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 2024

Subject: Structure, Spectroscopy and Kinetics   *Subject Code(s): CHS 1201*
Full Marks: 50   *Time Allotted: 3 h*

Part I: Physical Chemistry [25 marks]

1. 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]

2. a) Calculate the ratio, $N_{v=1}/N_{v=0}$, of molecules in the $v = 1$ and $v = 0$ vibrational states for carbon monoxide, CO, at 25.0°C. Assume a harmonic oscillator with $\omega_e = 2169.8 \; cm^{-1}$
   [Hint: at 25.0 °C, $kT = 207.2 \; cm^{-1}$]   [marks – 1]
   b) Calculate the ratio $N_{J=1}/N_{J=0}$ of molecules in the $J = 1$ and $J = 0$ rotational levels for carbon monoxide, CO, at 25.0°C. Assume a rigid rotor with
   $B = 1.932 \; cm^{-1}$ [Hint: at 25.0°C, $kT = 207.2 \; cm^{-1}$]   [marks – 1]
   c) Derive an expression for J_{max} for rotation distribution where the population is highest. What is the value of J_{max} for CO at 25.0°C.
   [Hint: at 25.0°C, $kT/hc = 205.83 \; cm^{-1}$]   [marks – 2.5]

3. a) Explain the basic principle of operation of a time-of-flight mass spectrometer (include derivations of relevant expressions).   [marks – 3]
   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?
        [marks – 2]

4. a) When ln(k) was plotted against (1/T) for a reaction a linear curve was obtained with slope -3.27x10^4 K. Find E_a. [R = 8.314 J mol^{-1} K^{-1}].   [marks – 1]
   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.   [marks – 1]
   c) For a reversible reaction (as given below), with K = 2.92, the plot of
   $ln([A] - [A]_f)$ vs time has a slope of -3.1950x10^{-4} s^{-1}.   [marks – 1]

 $$A \rightleftharpoons B$$

   Find k_1 and k_{-1}

5. Look at the following schematic. Write rate equation for a) A, b) D   [marks – 1.5]
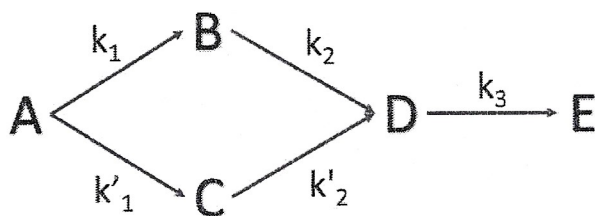
6. a) For the following reaction, prove that: $[B]:[C]:[D] = k_1:k_2:k_3$.   [marks – 2]
   b) Depict how concentrations of A, B, C and D for the above schematic will vary with time in one pictorial representation.   [marks – 1]
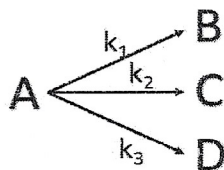

7. Discuss Michaelis – Menten kinetics of enzyme catalysis. What is the unit for Michaeli's constant (motivate your answer).   [marks – 2.5]

8. What is steady state approximation? In the reaction scheme given below, under what condition can steady state approximation be applied. Depict the variation of [B] vs time in a plot under steady state condition (motivate your answer).   [marks – 2]

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
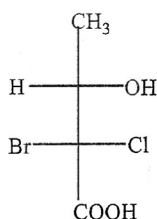
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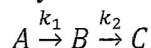
Part II: Organic Chemistry [25 marks]

Q1. Attempt the following questions

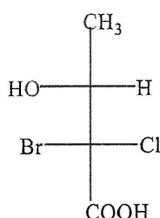**i)** The correct Fischer Projection Formula of the molecule **X** is
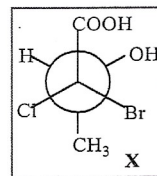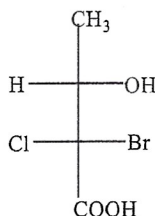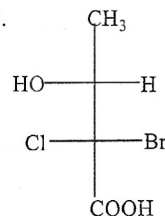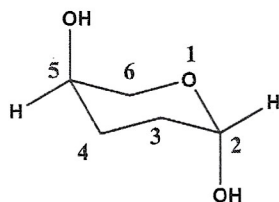

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A.

B.

C.

D.

ii) Which is the correct assignment of absolute configuration at C2 and C5 of the following molecule? Provide your answer by drawing a correct Fischer projection formula of the stereogenic centres.   **3**


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A. 2S, 5R
B. 2R, 5R
C. 2S, 5S
D. 2R, 5S
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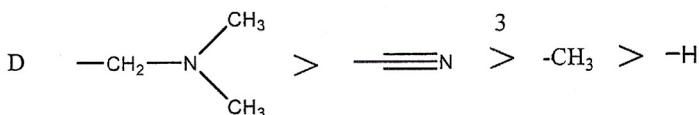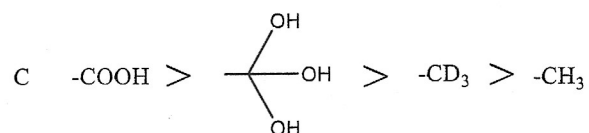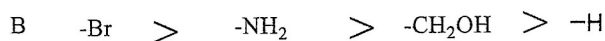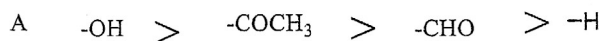
**iii)** Which one of the following statements regarding Fischer Projection formula drawn on a paper is **TRUE**?   **1**

A) Rotation of Fischer Projection formula on the plane of paper through 270° is permissible.

B) Rotation of Fischer Projection formula on the plane of paper through 90° is permissible.

C) Rotation of Fischer Projection formula on the plane of paper through 180° is permissible.

D) Interchange of one pair of ligands on a chiral center is permissible

iv) Which one of the following is the **INCORRECT** order of priority sequence of the ligands for assigning R/S configuration? Give reasons for your answer.   **1**

A $-OH > -COCH_3 > -CHO > -H$

B $-Br > -NH_2 > -CH_2OH > -H$

C $-COOH > \overset{OH}{\underset{OH}{\underset{|}{\overset{|}{C}}}} -OH > -CD_3 > -CH_3$

D $-CH_2-N\overset{CH_3}{\underset{CH_3}{\diagdown}} > \equiv N > -CH_3 > -H$

v) Draw the correct Fisher projection of C-2 and C-3 separately and then find which one of the A-D correctly describes their absolute configurations.
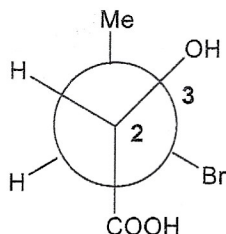
A) (2R,3R)-2-hydroxy-3-bromobutanoic acid
B) (2R,3S)-2-hydroxy-3-bromobutanoic acid
C) (2S,3R)-2-hydroxy-3-bromobutanoic acid
D) (2S,3S)-2-hydroxy-3-bromobutanoic acid

2

vi) The following molecules are

1
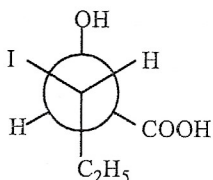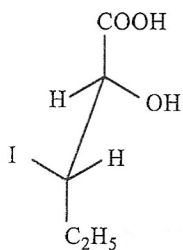
A. Enantiomer
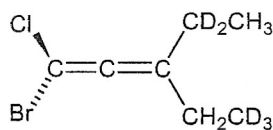B. Diastereomer
C. Homomer
D. Constitutional isomer

vii) Draw any chair conformation of cis-1,2-dimethyl cyclohexane. Flip the form that you have drawn. Find the relationship between the two forms. Show how you have arrived at the conclusion.
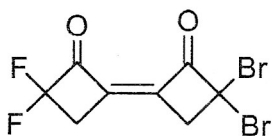
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viii) Draw the Newman projection looking through the chiral axis from any end and assign the absolute configuration.
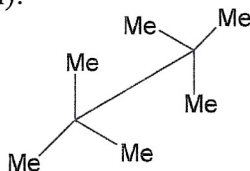
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ix) The absolute configuration of the following molecule is (show the priority sequence in the structure)

1

A. E
B. Z
C. R
D. S

4

x) The excess energy due to extra gauche butane interaction only that the following conformation has over most stable conformer of n-butane is (one gauche butane interaction energy is 0.9 kcal/mol). **2**

OR

Draw the preferred conformation of cis-1,4-di t-butyl cyclohexane. **2**

Q2. The Conformational energy profile diagram for the flipping process in a cyclohexane chair form is shown below: Consider the diagram and answer the following questions:

1+3+2
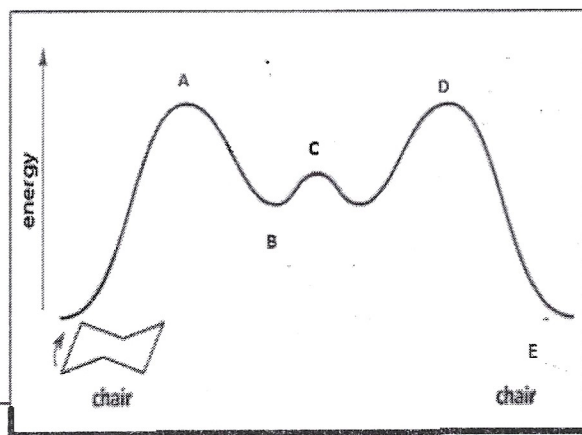
i) Identify the conformers (amongst A to E)

ii) Draw the structure of species A, B, C, D and E. Name them as chair-boat etc.

iii) Why is the chair form of cyclohexane more stable than the boat form? Calculate their approximate energy difference.

Q3. An optically pure compound of specific rotation +200° is mixed with **y%** of its enantiomer. The specific rotation of the mixture was found to be +60° under the same conditions. Calculate the value of **y**. **2**