CHM102A, General Chemistry, 2016-17 (II)
End Semester Examination

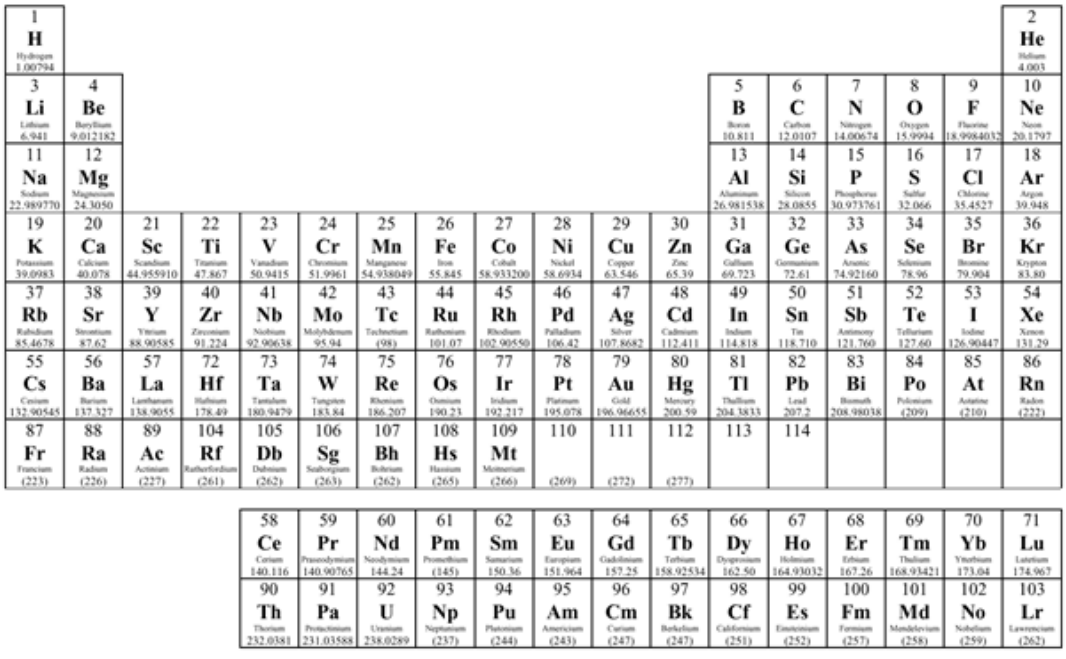
Date:	25-04-2017	Time:	9:00-11:00	Total Marks:	80
Roll #:				**Sect.:**	
Name:	**Answer Key**				

Instructions:

- This is a closed book exam. Answer ALL the questions.
- The answers should strictly be given in the space provided after each question.
- All rough works should be done on extra sheets provided. These should not be submitted after the examination.
- Mobile phones or any other digital gadgets are **STRICTLY NOT ALLOWED** during the examination.
- Sharing calculator is not allowed.
- The answers will not be graded if name, roll no. and section are not correctly filled in.
- I PLEDGE MY HONOUR AS A GENTLEMAN/LADY THAT DURING THE EXAMINATION I HAVE NEITHER GIVEN ASSISTANCE NOR RECEIVED ASSISTANCE.

Q. No.	Marks
1	
2	
3	
4	
5	
6	
7	
8	
Total	

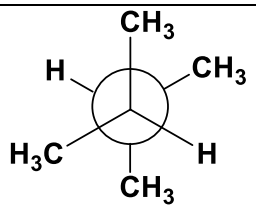
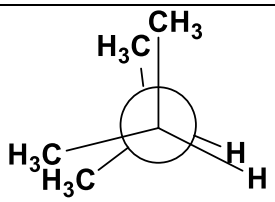
The Periodic Table of the Elements



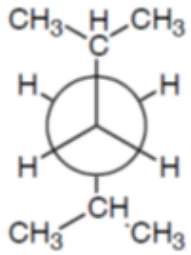
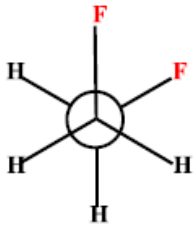
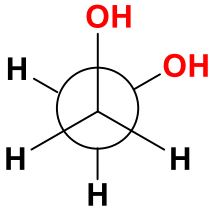
1. (a) Draw the Newman projections of the (i) most stable conformation and the (ii) least stable conformation of 2,3-dimethylbutane looking down the C2-C3 bond. **[2]**

Calculate the strain energy corresponding to each of these conformers. Energy cost for various interactions are given below: **[2]**

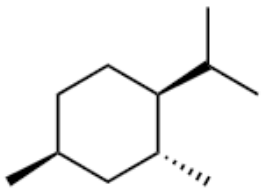
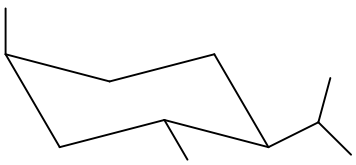
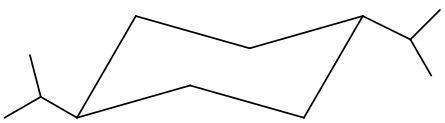
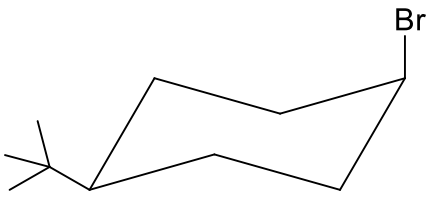
Interaction	H-H eclipsed	H-CH_3 eclipsed	CH_3-CH_3 eclipsed	CH_3-CH_3 gauche
Energy cost	1 kcal/mol	1.4 kcal/mol	2.6 kcal/mol	0.9 kcal/mol

Most stable conformer	**Least stable conformer**
	
Calculation of strain energy: 2 CH_3-CH_3 Gauche interactions =2 x 0.9 = **1.8 kcal/mol**	**Calculation of strain energy:** 2 CH_3-CH_3 eclipsed + 1 H-H eclipsed interactions = [2 x 2.6 + 1] = **6.2 kcal/mol**

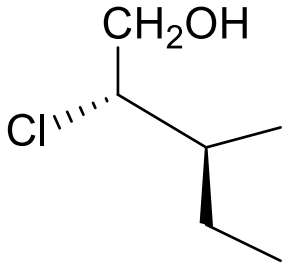
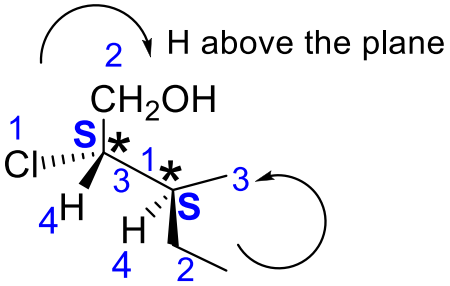
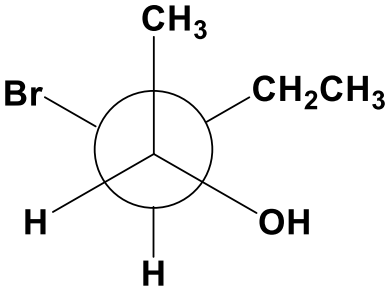
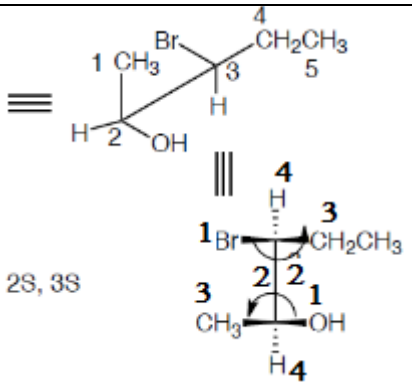
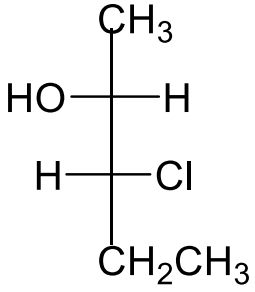
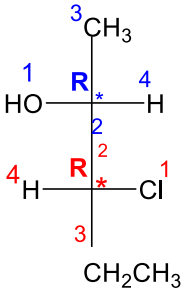
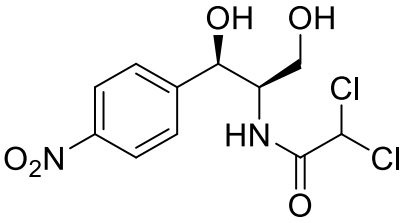
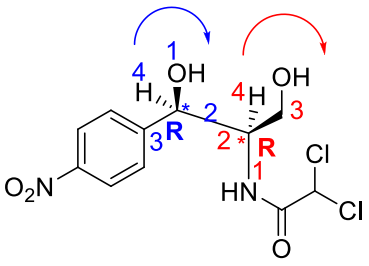
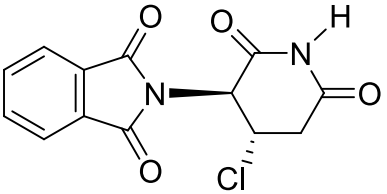
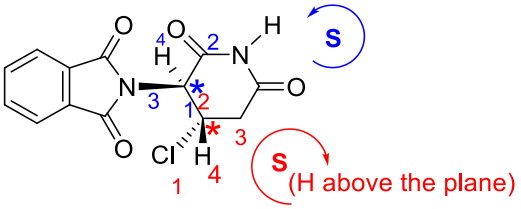
(b) Draw the Newman projection of the lowest energy conformation of (i) 2,5-dimethylhexane looking down the C3-C4 bond. (ii) 1,2-difluoroethane (iii) ethane 1,2-diol **[3]**

 (i)	(ii) 	 (iii)

(c) Draw the most stable chair conformation of following molecules: **[3]**

	
trans-1,4-diisopropylcyclohexane	
cis-1-bromo-4-*tert*-butylcyclohexane	

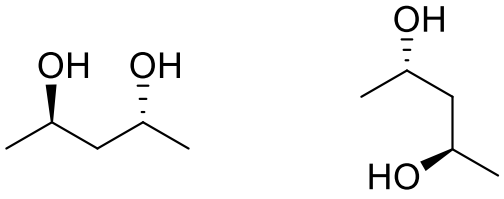
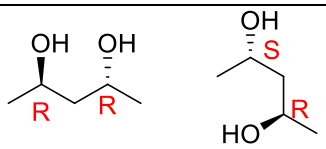
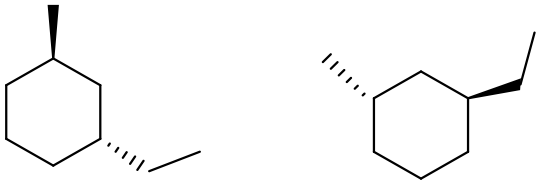
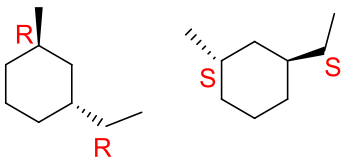
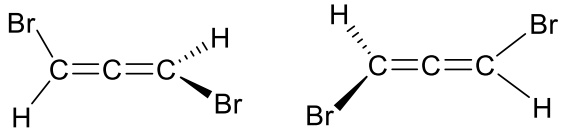
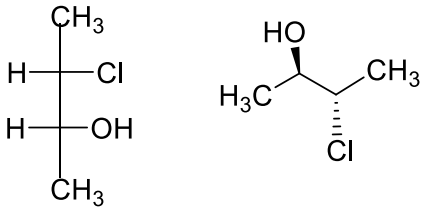
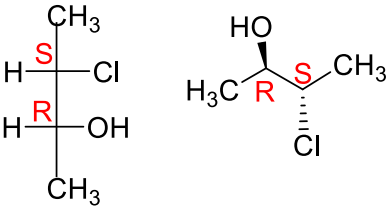
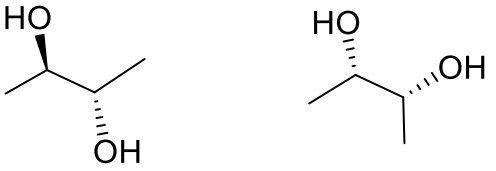
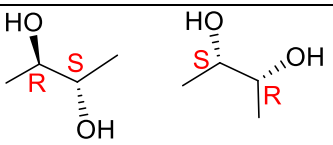
2. Assign the priorities of the atoms/groups attached to each asymmetric carbon centre(s) and **THEN** deduce the absolute configuration (***R*** or ***S***) to the chiral centre of each molecules given below: *No marks will be awarded unless you show your work out and then arriving respective configuration.* **[2 x 5 = 10]**

3. Identify the relationship between the following pair of molecules from the following options:

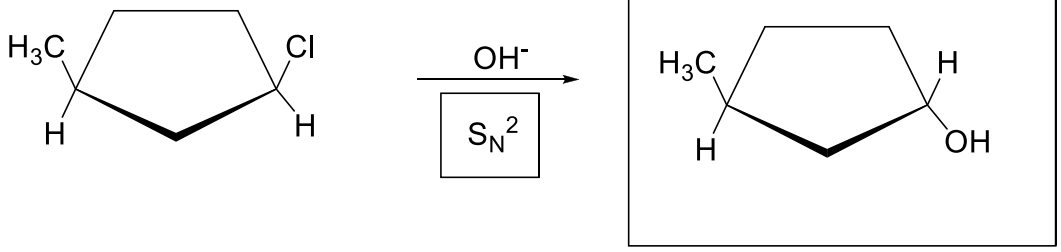
(i) enantiomers, (ii) diastereomers, (iii) conformers, (iv) atropisomers, (v) identical molecules.

[2 x 5 = 10]

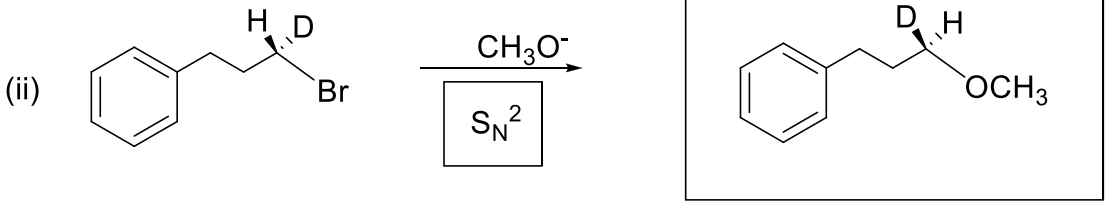
(i) 	 Diastereomers
(ii) 	 Enantiomers
(iii) 	Enantiomers
(iv) 	 Identical molecules/ conformers
(v) 	 Identical molecules/ conformers

4. (a) Draw the structures of the organic products, with appropriate stereochemistry, in the following reactions. Also indicate which type of reaction it is in the box provided below the arrow. **[4 x 1= 4]**

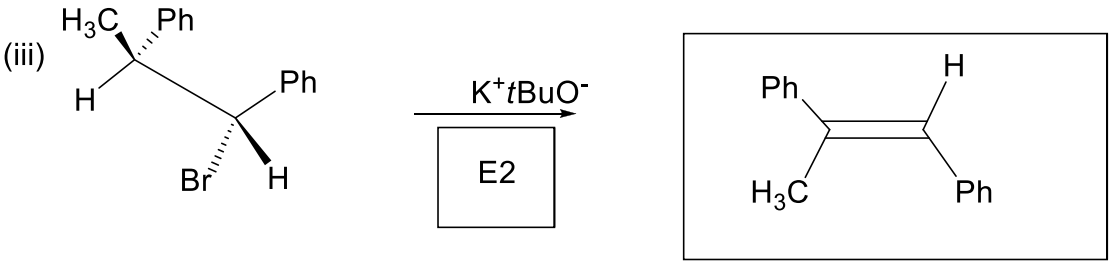
(i)



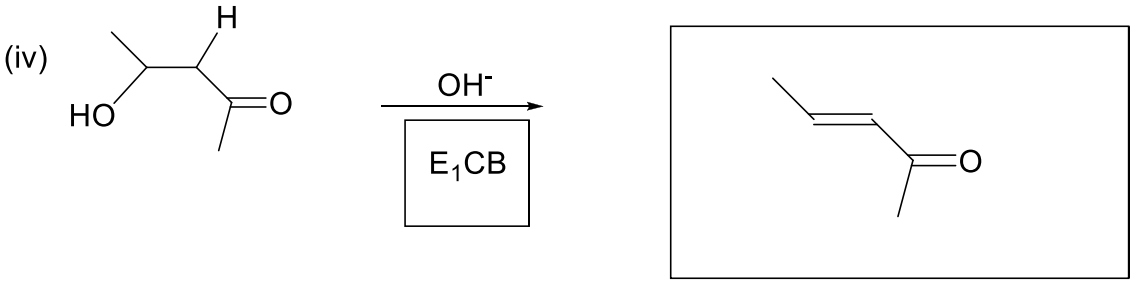
(ii)



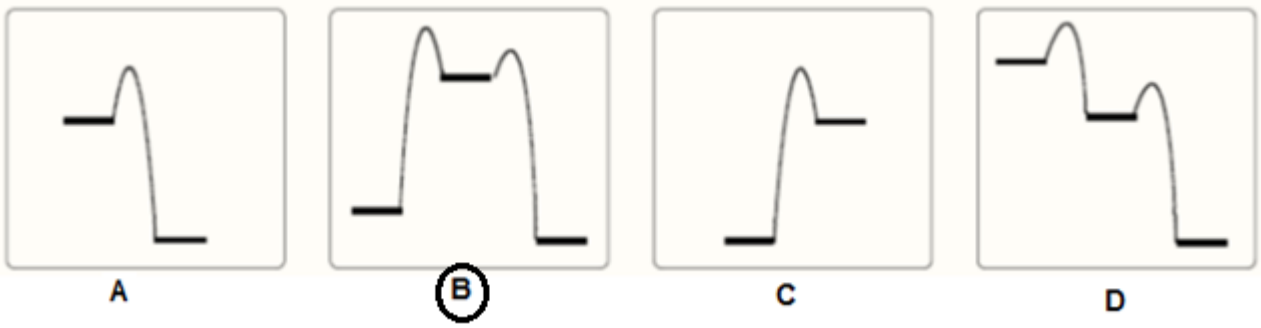
(iii)



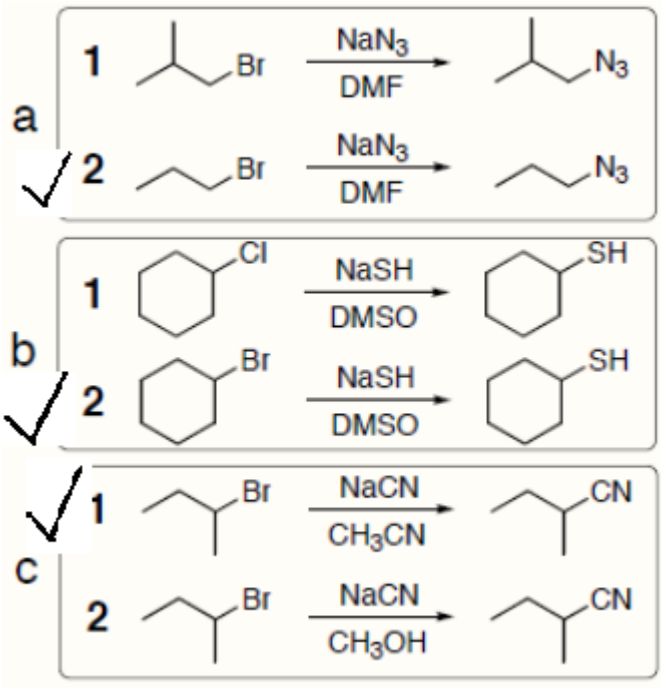
(iv)



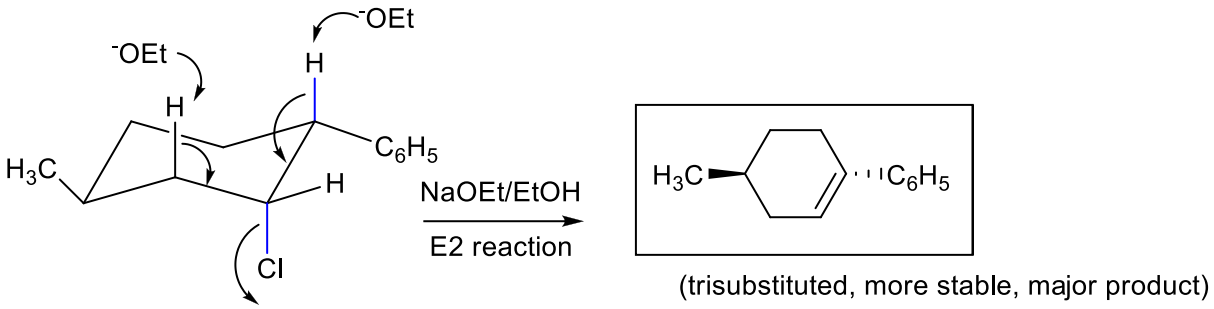
(b) Tick (√) which potential energy diagram best describes the substitution reaction of 1-bromo-1-methylcyclohexane with a cyanide ion? [Tick only one choice] **[1]**



(c) Only tick (√) the faster reaction in each pair (a, b, c) given below. **[3]**



(d) Draw the structure of the **major product** formed when the following compound is subjected to dehydrochlorination with sodium ethoxide in ethanol. **[2]**



(trisubstituted, more stable, major product)

5. ***IF ANSWER IS CORRECT AWARD MARK, NO WORKOUT NEEDED***

(i) Calculate the spin-only magnetic moment for $K_3[Fe(CN)_6]$. **[1 x 10 = 10]**

Ans: 1.73 B.M. [Fe(III), d^5 low-spin complex, electronic config. with one unpaired electron.

$\mu s.o = [n(n+2)]^{1/2}$ B.M. = $[(1(1+2)]^{1/2}$ B.M. = 1.73 B.M.]

(ii) Magnetic moment of $K_3[Mn(NO_2)_6]$ is 2.87 B.M. Predict whether it is high-spin or los-spin complex.

Ans: **Low-spin** (2.87 BM = 2 unpaired electrons , Mn^{3+}, d^4 low spin ($t_{2g}^4e_g^0$))

(iii) Which among the following metal carbonyl will dimerize: $Cr(CO)_6$, $Mn(CO)_5$, $Ni(CO)_4$.

Ans: $Mn(CO)_5$ (17 e- system, stabilize by getting 1 e- from Mn-Mn bond). All other 18 e^- system.

(iv) Which of the following metal ions will show regular octahedral structure? Ni(II) and Mn(III)

Ans: **Ni(II)**

Ni(II)-d^8 system, $t_{2g}^6e_g^2$, no orbital degeneracy, no J.T. distortion, regular octahedral structure.

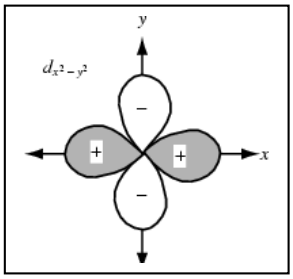
Mn(III)-d^4 system, h.s: $t_{2g}^3e_g^1$, l.s.: $t_{2g}^4e_g^0$, both cases having orbital degeneracy, show J.T. distortion.

(v) Identify the first-row transition metal (M) for the following 18-electron species: (η^4-C_8H_8)$M(CO)_3$

Ans: Fe (η^4-C_8H_8)$M(CO)_3$: 3 CO = 6, η^4-C_8H_8 = 4; Total = 10, need (18-10) = 8 e^- from M, M = Fe)

(vi) Draw the shape of the **most destabilized** d-orbital in **square planar** geometry with appropriate phase sign and axes.

Ans:



(no phase sign, zero mark)

(vii) Arrange the following octahedral complex ions in increasing order of their crystal field splitting parameter (Δ_o): $[Cr(H_2O)_6]^{3+}$, $[CrF_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)]_6]^{3+}$

Ans: $[CrF_6]^{3-}$ < $[Cr(H_2O)_6]^{3+}$ < $[Cr(NH_3)]_6]^{3+}$ < $[Cr(CN)_6]^{3-}$

(viii) Which among the following complex will have maximum value for molar extinction coefficient?

$[Cu(MeCN)_4](BF_4)$, $[Mn(H_2O)_6]Cl_2$, $K_2Cr_2O_7$, $K_2[CoCl_4]$, $[Ti(H_2O)_6]Cl_3$

Ans. $K_2Cr_2O_7$, LMCT transition, Spin and Laporte selection rule allowed.

(ix) Write down the electronic distribution in d-orbitals of gold for $[Au(SCN)_4]^-$

Ans: Au(III), d^8 square planar complex, electron distribution: **$(d_{xz}, d_{yz})^4$, $(dz^2)^2$, $(d_{xy})^2$, , $(d_{x^2-y^2})^0$ or**

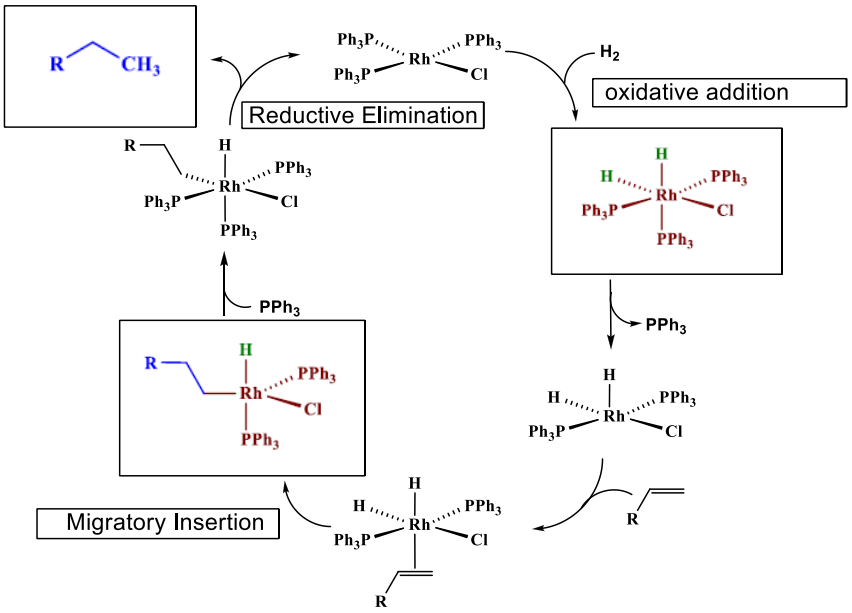
$(d_{xz})^2$, $(d_{yz})^2$, $(dz^2)^2$, $(d_{xy})^2$, $(d_{x^2-y^2})^0$

(x) Calculate the CFSE of $[NiCl_4]^{2-}$

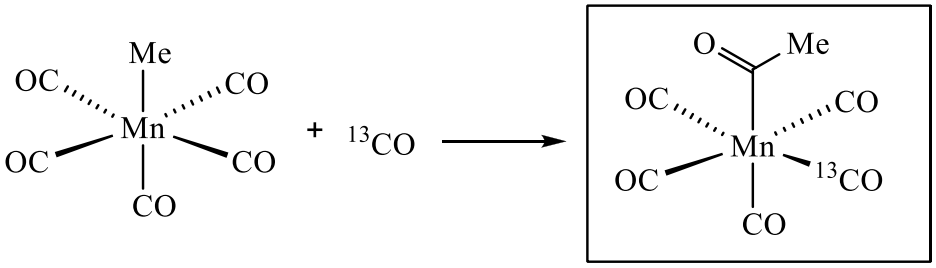
Ans: **$0.8\Delta_t$** or **$0.35\Delta_o$** (Ni(II) in tetrahedral geometry, config. $e^4t_2^4$, CFSE = (4 x 0.6)-(4 x0.4) Δ_t = **$0.8\Delta_t$** =-0.8 x 4/9 Δ_o = **$0.35\Delta_o$**) *(Ignore sign of CFSE)*

6 (a) Draw the structures of the missing species in the following catalytic cycle for Wilkinson catalyst and also write the type of respective reactions within the given boxes beside arrow. **[1x 6 =6]**

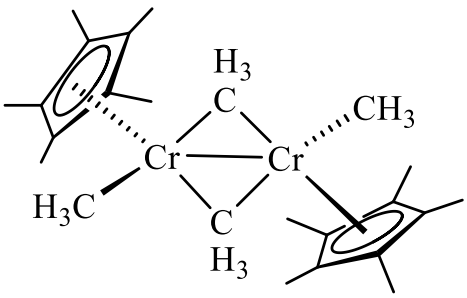
[Award 1 mark for each correct answer in the box]



(b) Consider the following migratory insertion reaction in presence of isotopically labelled CO (^{13}CO). Draw the structure of most probable isolable product indicating position of ^{13}CO. **[2]**



(c) Show the electron count around Cr in the following complex. **[2]**



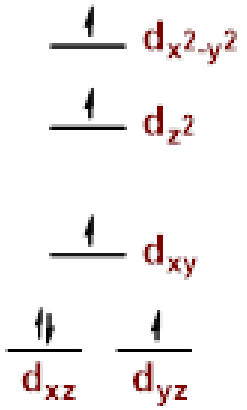
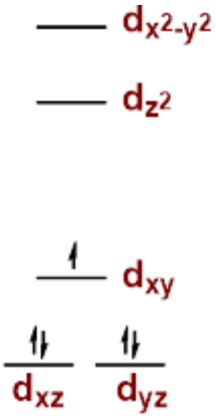
Neutral method
Cr(0) = 6 e
η^5-C_5Me_5 = 5 e
Terminal CH_3 = 1e
2 bridging CH_3 = 1e
Cr-Cr bond = 1e

Total = 14 e^-

Ionic method
Cr(III) = 3 e
η^5-C_5Me_5 = 6 e
Terminal CH_3 = 2 e
2 bridging CH_3 = 2 x 1e = 2 e
Cr-Cr bond = 1 e

Total = 14 e^-

7 (a) Draw the crystal field splitting diagram of iron present in deoxymyoglobin and oxymyoglobin with appropriate labelling of d-orbitals and filling up of the d-electrons of iron centre. **[2x2=4]**

deoxymyoglobin	**oxymyoglobin**
	

Note: Reverse order of d_{xz}/d_{yz} and d_{xy} in oxymyoglobin is also correct option.

Note: Ignored order splitting of d_{xz}/d_{yz} and d_{xy} in oxymb, even if all are degenerate is also correct option.

(b) Calculate the spin-only magnetic moment ($\mu_{s.o.}$) for deoxymyoglobin. **[2]**

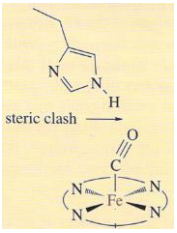
Ans. In deoxyMb, **Fe(II): d^6 high-spin, 4 unpaired electrons (n), $\mu_{S.O} = [n(n+2)]^{1/2} = 4.89$ B.M.**

(c) Consider the binding of O_2 and CO with given substrates. Write down which of these molecules will have higher binding affinity with the given substrates. **[2]**

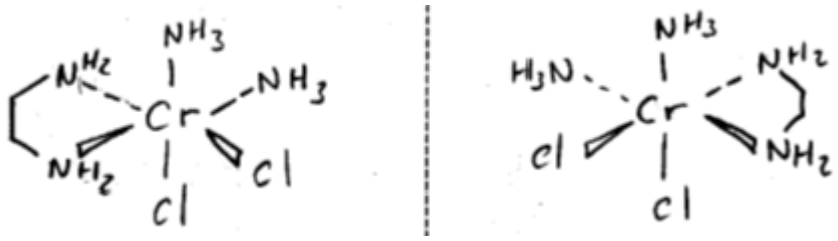
Substrate	**Higher binding affinity**
Free heam group	CO
Myoglobin	CO

(d) Briefly explain the role of distal histidine present in the active site of myoglobin during binding of CO with myoglobin. **[2]**

Distal histidine reduces the affinity of CO towards binding to iron centre in Mb by enforcing bending of otherwise favourable linear Fe-C-O bond.



8. (a) Draw the optical isomer and it's mirror image of the complex ion $[Cr(en)(NH_3)_2Cl_2]^+$. The dashed line represents mirror plane. **[2]**



(b) Which among the following complexes will absorb radiation of shortest wavelength. **ONLY** Tick the correct option. **[2]**

(A) $[Co(H_2O)_6]^{3+}$ **(B)** $[CoI_6]^{3-}$ **(C)** $[Co(NH_3)_6]^{3+}$

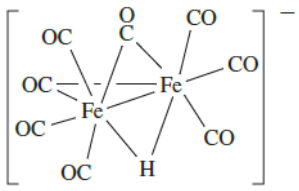
√(D) $[Co(en)_3]^{3+}$ **(E)** $[Co(H_2O)_6]^{2+}$ **(F)** $[Co(NH_3)_4]^{2+}$

(c) Which of the following compounds will exhibit lower stretching frequency for C-O bond (ν_{CO}): $[Ni(CO)_3(PF_3)]$ and $[Ni(CO)_3P(t\text{-}Bu)_3]$. Briefly explain your answer. **[2]**

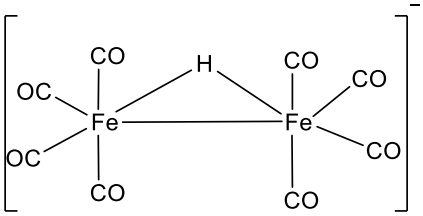
$[Ni(CO)_3P(t\text{-}Bu)_3]$ will exhibit lower ν_{CO}. $P(t\text{-}Bu)_3$ is a better σ-donor ligand the PF_3, so more electron density will be donated to π* anti-bonding orbital of CO, thus C-O bond strength will decrease and thus lower stretching frequency for C-O bond.

(d) Deduce the structure of $[HFe_2(CO)_8]^-$ which obeys 18-electron rule and bothe the Fe have identical coordination environment. Draw the structure and clearly show your electron count per Fe in this molecule. **[2+2]**

Draw the structure in this box **Show your electron count in this box**



Option-A



Option-B

Option –A
Fe (0) = 8 e
3 terminal CO = 3 x 2e = 6 e
2-μ-CO = 2 x 1e per Fe
Fe-Fe bond = 1e per Fe
μ-H = ½ e per Fe
Negative charge (-1) = ½ e

Total = 18 e per Fe

Option-B:
Fe (0) = 8e, 4 terminal CO = 8 e, Fe-Fe bond = 1 e,
μ-H = ½ e per Fe, Negative charge (-1) = ½ e

Total = 18 e^-

-END-