1212-19-503-009

Code No.0038/CORE

FACULTY OF SCIENCE

M. Sc. I – Semester Examination, January/February 2020

Subject: Chemistry

Paper – I: Inorganic Chemistry

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

Note: Answer all questions from Part–A and Part–B. Each question carries 8 marks in Part–A and 12 marks in Part – B.

PART – A (4 x 8 = 32 Marks)

(Short Answer Type)

1. (a) Define symmetry element and symmetry operation.
   (b) Write the symmetry elements and assign point group for the following molecules.
   (i) CH_3Cl (ii) $[PtCl_4]^{2-}$

2. (a) Sketch the d-orbital splitting in square planar and tetragonal complexes.
   (b) Calculate CFSE of high spin d^6 and d^7 octahedral metal complexes.

3. (a) Discuss briefly the ligand effects on stability constants of metal complexes.
   (b) Define ternary metal complexes and explain their formation.

4. (a) Explain the ligational properties of CO in Metal carbonyls.
   (b) Write a short note on chemical fixation of dinitrogen.

PART – B (4 x 12 = 48 Marks)

(Essay Answer Type)

5. (a) Explain the correlation between symmetry and dipole moment properties.
   (b) Discuss improper rotational axis of symmetry with suitable examples.

   OR

   (c) Explain descent in symmetry with substitution by taking suitable examples.
   (d) Explain the following point groups giving two examples each
   (i) C_n (ii) Dnd (iii) C_{nh}

6. (a) Explain the salient features of crystal field theory.
   (b) Explain quenching of orbital angular momentum.

   OR

   (c) Describe the determination of magnetic susceptibility of metal complexes by Guoy's method.
   (d) Discuss the applications of magnetic moment data.

7. (a) What is Jahn-Teller effect? How it effects on stability constants of metal complexes?
   (b) Write the determination of the stability constant by p^H metric method.

   OR

   (c) Explain Macrocyclic and Cryptate effects on stability constants of metal complexes.
   (d) Explain step-wise and simultaneous equilibria with suitable examples.

8. (a) Draw the molecular orbital diagram of CO and indicate its bonding in metal carbonyls.
   (b) Write the structural aspects of Ru(II) and Os(II) dinitrogen complexes.

   OR

   (c) Explain stereochemical control of valence in $[Co(diars)_2(NO)]^{2+}$ and $[Co(diars)_2(NO)(SCN)]^{+}$.
   (d) What is 18 electron rule? Mention its application in $Co_2(CO)_8$, $Fe_2(CO)_9$ and $Mn_2(CO)_{10}$ complexes.

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121219-503-009

Code No.0040/CORE

FACULTY OF SCIENCE

M. Sc. I – Semester Examination, January/February 2020

Subject: Chemistry

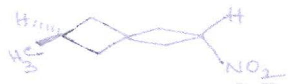
Paper – II: Organic Chemistry

Time: 3 Hours — Max. Marks: 80

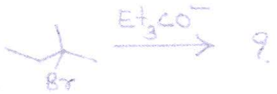
Note: Answer all questions from Part–A and Part–B. Each question carries 8 marks in Part–A and 12 marks in Part – B.

PART – A (4 x 8 = 32 Marks)
(Short Answer Type)

1. (a) What is desymmetrisation? Explain with suitable examples.
   (b) Assign R,S-configuration to the following.



2. (a) Predict the product of the following

   (i) Fumaric acid $\xrightarrow{Br_2}$? (ii)


(Major Product)

   (b) How the product isolation helps in determination of reaction mechanism? Explain with a suitable example.

3. (a) Write the preferred conformation of the following and give reasons.
   (i) Propylene (ii) 1,2-dibromoethane.
   (b) Define conformational enantiomers and give two examples.

4. (a) Discuss the reactivity of indole towards electrophiles.
   (b) Formulate the synthesis of Camphor.

PART – B (4 x 12 = 48 Marks)
(Essay Answer Type)

5. (a) What is chemical correlation method? Explain it with a suitable example.
   (b) Define and explain S_2-axis of symmetry with suitable examples.

OR

   (c) Discuss briefly about planar chirality.
   (d) Write a brief note on the use of spectral methods in determination of E, Z-configuration.

6. (a) Complete the following reactions and give mechanism.

   (i) Cis-2-pentene $\xrightarrow[H_2O]{KMnO_4 \;\; \bar{O}H}$? (ii) Meso-stilbene dibromide $\xrightarrow{^{\ominus}OEt}$?

   (b) Explain the use of isotopes in reaction mechanism with relevant examples.

OR

(c) Menthyl chloride gives 2-menthene by E2-elimination whereas by E1-elimination gives 3-menthene as major product. Explain.

(d) Explain the stereochemistry of pyrolytic eliminations taking any two suitable examples.

7. (a) Discuss the conformational analysis of butane with its potential energy diagram.

(b) The threo-2-(N,N-dimethylamino)-1,2-diphenyl ethanol showed $^3J_{H,H}$ of 10.5 Hz, whereas the corresponding erythro isomer showed 4.4Hz($^3J_{H,H}$) in ^{1}H-NMR spectrum. Explain.

OR

(c) How conformers are named according to Klyne-Prelog terminology? Explain with an example.

(d) Predict the product of the following and explain

(i) Erythro-3-Bromo-2-butanol $\xrightarrow{HBr}$?

(ii) Threo-3-phenyl-2-butyl acetate $\xrightarrow{\Delta}$?

8. (a) How the structure of papaverine is determined? Explain.

(b) Discuss the reactivity of quinolone towards electrophiles and nucleophiles.

OR

(c) Give any one method of synthesis of (i) Carbazole and (ii) Isoquinoline.

(d) Explain how the structure of α–terpeniol is determined.

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1212-19-503-009

Code No.0042/CORE

FACULTY OF SCIENCE

M. Sc. I – Semester Examination, January/February 2020

Subject: Chemistry

Paper – III: Physical Chemistry

Time: 3 Hours — Max. Marks: 80

Note: Answer all questions from Part–A and Part–B. Each question carries 8 marks in Part–A and 12 marks in Part – B.

PART – A (4 x 8 = 32 Marks)

(Short Answer Type)

1. (a) Give any two Maxwell relations and explain their significance.
   (b) Give the expression for entropy of mixing ΔS_{mix} when two ideal gases are mixed. Calculate ΔS_{mix} at 25^0C and 1 atm when 20 mol of He are mixed with 20 mol of Ne.

2. (a) Give the expression for Nernst equation for the reduction of Ag^+. If emf of the cell is 456 mV. calculate the change in Gibbs free energy ΔG.
   (b) Differentiate between activity, activity coefficient and mean ion activity coefficient.

3. (a) Show that $\psi = e^{-ikx}$ is a normalized function.
   (b) Write down the time independent Schrodinger wave equation and explain the terms.

4. (a) What is primary salt effect? Explain.
   (b) Discuss the significance of Hammond's postulate.

PART – B (4 x 12 = 48 Marks)

(Essay Answer Type)

5. (a) Explain the following with an example
   (i) Material equilibrium (ii) Phase equilibrium.
   (b) Explain the steps involved in the determination of standard entropy of a gas at room temperature from heat capacity data.

   OR

   (c) Derive Gibbs-Helmholtz equation and explain its usefulness.
   (d) Calculate the vapour pressure of benzene at 20^0C(293K) given its normal boiling point at 80^0C (353 k) and $\Delta H_{vap} = 30.8$ kj mol^{-1}.

6. (a) What are chemical cells? Derive the expression for the emf of the cell Pt $|H_{2(g)}$ (P_{H2}), $HCl(a_{HCl})$, AgCl / Ag.
   (b) How does quinhydrone electrode act as an indicator electrode for acid base titration?

   OR

   (c) Explain the postulates of Debye-Huckel theory of electrolytic solutions.
   (d) Calculate the mean activity coefficient of 0.01 M $ZnCl_2$ aq. solution using Debye-Huckel Limiting Law. The value of A is 0.5091.

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7. (a) Calculate the de Broglie wavelength of N_2 molecule moving with a velocity of 6.62×10^5 cm s^{-1}.
   (b) What are observables? Give operator forms of various observables for particle in a box.

OR

   (c) Write the schrodinger wave equation for particle in a box. Give the expression for energy, wave function Ψ and sketch the plots of Ψ and Ψ^2 for various quantum numbers.
   (d) Prove that eigen values of Hermitian operator are always real.

8. (a) What are various thermodynamic formulations of transition state theory.
   (b) Write the mechanism of H_2-Br_2 reaction and derive the rate law.

OR

   (c) Discuss how Hammett substituent constant and reaction constant are useful in understanding the mechanism of reactions.
   (d) Discuss the kinetics of the reaction $A \rightarrow B \rightarrow C$. Sketch the concentration versus time plots.

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1212-19-503-009

Code No. 0044/CORE

FACULTY OF SCIENCE

M. Sc. I – Semester Examination, January/February 2020

Subject: Chemistry

Paper – IV: Analytical Techniques & Spectroscopy-I

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

Note: Answer all questions from Part–A and Part–B. Each question carries 8 marks in Part–A and 12 marks in Part – B.

PART – A (4 x 8 = 32 Marks)
(Short Answer Type)

1. (a) Write a note on derivatization technique.
   (b) What is the relationship between capacity factor (k') and partition coefficient (K).
2. (a) The ^{1}H-nmr spectrum of an organic compound gave a quartet when recorded using 200 MHz nmr spectrometer. The positions of quartet are at 185, 195, 205 and 215 Hz away from TMS signal. Calculate the chemical shift and coupling constant.
   (b) Write a note on signal integration. What information can be deduced from signal integration?

3. (a) Calculate the reduced mass of $^{1}H^{127}I$. ($N = 6.023 \times 10^{23}$).
   (b) Write a note on complementary nature of IR and Raman spectra.

4. (a) Explain how cis-trans isomers can be identified from their electronic spectra.
   (b) Give an example each to (i) conjugated diene, (ii) conjugated triene, (iii) isolated triene and (iv) cross conjugated triene.

PART – B (4 x 12 = 48 Marks)
(Essay Answer Type)

5. (a) Explain how hydrocarbons present in a mixture can be qualitatively and quantitatively analyzed by GC.
   (b) A chromatogram of a mixture of A and B provided the following data:
   Length of column = 24.7 cm; $V_M = 1.37$ mL; $V_s = 0.164$ mL.

Compound	t_R(in min)	W(in min)
Solvent	3.1	-
A	13.3	1.07
B	14.1	1.16

   Calculate (i) the number of plates (N) for each peak and
   (ii) plate height of the column.

OR

   (c) The retention times of mobile phase and compound A are 2 and 14 min respectively. If the volumes of mobile phase (V_M) and stationary phase (V_s) are 1.4 and 0.17 mL respectively, calculate the partition coefficient (K_A) for compound A.
   (d) Describe the method of estimation of aspirin present in tablets by HPLC

6. (a) Discuss the application of ^{1}H-nmr spectroscopy in the conformation of electrophilic substitution mechanism.
   (b) Sketch the ^{1}H-nmr spectrum of ethyl benzoate and explain the splitting pattern. Show the coupling constant.

OR

   (c) What is the principle involved in magnetic resonance imaging (MRI)?
   (d) Draw the ^{1}H-nmr spectrum of $[HNi(OPEt_3)_4]^+$, and explain the splitting pattern.

7. (a) The rotational constant (B) of $^{14}N^{16}O$ is 1.67 cm^{-1}. If its reduced mass is 1.24×10^{-27} kg, calculate the bond length of $^{14}N^{16}O$.
   (b) Explain (i) fundamental band (ii) overtones and (iii) hot bands.

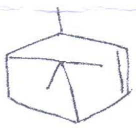
OR

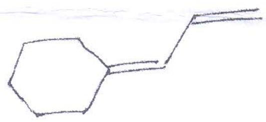
   (c) The vibrational frequency of $^{1}H^{79}Br$ is 2649 cm^{-1}. Calculate the vibrational frequency (in cm^{-1}) of $^{2}H^{79}Br$.
   (d) Explain quantum theory of Raman effect.

8. (a) Describe the selection rules for electronic spectra.
   (b) Explain how dissociation constant of a weak acid can be obtained from the application of Beer's law.

OR

   (c) Write about the solvent and structural influences on the absorption maxima of organic compounds.
   (d) Calculate the λ_{max} of the following compounds using Woodward-Fieser rules.

(i) 

(ii) 

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