

B.Sc. 5th Semester (Honours) Examination, 2024 (CBCS)**Subject : Chemistry****Course : CC-XI****(Inorganic Chemistry-IV)****Time: 2 Hours****Full Marks: 40***The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.***1. Answer any five questions:****2×5=10**

- (a) 10 Dq of $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is known from electronic spectrum to be 21000 cm^{-1} . The pairing energy of Mn^{3+} is 28800 cm^{-1} . Predict whether the complex is of high spin or low spin.
- (b) 'Addition of excess HCl to pale pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ changes the colour to blue while similar addition to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ has no effect.' — Comment.
- (c) What is nephelauxetic effect?
- (d) ' $[\text{Pt}(\text{NH}_3)_4]^{2+}$ is colourless and $[\text{PtCl}_4]^{2-}$ is red in the solution and the $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ — named Magnus' green salt is strongly coloured'. — Explain the observation.
- (e) The lanthanide elements show the common stable oxidation state of +3. Explain.
- (f) Draw the Orgel diagram of d^2 for O_h and T_d complexes.
- (g) Draw the crystal field splitting diagram for $[\text{Ni}(\text{dmg})_2]$; dmgH : dimethyl glyoxime.
- (h) 'Addition of ammonium thiocyanate to aqueous solution of uranyl nitrate produces deep red colouration'. — State reason.

2. Answer any two questions:**5×2=10**

- (a) (i) Using crystal field stabilization energy (CFSE) indicate spinels to be normal or inverse: Mn_3O_4 , Fe_3O_4
- (ii) Write the relationship between spectrum and magnetic moment of a transition metal complex. (2+2)+1
- (b) (i) Write 'True' or 'False' for the following statements and give reasons (any two):
 - Complexes of Cu^{2+} usually depart considerably from octahedral geometry.
 - In general, orbital contribution is more likely in square planar geometry than in octahedral geometry.
 - The ion $[\text{FeF}_6]^{3-}$ is colourless whereas $[\text{CoF}_6]^{3-}$ is coloured.
- (ii) 'The oxidising strength of $[\text{M}^{\text{VII}}\text{O}_4]^-$ ($\text{M} = \text{Mn}, \text{Tc}$ and Re) decreases and the energy of LMCT band position increases down the group.' — Explain. (1+1+1)

- (c) (i) Give one example of a magnetically concentrated substance.
- (ii) Calculate μ_{eff} for Eu^{3+} considering Lande splitting factor.
- (iii) 'Colours of Ln^{3+} (aqua) ions are less intense and sharp compared to the transition series elements.' — Comment'. 1+2+2
- (d) (i) What are the essential prerequisites for a coordination compound to be amenable to Spin Cross Over (SCO)?
- (ii) Distinguish between the possibilities in complex ions of $\Delta = 0$ and $\text{CFSE} = 0$. Give an example of each.
- (iii) What is meant by 'yl' ion? Give one example with respect to Mo. 2+2+(1/2+1/2)

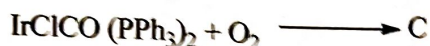
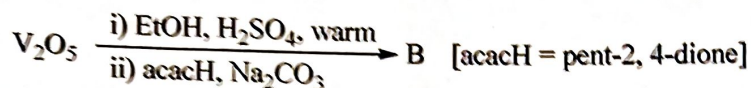
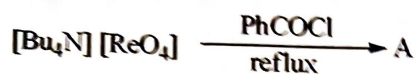
3. Answer any two questions:

10×2=20

- (a) (i) Show how does crystal field splitting take place in octahedral field and tetrahedral field. Why Δ_t is less than Δ_o ? Why are tetrahedral complexes always of high spin? Give an example of low spin tetrahedral complex. 2+1 1/2+1 1/2+1
- (ii) " OH^- ion is in the lower position than H_2O in spectrochemical series"— Explain. 2
- (iii) 'In high spin octahedral as well as in tetrahedral complexes, Co(II) contains three unpaired electrons. But the magnetic moments of its octahedral complexes are much higher (4.8 – 5.2 B.M.) in comparison to the tetrahedral ones (4.2 – 4.8 B.M.)'. — Comment. 2
- (b) (i) Calculate the spin only moment and spin plus orbital moment of chromium (III) ion. 3
- (ii) Which of the following should have comparatively more intense d–d transition? Explain.
- *trans* – $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ or *cis* – $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$
 - $\text{Ni}(\text{CO})_4$ or $\text{Fe}(\text{CO})_5$ 1 1/2+1 1/2
- (iii) 'More stable oxidation state of Cu is +2 while that of Au is +3'. — Explain it from CFT. 2
- (iv) Which of the following are expected to show Jahn–Teller distortion: $[\text{CuCl}_6]^{4-}$, $[\text{Cr}(\text{acac})_3]$, $\text{Cs}_2[\text{CuCl}_4]$ and $[\text{Co}(\text{CN})_6]^{4-}$ (low spin)? 2
- (c) (i) What happens when (any two): 2×2
- State the schematic steps for isolation of $[\text{Ni}(\text{diars})_2\text{Cl}_2](\text{ClO}_4)_2$ diars: o-phenylene bis(dimethyl arsine).
 - Sodium bismuthate is added to a solution of manganous sulphate in nitric acid medium.
 - On addition of H_2O_2 to an acidic (H_2SO_4) solution of $\text{K}_2\text{Cr}_2\text{O}_7$, a blue colour was developed which could be extracted into ether.

(ii) Draw the structure of the major products (A–C):

3



(iii) Draw the structure of Zeise's salt. Can you explain the lengthening of coordinated olefinic C–C bond in complex formed over the C–C bond in free ethylene? 1+2

(d) (i) Actinide compounds are much more covalent than lanthanides. — Why? Write the principle of separation of lanthanides by ion exchange method. 2+2

(ii) The colour and absorption spectra of a particular Ln^{3+} ions are more or less the same for the various types of ligands but transition metal ion shows different types of colours and absorption spectra for the different types of ligands. — Explain the fact. 2

(iii) Comment on the magnetic behaviour of solid AgO. How is the magnetic behaviour of Gd^{3+} and Lu^{3+} different from the rest of the lanthanides? $1\frac{1}{2}+1\frac{1}{2}$

(iv) What type of electronic transition is responsible for colour in lanthanides? 1