

U.G. 5th Semester Examination - 2020

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
- Show the d-orbital splitting in trigonal bipyramidal (tbp) ligand field.
 - What is curie temperature?
 - Calculate the magnetic moment of Ce³⁺ ion.
 - Arrange the following oxides in the increasing order of acidity MnO, Mn₃O₄, MnO₂ and Mn₂O₇ with brief explanation.
 - Define cis-effect.
 - Why CrO₄²⁻ and MnO₄⁻ are coloured ions and have different colors?
 - [Ti(H₂O)₆]³⁺ exhibits an absorption band at 20300cm⁻¹. Calculate the 10Dq value in KJ/mole.
 - What distortion is expected for octahedral d⁹-ion? State with reason.

[Turn over]

2. Answer any **two** questions: 5×2=10
- Write down two limitations of crystal field theory.
 - Explain with reason whether Mn₃O₄ exists in spinel or inverse spinel form. 2+3
 - Define ferrimagnetism with example.
 - Explain why the Ni²⁺ octahedral complexes show the magnetic moment higher than that of spin-only values? 2+3
 - Explain why radii are expected to decrease in the order d² > d³ > d⁴ > d⁵ > d⁶ in a given series of transition metal ions (M³⁺). Which kind of deviations are observed and why?
 - CuSO₄·5H₂O is blue whereas anhydrous CuSO₄ is colourless-Explain why? 3+2
 - Anomalous magnetic properties are exhibited by some lanthanide elements-Explain.
 - Explain the dissociative mechanism of substitution reaction in square planar complexes. 2½+2½
3. Answer any **two** questions: 10×2=20
- Why the aqueous solution of light pink coloured Co(II) chloride becomes deep blue upon addition of excess HCl?

- ii) The $[\text{CrF}_6]^{3-}$ exhibits absorption bands at 14900, 22700 and 34400cm^{-1} . Draw the Orgel diagram and assign the electronic transitions.
- iii) State and explain dynamic Jahn-Teller effect with example.
- iv) Calculate the CFSE in terms of Δ_0 for the complexes $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{NiCl}_4]^{2-}$. Then comment on their stabilities.
- 2+3+2+3
- b) i) State the Curie-Weiss law. Show the plot of $\frac{1}{\chi_M}$ vs T for ferromagnetic, antiferromagnetic and paramagnetic substances.
- ii) Explain why $\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ show diamagnetism.
- iii) A complex (molar mass = 0.395kgmol^{-1}) has density $1.92 \times 10^3\text{Kgm}^{-3}$ and magnetic susceptibility (k) at 293K is 6.7×10^{-4} . The diamagnetic correction is $2.5 \times 10^{-9}\text{mol}^{-1}\text{m}^3$. Calculate χ_M , μ_{eff} and number of unpaired electrons assuming $\mu_{\text{eff}} = \mu_{\text{spin}}$ only.
- 4+3+3

- c) i) In the first transition series electrons are gradually filled up in the 3d level with filled 4s² level. During ionization process will a 4s electron or a 3d electron be lost first? Give explanation on the basis of screening constant and effective nuclear charge citing an example.
- ii) Pt^{4+} is quite stable whereas Ni^{4+} is less stable—Explain.
- iii) Explain why the second and third rows of transition elements resemble each other much more closely than they resemble the first row, with respect to radii and oxidation states of the elements. 4+2+4
- d) i) What is trans effect? Explain π -bonding theory of trans effect.
- ii) Define kinetically inert and labile complex.
- iii) Although lanthanides usually exhibit +3 oxidation state but Eu^{2+} and Yb^{2+} have special stability—Explain.
- iv) Generally there is an increase in density from Ti to Cu in the first transition series. Explain. 3+2+2+3