

U.G. 5th Semester Examination - 2024

CHEMISTRY**[HONOURS]**

Course Code : CHEM-H-CC-T-11

Full Marks : 40

Time : $2\frac{1}{2}$ Hours*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.*

1. Answer any five questions: $2 \times 5 = 10$
- a) An octahedral complex absorbs at 432 nm. What would be its respective tetrahedral field splitting?
 - b) Define stoichiometric mechanism and intimate mechanism.
 - c) What is Calomel? Mention the change(s) observed when calomel is exposed to ammonia.
 - d) Which one will cause higher Crystal Field Splitting Parameter (Δ_0) for the same ligand in the same stereochemistry: Fe^{2+} or Fe^{3+} ? Give reason.

[Turn over]

e) Work out CFSE (Crystal Field Stabilisation Energy) for a d^6 metal ion in an octahedral complex in which $10Dq > P$. [P : pairing energy]

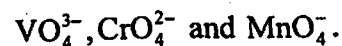
f) Give two examples of eight coordinated complexes of lanthanides.

g) Calculate the magnetic moment of Gd^{3+} ion.

h) Define cis-effect with example.

2. Answer any two questions: $5 \times 2 = 10$

a) i) Arrange the following oxoanions in the increasing order of oxidizing strength. Also write the decreasing order of the wavelength (λ) of LMCT transition of these species.



ii) What is OSSE (Octahedral Site Stabilisation Energy)? Give example.

2+3

b) i) Explain with reason whether Co_3O_4 exists as normal spinel or inverted spinel.

ii) $[NiCl_4]^{2-}$ is tetrahedral but $[PtCl_4]^{2-}$ is square planar although nickel and platinum belong to the same group in the periodic table. —Justify the contradiction. 3+2

c) i) Write the steps involved in the base hydrolysis of $[CoCl(NH_3)_5]^{2+}$.

ii) Differentiate between thermodynamic stability and kinetic stability. 3+2

d) i) Give proper reason: Actinoids form oxocations more frequently than lanthanoids.

ii) Why metallic radii of Eu and Yb are much larger than other lanthanoids? 3+2

3. Answer any two questions: $10 \times 2 = 20$

a) i) Justify or criticise: Gr 12 elements are not considered as transition metals.

ii) Elucidate the fact: High spin d^4 octahedral complexes undergo strong Jahn Teller distortion.

iii) Apply VBT to explain the structure and magnetic moment of $Li[Ti(bpy)_3]$.

iv) Indicate proper reason: Gold is a noble metal yet it forms auride (Au^-) ion like halogens. 3+3+2+2

b) i) Calculate effective magnetic moment (μ_{eff}) of $[Co(NO_2)_6]^{4-}$. Given: Spin-orbit coupling constant (λ) = -515 cm^{-1} ; crystal field splitting parameter ($10Dq$) = $12,000 \text{ cm}^{-1}$.

ii) Depict the structure of $Cr(II)$ acetate and indicate its salient features like bond order, state of hybridisation, magnetic behaviour.

- iii) Both V(II) and Cr(III) are d^3 metal ions —justify which one is more labile?

4+4+2

- c) i) What happens if $[\text{PtCl}_4]^{2-}$ is allowed to react (1) first with NH_3 and then with C_2H_4 , (2) first with C_2H_4 and then with NH_3 .

Write the geometries of the products.

- ii) Compare between spectrochemical series and nephelauxetic series.

- iii) Both Mn(II) and Fe(III) are d^5 metal ions. Which one is more labile and why?

4+4+2

- d) i) Write the name of the processes used for purification of nickel and zirconium from respective crude metals. Write the relevant chemical equations.

- ii) Interpret with the help of a diagram, the variation of lattice energy of +2 metal ions of 3d series in weak crystal field.

- iii) What happens when uranyl sulphate is treated with excess of Na_2CO_3 ?

4+4+2