

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR II SEMESTER,2005-2006

COMPREHENSIVE EXAMINATION

Course Title :Chemistry II

Course No:CHEMUC142

Date: 30.5.2006

Max Marks:120

Time:3 hrs

Weightage:40%

Note:1.Answer Section A in the main sheet , B and C in the additional sheets separately.

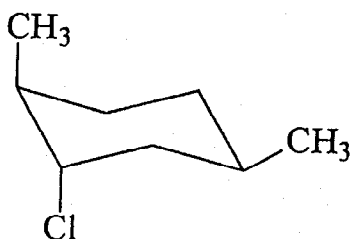
2. Answer briefly all parts of a question in continuation.

3. Useful atomic numbers:

Cr(24),Mn(25),Co(27),Fe(26),Ni(28),Cu(29),Zn(30)Pt(78)

SECTION -A

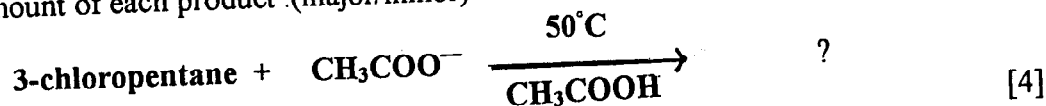
1. (i) Show by means of a diagram how the pattern of d-orbital splitting changes as an octahedral complex undergoes tetragonal distortion and eventually becomes a square planar complex. [3]
 - (ii) Pickout the species having greater Δ_o value from the following complex ions and give reason for your choice.
[Fe(C₂O₄)₃]⁴⁻ and [Fe(C₂O₄)₃]³⁻ [2]
 - (iii) On the basis of CFT, predict whether [Cu(NH₃)₄]²⁺ is square planar or tetrahedral. Show the distribution of d electrons of the central metal atom in the splitted d-orbitals. [4]
 - (iv) Calculate CFSE values in terms of Δ_o and P for high spin and low spin octahedral complexes of Fe(II). [4]
 - (v) Account for the following:
The magnitude of the crystal field splitting in tetrahedral complexes is considerably less than in octahedral fields. [2]
-
2. (i) Draw Newman projection of the chair and boat conformations of cyclohexane. Why is the boat conformation less stable than the chair conformation? [5]
 - (ii) Draw the ring- flipped form of the following structure. Circle the more stable of the two conformations. [2]



- (iii) Draw the most stable conformation of butane –Give the reason for its stability. [3]

3.(i) Starting from tert-butyl chloride how will you prepare tert-butyl alcohol? Give experimental conditions and write the mechanism clearly showing the electron transfer. [5]

(ii) Give the products that you would expect to be formed in the reaction given below. Predict the mechanism by which the product is formed and the relative amount of each product (major/minor)



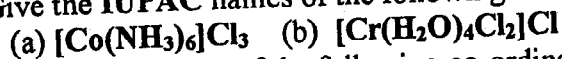
(iii) Why vinylic and phenyl halides are unreactive in $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ reactions? [2]

(iv) Justify - In general the trend in nucleophilicity among the halide anions in a protic solvent is as follows



SECTION-B

1.(i) Give the IUPAC names of the following complexes: [5]

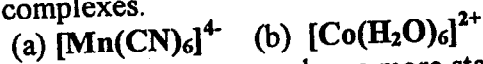


(ii) Write the structure of the following co-ordination complexes.

(a) Diamminedichloroplatinum(IV)chloride

(b) Sodium tetrachlorozincate(III) ion

(iii) Based on VBT show the electronic configuration, oxidation state of the central metal, type of hybridization, geometry and magnetic nature of the following complexes. [5]

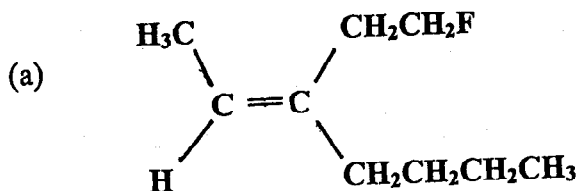


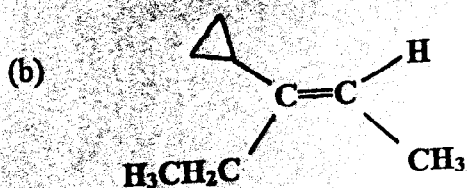
(iv) Why thalious compounds are more stable than thallic compounds? [3]

(v) Draw the structure of diborane and mention the nature, number of individual bonds. [2]

2.(i) Give the mechanism for anti-Markovnikov addition of hydrogen bromide to Propene. [5]

(ii) Determine the configuration of each of the following alkenes as Z or E as appropriate. [5]





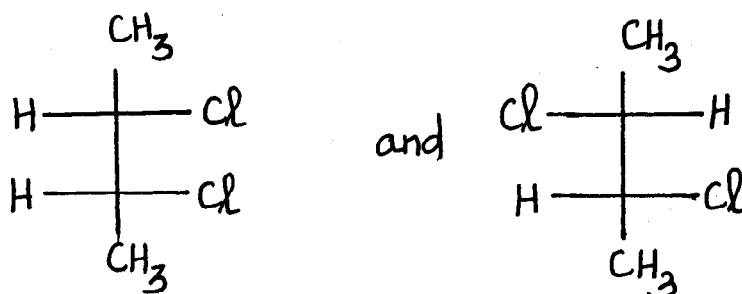
- (iii) Which of the following ion is aromatic/ antiaromatic? [5]
 (a) cyclononatetraenyl cation (b) [18]Annulene
- (iv) Give the reaction product formed during electrophilic addition of Hydrogen bromide to cis-3-Hexene. [5]

SECTION - C

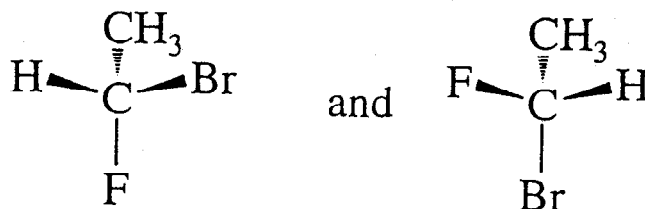
- 1.(i) Account for the following
 Cr^{2+} does not form a regular octahedral complex with a weak field ligand whereas Mn^{2+} forms a regular octahedral complex with that ligand. [4]
- (ii) Draw the structure of 1, 10-Phenanthroline clearly showing the donor atoms. [3]
- (iii) Calculate the magnetic moment and write the geometry of $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$. [3+3]
- (iv) Sketch the possible geometric isomers for $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$. [2]

- 2.(i) For each pair of the structures given below, identify whether they are identical or stereoisomers (enantiomers or diastereomers). [2+2]

(a)



(b)



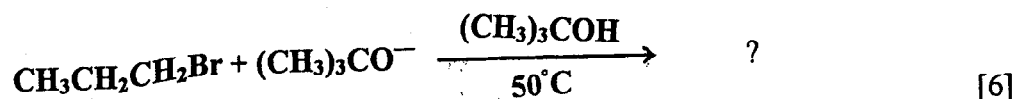
- (ii) Which of the following compounds are chiral.

- (a) 2-Chloro-2-methylpentane
 (b) 4-Chloro-2-methylpentane

[4]

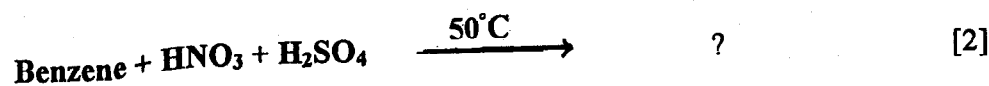
- (iii) Write the structural formula for all the stereo isomers of 1,3-dimethylcyclopentane. Label the pairs of enantiomers and meso compounds if they exist. [6]

- 3.(i) Give the product (or products) that you would expect to be formed in the following reaction. Give the mechanism by which the product is formed and predict the relative amount of each (i.e., would the product be the only product, the major product, or a minor product?).



- (ii) Write the structural formula for the following compound [3]
2-chloro-2-methyl-4-hexyn-3-one

- (iii) Give the structure of the major product of the following reaction:



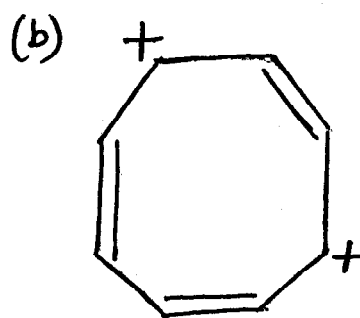
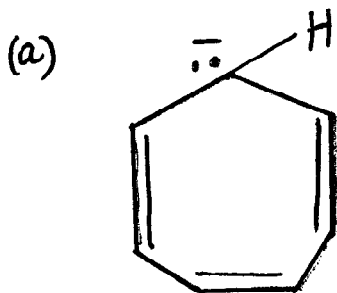
BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR II SEMESTER,2005-2006
Test - II (Open Book)

Course Title :Chemistry II
Date:14.5.2006
Time:50 min

Course No:CHEMUC142
Max Marks:60
Weightage:20%

- Note:1. Answer all questions
2. Show workings where ever necessary.

- 1.(i) Draw Newman projections for the most stable and least stable staggered conformations and the least stable eclipsed conformation, for the C2 - C3 bond of 2-methylbutane and label them.
(ii) Write chain mechanism accounting for the formation of 1,2-dichlorobutane from ethane. (6+5M)
2. Account for the following observations:
(i) HF, HCl and HI do not give anti-markovnikov addition products in the presence of peroxides.
(ii) Reaction of HCl with pent-2-ene gives 2 products but the corresponding reaction of pent-1-ene gives only 1 product.
(iii) Benzene reacts readily with nitric acid in the presence but not in the absence of Conc sulphuric acid. (3+3+3M)
- 3.(i) Use the Huckel rule to indicate whether the following planar species are aromatic or antiaromatic



- (ii) Give the structural formula and the name for the major alkylation product with proper mechanism.
Benzene + isobutylchloride $\xrightarrow{\text{AlCl}_3}$? (5+5M)

4.(i) Give the structural formula for the alkenes formed on dehydrobromination of the following alkyl bromides and underline the principal product in the reaction.

- (a) 2-bromo-2-methylpentane
(b) 3-bromo-2-methylpentane

(ii) Give the structural formula for the reactant that form 2-butene when treated with alcoholic KOH.

(iii) Arrange the following alkenes in order of increasing reactivity on addition of hydrohalogen acids:

- (a) $\text{H}_2\text{C}=\text{CH}_2$ (b) $(\text{CH}_3)_2\text{C}=\text{CH}_2$ (c) $\text{CH}_3\text{CH}=\text{CHCH}_3$ (6+2+2M)

5.(i) Explain which of the isomer, cis- or trans- 1, 3-dimethylcyclohexane, would have the larger heat of combustion?

(ii) On the basis of 0.9 kcal/mol per 1,3-diaxial methyl-hydrogen interaction or butane-gauche interaction, predict the potential energy difference between the pair of above stereoisomers. (4+3M)

6.(i) Write the structures of two chair conformations of 1-tert-butyl-1-methylcyclohexane. Which conformation is more stable? Explain your answer.

(ii) For the given reaction



Write the product and explain the reaction mechanism .

(6+7M)

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR SECOND SEMESTER,2005-2006

Make up -QUIZ II (Closed Book)

Course Title: Chemistry II
Date: 27.04.2006
Time: 30 min

Course No: CHEMUC142
Total Marks:30
Weightage: 10%

Name of the Student: _____

ID No: _____

Section : _____

Useful data:

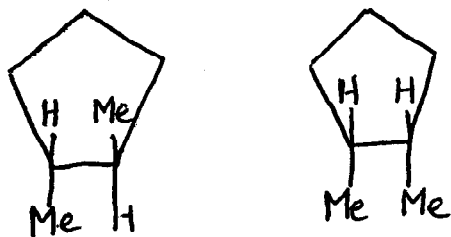
1. For multiple choice questions tick and underline the correct answer.

2. Useful atomic numbers: H(1), C(6), N(7), O(8)

1. The cis and trans forms (chair conformations) of 1,4 Dimethylcyclohexane are (2M)
- (a) enantiomers
 - (b) diastereomers
 - (c) chiral compounds
 - (d) none of the above

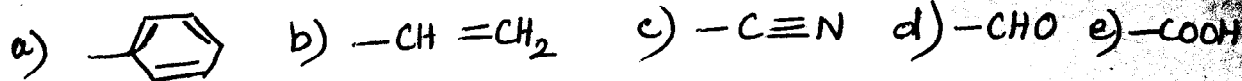
2. Give the structural formula of the chiral drug that is effective against typhoid fever. (2M)

3. Give the stereochemical relationship between the following structures (2M)



4. Write structural formulas for the stereoisomers of 3-chloro-1-butene. (2M)

5. Using the letter assigned to each group put the following functional groups in decreasing order of Cahn-Ingold-Prelog priority. (2M)



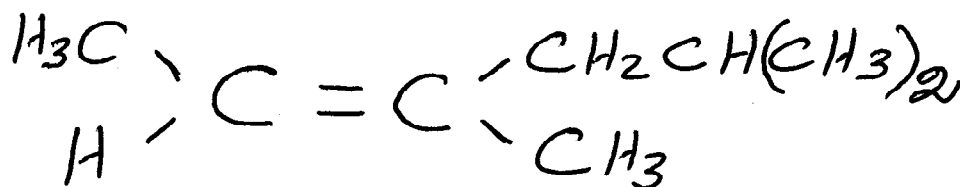
6. Meso compounds have (2M)

- (a) One chiral center
- (b) Two chiral centers
- (c) No chiral center
- (d) Optical activity

7. Which of the following show optical activity (2M)

- (a) Chloroethane
- (b) Chlorobromoethane
- (c) Chlorobromomethane
- (d) None of the above

8. Using the (E) - (Z) designation give IUPAC name for the following compound (2M)



9. Write structural formulas for

(a) A secondary amine with the formula C_3H_9N

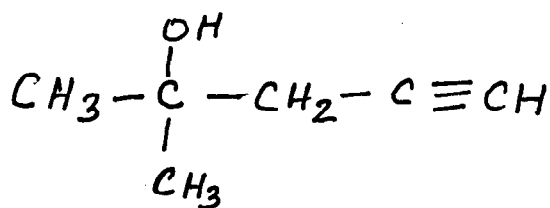
(2M)

(b) A tertiary amine with the formula C_3H_9N .

(2M)

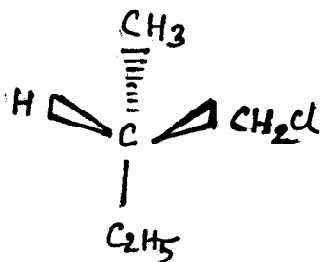
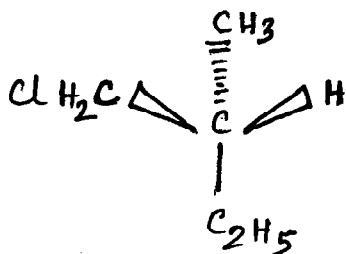
10. IUPAC name of

(2M)



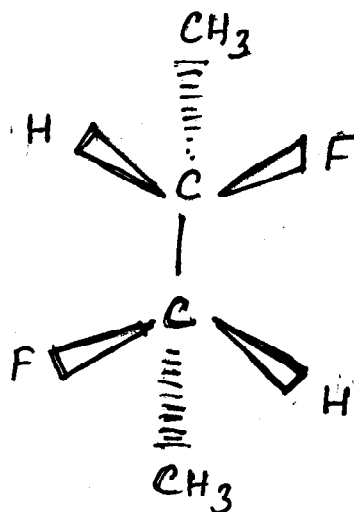
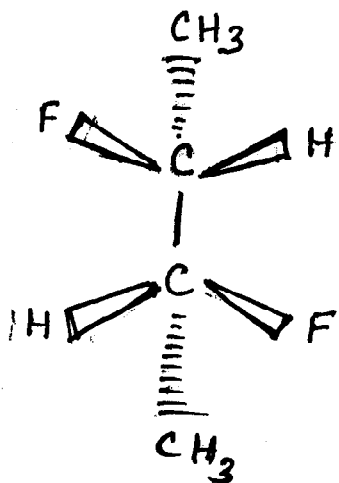
11. Cis,1,2-dimethylcyclohexane and trans 1,2-dimethyl cyclohexane are stereoisomers that are _____ . (2M)

12. Assign (R) or (S) designation to each of the following compounds. (2M)



13. Diastereomers have different -----properties. (2M)

14. Write the relationship between the stereochemical formulas of 2,3 difluorobutane. (2M)



BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR SECOND SEMESTER,2005-2006

A

QUIZ II (Closed Book)

Course Title: Chemistry II

Date: 18.04.2006

Time: 30 min

Course No: CHEMUC142

Total Marks:30

Weightage: 10%

Name of the Student: _____

ID No: _____

Section : _____

Set: **A**

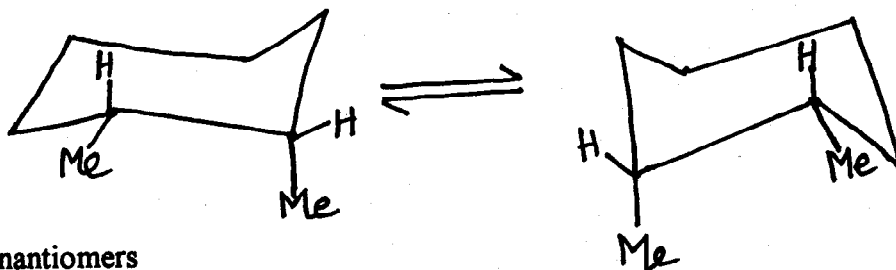
Useful data:

1. For multiple choice questions tick and underline the correct answer.
 2. Atomic numbers: H=1, C=6, N=7, O=8,

1. Which of the following pairs is an example of constitutional isomers
 (a) (R) -2-Butanol and (S) -2-Butanol
 (b) Cis-1,2-Dichloroethene and trans-1,2-Dichloroethene
 (c) 1-Chloropropane and 2-Chloropropane
 (d) Cis -1,2-Dimethylcyclopentane and trans-1,2-Dimethylcyclopentane (2M)

2. The (R) isomer of Ibuprofen (2M)
 (a) is an antihypertensive drug
 (b) has no anti-inflammatory action
 (c) is used for primary chronic arthritis
 (d) is used for typhoid fever

3. For the given chair conformations of 1,2-Dimethylcyclohexane, which of the following relationship is more appropriate (2M)



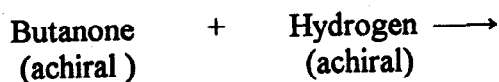
- (a) Enantiomers
 (b) Diastereomers
 (c) Configurational stereoisomers
 (d) Conformational stereoisomers

4. Which of the following is the correct order of priority according to the rules of Cahn-Ingold-Prelog system (2M)

- (a) $-\text{CH}(\text{CH}_3)_2 > -\text{C}(\text{CH}_3)_3 > -\text{CH}=\text{CH}_2 > -\text{H}$
 (b) $-\text{CH}=\text{CH}_2 > -\text{C}(\text{CH}_3)_3 > -\text{CH}(\text{CH}_3)_2 > -\text{H}$
 (c) $-\text{C}(\text{CH}_3)_3 > -\text{CH}=\text{CH}_2 > -\text{CH}(\text{CH}_3)_2 > -\text{H}$
 (d) $-\text{C}(\text{CH}_3)_3 > -\text{CH}(\text{CH}_3)_2 > -\text{CH}=\text{CH}_2 > -\text{H}$

5. The product of the following reaction is

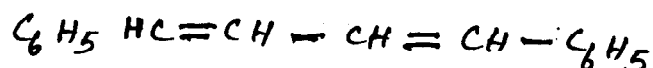
(2M)



- (a) (R)-2-butanol
- (b) (S)-2-butanol
- (c) Racemic butanol
- (d) None of the above

6. IUPAC name of

(2M)

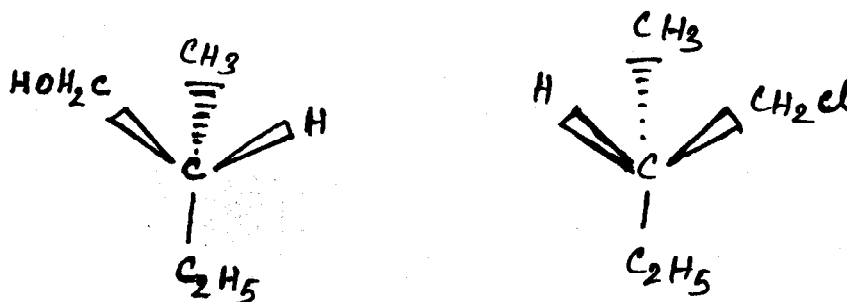


7. Stereo isomers whose molecules are nonsuperposable mirror images of each other are called _____.

(2M)

8. Assign (R) or (S) designation to each of the following compounds.

(2M)



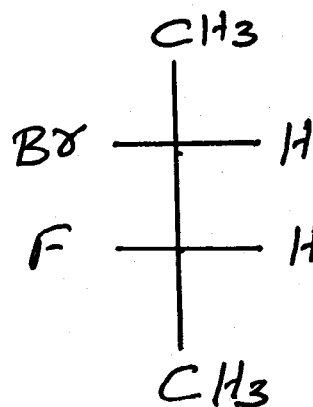
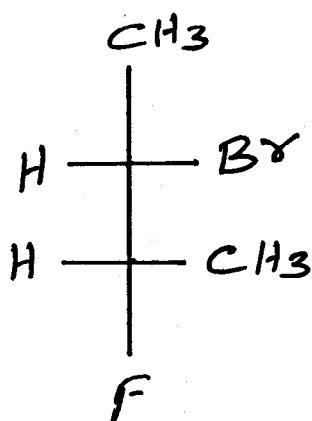
9. The total number of stereoisomers will not exceed _____ where n is equal to the number of tetrahedral stereogenic centers.

(2M)

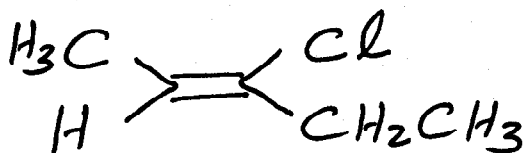
10. _____ is a chiral molecule that donot possess a tetrahedral atom with four different groups. (2M)

11. Write structural formula for a tertiary alcohol having the molecular formula $C_4H_{10}O$. (2M)

12. Identify the stereo chemical relationship between (2M)

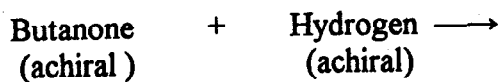


13. Using the (E)-(Z) designation give IUPAC name for the following compound: (2M)



5. The product of the following reaction is

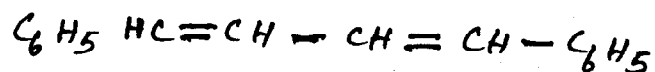
(2M)



- (a) (R)-2-butanol
- (b) (S)-2-butanol
- (c) Racemic butanol
- (d) None of the above

6. IUPAC name of

(2M)

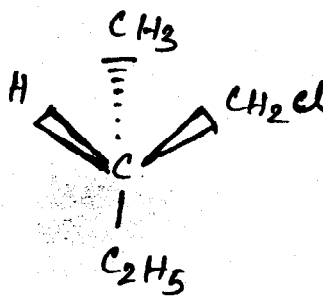
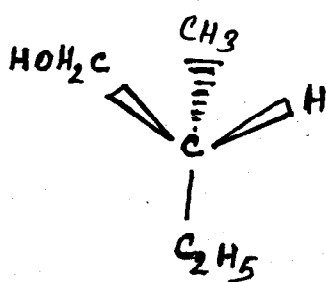


7. Stereo isomers whose molecules are nonsuperposable mirror images of each other are called _____.

(2M)

8. Assign (R) or (S) designation to each of the following compounds.

(2M)



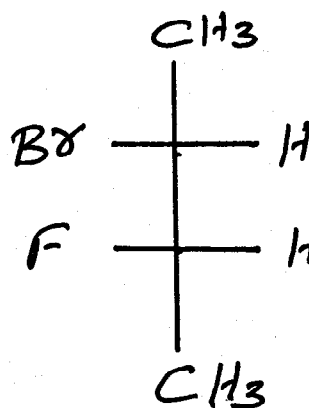
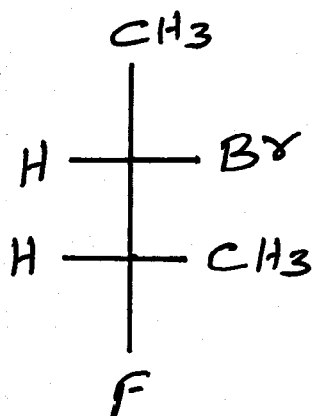
9. The total number of stereoisomers will not exceed _____ where n is equal to the number of tetrahedral stereogenic centers.

(2M)

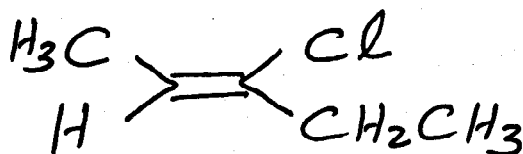
10. _____ is a chiral molecule that donot possess a tetrahedral atom with four different groups. (2M)

11. Write structural formula for a tertiary alcohol having the molecular formula $C_4H_{10}O$. (2M)

12. Identify the stereo chemical relationship between (2M)



13. Using the (E)-(Z) designation give IUPAC name for the following compound: (2M)



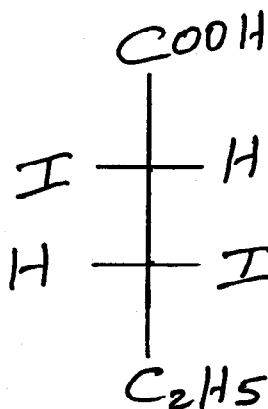
14. Which of the following show optical activity

(2M)

- (a) Chloroethane
- (b) Chloromethane
- (c) Chlorobromomethane
- (d) Chlorobromiodomethane

15. The configuration of

(2M)



is (a) (2R, 3R), (b) (2S, 3S), (c) (2S, 3R), (d) (2R, 3S).

BITS PILANI -DUBAI CAMPUS, KNOWLEDGE VILLAGE, DUBAI
I YEAR II SEMESTER, 2005-2006
Make-up Test - I (Closed Book)

Course Title :Chemistry II
Date: 5.04.2006
Time:50 min

Course No:CHEMUC142
Max Marks:60
Weightage:20%

- Note: 1. Answer all questions sequentially.
2. Show workings where ever necessary.
3. Useful atomic numbers:

Sc(21), Cr(24), Mn(25), Co(27), Fe(26), Ni(28), Cu(29), Zn(30), Rh(45), Pt(78)

1. For Pentaborane – 9 ,clearly state the no of bonds, nature of bonds, no of electrons included in each type of bonds. (10M)
2. (i) Account for the following observations.
(a) Complete methylation of diborane is not possible.
(b) Though the normal oxidation state of Ni is +2 , $[\text{Ni}(\text{CO})_4]$ with Ni(0) is stable.
(c) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ exchanges two of its water molecules more easily than the other four.
(ii) Give the energy level diagram of Rh^{2+} ion in an octahedral complex for which $\Delta_o > P$. (2+2+2+4M)
3. (i) Write the IUPAC name of the following coordination complexes.
(a) $[\text{CoCl}.\text{CN}.\text{NO}_2.(\text{NH}_3)_3]$
(b) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$
(ii) Why does $[\text{CoF}_6]^{3-}$ give a high spin complex?
(iii) $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral-Why? (3+3+4 M)
4. (i) Show that the octahedral complexes of Fe^{2+} are outer orbital complex.
(ii) Account for the fact that $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
(iii) Complex of Calcium with EDTA is used to treat lead poisoning-Why? (4+4+2M)

5. (i) Draw the isomers of an octahedral complex which has three identical bidentate Ligands.
(ii) Draw all the structures of isomers of Pt-glycine complex. (4+6M)
6. (i) Point out two major limitations of CF Theory.
(ii) Calculate CFSE in units of Δ_0 and give the CF splitting diagram for a Fe^{2+} ion in tetrahedral and low-spin octahedral ligand field. (2+8M)

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR II SEMESTER,2005-2006
Test - I (Closed Book)

Course Title :Chemistry II
Date: 26.03.2006
Time:50 min

Course No:CHEMUC142
Max Marks:60
Weightage:20%

- Note: 1. Answer all questions sequentially.
2. Show workings where ever necessary.
3. Useful atomic numbers:

Ti(22), Cr(24),Mn(25),Co(27),Fe(26),Ni(28),Cu(29),Zn(30),Pt(78)

- 1.(i)For Tetraborane, draw the following table in your answer book and fill up the blanks of the last 3 columns.

S.No	Nature of bonds	Total no of bonds	$3C-2e^- / 2C-2e^-$	Total no of valency electrons
1	Hydrogen bridge bonds			
2	Covalent bonds			
3	B—B bonds			

- (ii)Account for the following observation.
Ga has higher ionization energy than Al.

(7.5+2.5M)

- 2.(i)On the basis of CFT , predict whether $[Pt(en)_2]^{2+}$ ion is square planar or tetrahedral. Show the distribution of d electrons of the central metal atom in the splitted d -orbitals .

- (ii)For $[Cr(H_2O)_6]^{2+}$ ion, the mean pairing energy (P) is found to be equal to $23,500 \text{ cm}^{-1}$. The magnitude of Δ_o is $13,900 \text{ cm}^{-1}$. Calculate the CFSE for this complex ion corresponding to high spin and low spin state. Which state is more stable. Why ?

(4+6 M)

3. (i) Write the formula of the following coordination complexes.

- (a) Pentamminenitrito cobalt(III)chloride
(b) Potassiumtrioxalatoaluminate(III)

- (ii) Write any two limitations of V.B. theory.

- (iii) $K_2[PtCl_6]$ is a well known compound but corresponding Ni compound does not exist - Why ?

(2+2+3+3M)

- 4.(i) If Hexafluoroferrate(III) ion is an outer orbital complex. Find the number of unpaired electrons in it. (electronic configurations of metal, metal ion and the complex should be shown.)
- (ii) Identify the complex which is expected to be coloured and explain. (electronic configuration of complexes should be shown)
- (a) $\text{Ti}(\text{NO}_3)_4$
(b) $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$
- (iii) Draw the structure of 1,10 phenanthroline ligand clearly indicating the donor atoms.
- (iv) Name the ligand that finds application in the treatment of dermatitis from chromium. (4+4+1+1M)
- 5.(i) Draw the structures of all possible isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.
- (ii) How will you distinguish the cis and trans isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$? (6+3M)
- 6.(i) Compare the magnetic properties of $[\text{Fe}(\text{CN})_6]^{4-}$ with those of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.
- (ii) Explain the Jahn – Teller effect in octahedral complexes of Cr^{2+} and Cu^{2+} showing the d – orbital splitting with electron occupancy. (4+7M)

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR II SEMESTER,2005-2006

MAKE -UP QUIZ - I (Closed Book)

Course Title :Chemistry II
Date: 15.03.2006
Time:30 min

Course No:CHEMUC142
Max Marks:30
Weightage:10%

Name of the Student : _____

ID No: _____

Section : _____

Set : **A**

Recheck Request:

Note: 1. Answer all questions

2. For multiple choice questions tick and underline the correct answer.

3. Show workings where ever necessary.

4. Question paper contains 6 pages.

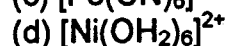
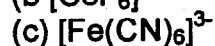
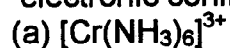
5. Useful atomic numbers:

Cr(24), Mn(25), Co(27), Fe(26), Ni(28), Cu(29), Zn(30)

1. Consider the coordination compound, $\text{Na}_2[\text{Pt}(\text{CN})_4]$. The Lewis acid

is _____ (1M)

2. In which one of the following species does the transition metal ion have d^3 electronic configuration? (2M)



3. Draw the structure of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (1M)

4. According to CF theory strong field ligands such as CN^- (2M)

(a) usually produce high spin complexes and small crystal field splittings.

(b) usually produce low spin complexes and small crystal field splittings.

(c) usually produce low spin complexes and high crystal field splittings.

(d) usually produce high spin complexes and high crystal field splittings.

5. Pick out the odd ligand from

(2M)

- (a) oxine
- (b) en
- (c) bipy
- (d) o-phen

6. A metal ion from the first transition series forms a tetrahedral complex which has a magnetic moment of 2.83 BM and a square planar complex which is diamagnetic. The metal ion is

(2M)

- (a) Co^{2+}
- (b) Fe^{2+}
- (c) Ni^{2+}
- (d) none of the above.

7. Write the formula of the following coordination complexes.

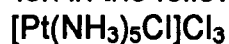
(1+1M)

a) tetraaquodichlorochromium(II) chloride

b) triamminechlorocyanonitro cobalt(III)

8. Write the oxidation number & co-ordination number of the metal ion in the following coordination complex

(2M)



9. Find out the state of hybridization of the central metal in the given complex based on VBT. (The electronic configurations of the neutral metal, metal ion and the complex should be shown.)
 $[\text{Cu}(\text{Cl}_4)]^{2-}$ (2M)
10. Using VBT, find out whether the following complex is paramagnetic/diamagnetic (electronic configuration should be shown)
 $[\text{Fe}(\text{CN}_6)]^{4-}$ (2M)
11. The number of donor atoms present in 2,2-dipyridyl ligand is _____ (1M)
12. Give any one application of EDTA as a chelating ligand. (1M)
13. According to VBT, if a sq. planar complex of Co^{3+} changes to tetrahedral configuration, by what factor its magnetic moment would change (2M)
- (a) 2 (b) $\sqrt{3}$ (c) $\sqrt{6}$ (d) No change

14. Tetragonal distortion of octahedral complexes occurs whenever the _____ and _____ orbitals are asymmetrically filled. (2M)

15. In Cu(II) complexes, the Cu^{2+} is six-coordinate with _____ short bonds and _____ long bonds. (2M)

16. Calculate the spin only magnetic moment for d^7 ion in square planar complex. (2M)

17. CFSE for d^6 electronic arrangement in tetrahedral ligand field (in terms of Δ_o) is _____ (2M)
