24MCHEH102 Reg No : .....

CHOICE BASED CREDIT SYSTEM

M. Sc. CHEMISTRY FIRST SEMESTER DEGREE EXAMINATION JANUARY 2025

Organic Chemistry -I

Duration: 3 Hours **Max Marks:70**

PART - A

1. Answer any TEN of the following : **(10×2= 20 Marks)**

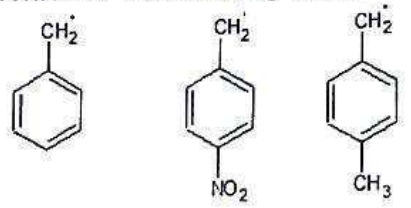
a) Chloroacetic acid is stronger than acetic acid. Why?

b) What are antiaromatic compounds? Give one example.

c) Maleic acid is much stronger acid than fumaric acid. Give reason.

d) Give an example for determination of reaction mechanism by identifying the products.

e) Which of the following is more stable? Give reason.



f) Give any two methods of generation of carbenes.

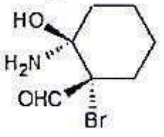
g) Give any one evidence which support aryne mechanism.

h) Identify the mechanism of hydrolysis of CH_3Cl and $(CH_3)_3CCl$.

i) 1-Bromo-3,3-dimethylbicyclo[2,2,2]octane is resistant towards reaction with ethoxide ion. Justify.

j) What is Prelog's rule? Give an example.

k) Assign R/S configuration for the following compound:



l) Give reason: Chair form of cyclohexane is stable than boat form.

PART - B

Answer any Five questions selecting at least one question from each unit. (5×10= 50 Marks)

UNIT - I

2. a) How hyperconjugation is used to explain the stability of alkenes and alkyl carbocations?

b) Write a note on inclusion compounds and fluxional molecules. **(5+5)**

3. a) Mention the rules governing resonance. Explain resonance in carboxylate and nitroethane.
   b) Compute the resonance energy of benzene from heat of hydrogenation. **(6+4)**

UNIT - II

4. a) Explain the methods of generation and reactions of carbanions.
   b) Describe the isotopic labelling method for determining the reaction mechanism. **(6+4)**

5. a) Explain the structure, generation and stability of carbon free radicals.
   b) Write a note on cross over experiments taking suitable examples. **(6+4)**

UNIT - III

6. a) Discuss the mechanism and stereochemistry of S_Ni reaction with appropriate example.
   b) Explain the factors influencing the mechanism of aliphatic nucleophilic substitution reactions.
   c) Write a note on Smiles rearrangement. **(4+3+3)**

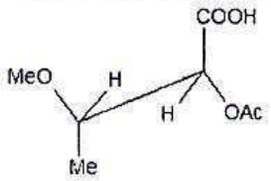
7. a) Write a note on i) SNAr Mechanism
      ii) allylic nucleophilic substitution reaction
   b) Explain the neighbouring group participation in the conversion of 2-Bromopropanoic acid to lactic acid. **(6+4)**

UNIT - IV

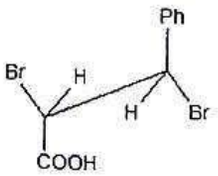
8. a) What is racemization? Explain various methods of producing racemic mixtures.
   b) Write a note on determination of configuration of geometrical isomers. **(6+4)**

9. a) Write the Newman projections for different distinct conformations of n- butane Discuss their chirality.
   b) Convert the following structures into Fischer projections:

i)



ii)



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24MCHEH103 Reg No : .....

CHOICE BASED CREDIT SYSTEM

M. Sc. CHEMISTRY FIRST SEMESTER DEGREE EXAMINATION JANUARY 2025

Physical Chemistry-I

Duration:3 Hours **Max Marks:70**

PART - A

1. Answer any TEN of the following : **(10×2= 20 Marks)**

a) State the assumption of local equilibria.

b) Define the terms: i) Chemical potential ii) Fugacity

c) The equilibrium constant K_C for reaction $H_{2(g)} + S_{(g)} \rightarrow H_2S_{(g)}$ is 20.2 atm^{-1} at 945°C and 9.1 atm^{-1} at 1065°C. Calculate $\Delta H°$.

d) Give the expression for Gibb's function in terms of partition function and explain the terms.

e) State Dulong-Petit's law and mention its drawbacks.

f) Calculate the translational partition function of an oxygen molecule at 298K confined to a 200cm^3 vessel. (Mass of oxygen = $16x3.348x10^{-27}$ kg, $k = 1.381x10^{-23}$ J K^{-1})

g) Give the schematic representation of the RRKM theory.

h) Give the limitations of continuous flow method of study of fast reactions.

i) The rate of a first order reaction is 6.0×10^{-5} s^{-1} at 298K and 10.5×10^{-4} s^{-1} at 318K. Calculate activation energy of the reaction.

j) Explain unimolecular photochemical kinetics.

k) Explain specific acid-base catalysis with an example.

l) Describe the Lineweaver-Burk method for determining V_{max} and K_{max}.

PART - B

Answer any Five questions selecting at least one question from each unit (5×10= 50 Marks)

UNIT - I

2. a) Deduce Duhem-Margules expression.
   b) Discuss the determination of fugacity of gas by graphical method. **(5+5)**

3. a) Explain the effect of concentration, temperature and pressure on the chemical equilibrium using suitable examples.
   b) In the formation of ammonia gas by Haber's process, what would happen if the volume of the container is decreased? Explain. **(6+4)**

UNIT - II

4. a) Explain Bose-Einstein condensation.
   b) Explain microcanonical, canonical and grandcanonical ensemble with suitable diagrams. **(5+5)**

5. a) Compare M-B, F-D and B-E statistics.
   b) Prove Liouville's theorem. **(5+5)**

UNIT - III

6. a) Explain the effect of ionic strength for reactions between ions.
   b) Derive an expression for elementary reactions in solutions given by CTST. **(5+5)**

7. a) Derive the rate expression for a reaction $A \rightarrow X \rightarrow Z$.
   b) Explain rate determing step taking the example of a consecutive reaction. **(6+4)**

UNIT - IV

8. a) Apply equilibrium treatment and derive the rate expression for a catalysed reaction.
   b) Relate the activation energy profile to the reaction rate and explain how a catalyst influences the profile. **(5+5)**

9. a) Describe the experimental process to study quantum yield in photochemistry.
   b) Explain the importance of the Frank-Condon principle in predicting photochemical behavior. **(5+5)**

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24MCHES104 Reg No : .....

CHOICE BASED CREDIT SYSTEM

M.Sc. CHEMISTRY FIRST SEMESTER DEGREE EXAMINATION JANUARY 2025

Spectroscopy I

Duration:3 Hours **Max Marks:70**

PART - A

1. Answer any SEVEN of the following : **(2×7= 14)**

a) Mention any two advantages of AAS over FES.

b) What is the role of a monochromator in AAS?

c) Why do excited molecules emit band spectra whereas excited atoms emit line spectrum?

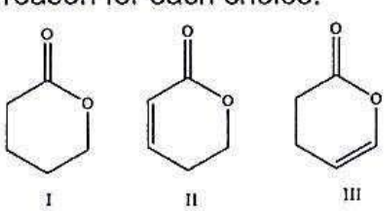
d) What are P, Q and R branches of rotation-vibration spectrum?

e) What type of molecules give rotational spectra? Which molecules show rotational spectra among HCl, CO, H_2 and O_2?

f) Write the working mechanism of the microwave oven.

g) How will you note the progress of oxidation of 2- propanol to propanone in infrared spectroscopy?

h) The carbonyl stretching absorptions for the following lactones are 1745, 1720, and 1760 cm^{-1}. Match the absorptions with the appropriate structure and give a reason for each choice.



I II III

i) Alkyl substitution in some molecules increases wavelength but intensity of absorption may increase. Justify this statement with a suitable example.

PART - B

Answer any Four questions selecting at least one question from each unit.

(14×4 = 56)

UNIT - I

2) a) Draw a schematic diagram of the instrumentation for AAS and explain its various parts.

b) List some of the advantages and disadvantages of AAS over FES.

c) Explain working of Graphite tube atomiser. **(5+5+4)**

3) a) Describe the interferences which could be present in flame photometry.
b) Explain the procedure used for the preparation of sample used for ICP-technique.
c) Draw a schematic diagram of the instrumentation for ICP-AES and explain its various parts. **(5+5+4)**

UNIT - II

4) a) Discuss the Morse equation for the energy of anharmonic oscillators.
b) Write a note on a diatomic molecule as an anharmonic oscillator
c) Illustrate the selection rules for vibrational transitions in a simple harmonic oscillator and anharmonic oscillator. **(5+5+4)**

5) a) Discuss the quantum theory of the Raman effect.
b) Write a note on Rayleigh scattering and Raman scattering.
c) Explain why N_2 is Raman active whereas some vibrations in CO_2 are Raman inactive. **(5+5+4)**

UNIT - III

6) a) Explain the principle and instrumentation of electronic spectroscopy.
b) Define the term 'chromophore'. How will you detect the presence of the carbonyl group in aldehydes and ketones?
c) Explain the following terms:
i) Bathochromic shift ii) Hypsochromic shift **(5+5+4)**

7) a) Rationalise the stretching vibrations (cm^{-1}) of the metal nitrogen bond in 2,2' bipyridyl and 1,10 phenanthroline complexes of the following transition metals.

M(II)	bipyridyl	o-phen
Fe(II)	423	530
Co(II)	264	288
Ni(II)	286	299
Cu(II)	297	300
Zn(II)	280	288

b) Explain the CO stretching frequency trend for the following complexes.
i) $[Ti(CO)_6]^{2-}$
ii) $[V(CO)_6]^-$
iii) $[Cr(CO)_6]$
iv) $[Mn(CO)_6]^+$
v) $[Fe(CO)_6]^{2+}$

c) Give reasons for the given IR data:

Complex	CO stretching frequency
$Mo(CO)_3(PF_3)_3$	2090, 2055
$Mo(CO)_3([P(OMe)_3]_3$	1977,1888
$Mo(CO)_3(triamine)_3$	1898,1758
$Mo(CO)_3(pyridine)_3$	1888,1746

(5+5+4)

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