



WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 5th Semester Examination, 2022-23

CEMACORIIT-CHEMISTRY (CC11)

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable
All symbols are of usual significance.*

UNIT-I

Answer any two questions from the following

12×2 = 24

1. (a) Find CFSE for d^6 systems in terms of Dq and pairing energy for high spin complexes. 2
- (b) CrF_6^{3-} shows absorption bands at 14900, 22700 and 34400 cm^{-1} respectively. Assign the bands. Find $10Dq$ value. 2+2
- (c) Give reasonable explanations to the following facts.
 - (i) FeF_6^{3-} ion is colorless, whereas, $[\text{Fe}(\text{CN})_6]^{3-}$ ion is colored. 2
 - (ii) Room temperature magnetic moment of Copper(II) sulfate pentahydrate is almost equal to the spin only moment of Cu(II) whereas that of Cu(II) acetate monohydrate is usually lower. 2
- (d) What is Nephelauxetic effect? 2
2. (a) 'Octahedral Cu(II) complexes are distorted' — Explain in the light of CFT using approximate energy diagram. 3
- (b) OH^- ion is in lower position than H_2O in spectrochemical series. Explain. 3
- (c) Explain with examples, how super-exchange and anti-ferromagnetic interactions influence the magnetic behaviour of co-ordination complexes. 3
- (d) Between cis- and trans- $[\text{Co}(\text{en})_2 \text{Cl}_2]^+$. Which one will give more intense d-d transition? Why? 3
3. (a) Diamagnetic complexes of cobalt(III) such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NO}_2)_6]^{3-}$ are yellow orange. In contrast paramagnetic complexes $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{OH}_2)_6]^{3+}$ are blue. Explain qualitatively the difference in color. 3
- (b) Which of the following complexes would you expect to suffer from a Jahn-Teller distortion: $[\text{CrI}_6]^{4-}$, $[\text{Cr}(\text{CN})_6]^{4-}$, $[\text{CoF}_6]^{3-}$ and $[\text{Mn}(\text{ox})_3]^{3-}$? Give reasons for your answers. 2
- (c) Which of the following pairs of complexes has higher Dq value and why? 3
 - (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Rh}(\text{NH}_3)_6]^{3+}$
 - (ii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
 - (iii) $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

- (d) How does pi bonding in metal ligand complexes influence the stability of oxidation states of transition metals? Give two examples with explanations. 2+2
4. (a) Pick up the ions which will undergo tetragonal distortion in octahedral field. Give reason of your choice. 3
 Fe^{+3} (High Spin), Co^{+2} (Low Spin) and Ni^{+2}
- (b) Chromium(II) acetate mono-hydrate is diamagnetic at room temperature. Explain. 3
- (c) Using an approximate Orgel diagram, explain the electronic spectrum of $\text{Ni}^{2+}(\text{aq})$ ion. 3
- (d) The observed magnetic moment for $\text{K}_3[\text{TiF}_6]$ is $1.70\mu\text{B}$. Calculate μ (spin-only) for this complex. Why is there a difference between calculated and observed values? 1+2

UNIT-II

Answer any one question from the following

16×1 = 16

5. (a) What is Lanthanide contraction? How does it influence the chemical behaviour of lanthanides? 3
- (b) Discuss the trend of variation of two important chemical properties in passing from 3d through 4d to 5d transition elements. 3
- (c) Actinides have a greater tendency to form complexes than lanthanides — Explain. 3
- (d) Why are the ionisation energies of 5d elements greater than those of 3d and 4d elements? 3
- (e) Although lanthanides usually exhibit +3 oxidation states, Eu^{2+} and Ce^{4+} have special stability. Give reason. 2
- (f) Bands from f-f transitions are sharp but those from d-d transitions are broad. Explain why. 2
6. (a) What are the basis of lanthanide separation? Give a brief outline of the separation of the lanthanide elements by the ion-exchange method. 1+3
- (b) Make critical comments on common and stable oxidation states of Cu, Ag and Au. 3
- (c) Oxo-cations are common with the actinides, but not with the lanthanides. Why? 3
- (d) ' La^{3+} and Lu^{3+} are diamagnetic while Sm^{3+} shows low magnetic moment' — Comment. 3
- (e) (+3) oxidation state is common for lanthanides in general while actinides can show variable oxidation states — Explain. 3

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