# CH31101_Chemistry of Transition Elements: End Semester Examination
## December 2018   Full Marks 80

1. (a) Calculate the rate constant for the electron transfer reaction noted below

$$[Co(bpy)_3]^{2+} + [Co(terpy)_3]^{3+} \rightarrow [Co(bpy)_3]^{3+} + [Co(terpy)_3]^{2+}$$
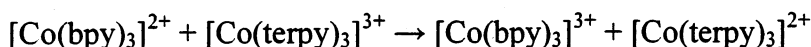
Where the rate constant for the self exchange reactions of $\{Co(bpy)_3\}^{2+/3+}$ and $\{Co(terpy)_3\}^{3+/2+}$ are 9 $M^{-1}$ $s^{-1}$ and 48 $M^{-1}$ $s^{-1}$ respectively. The electrochemical potential for the following reactions are 0.34 V and 0.31 V respectively. Collision frequency is $10^{22}$

(b) $[(Im)(Por)Fe^{II}]$ activates $O_2$ leading to a $Fe^{IV}= O$ species. Show the reaction mechanism with all the possible intermediates. Describe vibrational, paramagnetic resonance spectroscopy and magnetic properties of the reactants, intermediates and the products. Show mechanistically the product during the reaction between $Fe^{IV}= O$ species and $R_3C$-H.

(c) With the help of EPR spectroscopy how would you establish that a dinuclear mixed valence compound is valence localised $\{V^{IV}-V^V\}$ or valence delocalised $\{V_2\}^{9+}$ core motif.

(d) "TEMPO" exhibits an EPR transition at 348 mT with an isotropic g value of 2.003 when placed in an Q-band (34.18 GHz) EPR spectrometer. Calculate the operating frequency at which the resonance occurred.

(e) Describe Axial Zero-field Splitting (ZFS). How would you distinguish with the help of EPR spectroscopy that a compound with S=1 spin state having axial zero-field splitting or not. Explain with proper transitions. How would you determine Spin-Hamiltonian parameter "D" from the spectrum?

$$6+ 10 + 4 + 2 + 5 = 27$$

2. (a) $[(Cyclam)Mn^{VI}(N)(NCCH_3)]^{3+}$ exhibits an isotropic EPR spectrum when measured at 9.32GHz X-band spectrometer and depicts a g = 2.0. Calculate the frequency at which the resonance would occur? How many lines of hyperfine due to Mn is expected? Show the possible hyperfine transitions considering both $\nabla m_S$ and $\nabla m_I$. Draw the spectrum.

(b) Draw the d-orbital splitting of $[(Cyclam)Cr(N)(NCCH_3)]^{2+}$ .The molecule exhibits electronic transitions at440 ($\varepsilon$ = 30), 404 ($\varepsilon$ = 46), 365 ($\varepsilon$ = 18) & 273 ($\varepsilon$ = 3800) nm. Show the splitting of the spectroscopic terms. Assign these electronic transitions. Calculate 10Dq, Dt & Ds parameters. The molecule exhibits an EPR spectrum with a $g_{av}$ = 1.969. Calculate the spin-orbit coupling constant of the molecule.

(c) $[CoCl_4]^{2-}$ exhibits three electronic transitions at 4352 cm$^{-1}$, 7830 cm$^{-1}$ & 16400 cm$^{-1}$. Deduce the value of inter-electronic repulsion parameter and the covalency parameter. (Free ion value B for Co$^{II}$ is 971). The compound exhibits room temperature $\mu_{eff}$ = 4.54 Bohr Magnetron. Calculate the spin orbit coupling constant of Co$^{II}$ in this particular compound.

(d) [Cu(por)] exhibits 9 line hyperfine whereas [Mo(O)(por)](BF$_4$) does not exhibit such 9 line hyperfine though both of them having an unpaired electron with S=1/2. How would you explain?

$$9 + 9 + 5 + 4 = 27$$

**3. (a)** K$_3$[CrF$_6$] exhibits three d-d transitions at 14900, 22400 and 30500 cm$^{-1}$. The compound displays an EPR spectrum with $g_{av}$ = 1.97. Calculate spin-orbit coupling constant of the above mentioned compound.

**(b)** The energy trend in MLCT transitions are $CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$. Explain with the help of MO diagram.

**(c)** [Co(H$_2$O)$_6$]Cl$_2$ exhibits faint pink colour when dissolved in water. If HCl is added in this solution the colour changes to deep blue. Explain the reason for the colour change and the intensity of the colour described herein.

**(d)** [Re$_2$Cl$_8$]$^{2-}$ is diamagnetic although Re$^{III}$ is paramagnetic. Explain it with the help of MO diagram. What will be the bond order in the following species [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$] (A) and [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]$^+$ (B). Among the A and B which of the species can be probed by EPR spectroscopy and why?

**(e)** The g value of the paramagnetic transition metal complexes often deviated from $g_{s.o}$ value of 2. Describe with pictorial representation that a deviation from octahedral geometry can lead to an anisotropic g values.

$$3 + 7 + 4 + 8 + 4 = 26$$