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

M Sc DEGREE END SEMESTER EXAMINATION MAY - 2015

SEMESTER – 2 **M Sc CHEMISTRY/APPLIED CHEMISTRY**

COURSE: **P2CHET05, PCPHT05 - COORDINATION CHEMISTRY**

Time 3 Hours Max. Marks 75

SECTION A

(Answer any **ten** questions, each question carries **2** marks)

1. Lanthanide complexes show sharp electronic spectral bands whereas the spectral bands of transition metal complexes are generally broad. Give reasons.
2. Arrive at the ground state term symbol of V^{3+} and, Mn^{2+}
3. Predict the number of peaks observed in the electronic spectra of $[Ti(H_2O)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$.
4. What is transition moment integral? Explain its significance.
5. $[Ni(CN)_4]^{2-}$ is thermodynamically stable but kinetically labile. What do you mean by this? What is transition moment integral? Explain its significance.
6. The measured magnetic moment of copper(II) acetate dehydrate at room temperature is less than the spin only value. Explain why?
7. What is spectrochemical series? Why OH^- comes before water in the series, in spite of the negative charge?
8. What is nephelauxetic ratio? Point out its significance.
9. Why Δt is lower than Δo? What are the factors affecting the magnitude of Δ?
10. What is Jahn-Teller distortion? How it happens?
11. Differentiate between macrocyclic effect and chelate effect with examples.
12. Cerium(III) with f^1 configuration is colourless, whereas cerium (IV) with f^0 configuration is orange red in colour. Why?
13. Differentiate between ferromagnetism and antiferromagnetism.

(2 x 10 = 20)

SECTION B

(Answer any **Five** questions. Each question carries **5** marks)

14. Jahn-Teller distortion observed in t_{2g} state is very small compared to e_g state. Why? Site examples of complex systems involving slight distortion, maximum distortion and no distortion.
15. What is linkage isomerism? Discuss the different factors affecting linkage isomerism.

16. What is absolute configuration of a coordination compound? Discuss the role of CD and ORD in reaching absolute configuration.
17. Explain how IR spectroscopy used to identify the different bonding modes of CO in metal carbonyls. The C-O stretching frequency for $[Ni(CO)_4]$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$ are 2060, 1890 and 1790 cm^{-1} respectively. Account for the observation

18. 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?
19. What are ligand field and charge transfer excited states of metal complexes? Illustrate the reactions initiated by excitation of this states in metal complexes?
20. What are Orgel diagrams? Draw the Orgel diagrams of $\mathbf{d^2}$ and $\mathbf{d^4}$ ions in octahedral and tetrahedral ligand field?
21. Discuss briefly the mechanism of outer-sphere electron transfer reactions? How can Marcus theory be used to explain it?

(5 x 5 = 25)

SECTION C

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

22. (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? Alsowrite the configuration corresponding to these states. (9)

(b). Compare and contrast the electronic spectra of 3d, 4f and 5f block elements in terms of appearance, multiplicity and half height width.(6)

23. (a). The electronic spectrum of $[CoF_6]^{3-}$ shows an absorption peak at 13,000cm^{-1}..Assign the peak with the help of Orgel diagram. (9)

(b). Explain the origin of the pale pink color of $[Mn(H_2O)_6]^{2+}$. (6)

24. (a). 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)

25.(a). What is trans effect? Keeping trans effect, suggest method for preparing three different isomers of $[Pt(NH_3)(py)(Br)(Cl)]$ from $[PtCl_4]^{2-}$. (9)

(b). What is base hydrolysis? Explain its mechanism using $[Co(NH_3)_5Cl]$example. (6)

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