INORGANIC CHEMISTRY - II (SEMESTER - 2)

CS/INT.PBIR(CH)/SEM-2/CH-424/09

1. ....
   Signature of Invigilator

2. ....
   Signature of the Officer-in-Charge

Reg. No.

Roll No. of the Candidate

- -

CS/INT.PBIR(CH)/SEM-2/CH-424/09
ENGINEERING & MANAGEMENT EXAMINATIONS, MAY – 2009
INORGANIC CHEMISTRY - II (SEMESTER - 2)

Time : 3 Hours]   [Full Marks : 50

INSTRUCTIONS TO THE CANDIDATES :

1. This Booklet is a Question-cum-Answer Booklet. The Booklet consists of **36 pages**. The questions of this concerned subject commence from Page No. 3.

2. You have to answer the questions in the space provided marked 'Answer Sheet'. Write on both sides of the paper.

3. **Fill in your Roll No. in the box** provided as in your Admit Card before answering the questions.

4. Read the instructions given inside carefully before answering.

5. You should not forget to write the corresponding question numbers while answering.

6. Do not write your name or put any special mark in the booklet that may disclose your identity, which will render you liable to disqualification. Any candidate found copying will be subject to Disciplinary Action under the relevant rules.

7. **Use of Mobile Phone and Programmable Calculator is totally prohibited in the examination hall.**

8. You should return the booklet to the invigilator at the end of the examination and should not take any page of this booklet with you outside the examination hall, **which will lead to disqualification**.

9. Rough work, if necessary is to be done in this booklet only and cross it through.

No additional sheets are to be used and no loose paper will be provided

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Marks Obtained

Question Number										Total Marks	Examiner's Signature
Marks Obtained											

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Head-Examiner/Co-Ordinator/Scrutineer

31003 (27/5)

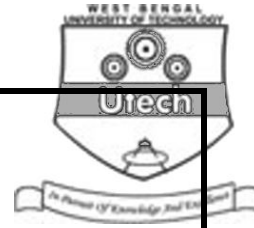DO NOT WRITE ON THIS PAGE

ENGINEERING & MANAGEMENT EXAMINATIONS, MAY – 2009
INORGANIC CHEMISTRY - II
SEMESTER - 2

Time : 3 Hours]   [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.

[There are three groups (A, B and C) in this paper. Use of calculator may be allowed]

GROUP - A

*[**Instruction :** There are **Five** questions in this group. Q. 1 is compulsory. Answer any **Three** from Q. 2 - Q. 5]*

1.   Nickel forms a 2 : 1 (ligand : metal) complex with the tridentate ligand 1, 4, 7-triazacyclononane. At 20°C the complex has μ_{eff} = 2.0 µB and at 150 K it exhibits an EPR spectrum. The UV-Vis spectrum has clear peaks at 18000 and 24000 cm $^{-1}$, each with ε of < 100 M^{-1} cm^{-1}. There is also a shoulder at about 28500 cm $^{-1}$ with about the same ε that is partially obscured by a more intense peak at higher energy.

   a)   What is the chemical formula of the complex that was formed ? Explain the magnetic moment and assign the UV-Vis spectrum assuming an effective O_h geometry. Calculate 10 Dq value for the tridentate ligand.

   b)   What effect did you expect to see in the UV-Vis spectrum, but which was not observed ? Why not ?   5

2.   a)   Show that the ground state term of Er^{3+} is $^4I_{15/2}$. What magnetic moment would you expect for $Er_2 (SO_4)_3 . 8H_2 O$?   2

   b)   Show that for a copper (II) dimer, the susceptibility is given by :

$$\chi_m = \frac{3g^2 (2e^{2J/T})}{8T (1 + 3c^{2J/T})}$$

3

3. a) What kind of exchange interaction is expected for a heterodinuclear V (IV)-Cu(II) complex where the six-coordinate metal centers are bridged by hydroxo ligand ?

1

   b) Predict the low temperature effective magnetic moments for the following compound assuming (a) antiferromagnetic exchange and (b) ferromagnetic exchange between magnetic centers. Determine the limiting high temperature effective magnetic moment for the complex. (Hint : assume that all ions as spin-only with $g = 2$]

   [Fe (OMe) (OAe)] $_{10}$ 2

   c) Write down the Hamiltonian for exchange interaction between the magnetic ions arranged in the corner of a symmetriccal square. Determine the spin states [S_T] for a square of interacting Ni (II) ions.   2

4. a) The gas-phase ion V $^{3+}$ has a ^3F ground term. The ^1D and ^3P terms lie, respectively, 10,642 and 12,920 cm $^{-1}$ above it. The energies of the terms are given in terms of Racah parameters as $E (^3F) = A - 8B$, $E (^3P) = A + 7B$, $E (^1D) = A - 3B + 2C$. Calculate the values of B and C for V $^{3+}$.   1

   b) Which of the following shows smaller value of Racah parameter, B' :

   [Co (NH $_3$) $_6$] $^{3+}$ and [Co (CN) $_6$] $^{3-}$.   1

   c) Assign the state terms for [Pt (CN) $_4$] $^{2-}$ in case of two-singly occupied, non-degenerate orbitals.   3

5. Close analysis of the electronic spectrum of [Ni (H $_2$ O) $_6$] $^{2+}$ reveals absorption maxima at 8,600, 13,500 and 25,300 cm $^{-1}$. There are also two exremely weak bands at 15,400 and 18,400 cm $^{-1}$. Consult the appropriate Tanabe Sugano diagram and assign all these transitions. Estimate 10Dq and B.   5

GROUP - B

[Instruction : There are **Three** questions in this group. Answer any **Two**]

1. a) How do the structures of UO $_2$ $^{2+}$ and WO $_2$ $^{2+}$ differ and why ?   2

   b) Write down the structure, conformation and magnetic property of Uranocene.   2

   c) How does the organolanthanide Sm (C $_5$ Me $_5$) $_2$ capture nitrogen ?   1

2. a) What could be the element of $^{238}U_{92}$ undergoes decay as follows : one α–emission followed by two β and another one α particles ? 2

b) Mention the essential step for the production of element beyond Pu. 1

c) "No^{2+} (aq) is specially, stable and most stable state for No in aqueous" — represents this fact in terms of Forst diagram and how do you get the potential of No^{2+} / No^{3+} couple from the diagram ? 2

3. a) Among Nd (III) and Tb (III) which metal ion forms complex with 18-crown-6 (*i.e.* 18–*C*–6) having formula of [Ln (18–*C*–6) (NO$_3$)$_3$] and why ? 2

b) "Ln^{3+} may replace Ca^{2+} in its binding sites in proteins" – briefly justify this statement. 2

c) Which lanthanide metal ion is used as MRI (Magnetic resonance imaging) agent and what is the role of the complex in this imaging technique ? 1

GROUP - C

*[Instruction : There are **Five** questions in this group. Answer any **Four**]*

1. a) Explain why the Fe–C distance lengthens for [Cp$_2$ Fe]$^+$, while the Co-C distance shortens for [Cp$_2$ Co]$^+$.

b) The indenyl ligand family shows much enhanced substitution reaction rates than cyclopentadienyl family. Explain.

5

2. a) Write a short note on Wilkinson's catalyst with proposed mechanism.

b) Explain the following results :

5

3.   a)   Sketch out a detailed mechanism and label each step for the following overall reaction.

   b)   Explain the anomalous C-C bond distances observed for following metal complexes.   5

4.   a)   To which of the following (each with a single open coordination site) will trifluoroethylene bind most strongly ? Why ?

b) Explain briefly the advantages of using of phosphine modified catalysits, compared to the traditional HCo $(CO)_4$ catalyst, for the hydroformylation reaction. 5

5. a) Briefly explain the role of additives in the carbonylation of methanol for the production of acetic acid.

b) Write a short note on Heck reaction with proposed mechanism of Pd (0) catalytic process. 5

Table

END