Reg. No : ....   Name: **P205**

MSc DEGREE END SEMESTER EXAMINATION APRIL 2016
SEMESTER -2**: CHEMISTRY/APPLIED CHEMISTRY**
COURSE: **P2CHET05, P2CPHT05- CO-ORDINATION CHEMISTRY**
(Common for Regular-2015 Admission/Supplementary-2014 Admission)

Time Three Hours   Maximum Marks 75

SECTION A
Answer **any ten** questions, each question carries 2 marks

1. Arrive at the ground state term symbol of Cr^{3+} and Mn^{2+}
2. What is transition moment integral? Explain its significance.
3. Which electronic transition would you expected to be more intense and why? $^3A_{2g} \rightarrow {}^3T_{2g}$ in a Ni(II) octahedral or $^3T_1 \rightarrow {}^3T_2$ in a Ni(II) tetrahedral complex.
4. $[Ni(CN)_4]^{2-}$ is thermodynamically stable but kinetically labile. Explain
5. The measured magnetic moment of copper(II) acetate dehydrate at room temperature
   is less than the spin only value. Explain why?
6. What is nephelauxetic ratio? Point out its significance.
7. Compare the molar atomic volume and density of Cerium and Europium with other lanthanides and explain the logic behind it
8. The formula used for calculating the magnetic moment of 3d series is not suitable for 4f series. Why? Suggest the most reasonable formula for working out the magnetic moment of lanthanides.
9. What is CFSE? Calculate the CFSE of d^7 high spin and d^7 low spin situations.
10. Differentiate between macrocyclic effect and chelate effect with examples.
11. Why lanthanides give fewer complexes than actinides and d-block elements?
12. Differentiate between ferromagnetism and antiferromagnetism.
13. Distinguish between LMCT and MLCT.

(2 x 10 = 20)

SECTION B

Answer **any five** questions. Each question carries 5marks

14. Jahn-Teller distortion observed in t_{2g} state is very small compared to e_g state. Why is it so? Explain why $[Cu(en)_3]^{2+}$ is less stable than $[Cu(en)_2(H_2O)_2]^{2+}$.

15. Discuss the crystal field splitting of d levels in TBP and Sq. Pyramidal complexes.

16. What is linkage isomerism? Discuss the different factors affecting linkage isomerism.

17. What is absolute configuration of a coordination compound? Discuss the role of CD and ORD in reaching absolute configuration.

18. Explain how IR spectroscopy can be used to identify the different bonding modes of CO in metal carbonyls. The C-O stretching frequency for $[Ni(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$ are 2060 and 1790 cm^{-1} respectively. Account for this observation.

19. What are Orgel diagrams? Draw the Orgel diagrams of **d²** and **d⁴** ions in octahedral and tetrahedral ligand field?

20. The electronic spectrum of $[CoF_6]^{3-}$ shows an absorption peak at 13,000cm^{-1}. Assign the peak with the help of Orgel diagram

21. Explain the Gouy method for determination of magnetic susceptibility.

(5 x 5 = 25)

SECTION C

Answer **any two** questions. Each question carries 15marks

22. (a). Discuss briefly the mechanism of outer-sphere electron transfer reactions? How canMarcus theory be used to explain it?(9)

(b).What is trans effect? Keeping trans effect, suggest method for preparing threedifferent isomers of $[Pt(NH_3)(py)(Br)(Cl)]$ from $[PtCl_4]^{2-}$. (6)

23. (a).For Mn^{2+} ion the electro pairing energy is about 28.000cm^{-1}. Δo value for the complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ are 21,000 cm^{-1} and 38,000cm^{-1} respectively. Do these complexes have high spin or low spin configuration?

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Also write the configuration corresponding to these states.
(9)

(b).The Racah parameter, B, for $[Co(CN)_6]^{3-}$ is $460cm^{-1}$ and the same for $[Co(NH_3)_6]^{3+}$ is $615cm^{-1}$. Explain.

24. (a).Discuss the postulates of MO theory as applied to co-ordination compounds. How are Group orbitals constructed for the formation of MO in an octahedral complex?   (9)

(b).Explain why the two spin allowed ligand field transitions of $[Cr(NCS)_6]^{3-}$ are at lower energy than those of $[Cr(NH_3)_6]^{3+.}$ [6]

25.(a).What are TS diagrams? Discuss the merits and demerits b) Explain why both the low spin a $[Fe(CN)_6]^{4-}$ and high spin $[Fe(H_2O)_6]^{2+}$ are colourless c) Explain why the two spin allowed ligand field transitions of $[Cr(NCS)_6]^{3-}$ are at lower energy than those of $[Cr(NH_3)_6]^{3+.}$ d) The Racah parameter, B, for $[Co(CN)_6]^{3-}$ is $460cm^{-1}$ and the same For $[Co(NH_3)_6]^{3+}$ is $615cm^{-1}$. Explain.
(9)

(b).Predict the spin only magnetic moment of the following complex ions and explain whether any deviation is expected from the spin only value.1. $[Fe(CN)_6]^{3-}$
2.$[Fe(NH_3)_6]^{3+}$ 3. $[Cr(H_2O)_6]^{3+}$ 4. $[Cr(CO)_6]$ (6)

(15 x 2 = 30)

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