

CHEM F214: Inorganic Chemistry-II
Max. Time: 90 mins.

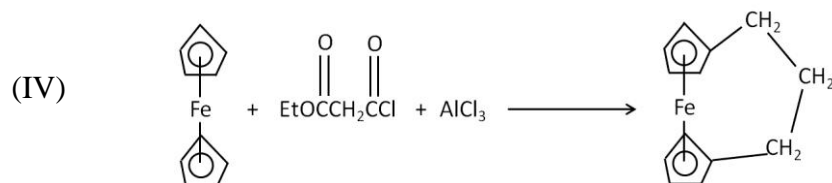
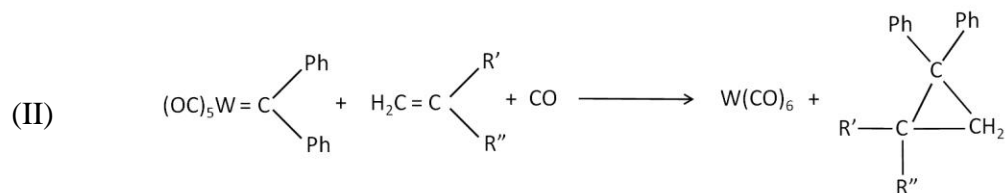
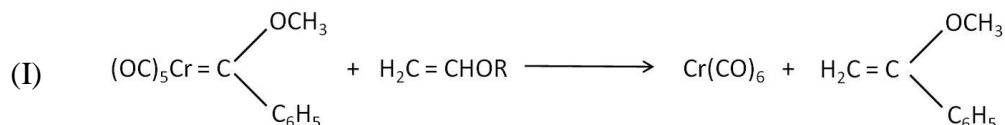
(Open Book)

Max. Marks: 50
Date: 07.05.2022

Instructions to the students:

1. There are **four questions** in all. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. Write brief answers to the point with proper justifications.
4. Atomic number of Co = 27, Fe = 26, Ni = 28, Mn = 25, Cu = 29, Pt = 78, Al = 13, Cr = 24, V = 23.

Q. 1. Write the mechanism in the following reaction. Write each step clearly with proper structure. Indicate the intermediate formed, reagents used and type of reaction occurring at each step. **[3+3+3+4]**



Q. 2. (a) Justify the following statement. "The rates of hydrolysis reaction of the four complexes e.g., $[PtCl_4]^{2-}$, $[Pt(NH_3)Cl_3]^{-}$, $[Pt(NH_3)_2Cl_2]$, and $[Pt(NH_3)_3Cl]^{+}$ vary only by a factor of two (a small effect), although the charge on the reactant Pt(II) complex varies".

(b) For the following polynuclear complex, indicate the total number of electrons, determine the number of M-M bonds present, and predict a structure. $\mu - CO - [(\eta^4 - C_4H_4)Fe(CO)]_2$

(c) Justify the following statement. "Ligands such as NO_2^- , $[NCS]^-$, and N_3^- etc. are as strong nucleophiles as OH^- , but they do not influence the rate of hydrolysis of ammine octahedral complexes".

(d) Consider a complex formation of $[Cr(en)_2(H_2O)_2]^{2+}$ from $[Cr(H_2O)_6]^{2+}$. What is/are the driving force (s) behind the conversion of $[Cr(H_2O)_6]^{2+}$ to $[Cr(en)_2(H_2O)_2]^{2+}$ complex? Calculate the overall formation constant (β) in "log₁₀" form for $[Cr(en)_2(H_2O)_2]^{2+}$ complex at 40 °C, if the standard enthalpy and entropy changes are -8.1 kJ/mol and 0.152 kJ/mol, respectively [$R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$]? **[3+3+3+3]**

Q. 3. (a) Fumarate ion is used as a food additive and an acidity regulator. Structure of fumarate ion is given in Figure 1. Answer the following questions for fumarate ion.

(I) Identify the presence of probable symmetry elements and point group.

(II) Find the number and symmetry species of the Raman and infrared active vibrations of the ion. Show all the steps clearly during the calculation of Raman and IR active vibrations.

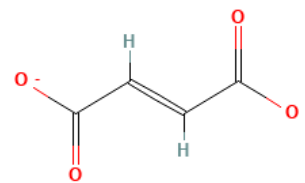


Figure 1

(b) Consider the octahedral (O_h), square pyramidal (C_{4v}), and seesaw (C_{2v}) species for AB_6 case, where A and B are central metal and ligands, respectively.

Show that the loss of orbital degeneracy is a characteristic result of reducing the symmetry from O_h to C_{2v} for AB_6 case.

(c) Comment on the dipole moments of cis- and trans- form of N_2F_2 based on the symmetry point of view. [6+3+3]

Q. 4. (a) Chrome yellow is a yellow pigment in paints using lead(II) chromate. The electronic spectrum of chrome yellow shows approximately four distinct bands at 256 nm, 360 nm, 500 nm, and a broad band at 780 nm. What is the reason for color in chrome yellow and assign the bands by showing the transitions in molecular orbital diagram with proper labeling.

(b) The complex $[Fe(H_2O)_6]^{2+}$ displays two overlapping absorption bands (Figure 2) in electronic spectrum. Provide a justification for this phenomena.

(c) Hexaquaairon (III) is nearly colorless. On the addition of potassium thiocyanate a blood red color develops. Explain.

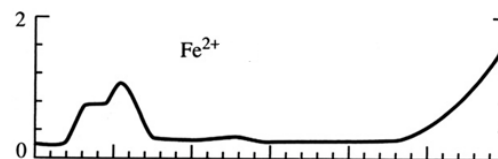


Figure 2

(d) Consider a complex, $Ni(NH_3)_4(NO_3)_2(H_2O)_2$ shows both paramagnetic and diamagnetic behaviour. Justify the statement with proper reasoning. [4+3+3+3]

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