Indian Association for the Cultivation of Science

(Deemed to be University under *de novo* Category)

Master's/Integrated Master's-PhD Program/Integrated Bachelor's-Master's Program/PhD Course

End-Semester Examination-Spring 2023

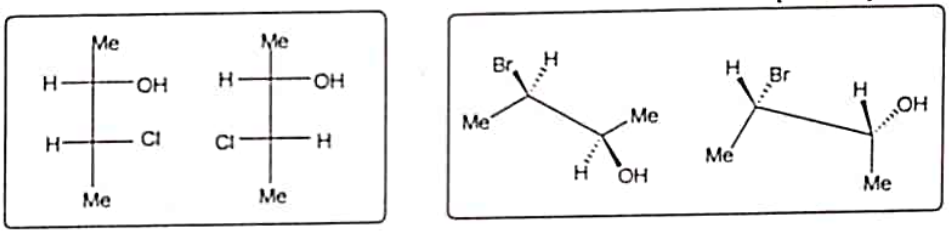
Subject: Structure, Spectroscopy and Kinetics ***Subject Code(s): CHS 1201***

Full Marks: 50 ***Time Allotted: 3 h***

Part I: Organic Chemistry [25 marks]

1. a) Indicate the relationship between the compounds of the following pairs as identical or enantiomers or diastereomers. Show how you have arrived at the answer.

[1+1= 2]

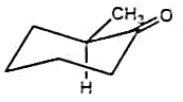


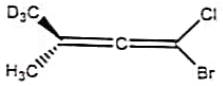
b) How many stereogenic center(s) is(are) present in each of the following molecules? Indicate them in the structures. Which one of these possesses any improper element of symmetry? Identify that symmetry element. **[2+2=4]**

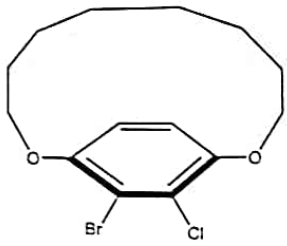
A is a substituent with stereogenic centre in R or S configuration

c) How many planes of symmetry does each of the following molecules possess? Show them in the structures. **[3]**

d) Assign ***R/S*** configuration to the following molecules showing the priority sequences and the method followed. **[2+2+2=6]**

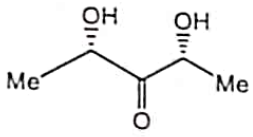


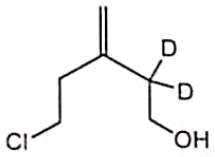




PTO

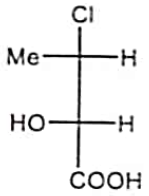
e) Assign ***Re/Si*** descriptors to **the beta faces** to the following structures: **[1+1= 2]**

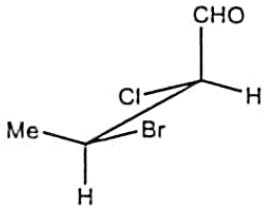




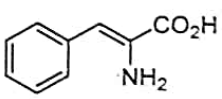
OR

Assign aldol-based *threo/erythro* descriptors to the following molecules: **[1+1= 2]**





2. A mixture of two diastereoisomeric unsaturated amino acids A (structure shown) and B, on catalytic hydrogenation, gives two stereoisomers C and D. Write the structures of B, C and D. Comment on the stereochemical relationship between C and D. Also assign E/Z configuration to A and B. **[2+1=3]**



+ it's diastereomer $\xrightarrow{H_2,\ cat.}$ **C + D** with molecular formula $C_9H_{11}NO_2$

A **B**

3. **ANSWER ANY TWO** **[2.5+2.5=5]**

a) Explain the greater stability of a cyclohexane chair form over its boat form by calculating their energy difference.

b) Draw the two chair conformations of methyl cyclohexane and comment on their relative stability.

c) Why does a cyclobutane ring takes up a puckered conformation? Draw the conformation and provide experimental evidence to support the non-planar structure.

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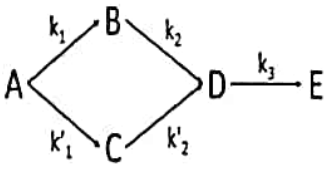
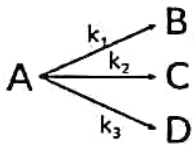
Part II: Physical Chemistry [25 marks]

1. Look at the following schematic. Write rate equation for a) A, b) D:
[1.5]



2. a) For the following reaction, prove that: [B]:[C]:[D] = $k_1:k_2:k_3$.
b) Depict how concentrations of A, B, C and D for the above scematic will vary with time in one pictorial represtation.
[2+1]



3. a) For an n^{th} order reaction derive $t_{1/2}$.
b) If the half-life for the reaction,

$$C_2H_5Cl \rightarrow C_2H_4 + HCl$$

is the same when initial concentration of C_2H_5Cl is 0.0050 M and 0.0078 M, what is the rate law for the reaction.
[1.5+1]

4. For an autocatalytic process given by A→ B, derive expressions for [A] vs time and [B] vs time. [3.5]

5. Explain the basic principle of operation of a time-of-flight mass spectrometer (include derivations of relevant expressions).
[3.5]

6. What is Frank-Condon principle? Discuss the operation of this principle for
a) internuclear distances equal in the upper and the lower states,
b) upper state electronic distance a little greater than in the lower state,
c) upper state distance considerably greater than the lower.
Also sketch vibronic spectra in each case.
[marks – 3.5]

7. Derive an expression for J_{max} for rotation distribution where the population is highest. [3]

8. a) If spin of a nucleus is ½, derive an expression for ΔE that results on application of a magnetic field along z-axis. Plot the dependence of E as a function of B_z.
b) Explain Larmor Precision.
[3+1.5]