

**BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI**

**II Semester, 2017-2018**

**Course No.: CHEM F111**

**Course Title: General Chemistry**

**Max. Marks: 15**

*Assignment Set 2 [based on Lecture Nos.: 17–29 in the course handout]*

*Instructions to the students: The following problems should be solved as home assignment within a week of distribution.*

**Que 1:** (a) Compound A,  $C_8H_{12}O$ , shows IR band at  $1686\text{ cm}^{-1}$ . It decolorizes bromine in carbon tetrachloride and gives positive results to iodoform test. However, one mole of compound A on ozonolysis gives only one mole of a single product. What is the structure of compound A. [10]

(b) A compound  $CoCl_3 \cdot 4NH_3$  has one ionisable chloride ion. Draw the structure of possible isomer(s). Comment on the optical activity of the isomer(s). [5]

**Que 2:** (a) Compound A ( $C_6H_8$ ) reacts with two molar equivalents of hydrogen in the presence of a catalyst to produce B ( $C_6H_{12}$ ). The proton-decoupled  $^{13}C$  spectrum of A consists of two singlets, one at  $\delta$  26.0 and one at  $\delta$  124.5. In the  $^{13}C$  spectrum of A the signal at  $\delta$  26.0 appears as a  $CH_2$  group and the one at  $\delta$  124.5 appears as a CH group. Propose structures for A and B. [10]

(b) Draw the crystal field splitting of  $[Co(NH_3)_6]^{3+}$  in the octahedral environment and calculate the CFSE in  $\Delta_o$  unit. [5]

**Que 3:** Predict the structure and hybridization with the help of Valence Bond Theory of (i)  $[AgI_2]^-$  (diamagnetic) (ii)  $Fe(CO)_5$  (diamagnetic) (iii)  $FeO$  (paramagnetic with 2 unpaired electrons) and (iv)  $[Cu(NH_3)_4]^{2+}$  (paramagnetic with 1 unpaired electron). Explain a typical drawback of this theory. [3×4 +3]

**Que 4:** (a) Write the electron splitting pattern and calculate the CFSE of the following complexes. [3×4]

(i)  $[Fe(H_2O)_6]^{2+}$  (ii)  $[Fe(CN)_6]^{4-}$  (iii)  $[CoF_6]^{3-}$  (iv)  $[Co(NH_3)_6]^{3-}$

(b) In octahedral complex of Cu(II) fluoride, the  $Cu^{2+}$  ion has four  $F^-$  at  $1.92\text{ \AA}$  and two  $F^-$  at  $2.22\text{ \AA}$ . Why? [3]

**Que 5:** (a) Draw all the geometric and optical isomers of complex ion,  $[CoBr_2(dipy)(NH_3)_2]^+$ . [4×2]

(b) Calculate the magnetic moment of  $K_3[Co(C_2O_4)_3]$  complex. [3]

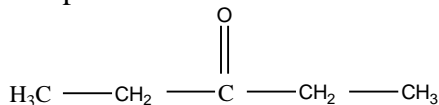
(c) Explain why CO forms low spin complexes whereas  $H_2O$  ligands form high spin complexes in octahedral field. [4]

**Que 6:** (a) An organic compound "A" with molecular Formula:  $C_7H_{12}O_3$  has following spectral data: IR peaks ( $cm^{-1}$ ): 1735 (s) and 1710 (s).  $^1H$  NMR ( $\delta$ ): 1.06 (3H, Triplet), 2.49 (2H, Quartet), 3.41 (2H, Singlet), 4.12 (2H, Quartet), and 1.3 (3H, Triplet). Determine the structure of the compound "A" assigning all the IR and NMR signals. [8]

(b) Consider the following compound and answer the following questions.

(i) How many  $^1H$  NMR signal are possible for this molecule? [2]

(ii) How many  $^{13}C$  NMR signal are expected for this molecule? Which carbon will be most deshielded? [2]



(iii) In the above compound, the chemical shift of the  $CH_3$  and  $CH_2$  protons are  $\delta = 1.20$  and  $3.80$ , respectively. What is the difference in local magnetic field between the two regions of the molecule when the applied field is  $3.0\text{ T}$ ? [3]

**Que 7:** Example of few six coordinated high-spin octahedral complexes are  $FeF_2$ ,  $K_3[CoF_6]$ ,  $[Fe(H_2O)_6]^{3+}$ , and  $[Cr(H_2O)_6]^{2+}$ . The electronic spectrum of  $FeF_2$  shows absorptions at  $6990\text{ cm}^{-1}$  and  $10,660\text{ cm}^{-1}$ , while for  $K_3[CoF_6]$  the absorption values are at  $10,200\text{ cm}^{-1}$  and  $14,500\text{ cm}^{-1}$ . In the electronic spectrum of  $FeF_2$  and  $K_3[CoF_6]$  complexes the 2<sup>nd</sup> peak is more intense than 1<sup>st</sup> peak.  $[Cr(H_2O)_6]^{2+}$  also shows two absorptions, whereas, for  $[Fe(H_2O)_6]^{3+}$  multiple absorptions are present. All the octahedral complexes are either intense or pale colored as compared to the complexes of other oxidation state of these metals. Answer the following questions properly.

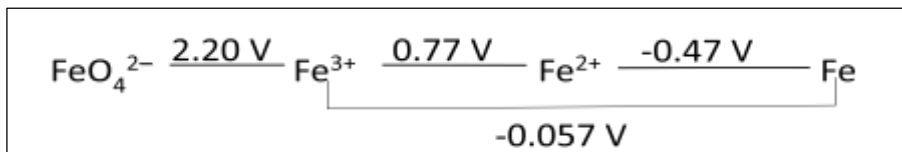
(a) How can you account for the presence of two bands in the electronic spectrum of  $K_3[CoF_6]$  complex? Specify all the possible transitions corresponding to the observed band in electronic transition. Justify in case of  $FeF_2$

complex why the 2<sup>nd</sup> peak is more intense than 1<sup>st</sup> peak. Provide your justification in terms of ground state term only. [5]

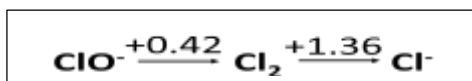
(b) Which of the above complex (s) shows pale color and why? [5]

(c) Which of the above four complex (s) show Jahn-Teller distortion? Explain whether  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  complex will undergo tetragonal elongation or compression. Justify your answer within 2-3 sentences. Starting from d-orbital diagram of regular octahedral geometry draw resultant splitting in the d-orbital of distorted  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  complex with proper labeling of all the d-orbitals. [5]

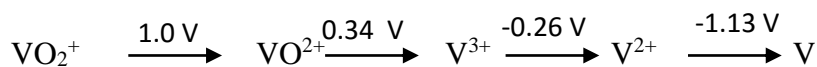
**Que 8: (a)** Iron can exist in two or more stable oxidation states. Latimer diagram of Fe in acidic solution in different oxidation state is given below. Calculate the standard reduction potential ( $E^0$ ) value for  $\text{FeO}_4^{2-}$  to Fe reaction and write the involved balanced chemical reaction? [5]



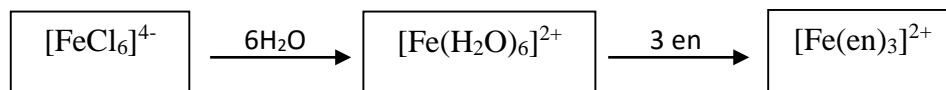
(b) Based on the reduction potential value from Latimer diagram of Cl species, the conversion of  $\text{Cl}_2$  to  $\text{ClO}^-$  is not spontaneous, however,  $\text{Cl}_2$  converts to  $\text{ClO}^-$ . Justify your answer. [5]



(c) Convert the following Latimer diagram for vanadium into Frost diagram by mentioning the coordinates of the different points. Identify the most effective oxidizing agent and most stable oxidation state of V. [5]



**Que 9:** Consider the following octahedral complexes and answer the following questions.



(a) Based on the ground state term in  $[\text{FeCl}_6]^{4-}$  complex theoretically how many band is/are expected in electronic spectrum? Assign the electronic transition starting with ground state term. [5]

(b) Do you expect any distortion (either tetragonal elongation or compression) in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  complex? Justify your answer briefly. [5]

(c) What is/are the driving force (s) behind the conversion of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  to  $[\text{Fe}(\text{en})_3]^{2+}$  complex? Calculate the overall formation constant ( $\beta$ ) for  $[\text{Fe}(\text{en})_3]^{2+}$  at 35 °C, if the standard enthalpy and entropy changes are -8.1 kJ/mol and 0.152 kJ/mol, respectively? [5]

**Que 10: (a)** Determine effective atomic number of iron in  $\text{Fe}(\text{NO})_2(\text{CO})_2$  and  $\text{Fe}(\text{C}_5\text{H}_5)_2$  complexes? Distinguish between the possibilities in complex ions of  $\Delta = 0$  and  $\text{CFSE} = 0$ . Provide an example for each. [5]

(b) Calculate CFSE for Ni(II) and Zn(II) in terms of  $\Delta$  in square planar field, tetrahedral field, and octahedral field? [5]

(c) What is the spinel structure for  $\text{NiCr}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  mixed oxides? [5]

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