

2024

CHEMISTRY — HONOURS

Paper : CC-10

(Inorganic Chemistry-4)

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer *question no. 1* and *any eight* questions from the rest.1. Answer *any ten* questions :

1×10

- Write down the R-S term for the state with $L = 3$ and $S = 3/2$.
- Find the number of unpaired electrons in $[\text{FeCl}_4]^-$.
- Predict the energy order of the following set of terms : ^3P , ^5D , ^3H , ^1I , ^1G .
- In $[\text{PtCl}_6]^{2-}$ complex, between Δ and P which one is less in value?
- Predict the origin of deep red colour of HgS .
- Identify the inert complex in terms of ligand substitution reaction :
 $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.
- Find x in $\text{K}_x[\text{V}(\text{Ox})_3]$ from its μ_{eff} value of 2.80 BM. [$\text{Ox} \Rightarrow \text{Oxalate ion}$]
- Give two uses of Lanthanides.
- Arrange the following in order of increasing Trans effect :
 H^- , C_2H_4 , SCN^- , Pyridine.
- Give example of a compound where dynamic Jahn-Teller distortion persists.
- Identify the M^{4+} actinide ion with electronic configuration : $[\text{Rn}]5f^0 6d^0 7s^0$.
- Between Ce^{3+} and Ce^{4+} which one is paramagnetic?

- $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is paramagnetic ($\mu = 2.90$ BM) whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic. – Explain.
 - Square planar and octahedral complexes generally adopt TBP and square pyramidal geometry in transition states, respectively in ligand substitution reaction. Explain qualitatively. 3+2
- Define spin-state equilibrium and explain the drop in magnetic moment in *tris*(N,N-dialkylthiocarbamato)iron(III) from 5.8 BM at 300 K to 4.0 BM at 78 K.
 - Predict and justify which ion forms stronger complex with EDTA : Yb(III) or Ce(III) . 3+2

Please Turn Over

4. (a) How will you prepare $[\text{PtCl Br}(\text{NH}_3)(\text{Py})]$ from $[\text{PtCl}_4]^{2-}$, where Py and NH_3 are trans to each other?
 (b) Why MnSO_4 is faintly pink? 3+2
5. (a) Explain which one of each pair is comparatively more intense in colour :
 (i) *cis*- and *trans*- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
 (ii) $[\text{CoCl}_4]^{2-}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
 (b) $[\text{Cr}(\text{CN})_6]^{4-}$ is inert while $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is labile with respect to ligand substitution reaction. – Explain. 3+2
6. (a) An octahedral Ni(II) complex shows d-d absorption bands with $\lambda_{\text{max}} \approx 325, 550$ and 900 nm.
 (i) Assign the electronic transitions using Orgel diagram.
 (ii) Which bands are in visible region and uv end of the spectrum?
 (b) Predict and justify the product :

$$[\text{Pt}(\text{NO}_2)\text{Cl}_3]^{2-} + \text{NH}_3 \longrightarrow \text{A, Draw the structure of A.}$$
 3+2
7. (a) Find out the magnetic moment value of Eu^{3+} . Explain why the experimental value is higher than the calculated value.
 (b) How would you explain the trends in LMCT transition energy to explain the colour?
 MnO_4^- (pink) < ReO_4^- (colourless). 3+2
8. (a) Electronic absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ (stable under acidic condition), shows two well separated bands (430nm and 650nm) assigned to d-d transitions in visible region whereas that of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ consist of one band (λ_{max} at 490 nm) with a shoulder (580nm). — Explain.
 (b) How the mechanisms of substitution reactions can be predicted from the $\Delta S^\ddagger$ and $\Delta V^\ddagger$ values? 3+2
9. (a) The order of stepwise formation constant runs as : $K_1 > K_2 < K_3$ when Fe^{2+} reacts with 1,10-phenanthroline. – Justify.
 (b) Why there is 10% reduction in inter electronic repulsions in going from gaseous Ni^{2+} to $[\text{NiF}_6]^{4-}$ ion? 3+2
10. (a) CO is placed in higher position in spectrochemical series compared to NH_3 . – Explain in the light of MO theory.
 (b) Mention two differences in spectral features between Lanthanide and Actinide ions. 3+2

11. (a) For Co(II) complexes, $\mu_{\text{obs}}(\text{Oh}_{\text{h.s.}}) > \mu_{\text{obs}}(\text{td})$ although both have same number of unpaired electrons. – Justify.
- (b) Why WF_6 and WCl_6 are stable but CrF_6 is not? 3+2
12. (a) Compare the variation in coordination number as well as geometry of transition metal complexes along a group.
- (b) Which of the following complexes are expected to show Jahn Teller distortion?
 $[\text{CrCl}_6]^{4-}$, $[\text{Cr}(\text{CN})_6]^{4-}$, $[\text{CoF}_6]^{3-}$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. 3+2
13. (a) Explain : Lanthanide elements show the common stable oxidation state of +3 whereas actinide elements exhibit wide range of oxidation states.
- (b) Write down the factors on which associative and dissociative mechanism depend in ligand substitution reaction. 3+2
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