BIOCHEMICAL ENERGY PRODUCTION

Living organisms use carbohydrates as their source of energy. Plants make their own carbohydrates through photosynthesis. Animals, on the other hand, obtain carbohydrates by eating plants or other animals. Plants and animals transform carbohydrates into fats, which also can be used as sources of energy. The extraction of chemical energy from these compounds is called **metabolism.**

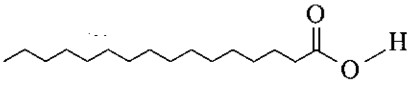
Metabolism involves highly spontaneous oxidation reactions, as illustrated by glucose (a carbohydrate) and palmitic acid (a fat):

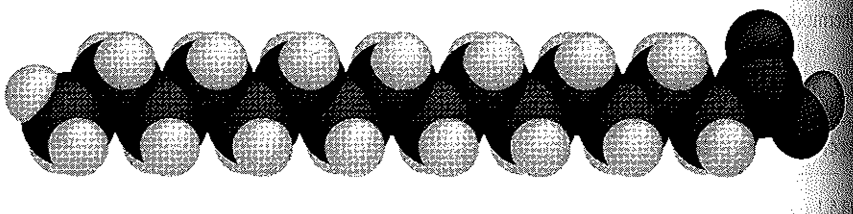
Glucose and other important carbohydrates are discussed in Section 11.6.

Glucose: $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$ $\Delta G° = -2870\ \text{kJ}$

Palmitic acid: $C_{15}H_{31}CO_2H + 23\ O_2 \rightarrow 16\ CO_2 + 16\ H_2O$ $\Delta G° = -9790\ \text{kJ}$

Palmitic acid:





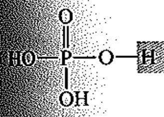
The negative standard free energy changes of these reactions arise because the relatively weak O=O bond in molecular oxygen is converted into stronger O—H and C=O bonds in H_2O and CO_2. Entropy also favors these reactions because gaseous oxygen converts a solid into gaseous CO_2 and liquid H_2O. Not only are the products in more disordered phases, but there are also more molecules on the product side of the equation than on the side of the starting materials.

The large amount of energy stored in molecules such as glucose and palmitic acid means that a little fat or carbohydrate goes a long way as a fuel for life processes. However, a living cell would be destroyed quickly if all the energy stored in these molecules were released in a single reaction. To utilize energy-rich molecules without being destroyed, cells use elaborate chains of sequential reactions that allow this stored energy to be harvested a little at a time. Part of this energy is released as heat that maintains our constant body temperature as it is dissipated to the surroundings. Another portion of the energy is stored in other high-energy molecules that the body uses as "power sources" for the many reactions that occur within cells. In addition to storing the energy produced in metabolism, these high-energy species serve as energy transport molecules, moving to different regions of the cell where energy is required for cell functions.

The most important of these energy transport molecules is **adenosine triphosphate (ATP).** Some of the energy released during the oxidation of glucose is used to drive a condensation reaction in which adenosine diphosphate (ADP) and phosphoric acid link together and eliminate water. This reaction stores chemical energy, as indicated by its positive standard free energy change:

$$\text{ADP} + H_3PO_4 \rightarrow \text{ATP} + H_2O \qquad \Delta G° = +30.6\ \text{kJ}$$

The molecular details of this reaction are illustrated in Figure 13-17. Although ATP is a complex molecule, notice that the adenosine portion does not change as this reaction occurs. The condensation reaction merely adds an additional phosphate group to the end of an existing chain.



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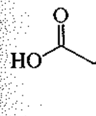

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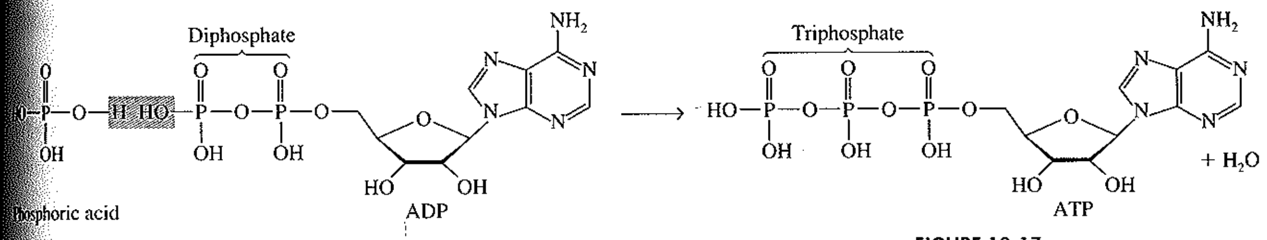


FIGURE 13-17
Phosphoric acid reacts with ADP to produce water and ATP. Because a P—O—P linkage is weaker than a P—O—H linkage, this reaction is endothermic by about 30 kJ/mol. Notice that the adenosine portion of the molecule remains intact during this reaction.

The right-hand portion of the ATP molecule is adenosine. It contains adenine, an important biochemical building block introduced in Section 11.7.

The exact processes by which carbohydrates and fats are converted to CO_2 and H_2O depend on the conditions and the particular needs of the cell. Each possible route involves a complex series of chemical reactions, many of which are accompanied by the conversion of ADP to ATP. Glucose, for example, can convert as many as 36 ADP molecules into ATP molecules as it is oxidized to CO_2 and H_2O:

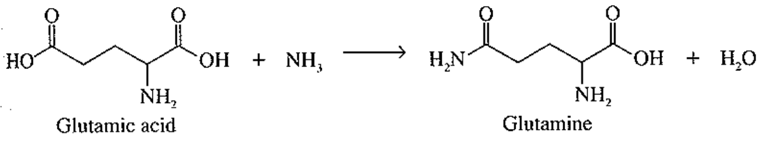
$$C_6H_{12}O_6 + 6\ O_2 + 36\ ADP + 36\ H_3PO_4 \rightarrow 6\ CO_2 + 36\ ATP + 42\ H_2O$$

COUPLED REACTIONS

Cells use the energy stored in ATP molecules to drive reactions that would otherwise be nonspontaneous under physiological conditions. This is accomplished by coupling the nonspontaneous reaction with the conversion of ATP back to ADP and phosphoric acid:

$$ATP + H_2O \rightarrow ADP + H_3PO_4 \qquad \Delta G^o = -30.6\ kJ$$

Coupled reactions share a common intermediate that transfers energy from one reaction to the other. For example, the amino acid glutamine is synthesized in cells by reacting ammonia with another amino acid, glutamic acid.



This reaction is thermodynamically unfavorable, $\Delta G^O = +14$ kJ. The reaction is driven by coupling it with the conversion of ATP into ADP.

$$\text{Glutamic acid} + NH_3 \rightarrow \text{Glutamine} + H_2O$$

$$ATP + H_2O \rightarrow ADP + H_3PO_4$$

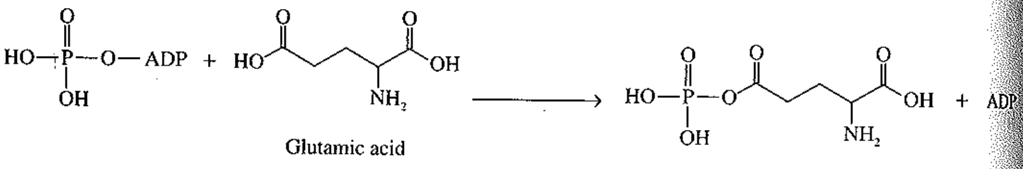
$$\textit{Net:}\quad \text{Glutamic acid} + ATP + NH_3 \rightarrow \text{Glutamine} + ADP + H_3PO_4$$

The net energy change for the coupled process is the sum of the ΔG^o values for the individual reactions:

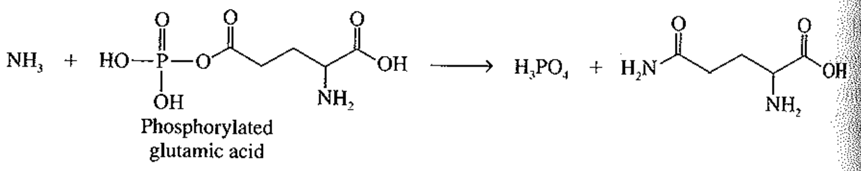
$$\Delta G^o_{rxn} = \Delta G^o_{glutamine} + \Delta G^o_{ATP} = 14\ kJ + (-30.6\ kJ) = -17\ kJ$$

The negative value of ΔG^o_{rxn} shows that the free energy released in the ATP reaction is more than enough to drive the conversion of glutamic acid into glutamine.

Although the coupled reactions can be represented by the net reaction, this process actually occurs in steps. In the first step of the coupled reaction, a phosphate group is transferred from ATP to glutamic acid:



Next, an ammonia molecule reacts with the phosphorylated form of glutamic acid, producing phosphoric acid and glutamine:



Overall, one molecule of ATP is converted to ADP and phosphoric acid for each molecule of glutamine produced from glutamic acid.

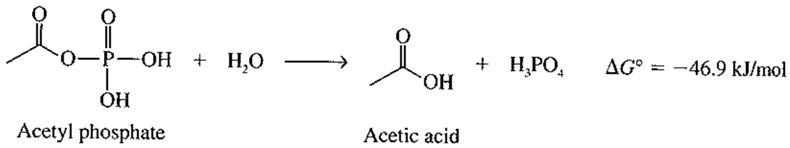
Coupled biochemical reactions occur on the surface of an enzyme. As we describe in Chapter 11, enzymes are huge proteins that catalyze an immense variety of biochemical reactions. The surface area of an enzyme has a particular shape that accommodates the various molecules that must react in a coupled reaction.

A catalyst is a chemical species that makes a reaction go faster than it would in the absence of a catalyst. Enzymes and other catalysts are discussed in Chapter 14.

Coupled reactions are also involved in the synthesis of ATP. Sample Problem 13-11 illustrates one of these energy-storing reactions.

SAMPLE PROBLEM 13-11 ATP-FORMING REACTIONS

One of the biochemical reactions that produces ATP involves the conversion of acetyl phosphate to acetic acid and phosphoric acid:



$\Delta G° = -46.9$ kJ/mol

Write the overall balanced equation, and show that the coupled reaction is spontaneous.

METHOD: A coupled process links a spontaneous reaction with a nonspontaneous one. In this case the energy released in the acetyl phosphate reaction provides the energy needed to drive the conversion of ADP to ATP.

Although the standard free energy change of the ADP/ATP reaction is 30.6 kJ/mol under *standard* conditions, the concentrations of the phosphate species in cells are far from 1 M. This causes the free energy to vary from its standard value. Typically, the conversion of ATP to ADP *in a living cell* releases around 50 kJ/mol of energy.

Combining the two reactions gives the overall balanced equation:

$$\begin{array}{c} \text{Acetyl phosphate} \qquad\qquad \text{Acetic acid} \\ CH_3CO_2PO_3H_2 + \cancel{H_2O} \rightarrow CH_3CO_2H + \cancel{H_3PO_4} \\ ADP + \cancel{H_3PO_4} \rightarrow ATP + \cancel{H_2O} \\ \hline \textit{Net}: CH_3CO_2PO_3H_2 + ADP \rightarrow CH_3CO_2H + ATP \end{array}$$

The net energy change for the coupled process is the sum of the $\Delta G°$ values for the individual reactions:

$$\Delta G°_{rxn} = \Delta G°_{\text{acetyl phosphate}} + \Delta G°_{ATP} = -46.9 \text{ kJ} + 30.6 \text{ kJ} = -16.3 \text{ kJ}$$

The negative value of $\Delta G°_{rxn}$ shows that the free energy released in the acetyl phosphate reaction is more than enough to drive the conversion of ADP to ATP.

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ENERGY EFFICIENCY

Cells store the energy that is released during the oxidation of glucose by converting ADP into ATP. The storage process cannot be perfectly efficient, however, because each step in the reaction sequence must have a negative free energy change. In practical terms, this requires that some energy be released to the surroundings as heat.

The complete balanced equation for glucose oxidation coupled with ATP production under normal physiological conditions is:

$$C_6H_{12}O_6 + 6\ O_2 + 36\ ADP + 36\ H_3PO_4 \rightarrow 6\ CO_2 + 42\ H_2O + 36\ ATP$$

According to this equation, the oxidation of 1 mol glucose yields 36 mol ATP. We can determine the overall free energy change for this process from the values for its uncoupled parts:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \qquad \Delta G^\circ = -2870\text{ kJ}$$

$$36\ (ADP + H_3PO_4 \rightarrow ATP + H_2O) \qquad \Delta G^\circ = (36\text{ mol})(-30.6\text{ kJ/mol}) = +1100\text{ kJ}$$

$$\Delta G_{\text{overall}} = -2870\text{ kJ} + 1100\text{ kJ} = -1770\text{ kJ}$$

Although 1100 kJ of energy is stored in this coupled process, 1770 kJ of energy is "wasted." Thus cells harness 38% of the chemical energy stored in glucose to drive the biochemical machinery of metabolism. The remaining 62% is dissipated as heat, raising the entropy of the surroundings as the living cell organizes itself and its immediate environment.

Fats such as palmitic acid are metabolized through pathways similar to the ones used for the oxidation of glucose. The complete oxidation of 1 mol of palmitic acid molecule liberates 9790 kJ of free energy and produces 130 ATP molecules. You should be able to verify that this metabolic process has about the same efficiency as the oxidation of glucose.

One mole of glucose releases 2870 kJ of free energy, whereas one mole of palmitic acid releases much more free energy, 9790 kJ. Although some of this extra energy results from its larger molecular size, palmitic acid also releases more energy per atom of carbon than glucose. Glucose oxidation releases about 480 kJ/mol of carbon atoms, whereas palmitic acid releases about 610 kJ/mol of carbon atoms. Organisms convert carbohydrates into fats because fats store more energy per unit mass.

SECTION EXERCISES

13.6.1 Nitrogen-fixing bacteria react N_2 with H_2O to produce NH_3 and O_2 using ATP as their energy source. Approximately 24 molecules of ATP are consumed per molecule of N_2 fixed. What percentage of the free energy derived from ATP is stored in NH_3?

13.6.2 The hydrolysis of ATP to ADP has $\Delta H^\circ = -21.0$ kJ/mol, whereas $\Delta G^\circ = -30.6$ kJ/mol at 298 K. Calculate ΔS° for this reaction. What happens to the spontaneity of this reaction as the temperature is increased to 37 °C?

13.6.3 In running a mile, an average person consumes about 500 kJ of energy.
  a. How many moles of ATP does this represent?
  b. Assuming 38% conversion efficiency, how many grams of glucose must be "burned"?