VISION OF THE INSTITUTION
To build jeppiaar engineering college as an institution of academic excellence in technological and management education to become a world class university.

MISSION OF THE INSTITUTION

<table>
<thead>
<tr>
<th>M1</th>
<th>To excel in teaching and learning, research and innovation by promoting the principles of scientific analysis and creative thinking.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2</td>
<td>To participate in the production, development and dissemination of knowledge and interact with national and international communities.</td>
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<tr>
<td>M3</td>
<td>To equip students with values, ethics and life skills needed to enrich their lives and enable them to meaningfully contribute to the progress of society.</td>
</tr>
<tr>
<td>M4</td>
<td>To prepare students for higher studies and lifelong learning, enrich them with the practical and entrepreneurial skills necessary to excel as future professionals and contribute to Nation's economy.</td>
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</tbody>
</table>

PROGRAM OUTCOMES (POS)

<table>
<thead>
<tr>
<th>PO 1</th>
<th>Engineering knowledge: Apply the knowledge of mathematics, science, engineering fundamentals, and an engineering specialization to the solution of complex engineering problems.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO 2</td>
<td>Problem analysis: Identify, formulate, review research literature, and analyze complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences, and engineering sciences.</td>
</tr>
<tr>
<td>PO 3</td>
<td>Design/development of solutions: Design solutions for complex engineering problems and design system components or processes that meet the specified needs with appropriate consideration for the public health and safety, and the cultural, societal, and environmental considerations.</td>
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<tr>
<td>PO 4</td>
<td>Conduct investigations of complex problems: Use research-based knowledge and research methods including design of experiments, analysis and interpretation of data, and synthesis of the information to provide valid conclusions.</td>
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<tr>
<td>PO 5</td>
<td>Modern tool usage: Create, select, and apply appropriate techniques, resources, and modern engineering and IT tools including prediction and modeling to complex engineering activities with an understanding of the limitations.</td>
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<tr>
<td>PO 6</td>
<td>The engineer and society: Apply reasoning informed by the contextual knowledge to assess societal, health, safety, legal and cultural issues and the consequent responsibilities relevant to the professional engineering practice.</td>
</tr>
<tr>
<td>PO 7</td>
<td>Environment and sustainability: Understand the impact of the professional engineering solutions in societal and environmental contexts, and demonstrate the knowledge of, and need for sustainable development.</td>
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<tr>
<td>PO 8</td>
<td>Ethics: Apply ethical principles and commit to professional ethics and responsibilities and norms of the engineering practice.</td>
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<td>PO 9</td>
<td>Individual and team work: Function effectively as an individual, and as a member or leader in diverse teams, and in multidisciplinary settings.</td>
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<tr>
<td>PO 10</td>
<td>Communication: Communicate effectively on complex engineering activities with the engineering community and with society at large, such as, being able to comprehend and write effective reports and design documentation, make effective presentations, and give and receive clear instructions.</td>
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<tr>
<td>PO 11</td>
<td>Project management and finance: Demonstrate knowledge and understanding of the engineering and management principles and apply these to one’s own work, as a member and leader in a team, to manage projects and in multidisciplinary environments.</td>
</tr>
<tr>
<td>PO 12</td>
<td>Life-long learning: Recognize the need for, and have the preparation and ability to engage in independent and life-long learning in the broadest context of technological change.</td>
</tr>
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</table>
VISION OF THE DEPARTMENT
- To pursue excellence in producing bioengineers coupled with research attributes.

MISSION OF THE DEPARTMENT

| M1  | To impart quality education and transform technical knowledge into career opportunities. |
| M2  | To establish a bridge between the program and society by fostering technical education. |
| M3  | To generate societal conscious technocrats towards community development |
| M4  | To facilitate higher studies and research in order to have an effective career / entrepreneurship. |

PROGRAM EDUCATIONAL OBJECTIVES (PEOS)

| PEO - 1 | To impart knowledge and produce competent graduates in the field of biotechnology |
| PEO - 2 | To inculcate professional attributes and ability to integrate engineering issues to broader social contexts. |
| PEO - 3 | To connect the program and community by fostering technical education. |
| PEO - 4 | To provide a wide technical exposure to work in an interdisciplinary environment |
| PEO - 5 | To prepare the students to have a professional career and motivation towards higher education. |

PROGRAM SPECIFIC OUTCOMES (PSOS)

| PSO 1 | Professional Skills: This programme will provide students with a solid foundation in the field of Biological Sciences and Chemical engineering enabling them to work on engineering platforms and applications in Biotechnology as per the requirement of Industries, and facilitating the students to pursue higher studies |
| PSO 2 | Problem-solving skills: This programme will assist the students to acquire fundamental and problem solving knowledge on subjects relevant to Biotechnology thereby encouraging them to understand emerging and advanced concepts in modern biology |
| PSO 3 | Successful Career and Entrepreneurship: Graduates of the program will have a strong successful career and entrepreneurial ability with the blend of inputs from basic science, engineering and technology, thereby enabling them to translate the technology and tools in various industries and/or institutes |
OBJECTIVES:
To enable the students
1. To know in detail about the elements of atom, charges and their bonding rule.
2. To understand the various kinetic properties and types of reaction mechanisms
3. To understand the possible bio-organic reactions involved in biosynthesis

UNIT I BONDING AND STEREOCHEMISTRY

UNIT II MECHANISMS OF SUBSTITUTION AND ADDITION REACTIONS
SN1 and SN2 reactions on tetrahedral carbon - nucleophiles - mechanism - steric effects – nucleophilic addition on Acetals and ketals -Aldehyde and ketone groups – reactions of carbonyl group with amines- acid catalyzed ester hydrolysis – Saponification of an ester hydrolysis of amides. Ester enolates - claisen condensation – Michael condensation.

UNIT III KINETICS AND MECHANISM

UNIT IV CATALYSIS
Reactivity – Coenzymes – Proton transfer – metal ions – Intra molecular reactions – Covalent catalysis – Catalysis by organized aggregates and phases. Inclusion complexation

UNIT V BIOORGANIC REACTIONS
Timing of Bond formation and fission – Acyl group transfer – C-C bond formation and fission – Catalysis of proton transfer reactions – Transfer of hydride ion – Alkyl group. Transfer – Terpene biosynthesis – Murrfield state peptide synthesis – Sanger method for peptide and DNA sequencing.

TOTAL: 45 PERIODS
OUTCOME:
On completion of this course, the students will learn the basics principles of chemical Bonding, Stereochemistry of Bio-organic molecules and their kinetics, mechanisms of reactions and catalysis.

TEXT BOOKS:

REFERENCE:

<table>
<thead>
<tr>
<th>CO NO</th>
<th>COURSE OUTCOME</th>
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<td>To know in detail about the elements of atom, charges and their bonding rule.</td>
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<td>C203.2</td>
<td>To understand the various kinetic properties and types of reaction mechanisms</td>
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<td>C203.3</td>
<td>To understand the possible bio-organic reactions involved in biosynthesis</td>
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<td>C203.4</td>
<td>To understand the importance of metal ions in the biological role</td>
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<tr>
<td>C203.5</td>
<td>Knowledge gain in various techniques to study the biological substances</td>
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<td>2.</td>
<td>Resonance Acids and Bases - Arrhenius and Bronsted Lowry Theories - Acid Base equilibria -</td>
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<td>3.</td>
<td>SP3 hybridization</td>
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<td>Nucleophilic addition on Acetals and ketals</td>
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<td>9.</td>
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<td>Acid catalyzed ester hydrolysis – Saponification.</td>
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<td>Arrhenius equation and Eyring equation -</td>
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<td>18.</td>
<td>ΔG, ΔS, ΔH, Thermodynamics of coupled reactions</td>
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<td>Acyl group transfer</td>
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<td>Catalysis of proton transfer reactions</td>
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<td>28.</td>
<td>Transfer of hydride ion</td>
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<td>29.</td>
<td>Alkyl group Transfer</td>
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<td>30.</td>
<td>Terpene biosynthesis</td>
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UNIT I
BONDING AND STEREOCHEMISTRY
Atoms Electrons and orbitals - Covalent Bonds - Octet rule - Polar covalant Bonds - Electronegativity- formal charge - Resonance Acids and Bases - Arrhenius and Bronsted Lowry Theories - Acid Base equilbria - SP3 hybridization - Conformations analysis ethane, butane and cyclohexane - Cis- trans isomerism. Stereochem activity around the tetrahedral carbon – optical activity - Conformation of the peptide bond.

PART-A
1. What is valence electrons of an atom.
   These are the outermost electrons, the ones most likely to be involved in chemical bonding and reactions. For second-row elements these are the $2s$ and $2p$ electrons. Because four orbitals ($2s$, $2px$, $2py$, $2pz$) are involved, the maximum number of electrons in the valence shell of any second-row element is 8. Neon, with all its $2s$ and $2p$ orbitals doubly occupied, has eight valence electrons and completes the second row of the periodic table.

2. What is polar covalent bond?
   Electrons in covalent bonds are not necessarily shared equally by the two atoms that they connect. If one atom has a greater tendency to attract electrons toward itself than the other, and the electron distribution is polarized, and the bond is referred to as a polar covalent bond.

   Cahn–Ingold–Prelog system otherwise called as the sequence rules.
   - Arrange the atoms according to their decreasing precedence
   
   | HO− | > | CH₃CH₂− | > | CH₃− | > | H− |
   | (highest) | | (lowest) |
   - Orient the molecule so that the lowest ranked substituent points away from you.
   - If the order of decreasing precedence of the three highest ranked substituents appears in a clockwise sense, the absolute configuration is $R$ (Latin rectus, “right,” “correct”). If the order of decreasing precedence is anticlockwise, the absolute configuration is $S$ (Latin sinister, “left”).

4. What is conformation?
   Conformations are different spatial arrangements of a molecule that are generated by rotation about single bonds. Eg. H₂O₂

5. Define Pauli exclusion principle
   Two electrons may occupy the same orbital only when they have opposite, or “paired,” spins.

6. Define Atomic number.
   The atomic number of a chemical element is the number of protons found in the nucleus of an atom of that element, and therefore identical to the charge number of the nucleus.

7. Define Hund’s rule.
Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

8. **Define ionization energy**

   The amount of energy that must be added to an atom to remove an electron is ionization energy. The ionization energy of sodium, for example, is 496 kJ/mol (119 kcal/mol).

9. **Define octet rule (2015)**

   Atoms of low atomic number tend to combine in such a way that they each have eight electrons in their valence shells, giving them the same electronic configuration as a noble gas.

10. **Define electronegativity**

    The tendency of an atom to draw the electrons in a covalent bond toward itself is referred to as its electronegativity. An electronegative element attracts electrons

11. **What do you mean by formal charges?**

    A formal charge is the charge assigned to an atom in a molecule, assuming that electrons in a chemical bond are shared equally between atoms, regardless of relative electronegativity.

12. **What is resonance?**

    Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule.

13. **How does resonance influence the ability of a base to share electrons with a proton?**

    A base that has resonance delocalization of the electron pair that is shared with the proton will be less basic than a base without resonance. Since a weaker base has a stronger conjugate acid, a compound whose conjugate base enjoys resonance stabilization will be more acidic.

14. **Which O-H proton is more acidic, ethanol (CH3CH2OH) or acetic acid (CH3CO2H)?**

    Because acetate ion has resonance that delocalizes the electron pair to be shared with a proton and ethoxide ion does not, acetate ion is a weaker base than ethoxide ion.

15. **Define Arrhenius and Bronsted Lowry theories.**

    **Arrhenius theory:** Acids are substances which produce hydrogen ions in solution.
    Bases are substances which produce hydroxide ions in solution.
    **Bronsted Lowry theories:** An acid is a proton (hydrogen ion) donor.
    A base is a proton (hydrogen ion) acceptor.

16. **Write about sp³ hybridisation**

    In ethane, each methyl group consists of an sp³-hybridized carbon attached to three hydrogens by sp³–1s σ bonds. Overlap of the remaining half-filled orbital of one carbon with that of the other generates a σ bond between them. In general, carbon will be sp³-hybridized when it is directly bonded to four atoms.

17. **What are stereoisomers?**
**Stereoisomers** are isomers that have their atoms bonded in the same order—that is, they have the same constitution, but they differ in the arrangement of atoms in space.

18. **Draw the Newman and sawhorse projections of ethane**

![Newman and sawhorse projections of ethane](image)

19. **Draw the Newman projection of butane**

![Newman projection of butane](image)

20. **What is meant by torsional strain?**

The destabilization that comes from eclipsed bonds on adjacent atoms is called **torsional strain**.

![Torsional strain](image)

21. **Draw the Axial and equatorial bonds in cyclohexane.**

![Axial and equatorial bonds in cyclohexane](image)

22. **Define D,L isomers?**

Rotation of the plane of polarized light in the clockwise sense is taken as positive (+), and rotation in the anticlockwise sense is taken as a negative (-) rotation. The classical terms for positive and negative rotations are dextrorotatory (D) and levorotatory (L).

23. **Write a note on optical activity**

Optical activity is the ability of a chiral substance to rotate the plane of **plane-polarized light** and is measured using an instrument called a **polarimeter**. To be optically active, the sample must contain a chiral substance and one enantiomer must be present in excess of the other. A substance that does not rotate the plane of polarized light is said to be optically inactive. All achiral substances are optically inactive.

24. **Draw the conformation of peptide bond.**

![Peptide bond](image)

25. **Define configuration and specify the R and S isomers.**

(Nov 2011)
The arrangement of atoms that characterizes a particular stereoisomer is called its configuration. The four groups attached to the asymmetric carbon atom are numbered 1,2,3,4 and ranked according to a set of sequence rules and if the view with respect to Fischer projection is clockwise it is specified as R isomer and in anti-clock wise it is S isomer.

26. What is the Aufbau principle with example? (Dec 2016)

   The Aufbau Principle states that electrons enter the lowest energy orbitals first.
   • The lower the principal quantum number (n) the lower the energy.
   • Within an energy level, s orbitals are the lowest energy, followed by p, d and then f.
     F orbitals are the highest energy for that level.

27. Give details about energy level.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Sub-level</th>
<th>Type of sub</th>
<th># of Orbitals</th>
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<tbody>
<tr>
<td>S</td>
<td>Sphere</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>P</td>
<td>Dumbbell</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>4-Lobed</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>F</td>
<td>6-8 Lobed</td>
<td>14</td>
<td>7</td>
</tr>
</tbody>
</table>

28. What do I mean by “electron configuration?”

   The electron configuration is the specific way in which the atomic orbitals are filled.
   The electron configuration reveals where all the electrons “live.”

29. Define Valence electrons of an atom.

   These are the outermost electrons, the ones most likely to be involved in chemical bonding and reactions. For second-row elements these are the 2s and 2p electrons. Because four orbitals (2s, 2px, 2py, 2pz) are involved, the maximum number of electrons in the valence shell of any second-row element is 8. Neon, with all its 2s and 2p orbitals doubly occupied, has eight valence electrons and completes the second row of the periodic table.

30. What is Chemical Bond and ionic bond?

   The attractive force between atoms in a compound is a chemical bond.
   Ionic bond, is the force of attraction between oppositely charged species (ions).
   Ions that are positively charged -cations;
   Ions that are negatively charged are anions

31. What is Hammond’s postulate? (Dec 2016)

   It states that that for any single reaction step, the geometry of the transition state for that step resembles the side to which it is closer in free energy.(It states that if there is an unstable intermediate on the reaction pathway, the transition state for the reaction will resemble the structure of this intermediate).

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PART – B

1. Explain about atom, electron, orbital, bonding, electronegativity and formal charge.
   Organic Chemistry by Carey and Giuliano- 3-16

2. Discuss about acid-base equilibria and give Arrhenius and Bronsted Lowry theories.
   Organic Chemistry by Carey and Giuliano- 32-45

   Organic Chemistry by Carey and Giuliano- 63-65

4. Explain in detail about the various conformational analysis of ethane, butane and cyclohexane.
5. Write an essay on “optical activity and chirality”.
   Organic Chemistry by Carey and Giuliano- 278-310

   Class notes.

PART – B

1. Explain diagrammatically and energetically the conformers of ethane, and n-butane.
   (Dec 2016)
   Organic Chemistry by Carey and Giuliano- 102-120

2. Explain Stereochemical activity around tetrahedral carbon. (Dec 2016)
   Organic Chemistry by Carey and Giuliano- 278-310

3. Explain Conformation of the peptide bond. Why is trans confirmation stable? (Dec 2016)
   Class notes.
UNIT II
MECHANISMS OF SUBSTITUTION AND ADDITION REACTIONS
SN1 and SN2 reactions on tetrahedral carbon- nucleophiles- mechanism steric effects – nucleophilic addition on Acetals and ketals -Aldehyde and ketone groups – reactions of carbonyl group with amines- acid catalyzed ester hydrolysis – Saponification of an sterhydrolysis of amides. Ester enolates - claisen .condensation – Michael condensation.

PART-A

1. **What are cyanohydrins?**
The product of addition of hydrogen cyanide to an aldehyde or a ketone contains both a hydroxyl group and a cyano group bonded to the same carbon. Compounds of this type are called cyanohydrins.

   ![Cyanohydrin Reaction]

2. **What are hemiacetals and acetals? Describe its formation.**
The product of nucleophilic addition of the alcohol to the carbonyl group of an aldehyde is called a hemiacetal. The reaction of one mole of the aldehyde with two moles of alcohol give geminal diethers known as acetals.

   ![Hemiacetal and Acetal Reaction]

3. **What is Wittig reaction?**
The Wittig reaction uses phosphorus ylides (called Wittig reagents) to convert aldehydes and ketones to alkenes.

   ![Wittig Reaction]

4. **Write the ester formation of ketone through Baeyer–Villiger oxidations**
An oxygen from the peroxy acid is inserted between the carbonyl group of a ketone and one of the attached carbons of the ketone to give an ester. Reactions of this type are known as Baeyer–Villiger oxidations.

   ![Baeyer-Villiger Oxidation]

5. **What is Fischer esterification.**
In the presence of an acid catalyst, alcohols and carboxylic acids react to form an ester and water. This is the Fischer esterification.

   ![Fischer Esterification]
6. **How do you prepare an ester from acyl chloride?**
Alcohols react with acyl chlorides by nucleophilic acyl substitution to yield esters. These reactions are typically performed in the presence of a weak base such as pyridine.

![Reaction diagram](image)

7. **Write the reaction of ester with amines?**
Esters react with ammonia and amines to form amides.

![Reaction diagram](image)

8. **Write the reaction of acid catalysed ester hydrolysis.**
Acid-catalyzed hydrolysis is an equilibrium-controlled process, the reverse of the Fischer esterification.

![Reaction diagram](image)

9. **Write the reaction of ester hydrolysis in base.**
Ester hydrolysis in aqueous base is *irreversible*.

![Reaction diagram](image)

10. **What is saponification?**
Saponification is a process that produces soap, usually from fats and lye. In technical terms, saponification involves base (usually caustic soda NaOH) hydrolysis of triglycerides, which are esters of fatty acids, to form the sodium salt of a carboxylate.

![Reaction diagram](image)

11. **How amides can be prepared?**
Amides are readily prepared by acylation of ammonia and amines with acyl chlorides, anhydrides, or esters.

![Reaction diagram](image)
12. What are lactams? 
**Lactams** are cyclic amides and are analogous to lactones, which are cyclic esters.

![Lactams](image1)

13. Write the reaction of amide hydrolysis in water

![Reaction](image2)

14. Write the reaction of amide hydrolysis in acid

![Reaction](image3)

15. What is Claisen condensation? 
On treatment with alkoxide bases, esters undergo self-condensation to give a β-keto ester and an alcohol.

![Claisen Condensation](image4)

16. What is Michael reaction? 
A synthetically useful reaction known as the **Michael reaction**, or **Michael addition**, involves nucleophilic addition of carbanions to α,β-unsaturated ketones. The most common types of carbanionic used are enolate ions derived from β-diketones. These enolates are weak bases and react with α,β-unsaturated ketones by conjugate addition.

![Michael Reaction](image5)

17. What is Dieckmann cyclization? 
Esters of **dicarboxylic acids** undergo an intramolecular version of the Claisen condensation when a five- or six-membered ring can be formed.

![Dieckmann Cyclization](image6)
18. What is SN2 reaction?
In the reaction,
\[
\text{CH}_3\text{Br} + \text{HO}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^- \\
\text{Methyl bromide} \quad \text{Hydroxide ion} \quad \text{Methyl alcohol} \quad \text{Bromide ion}
\]
Hughes and Ingold interpreted second-order kinetic behavior to mean that the rate determining step is *bimolecular*, that is, that both hydroxide ion and methyl bromide are involved at the transition state. The symbol given to the detailed description of the mechanism that they developed is SN2, standing for substitution nucleophilic bimolecular.

19. Name some nucleophile candidates for nucleophilic substitution reactions of alkyl halides
Alkoxide ion, Carboxylate ion, Hydrogen sulfide ion, Cyanide ion, Azide ion, Iodide ion.

20. What is SN1 reaction?
Hughes and Ingold observed that the hydrolysis of *tert*-butyl bromide, which occurs readily, is characterized by a first-order rate law:
\[
\text{(CH}_3\text{)}_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3\text{)}_3\text{COH} + \text{HBr}
\]
They found that the rate of hydrolysis depends only on the concentration of *tert*-butyl bromide. SN1, stands for substitution nucleophilic unimolecular, is a first-order kinetic reaction with a unimolecular rate-determining step.

E2 reaction proceeds with a second order kinetics (Hughes and Ingold), with a single step: base pulls a proton away from carbon; simultaneously a halide ion departs and the double bond forms.
E1 reactions follows the first order kinetics, where the bond-breaking and bond-making occurs. In step(1) the substrate undergoes slow heterolysis to form halide ion and a carbocation. In step (2) the carbocation rapidly loses a proton to the base and forms an alkene.

22. Define Walden inversion. (Nov/Dec 2012)
Walden inversion is the inversion of a chiral center in a molecule in a chemical reaction. Since a molecule can form two enantiomers around a chiral center, the Walden inversion converts the configuration of the molecule from one enantiomeric form to the other.

23. Write the factors influencing SN2 reactions.
- The rate of an SN2 reaction depends upon 4 factors:
  1. The nature of the substrate (the alkyl halide)
  2. The power of the nucleophile
  3. The ability of the leaving group to leave
  4. The nature of the solvent

24. Write the factors influencing SN1 reactions.
- The rate of an SN1 reaction depends upon 3 factors:
  1. The nature of the substrate (the alkyl halide)
  2. The ability of the leaving group to leave
  3. The nature of the solvent
  - The rate is independent of the power of the nucleophile.

25. What is steric hindrance and steric effect?
Steric hindrance is the stopping of a chemical reaction which might be caused by a molecule's structure.
Steric effect is an influence on a reaction's course or rate determined by the fact that all of the atoms within a molecule occupy space, thus certain collision paths are either disfavored or favored.
26. Give an example of a Claisen condensation reaction. (Dec 2016)

![Figure 21.1: The mechanism of the Claisen condensation of ethyl acetate.](image)

27. What is Barnase? (Dec 2016)

**Barnase** (a portmanteau of "Bacterial" "Ribonuclease") is a bacterial protein that consists of 110 amino acids and has ribonuclease activity. It is synthesized and secreted by the bacterium Bacillus amyloliquefaciens, but is lethal to the cell when expressed without its inhibitor barstar.

28. What is solvolysis?

Solvolysis reactions are substitutions in which the nucleophile is the solvent in which the reaction is carried out. Solvolysis in *water converts an alkyl halide to an alcohol*.

29. Give the structure of the carbonyl group.

Hybridization of the carbonyl carbon is $sp^2$.
- Geometry of the carbonyl carbon is *trigonal planar*
- Attack by nucleophiles will occur with equal ease from either the top or the bottom of the carbonyl group.
- The carbonyl carbon is *prochiral*. That is, the carbonyl carbon is not the center of chirality, but it becomes chiral as the reaction proceeds.

30. What is cyanohydrins?

The product of addition of hydrogen cyanide to an aldehyde or a ketone contains both a hydroxyl group and a cyano group bonded to the same carbon. Compounds of this type are called cyanohydrins.
PART – B

1. Elaborate SN1 and SN2 reactions on tetrahedral carbon
   Organic Chemistry by Carey and Giuliano- 326-347.
2. Explain about nucleophilic addition reaction with Acetals and ketals.
   Organic Chemistry by Carey and Giuliano- 742-743.
3. Discuss Hydration mechanism of aldehydes and ketones in acidic and basic solution.
   Organic Chemistry by Carey and Giuliano- 738-739.
4. Describe acid and base catalyzed ester hydrolysis (2015)
   Organic Chemistry by Carey and Giuliano- 830-834.
5. Write in detail about reactions of carbonyl group with amines, ester hydrolysis in base(saponification), hydrolysis of amides. (2015)
   Organic Chemistry by Carey and Giuliano- 746-751; 832-834; 843-845.
   Organic Chemistry by Carey and Giuliano- 882-884; 910-912.

PART – C

1. Explain the mechanism of an elimination reaction with an example. Explain the effect of steric hindrance on the rate of SN2 reactions.
   Organic Chemistry by Carey and Giuliano- 326-347.
2. Explain reaction of carbonyl groups with amines, with an example. Explain the SN1 mechanism of nucleophilic substitution with hydrolysis of ter-butyl bromide along with energy diagram.
   Organic Chemistry by Carey and Giuliano- 738-739.
3. Explain condensation reactions.
   Organic Chemistry by Carey and Giuliano- 882-884; 910-912.
UNIT III
KINETICS AND MECHANISM

PART-A

1. **What is blind alley intermediate?**
Blind alley intermediate which does not lead to product formation.

   ![Blind alley intermediate diagram]

2. **Define Curtin-Hammets principle.**
The Curtin–Hammett principle applies to systems in which different products are formed from two substrates in equilibrium with one another. The rapidly interconverting reactants can be enantiomers, diastereomers, or constitutional isomers. Product formation must be irreversible, and the different products must be unable to interconvert.

   For example, given species A and B that equilibrate rapidly while A turns irreversibly into PA, and B turns irreversibly into PB:

   ![Reaction diagram]

   \[ PA \xrightleftharpoons[k_A]{k_1} A \xrightarrow{k_2} B \xrightarrow{k_B} PB \]

   \( K \) is the equilibrium constant between A and B, and \( k_1 \) and \( k_2 \) are the rate constants for the formation of PA and PB, respectively. When the rate of interconversion between A and B is much faster than either \( k_1 \) or \( k_2 \), then the Curtin–Hammett principle tells us that the PA:PB product ratio is not equal to the A:B reactant ratio, but is instead determined by the relative energy of the transition states. If reactants A and B were at identical energies, the reaction would depend only on the energy of the transition states leading to each respective product. However, in a real-world scenario, the two reactants are likely at somewhat different energy levels, although the barrier to their interconversion must be low for the Curtin–Hammett scenario to apply. In this case, the product distribution depends both on the relative quantity of A and B and on the relative barriers to products PA and PB.

3. **Give rate law and its mechanism.**

   **Rate law and Mechanism**
   - Need mechanistic hypothesis
   - Steady state assumption
   - Unimolecular decomposition of A/reaction of A with solvent
     \[
     \begin{align*}
     &A \xrightarrow{k_1} I \xrightarrow{k_2} P \xrightarrow{k_2} (2)
     \\
     \text{Rate} & = -d[A]/dt = d[P]/dt = [A]k_1k_2/(k_1+k_2) + k'[A] \quad \ldots (5)
     \end{align*}
     \]

   Rate laws are used in chemical engg. But knowledge is imp. To control the chemical flux in a process.
4. Write Bodenstein attribute towards steady state and non-steady state.
   Steady state and non-steady state
   • ‘I’ can be predicted from k1, k-1 and k2 and intial [A].
   • K-1 or k2 > k1 ; [I] is very small.
   • Time dependency of A and P are first order.
   Bodenstien attribute:
   • When the concentration of the intermediate is very much smaller than that of reactants or products, the concentration of intermediates can be considered constant at a ‘steady state’ i.e
   • Rate of formation = rate of break down.
   • From equation 2 eqn 4a, 4b & 4c is obtained
     \[ \frac{d[I]}{dt} = [A] k1 - [I](k_1^{-1}+k2) = 0 \ghtarrow (4a) \]
     Steady state condition: \( k1[A] = (k_1^{-1}+k2)[I] \ghtarrow (4b) \]
     \( [I] = \frac{k1 [A]}{(k_1^{-1}+k2)} \ghtarrow (4c) \)

5. What is microscopic reversibility?
   In any equilibrium process, the sequence of intermediates and transition states encountered as reactants proceed to products in one direction must also be encountered, and in precisely the reverse order, in the opposite direction. This is called the principle of microscopic reversibility.

   If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.

7. Define Hammond’s postulate. (Nov 2011)
   It states that that for any single reaction step, the geometry of the transition state for that step resembles the side to which it is closer in free energy. (It states that if there is an unstable intermediate on the reaction pathway, the transition state for the reaction will resemble the structure of this intermediate).

8. What are the methods that are used to determine to Reaction Mechanism?
   • Kinetic Methods
   • Non-Kinetic Methods

9. What are the non kinetic methods of study of reaction mechanism?
   a) Identification of product
   b) Identification of intermediate
   c) Isotopic labeling
   d) Stereo chemical evidences

10. How will you determine reaction kinetics based on isotopic labeling?
    Carbon has two isotopes . \( ^{14}C \) is the radioactive. So we label the C in RCOO- as \( ^{14}RCO \) but in the product \( ^{14}COOH \) is present in alkylcyanide.

11. How will you determine acyloxygen in ester hydrolysis?
    \( ^{18}O \) in the products is found out by the help of mass spectrum i.e., the acid and the alcohol are analysed and the heavy isotope \( ^{18}O \) is present in the acid i.e., confirms the acyloxygen cleavage present.
12. **Write the Arrhenius equation.**
\[ k = A e^{-\frac{E_a}{RT}} \]
K = Rate constant of a chemical reaction; A = Arrhenius constant; Ea = Activation energy; R = gas constant; T = Temperature

13. **Write the Eyring equation.**
\[ k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \]
k = reaction rate constant; T = absolute temperature; R = gas constant; \( k_B \) = Boltzmann constant; \( h \) = Planck’s constant; \( \Delta G^\ddagger \) is the Gibbs energy of activation

14. **Write transition state theory.**
According to the theory, in between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state. During the transition state, the reactants are combined to form a species called the activated complex. The theory suggests that there are three major factors that determine whether a reaction will occur or not:
1. The concentration of the activated complex (the species of the transition state)
2. The rate at which the activated complex breaks apart
3. The way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

15. **What is a transition state?**
The transition state of a chemical reaction is a particular configuration along the reaction coordinate. It is defined as the state corresponding to the highest potential energy or free energy (\( \Delta G \)) along this reaction coordinate.

16. **Write the difference between kinetic product and thermodynamic product.**
Thermodynamic product- it is the most stable product. The thermodynamic product predominates when the reaction is reversible (thermodynamic control)
Kinetic product- It is the product that is formed most rapidly. The kinetic product predominates when the reaction is irreversible (kinetic control)

17. **Write the Diels–Alder reaction.**
The Diels–Alder reaction is the conjugate addition of an alkene to a diene. The alkene that adds to the diene is called the **dienophile**. Because the Diels–Alder reaction leads to the formation of a ring, it is termed a **cycloaddition** reaction. The product contains a cyclohexene ring as a structural unit.

18. **What is kinetic isotope effect?**
**Kinetic isotope effect** (KIE) refers to the change in the rate of a chemical reaction upon substitution of an atom in the reactants with one of its isotopes. Formally, it is defined as the ratio of rate constants for the reactions involving the light (\( k_L \)) and the heavy (\( k_H \)) isotopically substituted reactants
\[ KIE = \frac{k_L}{k_H} \]

19. **What are primary and secondary isotope effects?**
**Primary isotope effect**: isotope effect attributed to a bond breaking event at X–H/X–D bond.
**Secondary isotope effect**: isotope effect attributed to rehybridization or substitution remote from bonds undergoing reaction in the transition state.
20. What are the types of secondary isotope effects?

**α or β secondary isotope effects**: based on whether the isotope is on a position α or β to the bond that is changing. α effect occurs when the atom undergoing reaction has the associated isotope. β effect occurs when the associated isotope is on the atom neighboring that which is undergoing reaction.

21. How is equilibrium constant and free energy related?

\[ \Delta G^\circ = -RT \ln K_{eq}, \]

where \( \Delta G^\circ \) = change in standard gibbs free energy; \( R \) = gas constant; \( T \) = temperature; \( K_{eq} \) = equilibrium constant

22. What is Curtin-Hammett Principle?

If the rates of reaction are much slower than the rate of interconversion, the Curtin-Hammett principle states that the product distribution is controlled by the difference in standard Gibbs energies of the respective transition states. For a reaction,

\[ \frac{P_1}{P_2} = e^{\frac{(E_{A1} - E_{A2}) + \Delta G(1,2)}{RT}} \]

the CH principle states,

23. What are the methods to determine the reactive intermediates?

(a) Various spectroscopic: e.g. electronic absorption, emission, NMR, ESR, IR, microwave spectroscopy, etc (b) Using trapping reagents (c) Crossover experiments (d) Isotopic labeling (e) Stereochemistry analysis (f) Solvent Effects

24. What are steric isotopic effects?

The steric isotope effect is a SKIE that does not involve bond breaking or formation. This effect is attributed to the different vibrational amplitudes of isotopologues (molecules that differ only in their isotopic composition). D is smaller than H in van der Waals radius, therefore isotope effects can be observed in systems where steric hinderance is significant.

25. Write the Hammett equation.

\[ \log \left( \frac{K_X}{K_H} \right) = \rho \sigma_X \]

\( K_X \) = ionization constant; \( K_H \) = acidity constant for benzoic acid; \( \rho \) = reaction constant; \( \sigma_X \) = substituent constant

26. Define microscopic reversibility. (Dec 2016)

The principle of microscopic reversibility, when applied to a chemical reaction that proceeds in several steps, is known as the principle of detailed balancing. Basically, it states that at equilibrium each individual reaction occurs in such a way that the forward and reverse rates are equal

27. Name any two isotopes used to detect intermediates in a reaction. (Dec 2016)

Carbon has two isotopes. C14 is the radioactive. So we label the C in RCOO- as RC14OO but in the product C14 is present in alkylcyanide.

\[ 14^{RCOO^-} + BrCN \rightarrow 14^{RCN} + CO_2 + Br^- \]

O18 in the products is found out by the help of mass spectrum i.e., the acid and the alcohol
are analysed and the heavy isotope $O^{18}$ is present in the acid i.e., confirms the acyloxygen cleavage present.

28. Aaa
29. A
30. A
31. A
32. A
33.

PART-B

1. **Elaborate Kinetic method – Rate law and mechanism.**

   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 29-38.

3. **Discuss about Microscopic reversibility – Kinetic and thermodynamic reversibility.**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 42-45.

4. **Discuss Primary and secondary isotopes effects.**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 86-95.

5. **Derive Arrhenius equation Eyring equation. (2015)**
   Class notes

6. **Discuss in detail about $\Delta G, \Delta S, \Delta H$, Thermodynamics of coupled reactions**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 43-45. And Class notes

PART-C

1. **Write short notes on Rate law and mechanism. (Dec 2016)**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 22-28

2. **Write short notes on Primary and secondary isotopes. (Dec 2016)**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 86-95.

3. **Write short notes on Microscopic reversibility and Eyring equation (Dec 2016)**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 42-45. Class notes
UNIT IV
CATALYSIS

PART-A
1. What are Cofactors, prosthetic groups and Coenzymes?
Cofactors are non-proteinogenic compounds that are required for the catalytic activity of enzymes and which can bind to the enzyme either in a covalent or non-covalent bond. In the covalent bond, when the cofactor is permanently bound to the enzyme, the cofactor is called a prosthetic group. In case of a non-covalent binding of the cofactor to the enzyme it is called a coenzyme.

2. What are NAD, NADP?
NAD, NADP (Nicotinamide adenine dinucleotide, Nicotinamide adenine dinucleotide phosphate): Coenzymes functioning as carriers of hydrogen atoms an electrons in some oxidation – reduction reactions.

3. Define protein.
A biological macromolecule which composed of monomers of aminoacid. All aminoacids are linked by a peptide bond (CONH) to form a polypeptide. Proteins are employed as therapeutic agents, catalyst and materials.

4. What is the mechanism of proton transfer?
Proton transfer can catalyze reaction by stabilizing reactive intermediate either by neutralizing a strongly basic intermediate or by ionization of strongly acidic intermediate.

5. What are the types of catalysts?
a) Heterogeneous catalysts b) Homogeneous catalysts c) Electro catalysts d) Organocatalysis e) Biocatalysts (enzymes)

6. What is biocatalysis? Give an example
Biocatalysis is the use of natural catalysts, such as a catalytic protein which is most of the time referred to as an enzyme, to perform chemical transformations on organic compounds or biochemical reaction inside the living cells. Eg: Urease is an enzyme that catalyzes the conversion of urea to ammonia and carbon dioxide.

7. What is covalent catalysis?
In covalent catalysis, the enzyme contains a reactive group, usually a nucleophilic residue which reacts with the substrate through a nucleophilic attack.

8. What is pKa?
An acid dissociation constant, $K_a$, is a quantitative measure of the strength of an acid in solution. It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions. $pK_a = -\log_{10} K_a$

9. Describe a proton transfer mechanism in enzyme catalysis?
The initial step of the catalysis of serine protease involves the histidine of the active site accepting a proton from the serine residue. This prepares the serine as a nucleophile to attack the amide bond of the substrate. This mechanism includes donation of a proton from serine (a base, pKa14) to histidine (an acid, pKa6), made possible due to the local environment of the bases.

10. Name some nucleophilic groups of enzymes.
Carboxylates (Aspartate, glutamate), thiol (cystine), hydroxyl (Serine, tyrosine)

11. Describe the Schiff base formation in covalent catalysis of enzymes.
Schiff bases appear to be an important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate. The
condensation of a primary amine in an enzyme usually that of a lysine residue, with a carbonyl group of the substrate to form an imine, or Schiff base.

12. **How metal ion helps in enzyme catalysis?**

Metals ions act as electrophilic catalysts, stabilizing the increased electron density or negative charge that can develop during reactions. Or provide a powerful nucleophile at neutral pH. Coordination to a metal ion can increase the acidity of a nucleophile with an ionizable proton.

\[
M^{2+} + \text{Nu}H \rightleftharpoons M^{2+}(\text{Nu}H) \rightleftharpoons M^{2+}(\text{Nu}^-) + H^+
\]

13. **Give some examples for enzymes involved in metal ion catalysis.**

Carboxypeptidase A, Carbonic anhydrase, Enolase, Thermolysin

14. **How proximity and orientation effect the enzyme catalysis?**

This increases the rate of the reaction as enzyme-substrate interactions align reactive chemical groups and hold them close together. This reduces the entropy of the reactants and thus makes reactions such as ligations or addition reactions more favorable, there is a reduction in the overall loss of entropy when two reactants become a single product. This effect is analogous to an effective increase in concentration of the reagents. The binding of the reagents to the enzyme gives the reaction intramolecular character, which gives a massive rate increase.

15. **Compare intermolecular reaction rate with intramolecular reaction rate with an example.**

**Intermolecular Bi molecular Reaction of Imidazole with p-Nitrophenylacetate**

**Intramolecular Bi molecular Reaction of Imidazole with p-Nitrophenylacetate**

\[
\text{Intramolecular Rate} = 24 \times \text{Intermolecular Rate}
\]

16. **What is Lineweaver – Burk plot?**

If is the reciprocal of Michalis Menton approximation, A plot of 1/V versus 1/[S] gives slope of Km/V_max; and Y-intercept of 1/V_max and X intercept of -1/Km

17. **Write the Michaelis menten equation.**

\[
v = \frac{d[P]}{dt} = \frac{V_{\text{max}}[S]}{K_m + [S]}
\]

18. **What is the significance of Km in Michaelis menten equation?**

- Km is a dissociation constant, so the smaller the Km the stronger the interaction between E and S.
- If vo is set equal to 1/2 Vmax, then the relation Vmax /2 = Vmax[S]/Km + [S] can be simplified to Km + [S] = 2[S], or Km = [S]. This means that at one half of the maximal velocity, the substrate concentration at this velocity will be equal to the Km.
- Each enzyme has a characteristic Km for a given substrate that show how tight the binding of the substrate is to the enzyme.

19. **What is turnover number?**

The constant, k_cat (sec^{-1}), is called the turnover number because under saturating substrate conditions, it represents the number of substrate molecules converted to product in a given unit of time on a single enzyme molecule.

20. **What is an inclusion compound?**

An inclusion compound (Clathrate) is a complex in which one chemical compound (the "host") forms a cavity in which molecules of a second "guest" compound are located. Covalent or ionic bonds are not necessary for the inclusion complex.

21. **What is cyclodextrin? Mention its uses.**
Cyclodextrins are host molecules which form monomolecular inclusion compounds. Cyclodextrins are cyclic oligosaccharides which consist of 6(α-Cyclodextrins), 7 (β Cyclodextrins) or 8(γ Cyclodextrins) glucopyranose units. Due to the hydrophilic outside the Cyclodextrin can be dissolved in water. The apolar cavity inside Cyclodextrin provides a hydrophobic matrix, that entrap variety of guest molecules, thereby forming inclusion complex.

22. What is the principle of Phase transfer catalysis (PTC)?
The principle of PTC is based on the ability of certain phase-transfer agents (the PT catalysts) to facilitate the transport of one reagent from one phase into another (immiscible) phase wherein the other reagent exists. Thus, reaction is made possible by bringing together the reagents which are originally in different phases.

23. List out applications of Immobilized enzyme. (Nov/Dec 2011)
Production of L amino acids from D,L-acyl amino acids using Aminoacylase.
Production of high fructose corn syrup from starch using α amylase, glucoamylase
Production of aspartic acid from fumaric acid using Aspartase

24. What is meant by encapsulation?
The entrapping or occlusion of an enzyme is achieved within the lattice of the polymerized gel (Polyacrylamide).

25. Define Damkohler Number. (Nov/Dec 2102)
\[ \frac{\text{reaction rate}}{\text{convective mass transport rate}} = D_H \]

26. Give an example of phase transfer catalysis. (Dec 2016)
The principle of PTC is based on the ability of certain phase-transfer agents (the PT catalysts) to facilitate the transport of one reagent from one phase into another (immiscible) phase wherein the other reagent exists. Thus, reaction is made possible by bringing together the reagents which are originally in different phases.

Eg. Extraction of penicillin with organic solvent

27. What are coenzymes and give an example. (Dec 2016)
NAD, NADP (Nicotinamide adenine dinucleotide, Nicotinamide adenine dinucleotide phosphate): Coenzymes functioning as carriers of hydrogen atoms and electrons in some oxidation – reduction reactions

28. What is reaction intermediates?
If a reaction occurs in more than one step, it must involve species that are neither the reactant nor the final product. These are called reaction intermediates or simply “intermediates”.

29. Give the schematics for the free energy change associated with reaction intermediates.
Each step has its own free energy of activation in a complete reaction when the reaction occurs step wise manner. The complete diagram for the reaction shows the free energy changes associated with an intermediate.

30. What is Diels-Alder adduct?
The Diels–Alder reaction is the conjugate addition of an alkene to a diene. Using 1,3-butadiene as a typical diene, the Diels–Alder reaction may be represented by the general equation:
The alkene that adds to the diene is called the **dienophile**. Because the Diels–Alder reaction leads to the formation of a ring, it is termed a **cycloaddition** reaction.

**PART-B**

1. **Explain about Coenzymes.**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 166-174.

2. **Discuss in detail about Proton transfer.**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 174-179.


4. **Describe Intra molecular reactions.**

5. **Explain about Covalent catalysis**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 198-199.

6. **Describe Catalysis by organized aggregates and phases Inclusion Complexation**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 199-212.

**PART-C**

1. **Explain in detail about proton transfer mechanism with the help of a co-enzyme catalyzed reaction. (Dec 2016)**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 174-179.

2. **Explain in detail the mechanism of covalent catalysis with an example that you have studied. (Dec 2016)**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 198-199.

3. **Describe Catalysis by organized aggregates and phases Inclusion Complexation**
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 199-212.
UNIT V
BIOORGANIC REACTIONS
Timing of Bond formation and fission – Acyl group transfer – C-C bond formation and fission – Catalysis of proton transfer reactions – Transfer of hydride ion – Alkyl group. Transfer – Terpene biosynthesis – Merrifield state peptide synthesis – Sanger method for peptide and DNA sequencing.

PART A

1. What is protein sequencing?
Protein sequencing is a technique to determine the amino acid sequence of a protein, as well as which conformation the protein adopts and the extent to which it is complexed with any non-peptide molecules.

2. What is N-terminal amino acid sequencing?
N-terminal amino acid analysis: Determining which amino acid forms the N-terminus of a peptide chain is useful for two reasons: to aid the ordering of individual peptide fragments’ sequences into a whole chain, and because the first round of Edman degradation is often contaminated by impurities and therefore does not give an accurate determination of the N-terminal amino acid. A generalised method for N-terminal amino acid analysis follows:
1. React the peptide with a reagent that will selectively label the terminal amino acid.
2. Hydrolyse the protein.
3. Determine the amino acid by chromatography and comparison with standards.

3. What is C-terminal amino acid sequencing?
C-terminal amino acid analysis: The number of methods available for C-terminal amino acid analysis is much smaller than the number of available methods of N-terminal analysis. The most common method is to add carboxypeptidases to a solution of the protein, take samples at regular intervals, and determine the terminal amino acid by analysing a plot of amino acid concentrations against time. This method will be very useful in the case of polypeptides and protein-blocked N termini. C-terminal sequencing would greatly help in verifying the primary structures of proteins predicted from DNA sequences and to detect any posttranslational processing of gene products from known codon sequences.

Sanger’s strategy can be outlined as follows:
1. Determine what amino acids are present and their molar ratios.
2. Cleave the peptide into smaller fragments, separate these fragments, and determine the amino acid composition of the fragments.
3. Identify the N-terminal and the C-terminal amino acid in the original peptide and in each fragment.
4. Organize the information so that the amino acid sequences of small fragments can be overlapped to reveal the full sequence.
5. **Give the Sanger’s sequencing reaction.**

The reaction is carried out by mixing the peptide and 1-fluoro-2,4-dinitrobenzene in the presence of a weak base such as sodium carbonate. In the first step the base abstracts a proton from the terminal H,N group to give a free amino function. The nucleophilic amino group attacks 1-fluoro-2,4-dinitrobenzene, displacing fluoride.

6. **What is bond fission?**

The breaking of the covalent bond of a molecule to form two or more fragment species is called bond fission.

7. **What are the types of bond fission?**

1) Homolytic fission
2) Heterolytic fission

8. **What is homolytic fission?**

In hemolytic fission, one electron of the shared pair in the covalent bond goes with each of the bonded atoms forming free radicals. Organic reactions which proceed by hemolytic fission are called free radical reactions/nonpolar reactions.

9. **What is heterolytic fission?**

In heterolytic fission, the bonding electron pair is shifted to the more electronegative atom. Heterolytic fission normally occurs in solution phase, in presence of polar solvents. The organic reactions which proceed by heterolytic fission are called ionic/polar reactions.

10. **What are oligomeric proteins? Give examples.**

Oligomeric proteins consists of two or more polypeptide chains, which are usually linked to each other by non-covalent interactions and never by peptide bonds. The molecular weight is usually in excess of 35,000. E.g.: lactate dehydrogenase, lactose synthase, pyruvate dehydrogenase and tryptophan synthase.

11. **Differentiate between peptide and amide bond.**

N-substituted amide bond is peptide bond.
R-CO-NH₂ (amide bond) → R-CO-NH-R (peptide bond)

12. **Mention the different kinds of non covalent bonding interaction that stabilizes the protein structure. (May 2011).**

A number of non-covalent interactions such as hydrogen bonding, ionic interactions, Van Der Waals forces, and hydrophobic packing helps to stabilize the protein structure.

13. **What is solid state peptide synthesis (Dec '2012)**

SSPS allows the synthesis of natural peptides which are difficult to express in bacteria, the incorporation of unnatural amino acids, peptide/protein backbone modification, and the synthesis of D-proteins, which consist of D-amino acids.
14. **What are terpenes? Give an example.**
**Terpene,** any of a class of hydrocarbons occurring widely in plants and animals and empirically regarded as built up from isoprene, a hydrocarbon consisting of five carbon atoms attached to eight hydrogen atoms ($\text{C}_5\text{H}_8$).

\[
\text{(CH}_3\text{)}_2\text{C}==\text{CHCH}_2\text{CH}_2\text{CH}==\text{CH}_2
\]

Myrcene

15. **Write the classification of terpenes based on number of carbon atoms.**
Monoterpene(C-10), Sesquiterpene(C-15), Diterpene (C-20), Sesterpene(C-25), Triterpene(C-30) and Tetraterpene(C-40)

16. **Classify amino acids based on polarity.** (May 2011).
Based on polarity, amino acids are classified into four groups as follows,
Non-polar amino acids- alanine, valine, leucine, isoleucine, phenyl alanine, glycine, tryptophan, methionine and proline.
Polar amino acids with no charge-serine, threonine, tyrosine, cysteine, glutamine and asparagine.
Polar amino acids with positive charge- lysine, arginine and histidine.
Polar amino acids with negative charge- aspartic acid and glutamic acid

17. **How amino acids exhibit the behavior of zwitter ion?**
An amino acid has both a basic amine group and an acidic carboxylic acid group. There is an internal transfer of a hydrogen ion from $–\text{COOH}$ group to the $–\text{NH}_2$ group to leave an ion with both a negative an positive charge, thereby behaving as a zwitter ion

18. **Write about the C-C bond formation in synthesis of geranyl pyrophosphate**
Using the $n$-electrons of C-C double bond, isopentenyl pyrophosphate acts as a nucleophile and displaces pyrophosphate from dimethylallyl pyrophosphate.

The tertiary carbocation formed in this step can react according to any of the various reaction pathways available to carbocations. One of these is loss of a proton to give a double bond.

19. **How amino groups are protected in SSPS?**
The reactivity of an amino group is suppressed by converting it to an amide, and amino groups are most often protected by acylation. The benzyloxycarbonyl group is one of the most often used amino-protecting groups. It is attached by acylation of an amino acid with benzyloxycarbonyl chloride.

20. **What is DNA sequencing?**
**DNA sequencing** is the process of determining the precise order of nucleotides within a DNA molecule. It includes any method or technology that is used to determine the order of the four bases—adenine, guanine, cytosine, and thymine—in a strand of DNA.
21. Write the Sanger’s strategy for amino acid sequencing.
- Determine what amino acids are present and their molar ratios.
- Cleave the peptide into smaller fragments, separate these fragments, and determine the amino acid composition of the fragments.
- Identify the N-terminal and the C-terminal amino acid in the original peptide and in each fragment.
- Organize the information so that the amino acid sequences of small fragments can be overlapped to reveal the full sequence.

22. Sort the methods available for the determination of the primary structure.
   a) Sequencing from the N-terminus (Edmann degradation) 
b) Mass spectroscopy 
c) Fragmentation of a protein as peptide. 
d) Mapping the positions of residues  
e) Purification of peptide: Diagonal techniques 
f) Disulfide bonds location determination

23. What are restriction enzymes?
An enzyme produced chiefly by certain bacteria, that has the property of cleaving DNA molecules at or near a specific sequence of bases.

24. What are the steps involved in sanger di-deoxy method of sequencing.
- Ability to synthesize faithfully a complementary copy of a single stranded DNA template using a synthetic 5’end labeled oligodeoxynucleotide as primer.
- Polymerization using low concentration of one the 4ddNTPs and in higher concentration of normal dNTPs, termination of growing point of the DNA chain using 2’3’-dideoxy nucleotide triphosphate as substrate,
- Separation of fragment using gel electrophoresis,
- Analyzing the separated fragments using autoradiography

25. What is an isoelectric point (pI)?
The pH of an aqueous solution at which the concentration of the zwitterions is a maximum is called the isoelectric point (pI).

26. What is the effect of temperature on the stereochemistry of enzymatic reactions. (Dec 2016)
Stereoselectivity decreases at higher temperatures and in the presence of NADP analogues.

27. Give examples of haemolytic and heterolytic reactions. (Dec 2016)
Most organic transformations involve the movement of electron pairs (heterolytic reactions). There are a few important addition reactions, however, in which the electron reconfiguration involves the movement of single electrons. Whereas heterolytic bond cleavage leads to ion pairs, homolytic bond cleavage results in unpaired electrons – or free radicals. Some weak bonds have a tendency to fragment homolytically (e.g., peroxides, halogens). Chemists use a slight variation of curved arrow notation to show the movement of single electrons. For eg. heterolytic vs. homolytic fragmentation of Br2.

28. Give the structure of zwitter ion.
29. Define protein sequencing.
   protein sequencing is a technique to determine the amino acid sequence of a protein, as well as
   which conformation the protein adopts and the extent to which it is complexed with any non-
   peptide molecules.

30. Give the type of amino acid sequencing.
   N-terminal amino acid analysis
   C-terminal amino acid analysis

PART-B

1. Elaborate Timing of Bond formation and fission with an example of C-C bond
   formation and fission
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 232-
   235.

2. Explain about Acyl group transfer
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 215-
   224.

3. Discuss Catalysis of proton transfer reactions
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 224-
   232.

4. Describe Transfer of hydride ion
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 235-
   239.

5. Write in detail about Alkyl group Transfer and Terpene biosynthesis (2015)
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 240-
   245.
   Organic Chemistry by Carey and Giuliano- 1090-1100.

6. Explain Merrifield state peptide synthesis – Sanger method for peptide and DNA
   sequencing. (2015)
   Organic Chemistry by Carey and Giuliano- 1153-1155; 1198-1200.

PART-B

1. Explain in detail about terpene biosynthesis. Explain solid phase peptide
   biosynthesis with a diagram.
   Organic Chemistry by Carey and Giuliano- 1153-1155;

2. Explain Sanger’s methods for DNA sequencing.
   Organic Chemistry by Carey and Giuliano- 1198-1200

3. Discuss about transfer of alkyl group and hydride ion.
   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 235-
   245
4. **What is the Aufbau principle with example?**
   The Aufbau Principle states that electrons enter the lowest energy orbitals first.
   - The lower the principal quantum number \( n \) the lower the energy.
   - Within an energy level, s orbitals are the lowest energy, followed by p, d and then f. F orbitals are the highest energy for that level.

5. **What is Hammond’s postulate?**
   It states that that for any single reaction step, the geometry of the transition state for that step resembles the side to which it is closer in free energy. (It states that if there is an unstable intermediate on the reaction pathway, the transition state for the reaction will resemble the structure of this intermediate).

6. **Give an example of a Claisen condensation reaction.**

   ![FIGURE 21.1 The mechanism of the Claisen condensation of ethyl acetate.](image)

   **Overall reaction:**
   \[
   2\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{C}═\text{CH}_2\text{COCH}_3 + \text{CH}_3\text{CH}_2\text{OH}
   \]

   **Step 1:** Proton abstraction from the \( \alpha \) carbon atom of ethyl acetate to give the corresponding enolate.

   **Step 2:** Nucleophilic addition of the ester enolate to the carbonyl group of the neutral ester. The product is the anionic form of the tetrahedral intermediate.

7. **What is Barnase?**
   Barnase (a portmanteau of "Bacterial" "Ribonuclease") is a bacterial protein that consists of 110 amino acids and has ribonuclease activity. It is synthesized and secreted by the bacterium Bacillus amyloliquefaciens, but is lethal to the cell when expressed without its inhibitor barstar.

8. **Define microscopic reversibility.**
   The principle of **microscopic reversibility**, when applied to a chemical reaction that proceeds in several steps, is known as the principle of detailed balancing. Basically, it states that at equilibrium each individual reaction occurs in such a way that the forward and reverse rates are equal.
2. Name any two isotopes used to detect intermediates in a reaction.

Carbon has two isotopes. C\textsuperscript{14} is the radioactive. So we label the C in RCOO\textsuperscript{-} as RC\textsubscript{14}OO but in the product C\textsuperscript{14} is present in alkylcyanide.

O\textsuperscript{18} in the products is found out by the help of mass spectrum i.e., the acid and the alcohol are analysed and the heavy isotope O\textsuperscript{18} is present in the acid i.e., confirms the acyloxygen cleavage present.

3. Give an example of phase transfer catalysis.

The principle of PTC is based on the ability of certain phase-transfer agents (the PT catalysts) to facilitate the transport of one reagent from one phase into another (immiscible) phase wherein the other reagent exists. Thus, reaction is made possible by bringing together the reagents which are originally in different phases.

Eg. Extraction of penicillin with organic solvent

4. What are coenzymes and give an example.

NAD, NADP (Nicotinamide adenine dinucleotide, Nicotinamide adenine dinucleotide phosphate): Coenzymes functioning as carriers of hydrogen atoms an electrons in some oxidation – reduction reactions

5. What is the effect of temperature on the stereochemistry of enzymatic reactions.

stereoselectivity decreases at higher temperatures and in the presence of NADP analogues.

6. Give examples of haemolytic and heterolytic reactions.

Most organic transformations involve the movement of electron pairs (heterolytic reactions). There are a few important addition reactions, however, in which the electron reconfiguration involves the movement of single electrons. Whereas heterolytic bond cleavage leads to ion pairs, homolytic bond cleavage results in unpaired electrons – or free radicals. Some weak bonds have a tendency to fragment homolytically (e.g.,
peroxides, halogens). Chemists use a slight variation of curved arrow notation to show the movement of single electrons. For eg., heterolytic vs. homolytic fragmentation of Br2.

![Diagram showing heterolytic and homolytic fragmentation of Br2.]

**Part-B**

7. a) Explain diagrammatically and energetically the conformers of ethane, and n-butane.

   Organic Chemistry by Carey and Giuliano- 102-120

   (OR)

   b) Explain

   (i) Stereochemical activity around tetrahedral carbon

   Organic Chemistry by Carey and Giuliano- 278-310

   (ii) Conformation of the peptide bond

   Class notes.

8. a) Explain the mechanism of an elimination reaction with an example. Explain the effect of steric hindrance on the rate of SN2 reactions.

   Organic Chemistry by Carey and Giuliano- 326-347.

   (OR)

   b) Explain reaction of carbonyl groups with amines, with an example. Explain the SN1 mechanism of nucleophilic substitution with hydrolysis of ter-butyl bromide along with energy diagram.

   Organic Chemistry by Carey and Giuliano- 738-739.

9. a) Write short notes on

   (i) Rate law and mechanism.

   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 22- 28

   (ii) Primary and secondary isotopes.

   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams– 86- 95.

   (OR)

   b) Write short notes on

   (i) Microscopic reversibility

   Organic and Bioorganic mechanisms by Michael Page and Andrew Williams – 42- 45.

   (ii) Eyring equation.

   Class notes

10. a) Explain in detail about proton transfer mechanism with the help of a coenzyme catalyzed reaction.
b) Explain in detail the mechanism of covalent catalysis with an example that you have studied.

11. a) Explain in detail about terpene biosynthesis. Explain solid phase peptide biosynthesis with a diagram.
   (OR)
   b) Explain Sanger’s methods for DNA sequencing.

Part-C

12. a) Explain the stereochemistry of methyl methylene transformation with malate synthase reaction.
   (OR)
   b) Write a detailed account of the stereochemistry of nucleophilic reactions and chiral phosphate.

B.E./B.Tech. DEGREE EXAMINATION, NOVEMBER/DECEMBER 2017
Third Semester
Biotechnology
BT 6302 – BIOORGANIC CHEMISTRY
(Regulations 2013)

Time : Three Hours

Maximum : 100 Marks

Answer ALL questions.

PART – A

(10×2=20 Marks)

1. State the Octet rule.

2. Define Electronegativity.

3. What are nucleophiles ? Give an examples.


5. What is rate law ?

6. What is meant by transition state ?

7. Write any two properties of a catalyst.

8. What are co-enzymes ?

9. What do you mean by proton transfer reactions ?

10. What are peptides ?
PART – B

11. a) Describe the following concepts of acids and bases.
   i) Arrhenius concept
   ii) Lowry Bronsted concept.
   
   (OR)

   b) Explain the conformational analysis of cyclohexane.

12. a) Explain the mechanism of the following reactions:
   i) Claisen condensation
   ii) Michael condensation.
   
   (OR)

   b) i) Describe the mechanism of SN1 reaction.
   ii) Compare SN1 and SN2 reactions.

13. a) What are primary and secondary isotopic effects? Explain.
   
   (OR)

   b) i) Describe the significance of entropy of activation, free energy of activation
       and enthalpy of activation.
       ii) Write notes on thermodynamically coupled reactions.

14. a) What is covalent catalysis? Discuss its significance.
   
   (OR)

   b) Describe the mechanism of intramolecular reactions with suitable examples.

15. a) Explain the catalysis of proton transfer reactions.
    
    (OR)

   b) Explain the Sanger method of Peptide sequencing.

PART – C

16. a) Explain the kinetic method of analysis and its importance.
    
    (OR)

   b) Explain the applications of bioorganic reactions and catalytic reactions.