BITS, PILANI - DUBAI
I YEAR SECOND SEMESTER,2009-2010
COMPREHENSIVE EXAMINATION (Closed book)

Course Title: Chemistry-II **Course No: CHEM C142**
Date: 20.5.2010 **Total Marks: 120**
Time: 3 hours **Weightage: 40%**

Note: 1. Answer Part A, B and C separately.
2. Answer briefly all parts sequentially
3. Useful atomic numbers: C(6),Cl(17), Br(35) ,I (53), Cr(24), Mn(25), Co(27), Fe(26), Ni(28), Cu(29)
4. Question paper contains 3 pages

PART –A

1.(i) Clearly show the d-orbital splitting (with electronic arrangements) of Co^{2+} in tetrahedral and square planar complexes.
(ii) Calculate the CFSE in terms of Δ_o for a d^8 system in octahedral and tetrahedral complexes. Which is more stable? Why ? **[4+3M]**

2. (i) When methane is chlorinated among the products found are traces of chloroethane.Indicate clearly the stepwise mechanism for the formation of chloroethane.
(ii) Complete the following reactions clearly writing the structure and name of the products obtained. **[9+8M]**

(a) Propene + HBr $\xrightarrow{ROOR}$?

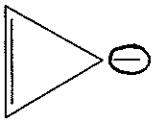
(b) 1-butene $\xrightarrow{\text{cold } H_2SO_4}$? $\xrightarrow{H_2O\text{ , heat}}$?

(c) 2 -pentyne $\xrightarrow[H_2O\text{ , heat}]{KMnO_4\text{ ,KOH}}$? + ?

(d) 1-hexyne $\xrightarrow[CCl_4]{Cl_2}$? $\xrightarrow[CCl_4]{Cl_2}$?

3. (i)Write the formula of tetrathiocyanato-N-Zinc (II)
(ii)For the following complexes, identify their structure and account for it using VBT.
(a) $Ni(CO)_4$ (b) $Ni(CN)_4^{2-}$ **[2+3+3 M]**

4. (i)Predict and justify if the following compounds are aromatic/anti aromatic / non-aromatic

(a) Pyridine (b) Cyclopentadienyl anion (c) 

(ii)For the following reactions, predict the mechanism followed and give the major and minor products formed .

(a) 2-iodo-2-methylbutane + CH_3OH $\xrightarrow{\text{Heat}}$

(b) 2-bromo-2-methylhexane + CH_3ONa $\longrightarrow$ **[6+6+4 M]**

PART-B

1. (i) Draw the structure of following ligands indicating the coordination site(s)
(a) 2,2'-Dipyridyl (b) oxalate ion
(ii) Give any three examples of biologically important chelates.
(iii) Draw the structure of optical isomers of dichlorobis(ethylenediamine) cobalt(III)ion . **[3+3+4M]**

2. (i) Name the following compounds using **E-Z-** nomenclature

(a)

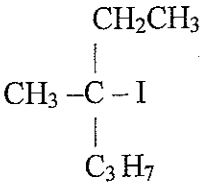
(b)

(ii) Write the mechanism for the formation of t-butyl benzene from benzene. **[6+8M]**

PART-C

1.(i) Draw all the possible conformations of butane. Explain the energy relationships among conformations of butane using the potential energy diagram.
(ii) Write the number of **B-B** , **B-B-B** and **B- H -B** bonds in pentaborane -9. **[8+6M]**

2. (i) Discuss the mechanism for the racemisation of the following compound with methanol in the S_N1 reaction



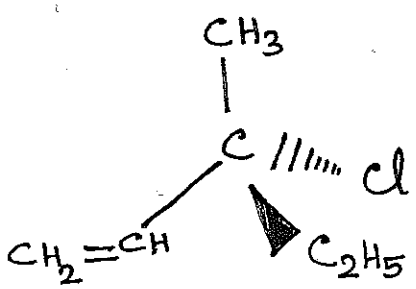
(ii) Give the decreasing order of halide nucleophilicity in protic solvents with proper justification. **[4+6M]**

3. (i) Depict the symmetrical and asymmetrical electronic arrangement of a d^6 octahedral system.

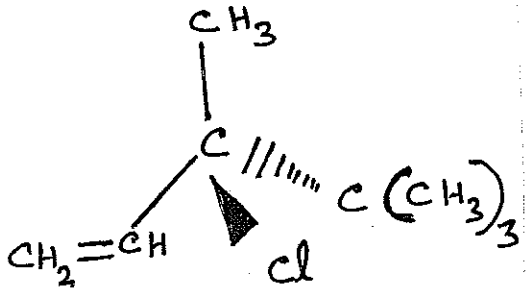
(ii) Give the reason for the tetragonal distortion in octahedral complexes .

(iii) Assign the **R** or **S** configuration for the following compounds. Also indicate the priority order of the groups. **[4+2+4M]**

(a)



(b)



4. (i) Draw the Fisher-Projections of enantiomers of 2,3-dibromopentane and assign the configuration.

(ii) Give the **IUPAC** names of following compounds.

(a) $CH_3COOC_3H_7$ (b) $CH_3N(C_6H_5)_2$

(iii) Write the structure of the following compounds.

(a) 2,2'-dimethylbutane-1-ol

(b) 3-cyano-2-hydroxy-5,5-dimethylheptane. **[6+4+4M]**

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BITS PILANI,DUBAI
I YEAR SECOND SEMESTER,2009-2010
TEST- 2 (Open book)

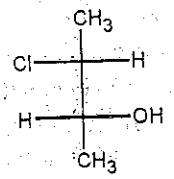
Course Title :Chemistry-II **Course No:CHEM C142**
Date:11.4.2010 **Total Marks:60**
Time: 50 min **Weightage:20%**

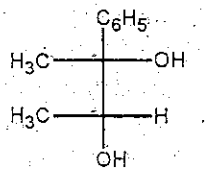
1.Answer all questions sequentially.
2. Only prescribed Text book and original hand written Notes are allowed.
3. Question paper has 2 pages.

1.(i) Write the factors that contribute to the ring strain of cyclopropane.
(ii) Draw the chair conformations for cis and trans -1-fluoro-3-cyanocyclohexane. Indicate which will be more stable with suitable reasons.

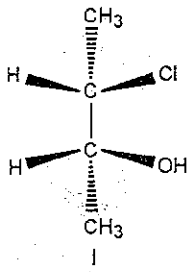
[4+8M]

2. (i) Assign R,S designation to the following compounds

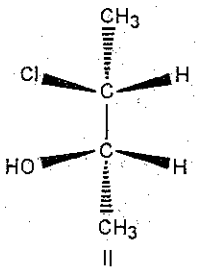
(a) 

(b) 

(ii)Identify the structural relationship between the following pair of compounds (Enantiomeric/diasteromeric/same)



I

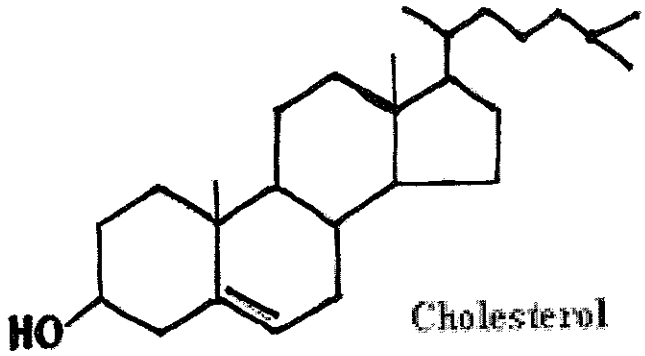


II

(iii)Does hepta-3,4-diene exhibit enantiomerism? Justify your answer. **[4+4+4M]**

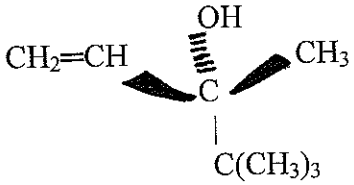
3. (i) Draw the enantiomers of 1,1-chlorobromoethane and assign the R and S configuration.

(ii)Indicate the number of stereocentres and the number of possible stereoisomers possible for the cholesterol molecule given below.



Cholesterol

(iii) Assign R and S configuration and clearly show the priority of groups at the chiral centre for the following molecule.

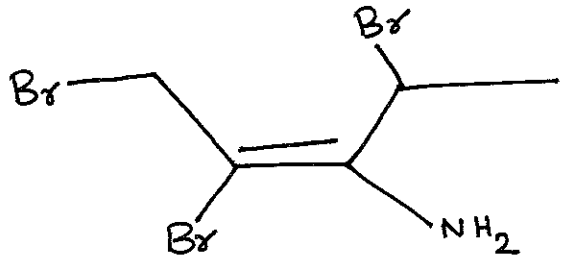


[4+4+4M]

4. (i)A solution containing one mole of (—) epinephrine give an optical rotation of —50 °. On adding 0.5 mole of (+) epinephrine, the rotation exhibited by the mixture was found to be —31°. What will be the optical rotation, if one mole of (+) epinephrine is added to the solution ?

(ii) Draw the structure of (a)(Z)-1-Iodo-2-pentene (b)(E)-1,3-Diiodo-2-pentene

(iii) Name the following compound according to the (E)–(Z) convention. **[3+6+3M]**



5. Draw the Newman projection of all possible conformers of n-hexane and comment on their relative stability using a relative potential energy diagram. **[12M]**

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BITS, Pilani - DUBAI
I YEAR SECOND SEMESTER,2009-2010

TEST- 1 (Closed book)

Course Title :Chemistry-II **Course No:CHEM C142**
Date: 28.2.2010 **Total Marks:75**
Time: 50 min **Weightage:25%**

Note:1. Answer all questions
2. Show workings whereever necessary.
3.Useful atomic numbers: Ti(22),Cr(24),Mn(25), Fe(26),Co(27),Ni(28),Cu(29)

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1. (i) For $[Mn(CN)_6]^{3-}$ ion,the mean pairing energy (P) is found to be equal to 28,000 cm^{-1} .The magnitude of Δ_o is 38,500 cm^{-1} .Draw the CF splitting diagram for this complex ion .Calculate the CFSE for this complex ion corresponding to high spin and low spin state.Which state is more stable.why?
(ii) Show the splitting of d orbitals in an octahedral field with tetragonal distortion.
[8+7M]

2. (i) Write the IUPAC names of the following coordination complexes.
(a) $[CoCl_2(NH_3)_4]_3[Cr(CN)_6]$ (b) $K_3[Fe(C_2O_4)_3]$
(ii) Write the formula of the following coordination complex.
Tetraaquairon(III)-μ-dihydroxotetraaquoiron(III)sulphate
(iii) Based on VBT show the oxidation state, type of hybridization, magnetic property of the complex $[Cr(NH_3)_6]^{3+}$
[3+3+3+6M]

3. (i) Write the reason for the fact that tetrahedral crystal field splitting is 4/9 th of the octahedral crystal field splitting.
(ii)Why t_{2g} orbitals are closer to the ligands than the e_g orbitals in tetrahedral complexes?
(iii)Draw the CF splitting diagram and calculate the CFSE in terms of Δ_t and Δ_o for the complex $[FeF_4]^{2-}$.
[5+4+6M]

4. (i) Write the structure of the following chelating ligands and indicate their donor atoms. (a) Acetylacetonate (b) Dimethylglyoxime.
(ii) Mention any two chelates that find application in day-to-day life.
(iii)Explain the origin of color in Ti^{3+} complexes based on Crystal Field Theory.
[4+4+7 M]

5. (i)Which of the following complexes will have distorted octahedral structure, Justify.(a) $[Co(CN)_6]^{4-}$ (b)$[MnF_6]^{4-}$
(ii)Using CFT predict whether the following complexes will have square planar or tetrahedral geometry (a) $Ni(CO)_4$ (b) $[Ni(CN)_4]^{2-}$ also show the d electron splitting of the central metal in the complex.
[7+8M]

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A

BITS, PILANI – DUBAI

SECOND SEMESTER 2009 – 2010

Course Code: CHEM C142 **FIRST YEAR Quiz-II (closed book)** Date: 29.4.2010
Course Title:Chemistry II Max Marks: 21
Duration : 20 minutes Weightage: 7 %

Name: ..... **ID No:** ..... **Sec / Prog:** .....

Instructions: (if any) Over writing will be taken as wrong answer

1. Which can act as a strong nucleophile methoxide ion or acetate ion ? **(2M)**

2. Which is the best and poorest leaving group among halide ions ? **(2M)**

3. Write the product of the reaction between methanol & t-butyl chloride. Name the mechanism of the reaction. **(2M)**

4. Hydrolysis of methyl bromide takes place much faster in presence of sodium iodide. Justify. **(2M)**

5. Which alkyl halide would you expect to react faster by S_N2 Mechanism

$(CH_3)_2CHCH_2CH_2Cl$ or $CH_3CH_2CH(CH_3)CH_2Cl$? **(2M)**

6 .In ethanol which will be a better nucleophile OH^- or SH^-? **(2M)**

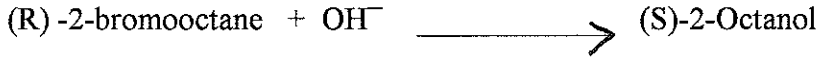
7.Identify the protic solvents from the following : **(2M)**
Dimethyl formamide, ethylene glycol , acetonitrile , ammonia

8.On the basis of Zaitsev's rule, write the major and minor product of the reaction between tert-pentyl bromide and ethanol. **(2M)**

9. List the following alkyl halide in the order of decreasing reactivity in the E1 reaction **(2M)**
2-bromo-2-methyl butane, 1-bromopentane , 3-bromopentane

10. Identify in which of the following solvents the rate of the E1 reaction would be greater . Water , hexane. **(2M)**

11. Predict the mechanism of the following reaction. **(1M)**



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A

BITS, PILANI – DUBAI

SECOND SEMESTER 2009 – 2010

Course Code: CHEM C142 **FIRST YEAR Quiz-1(closed book)** Date: 18.3.2010
Course Title:Chemistry II Max Marks: 24
Duration : 20 minutes Weightage: 8 %

Name: ..... **ID No:** ..... **Sec / Prog:** .....

Instructions: (if any) Over writing will be taken as wrong answer

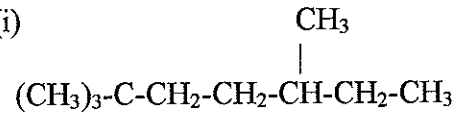
1. Give any two experimental methods that confirms the fact that in diborane four of the H atoms are in a different environment from the other two. **(2M)**

2. Write the number of terminal B-H bonds and the number of bridging B-H-B bonds in Pentaborane -11. **(2M)**

3. How many valence electrons are present in Decaborane -14. **(1M)**

4. Write the IUPAC name of the following compounds **(3M)**

(i)

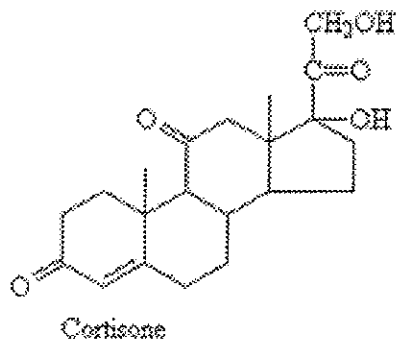


(ii) CH_3-CH=CH-CH_2Br

5. Write the structure of the following compound (IUPAC name is given). **(2M)**
2-Ethylprop-2-ene-1-ol

6. Write the structure of 4-hydroxy-4-methyl-2-pentanone. **(1M)**

7. Identify the different types of functional groups present in the following compound. **(3M)**



Cortisone

8. What is the trend of first ionization energy of the elements from B to Tl? **(2M)**

9. Comment on the spontaneity of the following reaction on the basis of electropositive character. **(2M)**

$Al^{+3} + 3e^{-} \rightarrow Al$ $\quad (E^{o} = -1.66 \text{ volts})$

10 .Tl (I) compounds are more stable than Tl (III) compounds. Why? **(1M)**

11. Mention any one method that can be used to distinguish between cis and trans isomer of a Complex. **(2M)**

12. Draw the geometrical isomers of $[Co(NH_3)_4 Cl_2]^{+}$ **(3M)**

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