

BITS PILANI-DUBAI CAMPUS, KNOWLEDGE VILLAGE, DUBAI
I YEAR SECOND SEMESTER, 2004-2005

COMPREHENSIVE EXAMINATION (Closed book)

Course Title: Chemistry II

Course No: CHEMUC142

Date: 26.5.2005

Total Marks: 40

Time: 3hrs

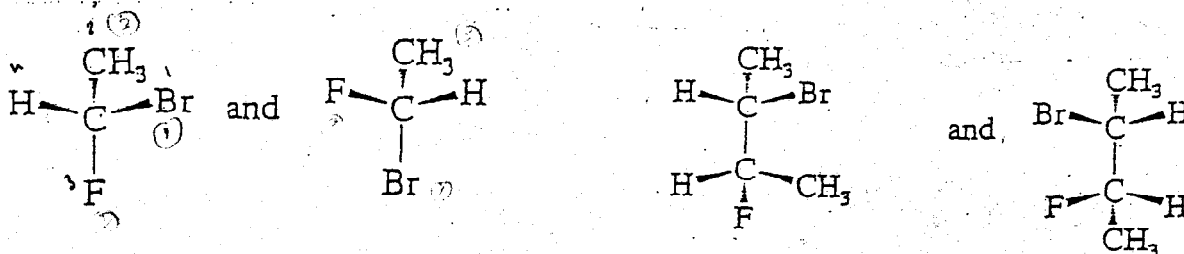
Weightage: 40%

1. Answer all parts of a question in continuation.
2. Use periodic table attached for information you may require.
3. Do not redraw shapes and structures.
4. Answer SECTION-A in the main sheet and SECTION-B in the additional sheet separately

SECTION -A

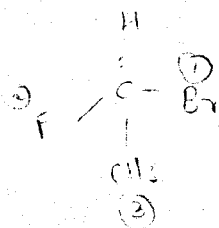
1. (i) Draw the structure of salicylaldehyde anion and 2, 2'-Dipyridyl clearly showing the donor atoms.
 (ii) Complete methylation of diborane is not possible. Why?
 (iii) Draw Newmann projections for chair and boat conformations of cyclohexane.
 (iv) Write the chemical formula of the following complex ions
 (a) tetraoxalato di- μ -hydroxo dichromium (III) ion
 (b) pentamminechlorocobalt(III) ion (1+1+1+1.5)

2. (i) $10 Dq$ of $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is known from electronic spectrum to be $21,000 \text{ cm}^{-1}$. The pairing energy of Mn(III) is $28,800 \text{ cm}^{-1}$. Calculate the CFSE and predict whether the given complex ion is high spin or low spin.
 (ii) On the basis of CFT predict the geometry of the following complex ions and show the distribution of d electrons of the central metal atom in the splitted d-orbitals
 (a) $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (b) $[\text{Co}(\text{Cl})_4]^{2-}$ ion
 (iii) Identify the relationship between the following structures by describing them as representing enantiomers, diastereomers, constitutional isomers or two molecules of the same compound. (3+3+1)

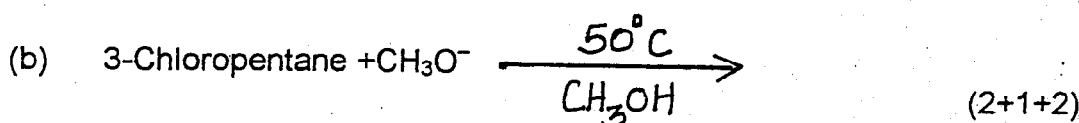
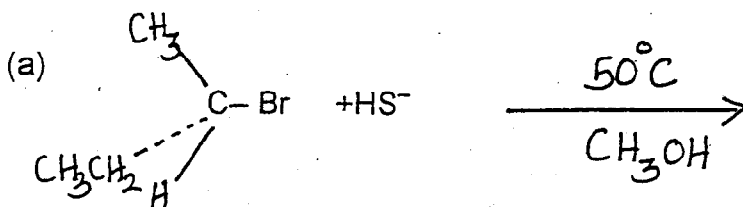


(a)

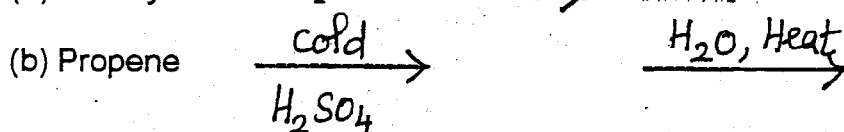
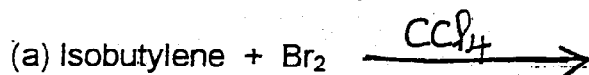
(b)



3. (i) Write a mechanism for the peroxide initiated addition of HBr to propene.
 (ii) Write the number of covalent bonds and closed B—B—B bonds in pentaborane-11.
 (iii) Give the products that you would expect to be formed in each of the following reactions. Predict the mechanism (S_N^1 , S_N^2 , E1, E2), major and minor product.



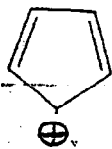
4. (i) Outline all steps in a mechanism showing how tert-butyl alcohol is formed in the acid-catalyzed hydration of 2-methylpropene.
 (ii) Complete the following reactions



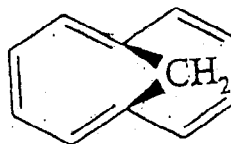
SECTION - B

5. (i) Name any two aromatic compounds that occur in living systems.
 (ii) Write the two conformations of trans-1-tert butyl-3-methylcyclohexane and designate which conformation would be the more stable.
 (iii) How many stereoisomers can exist for 4-methyl-2-hexene? Which of these stereoisomers would be expected to be optically active. (1+1.5+2.5)
6. (i) Arrange the following nucleophiles in decreasing order of their reactivity
 ROH , RO^- , H_2O , HO^- , RCO_2^-
 (ii) Write the structural formulae for the following compounds
 (a) 2-chloro-2-methyl-4-hexyn-3-one
 (b) 6-cyano-3-oxo-4-heptenal

(iii) Indicate which one of the following is aromatic or non aromatic.



(a)



(b)

(1+2+1)

7. (i) Account for the following

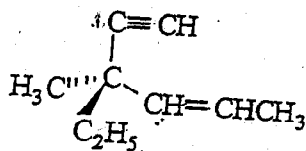
(a) Cr^{2+} does not form a regular octahedral complex with a weak field ligand whereas Mn^{2+} forms a regular octahedral complex with that ligand.

(b) The mode of splitting of d-orbitals in an octahedral field is just the reverse of that in a tetrahedral field.

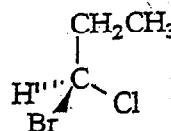
(ii) What happens when cis-1-chloro-3-methylcyclopentane reacts with hydroxide ion in an $\text{S}_{\text{N}}2$ reaction? Write the structure of the product and the transition state for the reaction.

(iii) Assign (R) and (S) designation to the stereocentre in each of the following molecules.

(1.5+1.5+1.5+1.5)



(a)



(b)

8. (i) Draw the most stable conformation of butane and give reasons for its stability.

(ii) Sketch the possible geometric isomers for $[\text{Cr}(\text{NH}_3)_2\text{Cl}_4]^-$. Which of these isomers will exhibit optical isomerism.

(iii) Outline the mechanism for the synthesis of 2-methylpropene from a tert-butyl halide.

(1+1.5+2.5)

*****GOOD LUCK*****

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR SECOND SEMESTER,2004-2005

TEST – 2 (Open Book)

Course Title :Chemistry II
Date: 10.4.2005
Time:50 min

Course No:CHEM UC142
Max Marks:20
Weightage:20%

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1. Answer in brief and to the point.
 2. Answer all parts of a particular question together.
 3. Do not redraw shapes and structures.
-

1. Give the **common** and **IUPAC** names of the following compounds

- (i) $\text{H}_2\text{C} = \text{CHOCH}_2\text{C}_6\text{H}_5$
- (ii) $\text{CH}_3\text{COCH}(\text{CH}_3)_2$

(3)

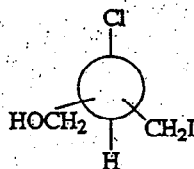
2. With reference to the structure of **pentaborane -9** clearly state the number of bonds, nature of bonds, number of electrons included in each type of bonds .

(4)

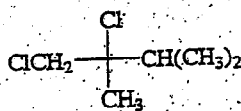
3. Specify configuration (**R/S**) of the molecules given below, clearly mentioning the priority of the groups attached to the chiral center.

(3)

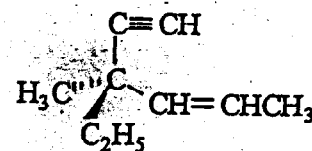
(i)



(ii)

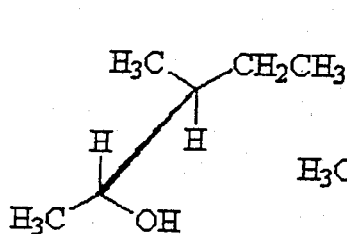
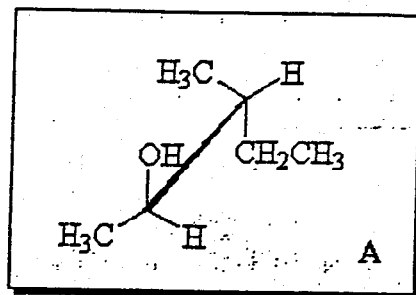


(iii)

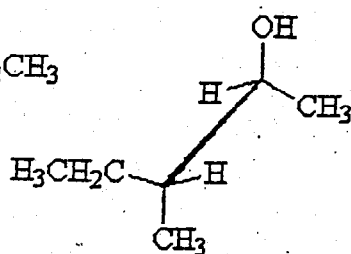


4. Identify the relation of each of the structures (B to E) to the structure A shown below as identical (ID), enantiomeric (ENT) and diastereomeric (DIA).

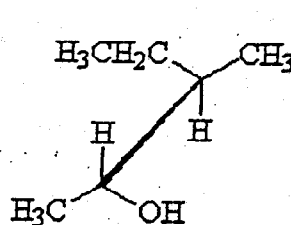
(3)



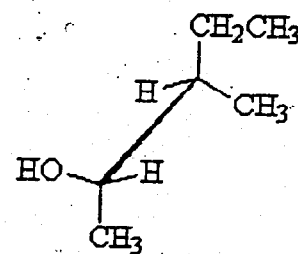
B



C



D



E

5. Give the structural formula of

- (i) (E)-6-fluoro-3,7-dimethyl-3-octene
- (ii) (Z)-1-iodo-2-bromo-3-methyl-1-hexene

(2)

6. Arrange the following substituents in decreasing order of priority

- (i) $-\text{CH}_2\text{NH}_2$, $-\text{NO}_2$, $-\text{C}\equiv\text{N}$, $-\text{NH}_2$
- (ii) $(\text{CH}_3)_2\text{CH}$ and cyclohexyl

(2)

7. Write appropriate structural formulas for

- (i) a cyclic molecule that is a constitutional isomer of cyclohexane
- (ii) molecule with the formula C_6H_{12} that contain one ring and are enantiomers of each other.
- (iii) molecule with the formula C_6H_{12} that contain no ring and that are diastereomers of each other.

(3)

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR SECOND SEMESTER,2004-2005

Name of the student :

ID No & Sec :

QUIZ (Closed Book)

Course Title :Chemistry II

Date: 15.3.2005

Time:30 min

Course No:CHEMUC142

Total Marks:20

Weightage:10%

1. For multiple choice questions tick and underline the correct answer.
2. Useful atomic numbers :Cr(24), Mn(25), Co(27), Fe(26), Ni(28), Cu(29), Zn(30)

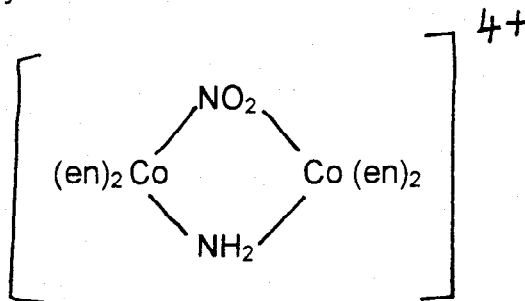
1. Which of the following is not a chelating ligand? (1M)
(a) ethylene diamine (b) EDTA (c) oxalate (d) pyridine
2. Indicate the oxidation state of the central metal ion in each of the following complex ions (1M)
(a) $[\text{Cr}(\text{NH}_3)_4(\text{CO}_3)]^+$
(b) $[\text{Cr}(\text{en})_3]^{2+}$
3. The number of isomers possible for square planar complex $[\text{PtClBr}(\text{NH}_3)]^-$ (1M)
(a) 2 (b) 3 (c) 4 (d) 6
4. Which of the following ligands does not contain donor nitrogen atom? (1M)
(a) ammine (b) nitrito (c) isothiocyanato (d) nitrosyl

5. Which of the following will have distorted octahedral structure?

- (a) $[\text{Co}(\text{CN})_6]^{4-}$ (b) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (c) $[\text{MnF}_6]^{4-}$ (d) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (1M)

6. Sketch the optically active isomers of

(1M)



7. A divalent metal ion of the first transition series forms an octahedral complex with a magnetic moment of 4.9 BM and another octahedral complex which is diamagnetic. The metal ion is

- (a) Fe^{2+} (b) Co^{2+} (c) Mn^{2+} (d) Ni^{2+} (1M)

8. Which of the following complex is tetrahedral?

- (i) $[\text{PtCl}_4]^{2-}$ (ii) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (iii) $[\text{MnBr}_4]^{2-}$ (iv) none of the above. (1M)

9. Why crystal field theory is not applied to complexes of main group metals?

(1M)

10. The aqueous solution of the salt will be coloured in the case of
(a) $Zn(NO_3)_2$ (b) $LiNO_3$ (c) $Co(NO_3)_2$ (d) none of the above (1M)

11. $Ni(CO)_4$ is
(a) square planar and paramagnetic
(b) tetrahedral and diamagnetic
(c) square planar and diamagnetic
(d) tetrahedral and paramagnetic (1M)

12. Polydentate ligands are also called as _____ (1M)

13. Thallium shows different oxidation states because of _____ (1M)

14. Predict whether the following statements are true or false
(a) All complexes exist as ions. (1M)
(b) The complex formation in solution brings change in conductance.

15. A bidentate ligand having one acidic and one coordinating group is
(a) en (b) glycine (c) oxalate (d) bipy (1M)

16. The number of ligands which are directly bonded to the metal ion is known as
(a) oxidation state (b) coordination sphere (c) valency (d) coordination number (1M)

17. Give a simple test to distinguish between the two enantiomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. (1M)

18. Write the chemical formula of the complex ion Tetraamminesulphatocobalt (III) ion (1M)

19. The alkali metal tetrahydridoborates act as _____ in both inorganic and organic chemistry. (1M)

20. Write the structure of the metal complex formed between Cu(II) and glycinate ions. (1M)

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR SECOND SEMESTER,2004-2005

MAKE UP TEST – 1 (Closed Book)

Course Title :Chemistry II
Date: 8.3.2005
Time:50 min

Course No:CHEM UC142
Max Marks:20
Weightage:20%

-
1. Answer in brief and to the point.
 2. Answer all parts of a particular question together.
 3. Useful atomic numbers :Cr(24),Mn(25),Fe(26),Co(27),Ni(28)

1. Write the chemical formula of the following complex ions

(i) Tetraoxalato di- μ -hydroxodichromium(III)ion

(ii) Potassium pentachloronitridoosmate(IV)

(iii) Diamminetetakis(isothiocyanato)chromate(III)ion

(3)

2. Calculate in kJmol^{-1} , the crystal field stabilization energy (CFSE) attained by Fe^{2+} ions in an octahedral environment of oxide ions (O^{2-}). Sketch the CFT diagram of Fe^{2+} ion corresponding to the octahedral environment of oxide ions (O^{2-}). Given that Δ_o for Fe^{2+} in O^{2-} environment = 124 kJmol^{-1} . (5)

3. Predict on the basis of CFT, whether the complex bis(dimethylglyoximate) nickel(II) is square planar, tetrahedral or octahedral. Give energy level diagram showing the distribution of d – electrons of the central metal in the splitted d – orbitals. (3)

4. Account for the following :

(i) Though the normal oxidation state of Ni is +2 $[\text{Ni}(\text{CO})_4]$ with Ni(0) is stable.

(ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion is more stable than $[\text{Co}(\text{NH}_3)_6]^{2+}$ ion but $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ion is less stable than $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion.

(iii) $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ is a salt but $\text{K}_4[\text{Fe}(\text{CN})_6]$ is a complex compound. (1+2+1)

5. (i) Draw the structure of the acetylacetonato ion clearly showing the donor atoms.

(ii) Mention any 2 applications of EDTA as chelating agent (2)

6. On the basis of VB theory predict the type of hybridization of the complex $[\text{Co}(\text{NO}_2)_6]^{3-}$. Calculate the value of μ_s for this complex. Draw the shape of the complex. (3)

BITS PILANI -DUBAI CAMPUS,KNOWLEDGE VILLAGE ,DUBAI
I YEAR SECOND SEMESTER,2004-2005

TEST – 1 (Closed Book)

Course Title :Chemistry II
Date: 27.2.2005
Time:50 min

Course No:CHEM UC142
Max Marks:40
Weightage:20%

-
1. Answer in brief and to the point.
 2. Answer all parts of a particular question together.
 3. Useful atomic numbers :Ti(22),Cr(24),Mn(25),Fe(26),Co(27),Ni(28),Cu(29)

1. Write the chemical formula of the following complex ions

- (i) Potassium hexacyanonickelate(0)
- (ii) Tetrakis(ethylenediamine) di- μ -hydroxodichromium(III)
- (iii) Triamminechlorocyanonitrocobalt(III)
- (iv) Sodium bis(thiosulphato)argentate(I) (4)

2. (i) Point out any two limitations of VB theory in explaining the properties of coordination complexes.

- (ii) In the compound $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ what is the oxidation state of the metal ion? What ions are expected to be formed in solution. (2+2)

3. (i) On the basis of CF theory draw energy level diagrams indicating the number of unpaired electrons in octahedral complex of d^4 ion when $\Delta_o > P$.

(ii) Account for the following.

- (a) Tetragonal elongation is much more common than tetragonal compression.
- (b) In the crystal of CuF_2 , all Cu – F distances are not equal. (3+2+2)

4. On the basis of VB theory answer the following questions for the complex



- (a) Predict the type of hybridization and geometry of the complex.
- (b) Calculate the value of μ_s for this complex. Draw the shape of the complex

(3+2)

5. (i) On the basis of CF theory predict whether the ion $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar or tetrahedral and show the distribution of d electrons of the central metal atom in the splitted d – orbitals.

(ii) Explain the origin of colour in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ using crystal field theory. (3+3)

6. For the $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, the mean pairing energy (P) is found to be $23,500 \text{ cm}^{-1}$. The magnitude of Δ_0 is $13,900 \text{ cm}^{-1}$.

(a) Sketch the CFT diagram of Cr^{2+} ion corresponding to high spin and low spin states.

(b) Calculate the CFSE of this complex ion corresponding to high spin and low spin states.

(c) Which state is more stable? Why? (8)

7. (i) Calculate the CFSE of d^7 (tetrahedral) ion (in terms of Δ_0 values).

(ii) Draw the structure of the following ligands clearly showing the donor atoms

(a) Dimethylglyoxime anion (b) EDTA^{4-} ion (2+4)
