

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

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 × 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 $\gg \gg kT$.

(b) In how many sets the d orbitals are splitted in a field of D_{4h} symmetry. Show 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 stoichiometric mechanisms operative in electron transfer reactions? Explain each of the mechanisms.

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

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

Explain the k_1 pathway.

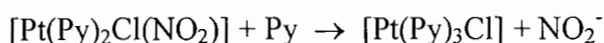
(c) Draw the potential energy curves for zero free energy change and non-zero free energy change electron transfer reactions.

$$3 + 3 + 4 = 10$$

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

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

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



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

(c) Use the trans effect to suggest synthesis of cis- and trans- $[\text{PtCl}_2(\text{NH}_3)_2]$.

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



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

$$3 + 3 + 2 + 2 = 10$$