3.1 Metabolism and Energy

All plants, animals, fungi, protists, and prokaryotes are in a constant struggle for survival. Throughout their life, organisms grow, protect themselves from danger, and reproduce. All of these processes require energy. Mammals and birds, which are endothermic, also need energy to maintain elevated body temperatures (**Figure 1**). Living organisms must continually capture, store, and use energy to perform this multitude of functions. Both prokaryotic and eukaryotic cells use ATP molecules to supply energy for their cellular work. In eukaryotic cells, most of the ATP is produced by mitochondria.

You can think of cells as microscopic chemical factories. For life processes to occur, thousands of chemical reactions take place within these microscopic factories. In some of the chemical reactions, large molecules (polymers such as DNA) are built from small molecules (monomers such as nucleotides). In other chemical reactions, polymers (such as amylose) undergo hydrolysis into monomers (such as glucose). The sum of these processes within an organism is called its **metabolism.**

Figure 1 Japanese macaques, often called snow monkeys, expend a significant amount of energy to keep warm in their snowy environment. They forage for food to supply this energy.

metabolism the sum of all chemical reactions in a cell or organism

Energy—The Ability to Do Work

Work is performed when energy is used to move an object against an opposing force, such as friction or gravity. For example, it takes energy for a car to travel along a highway, and it takes energy for a mountain climber to climb a steep slope. These are observable physical activities that require energy. On a much smaller scale, it also takes energy to link amino acids into a chain to form a protein, or to pump sucrose across a cell membrane.

There are many forms of energy, including chemical, electrical, mechanical, light, and thermal. Energy is defined as the capacity to do work. Each form of energy can be converted to other forms of energy. In a battery, for example, chemical energy is converted to electrical energy. In a flashlight bulb, this electrical energy is converted to light and thermal energy. In nature, during the process of photosynthesis, light energy from the Sun is converted to chemical energy (stored in sugar) by organisms. Most living organisms obtain energy in one of two ways: by obtaining it directly from the Sun through photosynthesis, or by consuming energy-rich molecules within food webs that began with photosynthesis.

Kinetic Energy and Potential Energy

kinetic energy the energy of motion

potential energy the stored energy that an object possesses as a result of its position relative to other objects or to its internal structure

All energy exists in one of two states. **Kinetic energy** occurs as a result of motion. Waves in the ocean, falling rocks, molecules and ions moving in a solution, or heart muscles contracting with every heartbeat are examples of kinetic energy. The kinetic energy that is present in movement is useful because it can perform work by making other objects move.

Potential energy is stored within an object and is dependent on the object's location or chemical structure. Chemical potential energy is stored in the electrons and protons that make up atoms and molecules. The electrons are often involved in chemical bonds. A bond results when electrons are simultaneously experiencing a force of attraction to protons in the nuclei of two atoms. Chemical potential energy is available and can be released or absorbed during a chemical reaction. It is stored in food molecules such as glucose. When food molecules are broken down, usable energy is released to power the functioning of cells in an organism—to do cellular work.

Another type of potential energy is gravitational potential energy. For example, a cyclist perched at the top of a hill has potential energy as a result of the high elevation (**Figure 2**). The gravitational pull of Earth at the high elevation is what gives the cyclist the potential energy. Similarly, a diver about to dive from a platform also has potential energy due to the force of gravity from Earth and her height above the surface of the water. The diver gains potential energy as her muscles work to climb the ladder and reach the top of the platform. When work is done, energy is transferred from one body or place to another. When she dives from the platform, the diver's speed increases and

Figure 2 This cyclist has gravitational potential energy as a result of his location at the top of the hill.

she gains kinetic energy. She also loses potential energy as the distance between her and the water surface decreases (**Figure 3**). Therefore, as the diver plunges toward the water, some of her potential energy is converted to kinetic energy.

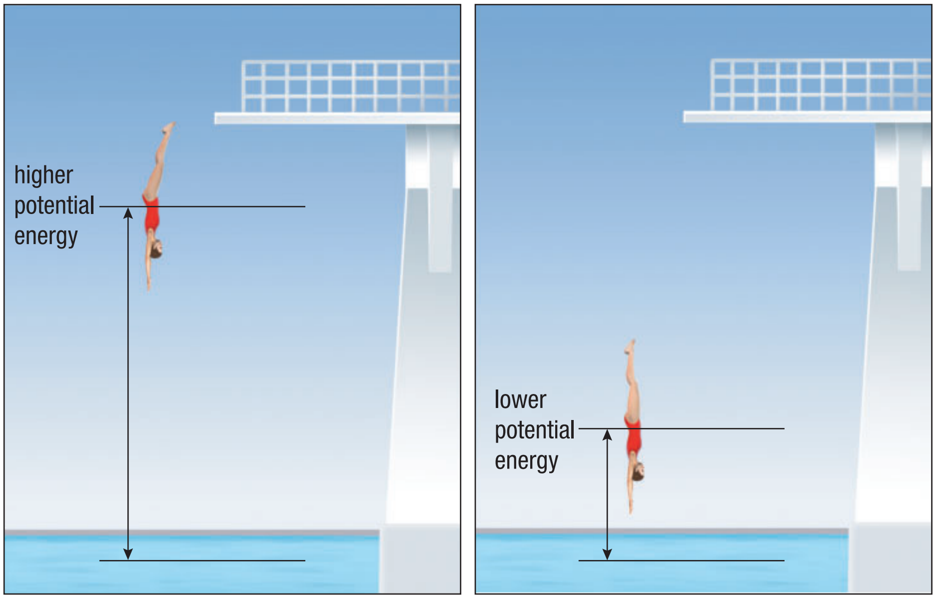


Figure 3 As the diver falls, her gravitational potential energy decreases.

The First Law of Thermodynamics

The diver example illustrates a fundamental law of nature known as the **first law of thermodynamics**: energy in the universe can be converted and transformed from one form to another, but energy cannot be created or destroyed—the total energy remains constant. This is also known as the law of energy conservation.

first law of thermodynamics principle that states that energy can be transferred or transformed, but it cannot be created or destroyed

The First Law of Thermodynamics

The total amount of energy in any closed system is constant. Energy cannot be created or destroyed; it can only be converted from one form to another. If a physical system gains an amount of energy, another physical system must experience a loss of energy of the same amount.

By converting sunlight into chemical energy, green plants act as energy transformers. During photosynthesis, plants capture light energy from the Sun. The plants then convert some of the light energy into chemical potential energy. The potential energy is stored in plant cells in the form of carbohydrates and other energy-rich molecules. The energy in these molecules is stored or is passed on to other organisms that rely on plants as a food source. In this manner, chemical energy is passed from plants to other organisms. Living organisms then convert the chemical energy into other forms of energy. For example, when woodland caribou living in northern Ontario consume plant material, chemical energy from the plants can later be converted to mechanical energy, which is used to contract muscles for movement (**Figure 4**). The caribou use this mechanical energy to move.

Figure 4 Caribou convert chemical energy from the food they eat into other forms of energy.

Energy and Chemical Bonds

Conversion of energy from one form into another depends on the breaking and forming of chemical bonds in a chemical reaction. During a chemical reaction, the amount of potential energy that is available changes. In the earlier example of the diver, the amount of potential energy was directly related to the height of the diver above the water. The higher the elevation, the greater the potential energy of the diver. In a similar way, the potential energy of electrons depends on their location with respect to positively charged atomic nuclei. Like the diver, the farther away electrons are from the nucleus of an atom, the more potential energy they have. The potential energy of outer electrons increases when they absorb energy, move farther from the nucleus, and reach an "excited" state. However, unlike the diver being pulled by Earth's gravitational force, there is not just one source of attraction; there are many sources, from many different atomic nuclei. These nuclei may vary in their forces of attraction. When electrons are strongly attracted to two nuclei at the same time, the resulting forces are called a chemical bond.

Energy Changes during a Chemical Reaction

During a chemical reaction, some of the bonds between atoms in the reactant molecules must be broken, and new bonds form between atoms in the product molecules. For bonds to break in the reactant molecules, energy must be absorbed because energy is required to pull an electron away from an atom. When bonds are formed between the atoms of product molecules, energy is released. Just as the diver loses potential energy as she gets closer to Earth, an electron loses potential energy as it gets closer to a nucleus. When methane, CH_4, burns, for example, all the bonds in the methane and oxygen molecules are broken as energy is absorbed (**Figure 5**). New bonds then form between carbon and oxygen atoms to make carbon dioxide, CO_2, and between hydrogen and oxygen atoms to make water, H_2O. As these products form, energy is released. Thus, the reaction involves both the absorbing and releasing of energy.

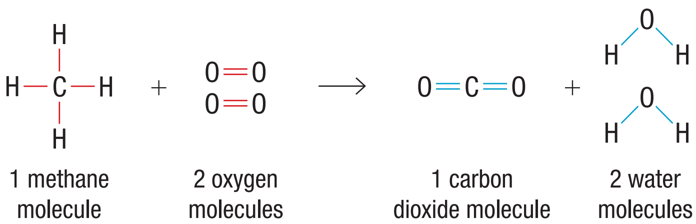


Figure 5 The combustion of methane gas. Bonds broken are shown in red; bonds formed are shown in blue.

As bonds break and new bonds form, the positions of some electrons in the atoms change. The change in potential energy of these electrons accounts for the change in energy during a chemical reaction. To break a bond, electrons must be pulled away from the nucleus of an atom. This action of pulling away always requires energy but at the same time increases the electrons' potential energy. Therefore, the breaking of bonds always requires additional energy. However, when electrons form a new bond, they move closer to the nucleus of another atom and release energy (like the diver falling down toward Earth). The released energy can be converted to different forms, including thermal, light, vibrational, or mechanical energy. For example, the light and thermal energy that comes from the flame of a burning candle is the result of electrons involved in bond formation.

Bond Energy

Bond energy is a measure of the strength or stability of a covalent bond. It is measured in units of kilojoules per mole (kJ/mol) and is equal to the amount of energy absorbed per mole when the bond between atoms is broken. A **mole** is a standard quantity equal to approximately 6.022×10^{23}. This value, also called Avogadro's number, is used in chemistry when considering numbers of extremely small particles. The bond energy value is equal to the amount of energy released per mole when the same bonds form. The energy needed to break a bond reflects the relative strength of the bond. For example, if it takes 799 kJ/mol to break a double bond between carbon and oxygen (C=O), this bond is roughly twice as strong as the C–H bond (411 kJ/mol). Therefore, roughly twice as much energy is released when C=O bonds form.

bond energy the minimum amount of energy that is required to break a particular type of bond; measured in kJ/mol of bonds

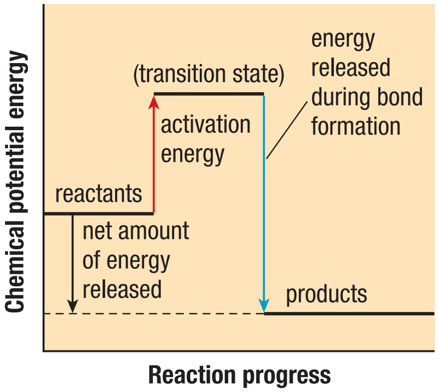
mole the number (approximately 6.022×10^{23}) of atoms or molecules whose mass in grams is equal to the atomic mass of one such particle in atomic mass units; one carbon atom has a mass of 12 AU, and, therefore, one mole of carbon atoms has a mass of 12 g

Table 1 lists the average bond energies of the most common types of chemical bonds found in biological molecules. The values are averages because actual bond energies vary depending on the other atoms in the molecules. For example, the bond energy of the O–H bond will vary depending on what other atoms the O forms a bond with.

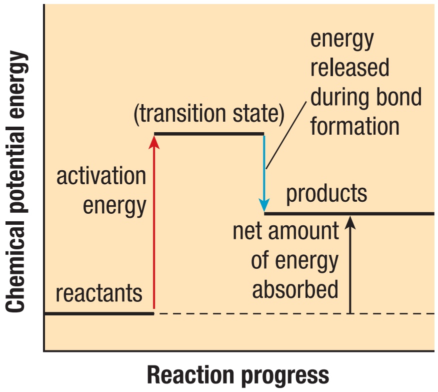
All chemical reactions involve the absorption of energy as bonds break in the reactants and the release of energy as bonds form in the products. Therefore, energy is always required to start a reaction, even if there is an overall release of energy in the chemical reaction. The **activation energy (E_a)** of a reaction is the minimum amount of energy needed to break bonds in the reactants and start the chemical reaction. For example, there must be a spark or a match to start a fire and the process of combustion. Although this may be a small amount of energy, it is enough to break the first bonds and initiate the chemical reaction. Once the reaction begins, it releases enough energy to break bonds in other reactant molecules and keep the process going.

The **transition state** of a chemical reaction is the temporary condition in which bonds in the reactants have reached their breaking point and new bonds are ready to form in the products. The activation energy of a reaction is equal to the difference between the potential energy of the reactants and the potential energy during the transition state (**Figure 6(a)**). As products are formed in a reaction, energy is always released. If the bonds that form in the products are stronger than the bonds in the reactants, the energy released as the bonds form will be greater than the energy absorbed as the bonds were broken. This type of reaction, in which there is a net release of energy, is an **exothermic reaction**. Figure 6(a) shows a potential energy diagram for an exothermic reaction. As you can see, the chemical potential energy of the products is less than the chemical potential energy of the reactants. Also, the energy released when forming the products is greater than the energy absorbed when breaking the bonds in the reactants.

In other reactions, the energy absorbed in breaking the bonds of the reactants may be greater than the energy released as new bonds are formed in the products. This results in a net absorption of energy. The reaction is called an **endothermic reaction**. **Figure 6(b)** shows a diagram of the energy changes during an endothermic reaction. Note that the potential energy of the products is greater than the potential energy of the reactants. This means that the activation energy required to break the bonds and start the reaction is greater than the energy released when products are formed.



(a) exothermic reaction



(b) endothermic reaction

Figure 6 Changes in energy during (a) exothermic and (b) endothermic reactions: The activation energy that is required to initiate the reaction is represented by the red arrow. The energy that is released by the products forming is represented by the blue arrow. The overall energy change for the reaction is represented by the black arrow.

In the following tutorial, you will calculate the net energy change in simple exothermic and endothermic chemical reactions.

Table 1 Average Bond Energies

Bond type	Average bond energy (kJ/mol)
H–H	436
C–H	411
O–H	459
N–H	391
C–C	346
C–O	359
C=O	799
O=O	494

activation energy (E_a) the minimum amount of energy that chemical reactants must absorb to start a reaction

transition state a temporary condition during a chemical reaction in which the bonds in the reactants are breaking and the bonds in the products are forming

exothermic reaction a chemical reaction in which energy is released, leaving the products with less chemical potential energy than the reactants

endothermic reaction a chemical reaction in which energy is absorbed, giving the products more chemical potential energy than the reactants

LEARNING **TIP**

Calculating Molar Mass

The molar mass of a compound is the mass of one mole (6.022×10^{23} molecules) of the compound. This is the sum of all the molar masses of all the atoms in a molecule of the compound. For the compound NaCl, the molar mass (taken from the atomic mass shown in the periodic table) equals the mass of one mole of Na (23 g/mol) added to the mass of one mole of Cl (35.5 g/mol). Thus, the molar mass of NaCl is 58.5 g/mol.

Tutorial 1 Estimating Energy Changes during a Chemical Reaction

In this tutorial, you will calculate the energy changes that occur during simple reactions, such as the combustion of methane, the decomposition of water, and the reactions that occur when we consume energy-rich foods. By calculating the net change in energy in the chemical reaction between the reactants and the products, you will be able to determine whether a reaction is exothermic or endothermic.

Sample Problem 1: The Combustion of Methane

Determine the energy changes, per gram of methane, that occur during its complete combustion.

Step 1. Write and balance the chemical equation:

methane gas + oxygen gas → carbon dioxide gas + water

This equation can be written using the chemical formulas of each molecule:

$CH_4 + O_2 \rightarrow CO_2 + H_2O$

The chemical equation must be balanced so that there is the same number of each type of atom on both sides of the arrow. The balanced equation looks like this:

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

Step 2. Examine the bond arrangements of the reactants and the products.

During the combustion of methane gas, all of the original C–H and O=O bonds in the reactants are broken. You know this because there are no bonds of these types in the final products. Therefore, all the bonds in the products are newly formed during the reaction. To determine all the bonds that are in both the reactants and the products, it is helpful to draw the structure of each chemical (**Figure 7**).

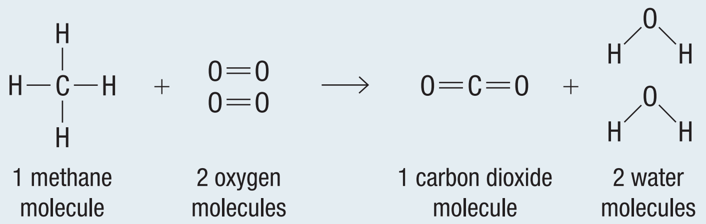


Figure 7 Structural diagram showing all the bonds in a methane combustion reaction

Step 3. Calculate the net energy change.

Use the bond energy values listed in Table 1 (page 129) to estimate the energy changes that occur when reactant bonds are broken and when product bonds are formed. At the start of the reaction, four C–H bonds and two O=O bonds are broken. Using Table 1, calculate the total energy absorbed by adding the energies required to break each bond as follows:

4(C–H bond energy) + 2(O=O bond energy) = total bond energy of 1 mol of methane and 2 mol of oxygen

4(411 kJ/mol) + 2(494 kJ/mol) = 2632 kJ absorbed during the breaking of reactant bonds

This is the energy that was required to pull apart all of the bonds in the reactants. However, during the reaction, six new bonds form: two C=O bonds and four H–O bonds. When these bonds form, energy is released. The amount of energy released is calculated as follows:

2(C=O bond energy) + 4(H–O bond energy) = total bond energy of 1 mol of carbon dioxide and 2 mol of water

2(799 kJ/mol) + 4(459 kJ/mol) = 3434 kJ released during the formation of product bonds

With these values, you can determine the net energy change for the combustion of methane. In this reaction, the energy released when bonds are formed is greater than the energy absorbed when bonds are broken. The net energy change is the difference between the energy released by bonds forming and the energy absorbed to break bonds, where BE is bond energy:

$$BE_{released} - BE_{absorbed} = \text{net energy released by reaction}$$

$$3434 \text{ kJ} - 2632 \text{ kJ} = 802 \text{ kJ}$$

Based on the balanced equation, the value of 802 kJ represents the energy released by burning one mole of methane gas. Since methane has a mass of 16 g/mol, you can also express this energy value as

$$\frac{802 \text{ kJ/mol methane}}{16 \text{ g/mol}} = 50 \text{ kJ/g of methane}$$

Since the overall value represents a net release of energy, you know that the combustion of methane gas is an exothermic reaction. The thermal energy released by the reaction can be used to heat our homes.

Sample Problem 2: The Decomposition of Water

Determine the net energy change that occurs during the decomposition of water into hydrogen and oxygen gas. Express your answer in units of kJ/g of water.

Step 1. Write and balance the chemical equation:

water $\rightarrow$ hydrogen gas + oxygen gas

This equation can be written using the chemical formulas of the molecules involved:

$$H_2O \rightarrow H_2 + O_2$$

The balanced chemical equation looks like this:

$$2\,H_2O \rightarrow 2\,H_2 + O_2$$

Step 2. Examine the bond arrangements of the reactants and the products.

Now that you know the chemical formulas for the reactants and products, look at the bond arrangements of each. **Figure 8** shows the structure of each molecule.

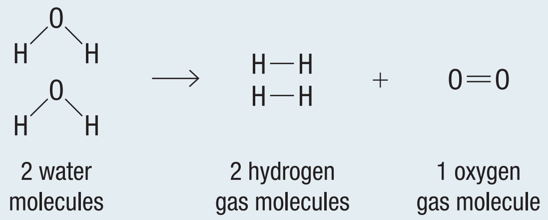


Figure 8 Structural diagram of the decomposition of water, with all the bonds shown

In the reactant, water, O–H bonds are broken. The bonds that form in the products are O=O bonds and H–H bonds. All of the bonds in the reactant are broken, and all of the bonds in the products are newly formed.

Step 3. Calculate the net energy change.

Use the bond energy values (Table 1, page 129) to estimate the energy changes that occur when bonds are broken and formed. You see that four O–H bonds in the reactants are broken.

Therefore, you can calculate the total energy absorbed by adding the energies required to break each bond as follows:

4(O–H bond energy) = total bond energy of 4 O–H bonds in 2 molecules of water

4(459 kJ/mol) = 1836 kJ absorbed in the breaking of reactant bonds

This is the energy required to pull apart the bonds in the reactant molecules. However, during the reaction, two H–H bonds and one O=O bond are formed. When these bonds form, energy is released. The amount of energy released is calculated as follows:

2(H–H bond energy) + 1(O=O bond energy) = total bond energy of 2 molecules of hydrogen and 1 molecule of oxygen

2(436 kJ/mol) + 1(494 kJ/mol) = 1366 kJ released during the formation of product bonds

In this reaction, the energy absorbed when breaking the O–H bonds in the reactants is greater than the energy released by the formation of bonds in the products. The net energy change is the difference between the energy released by bond formation and the energy absorbed by bond breakage, where BE is bond energy. For convenience, you can rearrange the equation to obtain a positive value for the energy absorbed during the reaction:

$BE_{absorbed} - BE_{released}$ = net energy absorbed by reaction

1836 kJ – 1366 kJ = 470 kJ

Based on the balanced equation, this is the energy required to decompose two moles of water. The mass of one mole of water is 18 g, so the mass of two moles is 36 g. Therefore, you can also express this energy value as

$$\frac{470\ \text{kJ}}{36\ \text{g}} = 13\ \text{kJ/g of water}$$

In the decomposition of water molecules, energy must be provided from an outside source. This reaction is not a source of energy (like burning methane in Sample Problem 1), but rather an energy consumer. Therefore, you know that the decomposition of water is an endothermic reaction.

Investigation 3.1.1

The Energy Content of Foods (p. 156)
In Investigation 3.1.1, you will perform a quantitive analysis to determine the energy content of various types of food.

Sample Problem 3: The Energy Content of Food

Determine the net energy change that occurs during the complete oxidation of the simple fatty acid, butanoic acid (C_3H_7COOH). You will estimate the energy change that occurs when this food molecule is completely oxidized. Assume that the complete oxidation of any compound containing carbon, hydrogen, and oxygen atoms will result in the formation of carbon dioxide and water. CAREER LINK

Step 1. Write and balance the chemical equation.

The basic chemical reaction is as follows:

butanoic acid + oxygen gas → carbon dioxide gas + water

Rewrite the equation using the chemical formulas of the molecules involved:

$C_3H_7COOH + O_2 \rightarrow CO_2 + H_2O$

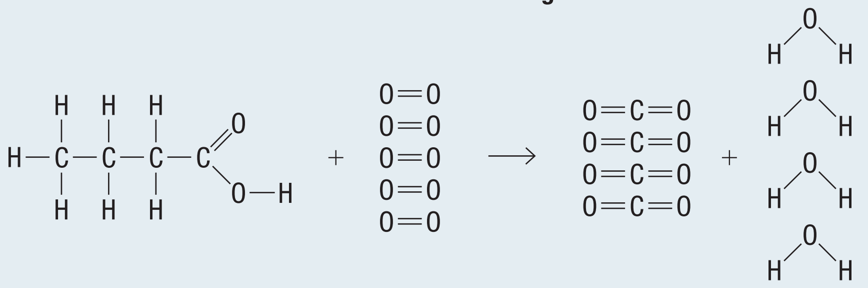
The balanced equation for this reaction is as follows:

$C_3H_7COOH + 5\ O_2 \rightarrow 4\ CO_2 + 4\ H_2O$

Step 2. Examine the bond arrangements of the reactants and the products.

Use the diagram to determine the numbers and kinds of bonds that are broken and formed. Assume that all the bonds in the reactants are broken and all the bonds in the products are newly formed.

The structure of each molecule is shown in **Figure 9**.



1 butanoic acid molecule | 5 oxygen gas molecules | 4 carbon dioxide gas molecules | 4 water molecules

Figure 9 Structural diagram of the reaction for the oxidation of butanoic acid. All bonds are shown.

Step 3. Calculate the net energy change.

The bonds in the reactants that are broken are three C–C bonds, seven C–H bonds, one C=O bond, one C–O bond, one O–H bond, and five O=O bonds. Using the values from Table 1 (page 129), calculate the total energy absorbed by adding the energies required to break each bond as follows:

$3(346 \text{ kJ/mol}) + 7(411 \text{ kJ/mol}) + 799 \text{ kJ/mol} + 359 \text{ kJ/mol} + 459 \text{ kJ/mol} + 5(494 \text{ kJ/mol}) = 8002 \text{ kJ}$ absorbed during the breaking of reactant bonds

The bonds that are formed in the products are eight C=O bonds and eight O–H bonds. When these bonds are formed, energy is released. The amount of energy released is calculated as follows:

$8(799 \text{ kJ/mol}) + 8(459 \text{ kJ/mol}) = 10\,064 \text{ kJ}$ released during the formation of product bonds

Therefore, the energy released by the formation of bonds in the products is greater than the energy added by breaking the bonds in the reactants. The energy released is

$10\,064 \text{ kJ} - 8002 \text{ kJ} = 2062 \text{ kJ}$

One mole of butanoic acid has a mass of 88 g/mol, so the energy content per gram is

$$\frac{2062 \text{ kJ/mol}}{88 \text{ g/mol}} = 23 \text{ kJ/g of butanoic acid}$$

The overall oxidation reaction releases energy; therefore, the oxidation of butanoic acid is an exothermic reaction.

Practice

1. Calculate the energy released per gram of propane when it is burned in a combustion reaction. The chemical formula for propane is C_3H_8 (**Figure 10**). T/I [ans: 46 kJ/g]
2. Calculate the energy released by the burning, or oxidation, of 1 g of glucose, $C_6H_{12}O_6$ (**Figure 11**). T/I [ans: 15 kJ/g]

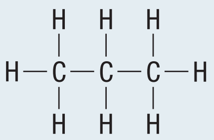


Figure 10 Chemical structure of propane

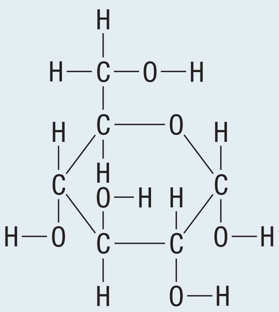


Figure 11 Chemical structure of glucose

3. Compare the energy released, per gram, during the complete combustion of butanoic acid (Sample Problem 2) with the energy released during the complete combustion of methane (Sample Problem 1). Which substance has more potential energy? Explain to a classmate how you came to your conclusion. T/I C

The Second Law of Thermodynamics

second law of thermodynamics principle that states that every time energy is converted to another form, some of the energy becomes unusable

If energy is neither created nor destroyed, why do organisms have to keep replenishing their energy supply? According to the **second law of thermodynamics**, in every energy transfer or conversion, some of the useful energy in the system becomes unusable; that is, it is unavailable to do work. The unusable energy is usually in the form of thermal energy, which is the energy associated with random molecular motion. This is one reason why machines are never 100 % efficient. For example, the engine of a car converts only about 25 % of the potential energy in gasoline into the kinetic energy that makes the car move. Likewise, only a portion of the energy in a laptop computer battery is used to run the computer. If you touch a car engine or laptop computer that has been in use, it is obvious that the remaining energy is being lost to the surroundings as thermal energy. This concept of energy efficiency also applies to living cells. As you will see in Chapter 4, through the process of cellular respiration, cells are able to convert about 40 % of the potential energy in glucose into a form usable for metabolism; the remainder is lost as thermal energy. In many cases, including in living cells, this thermal energy cannot be harnessed to do work; instead, it is simply lost to the environment (**Figure 12**).

Figure 12 A runner converts only 40 % of the energy from glucose into a useful form. Most of the energy is unused and given off as thermal energy in the form of body heat.

The Second Law of Thermodynamics

In every energy transfer or conversion, some of the useful energy in the system becomes unusable and increases the entropy of the universe.

entropy a measurement of disorder in a system

Whether referring to a car or to the cells of a living organism, the release of unusable energy, in the form of random particle motion during an energy transformation, leads to an increase in the disorder, or randomness, of the system. In the field of thermodynamics, the degree of disorder is a measurable quantity called **entropy**. The total entropy of a system and its surroundings increases whenever there is any change, such as a chemical reaction. Therefore, all systems in the universe tend toward disorder. Disorder increases when an orderly arrangement of objects becomes more randomly assorted. For example, no matter how much energy you may expend to tidy up your room, it always gets messy again.

At the level of chemical and physical changes, an increase in entropy is usually associated with a breaking down of large particles into smaller particles, or the spreading out of particles. When ice melts, a large crystal structure is broken down into countless individual molecules. When liquid water evaporates, the water molecules that were in close contact as a liquid spread out over large distances. Likewise, when a substance in solution diffuses from an area of higher concentration to an area of lower concentration, its molecules become more randomly distributed, corresponding to an increase in entropy. In chemical reactions, entropy increases when

- solids react to form liquids or gases
- liquids react to form gaseous products
- the total number of product molecules is greater than the total number of reactant molecules

Figure 13 (a) A flower and (b) the compound eye of an insect, such as this fly, are highly ordered structures.

One characteristic of all living things is that they are highly ordered structures. A flower, the compound eye of an insect, and the human brain are all very highly ordered structures (**Figure 13**). Living cells have the ability to create order from a disordered arrangement. For example, individual nucleotide molecules link together to synthesize DNA, a highly ordered macromolecular structure. Proteins are very ordered structures constructed from many small amino acid building blocks.

These examples may seem to suggest that living organisms do not follow the second law of thermodynamics. This is *not* true. Just as you can expend energy to tidy your room when it becomes disorderly, living cells can, by expending energy, establish and maintain complex and orderly structures and processes. In other words, it is possible to maintain a level of low entropy in a system; however, it requires energy. This energy may be in the form of chemical potential energy in a sandwich (**Figure 14**) or in photons of light absorbed by a green plant. Living things bring in energy and matter and use them to establish order out of disorder. It is understandable why elite athletes need to eat a lot of energy-rich food, but even people who do not have a high energy demand for movement need to ingest enough food to supply energy, simply to maintain their cells in a highly ordered state.

According to the second law of thermodynamics, the overall entropy of the system always increases. The thousands of chemical reactions that take place to maintain order in a living system release energy in the form of thermal energy and the by-products of metabolism, such as carbon dioxide. These by-products and released energy increase the entropy of the surroundings, but the living organisms themselves maintain order. Therefore, entropy of the organism decreases, but the overall entropy of the universe increases.

Figure 14 The average person needs to ingest between 9000 and 12 000 kJ per day. A significant amount of this energy is used to maintain the order within our cells. We eat food to maintain low entropy.

Spontaneous Changes

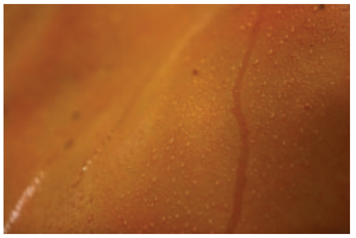
The first and second laws of thermodynamics allow us to predict whether a given chemical or physical change can occur without the continuous input of additional energy. A **spontaneous change** is one that will continue to occur on its own once it is underway. Unlike in everyday language where the word "spontaneous" means that some event can and will happen on its own, in thermodynamics, spontaneous means only that a change will continue to happen on its own once it is underway. For example, a match will not suddenly burst into flame. However, once a match is lit, it will continue to burn on its own without any continual addition of energy. Therefore, the burning of a match is classified as a spontaneous change. Similarly, a diver high on a diving board will not begin his dive until he jumps—but once he jumps, his falling motion will continue on its own. Therefore, we say that diving into a swimming pool is a spontaneous change.

spontaneous change a change that will, once begun, continue on its own under a given set of conditions; does not require a continuous supply of energy

A non-spontaneous reaction cannot occur without a continual input of energy. For example, if you heat a pot of water until it starts boiling and then take it off the heat source, the water will not continue to boil. Under normal conditions, you would describe the boiling of water as a non-spontaneous change. The water will only boil if there is a continuous addition of energy. To revisit the messy room analogy, you could describe the change from a tidy room to a messy room as a spontaneous change because it can happen "on its own." However, a change from a messy room to a tidy room is not spontaneous; it will only occur when there is a continual supply of energy—from you!

Physical changes that are thermodynamically spontaneous may occur at various rates—ice will melt quite slowly at 1 °C but will melt much more rapidly at 50 °C. Spontaneous chemical change may also be very slow, as when rust forms on a nail, or very fast, as when a match burns. To determine whether a change will occur spontaneously, you must take three factors into account: energy changes, entropy, and temperature (**Table 2**, next page). Exothermic changes that are accompanied by an increase in entropy occur spontaneously, since both the change in energy (energy is released during the change) and the change in entropy (increase) are favourable. A favourable change means that it does not require an additional supply of energy. Energy is needed for endothermic changes and for changes that increase order (decrease entropy). Endothermic changes accompanied by a decrease in entropy do not occur spontaneously; neither the change in energy (the overall change requires an addition of energy) nor the change in entropy (an increase in order requires an addition of energy) is favoured. In changes in which the energy change is exothermic (favoured) and the entropy decreases (not favoured), and in changes in which the energy change is endothermic (not favoured) but entropy increases (favoured), the spontaneity of the changes depends on the temperature at which they occur.

Table 2 Factors Influencing Spontaneous and Non-spontaneous Changes

	Exothermic change (favoured)	Endothermic change (not favoured)
Increase in entropy (favoured)	spontaneous at all temperatures  example: wood burning	spontaneous at high temperatures; not spontaneous at low temperatures  example: sweat evaporating from the surface of the skin
Decrease in entropy (not favoured)	spontaneous at low temperatures; not spontaneous at high temperatures  example: water freezing	not spontaneous at any temperature; requires a continuous input of energy to proceed  example: glucose being synthesized during photosynthesis

Gibbs Free Energy

free energy energy that can do useful work; also called Gibbs free energy

According to the second law of thermodynamics, energy transformations are never 100 % efficient. Some energy is always lost to the environment, which leads to an increase in entropy. The energy that is not lost, or the portion that is still available to do work in the given system, is called **free energy**. The free energy value of a chemical reaction provides us with useful information in the study of metabolism. Free energy values tell us which types of reactions provide fuel to our bodies—fuel that releases the energy needed for cellular work. Free energy is represented by the symbol *G*, in recognition of the physicist who developed the concept, Josiah Willard Gibbs.

The concept of free energy applies to both chemical and physical processes. Therefore, free energy may be released during a chemical reaction or during a physical act, such as water spilling over a waterfall. In fact, all processes in our universe require a source of free energy. However, at the completion of a process, there is a reduction in the amount of free energy that is available in a given system.

In living organisms, free energy is responsible for the chemical and physical work required in activities such as the synthesis of molecules, reproduction, and movement. The change in free energy (ΔG) can be represented by the following equation:

$$\Delta G = G_{\text{final state}} - G_{\text{initial state}}$$

The value of ΔG can be calculated for any chemical reaction. We can use bond energy changes to quantify the total amount of energy released from a reaction, but we know, from the second law of thermodynamics, that some of this energy is lost and therefore unavailable to do work. For example, when an organism oxidizes one mole of butanoic acid, it releases approximately 470 kJ of energy. However, not all of this energy is free energy that is available to do work. Processes in the cell can only use a portion of the energy, and the rest is released as thermal energy.

The change in free energy (ΔG) represents the difference in the free energy of the final state of molecules as compared to the free energy of the initial state. Therefore, a negative ΔG value indicates that the free energy of the products of a reaction is less than the free energy of the reactants. The energy released during a reaction with a negative ΔG can be used to do work in other reactions that require energy. Conversely, a positive ΔG value indicates that the products have more free energy than the reactants. These products must have obtained free energy from an external source. A reaction with a negative ΔG gives off free energy, which is then available to do work. A reaction with a positive ΔG must gain free energy to occur. Free energy must be supplied for this type of reaction to happen—it cannot happen on its own. Therefore, reactions with a negative ΔG occur spontaneously, and reactions with a positive ΔG do not (**Figure 15**).

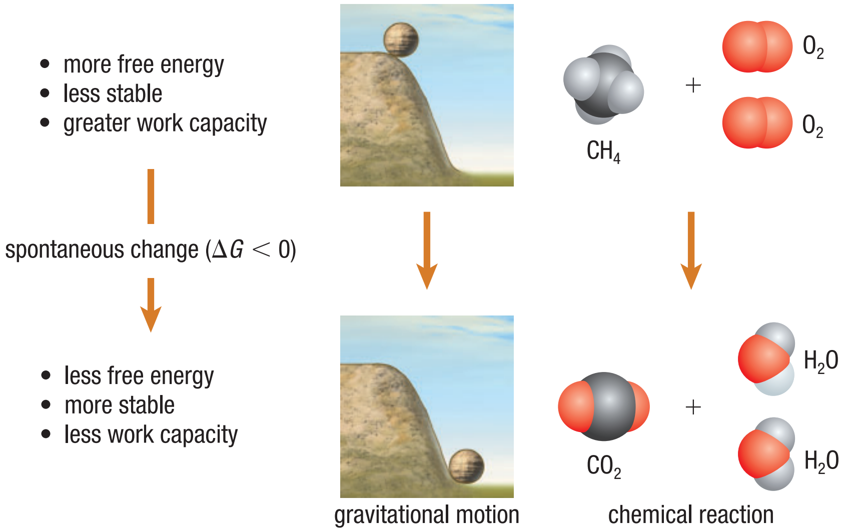


Figure 15 This diagram shows the relationship between free energy, stability, and work capacity. Unstable systems (top) have a high value of free energy and a greater capacity to do work because they have a higher potential energy. They can spontaneously change into the more stable system (bottom) with less free energy. The free energy that was released could have been used to do work.

The oxidation of glucose is an example of a reaction that releases free energy:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \quad \Delta G = -2870 \text{ kJ/mol of glucose oxidized}$$

The negative ΔG value indicates that the reaction is spontaneous. Free energy is released during the reaction, so the products have less free energy than the reactants. There is also an increase in entropy because there are more molecules of the products than molecules of the reactants.

Plants combine CO_2 and H_2O to create sugars through the process of photosynthesis. This reaction is the opposite of glucose oxidation and is an example of a chemical reaction that has a positive ΔG value:

$$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2 \quad \Delta G = +2870 \text{ kJ/mol of glucose formed}$$

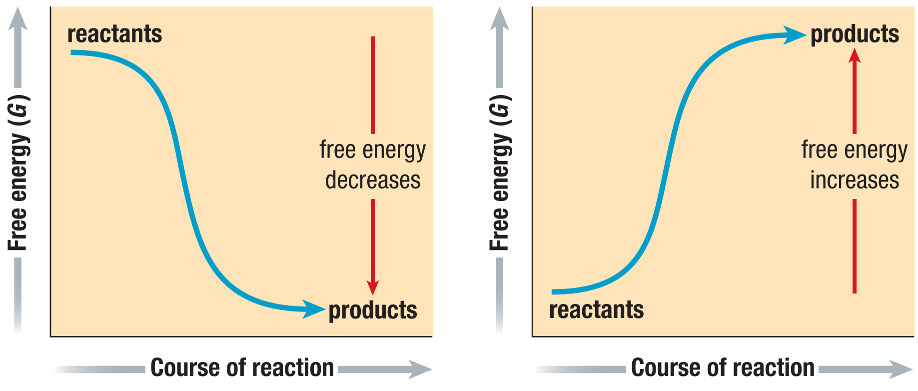
The positive ΔG value indicates that the reaction is not spontaneous—it must gain free energy to occur. Keep in mind that a process resulting in an increase in free energy can never occur spontaneously. In this particular reaction, plant cells are able to use light to supply free energy and make the reaction proceed.

Every reaction falls into one of two groups, based on the free energy of the reactants and the products. An **exergonic reaction** releases free energy. The ΔG value is negative in this type of reaction because the products contain less free energy than the reactants (**Figure 16(a)**, next page). Exergonic reactions can do work because they act as a source of free energy. Releasing free energy gives cells the ability to do work—to move, to grow, and to reproduce. An example of an exergonic reaction is the burning

exergonic reaction a chemical reaction that releases free energy; the products have less free energy than the reactants of wood. A major component of wood is cellulose, which is a large carbohydrate composed of linked glucose molecules. We can think of these glucose molecules, along with oxygen gas molecules, as the reactants in the process that contain a lot of potential energy. Burning the wood releases free energy from these glucose molecules.

endergonic reaction a chemical reaction that absorbs free energy; the products have more free energy than the reactants

The second type of reaction is an **endergonic reaction**, in which the products contain more free energy than the reactants (**Figure 16(b)**). The ΔG value for these reactions is positive, and the reactants in an endergonic reaction must absorb free energy from the surroundings to transform into the products. An example of an endergonic reaction is the conversion of carbon dioxide and water into glucose and oxygen gas. This reaction requires an input of free energy.



(a) exergonic reaction **(b)** endergonic reaction

Figure 16 (a) In an exergonic reaction, free energy is released. The products have less free energy than was present in the reactants, and the reaction proceeds spontaneously. (b) In an endergonic reaction, free energy is gained. The products have more free energy than was present in the reactants. An endergonic reaction is not spontaneous: it proceeds only if energy is supplied by an exergonic reaction.

Coupled Reactions

Every type of cell in every organism continuously carries out thousands of exergonic and endergonic reactions. Exergonic reactions release free energy and therefore can proceed spontaneously. Endergonic reactions require a supply of free energy and therefore cannot proceed on their own. Cells are able to make endergonic reactions happen by supplying them with the free energy released by an exergonic reaction. In other words, cells couple exergonic reactions to endergonic reactions. This is called **energy coupling**. For example, consider the following generic chemical reactions:

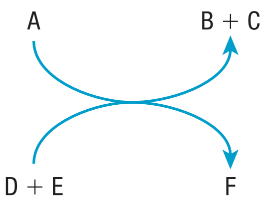
energy coupling the transfer of energy from one reaction to another in order to drive the second reaction

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C} \quad \Delta G = -5\ \mathrm{kJ/mol}$$

During this exergonic reaction, 5 kJ of free energy is released from the overall reaction. A second endergonic reaction requires the addition of 4 kJ of free energy:

$$\mathrm{D} + \mathrm{E} \rightarrow \mathrm{F} \quad \Delta G = +4\ \mathrm{kJ/mol}$$

The energy required by reactants D and E to produce F can be supplied by the first exergonic reaction. We say that the first reaction is coupled to the second reaction (**Figure 17**).



$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C} \qquad \Delta G = -5\ \mathrm{kJ/mol}$$

$$\mathrm{D} + \mathrm{E} \rightarrow \mathrm{F} \qquad \Delta G = +4\ \mathrm{kJ/mol}$$

Coupled reactions: $\mathrm{A} + \mathrm{D} + \mathrm{E} \rightarrow \mathrm{B} + \mathrm{C} + \mathrm{F} \qquad \Delta G = -1\ \mathrm{kJ/mol}$

Figure 17 An exergonic reaction can be coupled to an endergonic reaction to provide free energy.

When combined, the coupled reactions have a net negative ΔG. Free energy is released and both reactions, when coupled, can occur spontaneously. For an endergonic reaction to proceed, it must be coupled with an exergonic reaction that releases more free energy than the endergonic reaction requires. In cells, all endergonic reactions are coupled to such exergonic reactions.

The sum of all individual reactions is an organism's metabolism. In metabolism, individual reactions tend to be part of a metabolic pathway, which is a series of sequential reactions in which products of one reaction are used immediately as reactants for the next reaction in the series. In a **catabolic pathway**, complex molecules are broken down into simpler compounds, thereby releasing free energy. An example of a catabolic pathway is cellular respiration, in which energy is extracted from the breakdown of food such as glucose. This is discussed in detail in Chapter 4. In contrast, an **anabolic pathway** (often called a biosynthetic pathway) consumes free energy to build complicated molecules from simpler molecules. Examples of anabolic pathways include photosynthesis, which is covered in Chapter 5, and the synthesis of macromolecules such as proteins and nucleic acids.

catabolic pathway a pathway in which energy is released and complex molecules are broken down into simple molecules

anabolic pathway a pathway in which energy is supplied to build complex molecules from simple molecules

The overall ΔG of an anabolic pathway is positive, whereas the overall ΔG of a catabolic pathway is negative. However, any one pathway may be made up of a number of individual chemical reactions. Some of these reactions may not have the same sign (positive or negative) for ΔG as the overall pathway (**Figure 18**). Regardless of the overall ΔG value for an entire pathway, each endergonic step can proceed only if it is coupled with an exergonic reaction.

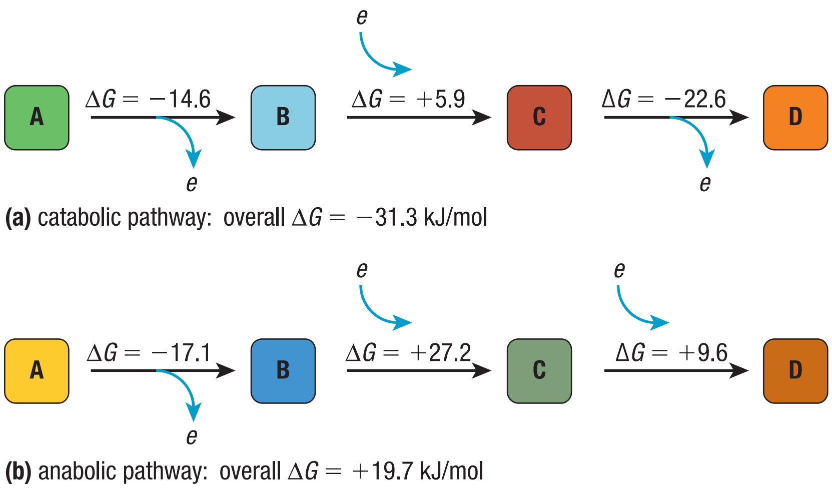


Figure 18 Examples of a catabolic pathway and an anabolic pathway: (a) The catabolic pathway has three steps. Free energy is released in the first and last steps and added in the middle step. The middle step is endergonic and must be coupled with an exergonic reaction (not shown). The overall change in free energy from A to D is negative. (b) The anabolic pathway also has three steps, but the overall change in free energy is positive. While the first step is exergonic, releasing energy and proceeding spontaneously, the next two steps are endergonic and must be coupled with exergonic reactions to supply the needed free energy.

All living things perform numerous activities that result in an increase in the free energy ($+\Delta G$) of the products or substances involved—they move, grow, repair and reproduce. These activities need a continuous supply of free energy. Cells need a constant, convenient source to provide this free energy. As you are about to learn, free energy is usually supplied by the energy carrier molecule ATP.

3.1 Review

Summary

- Energy is the ability to do work. All living things require a constant supply of energy.
- The first law of thermodynamics states that energy transforms from one form to another or transfers from one object to another, but it is neither created nor destroyed.
- During a chemical reaction, bonds in the reactants break and bonds in the products form. For the bonds in the reactants to break, energy must be absorbed. As bonds form, energy is released.
- The second law of thermodynamics states that in every transfer and conversion of energy, there is less energy available to do work. The total entropy of a system and its surroundings always increases.
- Gibbs free energy (G) is the energy in a system that is still available to do work after a reaction occurs.
- Exergonic reactions have a negative ΔG value, are spontaneous, and release free energy.
- Endergonic reactions have a positive ΔG value, are not spontaneous, and absorb free energy. They must be coupled with an exergonic reaction to proceed.
- Metabolic pathways are a series of chemical reactions. Catabolic pathways result in an overall decrease in free energy—free energy is released. Anabolic pathways result in an overall increase in free energy—free energy is absorbed.

Questions

1. Explain the relationship between the terms in each pair:
   (a) energy and work
   (b) potential energy and kinetic energy
   (c) free energy and spontaneous changes K/U
2. Describe the relationship between bond energy and energy changes that occur during a chemical reaction. K/U
3. (a) Calculate the overall energy change in the combustion of ethane, C_2H_6. Is it an exothermic reaction or an endothermic reaction?
   (b) Compare the energy released per gram from ethane with the energy released from glucose and butanoic acid. (See Tutorial, page 132.)
   (c) Based on these examples, predict which compounds contain more energy per gram: hydrocarbons, fats, or carbohydrates. K/U T/I
4. If the activation energy of a reaction is 1250 kJ/mol, and the energy released by the formation of products in the reaction is 1386 kJ/mol, what type of reaction has taken place? T/I
5. Explain how organisms can grow and create internal order without violating the second law of thermodynamics. K/U T/I
6. Is the releasing of light by a firefly endergonic or exergonic? Explain how such a process abides by the first and second laws of thermodynamics. K/U
7. In your own words, describe the difference between anabolic and catabolic pathways. K/U C
8. For each of the following, state whether the event or process is spontaneous or non-spontaneous, and under what conditions you would expect it to occur. T/I
   (a) Organic food waste decomposes.
   (b) A bacterial cell propels itself through water using a flagellum.
   (c) Honey bees perform a hydrolysis reaction to convert sucrose into a mixture of glucose and fructose.
   (d) Electric eels generate powerful electric fields to stun their prey and to defend themselves.
9. (a) Describe the first and second laws of thermodynamics.
   (b) Explain why some people might mistakenly think that living things do not obey the second law. K/U
10. Which of the following processes are spontaneous? Give an example of each spontaneous process. K/U T/I A
    (a) an exothermic process that increases entropy in a setting with a low temperature
    (b) an exothermic process that decreases entropy in a setting with a high temperature
    (c) an endothermic process that increases entropy in a setting with a high temperature
    (d) an endothermic process that decreases entropy in a setting with a low temperature