Long Answers to Review Questions

Chapter 2

1. Chemical work is in the form of biosynthesis of new organic molecules; osmotic work is done by differential solute concentrations across biological membranes; and mechanical work is in the form of muscle contraction or flagellar rotation.
2. Redox reactions are a form of chemical work, which can be used to synthesize important biomolecules with energy made available through electron transfer. Chemical work is also vital for an organism to maintain homeostasis.
3. In photosynthesis, a series of coupled redox reactions result in an electrochemical proton gradient across the chloroplast membrane. The energy from this gradient is used to drive the phosphorylation of ADP to form ATP. The ATP formed in the culmination of these reactions can then be used to convert carbon dioxide into glucose, which can be used by plants or the animals that eat those plants.
4. The equation that describes the change in Gibbs free energy is $\Delta G = \Delta H - T\Delta S$, where ΔG defines the free energy change between reactants and products of a specific reaction, ΔH is the change in enthalpy, T is the temperature, and ΔS is the change in entropy. A favorable reaction is one in which the sign of ΔG is negative. This equation shows that both ΔH and ΔS contribute to the overall change in free energy and that the temperature (T) amplifies or decreases the entropic change of the reaction.
5. A reaction that is unfavorable under standard conditions might still proceed in a living system, if the actual conditions make it possible. The spontaneity of a reaction is determined by the actual free energy change ΔG. The standard free energy change and the initial concentrations of reactants and products both contribute to the actual free energy change (see Equation 2.14). In cells, if product concentrations are low and reactant concentrations are high ([products]/[reactants] < 1), the second

term of Equation 2.14 will be negative. If it is sufficiently negative to overcome a positive $\Delta G^{\circ\prime}$, then the reaction will be spontaneous with $\Delta G < 0$.

6. Water is less dense as a solid than as a liquid. This means that ice will float. If ice were denser, it would sink to the bottom of the ocean, resulting in an upwelling of cold water, which would also freeze and sink. This process would continue until all of the water was frozen solid. Water is in its liquid state for a wide range of temperatures, particularly those found on Earth. This is critical to the oxygen concentration found on Earth because oxygen is largely dependent on the photosynthetic algae that flourish in the oceans. Water is a fantastic solvent because of its polar nature and hydrogen-bonding abilities, which are important for biological systems.
7. (1) *Hydrogen bonds* form between a donor group, consisting of a hydrogen atom attached to an electronegative atom, and a hydrogen-bond acceptor, which is an electronegative atom. The most common electronegative atoms involved in hydrogen bonding are oxygen, nitrogen, and sulfur. (2) Electrostatic *ionic interactions* occur between two atoms with opposite charges. The strength of the interaction depends upon the environment of the ions participating in the bond and the distance between the ions themselves. (3) van der Waals interactions occur between nonpolar molecules and arise from the creation of temporary dipoles due to fluctuation in electron clouds. If dipoles align with opposite signs at the appropriate distance, an interaction can occur. van der Waals interactions are quite weak but can occur simultaneously with a variety of atoms, thus having a strong cumulative effect. (4) The *hydrophobic effect* is driven by the tendency for hydrophobic molecules to pack close together in solution. Water molecules maintain an ordered structure around hydrophobic molecules, thus decreasing entropy. By packing close together, hydrophobic molecules decrease their overall surface area, which decreases the number of water molecules that are involved in an ordered structure. This increases the entropy of the system, making the formation of such structures favorable.
8. Colligative properties are properties of solutions related to numbers of solute particles. These properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure.
9. The pH scale is a logarithmic scale. A value of 0–6.5 is considered acidic, whereas a value of 7.5–14 is considered basic. Anything in between these two ranges (that is, 6.5–7.5) is considered to be neutral.
10. Amphipathic molecules contain hydrophobic and hydrophilic regions. Amphipathic lipids are crucial for life because they form biological membranes with a hydrophobic region that is relatively impermeable to polar molecules. These membranes are necessary for the separation of the inside of cells from the environment and for compartmentalization within cells where specific reactions can occur.
11. (1) *Phospholipid monolayers* have the polar head groups of their phospholipids pointed toward water with their tails pointed toward air or a hydrophobic

environment. (2) *Phospholipid bilayers* create a hydrophobic barrier between two aqueous compartments, which is characteristic of biological membranes. (3) *Micelles* have the hydrophobic tails of the lipids packed in the center of a globular sphere, with the polar head groups facing outward toward water. (4) *Liposomes* are spherical structures formed by a lipid bilayer that surrounds an aqueous center.

The organization of these structures such that the hydrophobic regions interact with each other increases entropy, thus favoring their formation, which is consistent with the hydrophobic effect.

12. (1) The *plasma membrane* is the lipid bilayer that surrounds every cell. (2) The *endomembrane* consists of structurally related intracellular membrane networks and vesicles. (3) *Chloroplast and mitochondrial membranes* enclose the enzymes that convert energy into a usable form for organisms. These membranes separate the inside of these organelles from the cytoplasm, which is a very different environment.

Long Answers to Challenge Problems

Chapter 2

1. Plants (at night) and animals (all of the time) metabolize nutrients (carbohydrates) by the process of aerobic respiration.
2. The second law of thermodynamics states that all natural processes in the universe tend toward disorder (entropy) in the absence of energy input. Many types of biochemical reactions in living organisms are maintained at a steady state that is far from equilibrium with the environment. This is done by photosynthetic organisms that harness energy released from the Sun (thermonuclear fusion reactions) and convert it to chemical energy in the form of ATP, NADPH, and glucose. Chemical energy is used by all organisms to restrain entropy and avoid reaching equilibrium with the environment (death).
3. a. The notation $\Delta G^{\circ\prime}$ refers to the biochemical standard free energy change of a reaction, which is experimentally determined under physiologic conditions (298 K, 1 atm, 1 M of each reactant and product, pH 7) by allowing the reaction to go to equilibrium and then measuring the steady-state concentrations of reactants and products. The difference in free energy under these two conditions (1 M concentration and at equilibrium) is expressed in units of kilojoules (kJ). The value of ΔG is the actual free energy change in a reaction that is calculated from the known $\Delta G^{\circ\prime}$ value and the initial concentrations of reactants and products.

   b. When a reaction is at equilibrium, $\Delta G = 0$, and $\Delta G^{\circ\prime}$ is described by the equation:

$$\Delta G = \Delta G^{\circ\prime} + RT\ln\frac{[\mathrm{B}]_{\mathrm{actual}}}{[\mathrm{A}]_{\mathrm{actual}}} = 0$$

$$\Delta G^{\circ\prime} = -RT\ln\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}$$

c. Enzymes are catalysts and only affect the rates of chemical reactions. The change in free energy (ΔG), change in standard free energy ($\Delta G^{\circ\prime}$), and the equilibrium constant (K_{eq}) are all unchanged in the presence of an enzyme.

4. a. $K_{eq} = [B]/[A] = 1 \times 10^5$

The total number of moles of A plus B must stay constant throughout the reaction.

Therefore, [A] + [B] = 1.000 M + 0.001 M = 1.001 M.

$$K_{eq} = [B]/[A] = 1 \times 10^5 = 100{,}000$$

Rearrange to get [B] = 100,000[A] and substitute for [B] in [A] +[B] = 1.001 M:

$[A] + 100{,}000[A] = 1.001\text{ M}$

$100{,}001[A] = 1.001\text{ M}$

$[A] = 1.000989 \times 10^{-5}\text{ M}$

$[B] = 1.000989\text{ M}$

b. At equilibrium, $\Delta G = 0$ and therefore

$$\Delta G = \Delta G^{\circ\prime} + RT\ln\frac{[B]_{eq}}{[A]_{eq}} = 0, \text{ and}$$

$$\Delta G^{\circ\prime} = -RT\ln K_{eq}$$

$$\Delta G^{\circ\prime} = -(8.3 \times 10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1})(298\text{ K})\ln 1 \times 10^5$$

$$\Delta G^{\circ\prime} = -28.5\text{ kJ mol}^{-1}$$

c. $$\Delta G = \Delta G^{\circ\prime} + RT\ln\frac{[B]_{actual}}{[A]_{actual}} = 0$$

$$\Delta G = -28.5\text{ kJ mol}^{-1} + (8.3 \times 10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1})(298\text{ K})\ln\frac{15 \times 10^{-2}\text{ M}}{5 \times 10^{-5}\text{ M}}$$

5. a. Pathway 1: A $\rightleftharpoons$ B $\rightleftharpoons$ E $\rightleftharpoons$ F

Pathway 2: A $\rightleftharpoons$ B $\rightleftharpoons$ C + D $\rightleftharpoons$ F

b. Pathway 1 has a $\Delta G^{\circ\prime}$ = −10 kJ/mol, and pathway 2 has a $\Delta G^{\circ\prime}$ = +4 kJ/mol; therefore, pathway 1 is more likely to proceed based on a favorable $\Delta G^{\circ\prime}$ value.

6. a. $$\text{Energy charge (EC)} = \frac{[ATP] + 0.5[ADP]}{[ATP] + [ADP] + [AMP]}$$

$$= \frac{1.25\text{ mM} + 0.5(0.35\text{ mM})}{1.25\text{ mM} + 0.35\text{ mM} + 0.125\text{ mM}}$$

$$= 0.83$$

b. $$K_{eq} = \frac{[\text{ATP}][\text{AMP}]}{[\text{ADP}][\text{ADP}]}$$

$$K_{eq} = \frac{(1.25\ \text{mM})(0.12\ \text{mM})}{(0.35\ \text{mM})^2} = 1.22$$

7. The energy charge of the cell refers to the relative concentrations of ATP, ADP, and AMP. When the energy charge is high, it means that ATP concentrations are high relative to AMP and ADP. Anabolic pathways (biosynthesis) require ATP; therefore, a high energy charge in the cell leads to increased flux through anabolic pathways. In contrast, when the energy charge is low, flux is increased through catabolic pathways to replenish ATP levels and achieve homeostasis.

8. $$\text{Glucose} + \text{P}_i \rightleftharpoons \text{Glucose-6-phosphate} \qquad \Delta G^{\circ\prime} = +13.8\ \text{kJ/mol}$$

$$\text{ATP} \rightleftharpoons \text{ADP} + \text{P}_i \qquad \Delta G^{\circ\prime} = -30.5\ \text{kJ/mol}$$

$$\text{Glucose} + \text{ATP} \rightleftharpoons \text{Glucose-6-phosphate} + \text{ADP} \qquad \Delta G^{\circ\prime} = -16.7\ \text{kJ/mol}$$

9. The water molecules hydrogen bond with each other to form a cage-like structure around the hydrophobic limonene molecule. This process increases the order of the water molecules, which is an entropically unfavorable process, and therefore ΔS is negative.

10. Water molecules in ice are oriented such that maximum hydrogen bonding between water molecules occurs. Protons move through ice (and water) via proton hopping.

11. The four noncovalent interactions are (1) hydrogen bonds, (2) ionic interactions, (3) van der Waals interactions, and (4) hydrophobic effects. Hydrogen bonds are directly formed between H_2O and biomolecules and between H_2O molecules themselves, whereas hydrophobic effects are indirectly caused by H_2O through the promotion of "water-avoiding" interactions between nonpolar molecules.

12. a. Using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

$$7.4 = 6.1 + \log\frac{[\text{HCO}_3^{\ -}]}{[\text{CO}_2(\text{aq})]}$$

$$7.4 - 6.1 = 1.3 = \log\frac{[\text{HCO}_3^{\ -}]}{[\text{CO}_2(\text{aq})]}$$

$$10^{1.3} = 10^{\frac{[\text{HCO}_3^{\ -}]}{[\text{CO}_2(\text{aq})]}}$$

$$\frac{[\text{HCO}_3^{\ -}]}{[\text{CO}_2(\text{aq})]} = \frac{20}{1}$$

b. $0.025\ \text{M} = 2.5 \times 10^{-2}\ \text{M} = [\text{HCO}_3^{\ -}] + [\text{CO}_2(\text{aq})]$

$$\frac{2.5 \times 10^{-2}\ \text{M}}{20 + 1} = [\text{CO}_2(\text{aq})] = 1.19 \times 10^{-3}\ \text{M}$$

$$[\text{HCO}_3^{\ -}] = 2.5 \times 10^{-2}\ \text{M} - 1.19 \times 10^{-3}\ \text{M} = 2.38 \times 10^{-2}\ \text{M}$$

13. The spot disappears because the proteins laterally diffuse in the plane of the membrane. Therefore, eventually the bleached molecules diffuse out of the laser-treated area and are replaced by fluorescent molecules. The rate of lateral protein diffusion in the plasma membrane can be determined using this experimental approach.
14. For the fatty acid to form a micelle, it must have a charged polar head group. This will only occur when the carboxyl group has ionized, that is, $COOH \rightarrow COO^- + H^+$, and this will only occur at pH values higher than the pK_a.