Exam Code: 210401 **Paper Code: 8361 (50)**

Programme: M. Sc. (Chemistry) Sem-I

Course Title: Ligand Field Theory

Course Code: MCHL-1081

Time Allowed: 3 Hours **Max Marks: 40**

Instructions:

Attempt five question in all selecting at least one question from each section. The Fifth question may be attempted from any section.

Unit-1

1. a) What are Symmetry elements. Also discuss their types. 4

b) How is Group theory helpful in understanding σ (Sigma) and π (pi) Bonding in square planar Transition metal complexes. 4

2. a) What are the rules, that help in determination of irreducible representation of any symmetry point group. 4

b) Construct a character tables for C_{2v} . Point group by taking H_2O as an example. 4

Unit-2

3. Discuss Sigma (σ) and pi (π) bonding in square planar complexes by constructing a composite molecular orbital diagram for $[PtCl_4]^{2-}$ 8

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

   b)What are electron repulsion parameter. Give their types. 4

Unit-3

5. a) Give an evaluation of strong crystal field term of d^2 – configuration in tetrahedral crystal field wing group Theory. 4

   b) How the selection rules are relaxed in centrosymmetric and Non-centrosymmetric molecules. 4

6. a) What is quenching of orbital angular momentum and what are its consequences on the help of transition metal complexes. 6

   b) Give an importance of Tanabe-Sugano diagram (TS). 2

Unit-4

7. a) Write short notes on
   (i) Spectrochemical series
   (ii) Nephelauxetic series 4

   b) Give comments on spectra of cis and trans $[Co(en)_2X_2]^+$ 4

8. a) Why do electronic spectra of $[V(H_2O)_6]^{3+}$, show only two absorption band against three predicted for the system. 4

   b) Discuss the factors that influencing band widths. 4

Exam Code : 210401 **Paper Code : 8362 (50)**

Programme : M.Sc. (Chemistry) Semester-I

Course Title : Organic Reaction Mechanism-I

Course Code : MCHL-1082

Time Allowed : 3 Hours **Max Marks : 40**

NOTE: Attempt any five questions selecting at least ONE from each unit.

UNIT-1

1) a) What are alternant and non-alternant hydrocarbons? Give one example of each.
b) Explain why cyclopentadiene is more acidic than 1,3-cyclohexadiene?
c) Explain why a substituent such as nitro bonded to *ortho* or *para* position has a much greater effect on the acidity of phenol than a benzoic acid.
d) Define benzenoid and non-benzenoid compounds with one example of each.

(2,2,2,2)

2) a) Comment upon the optical activity of biphenyls containing four large groups in the *ortho* positions taking two examples where either of the two benzene rings is symmetrically and unsymmetrically substituted. Is it necessary to have four large groups in *ortho* positions?
b) Describe briefly enantiotopic and diasterotopic terms with suitable examples.

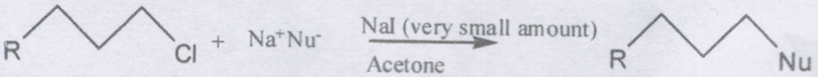
(5,3)

UNIT-II

3. a) Discuss briefly the role of solvent on the strength of an acid or a base.
b) Why some of the first order nucleophilic substitutions (SN^1) do not give completely racemized product rather give 5 to 20 % inverted product. Explain?
c) Discuss SET Mechanism with one example.

(3,3,2)

4. a) A common procedure to increase the rate of an S_N2 reaction is to add a very small amount of NaI. How does it act to increase the rate, and why is only a catalytic amount necessary? Explain with the following example:



b) The S_N2 substitution of an axial substituent is faster than that of an equatorial substituent. Explain.

c) Explain why ethanolysis of 2-(p-hydroxyphenyl)ethyl bromide in the presence of ethoxide ion is 10^6 times faster than that of 2-(p-methoxyphenyl)ethyl bromide.

3,2,3.

UNIT-III

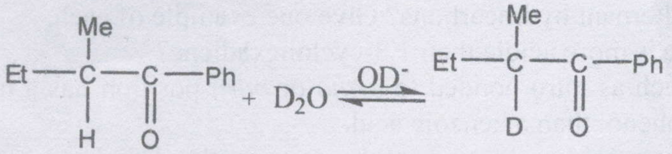
5. a) Discuss the mechanism of a nucleophilic substitution at an aliphatic trigonal carbon atom.
b) Write note on ambident nucleophiles and ambident substrates.

3,5

5. a) Explain why $CHCl_3$ is more reactive than CHF_3 in S_E1 reaction?
b) Explain giving mechanism the formation of the given products in the following reactions:

$$CH_3COCHBrCH_3 \xleftarrow{Br_2/H^+} CH_3COCH_2CH_3 \xrightarrow{Br_2/OH^-} BrCH_2COCH_2CH_3$$

c) Outline the mechanism for the following reaction



$$Et-\overset{Me}{\underset{H}{C}}-\underset{O}{\underset{\|}{C}}-Ph + D_2O \overset{OD^-}{\rightleftharpoons} Et-\overset{Me}{\underset{D}{C}}-\underset{O}{\underset{\|}{C}}-Ph$$

2,3,3

UNIT-IV

7) a) At which position naphthalene undergoes electrophilic substitution preferably. Explain with suitable reasoning.
b) Out of benzene and naphthalene which is more reactive towards electrophilic substitution. Justify your answer.
c) Which is the most widely accepted mechanism for aromatic electrophilic substitution? Write various steps of this mechanism and give evidences in support of this mechanism.

2,2,4

8) a) Write short notes on the following
   a. Sommelet-Hauser rearrangement
   b. Von Richter rearrangement

(4,4)

Exam Code: 210401 **Paper Code: 8363 (50)**

Programme: M.Sc. (Chemistry) Sem: I

Course Title: Physical Chemistry - Thermodynamics

Course Code: MCHL-1083

Time Allowed: 3 Hours **Max Marks: 40**

Instructions to the candidates:

1. **There are four Sections A, B, C and D. Candidates are required to attempt five questions in all, selecting at-least one question from each Section and fifth question may be attempted from any of the Section.**

Section A

Q 1 (a) Derive the Gibbs Duhem equation. 3

(b) The concept of fugacity is introduced with the help of equation $\mu_i = \mu_i^* + RT\ln(f_i / f_i^0)$. Deduce an expression to calculate the fugacity of a non-ideal gas that obeys the van der Waals equation of state $(P + a/V_m^2)(V_m - b) = RT$. 5

Q 2 (a) The value of an aqueous solution of potassium chloride at 298.15 K is given by $V\ (cm^3) = 1000 + 18\,m + 1.44\,m^{1/2} + 0.20\,m^2$ where m is the molality i.e. the moles of solute (n_2) per kg of the solvent. Calculate the partial molar volume of the components for $m = 0.2$ mol kg^{-1}. 3

(b) Discuss the term Gibb's free energy. What is its physical significance? IN other words briefly describe why it is called free energy? 3

(c) Justify the statement "Entropy of the universe is increasing". 2

Section B

Q 3 (a) Define excess thermodynamic functions and derive expressions for μ^E, S^E, H^E, and V^E. 4

(b) Describe the principle of equal a priori probability. 2

(c) Define the ionic strength and calculate the ionic strength of (i) 0.15 molal KCl and (ii) 0.2 molal $BaCl_2$ solution. 2

Q 4 (a) What do you understand by thermodynamic probability? Derive the relationship between entropy and thermodynamic probability. 3

(b) Calculate the mean activity coefficients $\gamma_\pm$ of (i) 0.01 molal NaCl and 0.001 molal Na_2SO_4 solutions. 3

(c) How the composition of ternary systems can be computed using triangle plot? 2

Section C

Q 5 (a) Derive expression for rotational contribution to molar entropy and molar enthalpy. 4

(b) Derive the expression for probability distribution of particles obeying Fermi Dirac statistics.. 4

Q 6 (a) Discuss the theory of black body radiation and deduce the Planck radiation law in terms of frequency. 6

(b) If each square cm of sun's surface radiates energy at the rate 1.5×10^3 cal s^{-1} cm^{-2} and Stefan's constant is 5.7×10^{-5} erg s^{-1} cm^{-2} K^{-1}, calculate the temperature of the sun. 2

Section D

Q 7 (a) Show that for steady state close to equilibrium, entropy production is minimum.. 3

(b) Write the equation for entropy production for thermo osmosis phenomenon and show that rate of entropy production is the sum of product of fluxes and forces. 5

Q 8 (a) Discuss the limitations of linear thermodynamics of irreversible phenomenon. 3

(b) What is understood by a conjugate pair of fluxes and forces? Taking one example illustrate how will you such a pair? 3

(c) What are linear laws in irreversible thermodynamics? Discuss by taking example. 2

Exam Code: 210401 **Paper Code: 8364 (50)**

Programme: M. Sc. (Chemistry) Sem-I

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

Course Code: MCHL-1084

Time Allowed: 3 Hours **Max Marks: 60**

Instructions:

Attempt five questions in all selecting at least one question from each section. The Fifth question may be attempted from any section. All questions carry equal marks.

Section-A

1. a) A compound C_3H_7Cl could give two isomeric structures. How will you distinguish them by ^{1}H-NMR Spectrum. 4

   b) TMS is used as reference compound both in ^{1}H-NMR & ^{13}C-NMR spectroscopy. Justify the statement with reason. 4

   c) Compare the ^{1}H-NMR spectrum of pure & acidified ethanol. 4

2. a) There are three isomeric ethers with molecular formula $C_4H_{10}O$, Name them and state how many signals will arise in ^{13}C-NMR spectrum of each.4

b) Define chemical shift & spin-spin splitting in NMR. 4

c) Write a short note on spin lattice relaxation. 4

Section-B

3. a) A compound $C_4H_{10}O$ gave the following data, predict the structure & assign the data

$\frac{m}{z}$= 74, 59, 45, 31, 29 4

b) What shall be the major peaks in the mass spectrum of $C_6H_5COCH_3$. Give fragments and their structure. 4

c) What is Frank Codon principle. 4

4. a) What is the effect of solvent polarity on the UV visible spectrum of organic compounds? 4

b) What is the effect of the conjugation on the U.V –visible spectrum of enones. 4

c) Explain:-

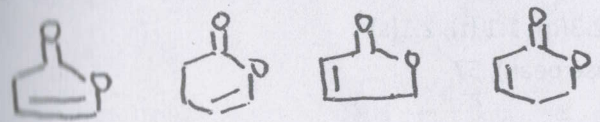
(i) Mc Lafferty rearrangement

(ii) FAB 4

Section-C

5. a) Two compounds A & B were reduced with $NaBH_4$ to give primary alcohol & secondary alcohol. How will you distinguish A & B on the basis of IR spectra. 4

b) Give below are lactones & their c=0 absorptions (IR spectrum) diagram 4



$\bar{\nu}_{c=0}$ (cm^{-1}) 1720, 1800, 1750, 1760

c) Why conjugation does not reduce c=0 absorption frequency in amides.4

6. a) What is the effect of ring size on c=c absorption frequency of external double bond. 4

b) What is the effect of electro negativity on the IR spectra of organic compounds. 4

c)How IR is used to distinguish between mono substituted, Ortho-, meta- & para- disubstituted benzene rings. 4

Section-D

7. a) Deduce the structure of the compound on the basis of following spectral data,

Molecular formula: $C_3H_5BrO_2$

IR: 1715 cm^{-1}

^{1}H-NMR($CDCl_3$): 8(ppm) : (1.75,d,3H), (4.4, q, 1H), (12.2, s, 1H)

^{13}C-NMR($CDCl_3$): 8(ppm): 21.9, 42.4, 171.9 6

b) Deduce the structure of the compound with the following data spectural formula

IR: 171B & 3010 cm^{-1}

NMR (8,ppm): 2.3(q), 1.1 (t), 2.1(s)

m/z= 72, 43 (base peak), 57 6

8. a) Deduce the structure of the compound with the following data

Molecular formula: $C_{14}H_{12}O_2$

IR(cm^{-1}): 1690, 1021, 935

^{1}H-NMR(8, ppm): 10.75(s,1H), 7.9 (d,2H), 7.3-7.5(m,5H), 7.1(m, 2H), 5.1 (s, 2H)

^{113}C-NMR (proton decoupled) (8,ppm) : 191, 166.5, 130.9, 141.2, 129.2, 129, 127.9, 127.2, 70.9 6

b) Deduce the structure of the compound with following spectral data,

IR (cm^{-1}) : 3200-3400 (broad & strong), 1100-1300

NMR (8,ppm): 0.9 (t), 1.5 (sextet), 3.6 (t), 3.2 (s)

m/z: 60, 31 (Base peak) 6

Exam Code: 210401 **Paper Code: 8365** **(50)**

Programme: M. Sc. (Chemistry) Sem-I

Course Title: Computer for Chemists- Theory

Course Code: MCHM-1135

Time Allowed: 3 Hours **Max Marks: 40**

Instructions:

Attempt five question in all selecting at least one question from each section. The Fifth question may be attempted from any section.
The Students are allowed to use Non-programmable calculator.

Section-A

1. Write note on
   a. Principle of programming
   b. Modulus operator (4,4)

2. What is the role of Arithmetic operators in programming. Also discuss the priority of arithmetic operators. 8

Section-B

3. How to convert integers to floating point numbers and vice-versa. 8

4. Write a program to find the Largest number from 3 numbers. Also draw Flow Chart of it. 8

Section-C

5. Explain user defined functions and its categories. 8

6. Explain the working of While-loop in detail. 8

Section-D

7. What are Multidimensional Arrays. How to declare Multidimensional Arrays. 8

8. Write a program to sort the elements of Array. 8