Question 1: (a) Give an example of the following and draw their biochemical structures (any three): (3×5=15) (i) Non reducing disaccharide (ii) Sugar derivative in fungal cell wall (iii) Epimer (iv) Essential fatty acid (b) Define entropy and enthalpy. Write a mathematical expression relating these two terms. (1+2=3)

(a) Give an example of the following and draw their biochemical structures (any three): I cannot generate biochemical structures (diagrams). However, I can provide the example and a detailed description of the biochemical structure for each.

- **(i) Non-reducing disaccharide:**
    - **Example:** Sucrose
    - **Biochemical Structure Description:** Sucrose is a disaccharide composed of one molecule of α-D-glucose and one molecule of β-D-fructose. The anomeric carbon of glucose (C1 of the α-glucose) is linked to the anomeric carbon of fructose (C2 of the β-fructose) by an α,β-(1→2) glycosidic bond. Because the anomeric carbons of both monosaccharides are involved in the glycosidic bond, neither can open to form an aldehyde group, which is why sucrose is a non-reducing sugar.
- **(ii) Sugar derivative in fungal cell wall:**
    - **Example:** N-acetylglucosamine (NAG)
    - **Biochemical Structure Description:** N-acetylglucosamine is an amino sugar derivative of glucose. It is essentially glucose where the hydroxyl group on C2 is replaced by an acetylated

amino group ($-NHCOCH_3$). In fungal cell walls, multiple N-acetylglucosamine units are linked together by β-(1→4) glycosidic bonds to form chitin, which is a major structural component providing rigidity and protection to the fungal cell.

- **(iii) Epimer:**
    - **Example:** Glucose and Galactose
    - **Biochemical Structure Description:** Epimers are a pair of stereoisomers that differ in the configuration at only one chiral carbon atom, excluding the anomeric carbon (C1). Glucose and galactose are C4 epimers. This means their structures are identical except for the orientation of the hydroxyl group at the fourth carbon atom. In D-glucose, the hydroxyl group at C4 points to the right in the Fischer projection, while in D-galactose, it points to the left.

- **(iv) Essential fatty acid:**
    - **Example:** Linoleic acid
    - **Biochemical Structure Description:** Linoleic acid is an 18-carbon polyunsaturated fatty acid with two double bonds. Its chemical formula is $CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COOH$. The double bonds are located at the 9th and 12th carbons from the carboxyl end, both in the *cis* configuration, leading to the designation 18:2($\Delta^{9,12}$) or more commonly, an omega-6 ($\omega-6$) fatty acid. Humans cannot synthesize double bonds at these positions and thus must obtain it from their diet.

(b) Define entropy and enthalpy. Write a mathematical expression relating these two terms.

- **Entropy (ΔS):**
    - Entropy is a measure of the disorder or randomness of a system. A system with high entropy has many possible arrangements of its components and is considered more disordered. Processes that increase the disorder of a system tend to be spontaneous. In biological systems, entropy often increases with the breakdown of complex molecules into simpler ones or the dispersion of molecules.
- **Enthalpy (ΔH):**
    - Enthalpy is a measure of the total heat content of a system. In biochemical reactions, it primarily reflects the heat absorbed or released during a process at constant pressure.
    - An **exothermic** reaction releases heat into the surroundings, so ΔH is negative.
    - An **endothermic** reaction absorbs heat from the surroundings, so ΔH is positive.
- **Mathematical expression relating these two terms (Gibbs Free Energy Equation):** The relationship between entropy, enthalpy, and the spontaneity of a process at constant temperature and pressure is given by the Gibbs Free Energy equation: $\Delta G = \Delta H - T\Delta S$ Where:

- ΔG is the change in Gibbs Free Energy (a measure of spontaneity).
- ΔH is the change in Enthalpy.
- T is the absolute temperature in Kelvin.
- ΔS is the change in Entropy.

Question 2: (a) Differentiate between the following (any three): (3×5=15) (i) Starch and Cellulose (ii) Enantiomers and Diastereoisomers (iii) Phosphoglycerides and Sphingolipids (iv) Standard free energy change and Actual free energy change (b) What are anomers. Discuss giving an example. (1+2=3)

(a) Differentiate between the following (any three):

- **(i) Starch and Cellulose:**
  - **Starch:**
    - **Function:** Major energy storage polysaccharide in plants.
    - **Monomer Linkage:** Composed of α-D-glucose units linked by glycosidic bonds.
    - **Structure:** Consists of two main components:
      - **Amylose:** Linear, unbranched polymer of α-(1→4) glycosidic bonds.

- **Amylopectin:** Branched polymer with α-(1→4) glycosidic bonds in the main chain and α-(1→6) glycosidic bonds at branch points.

- **Digestibility:** Readily digestible by humans (e.g., by amylases) due to the α-linkages, which can be easily broken down.
- **Solubility:** Amylose is sparingly soluble in hot water, while amylopectin is insoluble but forms a stable dispersion.
- **Shape:** Tends to form helical or coiled structures.

- **Cellulose:**

  - **Function:** Major structural polysaccharide in plant cell walls, providing rigidity and strength.
  - **Monomer Linkage:** Composed of β-D-glucose units linked by β-(1→4) glycosidic bonds.
  - **Structure:** Linear, unbranched polymer. The β-linkages cause each glucose unit to be rotated 180 degrees relative to its neighbors, resulting in a straight, extended chain.
  - **Digestibility:** Indigestible by most animals (including humans) as they lack the enzyme cellulase to break down the β-(1→4) linkages. Digested by ruminants and some

other animals that harbor cellulase-producing microorganisms.

- **Solubility:** Insoluble in water due to extensive hydrogen bonding between parallel cellulose chains, forming strong microfibrils.
- **Shape:** Forms straight, rigid fibrils.

- **(ii) Enantiomers and Diastereoisomers:**
  - **Enantiomers:**
    - **Definition:** Stereoisomers that are non-superimposable mirror images of each other.
    - **Chiral Centers:** Must have at least one chiral center (carbon atom bonded to four different groups). If there are multiple chiral centers, all of them must have the opposite configuration for them to be enantiomers.
    - **Properties:** Possess identical physical properties (e.g., melting point, boiling point, density, solubility) except for their interaction with plane-polarized light (they rotate it in opposite directions to equal extents). They also react identically with achiral reagents.
    - **Biological Activity:** Often have different biological activities due to the chiral nature of biological systems (e.g., enzymes, receptors).
    - **Example:** D-glucose and L-glucose.

- **Diastereoisomers:**
  - **Definition:** Stereoisomers that are not mirror images of each other. They differ in the configuration at at least one, but not all, chiral centers.
  - **Chiral Centers:** Must have at least two or more chiral centers. If there are multiple chiral centers, at least one has the same configuration, and at least one has the opposite configuration.
  - **Properties:** Possess different physical and chemical properties (e.g., melting point, boiling point, density, solubility, optical rotation). They also react differently with both chiral and achiral reagents.
  - **Biological Activity:** Typically have different biological activities.
  - **Example:** D-glucose and D-galactose (C4 epimers), D-glucose and D-mannose (C2 epimers). Epimers are a specific type of diastereoisomer.

- **(iii) Phosphoglycerides and Sphingolipids:**
  - **Phosphoglycerides (Glycerophospholipids):**
    - **Backbone:** Glycerol-3-phosphate is the core backbone molecule.

- **Fatty Acids:** Two fatty acids are esterified to the first two carbons of glycerol. These fatty acids can be saturated or unsaturated, contributing to membrane fluidity.
- **Phosphate Group:** A phosphate group is esterified to the third carbon of glycerol.
- **Head Group:** A polar head group (e.g., choline, ethanolamine, serine, inositol) is attached to the phosphate group. This head group determines the specific type of phosphoglyceride and its charge.
- **Prevalence:** The most abundant class of lipids in biological membranes.
- **Examples:** Phosphatidylcholine, Phosphatidylethanolamine, Phosphatidylserine.

- **Sphingolipids:**
  - **Backbone:** Sphingosine, a complex amino alcohol, serves as the backbone molecule instead of glycerol.
  - **Fatty Acids:** One fatty acid is attached to the amino group of sphingosine via an amide linkage, forming a ceramide.
  - **Phosphate Group:** Some sphingolipids (sphingophospholipids) contain a phosphate group.
  - **Head Group:** A polar head group is attached to the primary hydroxyl group of sphingosine. This can be a

simple sugar (glycosphingolipids) or a phosphate group with an additional substituent (e.g., choline in sphingomyelin).

- **Prevalence:** Less abundant than phosphoglycerides, but particularly important in nervous tissue (e.g., myelin sheath).
- **Examples:** Sphingomyelin (a sphingophospholipid), Cerebrosides, Gangliosides (both glycosphingolipids).

- **(iv) Standard free energy change and Actual free energy change:**
  - **Standard Free Energy Change ($\Delta G^{0'}$ or ΔG^{o}):**
    - **Definition:** The change in Gibbs free energy for a reaction when all reactants and products are at **standard conditions**.
    - **Standard Conditions (Biochemical):**
      - Temperature: 25°C (298 K).
      - Pressure: 1 atmosphere.
      - Concentration: 1 M for all solutes (except H+, which is 10^{-7} M for pH 7.0, indicated by the prime ('). Water concentration is considered constant).
    - **Significance:** A constant value for a given reaction under defined conditions. It indicates the intrinsic tendency of a reaction to proceed and is used to compare the relative

favorability of different reactions. It does not predict the direction of a reaction under non-standard, physiological conditions.

- **Actual Free Energy Change (ΔG):**
  - **Definition:** The change in Gibbs free energy for a reaction under **actual, non-standard conditions** (i.e., the prevailing cellular concentrations of reactants and products, and potentially different temperatures and pressures).
  - **Calculation:** Calculated using the equation: $\Delta G = \Delta G^{0'} + RT\ln Q$, where Q is the reaction quotient.
  - **Significance:** Predicts the actual direction and spontaneity of a reaction within a living cell at any given moment. A negative ΔG indicates a spontaneous (exergonic) reaction in the forward direction under those conditions, a positive ΔG indicates a non-spontaneous (endergonic) reaction, and a ΔG of zero indicates equilibrium.

(b) What are anomers. Discuss giving an example.

- **Anomers:**
  - Anomers are a specific type of stereoisomer that differ in the configuration at the **anomeric carbon** (the new chiral center formed when a monosaccharide cyclizes to form a hemiacetal or hemiketal).

- The anomeric carbon is the carbon atom that was originally the carbonyl carbon (aldehyde or ketone) in the open-chain form of the sugar.
- The two anomeric forms are designated as α and β.

- **Discussion and Example (Glucose):**
  - When an aldohexose like D-glucose cyclizes to form a six-membered pyranose ring (glucopyranose), the hydroxyl group on C5 (or C4 for furanose) attacks the carbonyl carbon (C1 in aldoses). This intramolecular reaction forms a new stereocenter at C1.
  - **α-anomer:** In the cyclic structure, if the hydroxyl group on the anomeric carbon (C1) is on the **opposite side** of the ring from the CH_2OH group at C6 (or the highest numbered chiral carbon in general), it is designated as the α-anomer. In a Haworth projection, for D-sugars, the α-hydroxyl typically points **down**.
  - **β-anomer:** If the hydroxyl group on the anomeric carbon (C1) is on the **same side** of the ring as the CH_2OH group at C6, it is designated as the β-anomer. In a Haworth projection, for D-sugars, the β-hydroxyl typically points **up**.
  - **Example:** D-glucose in aqueous solution exists in equilibrium between its open-chain form and two cyclic anomers: α-D-glucopyranose and β-D-glucopyranose.
    - In α-D-glucopyranose, the -OH group at C1 is *down*.

    - In β-D-glucopyranose, the -OH group at C1 is *up*.
  - These anomers can interconvert in aqueous solution through a process called mutarotation, passing through the open-chain aldehyde intermediate. This explains why freshly prepared solutions of glucose have a changing optical rotation until equilibrium is reached between the α and β forms.

Question 3: (a) State true or false giving reason/s (any four): (4×3=12) (i) Deoxyribose is a modified monosaccharide (ii) All sugars are optically active (iii) All monosaccharides are reducing in nature (iv) Oleic acid is a polyunsaturated fatty acid (v) Lipids are better storage fuel than carbohydrates (b) Discuss how is free energy change of a chemical reaction related to the concentration of its reactants and products. (6)

(a) State true or false giving reason/s (any four):

- **(i) Deoxyribose is a modified monosaccharide**
  - **True.**
  - **Reason:** Deoxyribose is a modified form of the monosaccharide ribose. It is derived from ribose by the reduction of the hydroxyl group at the 2' carbon to a hydrogen atom. This structural modification is crucial as deoxyribose is the sugar component of DNA, while ribose is found in RNA.
- **(ii) All sugars are optically active**
  - **False.**

- **Reason:** To be optically active, a molecule must be chiral, meaning it cannot be superimposed on its mirror image. This requires the presence of at least one chiral carbon atom (a carbon atom bonded to four different groups). While most sugars, especially those with three or more carbon atoms (e.g., glyceraldehyde, glucose), are chiral and thus optically active, some simple sugars or sugar alcohols are not. For example, dihydroxyacetone, the simplest ketose (a three-carbon sugar), has no chiral carbons and is therefore optically inactive.

- **(iii) All monosaccharides are reducing in nature**
  - **True.**
  - **Reason:** All monosaccharides contain either a free aldehyde group (aldoses) or a free ketone group (ketoses). In aqueous solutions, these cyclic forms are in equilibrium with their open-chain forms, where the aldehyde or ketone group is exposed. The aldehyde group in aldoses (or the α-hydroxyketone group in ketoses, which can isomerize to an aldehyde in solution) can be oxidized by mild oxidizing agents (like Benedict's or Tollens' reagent). This ability to be oxidized means they can reduce other compounds, hence they are called reducing sugars.

- **(iv) Oleic acid is a polyunsaturated fatty acid**
  - **False.**
  - **Reason:** Oleic acid is an 18-carbon fatty acid with only **one** double bond (18:1, Δ^9). A polyunsaturated fatty acid (PUFA)

must contain **two or more** double bonds. Examples of polyunsaturated fatty acids include linoleic acid (two double bonds) and linolenic acid (three double bonds).

- **(v) Lipids are better storage fuel than carbohydrates**
    - **True.**
    - **Reason:** Lipids, particularly triglycerides, are highly reduced compounds compared to carbohydrates. The oxidation of lipids releases significantly more energy per unit mass than the oxidation of carbohydrates. This is because lipids have a higher proportion of C-H bonds and fewer oxygen atoms than carbohydrates. For instance, the complete oxidation of fats yields approximately 9 kcal/g, whereas carbohydrates yield about 4 kcal/g. Additionally, lipids are stored in an anhydrous form, while carbohydrates (like glycogen) are stored hydrated, meaning lipids provide more compact energy storage by weight.

(b) Discuss how is free energy change of a chemical reaction related to the concentration of its reactants and products.

The actual free energy change (ΔG) of a chemical reaction in a biological system is critically dependent on the concentrations of its reactants and products, and not just on the intrinsic properties of the molecules. This relationship is described by the equation:

$$\Delta G = \Delta G^{0'} + RT\ln Q$$

Where:

- ΔG is the actual free energy change under prevailing (non-standard) conditions. It determines the spontaneity and direction of the reaction *in vivo*.
- $\Delta G^{0'}$ is the standard free energy change, a constant value for a given reaction under defined standard conditions (1 M concentration for all solutes, 25°C, pH 7.0). It represents the intrinsic energy difference between products and reactants.
- R is the gas constant ($8.314 J \cdot mol^{-1} \cdot K^{-1}$).
- T is the absolute temperature in Kelvin.
- $\ln$ is the natural logarithm.
- Q is the **reaction quotient**, which represents the ratio of product concentrations to reactant concentrations at any given time (not necessarily at equilibrium). For a general reaction $aA + bB \rightleftharpoons cC + dD$, the reaction quotient Q is given by:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

How concentration affects ΔG:

1. **Effect of Reaction Quotient (Q) on ΔG:**
    - **When $Q < K_{eq}$ (Equilibrium Constant):** If the ratio of products to reactants is less than the equilibrium constant, meaning there are relatively more reactants and/or fewer products than at equilibrium, the $\ln Q$ term will be more negative (or less

positive). This makes ΔG more negative, driving the reaction forward (exergonic). Even if $\Delta G^{0'}$ is positive (unfavorable under standard conditions), a sufficiently low product-to-reactant ratio can make ΔG negative, allowing the reaction to proceed.

- **When $Q > K_{eq}$:** If the ratio of products to reactants is greater than the equilibrium constant, meaning there are relatively more products and/or fewer reactants than at equilibrium, the $\ln Q$ term will be more positive. This makes ΔG more positive, driving the reaction in the reverse direction (endergonic in the forward direction).
- **When $Q = K_{eq}$:** At equilibrium, $\Delta G = 0$. In this state, the rate of the forward reaction equals the rate of the reverse reaction, and there is no net change in concentrations of reactants and products. At equilibrium, Q becomes equal to K_{eq}, and the equation simplifies to $0 = \Delta G^{0'} + RT\ln K_{eq}$, which can be rearranged to $\Delta G^{0'} = -RT\ln K_{eq}$.

2. **Driving Unfavorable Reactions:** Many biochemical reactions that are endergonic under standard conditions ($\Delta G^{0'} > 0$) can be driven forward *in vivo* because the actual cellular concentrations of reactants are kept high and product concentrations are kept low.
   - **High Reactant Concentration:** If the cell maintains a high concentration of reactants, the denominator of Q becomes large, making Q small. This pushes $\ln Q$ to be negative, making ΔG more negative.

- **Low Product Concentration:** If the cell rapidly removes products as they are formed (e.g., by immediately using them in the next step of a metabolic pathway, or by converting them into another form), the numerator of Q remains small. This keeps Q small and $\ln Q$ negative, continuously pulling the reaction forward.
- **Coupling with Exergonic Reactions:** Crucially, endergonic reactions are often coupled with highly exergonic reactions (like ATP hydrolysis), where the overall ΔG of the coupled reactions becomes negative, allowing the unfavorable reaction to proceed. However, even in coupled reactions, the mass action ratio (Q) still plays a role in influencing the actual ΔG.

In summary, while $\Delta G^{0'}$ provides a baseline for a reaction's inherent favorability, the actual direction and spontaneity of a reaction in a living cell (ΔG) are dynamically determined by the prevailing concentrations of reactants and products, which continuously influence the reaction quotient Q. Cells finely regulate these concentrations to ensure metabolic pathways proceed in the desired direction.

Question 4: (a) Write short note on the following (any three): (3×5=15) (i) Energy rich compound (ii) Sphingomyelin (iii) Mutarotation (iv) Liposomes (b) What is pectin? Give its function : (1+2=3)

(a) Write short note on the following (any three):

- **(i) Energy-rich compound:**

- Energy-rich compounds, also known as high-energy compounds or high-energy phosphate compounds, are molecules that contain a particular type of chemical bond (often a phosphate bond) that, upon hydrolysis, releases a large amount of free energy (typically $\Delta G^{0'}$ values more negative than -25 kJ/mol or -6 kcal/mol).
- These compounds serve as the immediate currency of energy in biological systems, facilitating various endergonic (energy-requiring) cellular processes. The "high energy" does not refer to the bond strength itself, but rather to the large negative free energy change upon hydrolysis, driven by factors like resonance stabilization of the products, electrostatic repulsion in the reactant, and increased entropy.
- **Examples:**
  - **ATP (Adenosine Triphosphate):** The most common and direct energy currency in cells. Hydrolysis of the terminal phosphate bond to ADP + Pi releases significant energy.
  - **Phosphoenolpyruvate (PEP):** Has an extremely high phosphate group transfer potential.
  - **1,3-Bisphosphoglycerate:** An intermediate in glycolysis with high phosphoryl transfer potential.
  - **Creatine Phosphate:** An energy reserve in muscle cells, particularly for rapid ATP regeneration.

    - **Acetyl-CoA (Thioester bond):** The thioester bond is also considered an energy-rich bond due to its high standard free energy of hydrolysis.

  - These compounds are crucial for coupling exergonic (energy-releasing) metabolic reactions (like glucose oxidation) to endergonic cellular activities (like muscle contraction, active transport, biosynthesis, and nerve impulse transmission).

- **(ii) Sphingomyelin:**

  - Sphingomyelin is a type of sphingolipid, specifically a **sphingophospholipid**, meaning it contains a phosphate group. It is one of the major lipids found in animal cell membranes, particularly abundant in the myelin sheath that surrounds and insulates nerve cell axons.

  - **Structure:** It has a sphingosine backbone, to which a fatty acid is attached via an amide linkage (forming a ceramide). A phosphate group is then attached to the primary hydroxyl group of the sphingosine, and typically **choline** (less commonly ethanolamine) is linked to the phosphate group.

  - **Key Features:**

    - **No Glycerol:** Unlike phosphoglycerides, it does not have a glycerol backbone.

    - **Amide Linkage:** The fatty acid is attached by an amide bond, not an ester bond.

- **Phosphate-Choline Head Group:** The presence of the phosphocholine head group gives it amphipathic properties, similar to phosphatidylcholine.

- **Function:**
  - **Major Component of Myelin Sheath:** Its high concentration in myelin (up to 85% of its lipid content) is critical for the electrical insulation and efficient transmission of nerve impulses.
  - **Membrane Component:** Contributes to the structural integrity and fluidity of cell membranes, especially in eukaryotic cells.
  - **Signal Transduction:** Involved in cell signaling pathways.
  - **Pathogenesis:** Implicated in certain diseases like Niemann-Pick disease (due to defects in sphingomyelin metabolism) and multiple sclerosis (myelin degradation).

- **(iii) Mutarotation:**
  - Mutarotation is the change in the optical rotation of a solution when the anomeric form of a sugar interconverts in an aqueous solution until an equilibrium mixture of the α-anomer, β-anomer, and the open-chain form is established.
  - **Mechanism:** When cyclic monosaccharides (like glucose) are dissolved in water, the hemiacetal or hemiketal ring can

spontaneously open to the aldehyde or ketone form, and then re-close to form either the α or β anomer. This opening and closing occurs continuously.

- **Optical Rotation:** The α and β anomers of a sugar have different specific optical rotations. For example, freshly prepared α-D-glucose has a specific rotation of +112.2°, while β-D-glucose has a specific rotation of +18.7°. When either form is dissolved in water, the optical rotation of the solution gradually changes until it reaches an equilibrium value (+52.7° for glucose). This equilibrium value reflects the proportions of the α, β, and open-chain forms present in the solution.
- **Significance:** Mutarotation is an important characteristic of reducing sugars and demonstrates the dynamic nature of their cyclic structures in solution. It is also important in food chemistry and pharmaceutical applications where the stability of sugar forms can influence properties.

- **(iv) Liposomes:**
  - Liposomes are spherical vesicles composed of one or more concentric lipid bilayers, typically formed from phospholipids, enclosing an aqueous core. They spontaneously self-assemble when dry lipids are hydrated in an aqueous solution.
  - **Structure:** They have a hydrophobic lipid bilayer (similar to cell membranes) that forms the outer shell, and a hydrophilic interior (aqueous core). This amphipathic nature allows them to

encapsulate both hydrophilic substances (in the aqueous core) and hydrophobic substances (within the lipid bilayer).

- **Formation:** They are formed by sonication or extrusion of phospholipid suspensions, which causes the lipid molecules to arrange themselves into closed vesicles to minimize unfavorable interactions between the hydrophobic tails and water.
- **Types:** Can be unilamellar (single bilayer) or multilamellar (multiple concentric bilayers).
- **Applications:**
  - **Drug Delivery:** Widely used as drug delivery systems in medicine. They can encapsulate drugs (chemotherapeutics, antibiotics, genes) and deliver them to target cells or tissues, reducing systemic toxicity and improving efficacy.
  - **Gene Therapy:** Used to deliver genetic material (DNA, RNA) into cells.
  - **Cosmetics:** Used in cosmetic formulations to deliver active ingredients into the skin.
  - **Food Industry:** Used to encapsulate flavors, vitamins, and other food additives.

- **Research Tools:** Serve as excellent model systems for studying membrane structure, function, and protein-lipid interactions.
- **Vaccines:** Can act as adjuvants or carriers for vaccine antigens.

(b) What is pectin? Give its function: (1+2=3)

- **Pectin:**
  - Pectin is a complex heteropolysaccharide found primarily in the primary cell walls and middle lamella of plants, particularly in fruits (e.g., apples, citrus, berries) and vegetables. It is a family of polysaccharides rich in galacturonic acid residues.

- **Function:**
  a. **Cell Adhesion and Structural Support:** Pectin acts as a "glue" or cementing agent between plant cells, holding them together and contributing significantly to the structural integrity and rigidity of plant tissues. It provides mechanical strength and flexibility to the cell wall.

  b. **Water Retention and Turgor:** Due to its highly hydrophilic nature and ability to form gels, pectin plays a crucial role in water retention within plant tissues. This contributes to maintaining turgor pressure and preventing desiccation.

c. **Fruit Ripening:** During fruit ripening, enzymes (like pectinases) break down pectin, leading to the softening of the fruit. This process is essential for making fruits palatable.

d. **Dietary Fiber:** In the human diet, pectin acts as a soluble dietary fiber. It is not digestible by human enzymes but is fermented by gut bacteria. It contributes to satiety, helps regulate blood sugar levels, and can lower cholesterol.

e. **Gelling Agent in Food Industry:** Due to its excellent gelling properties, pectin is widely used in the food industry as a gelling, thickening, and stabilizing agent in jams, jellies, preserves, fruit preparations, and confectioneries. Its ability to form a gel in the presence of sugar and acid is the basis for these applications.

Question 5: (a) Explain why do the amphipathic lipid molecules form a bilayer structure? How does a bilayer differ from a monolayer? (3+3=6) (b) Glycogen with n branches have an n+1 non-reducing end and one reducing end. Explain. (5) (c) Explain the laws of thermodynamics with examples. (7)

(a) Explain why do the amphipathic lipid molecules form a bilayer structure? How does a bilayer differ from a monolayer?

- **Why Amphipathic Lipid Molecules Form a Bilayer Structure:**
    - Amphipathic lipid molecules (like phospholipids and glycolipids) have a dual nature: they possess both a hydrophilic (water-loving) head group and hydrophobic (water-fearing) hydrocarbon tails.

- When these molecules are placed in an aqueous environment, they spontaneously self-assemble into structures that minimize the unfavorable interactions between their hydrophobic tails and water, while maximizing favorable interactions between their hydrophilic heads and water.
- The most energetically favorable arrangement that achieves this is a **bilayer**. In a bilayer, two layers of lipid molecules are arranged tail-to-tail.
    - The **hydrophilic head groups** face outwards, interacting with the aqueous environment on both sides of the membrane (the extracellular fluid and the intracellular cytoplasm).
    - The **hydrophobic tails** are sequestered in the interior of the bilayer, away from water, forming a hydrophobic core.
- This arrangement reduces the free energy of the system by minimizing the surface area of hydrophobic regions exposed to water, making the bilayer a stable and thermodynamically favored structure for biological membranes. The formation is largely driven by the **hydrophobic effect** and the increase in entropy of water molecules that are released from ordered clathrate-like structures around exposed hydrophobic surfaces.

- **How a Bilayer Differs from a Monolayer:**
    - **Monolayer:**

- A monolayer is a single layer of amphipathic molecules where all the hydrophilic head groups face the aqueous phase on one side, and all the hydrophobic tails point away from the aqueous phase, often towards air or a hydrophobic surface.
- It is typically formed at an air-water interface or on the surface of a lipid droplet.
- It only has one hydrophilic surface interacting with water.
- Example: A layer of lipids on the surface of a micelle, or lipid layer surrounding a lipid droplet in a cell.

- **Bilayer:**

  - A bilayer consists of **two** parallel layers of amphipathic molecules arranged tail-to-tail.
  - It has two hydrophilic surfaces facing aqueous environments (one facing outside the cell, one facing inside the cell in a plasma membrane).
  - It forms a hydrophobic core in the middle, separating the two aqueous compartments.
  - It forms the fundamental structure of all biological membranes (plasma membrane, organelle membranes).
  - It is a stable, closed structure that encloses an aqueous compartment (e.g., cell lumen, liposome interior).

In essence, a monolayer is a single sheet of lipids with one hydrophilic face, while a bilayer is a double sheet of lipids with two hydrophilic faces, forming a barrier that separates two aqueous compartments.

(b) Glycogen with n branches have an n+1 non-reducing end and one reducing end. Explain.

- **Glycogen Structure:**
    - Glycogen is a highly branched homopolysaccharide of glucose, serving as the primary long-term energy storage in animals and fungi.
    - Glucose units are linked primarily by α-(1→4) glycosidic bonds, forming linear chains.
    - Branch points occur approximately every 8-12 glucose units, formed by α-(1→6) glycosidic bonds.
- **Reducing and Non-reducing Ends:**
    - **Reducing End:** A reducing end in a polysaccharide is defined by the presence of a free anomeric carbon (C1 of a glucose unit) that is not involved in a glycosidic bond and can therefore open to form an aldehyde group. This aldehyde group has the potential to be oxidized, hence "reducing."
    - **Non-reducing End:** A non-reducing end is any end of a glucose chain where the anomeric carbon (C1) is involved in a glycosidic bond with another glucose unit, and the terminal

glucose unit has a free hydroxyl group at C4 (or C6 for branch points) but its own C1 is part of a bond. More simply, it's the end of a chain where there's no free anomeric carbon available for oxidation.

- **Explanation of n+1 Non-reducing Ends and One Reducing End:**

  f. **The Single Reducing End:**

  - In a glycogen molecule, the very first glucose unit from which the entire structure begins to grow will have its C1 carbon involved in an α-(1→4) glycosidic bond with the next glucose unit.
  - However, the chain effectively grows *outward* from this initial glucose. As branching occurs, new chains extend from the C6 of other glucose residues.
  - Regardless of how many branches are formed, there will always be **only one** glucose unit within the entire glycogen molecule whose C1 carbon (the original anomeric carbon of the starting glucose) remains unsubstituted, giving it the potential to be a free reducing end. This single reducing end is the point of attachment for the enzyme glycogenin during synthesis, but it is typically depicted as having one such end for the entire macromolecule.

  g. **The n+1 Non-reducing Ends:**

- Every chain in a glycogen molecule has an end where the terminal glucose residue has a free C4 hydroxyl group (and its C1 is linked to the preceding glucose by an α-(1→4) bond). This is a **non-reducing end**.
- Consider a glycogen molecule that starts with one main chain. This main chain has one non-reducing end.
- When a branch is formed, an α-(1→6) linkage creates a new growing point. Each new branch effectively creates an **additional non-reducing end**.
- If there are 'n' branch points in a glycogen molecule, each branch effectively adds a new "arm" to the structure.
- Therefore, the total number of non-reducing ends will be the initial non-reducing end of the main chain plus one additional non-reducing end for each of the 'n' branches.
- Thus, if a glycogen molecule has 'n' branches, it will have **n + 1 non-reducing ends**.

- **Example Illustration:**
  - Imagine a simple linear glucose chain: Glucose-Glucose-Glucose-Non-reducing End. This has 1 reducing end (at the start) and 1 non-reducing end.
  - Now, add one branch (n=1): Reducing End - G - G - G - Non-reducing End | G - G - Non-reducing End This structure has 1 reducing end and 2 non-reducing ends (n+1 = 1+1 = 2).

- Add another branch (n=2): Reducing End - G - G - G - Non-reducing End | | G G - Non-reducing End | G - Non-reducing End This has 1 reducing end and 3 non-reducing ends (n+1 = 2+1 = 3).

The highly branched nature of glycogen, with its many non-reducing ends, is functionally significant because it allows for the rapid mobilization of glucose units during periods of high energy demand. Enzymes like glycogen phosphorylase act simultaneously on these multiple non-reducing ends, allowing for quick glucose release.

(c) Explain the laws of thermodynamics with examples.

- **Laws of Thermodynamics:** The laws of thermodynamics are fundamental principles governing energy and its transformations in physical and chemical systems. They are crucial for understanding biological processes.

- **1. First Law of Thermodynamics (Law of Conservation of Energy):**
  - **Statement:** Energy cannot be created or destroyed, only transformed from one form to another. In any physical or chemical process, the total amount of energy in the universe remains constant.
  - **Mathematical Expression:** $\Delta U = Q - W$ or $\Delta U = Q + W$ (depending on convention, where W is work done *by* or *on* the system). More commonly, in terms of changes: $\Delta E_{universe} = 0$.

- **Explanation:** This law means that energy is conserved. While it can change forms (e.g., chemical energy to heat, light, or mechanical energy), the total energy before and after a transformation is the same.
- **Biological Example:**
  - **Photosynthesis:** Plants convert light energy (solar energy) into chemical energy stored in the bonds of glucose (chemical energy). No energy is lost or gained, just converted.
  - **Cellular Respiration:** Glucose (chemical energy) is broken down to produce ATP (chemical energy), heat (thermal energy), and mechanical work (e.g., muscle contraction). The total energy input equals the total energy output in different forms. Your body doesn't "make" energy; it extracts and transforms it from the food you eat.

- **2. Second Law of Thermodynamics:**
  - **Statement:** In any spontaneous process, the total entropy (disorder/randomness) of the universe always increases. Processes tend to proceed from a state of order to a state of disorder.
  - **Mathematical Expression:** $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$ for a spontaneous process.

- **Explanation:** This law explains why certain processes occur spontaneously while others do not. For a process to be spontaneous, the overall disorder of the universe (system + surroundings) must increase. It implies that energy transformations are never 100% efficient; some usable energy is always converted into unusable energy (heat) that increases the entropy of the surroundings.
- **Biological Example:**
  - **Metabolism:** While living organisms appear highly ordered (decreasing system entropy), they achieve this by continuously performing energy-releasing reactions (e.g., breaking down complex food molecules). These exergonic reactions release heat into the surroundings, significantly increasing the entropy of the surroundings. The total entropy of the universe (organism + environment) therefore increases, consistent with the second law.
  - **Diffusion:** The movement of molecules from a region of higher concentration to lower concentration is a spontaneous process. This occurs because the random distribution of molecules increases the overall disorder (entropy) of the system.

- **3. Third Law of Thermodynamics:**

- **Statement:** The entropy of a perfect crystalline substance approaches zero as the absolute temperature approaches zero (0 Kelvin or -273.15°C).
- **Explanation:** This law provides a baseline for measuring entropy. At absolute zero, all atomic motion ceases, and a perfectly ordered crystalline structure would have minimal (approaching zero) disorder. This law is less directly applicable to biological systems, which are typically at much higher temperatures and are far from perfect crystalline structures.
- **Biological Relevance (Indirect):** While not directly applicable, it underpins the concept that true "zero entropy" is a theoretical limit and emphasizes the inherent molecular motion and disorder even at low biological temperatures, contributing to the understanding of molecular dynamics.

Question 6: (a) What feature of Archeal membrane lipids help them to survive in extreme environments. (6) (b) Define Gibbs free energy and comment on exergonic and endergonic reactions. (6) (c) Explain with an example how a thermodynamically unfavorable reaction can be driven in the forward direction. (6)

(a) What feature of Archael membrane lipids help them to survive in extreme environments.

Archaea are renowned for their ability to thrive in extreme environments (extremophiles), such as high temperatures (thermophiles), high salinity (halophiles), or very low pH (acidophiles). A key factor enabling their survival in such harsh conditions is the unique composition and structure of

their cell membrane lipids, which differ significantly from those of Bacteria and Eukarya.

- **Key Features of Archaeal Membrane Lipids for Extreme Environments:**

    h. **Ether Linkages (instead of Ester Linkages):**

        - In archaeal lipids, the hydrocarbon chains are attached to glycerol by **ether bonds** $(R - O - R')$, whereas in bacteria and eukaryotes, they are attached by **ester bonds** $(-COO-)$.

        - **Benefit:** Ether bonds are chemically much more stable than ester bonds, especially at high temperatures and extreme pH (both acidic and alkaline conditions). They are less susceptible to hydrolysis, preventing the membrane from falling apart in harsh environments.

    i. **Branched Isoprenoid Chains (instead of Straight-Chain Fatty Acids):**

        - The hydrocarbon chains in archaeal lipids are derived from **isoprenoid units** and are highly branched. These branches typically consist of methyl groups.

        - **Benefit:** The branching of the hydrocarbon chains makes the membrane more rigid and less fluid. This increased packing density and reduced flexibility contribute to the membrane's stability at high temperatures, preventing it

from becoming too fluid or "leaky." It also likely enhances resistance to oxidation and chemical attack.

j. **Glycerol Enantiomer (Glycerol-1-phosphate vs. Glycerol-3-phosphate):**

- Archaea use an enantiomeric form of glycerol, **sn-glycerol-1-phosphate**, as the backbone for their lipids, whereas bacteria and eukaryotes use sn-glycerol-3-phosphate.
- **Benefit:** While not directly contributing to extreme resistance itself, this fundamental difference in stereochemistry likely reflects a very ancient evolutionary divergence and contributes to the overall unique structural integrity and synthesis pathways of archaeal membranes.

k. **Formation of Lipid Monolayers (Diglycerol Tetraethers):**

- A remarkable feature of many hyperthermophilic and thermoacidophilic archaea is that their membrane lipids are not just phospholipids forming a bilayer. Instead, they often consist of **diglycerol tetraethers**. In these lipids, two glycerol molecules are linked by two long, branched isoprenoid chains that span the entire width of the membrane, forming a **single lipid monolayer**.
- **Benefit:** A lipid monolayer is significantly more stable and less permeable to ions and small molecules than a bilayer. This rigid, covalently linked structure is crucial for

maintaining membrane integrity and preventing cell lysis at extremely high temperatures and very low pH conditions, which would destroy typical lipid bilayers.

These distinct features of archaeal membrane lipids collectively provide the necessary stability and impermeability for archaea to thrive in environments that would be lethal to most other forms of life.

(b) Define Gibbs free energy and comment on exergonic and endergonic reactions.

- **Gibbs Free Energy (ΔG):**
    - Gibbs free energy is a thermodynamic potential that measures the maximum amount of reversible work that can be performed by a thermodynamic system at a constant temperature and pressure.
    - More commonly in biochemistry, the change in Gibbs free energy (ΔG) for a reaction is a measure of the spontaneity of that reaction. It represents the portion of the total energy change in a system that is available to do useful work.
    - It combines the concepts of enthalpy (ΔH, change in heat content) and entropy (ΔS, change in disorder) at a given temperature (T) via the equation: $\Delta G = \Delta H - T\Delta S$.
- **Comment on Exergonic and Endergonic Reactions:**
    1. **Exergonic Reactions:**
        - **Definition:** These are reactions that release free energy.

- ΔG **Value:** The change in Gibbs free energy (ΔG) for exergonic reactions is **negative** ($\Delta G < 0$).
- **Spontaneity:** Exergonic reactions are thermodynamically **spontaneous** under the given conditions. This means they will proceed in the direction written without the input of external energy.
- **Work:** The released free energy can be used to perform work (e.g., synthesize ATP, drive other reactions, power cellular processes).
- **Examples:**
  - Cellular respiration (oxidation of glucose to CO_2 and H_2O).
  - Hydrolysis of ATP to ADP + Pi.
  - Burning of fuel.

m. **Endergonic Reactions:**

- **Definition:** These are reactions that require an input of free energy to proceed.
- ΔG **Value:** The change in Gibbs free energy (ΔG) for endergonic reactions is **positive** ($\Delta G > 0$).
- **Spontaneity:** Endergonic reactions are thermodynamically **non-spontaneous** under the given

conditions. They will not proceed unless energy is supplied to them.

- **Work:** They require energy input from an external source, typically by being coupled to an exergonic reaction.
- **Examples:**
    - Synthesis of complex molecules from simpler precursors (e.g., protein synthesis from amino acids, DNA synthesis).
    - Active transport of molecules against their concentration gradient.
    - Muscle contraction.

In biological systems, exergonic reactions are often "coupled" with endergonic reactions. The energy released from an exergonic reaction (e.g., ATP hydrolysis) is used to drive an endergonic reaction, making the overall coupled process spontaneous.

(c) Explain with an example how a thermodynamically unfavorable reaction can be driven in the forward direction.

A thermodynamically unfavorable (endergonic) reaction, characterized by a positive ΔG, can be driven in the forward direction in living systems primarily through two mechanisms:

3. **Coupling with a Highly Exergonic Reaction (most common and effective):**

4. **Maintaining Low Product and High Reactant Concentrations (Mass Action Effect):**

Let's explain with an example focusing on **coupling**:

Example: The First Step of Glycolysis - Phosphorylation of Glucose

- **Unfavorable Reaction (Endergonic in isolation):** Glucose + Phosphate (Pi) ⇌ Glucose-6-phosphate + H_2O $\Delta G^{0'} = +13.8$ kJ/mol (positive, so non-spontaneous under standard conditions)

  If this reaction were to occur in isolation, it would not proceed significantly in the forward direction. The cell needs to make glucose-6-phosphate from glucose to begin glycolysis.

- **Coupling Reaction (Highly Exergonic):** The cell uses the hydrolysis of ATP, which is a highly exergonic reaction: ATP + H_2O ⇌ ADP + Pi $\Delta G^{0'} = -30.5$ kJ/mol (highly negative, so very spontaneous under standard conditions)

- **Coupled Reaction (Overall Favorable):** These two reactions are coupled together by the enzyme **hexokinase**. Hexokinase catalyzes the transfer of a phosphate group directly from ATP to glucose. The net effect is:

  Glucose + ATP → Glucose-6-phosphate + ADP

  To find the overall $\Delta G^{0'}$ for the coupled reaction, we sum the $\Delta G^{0'}$ values of the individual reactions:

Overall $\Delta G^{0'} = (\Delta G^{0'}_{\text{glucose phosphorylation}}) + (\Delta G^{0'}_{\text{ATP hydrolysis}})$ Overall $\Delta G^{0'} = (+13.8 \text{ kJ/mol}) + (-30.5 \text{ kJ/mol})$ Overall $\Delta G^{0'} = -16.7 \text{ kJ/mol}$

- **Explanation:**
    - The negative overall $\Delta G^{0'}$ of -16.7 kJ/mol indicates that the coupled reaction (glucose phosphorylation driven by ATP hydrolysis) is now **thermodynamically favorable and spontaneous** under standard conditions.
    - The large amount of free energy released by ATP hydrolysis "pulls" the otherwise unfavorable phosphorylation of glucose forward.
    - In the cell, this coupling is not just theoretical; it often involves a single enzyme (like hexokinase) that binds both substrates (glucose and ATP) and catalyzes both parts of the reaction, ensuring that the energy transfer is efficient.
- **Role of Concentration (Mass Action Effect):** Even for this coupled reaction, the actual ΔG in the cell is further influenced by the cellular concentrations of reactants and products. For instance, cells typically maintain high ATP concentrations and low ADP/Pi concentrations, which makes the ΔG of ATP hydrolysis even more negative than its standard value. Similarly, glucose concentration might be higher than glucose-6-phosphate, also favoring the forward reaction. This combination of energy coupling and favorable concentration gradients ensures that crucial metabolic pathways proceed efficiently in the desired direction.