# 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

**1.** (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 $[Pt(NH_3)_2(NO_2)_2]$ starting from $K_2PtCl_4$.

(b) Show d orbital splitting pattern of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$.

**2.** (a) In an octahedral $Ni^{2+}$ complex the absorption bands arising from d – d transitions occur at 10,750 $cm^{-1}$, 17,500 $cm^{-1}$ and 28,200 $cm^{-1}$. Assign the bands from the Orgel diagram.

(b) What type of CT has been observed in the following compounds?

Cds, $HgI_2$, [Fe (Phenanthroline)$_3$]$^{2+}$, Prussian blue.

**3.** (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 :

$CoCl_4^{2-}$, $CoBr_4^{2-}$, $CoI_4^{2-}$.

**4.** (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 $Mn_3O_4$?

**5.** (a) $[Co(NH_3)_6]^{3+}$ is diamagnetic and of orange yellow coloured while $[CoF_6]^{3-}$ is paramagnetic and blue. Explain the difference qualitatively.

(b) Draw the structures of all possible isomers of the complex $Ma_2b_2c_2$, where a, b and c are monodentate ligands.

**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 $K_2Cr_2O_7$. 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 $\left[\bar{\nu}\,(CO),\ cm^{-1}\right]$ in the following compounds :

| | $[Mo(CO)_6]$ | $[W(CO)_6]$ |
|---|---|---|
| $\left[\bar{\nu}\,(CO),\ cm^{-1}\right]$ | 1984 | 1960 |

**10.** (a) Explain the mechanism of the following reaction –

$CH_3Mn(CO)_5 + CO \rightarrow Mn(COCH_3)\ (CO)_5$.

(b) Compare the redox activities of $[Fe(Cp)_2]$ and $[Co(Cp)_2]$ complexes (Cp = Cyclopentadienyl anion).

**11.** (a) In free $CH_3CH = CH_2$ compound, $\nu_{c-c}$ is 1652 $cm^{-1}$.

But in the complex $K[PtCl_3CH_3CH = CH_2]$, $\nu_{c-c}$ is 1504 $cm^{-1}$. — Explain.

(b) Find out X and Y in the following compounds :

(i) $Mn(CO)_x(NO)_y$

(ii) $Fe(\eta^5 - C_5H_5)(CO)_x(NO)_y$ .

**12.** (a) Find out the number of metal-metal bonds in the following compounds.

(i) $Rh_6(CO)_{16}$

(ii) $Os_4(CO)_{14}$

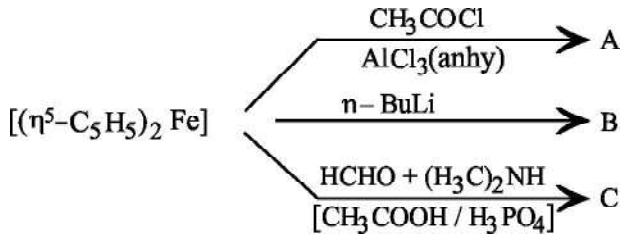
(iii) $[Fe_5(CO)_{15}]^{2-}$

(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 $IrCl_2(NO)(PPh_3)_2$.

**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 $E^{o}_{Fe^{3+}/Fe^{2+}}$ is 0.77V and $E^{o}_{Ce^{4+}/Ce^{3+}}$ is 1.44V.

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

**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 $H_2C_2O_4 . 2H_2O$, how many mililitres 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) $K_2Cr_2O_7$

(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 $N(CH_3)_3$ will be more basic?

(b) Precipitate of $Mg(OH)_2$ 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 :

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