Birla Institute of Technology & Science Pilani, Pilani Campus, Rajasthan 333 031

Comprehensive Examination, First Semester 2022-2023

Course No: CHEM F111 **Course Title: General Chemistry** **Date: 23 Feb 2023**

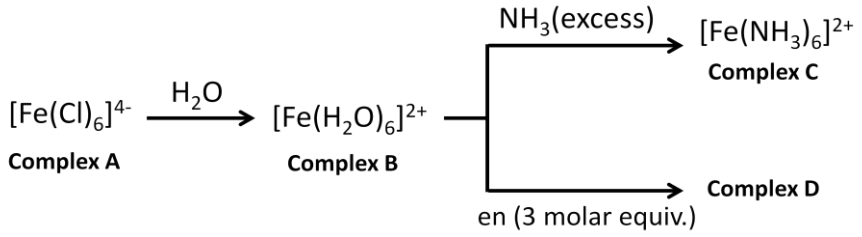
Maximum Marks: 48 **PART-A: CLOSED BOOK** **Max. Time: 70 min**

Given are commonly used data, notations have usual meanings; h = 6.626×10^{-34}J.s, k = 1.38×10^{-23}JK^{-1}.
At. No. Cr = 24, Fe = 26. R = 8.314 J/(mol.K)

Important Instructions

- **There are TWO questions printed on both sides of the question paper**
- **Answer all questions in the provided answer booklet only**
- **DO NOT use pencils for answering any part**
- **Start answering each question from a fresh page, all sub-sections together**
- **Part-B can be taken ONLY after submitting Part-A**

Q. 1. Consider the following conversion of an octahedral Fe^{2+} complex given schematically. Here, en = ethylenediamine; Cl^-, H_2O = weak ligand field, and NH_3, en = strong ligand field. Based on this scheme answer the following questions (**a** to **d**):



(a) Identify the type of distorted geometry (tetragonal elongation or compression) expected to observe for the complex **A**. Justify your answer in no more than 3-4 sentences. **[4]**

(b) Identify the ground state term of Fe^{2+} in the complex **B**. In the electronic spectrum of the complex **B,** theoretically, one transition is expected based on the ground state term. Using Mulliken symbols DRAW the Orgel energy level diagram for the electronic transition in the complex **B** with proper labeling. **[3]**

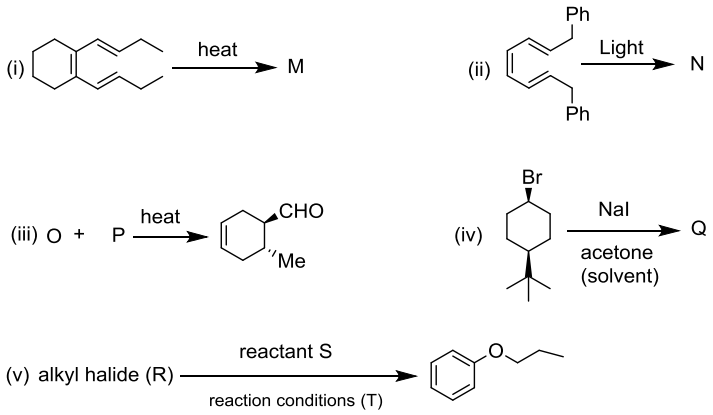
(c) (I) Calculate CFSE (**in cm^{-1}**) of the complex **C** if Δ_o = 11,400 cm^{-1}? Ignore the effect of pairing energy during the CFSE calculation. **(II)** Identify the magnetic behavior (paramagnetic or diamagnetic) of the complex ion **C** with one line justification. **[2+2]**

(d) (I) Identify the complex ion **D** and write the formula in a proper format (coordination complex form). **(II)** Identify the most stable complex out of **A** to **D** and justify your answer in one sentence. **(III)** Calculate the overall formation constant (**β**) for complex **D** at 28 ^oC, if the standard enthalpy and entropy changes are -13 kJ/mol and 0.19 kJ/mol/K, respectively? **[6]**

(e) (I) Find the strength (**in T**) of the required magnetic field of a NMR instrument for a proton (^1H) nucleus to resonate at the operating frequency 30.5 MHz. Given, nuclear magnetic moments (μ_I) of ^1H is 2.7927 μ_N; I = 1/2 for ^1H nucleus; and $\mu_N = 5.05 \times 10^{-27}$ JT^{-1}. **(II)** The CH_3- and CH_2- protons of CH_3-CH_2-Cl are 118 Hz and 185 Hz downfield shifted from TMS, respectively, in a 80 MHz NMR spectrometer. What will be the frequency shifts (**in Hz**) of those same protons in a 300 MHz NMR spectrometer? **[3+4]**

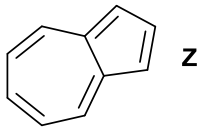
DO NOT SCRIBBLE ON THE QUESTION PAPER

Q. 2 (a) Write the structures (with appropriate stereochemistry wherever applicable) of reactant/major product (M, N, O, P, Q, R & S) and reaction conditions (T) for the following transformations. **[11]**

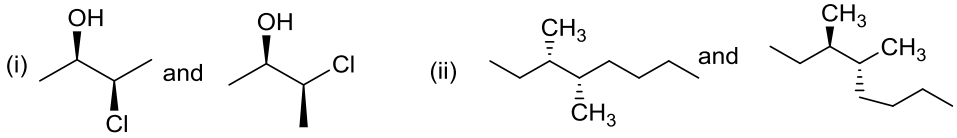


(b) Identify the major and minor products for the elimination reactions of compounds **X** and **Y** with sodium ethoxide. Briefly explain the formation of the appropriate product(s) by drawing Newman projection of the conformations of **X** and **Y** involved in the elimination reaction. Also determine in each case if the reaction is stereoselective or stereospecific. **[6]**

(c) Azulene (**Z**) shows a relatively large dipole moment (1.08 debye). Briefly explain why dipole moment arises in **Z** even though it is composed of carbon-carbon and carbon-hydrogen bonds. Also, write the number of π electrons in Azulene. **[3]**



(d) Identify whether the following pairs of compounds are enantiomers, diastereomers or identical. **[4]**



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