[Time: 2 ½ Hours]   **Revised course**   **[Total Marks: 60]**

N. B: 1. **All** questions are **compulsory**.
          2. **Answers to the same question must be written together.**
          3. **Figures** to the **right** indicate **full marks**.

Q. 1   (a)   Attempt any **two** of the following: -   8
       (i)   The change in the reaction mechanism of a reaction can be explained with Hammett's equation. Justify the statement with a suitable example.
       (ii)   Establish the structure-reactivity correlation for the phenomenon shown by *p*-substituted phenols with electron withdrawing groups during their dissociation in water.
       (iii) Explain Grunwald-Winstein equation.
       (iv)   Match the columns and justify your answer.

	Acid ionization in water		ρ
I)	C_6H_5COOH	A)	1.20
II)	$C_6H_5CH=COOH$	B)	0.47
III)	$C_6H_5CH_2COOH$	C)	0.49
IV)	$C_6H_5CH_2CH_2COOH$	D)	1.0
		E)	0.21

      (b)   Attempt any **one** of the following: -   4
       (i)   Establish the equation for the structure-activity relationship for compounds for which Hammett's equation is not applicable.
       (ii)   Explain Yukawa-Tsuno Equation.

Q. 2   (a)   Attempt any **two** of the following: -   8
       (i)   Describe the various strategies adopted for antibody catalysis in terms of molecular recognition.
       (ii)   Discuss the structural features of calixarenes and give any one method of synthesis.
       (iii) What is molecular self-assembly? Explain the process based on hydrogen bonds.
       (iv)   Enzymes exhibit the concept of molecular recognition. Justify with suitable example.

      (b)   Attempt any **one** of the following: -   4
       (i)   Discuss the structural features of cyclodextrins and explain how they act as hosts in the phenomenon of molecular recognition.
       (ii)   What are molecular clefts? Explain any one with suitable example.

Q. 3   (a)   Attempt any **two** of the following: -   8
       (i)   What is resolution of racemates? Explain resolution of an alcohol through acid succinate.
       (ii)   Explain how to calculate optical purity and enantiomeric excess.

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(iii) Discuss chemical transformation involving the chiral centre involving Walden inversion and molecular rearrangement.

(iv) How does octant rule and axial α-haloketone rule help in ascertaining molecular dissymmetry and chiroptical properties?

(b) Attempt any **one** of the following: -   4

(i) Explain resolution through kinetic asymmetric transformation with the help of reaction co-ordinates.

(ii) Write a note on determination of enantiomeric purity by using chiral solvating agents.

Q. 4 (a) Attempt any **two** of the following: -   8

(i) Explain with appropriate reactions stereochemistry involved in reaction of chiral aldehyde with chiral enolates.

(ii) Give synthesis of α-amino acid by Corey's diastereoselective hydrogenation of cyclic hydrazones.

(iii) Explain Sharpless enantioselective epoxidation.

(iv) What is asymmetric amplification? Explain with suitable examples.

(b) Attempt any **one** of the following: -   4

(i) What is asymmetric induction? Give structures of three natural product molecules in the chiral pool.

(ii) Illustrate the reactions enantioselective synthesis using chiral oxazolines.

Q. 5   Attempt any **four** of the following: -   12

(a) Explain the parameters: E_s and δ.

(b) What is Dimroth's equation? Explain its significance.

(c) What are crown ethers? Discuss their properties.

(d) Give the two principles governing the stability of synthetic molecular receptors.

(e) What is cotton effect? How will you use this effect to determine position of functional group in steroids?

(f) What are quasi-racemates? How does it help in determination of configuration? explain

(g) Give synthesis of L-DOPA using Knowles's method.

(h) Explain use of BINOL's in asymmetric transformaations.

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