Code No. 16038/CORE

# FACULTY OF SCIENCE

## M. Sc. I – Semester Examination, September 2021

## Subject: Chemistry

## Paper – I: Inorganic Chemistry

**Time: 2 Hours** **Max. Marks: 80**

### PART – A

**Note: Answer any five questions.** **(5 x 7 = 35 Marks)**

1 Show that $S_2$ = inversion centre
2 What are principle axis and subsidiary axis of symmetry? Give examples.
3 What are the salient features of crystal field theory?
4 Calculate CFSE of $[Mn(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$ complex ions.
5 State HSAB rule. Present Pearson's classification of hard and soft metal ions and ligands.
6 What are stepwise and overall stability constants? Discuss their interrelation.
7 Explain 18 electron rule with two examples.
8 Write a note on stereochemical control of valence in nitrosyl complexes with an example.

### PART – B

**Note: Answer any three questions.** **(3 x 15 = 45 Marks)**

9 (i) What is a dihedral plane? Explain it by taking allene as example.
(ii) Show all the symmetry elements present in $NH_3$ and $BCl_3$ molecules and assign their point groups.

10 (i) List out all the elements present in Td and Oh point groups and mention the order of the groups.
(ii) Explain the symmetry criteria for optical activity.

11 (i) Draw the d-orbitals crystal splitting diagram for tetragonally distorted octahedral and trigonal bipyramidal geometries.
(ii) Explain the magnetic properties of $[Co(NH_3)_6]^{3+}$, $Ni(CO)_4$ and $[Mn(H_2O)_6]^{2+}$ based on CFT.

12 (i) How magnetic moment data is useful for the determination of stereochemistry of the metal complexes. Give examples.
(ii) Explain briefly Guoy's method for the determination of magnetic moment.

13 (i) Explain the metal ion effects which influence the stability constants of complexes?
(ii) Explain cryptate effect and its effect on the stability constants of complexes.

14 (i) Discuss the principle involved in the polarographic method for the determination of stability constant of a metal complex.
(ii) Write a note on stability constants of ternary complexes.

15 (i) Draw the molecular orbital diagram of CO and discuss its donor and acceptor properties.
(ii) Discuss the structural aspects of $[IrCl(PPh_3)_2(CO)(NO)]^+$ complex ion.

16 (i) Write a note on chemical fixation of nitrogen.
(ii) What is back bonding? Present evidence for its presence in metal carbonyl Complexes?.

* * *

Code No.16040/Core

# FACULTY OF SCIENCE

## M.Sc. I – Semester (CBCS) Examination, September 2021

## Subject: CHEMISTRY

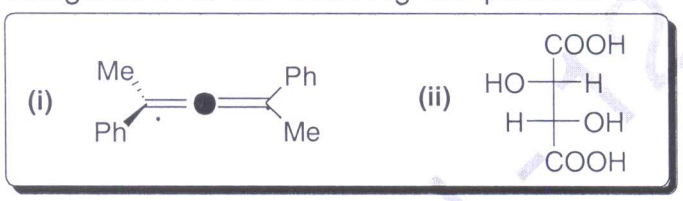
## Paper- II: Organic Chemistry

**Time: 2 Hours** **Max. Marks: 80**

### PART – A

**Note: Answer any five questions.** **(5x7 = 35 Marks)**

1. What is optical activity? Explain the criteria for molecules to show optical activity taking relevant Examples.
2. Assign the R, S-configuration to the following compounds.




3. Differentiate between α- and β- elimination reactions.
4. Elaborate on Bredt's rule with two examples.
5. Write about conformational enantiomers and configurational diastereomers with an example each.
6. Draw the preferred conformations for 2-amino ethanol and 1,2-di fluoro ethane and give the reason.
7. Write the Bischler-Napieralski synthesis of Isoquinoline and compare it with Pictet- Gams synthesis.
8. Discuss the Isoprene and Special Isoprene rules. Present their violations with one example for each .

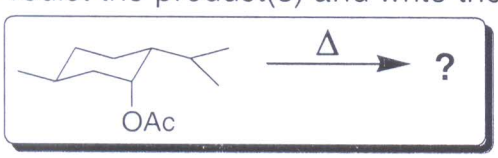
### PART – B

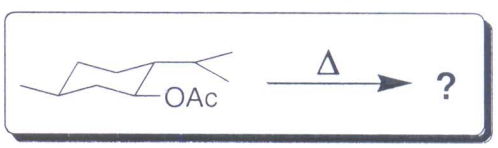
**Note: Answer any three questions.** **(3x15 = 45 Marks)**

9 (a) What is desymmetrisation? Explain it with any two suitable examples.
(b) Explain chemical correlation method in assigning the relative configuration.

10(a) Describe any two methods used in the resolution of racemic mixture.
(b) Write about atropisomerism in biphenyls.

11(a) Predict the product(s) and write the mechanism for these reactions .




(b) Comment on chemical trapping and isotopic labeling in establishing the mechanism of a reaction.

....2

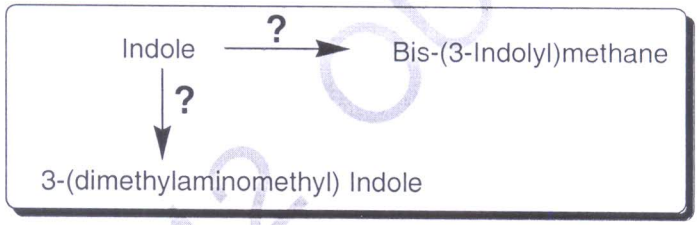
12(a) Discuss about elimination Vs sulestitation in $S_N2$ /E2 reactions.
(b) Write the mechanism involved in bromination and dihydroxylation across the carbon-carbon double bonds of trans-2-pentene.

13(a) Describe the Curtin-Hammett principle with energy profile Diagrams.
(b) Write a note on conformational stability and conformational equilibrium.

14(a) Discuss the application of spectral methods in the analysis of conformers.
(b) Describe the Klyne-Prelog terminology.

15(a) Write the synthetic scheme for the conversion of α-Terpineol to Terpenylic acid.
(b) What is Hoffmann's exhaustive methylation method ? Depict the fate of Tetrahydroisoquinoline and Piperidine in this process.

16 (a) Explain the synthesis of Camphoronic acid and Camphoric acid.
(b) Write the reagents, conditions and mechanism for the following conversions.




*****

Code No. 16042/CORE

# FACULTY OF SCIENCE

## M. Sc. I – Semester Examination, September 2021

## Subject: Chemistry

## Paper – III: Physical Chemistry

**Time: 2 Hours** **Max. Marks: 80**

### PART – A

**Note: Answer any five questions.** **(5 x7 = 35 Marks)**

1 Explain Clausius inequality
2 Derive Maxwell relation $[\partial S/\partial V]_T = [\partial P/\partial T]_V$
3 Derive Nernst equation for measuring the emf of a cell
4 Explain Bjerrum theory of ion association
5 Define operator give the expression for the following (a) $\hat{p}$ (b) $\hat{\nabla}^2$ (c) $\hat{H}$
6 Show that position x and momentum of the particle $p_x$ cannot be measured simultaneously.
7 Discuss the thermodynamic aspects of the transition state theory.
8 Explain the terms isokinetic temperature and iso selectivity rule.

### PART – B

**Note: Answer any three questions.** **(3 x 15 = 45 Marks)**

9 (a) Derive Clausius-Clapeyron equation.
(b) Explain measurement of partial molar volume from slope and intercept method.

10 (a) Derive an expression for variation of chemical potential with temperature.
(b) The equilibrium constant of reaction doubles on raising the temperature from 25 °C to 35 °C. Calculate the value of the $\Delta H^\circ$ of the reaction.

11 (a) What is liquid junction potential. Derive an expression for liquid junction potential.
(b) Explain how you will determine activity and activity coefficient from EMF measurement.

12 (a) Explain determination of PH of the solution using the quinhydrone electrode by EMF measurement in potentiometric titration.
(b) Explain Debye-Huckel theory of electrolytic solutions and write its limitations.

13 (a) Explain any three postulate of quantum mechanics.
(b) What is the ground state energy for an electron which is confined in one dimensional box having width of 0.2 nm.

14 (a) Derive an expression for normalized eigen function and total energy of a particle in three-dimensional box.
(b) Apply the results of particle in one dimensional box to explain the spectra of conjugated molecules.

15 (a) Explain the primary salt effect on the rate of reaction in solution.
(b) Show that Hammett and Taft equations are linear free energy relationships.

16 (a) Derive rate law for $H_2 + Br_2 \rightarrow 2HBr$.
(b) Write Swain-Scott equation and Edward equation. Explain the significance of the terms in the equation.

Code No. 16044/Core

# FACULTY OF SCIENCE

## M.Sc. I – Semester Examination, September 2021

## Subject: Chemistry

## Paper – IV: Analytical Techniques and Spectroscopy - I

**Time: 2 Hours** **Max. Marks: 80**

### PART – A

**Note: Answer any five questions.** **(5 x 7 = 35 Marks)**

1 What is differential migration rate? Explain.
2 Describe the principle and theory of Gas chromagraphy.
3 Define chemically equivalent and magnetically equivalent protons with suitable example each.
4 Interpret the NMR spectrum of ethyl acetate with integration and spin-spin coupling details.
5 Explain the classification of molecules based on the moment of inertia.
6 Define fundamental bands, overtones and hot bands.
7 Write about the types of electronic transitions with suitable example each.
8 Discuss the solvent and structural influences on absorption maximum.

### PART – B

**Note: Answer any three questions.** **(3 x 15 = 45 Marks)**

9 (a) Explain the plate theory in chromatography.
(b) Describe the drivatization techniques in GC.

10 (a) Write about the principle and working of UV detector and photodiode array detector.
(b) Explain the assay of paracetamol and asprin in tablets.

11 (a) What is coupling constant? Discuss the factors affecting the coupling constants.
(b) In benzaldehyde, two of the ring protons have resonance at 7.87 ppm and the other three have resonance in the range of 7.5 to 7.6 ppm. Explain.

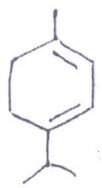
12 (a) Write about the proton exchange processes in NMR spectroscopy.
(b) Calculate the chemical shift in parts per million ($\delta$) for a proton that has resonance 128Hz down field from TMS on a spectrometer that operates at 60MHz.

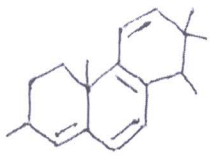
13 (a) Explain the rigid rotor model for diatomic molecules.
(b) The spacing between the neighbouring lines in the pure-rotational spectrum of gaseous HCl is 20.89$cm^{-1}$. Calculate the rotational constant B in $s^{-1}$.

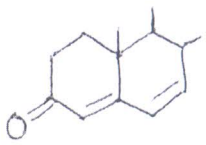
14 (a) Discuss the applications of IR spectroscopy in the identification of cis-trans isomerism and hydrogen bonding.
(b) Explain the principle of Raman spectroscopy, strokes and anti-strokes lines.

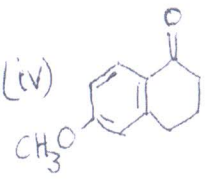
15 (a) Explain the following with suitable examples:
(i) chromophore (ii) auxochrome (iii) extent of conjugation on UV spectra.
(b) Discuss the electronic spectra of heterocyclic systems.

16 (a) Discuss the electronic spectra of polynuclear aromatic compounds.
(b) Calculate $\lambda$ max for the following molecules using Woodward-fieser rules:

(i) 

(ii) 

(iii) 

(iv) 


****