

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 H Hydrogen 1.00794																	2 He Helium 4.003	
3 Li Lithium 6.941	4 Be Beryllium 9.012182																	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050																	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80	
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29	
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)	
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114					
58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967					
90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)					

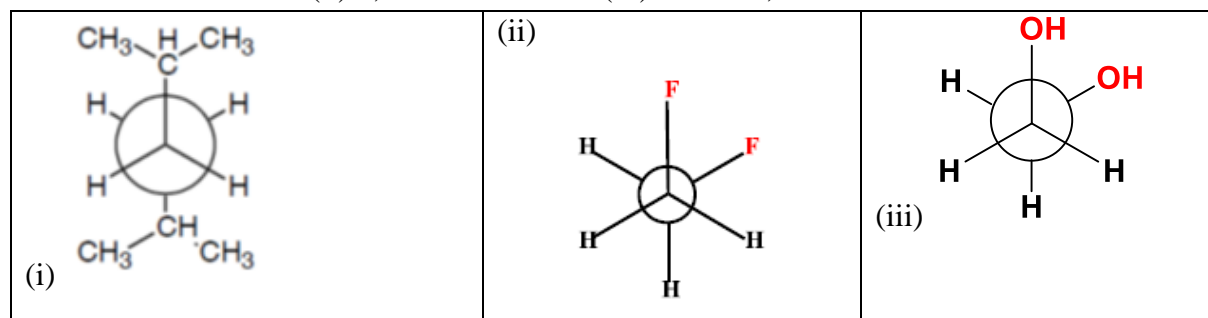
1. (a) Draw the Newman projections of the (i) most stable conformation and the (ii) least stable conformation of 2,3-dimethylbutane looking down the C2-C3 bond. [2]

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

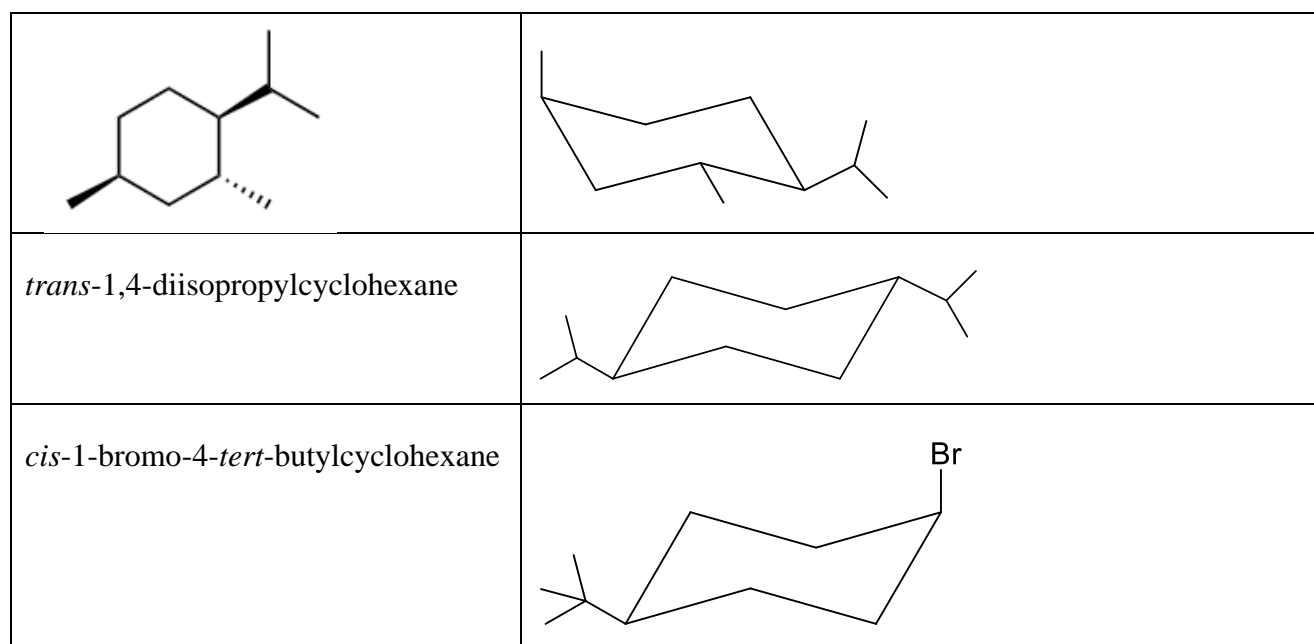
Interaction	H-H eclipsed	H-CH ₃ eclipsed	CH ₃ -CH ₃ eclipsed	CH ₃ -CH ₃ gauche
Energy cost	1 kcal/mol	1.4 kcal/mol	2.6 kcal/mol	0.9 kcal/mol

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]



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

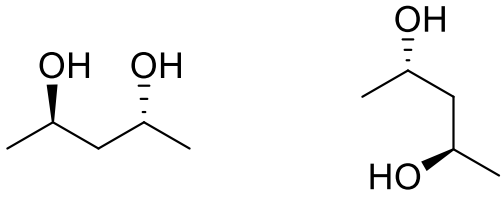
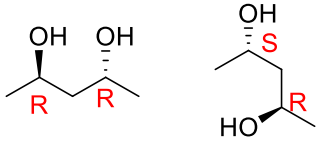
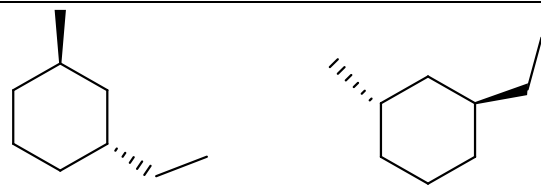
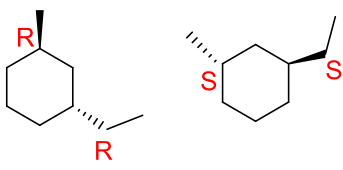
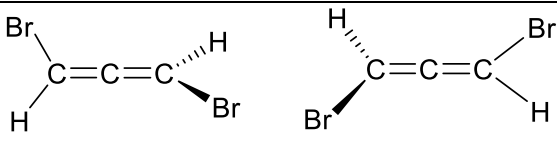
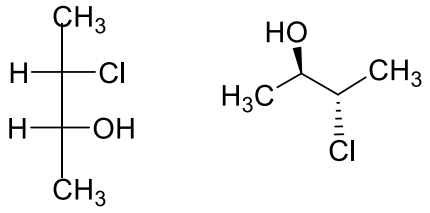
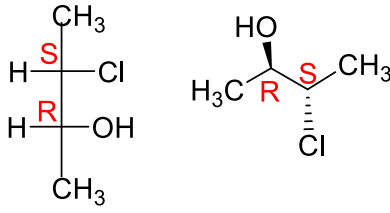
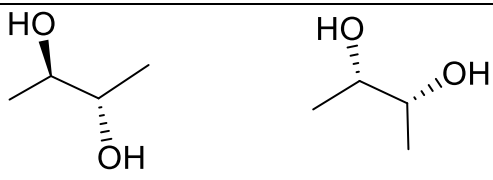
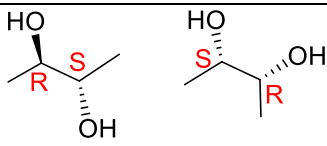


2. Assign the priorities of the atoms/groups attached to each asymmetric carbon centre(s) and **THEN** deduce the absolute configuration (**R** or **S**) to the chiral centre of each molecules given below: *No marks will be awarded unless you show your work out and then arriving respective configuration.*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

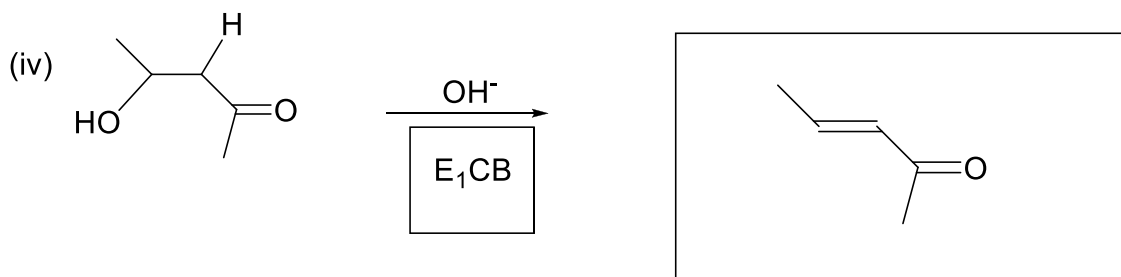
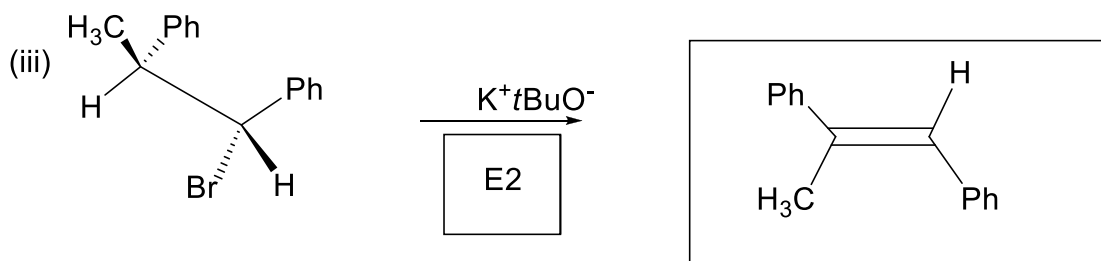
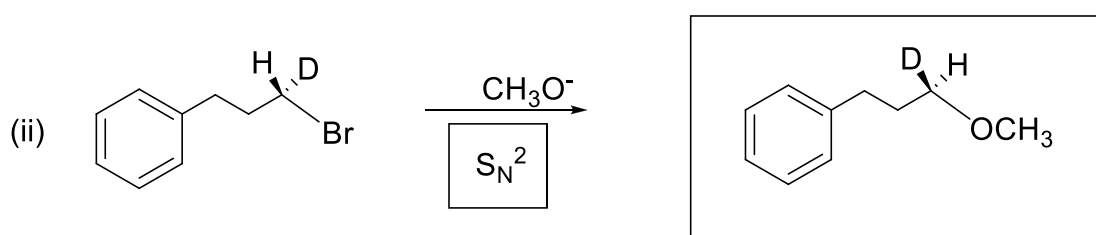
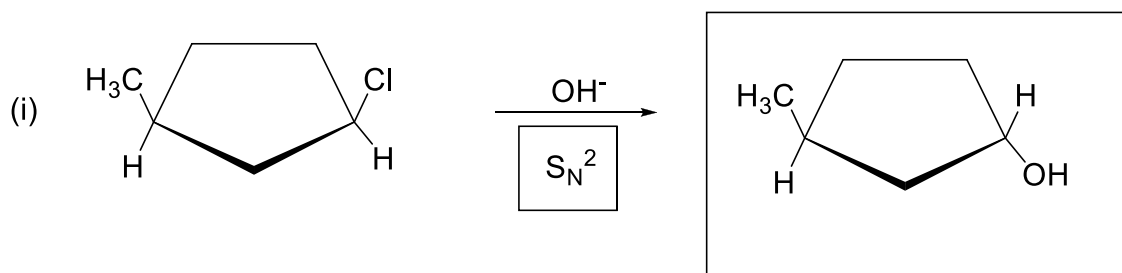
3. Identify the relationship between the following pair of molecules from the following options:

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

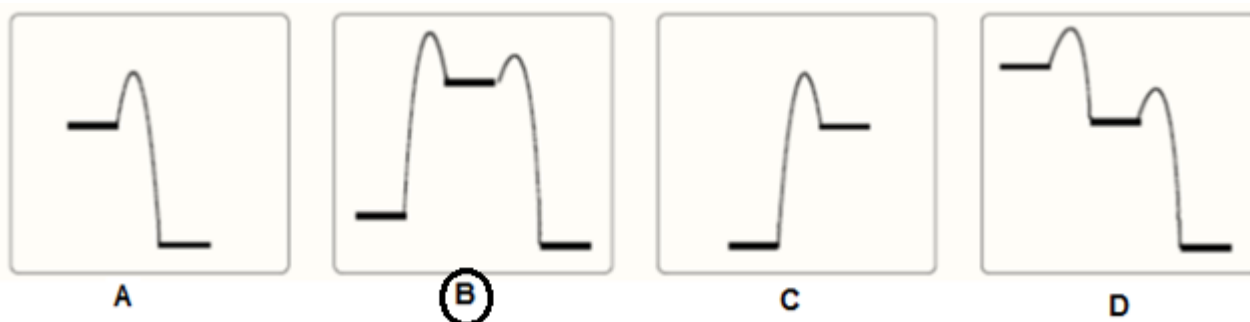
[2 x 5 = 10]

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

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]

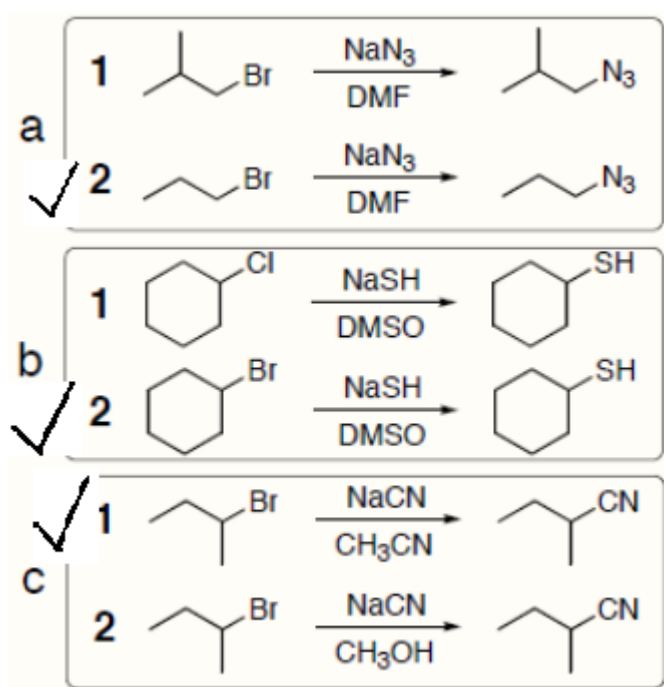


(b) Tick (✓) which potential energy diagram best describes the substitution reaction of 1-bromo-1-methylcyclohexane with a cyanide ion? [Tick only one choice] [1]

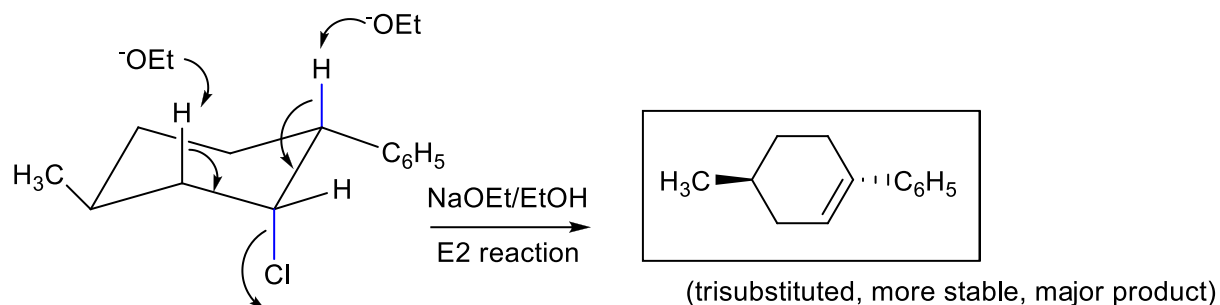


(c) Only tick (✓) the faster reaction in each pair (a, b, c) given below.

[3]



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



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

(i) Calculate the spin-only magnetic moment for $\text{K}_3[\text{Fe}(\text{CN})_6]$.

[1 x 10 = 10]

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

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

(ii) Magnetic moment of $\text{K}_3[\text{Mn}(\text{NO}_2)_6]$ is 2.87 B.M. Predict whether it is high-spin or low-spin complex.

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

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

Ans: $\text{Mn}(\text{CO})_5$ (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)-d⁸ system, t_{2g}⁶e_g², no orbital degeneracy, no J.T. distortion, regular octahedral structure.

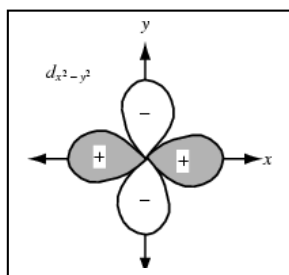
Mn(III)-d⁴ system, h.s.: t_{2g}³e_g¹, l.s.: t_{2g}⁴e_g⁰, both cases having orbital degeneracy, show J.T. distortion.

(v) Identify the first-row transition metal (M) for the following 18-electron species: (η^4 -C₈H₈)M(CO)₃

Ans: **Fe (η^4 -C₈H₈)M(CO)₃**: 3 CO = 6, η^4 -C₈H₈ = 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(H₂O)₆]³⁺, [CrF₆]³⁻, [Cr(CN)₆]³⁻, [Cr(NH₃)₆]³⁺

Ans: **[CrF₆]³⁻ < [Cr(H₂O)₆]³⁺ < [Cr(NH₃)₆]³⁺ < [Cr(CN)₆]³⁻**

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

[Cu(MeCN)₄](BF₄), [Mn(H₂O)₆]Cl₂, K₂Cr₂O₇, K₂[CoCl₄], [Ti(H₂O)₆]Cl₃

Ans. **K₂Cr₂O₇**, 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), d⁸ square planar complex, electron distribution: (**d_{xz}, d_{yz}**)⁴, (**d_z²**)², (**d_{xy}**)², , (**d_x²-y²**)⁰ or

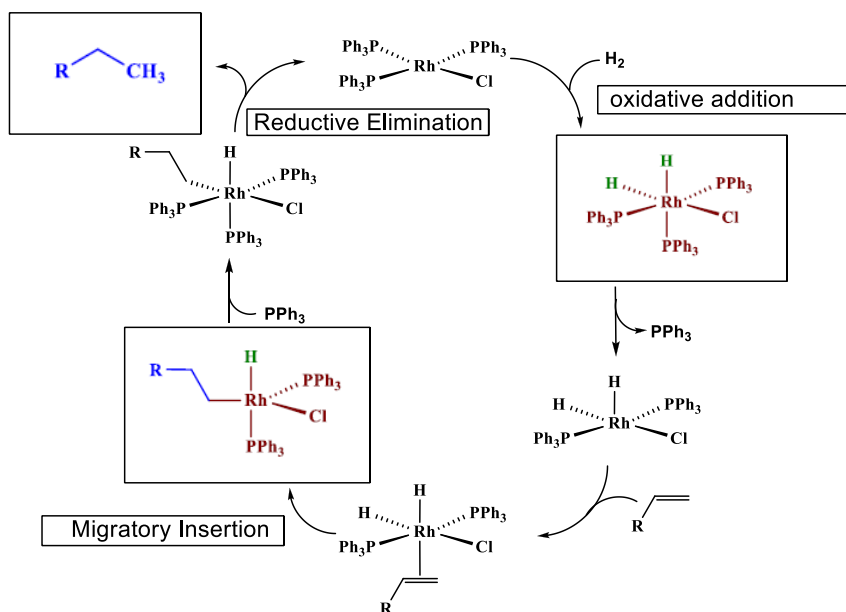
(**d_{xz}**)², (**d_{yz}**)², (**d_z²**)², (**d_{xy}**)², (**d_x²-y²**)⁰

(x) Calculate the CFSE of [NiCl₄]²⁻

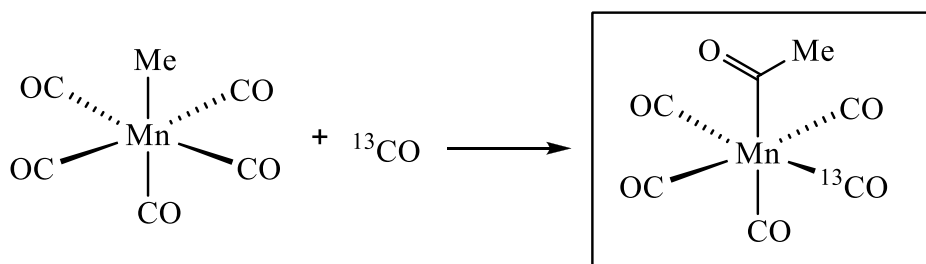
Ans: **0.8Δ_t or 0.35Δ_o** (Ni(II) in tetrahedral geometry, config. e⁴t₂⁴, CFSE = (4 x 0.6)-(4 x 0.4) Δ_t = **0.8Δ_t**
= -0.8 x 4/9 Δ_o = **0.35Δ_o**) (Ignore sign of CFSE)

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]

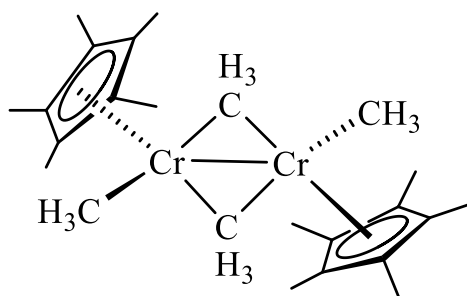
[Award 1 mark for each correct answer in the box]



(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
 $\eta^5\text{-C}_5\text{Me}_5$ = 5 e
 Terminal CH_3 = 1 e
 2 bridging CH_3 = 1 e
 Cr-Cr bond = 1 e

 Total = 14 e⁻

Ionic method

Cr(III) = 3 e
 $\eta^5\text{-C}_5\text{Me}_5$ = 6 e
 Terminal CH_3 = 2 e
 2 bridging CH_3 = 2 x 1 e = 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 oxymyoglobin, even if all are degenerate is also correct option.

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

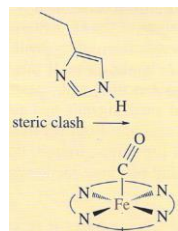
Ans. In deoxyMb, Fe(II): d^6 high-spin, 4 unpaired electrons (n), $\mu_{s.o.} = [n(n+2)]^{1/2} = 4.89$ B.M.

(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]

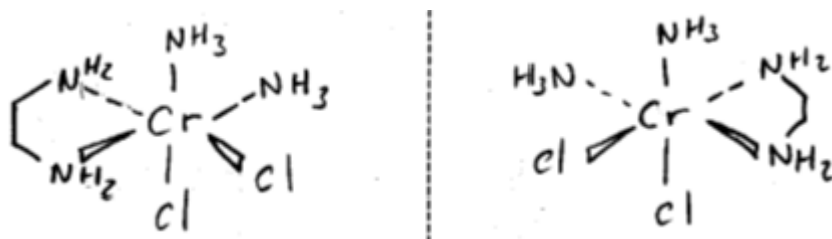
Substrate	Higher binding affinity
Free heme group	CO
Myoglobin	CO

(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 its mirror image of the complex ion $[\text{Cr}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$. 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) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{CoI}_6]^{3-}$ (C) $[\text{Co}(\text{NH}_3)_6]^{3+}$
☒ (D) $[\text{Co}(\text{en})_3]^{3+}$ (E) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (F) $[\text{Co}(\text{NH}_3)_4]^{2+}$

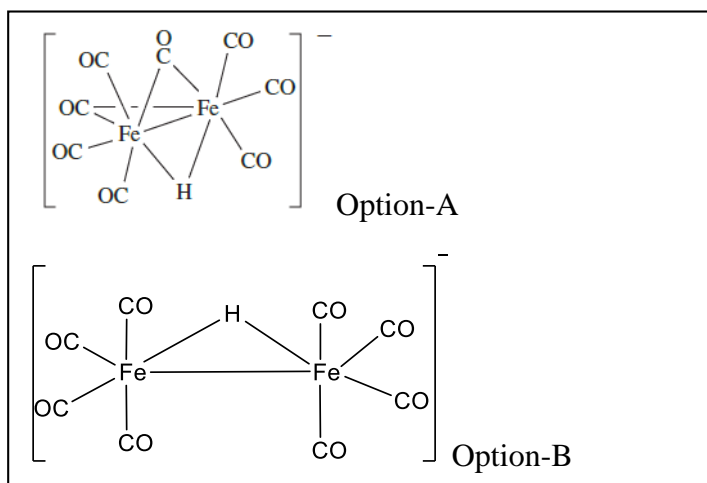
(c) Which of the following compounds will exhibit lower stretching frequency for C-O bond (ν_{CO}): $[\text{Ni}(\text{CO})_3(\text{PF}_3)]$ and $[\text{Ni}(\text{CO})_3\text{P}(t\text{-Bu})_3]$. Briefly explain your answer. [2]

$[\text{Ni}(\text{CO})_3\text{P}(t\text{-Bu})_3]$ will exhibit lower ν_{CO} . $\text{P}(t\text{-Bu})_3$ is a better σ -donor ligand than 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 $[\text{HFe}_2(\text{CO})_8]^-$ which obeys 18-electron rule and both 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
 $\text{Fe}(0) = 8\text{ e}$
 $3\text{ terminal CO} = 3 \times 2\text{ e} = 6\text{ e}$
 $2\text{-}\mu\text{-CO} = 2 \times 1\text{ e per Fe}$
 $\text{Fe-Fe bond} = 1\text{ e per Fe}$
 $\mu\text{-H} = \frac{1}{2}\text{ e per Fe}$
 $\text{Negative charge } (-1) = \frac{1}{2}\text{ e}$

Total = 18 e per Fe
 Option-B:
 $\text{Fe}(0) = 8\text{ e}$, $4\text{ terminal CO} = 8\text{ e}$, $\text{Fe-Fe bond} = 1\text{ e}$,
 $\mu\text{-H} = \frac{1}{2}\text{ e per Fe}$, $\text{Negative charge } (-1) = \frac{1}{2}\text{ e}$

Total = 18 e

-END-