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 2025

Subject: Structure, Spectroscopy and Kinetics	***Subject Code(s): CHS1201***
Full Marks: 50	***Time Allotted: 3 h***

Please write Part I and Part II in separate answer sheets, clearly labelled as part I and II.

Part I: Physical chemistry [25 marks]

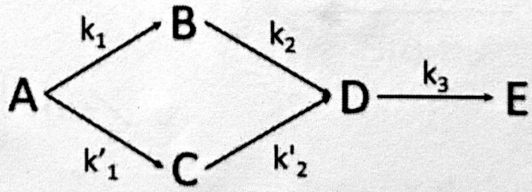
1. For a CO_2 molecule:
   a) How many modes of vibration are present? [0.5]
   b) How many of them are IR active? Explain your answer. [2.0]

2. a) For CO molecule, the first line in the rotational spectra is found to be 3.83235 cm^{-1}. Find its rotational constant. Assume rigid rotor. [0.5]
   b) Derive an expression for J_{max} for rotation distribution where the population is highest. [2.0]
   c) What is the value of J_{max} for CO at 25.0°C.
   [Hint: at 25.0°C, $kT/hc = 205.83\ cm^{-1}$] [1.0]

3. 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. [2.5]

4. a) Explain the basic principle of operation of a time-of-flight mass spectrometer (include derivations of relevant expressions). [3.5]
   b) In a time-of-flight mass spectrometer, the time-of-flight of H_2^+ is 4.2 μs. What can you say about the species whose time-of-flight is found out to be 10.3 μs? [2.0]

5. Look at the following schematic. Write rate equation for D. [1.0]



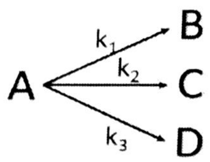
6. a) If the half-life for the reaction,

$$C_2H_5Cl \rightarrow C_2H_4 + HCl$$

is the same when initial concentration of C_2H_5Cl is 0.0050 M and 0.0080 M, what is the rate law for the reaction. [1.0]

b) When ln(k) was plotted against (1/T) for a reaction a linear curve was obtained with slope -3.27×10^{4} K. Find E_a. [$R = 8.314$ J mol^{-1} K^{-1}]. [1.0]

7. For the following reaction, [4.0]



a) Write rate equations with respect to A, B, C and D
b) prove that: [B]:[C]:[D] = $k_1:k_2:k_3$.
c) Depict how concentrations of A, B, C and D for the above schematic will vary with time in one pictorial representation.

8. See the reaction scheme: [4.0]

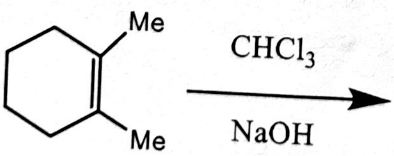
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

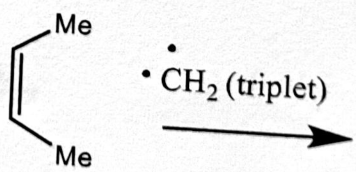
a) What is steady state approximation?
b) In the reaction scheme given above, under what condition can steady state approximation be applied.
c) Depict the variation of [A], [B] and [C] vs time in a plot under steady state condition (motivate your answer).

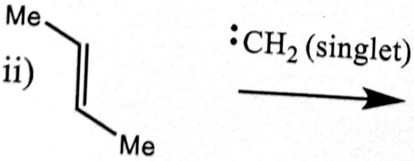
Part II: Organic Chemistry [25 marks]

1. A) Draw the structure of a bent carbene and a linear carbene, along with the state of hybridization. Explain the reason why one is bent and the other is linear. [2]

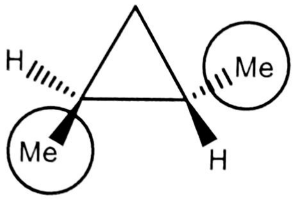
B) Draw the structure of the major product(s) in each of the following reactions. Provide the mechanism in each case and explain the stereoselectivity, if any. [6]

i) 

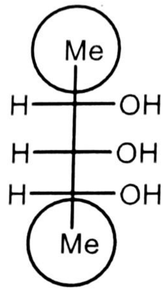
iii) 

ii) 

2. A) Find the stereochemical relation (topicity) of encircled groups in each of the foll owing molecules. Provide justification in support of your answer. **[4]**

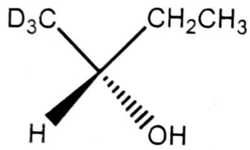


A



B

B) Assign *R/S*-descriptors to the sp^3-stereogenic centers present in the following molecules: **[5]**



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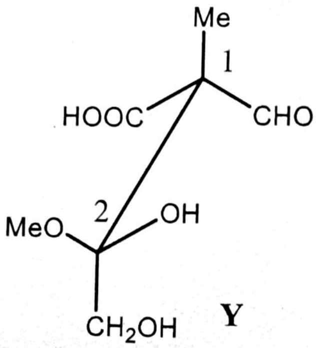

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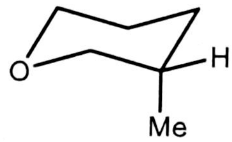

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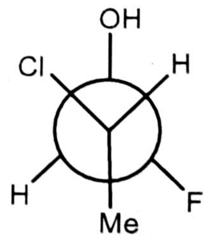

M

3. A) Draw the Chair and boat conformations of cyclohexane. Explain with reason why the chair form is more stable than the boat form. **[2]**

B) Draw any chair conformation of *cis*-1,2-dimethyl cyclohexane. How many extra gauche butane interactions it has over a cyclohexane chair form? Flip the chair form that you have drawn. Draw the mirror image of the flipped form. Find the stereochemical relationship between the three structures and hence comment on the optical activity of cis-1,2-dimethylcyclohexane. **[4]**

C) Draw the preferred conformation of cis and trans-4-t-butylcyclohexane-1-carboxylic acid. Which one is a stronger acid? Explain. **[2]**