Model Answers_CHM 113M End Sem Exam

1. (A) Determine the nature of the following spinel structure in $NiFe_2O_4$ in the context of CFSE. Show your calculation. **(4 Marks)**

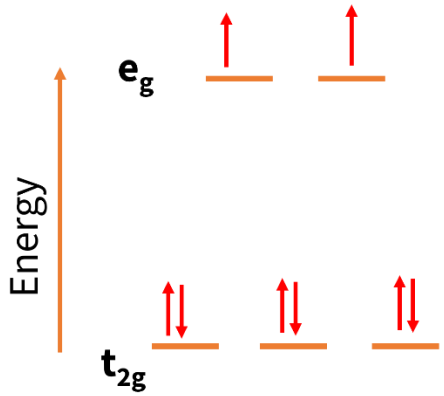
Ans. The CFSE for Ni^{2+} in octahedral sites ($t_{2g}^6e_g^2$) is $[6 \times (-0.4) + 2\ (0.6)]\Delta o$ = - **1.2 Δo**

while for tetrahedral sites the CFSE ($e^4t_2^4$) is $[4 \times (-0.6) + 4\ (0.4)]\Delta_t$ = - 0.8 Δt = - **0.36 Δo**

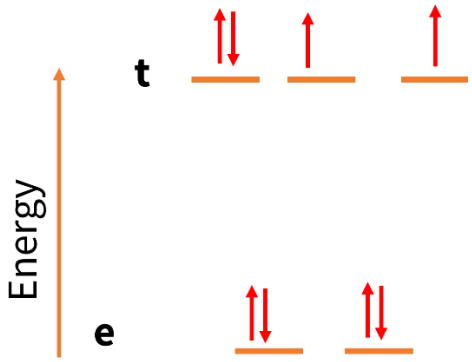
CFSE for Fe^{3+} (d^5) in a tetrahedral void, $e^2t_2^3$; **CFSE = 0**

In an octahedral void, $t_{2g}^3e_g^2$; CFSE = **0,** thus Fe^{3+} (d^5) has no site preference

So, Ni^{2+} would go to the octahedral sites, while one of the Fe^{3+} would go to the tetrahedral site, thus **$NiFe_2O_4$ ($Fe^{III}_{Tet}(Ni^{II}Fe^{III})_{Oct}O_4$ is an inverse spinel.**

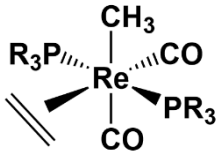


d-orbital splitting of Ni(II) in octahedral environment



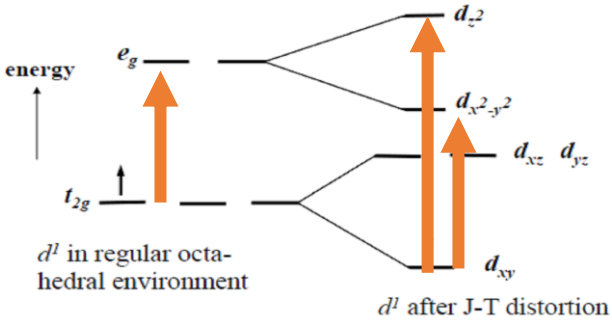
d-orbital splitting of Ni(II) in tetrahedral environment

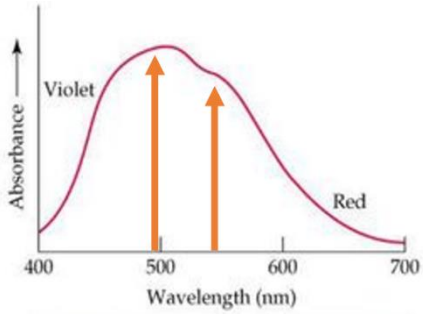
(B) Calculate valence shell electron counts in the following compounds using an ionic method. **(6 Marks)**

Compound	Valence shell electron counts (show calculations)
(i) $[(\eta^5\text{-Cp})Re(\eta^6\text{-}C_6H_6)]$	**η^5-Cp → 6 e⁻** **Re(I) → 6 e⁻** **η^6-C_6H_6 → 6 e⁻** **Total= 18 e⁻**
(ii) $Mn_2(CO)_{10}$	**Mn(0) → 7 e⁻** **5 C≡O → 10 e⁻** **Mn-Mn → 1 e-** **Total= 18 e⁻**
(iii) 	**Re(I) → 6 e⁻** **2PR_3 → 4 e⁻** **2C≡O → 4 e⁻** **CH_3^- → 2 e⁻** **CH_2=CH_2 → 2 e⁻** **Total= 18 e⁻**

2. (A) Draw the crystal field splitting diagram for $[Ti(H_2O)_6]^{3+}$ with appropriate labeling. Show the possible electronic transitions and sketch an absorption spectrum of the complex. **(4 Marks)**

Answer: $[Ti(H_2O)_6]^{3+}$ is a d^1 electronic system which is unsymmetrically filled, t_{2g}^1, thus undergoing J-T distortion which is Z-in or compressed distortion. As a result, it would show two electronic transitions, d_{xy} to $d_{x^2-y^2}$, and d_{xy} to dz^2. It shows two signals in electronic absorption spectrum.

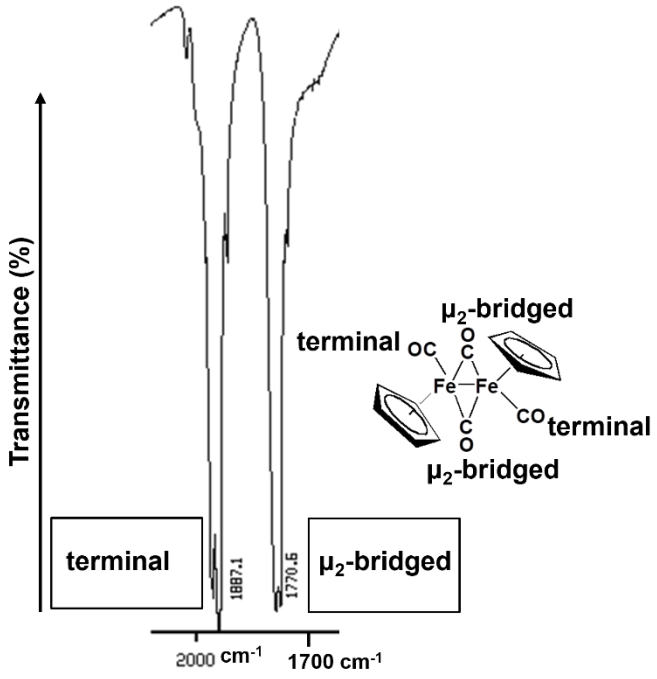




(B) Calculate the crystal field stabilization energy (CFSE) and spin-only magnetic moment for both compounds. **(4 Marks)**

	Compound	CFSE	Spin only magnetic moment
(i)	$NaFeCl_4$	**$2 \times -0.6 + 3 \times 0.4 = 0$**	**5.92 B.M.**
(ii)	$K_4[Fe(CN)_6]$	**$6 \times -0.4 = -2.4\ \Delta o$**	**0 B.M.**

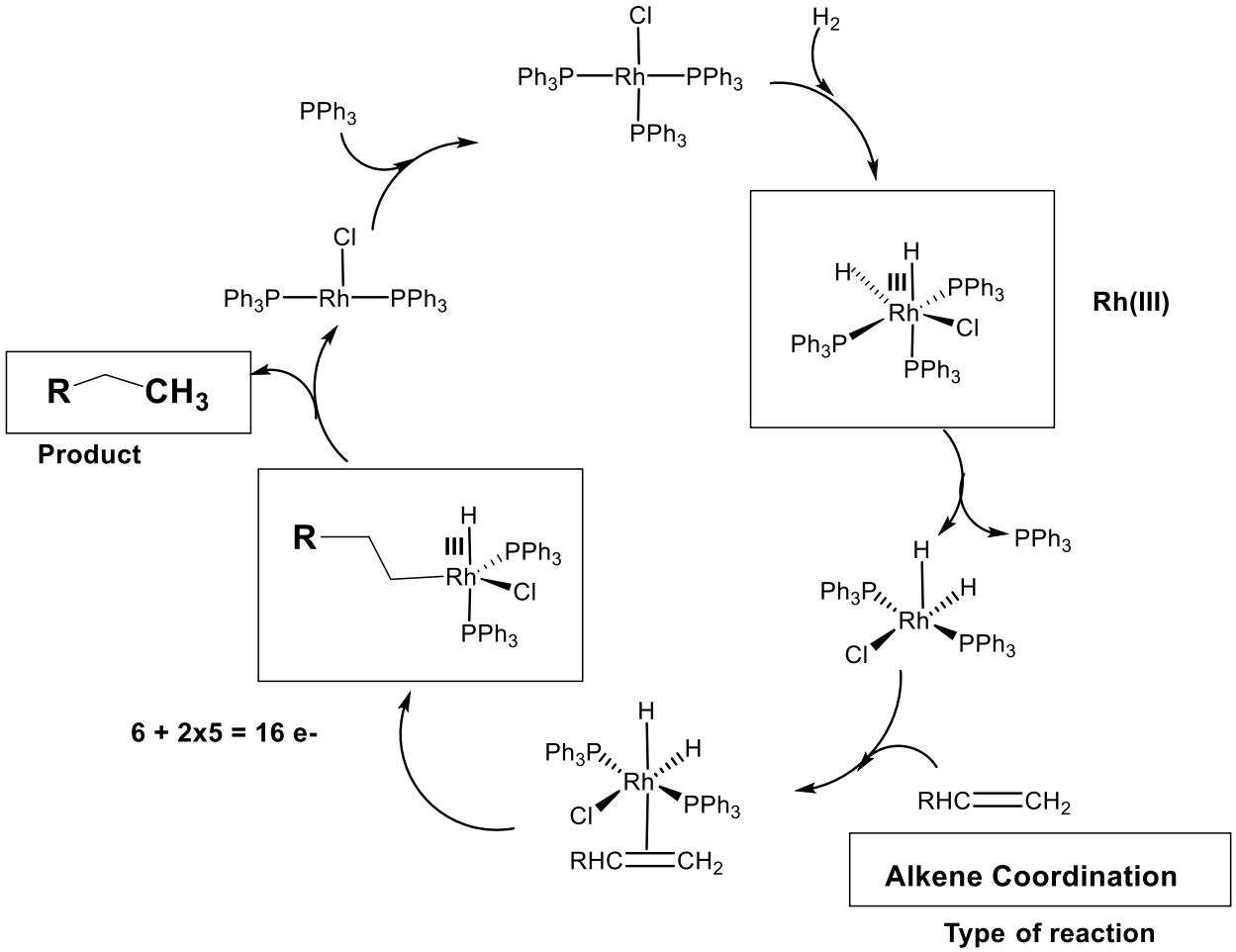
(C) Considering the FT-IR spectrum given below, assign the carbonyl stretching frequency, $\nu_{C\equiv O}$ of the iron-carbonyl compound. Write your answer in the boxes. **(2 Marks)**



3. (A) Fill out the table with the correct information. **(4 Marks)**

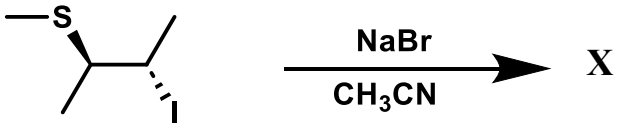
Complex	No. of unpaired electron(s) in the iron center	Comments on the magnetic property of the complex
(i) Deoxyhemoglobin	**4 No.**	**Paramagnetic, Spin-only magnetic moment = 4.89 B.M.**
(ii) Oxyhemoglobin	**1 No.**	**Diamagnetic due to anti-ferromagnetic between Fe^{3+} and superoxide radical anion**

(B) Fill out the boxes with the correct information considering the following catalytic cycle. **(6 Marks)**



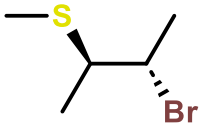
4. (A) The major product '**X**' with the correct stereochemistry in the following reaction is:

(2 Marks)



(Enantiopure)

Answer: **X =**

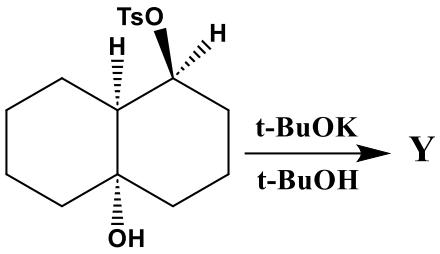


(B) The observed optical rotation of a solution containing 10 g of (*R*)-2-methyl-1-butanol in the 25 mL solvent is +5.4 ° at 25 °C. For this measurement, the D line of the sodium lamp and 10 cm polarimeter tube are used. What is the specific rotation of (*S*)-2-methyl-1-butanol? What is the % of the *R* isomer in the solution if a sample of 2-methyl-1-butanol shows a specific rotation of 6.75 deg·mL·g^{-1}·dm$^{-1?}$ Give your answer to 2 decimal places. **(3+2=5 marks)**

Answer: The specific rotation of (*S*)-2-methyl-1-butanol is **-13.5 deg·mL·g^{-1}·dm^{-1}**

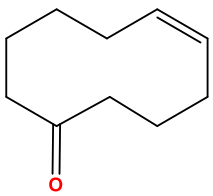
R isomer content is **75** **%**

(C) Write the major product 'Y' which contains a keto group in the following reaction. **(3 Marks)**



Answer:

Y =



(*Z*)-cyclodec-5-enone

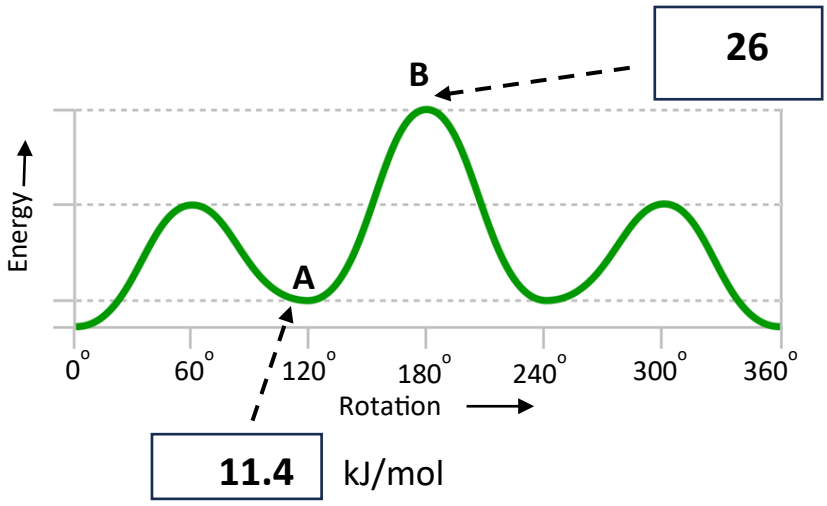
5. (A) The 'A' value of a monosubstituted cyclohexane derivative is 10 kJ/mol. Determine the % of the equatorial conformer at 25°C. Give your answer to 2 decimal places. R = 8.314 JK^{-1} mol^{-1}.

(3 Marks)

Answer: The equatorial content is **98.26** **%**

(B) The energy profile diagram of 2,3-dimethylbutane (by rotation along the C2-C3 bond) is given below. Calculate the energy of the conformers '**A**' and '**B**' (write in the box) using the interaction energy values provided. Give your answer to one decimal place.

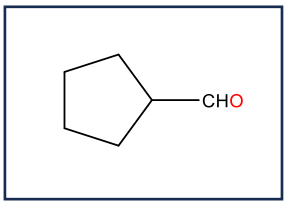
(4 Marks)

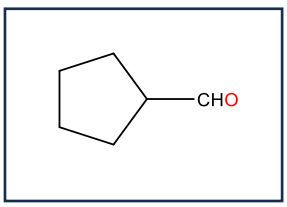


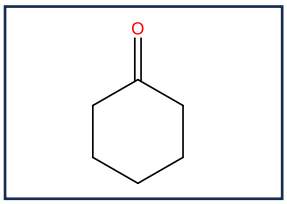
Interaction	Energy cost (kJ/mol)
H-H eclipsed	4
H-CH_3 eclipsed	6
CH_3-CH_3 eclipsed	11
CH_3-CH_3 Gauche	3.8

(C) Write the product(s) in the following reactions.

(1+2=3 Marks)

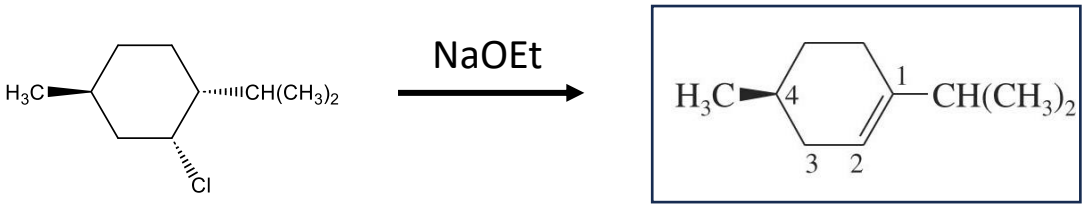
trans-2-Aminocyclohexanol $\xrightarrow{NaNO_2/HCl}$ 

cis-2-Aminocyclohexanol $\xrightarrow{NaNO_2/HCl}$ 

+ 

6. (A) Write the major product formed in the following elimination reactions.

(2+2=4 Marks)



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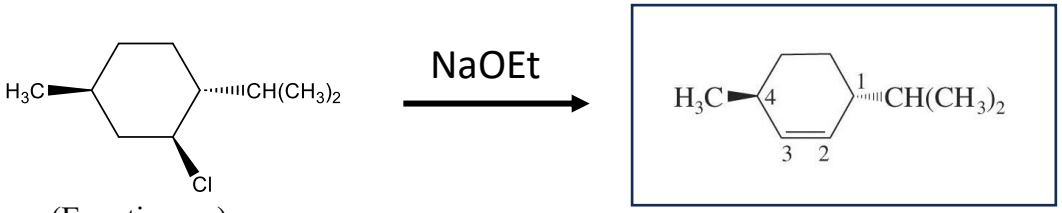
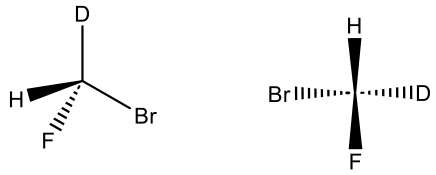


(Enantiopure)

(B) Identify the relationship between the compounds given in the following pairs as enantiomers, diastereomers, and the same molecule. Write in the box. **(2+2 =4 Marks)**

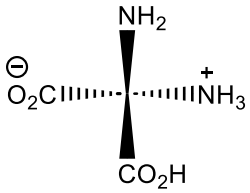


Enantiomers

Enantiomers

(C) Find out the absolute configuration of the chiral center in the following molecule.

(2 Marks)



Answer: The absolute configuration is ***S***