Final Year M.Sc., Degree Examinations

September / October 2015

(Directorate of Distance Education)

CHEMISTRY

PAPER: DECHEM 2.01: ANALYTICAL CHEMISTRY – V

Time: 3hrs.] *[Max. Marks: 75/85*

Note:

i) ***Scheme : 75 Marks : Answer PART – A, PART – B and PART – C***

ii) ***Scheme : 85 Marks : Answer PART – A, PART – B, PART – C and PART – D.***

PART – A

I. Answer any TEN of the following: 10 x 2 = 20 Marks

a) In C_{2V} point group show that $C_2(Z)$, $\sigma XZ = \sigma YZ$.

b) Identify the symmetry elements in the following molecules: H_2O and $Cr(CO)_6$.

c) Distinguish between hard ware and soft ware.

d) Classify the computers based on the operating principles.

e) Acidic solution of triethylamine shows no absorption due to $n \rightarrow \pi*$ transition. Explain.

f) Explain the NMR spectrum of [18] annulene and give suitable explanation.

g) What are the characteristics of electromagnetic radiation?

h) A dichloro hydrocarbon with molecular weight 113 shows three molecular ion peaks at 116, 114 and 112 in its mass spectrum. Why?

i) Define the terms: Fluorescence, singlet state, triplet state and intersystem crossing.

j) Direct interference is far less in AAS and FES. Give reasons.

k) What is meant by hyperfine splitting in ESR spectroscopy?

l) What is improper rotational axis? Give an example.

m) Mention the functions of flame in flame photometry.

n) What is meant by fluorescent quenching?

o) A compound $C_8H_{12}O_4$ is an ester and gives the following NMR spectral data: $\delta = 6.75(s,1H)$; $\delta = 4.15(q,2H)$; $\delta = 1.25(t,3H)$. Predict its structure.

Contd..... 2

PART – B

II. Answer any TWO questions: 2 x 8 = 16 Marks

2. a) Write the schematic representation of a computer system and label the various components. Describe the functioning of a central processing unit and output.

   b) Describe the mechanism of Mc-Lafferty rearrangement with suitable examples. (5 + 3)

3. a) What is 'g' value in ESR spectroscopy? Discuss the factors affecting it.

   b) Construction the multiplication table for C_{2V} point group. (5 + 3)

4. a) Discuss how mass spectrometry is helpful in providing molecular mass, formula and structural information of organic compounds from fragmentation patterns.

   b) How do temperature, pH, presence of oxygen and solvent polarity affect the intensity of luminescence. (5 + 3)

PART – C

III. Answer any THREE of the following questions: 3 x 13 = 39 Marks

5. a) Discuss Mulliken symbolism rules for the designation of non-degenerate irreducible representations in character table.

   b) Sketch the $^1H\ NMR$ spectrum of the following molecules and assign the peaks: *i*) $CH_3CHOHCH_3$ and *ii*) $CH_3CH_2CH_2CHO$

   c) Describe premix or laminar – flow burner used in AAS or FES. (5 + 5 + 3)

6. a) Briefly discuss about the various types of interferences encountered in flame photometry.

   b) Sketch and explain the salient features of the ESR spectra of i) Methyl radical and ii) copper bis salicylaldoxime complex.

   c) Explain chemical shift? Discuss the factors influencing the chemical shift. (5 + 5 + 3)

7. a) Discuss the effect of conjugation on UV-Visible spectra with suitable example.

   b) Establish the relation between fluorescence intensity and concentration of fluorescing substance. Why is the linearity lost at higher concentration?

   c) How do you represent groups using matrices? (5 + 5 + 3)

8. a) What is flow chart? What are the various symbols used to draw a flow chart? Explain with an example.

   b) Explain zero fields splitting and Kramer's degeneracy in ESR spectroscopy.

   c) Discuss the methodology involved in the simultaneous determination of Cu and Ni a mixture by spectrophotometry. (5 + 5 + 3)

Contd..... 3

9. a) Draw the schematic diagram of NMR instrument and label the components and explain its working.

   b) Give brief account of electron impact ionization and chemical ionization as ionization source in mass spectrometry.

   c) Identify the symmetry elements present in the following molecules and assign the appropriate point groups:
   i) H_2O_2 (cis, trans), ii) BF_3 iii) B_2H_6 and iv) $PtCl_4$ (5 + 5 + 3)

PART – D

Answer any ONE of the following questions: 1 x 10 = 10 Marks

10. a) What is an algorithm? Write the basic programme for the calculation of entropy and enthalpy of chemical reaction.

    b) Draw a labeled diagram of double focusing mass spectrometer and explain the function of each component. (5 +5)

11. a) Explain the basic difference between atomic emission and atomic absorption spectroscopy. Describe the quantitative relationships that form the basis of analysis by the two techniques.

    b) Explain the selection rules related to ESR spectroscopy. Show that when an electron spin is coupled with nuclear spin of a proton (I = ½) give a doublet with relative intensity of 1:1. (5 + 5)

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CHEMISTRY

PAPER: DECHEM 2.02: INORGANIC CHEMISTRY – VI

Time: 3hrs.] *[Max. Marks: 75/85*

Note:

i) ***Scheme : 75 Marks : Answer PART – A, PART – B and PART – C***

ii) ***Scheme : 85 Marks : Answer PART – A, PART – B, PART – C and PART – D.***

PART – A

I. Answer any TEN of the following: 10 x 2 = 20 Marks

a) Why d-block elements exhibit different oxidation states? Explain.

b) Define 18-electron rule with an example.

c) What is lanthanide contraction?

d) Why lanthanides and actinides are placed separately in the periodic table?

e) Name two effects of lead toxicity on human beings.

f) What are bridging ligands? Give examples.

g) Differentiate between ferro and anti-ferromagnetic materials.

h) Define isomer shift.

i) What are charge-transfer transitions? Mention their classification.

j) What are metal-nitrosyl compounds? Give examples.

k) Write the importance of calcium in biological systems.

l) What is water gas shift reaction?

m) Give the classification of nucleus based on charge distribution.

n) Explain Bohr effect.

o) What is spectrochemical series?

PART – B

II. Answer any TWO questions: 2 x 8 = 16 Marks

2. a) What are metal carbonyls? Discuss the preparation and structure of cobalt carbonyls.

b) Explain the separation of lanthanides by ion-exchange method. (4 + 4)

Contd..... 2

3. a) Discuss stepwise and overall stability constants of complexes.

   b) Briefly discuss the effect of temperature on magnetic properties. (4 + 4)

4. a) Discuss the Mossbauer spectrum of Prussian blue.

   b) Give the classification and structures of Fe-S proteins. (4 + 4)

PART – C

III. Answer any THREE of the following questions: 3 x 13 = 39 Marks

5. a) Explain the use of lanthanides as shift reagents.

   b) Discuss various types of reactions involved in the synthesis of co-ordination compounds?

   c) Using Orgel diagram explain the electronic spectra of $[V(H_2O)_6]^{3+}$. (4 + 4 + 5)

6. a) Briefly explain the determination of composition of Fe-1, 10-phenanthroline complex by spectrophotometry.

   b) Discuss the magnetic properties of $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[CoCl_4]^{2-}$.

   c) Explain the determination of magnetic susceptibility of a complex using Gouy method. (4 + 4 + 5)

7. a) Briefly discuss the factors affecting the metal-metal bonding.

   b) Write the mechanism of transport of oxygen by haemoglobin.

   c) Discuss the mechanism involved in Wacker process. (4 + 4 + 5)

8. a) With the help of an example, explain how structural information can be obtained from NQR spectrum.

   b) Discuss the synthesis, structure and bonding in ferrocene.

   c) What is Fisher-Tropsch reaction? Explain the mechanism of formation of hydrocarbons. (4 + 4 + 5)

9. a) Discuss the effect of magnetic field on Mossbauer spectra.

   b) List out the IUPAC rules for the nomenclature of co-ordination compounds.

   c) Discuss the isomerism observed in metal complexes with coordination number 6. (4 + 4 + 5)

PART – D

Answer any ONE of the following questions: 1 x 10 = 10 Marks

10. a) Write short notes on
    i) Spectral properties of actinide complexes
    ii) Irving-Williams series.

Contd..... 3

b) Differentiate between

i) Complementary and non-complementary electron transfer reactions.

ii) Homogeneous and heterogeneous catalysis (5 +5)

11. a) Discuss the following:

i) Importance and working of sodium/potassium pump.

ii) Antiferromagnetic coupling.

b) Explain the following:

i) Fluxional behavior of organometallic compounds

ii) Nitrogen fixation

(5 +5)

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CHEMISTRY

PAPER: DECHEM 2.03: ORGANIC CHEMISTRY – VII

Time: 3hrs.] *[Max. Marks: 75/85*

Note:

i) ***Scheme : 75 Marks : Answer PART – A, PART – B and PART – C***

ii) ***Scheme : 85 Marks : Answer PART – A, PART – B, PART – C and PART – D.***

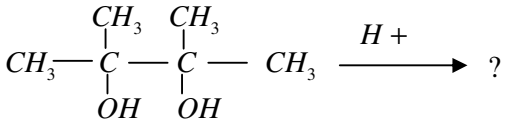
PART – A

I. Answer any TEN of the following: 10 x 2 = 20 Marks

a) What are the source of energy of activation in pericyclic reactions.

b) Give an example for sigmatropic rearrangement.

c) Complete the rearrangement and mention the name in the following



d) Give any two applications of chichibabin reaction in organic synthesis.

e) Mention the names of two kinds of nucleic acids found in cells.

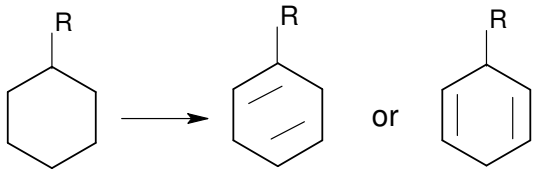
f) What are chromophore?

g) Mention any four categories of terpenes.

h) List out the different modes of stretching and bending vibrations.

i) What is the standard used in NMR and why?

j) Complete the following reaction & name it.



k) Give an example for electro cyclic reaction.

l) What is a coupling agent?

Contd..... 2

m) Define hypsochromic shift.

n) What is photo reduction?

o) Mention the uses of morphine and identify the class of alkaloid it belongs.

PART – B

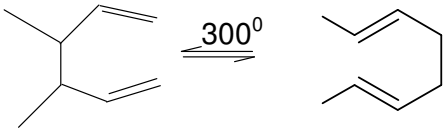
II. Answer any TWO questions: 2 x 8 = 16 Marks

2. a) What are the three features that are inter related in pericyclic reactions.

   b) Construct the λ molecular orbitals of Ethylene. (4 + 4)

3. a) Explain Beckmann rearrangement with Mechanism.

   b) Identify and write the mechanism of the following reaction. (4 + 4)



4. a) With a suitable example give acylation by Friedel-Crafts reaction.

   b) Aldehydes and ketones can be reduced by Wolf-Kishner reduction. Justify with an example. (4 + 4)

PART – C

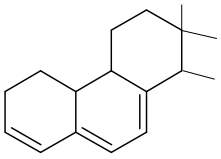
III. Answer any THREE of the following questions: 3 x 13 = 39 Marks

5. a) Summerise the types of excitation given by organic compounds.

   b) Discuss the HOMO-LUMO transition in 1, 3, butadiene.

   c) What is Paterno-Buchi reaction? Discuss its mechanism along with the stereo chemical consequences. (4 + 4 + 5)

6. a) Calculate the λ_{max} of the compound



   b) Brief the factors that influence chemical shift.

   c) How many types of orientation takes place when a proton is placed via magnetic field. ^{13}C is NMR active while ^{12}C is not. Justify. (4 + 4 + 5)

7. a) Give a method for the asymmetric epoxidation of allylic alcohols.

   b) Explain how Wittig reagent is useful in organic synthesis.

   c) With an example give the mechanism of Reimer – Tiemann reaction. (4 + 4 + 5)

Contd..... 3

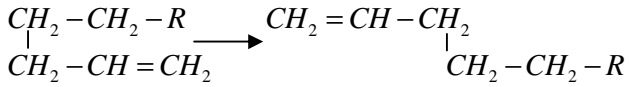
8. a) What are terpenes? How they are classified?

   b) Give an account of structural elucidation of morphine.

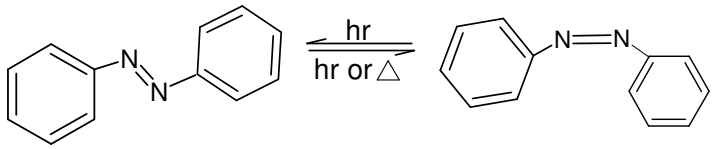
   c) Brief the salient feature of Genetic code. (4 + 4 + 5)

9. a) What is a photo sensitizer? List the useful features.

   b) Define sigmatropic rearrangement. Identify the class of sigmatropic rearrangement in the following



   c) Name the reaction given below



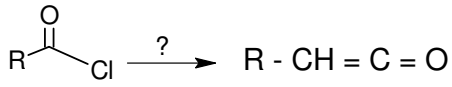
   and explain its synthetic utility. (4 + 4 + 5)

PART – D

Answer any ONE of the following questions: 1 x 10 = 10 Marks

10. a) i) State Woodward-Hoffmann rule for electrocyclic thermal reactions.
    ii) Brief the photochemical excitation of a molecule

    b) i) Complete the following reaction and name it. (2 + 3)



    ii) Differentiate Lossen & Hofmann rearrangements. (2 +3)

11. a) i) What do you mean by Finger print region?

    ii) Give one example for oppenauer oxidation and mechanism. (2 + 4)

    b) What is a nucleoside? Give examples. (4)

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CHEMISTRY

PAPER: DECHEM 2.04: PHYSICAL CHEMISTRY – VIII

Time: 3hrs.] *[Max. Marks: 75/85*

Note:

i) ***Scheme : 75 Marks : Answer PART – A, PART – B and PART – C***

ii) ***Scheme : 85 Marks : Answer PART – A, PART – B, PART – C and PART – D.***

PART – A

I. Answer any TEN of the following: 10 x 2 = 20 Marks

a) Explain the types of recording thermo balances for TGA.

b) Explain trans effect.

c) Explain the merits of liquid drop model.

d) What is binding energy? What is its effect on nuclear stability?

e) What are the limitations of the first law of thermodynamics?

f) What is the physical significance of entropy?

g) What are graft polymers? Explain with examples.

h) Explain the concept of molar masses of polymers.

i) What is meant by tacticity in polymers? Explain with suitable examples.

j) Why rate of reaction decreases with increase of charge on the complex?

k) Explain fission chain reaction.

l) What is meant by efficiency of heat engine?

m) Distinguish between IR and Raman Spectroscopy.

n) What is meant by zero point energy?

o) What are the factors affecting group frequencies and band shapes?

PART – B

II. Answer any TWO questions: 2 x 8 = 16 Marks

2. a) Write a note on thermometric titrations.

b) Explain the working principles of DSC. (4 + 4)

Contd..... 2

3. a) Describe the factors contributing the stability of nucleus.

   b) What are the criteria for reversible and irreversible processes? (4 + 4)

4. a) Give a brief classification of polymers.

   b) Give the preparation and properties of Terylene. (4 + 4)

PART – C

III. Answer any THREE of the following questions: 3 x 13 = 39 Marks

5. a) Describe the multiple heating rate method in TGA? What are the advantages of this method?

   b) What are simultaneous DTA – TGA curves? What are the factors affecting the DTA results? (7 + 6)

6. a) Explain the principle and working of Fricke Dosimeter.

   b) Write a note on Radiolysis of water.

   c) Describe Maxwells thermodynamic relations. (5 + 4 + 4)

7. a) Give the mechanism of base hydrolysis of octahedral complex.

   b) With suitable examples explain the factors affecting the vibrational frequencies. (8 + 5)

8. a) How do you determine the molar masses of polymers by light scattering method?

   b) Explain the derivation of entropy from Carnot cycle. (7 + 6)

9. a) Explain the 3^{rd} law of thermodynamics.

   b) Using rotational energy expression obtain energy level diagram of a rigid rotor. Explain the position of spectral lines.

   c) What are overtones and combination bands-explain. (4 + 5 + 4)

PART – D

Answer any ONE of the following questions: 1 x 10 = 10 Marks

10. a) Discuss the application of IR spectroscopy of organo transition complexes and co-ordination compounds.

    b) Explain the preparation and application of Nylon. (6 +4)

11. ***Write short notes on:*** (10)

    a) Anharmonicity constant
    b) Sampling technique for IR spectra
    c) Degree of polymerization
    d) Determination of H-bonding by IR spectra.

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