

U.G. 5th Semester Examination - 2024

## CHEMISTRY

[HONOURS]

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

Full Marks : 40

Time : 2½ 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: 2×5=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 ( $\Delta_0$ ) for the same ligand in the same stereochemistry:  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ? 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 ( $\lambda$ ) of LMCT transition of these species.  
 $VO_4^{3-}$ ,  $CrO_4^{2-}$  and  $MnO_4^-$ .
- 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 ( $\mu_{eff}$ ) of  $[Co(NO_2)_6]^{4-}$ . Given: Spin-orbit coupling constant ( $\lambda$ ) =  $-515 \text{ cm}^{-1}$ ; 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  $\text{NH}_3$  and then with  $\text{C}_2\text{H}_4$ , (2) first with  $\text{C}_2\text{H}_4$  and then with  $\text{NH}_3$ .  
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  $\text{Na}_2\text{CO}_3$  ?  
4+4+2
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