3$ = 100] 3+2

29. (a) Find out the amount of solid oxalic acid ($H_2C_2O_4.2H_2O$) required to make 250 mL of its solution having 0·05 (N) concentration.
(b) Give the balanced chemical equation for the standardization of $KMnO_4$ using oxalic acid. 3+2

Unit – II

Answer ***any two*** questions.

30. (a) Precipitation of ZnS does not occur when H_2S is passed in HCl medium but it does occur on addition of sodium acetate. —Why?
(b) Write down the Born equation and explain the terms involved. 3+2

31. (a) Arrange the following complexes in order of their increasing acidity:

$[Al(H_2O)_6]^{3+}$, $[Na(H_2O)_6]^{+}$, $[Mn(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$

(b) Though the lattice energy of CsF is much greater than the CsI, the former is more soluble in water than the later. —Explain. 3+2

32. (a) What happens when H_2S is passed through (i) $CuSO_4$, (ii) $K_2Cr_2O_7$ (iii) $SbCl_3$ solution in acid medium?
(b) The Group-IV metal requires NH_4OH-$(NH_4)_2CO_3$ for their selective precipitation as metal carbonates but Na_2CO_3 is not used for this purpose. —Justify. 3+2

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