INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR

Time: 3 Hrs.

Date of examination.....FN/AN Full Marks..... 50

Autumn Semester 2012 4th yr. M. Sc.

Subject No.CY41005 Subject name: Inorganic Chemistry: Principle, Structure & Reactivity

No. of Students: 57 Department: Chemistry

Answer all the questions. This question paper contains two pages.

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1. (i) Explain the following:

(a) "d – d transition in octahedral metal complexes are weak, whereas that of tetrahedral complexes are strong."

(b) "The magnetic susceptibility of transition metal complexes having A and E ground terms do not have any orbital contribution."

(c) "A solution of $Mn(CH_3COO)_2$ is almost colourless."

(d) "Formation constant of $[Co(NH_3)_6]^{3+}$ is less than that of $[Co(en)_3]^{3+}$ {en = ethylenediamine}."

(e) " For oxidative addition, the metal must be of Lewis acidic as well as Lewis Basic in character.} $2 \times 5 = 10$

2. (a) Derive an expression for μ_{eff} for the system where only first order Zeeman effect is operative (energy state specified by **J**). Assume that, other states lie at >>> kT.

(b) In how many sets the d orbitals are splitted in a field of D_{4h} symmetry. Sow the details of the calculation. The necessary character table is given below.

	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

$5 + 10 = 15$

3. (a) What is TIP? How does it arise?

(c) What is Eigen-Wilkins Mechanism?

(d) What is Fuoss-Eigen equation? 2 + 2 + 1 = 5

4. (a) What are the different type of stoicheometric mechanisms operative in electron transfer reactions? Explain each of the mechanisms.

(b) The rate law for the substitution of $[PtCl(dien)]^+$ by I^- is given by:

$$Rate = (k_1 + k_2[I^-])[\{PtCl(dien)\}^+]$$

Explain the k_1 pathway.

(c) Draw the potential energy curves for zero free energy change and non-zero free energy change electron transfer reactions.

3 + 3 + 4 = 10

5. (a) Calculate the rate constant for the outer sphere reaction: $Cr^{2+} + Fe^{3+}$ form the given data.

$k_{11} = 2 \times 10^{-5}$ L mol^{-1} sec^{-1}; $k_{22} = 4.0$ L mol^{-1} sec^{-1}; $E^{\Theta} = +1.18$ V

(b) The following activation parameters have been observed for the reaction:

$$[Pt(Py)_2Cl(NO_2)] + Py \rightarrow [Pt(Py)_3Cl] + NO_2^-$$

$k_2 = 7.35 \times 10^{-3}$ L mol^{-1} sec^{-1}. $\Delta H_2^{\#} = 49.3$ kJ/mol; $\Delta S_2^{\#} = -94$ J/ K mol; $\Delta V^{\#} = -8.8$ cm^3/K mol. What mechanistic information can be obtained from these values? Explain you answer.

(c) Use the trans effect to suggest synthesis of cis- and trnas- $[PtCl_2(NH_3)_2]$.

(d) Explain the observed trend in the rate constant of the following reaction.

$$[PtClL(PEt_3)_2] + H_2O \longrightarrow [Pt(H_2O)Cl(PEt_3)_2]$$

L = pyridine; k = 8×10^{-2} s^{-1}, L = 2-methylpyridine; k = 2×10^{-4} s^{-1} L = 2, 6-dimethylpyridine; k = 1.0×10^{-6} s^{-1}.

3+ 3 + 2 +2 = 10