

M.Sc. Final (Chemistry) Examination, Aug./Sept. 2008  
 Directorate of Correspondence Course  
 Analytical Chemistry – II  
 DECH EM : 2.01 – CHEMISTRY – V

Time : 3 Hours

Max. Marks : 75

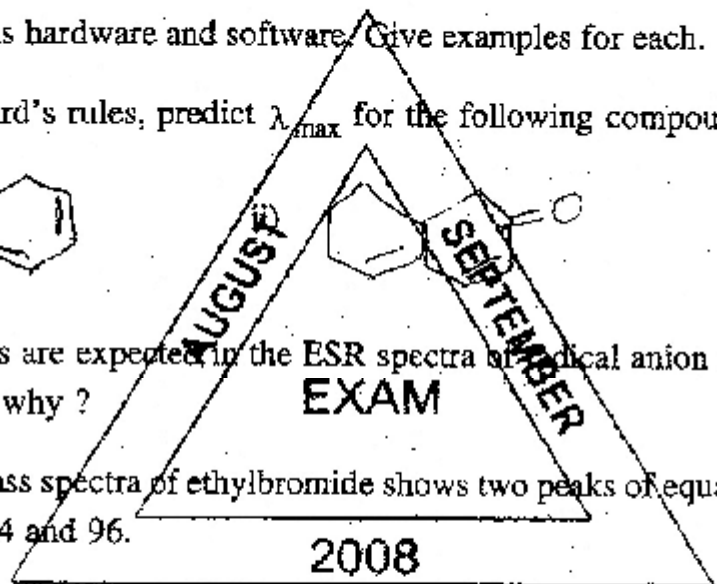
- Notes : 1) Answer any TEN questions from Part – A, TWO questions from Part – B and any THREE questions from Part – C.  
 2) Figures to the right indicate marks.

PART – A

(2×10=20 Marks)

1. Identify the symmetry elements in molecules  $H_2O$  and  $Cr(CO)_6$ .
2. Define the terms hardware and software. Give examples for each.
3. Using Woodward's rules, predict  $\lambda_{max}$  for the following compounds.



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4. How many lines are expected in the ESR spectra of radical anion derived from naphthalene and why?
  5. Explain why mass spectra of ethylbromide shows two peaks of equal intensity at  $m/e$  values of 94 and 96.
  6. Why are spectral interferences less severe in AAS than in FES?
  7. Define the terms : Singlet state, triplet state, quantum yield and intersystem crossing with respect to luminescence spectroscopy.
  8. NMR spectroscopy can be used to study the hydrogen bonding present in molecules. Explain.

P.T.O.



9. Explain the significance of molar extension coefficient.
10. What is an improper rotational axis? Give an example.
11. Distinguish between zero field and non-zero field splittings in ESR spectroscopy.
12. Classify the computers based on the operating principles.
13. How many signals would you expect in the proton NMR of  $\text{CH}_3\text{CH}_2\text{CH}_3$ ?
14. Write the principle of flame photometry.
15. What is the principle involved in mass spectrometry?

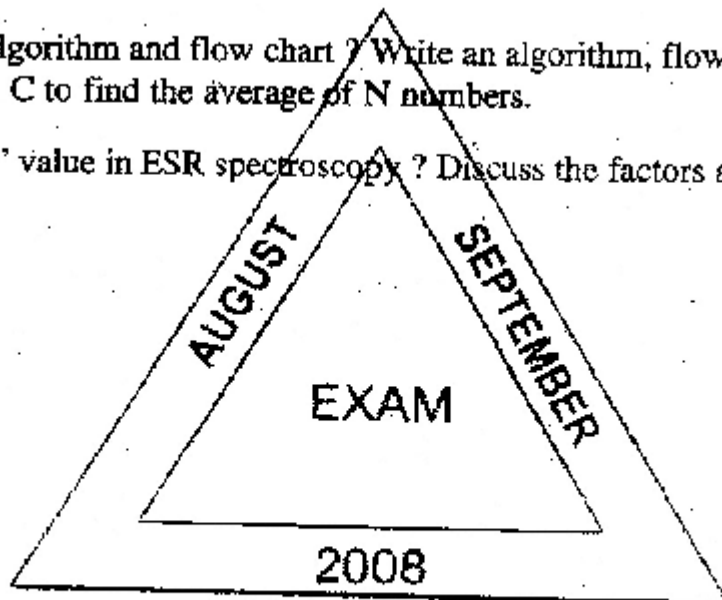
PART – B

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|--------|--|---|
| 16. a) | What are the effects of structural rigidity and paramagnetic impurities on fluorescence? | 4 |
| b)     | Explain the term hyper fine splitting with respect to ESR spectroscopy.                  | 4 |
| 17. a) | Derive an expression for fluorescence intensity and concentration of a compound.         | 4 |
| b)     | Compare atomic absorption spectroscopy with flame emission spectroscopy.                 | 4 |
| 18. a) | Give an account of the general rules useful for the interpretation of ESR spectrum.      | 4 |
| b)     | Explain <del>low level language and high level language.</del>                           | 4 |

PART – C

- |        |   |   |
|--------|---|---|
| 19. a) | Predict the high resolution $^1\text{H}$ – NMR spectrum of pure ethyl alcohol and explain the spin-spin splittings. | 7 |
| b)     | Discuss the mass spectral fragmentations of ethyl alcohol.  | 6 |

20. a) Outline the general analytical procedure for the determination of potassium in a sample of soil by flame photometric method. 7
- b) Construct the multiplication table for  $C_2V$  point group. 6
21. a) Draw the block diagram of a computer and discuss the function of each component. 7
- b) Draw a schematic diagram of a typical double-beam UV – vis spectrophotometer and explain the functions of various components. 6
22. a) What is Melasterty rearrangement ? Explain the fragmentation pattern of an organic compound involving this rearrangement with an example. 7
- b) State and explain Beer-Lambert Law. What are its limitations ? 6
23. a) What are algorithm and flow chart ? Write an algorithm, flow-chart and a program in C to find the average of N numbers. 7
- b) What is "g" value in ESR spectroscopy ? Discuss the factors affecting it. 6



M.Sc. Final Year (Chemistry) Examination, August/September 2008  
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 DE CHEM 2.02 : CHEMISTRY – VI  
 Inorganic Chemistry – II

Time : 3 Hours

Max. Marks : 75

- Notes : 1) Answer any TEN questions from Part – A. TWO questions from Part – B and any THREE questions from Part – C.  
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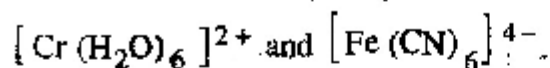
PART – A

(10×2=20)

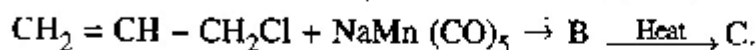
1. The common oxidation state of lanthanides is +3, but  $Ce^{4+}$  and  $Fu^{2+}$  are very stable. Explain why ?
2. Lanthanides have very low tendency to form complexes. Why ?
3.  $[CdCl_2 Br_2]^{2-}$  has no isomers, while  $[NiCl_2 Br_2]^{2-}$  has two isomers. What are the shapes of these complex ions ?
4. Tetrahedral complexes are more intense in colour compared to octahedral complexes. Why ?
5. Ligand substitution in square-planar complexes are faster than those in the octahedral complexes. Explain.
6. What are the isomerization and racemization reaction ?
7. What are coenzymes and prosthetic groups ?
8. Explain photoaquation with an example.
9. What is Bohr effect ? Explain.
10. Give biological importance of  $Ca^{2+}$  and  $Mg^{2+}$  ions.
11. Derive the ground state term symbols for  $Ni^{2+}$  and  $Mn^{3+}$  ions. Deduce their ground state J values.

P.T.O.

12. Calculate the spin-only magnetic moment value for the complexes



13. Identify the products in following reactions and write the structures.



14. What is reductive elimination? Point out its importance in a catalytic reaction.

15. Manganese carbonyl exists as  $\text{Mn}_2(\text{CO})_{10}$  but not as  $\text{Mn}(\text{CO})_5$  or  $\text{Mn}(\text{CO})_6$ . Explain.

### PART - B

16. a) Give an evidence for covalency in metal complex.

b) What are limitations of CFT? (4+4)

17. a) What are stepwise and over-all stability constants of complexes? Explain.

b) What are shift reagents? Explain their applications. (4+4)

18. a) Give a comparative account of relative stabilities of oxidation states, complex formation and spectral characteristics of titanium sub-group.

b) Explain the bonding and magnetic properties of  $[\text{FeF}_6]^{3-}$  and

$[\text{Fe}(\text{CN})_6]^{3-}$  complexes using VBT. (4+4)

### PART - C

19. a) Define the term stereochemical non-rigidity. How it can be detected?

b) What is meant by absolute configuration of metal complexes? How is it determined?

c) Set up the Orgel diagram for a complex where the metal has  $d^3$  electron configuration. Explain the salient features and limitations of this diagram.

(4+4+5=13)

20. a) Discuss the chemistry of hydrogenation of olefins using Wilkinson's catalyst.
- b) Give the basic principles of MOT of coordination compounds. Set up the MO energy diagram of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  involving  $\sigma$ -bonding only. (6+7=13)
21. a) Describe the role of photosynthesis – I and photosynthesis – II in cleavage of water.
- b) What are electron transfer reactions? Discuss the outer-sphere electron transfer reactions with example. (6+7=13)
22. a) Explain the structure of hemoglobin and myoglobin that enable them to transport molecular oxygen in biological system.
- b) Give the application of Mossbauer spectroscopy in the determination of structure of low spin and high spin ion complexes. (7+6=13)
23. a) Which compound would you expect to be more stable,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  or  $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$ . Give a possible explanation for the difference in the terms of simple bonding concepts.
- b) Discuss the determination of stability constant of complexes by spectrophotometric method. (7+6+13)

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 DE CHEM – 2.03 ORGANIC CHEMISTRY

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Notes : 1) Answer any TEN questions from Part – A, TWO questions from Part – B and any THREE questions from Part – C.

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## PART – A

Answer any TEN of the following :

(2×10=20)

1. How are cycloaddition reactions classified ?
2. Point out the salient features of sigmatropic rearrangement.
3. Write the structures of any two heterocyclic bases present in RNA and DNA.
4. Write Beckmann rearrangement with suitable example.
5. What isoprene rule ? Give an example.
6. What is the role of t-RNA in protein synthesis ?
7. Write a note on bonding and antibonding orbitals.
8. What are nucleotides and nucleosides ? Give an example for each.
9. What is Barton's reaction ? Give an example.
10. Write a note on chemical shift in NMR spectroscopy.
11. Write the mechanism for the Mannich reaction by taking suitable example.
12. What is an electrophilic rearrangement reaction ? Give an example.
13. Give the mechanism for Oppenauer oxidation.
14. Mention the range of stretching frequencies for – COOH group.
15. What are diens and dienophiles ? Give example for each.

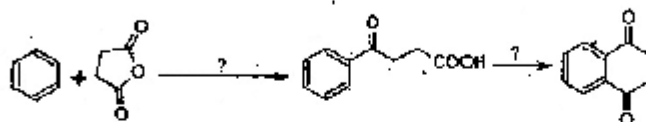
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## PART - B

Answer any two of the following :

(4+4=8×2=16)

16. a) Predict the suitable reagents and condition for the following synthesis.



- b) Give the mechanism for Michael addition and Birch reduction.

(4+4=8)

17. a) Write the general methods of structural elucidation of Morphine.

- b) Explain the mechanism of Friedel-Craft's alkylation with suitable example.

Comment on the role of anhydrous aluminum chloride and discuss the demerits of this reaction.

(4+4=8)

18. a) Point out the salient features of electrocyclic reactions. Electrocyclic reactions are compatibly stereoselective. Justify this statement by using appropriate example.

- b) Name the reaction and write the product with mechanism.

(4+4=8)



## PART - C

Answer any three questions of the following :

19. a) Discuss with mechanism

- i) Wittig reaction
- ii) Mannich reaction

- b) Define Woodward Hoffman rules for electro cyclic and cycloaddition reactions.

- c) Mention the different types of RNA and explain their role in the synthesis of protein.

(5+3+5=13)

20. a) What is Sharpless asymmetric epoxidation ? Give any one of its synthetic application with mechanism.
- b) How many types of protons are present in ethyl alcohol ? Explain by using a neat PMR spectrum.
- c) Explain internal conversion, intersystem crossing, fluorescence and phosphorescence by using a neat labelled Jablonski diagram. (4+4+5=13)
21. a) Write the primary structure of DNA and explain the importance of AT and GC pairing.
- b) Explain Benzil-benzilic acid rearrangement with suitable example.
- c) What is Fries rearrangement ? Give its any two synthetic applications with mechanism. (5+3+5=13)
22. a) Explain Norrish Type-I and Norrish Type-II reactions by taking suitable examples.
- b) Reaction between n-propyl chlorides and benzene in presence of Lewis acid results in the formation of isopropyl benzene. Give reason.
- c) Elucidate the structure of menthol. (5+3+5=13)
23. a) Explain the mechanism of Stork enamine reaction by taking a suitable example.
- b) Write the range of stretching frequencies for different functional groups present in phenol, nitrobenzene and benzonitrile.
- c) Explain Claisen and Cope rearrangement reactions by taking suitable examples for each. (4+4+5=13)

2008

M.Sc. II Year (Chemistry) Examination, August/September 2008  
Directorate of Correspondence Course  
DECHEM – 2.04 : PHYSICAL CHEMISTRY

Time: 3 Hours

Max. Marks: 75

- Notes :* 1) Answer **any TEN** questions from Part A, **TWO** questions from Part B and **any THREE** questions from Part C.  
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PART – A

(10×2=20)

1. What are the special features of a reference material used in DTA ? Give an example.
2. Distinguish between DTA and TGA.
3. What is the principle involved in DSC ? Explain.
4. Differentiate between inert and labile complexes.
5. Explain trans effect in kinetics of complex reactions.
6. State and explain second law of thermodynamics.
7. How polymers are classified ?
8. Explain the physical significance of entropy.
9. Calculate the entropy of mixing of one mole of oxygen gas and two moles of hydrogen gas assuming that no chemical reaction occurs and the gas mixture behaves ideally.
10. What is mass defect ?
11. State Born-Oppenheimer approximation.

P.T.O.



12. Distinguish between fundamental and overtone bands in IR spectroscopy.
13. Explain why the symmetric stretching vibration of  $\text{CO}_2$  is IR inactive but Raman active.
14. Differentiate Stokes Raman lines from antistokes Raman lines.
15. Explain nuclear fusion. Give example.

## PART - B

16. a) What is meant by nuclear fission ? Explain with suitable examples. 4
- b) Explain the term radiolysis. Discuss the mechanism involved in the radiolysis of water. 4
17. a) Explain base hydrolysis of Cr (III) complexes. 4
- b) Write a note on ligand displacement reactions taking an example. 4
18. a) Explain the terms, packing fraction and nuclear density. 4
- b) Give a brief description of the nuclear shell model. 4

## PART - C

19. a) Explain the features of thermogram of copper sulphate penta hydrate. 4
- b) Describe the factors influencing the TG results. 5
- c) Give a brief note on "thermometric titrations". 4
20. a) What is meant by efficiency of an heat engine ? Derive an expression for the same. 7
- b) Explain what is meant by change of entropy ( $\Delta S$ ) of a system. Show that

$$\Delta S = \frac{q_{\text{rev}}}{T} .$$

6

21. a) What is meant by number-average molar mass and mass-average molar mass of a polymer ? 4
- b) Describe the viscosity method for the determination of molar mass of macromolecules. 6
- c) Write a note on Nylon and Terylene polymers. 3
22. a) Show that for a rigid diatomic rotor, the moment of inertia is given by  $I = \mu r^2$ . 4
- b) Give an account of rotational spectra of diatomic molecules. 5
- c) Explain the terms zero point energy and anharmonicity constant. 4
23. a) Discuss the vibration-rotation spectra of diatomic molecules. 6
- b) The fundamental vibration frequency of HCl is  $2,890 \text{ cm}^{-1}$ . Calculate the force constant of the molecule. The atomic masses are  $^1\text{H} = 1.673 \times 10^{-27} \text{ kg}$ ;  $^{35}\text{Cl} = 58.1 \times 10^{-27} \text{ kg}$ . 3
- c) Write the applications of IR spectroscopy. 4

