Exam Code: 220401 **Paper Code: 1221**
(20)

Programme: Master of Science (Chemistry)
Semester-I

Course Title: Ligand Field Theory

Course Code: MCHL-1081

Time Allowed: 3 Hours **Max Marks: 80**

Note: Students are required to attempt five questions selecting one question from each section. The fifth question may be attempted from any section. Each question carries equal marks.

Section A

1. (a) Determine the symmetry point groups and symmetry operations of given molecules:
   - a) CH_3Cl
   - b) BrF_5
   - c) C_2H_6
   - d) H_3PO_4 8

(b) Discuss the qualitative spliting of P and D orbitals in tetrahedral complexes. 8

2. (a) For NH_3 molecule the reducible representation is given by :-

C3v	E	$2C_3$	$3\sigma v$
ζ	9	-1	3

Find the irreducible representations 8

b) Construct a character tables for C2v point group by taking H_20 as an example. 8

Section B

3. Discuss Sigma (σ) and pi (Π) bonding in Square Planar complexes by constructing a composite molecular orbital diagram for $[PtC14]^{2-}$ 16

4. (a) Write down all the energy terms that are possible for a free gaseous atom having configuration (i) $3d^4\ 4s^1$ (ii) $2s^2 2p^4$ 8

(b) Discuss spin orbit coupling parameters (λ) and (ξ) for ^3F terms of d^2 configuration of metal ion and their energy separation between different j states.

8

Section C

5. (a) Draw and discuss the qualitative corelation diagrams for d^2 octahedral and d^2 tetrahedral complexes. 8

   (b) The three absorption bands for $[Cr(H_2O)_6]^{3-}$ are observed in an electronic spectrum at 17400 cm_{-1}, 24700 cm^{-1} and 37800 cm^{-1}. Determine the values of B' and Δ_0 8

6. (a) Give an evaluation of strong crystal field terms of d^2-configuration in octahedral crystal field theory. 8

   (b) What is quenching of orbital angular momentum and discuss its effect on magnetic properties of A, E and T terms of metal complexes. 8

Section D

7. Discuss the utility of orgel diagrams. What are their limitations. Draw orgel diagrams for d^n configurations of metal ions in their transition metal complexes. 16

8. (a) Write short notes on
   (i) Spectrochemical series
   (ii) Nephelauxetic series

   Tunabe Sugano diagrams 8

(b) Give comments on spectra of [Mn $(H_2O)_6]^{2+}$ and $CuSO_4.5H_2O$. 8

Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		(z^2 , x^2-y^2)
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Exam Code: 220401 **Paper Code: 1222**
(20)

Programme: Master of Science (Chemistry)
Semester-I

Course Title: Organic Reaction Mechanism-I

Course Code: MCHL-1082

Time Allowed: 3 Hours **Max Marks: 80**

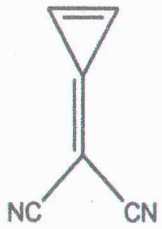
Note - Attempt five questions in all, selecting at least one question from each section. The fifth question may be attempted from any section. Each question carries 16 marks.

Section-A

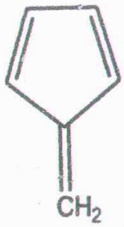
1. (a) What do you understand by racemisation and autorecamisation? (8)

   (b) Assign the following compounds whether they are aromatic/ non aromatic / antiaromatic and justify the reason? (8)

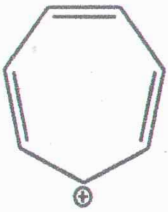
(i)



(ii)



(iii)



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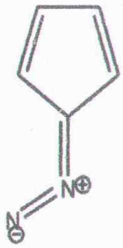

2. (a) Describe asymmetric synthesis. Also discuss enantioselective and diastereselective synthesis with example? (10)

   (b) Explain PMO theory with example of ethylene. (6)

Section-B

3. (a) Explain the methods to isolate and detect carbocation? Give suitable examples. (10)

   (b) Discuss neighbouring group participation by pi and sigma bonds? (6)

4. (a) Explain SET mechanism in detail for aliphatic nucleophilic substitution. (8)

   (b) Discuss isotope effects in reaction mechanism. (8)

Section-C

5. (a) Explain effect of leaving group, substrate structure and solvent polarity in reactivity of aliphatic nucleophilic substitution reactions. (10)

   (b)Explain the reaction of sulphur ylides with alkenes and unsaturated systems. (6)

6. (a) Give detail overview of SE2 (front and back) and SEi mechanism. Explain in detail with mechanism. (10)

   (b) Explain nucleophilic substitution at allylic and vinylic carbon. (~~10~~)(6)

Section-D

7. (a) Give brief overview of Fries rearrangement with example. (10)

   (b) Explain Von Richter and Smiles rearrangement. (6)

8. (a) Discuss the reactivity effect of substrates, leaving group and nucleophile in SNAr reactions?

(10)

(b) Discuss steric effect and ortho-para ratios in aromatic electrophilic substitution.

(6)

Exam Code: 220401 **Paper Code: 1223**

Programme: Master of Science (Chemistry)

Semester: I

Course Title: Physical Chemistry-Thermodynamics

Course Code: MCHL-1083

Time Allowed: 3 hours **Max. Marks: 80**

Note: Attempt five questions in all, selecting atleast one question from each section. The fifth question may be attempted from any section. Each question carries 16 marks.

Section A

1. (a) What do you mean by partial molar properties? Give two methods to determine the partial molar properties?

(b) State Zeroth, first, second and third law of thermodynamics in detail. (8, 8)

2. (a) Define the terms fugacity and activity. How are these related to chemical potential?

(b) How fugacity can be determined? (8, 8)

Section B

3. (a) Derive an expression for Debye-Huckel theory for strong electrolytes.

(b) Using Debye-Huckel theory, prove that how mean ionic activity coefficient relates to the ionic strength. (8, 8)

4. (a) Using Lagrange's method of undetermined multipliers, derive an expression for Maxwell-Boltzmann statistics.

(b) What are the different methods for the determination of partial molar volume. Deduce an expression for calculating partial molar volume by INTERCEPT method. (8, 8)

Section C

5. (a) What do you mean by partition function? Derive the value of the Internal energy in terms of partition function.

(b) Derive an expression for the molecular vibrational partition function of an ideal diatomic gas. (8, 8)

6. (a) Discuss Fermi Dirac statistics. Give its applications for metals.

(b) Derive an expression for the equilibrium constant of an ideal gaseous mixture in terms of partition functions of the reactants and products. (8, 8)

Section D

7. (a) Mention and prove Prigogine's principle of minimum entropy production.

(b) Derive the law of Onsager reciprocal relation. (8, 8)

8. (a) Define the terms: Flux, driving force, transport coefficient in detail with examples.

(b) Write short notes on the following:

I. Entropy production in open systems.

II. Electrokinetic effects in irreversible processes. (8, 8)

Exam Code: 220401 **Paper Code: 1224**

Programme: Master of Science (Chemistry) Semester - I

Course Title: Spectroscopy-A: Techniques for Structure Elucidation of Organic Compounds

Course Code: MCHL-1084

Time Allowed: 3 Hours **Max Marks: 80**

Note: -- Note: Attempt five questions in all, selecting atleast one question from each section. The fifth question may be attempted from any section.

SECTION-A

1. (a) Which compound is preferred as a standard in NMR spectroscopy and why. Also explain the number of signals observed in this standard? Explain instrumentation and working of Fourier transformation - NMR technique. (8)

(b) Write the principle of NMR spectroscopy and also describe the conditions necessary for the nuclei to be NMR active? (8)

2. (a) Predict the complete NMR spectrum of 3-Aminopentanol and 3,3-Diethylpentane. (8)

(b) What are lanthanide shift reagents. Explain the application of structure elucidation of simple organic molecules using Lanthanide shift? (8)

SECTION-B

3. (a) Describe the various factors affecting the absorption maxima in UV Visible spectroscopy. Explain why Aniline absorbs at 280 nm, but in acidic medium the main absorption band is seen at 203 nm? (8)

(b) Explain the conditions required for McLafferty rearrangement to occur in mass spectroscopy citing suitable example? (8)

4. (a) Explain Lambert- Beer law and Franck Condon principle and describe their relevance in UV Visible spectroscopy? (8)

(b) Describe some important features of mass spectra of aromatic hydrocarbons and amines with suitable example? (8)

SECTION-C

5. (a) Write a short note on Finger print region and explain the concept of Fermi Resonance with relevant example? (8)

(b) Define Infra-red spectroscopy. Describe the various molecular vibrations in the technique. What is the major requirement for Infra-red absorption to occur? (8)

6. (a) How will you study reaction kinetics by Infra-red spectroscopy. Also discuss the various types of stretching and bending vibrations which arise in aromatic compounds in their Infra-red spectrum? (8)

(b) Distinguish between the following pairs of compounds with the help of infra-red spectroscopy: (8)

(i) Ethanol and Diethyl ether (ii) Propanol and Propanone
(iii) Ethanol and Ethyl amine (iv) cis and trans Cinnamic acid

SECTION-D

7. (a) An organic compound with molecular formula C_4H_9NO gives the following spectral data
UV: λ_{max} 220 mμ ε_{max} 63.
IR: 3500 (m), 3402 (m), 2960 (w), 1682 (s), 1610 (s).
NMR: 9.0 τ doublet (23.2 squares); 7.9 τ septet (3.8 squares); 1.92 τ singlet (7.5 squares)
Determine the structural formula of the compound. (8)

(b) An organic compound A (molecular formula $C_9H_{10}O_2$) exhibit the following spectral data
UV: λ_{max} at 268 nm, 264 nm, 262 nm, 257 nm.
IR: 1745 (s), 1225 (br, s), 749 (s), 697 (s).
^{1}H NMR: 1.96 (3H, singlet); 5.00(2H, singlet); 7.22(5H, singlet)
Determine the structure of the compound A. (8)

8. (a) An organic compound with molecular formula C_7H_8Br gives primary alcohol on hydroboration. The spectral data of the compound is given below:
UV: λ_{max} 282 mμ ε_{max} 450.
IR: 3033 (m), 1646 (m), 1602 (m), 1582 (v), 820 (s) and 710 (m).
NMR: 2.62-2.74τ (asymmetrical pattern, 18.9 squares); 4.30τ (double doublet, 4.7 squares); 3.30τ (double doublet, 4.9 squares); 4.86τ (double doublet, 5.0 squares)
Determine the structure of the compound. (8)

(b) An organic compound with molecular weight 130 shows the following bands in the infra-red spectrum:
(i) 3082-2860 (m), (ii) 1825 (s), (iii) 1755 (m) and 1455 (m).
In its NMR spectrum, two signals result (i) Triplet 8.7 τ (7.3 squares, J = 7.1 cps) (ii) quartet 7.8 τ (4.9 squares, J = 7.1 cps).
Determine the structure of the compound. (8)

Exam Code: 220401 **Paper Code: 1225**

Programme: Master of Science (Chemistry) Semester: I

Course Title: Computer for Chemists

Course Code: MCHM-1135

Time Allowed: 3 Hours **Max Marks: 20**

Note: Attempt five questions in all, selecting atleast one question from each section. The fifth question may be attempted from any section. Each question carries 4 marks.

Section – I

1. Explain identifiers in C. What are the rules to write identifiers in C? 4
2. Explain Data types available in C. 4

Section – II

3. Explain logical and relational operators in C with programming examples. 4
4. Explain if else statement and nested if statement with programming examples in C. 4

Section – III

5. Explain for loop and do while loop with programming examples. 4
6. What do you mean by functions? Write a program in C demonstrating the role of function. 4

Section – IV

7. Write a program to sort an array in increasing order. 4
8. Explain Arrays. How they are useful? 4
