CHAPTER 8: ENERGY AND METABOLISM

CHAPTER SYNOPSIS

Living organisms transform potential energy into kinetic energy to survive, grow, and reproduce. The energy that the earth receives from the sun is transformed into heat energy as it warms the continents and the oceans. Various kinds of photosynthetic organisms also absorb this energy and convert it to potential energy in the form of chemical bonds.

Oxidation-reduction reactions are a class of reactions that pass electrons from one molecule to another. A molecule that is oxidized loses an electron; one that is reduced gains an electron. Oxygen is the most common electron acceptor in biological systems. Since the transfer of electrons is accompanied by a transfer of protons in the form of H^+ ions, oxidation generally involves the removal of hydrogen atoms and reduction involves the addition of hydrogen atoms. In biological systems, oxidation-reduction reactions are coupled to one another. In photosynthesis, carbon dioxide is reduced to form glucose, storing energy. In cellular respiration, the oxidation of glucose releases energy.

The First Law of Thermodynamics states that energy can be transformed from one state to another, but cannot be created or destroyed. The Second Law of Thermodynamics states that objects tend to move from a state of greater order to one of lesser order. Thus entropy, the measure of disorder in a system, is constantly increasing. The amount of free energy available to form chemical bonds is equal to the energy within a cell that is available to do work (enthalpy) minus the product of temperature and entropy. A reaction proceeds spontaneously when its change in free energy is a negative number.

The products of exergonic reactions contain less free energy than the reactants. Such reactions proceed spontaneously and release the excess usable free energy. The products of endergonic reactions have more free energy than the reactants, do not occur spontaneously, and require an input of energy to proceed. Fortunately, even exergonic reactions require an input of a small amount of activation energy to get started. Otherwise all combustible materials would have burned up long ago. This activation energy is required to destabilize the existing chemical bonds; something that occurs more readily in the presence of a catalyst.

Enzymes are biological catalyzing agents generally in the form of proteins and having names ending in *-ase*. An enzyme brings two substances together in the proper orientation and stresses certain bonds. It does not force a reaction to occur in a single direction but enhances the reaction in both directions. Although many reactions involve discrete enzymes, many complex pathways depend on multienzyme complexes to efficiently carry out their sequential reactions. Certain RNA reactions possess unique RNA catalysts called ribozymes, giving strength to the argument that RNA evolved prior to proteins. Enzyme activity is altered by several factors including temperature and hydrogen ion concentration (pH). A competitive inhibitor binds at the same site as the substrate, effectively inhibiting the reaction. Non-competitive inhibitors and activators bind to the allosteric site to alter reaction rates. Various cofactors are associated with most enzymes and may be in the form of metal ions or nonprotein, organic molecules called coenzymes. One of the more important coenzymes is nicotinamide adenine dinucleotide (NAD^+), a hydrogen acceptor that, when reduced, becomes NADH. This molecule is responsible for carrying the energy of an electron and a hydrogen throughout the cell.

The chief energy currency of cells is the molecule adenosine triphosphate, ATP. This molecule is composed of a five-carbon backbone to which an nitrogenous adenine base and a chain of three phosphate groups are attached. The covalent bonds linking the phosphate groups are high-energy bonds that are readily broken to release 7.3 kcal / mole of energy. All cells use ATP to drive their endergonic reactions. Cells do not store large amounts of ATP but possess a pool of ADP and phosphates so that they can make ATP whenever it is needed.

Living organisms organize their metabolic activities in reaction chains called biochemical pathways. The first metabolic pathways were anaerobic since oxygen was not present in the early atmosphere of the earth. The product of one reaction becomes the substrate for the next. The step-wise nature of a biochemical pathway reflects its evolution. Organisms rarely evolve new processes completely independent of other processes; rather they utilize the machinery that already exists and add to it or alter it slightly. The addition of new processes generally occurs at the beginning of the pathway; such a pathway evolves backwards. The final reactions evolved first, the beginning reaction is the most recent adaptation. The stepwise progression of pathways allows for more precise regulation.

There are many intermediate points at which the activity of the pathways can be increased or decreased. There have been five major events in the evolution of metabolic processes. The process of degradation where organisms began to harness energy in chemical bonds is the earliest. In glycolysis, the next process, glucose became a valuable energy source. Next, cells evolved photosynthesis to generate ATP from light energy. The process of nitrogen fixation developed to obtain nitrogen from the atmosphere for the synthesis of proteins and nucleic acids. Cyanobacteria evolved that used water to drive photosynthesis releasing oxygen as a byproduct. Finally, cells evolved that could harvest energy from organic molecules in the process of aerobic respiration.

CHAPTER OBJECTIVES

- Differentiate between kinetic and potential energy.
- Describe how oxidation and reduction are interrelated in chemical reactions.
- Understand The First Law of Thermodynamics and its impact on the amount of energy in the universe.
- Understand The Second Law of Thermodynamics and its relation to entropy and enthalpy.
- Explain the energy requirements of endergonic and exergonic reactions.
- Describe the importance of activation energy and how it can be altered.
- Explain the nature of enzymes and multi enzyme complexes, how they affect reactions, and the factors that affect their performance.
- Define competitive inhibition, noncompetitive inhibition, and activation. Know how each relates to the allosteric site.
- Understand the unique catalytic nature of and properties associated with ribozymes.
- Understand the structure of ATP and how it is able to drive biological reactions.
- Describe how a general biochemical pathway evolves over time.
- Know how the five major metabolic processes evolved over time.

KEY TERMS

activation energy
activator
active site
adenosine diphosphate (ADP)
adenosine triphosphate (ATP)
allosteric inhibitor
allosteric site
anabolism
biochemical pathway
catabolism
catalysis
coenzyme
cofactor
competitive inhibitor
endergonic reaction
energy
enthalpy (H)
entropy (S)
enzyme
enzyme-substrate complex
exergonic reaction
feedback inhibition
First Law of Thermodynamics
free energy (G)
heat
inhibitor
joule
kilocalorie (kcal)
kinetic energy
metabolism
nicotinamide adenine dinucleotide (NAD^+ NADH)
noncompetitive inhibitor
oxidation
oxidation-reduction reaction
pH optimum
potential energy
reduction
Second Law of Thermodynamics
substrate
temperature optimum
thermodynamics

CHAPTER OUTLINE

8.0 Introduction

I. LIFE VIEWED AS CONSTANT FLOW OF ENERGY

A. Required for Each of the Significant Properties of Life fig 8.1

B. Bioenergetics: How Energy Behaves in Living Systems

8.1 The laws of thermodynamics describe how energy changes

I. THE FLOW OF ENERGY IN LIVING THINGS

A. Energy Is the Ability to Do Work
1. Exists in two states fig 8.2
   a. Kinetic energy: Energy of motion
   b. Potential energy: Stored energy that has the capacity of moving
2. Living organisms transform potential energy into kinetic energy

B. Thermodynamics Is the Study of Energy
1. Energy is readily measured by its conversion into heat
2. Unit of heat:
   a. 1 kilocalorie (kcal)=1,000 calories
   b. 1 joule = 0.239 calories

C. Oxidation-Reduction
1. Life exists on earth because it is able to capture energy from the sun
2. Energy from the sun transformed into chemical energy
   a. Process called photosynthesis
   b. Done by plants, algae, and certain bacteria
   c. Combine water and carbon dioxide to make sugars
   d. Energy stored in covalent bonds between sugar atoms
3. Certain reactions pass electrons from one molecule to another
4. Oxidation: Atom or molecule loses an electron, becomes oxidized
   a. Oxygen strongly attracts electrons
   b. Oxygen is most common electron acceptor in biological systems
5. Reduction: Atom or molecule gains an electron and is reduced
6. Redox reactions occur together, electron transfers from one atom to other fig 8.3
7. Reactions play key role in flow of energy through biological systems fig 8.4
8. Light adds energy and boosts electron to higher energy level

II. THE LAWS OF THERMODYNAMICS

A. First Law of Thermodynamics
1. Energy can be transformed but not created or destroyed
2. Total amount of energy in the universe remains constant
3. Animals transfer food potential energy into their own chemical bonds fig 8.1
4. Energy is not lost but may be changed into other forms
   a. Converted to kinetic energy, light, electricity
   b. Also dissipated as heat
5. Heat harnessed to do work only via heat gradient
   a. Temperature difference between two areas
   b. Cells too small to maintain substantial internal heat differences

B. Second Law of Thermodynamics
   1. All objects tend to become less ordered, disorder is increasing
   2. Spontaneous conversion from order / low stability to disorder / stability fig 8.5

C. Entropy
   1. Measure of disorder of a system = S
   2. Universe has progressively become disordered since beginning, increasing entropy

III. FREE ENERGY

A. Bonds Between Atoms Hold Molecules Together
   1. Free energy: Energy available to break and form chemical bonds = G
   2. Enthalpy: Energy within a cell that is available to do work = H
   3. Temperature = T, absolute measured in K°

B. Free Energy = Ordering Influences – Disordering Influences
   1. $G = H - TS$
   2. Change in free energy: $\Delta G = \Delta H - T\Delta S$ fig 8.6
   3. Positive ΔG: Endergonic reactions
      a. Products contain more free energy than the reactants
      b. Reactions do not occur spontaneously, require input of energy
   4. Negative ΔG: Exergonic reactions
      a. Products contain less free energy or more disorder than reactants
      b. Reactions occur spontaneously, release excess usable free energy

IV. ACTIVATION ENERGY

A. Reactions Require an Input of Energy to Get Started
   1. Must break chemical bonds before new bonds can be created
   2. Activation energy: Required to destabilize existing chemical bonds fig 8.7a
   3. Rate of exergonic reaction depends on activation energy needed to start reaction
   4. Large activation energy, reaction proceeds slowly

B. Catalysis
   1. Stressing chemical bonds makes them easier to break fig 8.7b
   2. Catalyst: Substance that carries out catalysis
   3. Cannot violate basic laws of thermodynamics
   4. Accelerates reaction in both forward and reverse directions
   5. Direction of reaction dependent on free energy
   6. Analogy of bowling ball rolling down hill

8.2 Enzymes are biological catalysts

I. ENZYMES

A. Enzymes Carry Out Catalysis in Living Organisms
   1. Are generally proteins (or RNA) with specialized shapes
   2. Permit temporary associations with the molecules that are reacting
   3. Lower activation energy required for new bonds to form
      a. Bring two substrates together in the correct orientation
      b. Stress particular bonds of a substrate

4. Example: Formation of carbonic acid from carbon dioxide and water
   a. Reaction proceeds in either direction
   b. Reaction is slow because of a great activation energy
   c. Carbonic anhydrase: Enzyme that speeds the reaction
   d. Enzymes given the name of their substrate with the ending *-ase*

B. Thousands of Different Enzymes Exist
1. Each enzyme catalyzes a different reaction
2. Different cells contain different complements of enzymes

II. HOW ENZYMES WORK

A. Globular Protein Enzymes Possess Surface Clefts Called Active Sites fig 8.8
1. Enzymes are specific in their choice of substrate
2. Form enzyme-substrate complex
3. The substrate must fit precisely into the active site
   a. Amino acid side groups of an enzyme react with substrate
   b. Bond stressed or distorted, activation energy decreased
4. Substrate binding causes enzyme to slightly change shape
   a. Induced fit: Binding may induce shape adjustments in the protein fig 8.9
   b. Substrate itself may act as activator

III. ENZYMES TAKE MANY FORMS

A. Multienzyme Complexes
1. Groups of several enzymes that catalyze successive steps of a reaction
2. Assembly is non-covalently bonded
3. Example: Bacterial pyruvate dehydrogenase multienzyme complex fig 8.10
   a. Enzymes carry out three sequential reactions in oxidative metabolism
   b. Each complex has multiple copies of each enzyme, 60 subunits total
   c. Subunits work together
4. Increases catalytic efficiency
   a. Product of one reaction delivered to next; if released, would diffuse away
   b. Eliminates possibility of unwanted side reactions
   c. All reactions controlled as one unit
5. Example: Fatty acid synthetase complex
   a. Catalyzes synthesis of fatty acids from two-carbon precursors
   b. Includes seven enzymes and reaction intermediates

B. Not All Biological Catalysts Are Proteins
1. RNA catalyzes certain reactions involving RNA molecules
   a. RNA catalysts called ribozymes
   b. Accelerate reactions, show specificity to substrates
2. Two kinds of ribozymes
   a. Intramolecular catalysts have folded structures, act upon selves
   b. Intermolecular catalysts act on other molecules
3. Catalyzed reactions involve small RNA molecules
   a. Chip out unnecessary sections from RNA copies of genes
   b. Prepare ribosomes for protein synthesis
   c. Facilitate replication of DNA in mitochondria
4. RNA may have evolved before proteins and catalyzed their formation

IV. FACTORS AFFECTING ENZYME ACTIVITY

A. Temperature fig 8.11a
1. Increasing temperature increases random motion and rate of reaction
2. Beyond the temperature optimum the rate is not increased
3. Below optimum
   a. Hydrogen bonds and hydrophobic interactions not flexible
   b. Does not permit induced fit necessary for catalysis
4. Above optimum
   a. Forces too weak to maintain enzyme's shape
   b. Enzyme denatures
5. Human enzyme temperature optima range from 35°C to 40°C
6. Hot spring bacteria proteins have more stable enzymes, optima to 70°C

B. pH fig 8.11b
1. Hydrogen ion concentration disrupts bonds between oppositely charged amino acids
2. With more H^+ ions fewer negative, more positive charges occur
3. Most enzymes have a pH optimum of 6 to 8
4. Enzymes that function in acids retain 3-D shape when many H^+ present

C. Inhibitors and Activators
1. Activity dependent on presence of specific substances
   a. Substances bind to enzyme and change its shape
   b. When shape changes, activity is altered
2. Inhibitors bind to enzyme and decrease its activity
   a. Feedback inhibition: End product inhibits reaction early in pathway
   b. Competitive inhibitors bind at active site, same as substrate
   c. Noncompetitive inhibitors bind at different site fig 8.12
3. Allosteric site: Region where non-competitive inhibitor binds
4. Allosteric inhibitor binds to allosteric site to reduce enzyme activity fig 8.12b
5. Activators bind to allosteric sites
   a. Keep enzymes in active configuration
   b. Increase enzyme activity

D. Enzyme Cofactors
1. Many metallic trace elements are cofactors
2. Coenzymes are nonprotein organic molecules like vitamins
3. Serve as acceptors for electron pairs in redox reactions, shuttle energy
4. Example: Nicotinamide adenine dinucleotide (NAD^+) fig 8.13
5. Structure of NAD^+
   a. Composed of nucleotides NMP and AMP
   b. AMP acts as core, provides for enzyme shape recognition
   c. NMP is an active part, contributes site that readily accepts electrons
6. Important biological hydrogen acceptor
   a. NAD^+ acquires an electron and hydrogen to become reduced NADH
   b. NADH carries energy of electron and hydrogen around in cells

8.3 ATP is the energy currency of life

I. WHAT IS ATP?

A. Adenosine Triphosphate (ATP) Is the Chief Energy Currency of All Cells
1. Bulk of photosynthesis channeled into ATP production
2. Energy stores in fat and starch

B. Structure of the ATP Molecule
   1. Composed of three subunits fig 8.14
   2. Five-carbon ribose sugar serves as the backbone
   3. Adenine composed of two C—N rings attaches to the ribose
      a. Nitrogen has unshared electrons
      b. Weakly attracts hydrogen atoms
      c. Called a nitrogenous base (one of four in DNA)
   4. Triphosphate group attaches to the ribose

C. How ATP Stores Energy
   1. Key lies in triphosphate group
      a. Highly negatively charged, repel one another
      b. Covalent bonds linking phosphates are unstable
      c. Bonds are readily broken and energy transferred
   2. Usually only outer-most bond is broken
      a. ATP ADP + P_i + 7.3 kcal / mole
      b. Adenosine diphosphate = ADP
      c. P_i is inorganic phosphate group

D. How ATP Powers Energy-Requiring Reactions
   1. Cells use ATP in endergonic reactions
      a. Cleavage of P_i may release more energy than reaction consumes
      b. Overall energy change is exergonic, energy released
      c. Both reactions proceed
      d. ATP cleavage can power cell activities
   2. Not spontaneous reactions, products possess more energy than the reactants
   3. Instability of phosphate bond makes ATP poor long-term storage molecule
   4. Cells do not stockpile ATP but create it as needed
   5. Cells contain a pool of ATP, ADP, and P_i

8.4 Metabolism is the chemical life of a cell

I. BIOCHEMICAL PATHWAYS: THE ORGANIZATIONAL UNITS OF METABOLISM

A. Metabolism
   1. Sum of all chemical reactions carried out by an organism
   2. Anabolism: Expend energy to make or transform bonds
   3. Catabolism: Harvest energy when bonds broken

B. Reactions in Biological Systems Occur in Sequence
   1. Product of one reaction becomes substrate for another fig 8.15
   2. Organized units of metabolism
   3. Location of enzymes helps map out model of pathway

C. How Biochemical Pathways Evolved
   1. First primitive biochemical processes
      a. Energy-rich molecules scavenged from the environment
      b. Molecules were present in the existing organic soup
   2. Catalyzed reactions were simple, one-step processes
   3. Without energy-rich molecules only cells that synthesized own energy survived
   4. Energy-utilizing reaction became coupled to energy-producing reaction
   5. Evolution of pathways works backwards
      a. Occur one step at a time
      b. Final reactions generally evolve first, initial reaction evolves last

D. How Biochemical Pathways Are Regulated
   1. Output of pathways must be controlled
   2. Primitive organisms evolved feedback mechanisms
   3. End product binds to allosteric site on enzyme that catalyzes first reaction
      a. Binding to enzyme shuts down first reaction
      b. Effectively shuts down whole pathway
      c. Increase of cell products inhibits production of more product
   4. Called feedback inhibition fig 8.16

II. THE EVOLUTION OF METABOLISM

A. Degradation
   1. Occurred in most primitive life forms
   2. First major event: Needed to harness chemical bond energy
   3. Early utilization of ATP as energy carrier

B. Glycolysis
   1. Second major event: Breakdown of glucose
   2. One 6C glucose becomes two 3C molecules
      a. Occurs in series of ten steps with a net production of 2 ATP
      b. Break bonds and form new, less energetic ones
   3. Occurred early in history of life, unchanged, universal

C. Anaerobic Photosynthesis
   1. Third major event: Generate ATP from light energy
      a. Use light to pump protons out of cells
      b. Resulting proton gradient powers ATP production
      c. Called chemiosmosis
   2. Evolved in absence of oxygen
      a. Dissolved H_2S was source of hydrogen atoms
      b. Free sulfur released as byproduct

D. Nitrogen Fixation
   1. Fourth major event: Obtain nitrogen for protein and nucleic acid synthesis
      a. Elemental nitrogen derived from N_2 gas in atmosphere
      b. Requires breaking a triple bond
   2. Evolved in absence of oxygen
      a. Reaction only occurs in O_2 free environment
      b. Occurs in special compartments in bacterial cells

E. Oxygen-Forming Photosynthesis
   1. Fifth major event: Use H_2O instead of H_2S in photosynthesis
   2. Generates free O_2 as byproduct
   3. Developed in early cyanobacteria
   4. Resulted in 20% oxygen in present atmosphere

F. Aerobic Respiration
   1. Sixth major event: Harvest energy from organic molecules
   2. Utilizes proton pump like photosynthesis
      a. May have evolved from that process
      b. Electrons do not come from H_2O or H_2S
      c. Electrons derived from breakdown of organic molecules
   3. May have evolved first in purple nonsulfur bacteria
   4. Mitochondria are descendants of these bacteria

INSTRUCTIONAL STRATEGY

PRESENTATION ASSISTANCE:

As seen in figure 8.5, the condition of one's bedroom, office, or desk is related to the Second Law of Thermodynamics. There is a tendency for each of them to become more disorganized (increased entropy). Cleanup and organization requires the input of energy.

It is easier to see how reactions with negative free energy occur spontaneously if the equation is presented as $\Delta G = \Delta H + (-T\Delta S)$. For ΔG to be negative, disordering influences ($-T\Delta S$) must be larger than ordering influences (ΔH).

In relation to oxidation / reduction reactions, think of the reverse of what is expected. In reduction, an electron is GAINED. When oxygen does what it is best at, accepting electrons, it is REDUCED.

The lock and key analogy to enzyme action can be extended to include a master key system. Sometimes a key opens only one specific lock. A master or submaster key may be able to open several locks in a specific series. In addition, some high security doors may require two or more locks to be unlocked to gain access. This is similar to how cofactors help control enzyme activity. A multienzyme complex can be likened to a separate key ring used to open a series of rooms in a certain building. I personally keep my work, home, and car keys on separate rings. It makes any entry less cumbersome and prevents me from losing every thing all at once should I leave a set of keys somewhere!

On a social comparison, a catalyst is like a good party host / hostess (or a romantic match maker). He / she introduces two individuals that otherwise might not meet. The host / ess is not "used up" in the process, but if there are too many unfamiliar individuals, the host / ess can become "saturated" trying to pair up the guests.

The evolution of metabolic pathways resembles taking a factory that makes cars and altering it to make trucks. Many of the same machines and tools can still be used, but they may be used in a different order or a different way. New machines may be added to the factory to do things that are specifically oriented to making trucks.

VISUAL RESOURCES:

Any wooden or plastic interlocking puzzle can be used to show how an enzyme catalyzes a reaction by stressing bonds and altering chemical shapes. The puzzle cannot be taken apart until one knows the special twist or trick to it. Finding this may take hours. Once it is known, the puzzle can be done very rapidly — like an enzyme catalyzing a reaction.