

Chapter 3

Overall Energetics of Photosynthesis

ENERGY, ENTROPY, FREE ENERGY

The basic concept of physics is *energy*; that means, capacity to produce work. The basic law of physics is the law of conservation of energy (as the basic law of chemistry is that of conservation of matter). This law asserts that *the amount of energy in the universe is constant*. This sweeping statement is a generalization of the more restricted *first law of thermodynamics*, which proclaims the constancy of the sum of mechanical and thermal energy in systems containing energy only in these two forms.

According to the law of conservation of energy, the latter cannot be created or lost. However, different *forms* of energy, such as electromagnetic, chemical, or nuclear, are interconvertible. All of them can be converted to mechanical energy and made to produce work; that is, to impart acceleration to material bodies.

However, from the point of view of mutual convertibility of the different forms of energy, one important distinction exists. All forms of energy are *completely* interconvertible, except one: thermal energy. This is easy to understand, if one considers the molecular structure of matter. Thermal energy is the mechanical energy of the chaotic motion of atoms and molecules. Increase in intensity of this motion is what we call tem-

perature rise. The chaotic character of thermal agitation is the reason for the limited convertibility of thermal energy into other forms of energy. In a resting mass of gas or liquid, as many molecules move, at a given time, in one as in any other direction. The law of conservation of energy would not be violated if the thermal energy of a mass of water in the ocean would be converted into the kinetic energy of a ship riding this water. Water would cool down and the ship would speed forward. All that is needed for this is to give the chaotic motion of water molecules a preferred direction. We know from experience that this does not happen; and we never expect such conversion of disorder into order to occur spontaneously. This conviction is expressed in a fundamental principle that says, in essence, that order does not arise spontaneously out of disorder; to create order out of disorder, a certain amount of energy must be expended (that is, converted into heat). This is the *second law of thermodynamics*; it says that in a closed system (a system not exchanging energy with the surroundings) heat cannot be converted into work without some other change in the system involving an increase in disorder and balancing the increase in orderliness associated with the conversion of heat into work.

For precise formulation, this principle requires a quantitative measure of disorder. This measure is called *entropy*. (The measure of *order* is sometimes called *negentropy*.) The precise definition of entropy has to do with the fact that every orderly state of a system of many particles is in some way unique, while disorderly states can be realized in a multitude of different ways. For example, the state in which all girls sit on the right side and all boys on the left side of the classroom is more orderly than the state in which sexes are mixed at random. It is obvious that the first distribution can be arranged through fewer different individual seat assignments than the second. Entropy, S , is defined (apart from a proportionality constant, k) as the logarithm of the number (n) of different ways in which a particular state of an assembly of many particles can be achieved (Eq. 3.1).

$$S = k \ln n \quad (3.1)$$

(By taking the logarithm, \ln , rather than the number itself, entropy becomes, like energy, an *additive*, rather than a *multiplicative* property, so that the entropy of two systems together is equal to the sum of the entropies of the same two systems taken separately.)

The thermodynamic state of a system of many particles is thus defined (a) by its content in energy (E), and (b) by its content in entropy (S). The higher the entropy of a system, the more disorderly it is, and the less of its thermal energy is available for conversion into usable forms of energy—mechanical, chemical, or electric. The “usable” part of total energy (E) of a system is called its *free energy* (F). Thermal energy (heat) is the only kind of energy that is only partly free. A change in free energy (ΔF) in a process is related to the change in entropy (ΔS) and the change in the total energy (ΔH , or enthalpy) by the following equation:

$$\Delta F = \Delta H - T \Delta S \quad (3.2)$$

where T is the so-called absolute temperature. Its definition and implications will be discussed below.

In a closed system, spontaneous processes cannot go in the direction of decreasing entropy (that is, increasing order) because this would contradict the second law of thermodynamics. After every spontaneous process in such a system, entropy must increase. This means that a less probable, or more orderly, state must go over into a more probable, less orderly state.

When we deal, as we usually do, with systems that are *not* closed (systems that can exchange energy with the surroundings), more complex formulations of the second law of thermodynamics become necessary. One important case is that of a reactive system enclosed in a reservoir of constant temperature and exchanging heat with it, such as an organism in air. We can imagine, for example, a sphere, S_y , inside which a combustion, or another chemical reaction can be produced (see Fig. 3.1). Let this sphere be submerged in a water reservoir, R , so large that its temperature is practically unaffected by taking up, or supplying, the enthalpy of the reaction, ΔH . The process is thus conducted *isothermally*, the same temperature prevailing before and after the reaction; but a certain amount of thermal energy, ΔH , is transferred from the system to the reservoir or vice versa. If thermal energy is lost by the system to the reservoir, ΔH is given the negative sign ($-\Delta H$); a positive sign ($+\Delta H$) indicates that energy is acquired by the system from the reservoir.

Since entropy is additive, the change in total entropy of the reservoir and the system can be divided into two terms: one is the change in



FIG. 3.1 Isothermal reaction. (S_y , system; R , reservoir.) Thermal energy, ΔH , is passed *from* the reacting system, S_y , to the reservoir, R , if the reaction is exothermal; from the reservoir to the system if it is endothermal. The total change in *entropy* (disorder), ΔS , is $\Delta S_{S_y} + \Delta S_R$. The second term is equal to $-\Delta H/T$. For reaction to proceed, the total entropy (disorder) must increase: $\Delta S_{S_y} - \Delta H/T \geq 0$; or, $\Delta H - T\Delta S_{S_y} \leq 0$; or, $\Delta F \leq 0$.

the entropy of the reservoir, ΔS_R , caused by the addition or subtraction of thermal energy, ΔH ; it is positive for “exothermal” (heat-liberating) reactions, and negative for “endothermal” (heat-consuming) reactions. The second term is the change in entropy of the reacting system (ΔS_{S_y}). This term is positive if the reaction leads to a decrease of orderliness and negative if there is an increase in orderliness.

Since, together, the reacting system and the reservoir form a closed system, the condition that must be satisfied for the reaction to proceed is

$$\Delta S = \Delta S_{S_y} + \Delta S_R \geq 0 \quad (3.3)$$

The entropy increase in the reservoir, $+\Delta S_R$, caused by transfer of thermal energy, $-\Delta H$, from the system to a reservoir with a temperature T , or the entropy decrease in the reservoir, $-\Delta S_R$, associated with the transfer of energy $+\Delta H$ from the reservoir to the system, is proportional to ΔH (Eq. 3.4). Equation 3.4 provides the thermodynamic *definition*

of absolute temperature T : the proportionality constant in this equation is the reciprocal of T .

$$\Delta S_R = \frac{1}{T} (-\Delta H); \text{ or, } T \Delta S_R = -\Delta H \quad (3.4)$$

Equation 3.4 states that the lower the temperature of the reservoir, the greater is ΔS_R (change in entropy). In other words, the lower the temperature, the larger is the part of thermal energy of a reservoir not available for conversion into mechanical or other free energy. A given amount of thermal energy becomes less "useful" as the temperature decreases. We can rewrite Eq. 3.3 with the help of 3.4 as

$$\Delta S_{sy} - \frac{\Delta H}{T} > 0,$$

or, multiplying by T ,

$$T \Delta S_{sy} - \Delta H > 0 \quad (3.5)$$

or

$$\Delta F \equiv (\Delta H - T \Delta S_{sy}) < 0; \text{ or, } -\Delta F = -\Delta H + T \Delta S_{sy} > 0 \quad (3.6)$$

where ΔF is the change in *free* energy associated with the process (as in Eq. 3.2). The absolute value of $-\Delta F$ is greater than that of the $-\Delta H$ (enthalpy) of the process, if the entropy change, ΔS_{sy} , is positive; ΔF is smaller than ΔH if ΔS_{sy} is negative. We note that at $T = 0$ (absolute zero, -273°C), when all thermal motion stops, ΔF becomes equal to ΔH . Equation 3.5 is the form of the second law of thermodynamics most often applied to chemical reactions, because they are usually carried out without insulation from the atmosphere, the latter acting as a thermal reservoir. Equation 3.6 says that *in order for a reaction to proceed spontaneously, its free energy change, ΔF , must be negative*. ΔF is the chemical energy that can be converted into other useful forms of energy in the reaction. As noted above, the absolute value of $-\Delta F$ is greater than that of $-\Delta H$ if the reaction proceeds with a decrease in orderliness ($\Delta S_{sy} > 0$, that is, the second term in Eq. 3.6 is positive) and smaller if the reaction proceeds with an increase in orderliness ($\Delta S_{sy} < 0$, that is, the second term in Eq. 3.6 is negative). Thus for an isothermal reaction to proceed spontaneously, it must have either a sufficiently large *negative* ΔH (give off enough heat) or a sufficiently large positive ΔS (that is, it must lead to a sufficient increase in disorder) to make the sum $\Delta F = \Delta H - T \Delta S$ negative.

This explains why some endothermal reactions, which consume rather

than evolve heat, nevertheless proceed spontaneously. For example, some salts dissolve in water with consumption of heat (so that the solution cools down, if it is not supplied with heat from a reservoir). In this case, the increase in *entropy* (increase in disorder), caused by breakdown of the crystalline salt structure into free ions, overbalances the acquisition of heat energy needed to maintain constant temperature.

In chemical reactions with *large* enthalpy (ΔH) changes, the entropy term, $T \Delta S$, becomes relatively insignificant. For example, in photosynthesis, the stored energy ΔH , is about 112 Kcal/mole (Eq. 2.1), while the stored free energy, ΔF , is about 120 Kcal/mole. (This figure applies to open air conditions, when the proportions of CO_2 and O_2 are 0.03% and 21% respectively; the concentration of $\text{C}_6\text{H}_{12}\text{O}_6$, which also affects the free energy, is arbitrarily taken as 1 mole/liter.) The ΔF of photosynthesis is slightly greater than ΔH (that is, ΔS is negative), because the system consisting of large sugar molecules and small oxygen molecules is somewhat more orderly than the system consisting only of the small molecules, H_2O and CO_2 .

In order to increase the orderliness of a system, and thus to decrease its entropy, energy must be supplied from the outside. Inversely, useful energy can be extracted from a system if its entropy increases. When thermal energy is passed from a body of *higher temperature* to one of lower temperature, equalizing the average thermal energy of the molecules and thus destroying the orderliness inherent in the segregation of the faster from the slower molecules, some free energy can be derived from this passage. This is the principle on which the heat engines operate. The same is true of equalization of *pressure* or of *concentration* between two parts of a system. The amount of free energy available from various equalization processes depends on the degree of inequality in temperature, pressure, or concentration available in the system. This is why, in a heat engine, the amount of work that can be derived from the transfer of a certain amount of heat from a hot to a cold reservoir (the "efficiency" of the engine) is larger the greater the temperature difference between them.

When we say that life consumes energy, we really mean that it consumes *free* energy, since energy as such cannot be consumed. Every activity of an organism involves consumption of free energy. The locomotion of the body as a whole uses up some of it. So does every movement of its limbs and food propulsion through the digestive canal. So does

the beating of the heart, or the electric current that carries messages along the nerves and stores information in the brain. So does the maintenance of the body temperature of warm-blooded animals, since the difference between that temperature and the lower temperature of the surrounding medium represents free thermal energy.

The synthesis of the constituents of a living organism—proteins, fats, etc.—also consumes free energy. These complicated molecules may or may not contain more energy than the simpler organic molecules from which they are synthesized; but they always represent a higher degree of orderly arrangement of the atoms, and, therefore, contain less entropy. It is often said that complicated, orderly molecular systems contain a large amount of *information*. Information means, in this context, the same as negative entropy (negentropy)—a higher degree of orderliness.

A living organism is like a running clock. If it is not wound up, it will sooner or later run out of free energy and stop. If the clock of life on earth would be left to run down without rewinding, it would take less than one hundred years for all life on the planet to approach its end. First, green plants would die from starvation. Man and other animals who feed on plants would follow. And finally, bacteria and fungi feeding on dead animal and plant tissues would exhaust their food and die too.

PHOTOSYNTHESIS AND RESPIRATION

What is it that winds up the machinery of life on earth? The answer was given in Chapter 1: it is *photosynthesis*. As mentioned in Chapter 2, some terrestrial sources of free energy do exist—the heat of volcanoes or hot springs, the radioactivity of certain elements in the earth's crust. These sources, however, are rare and diffuse. The universal distribution of life on earth is bound to the infinitely more abundant extraterrestrial supply of free energy—the light energy streaming to the earth from the sun. The photosynthesis of plants is the process by which light winds up the clock of life.

This description is more sophisticated than that of Robert Mayer, quoted in the first chapter. Mayer saw in photosynthesis by plants the confirmation, on a giant scale, of the *first* law of thermodynamics: the

energy of life is derived from the energy of light. The second law of thermodynamics was not known at that time, and Mayer did not ask himself "why could not life exist on earth by continuously consuming the heat energy of the oceans and the atmosphere, and converting it into chemical energy?" The second law says that this is impossible. Living organisms cannot violate the entropy principle and create order out of disorder without a compensating process, so that the net result is an increase in entropy.

The free energy needed for life is provided in all organisms—except certain bacteria—by a reversal of photosynthesis. One often speaks of "energy content of organic matter" (meaning by this its combustion energy). This is a sloppy expression. The combustion energy is the energy available not in organic matter as such, but in the system (organic matter + oxygen). In order to supply energy for life processes, organic matter and oxygen (both originating in photosynthesis) must be given a chance to react back, reversing photosynthesis. This back reaction is *respiration*—a slow, regulated combustion. Life without oxygen, that is, anaerobic life, is possible only for certain microorganisms able to extract energy from chemical processes not requiring oxygen. Thus, yeast cells can use the energy of alcoholic fermentation. Certain cells in higher organisms, such as the muscle fibers, can obtain, in emergency, some energy in a similar fashion, by fermentation leading to lactic acid.

As respiration substrates, organisms can use either materials derived from food (animals), or materials they had themselves synthesized from carbon dioxide and water (plants). The latter process is called *endogenous respiration*. However, organic materials supplied from the outside can also be used by many plants. (Carnivorous plants can even digest insects!) This is called *exogenous respiration*. Only exogenous respiration is possible in animals.

In its overall chemical result, respiration is the reversal of photosynthesis. The two processes are different in that one represents an uphill transport of material, requiring massive supply of free energy from the outside, while the other runs downhill and needs no such supply.

The energy of light acts in photosynthesis similarly to the electrical energy operating a pump that lifts water into a higher reservoir (Fig. 3.2a). In Fig. 3.2b, the accumulated chemical energy is prevented from dissipation by the metastability of the system "organic matter plus oxygen." This system, while intrinsically unstable, does not react sponta-

neously—even a piece of dry wood needs a match to start it burning! In organisms, the back reaction goes through special channels (Figs. 3.2*b* and 3.3), the locks on which are opened by lockkeepers—biological catalysts (enzymes). These catalytic proteins permit the release of the accumulated energy in gradual steps, rather than in a single big rush.

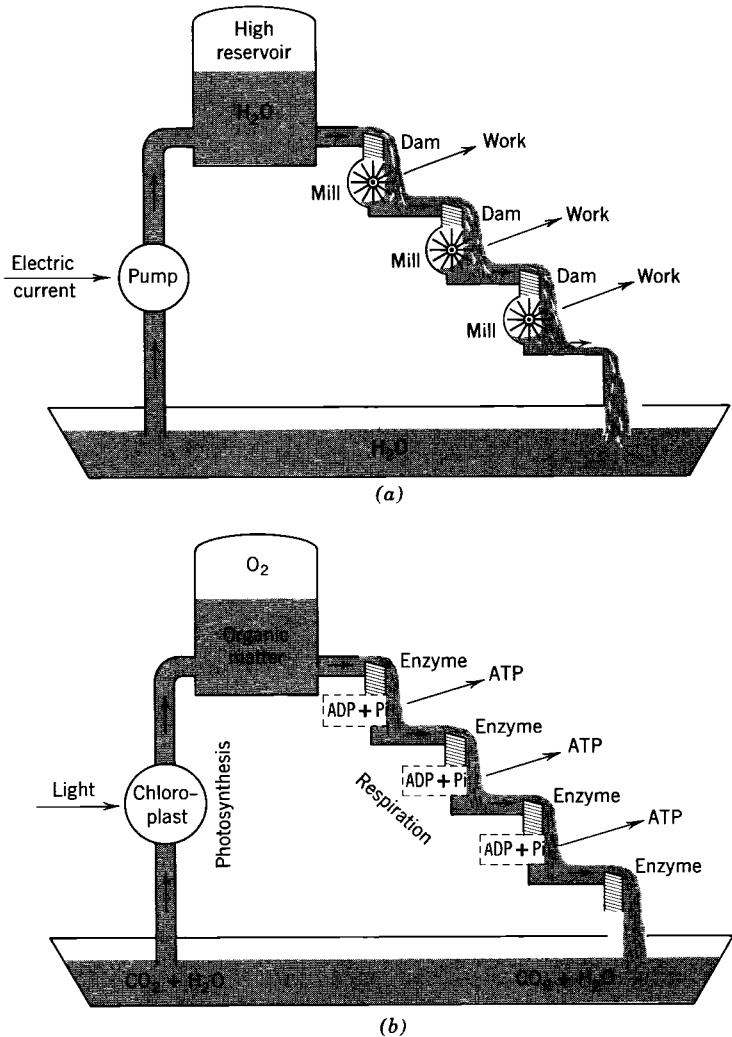


FIG. 3.2 (a) Pump and water wheels. (b) Photosynthesis and respiration. (ATP, adenosine triphosphate; ADP, adenosine diphosphate; P_i , inorganic phosphate.)

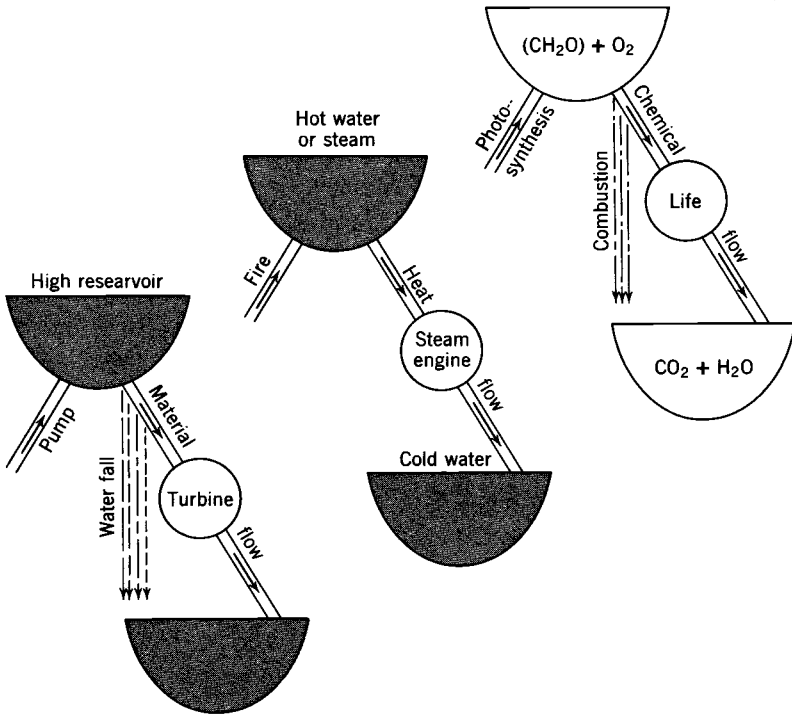
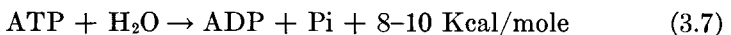


FIG. 3.3 Turbine, steam engine, life.

Such a rush would be equivalent to direct combustion (see Fig. 3.3), and even if it would not set the organism on fire, it is likely to damage it *locally*, and much of the released energy would go to waste. For its different chemical and physical functions, the organism requires small, measured amounts of energy. The respiration mechanism is fulfilling the task of releasing the free energy of the system (organic substrate + oxygen), in proper small units.

The most important energy currency in biology are the energy amounts carried by the so-called "high energy phosphate bonds" (see Chapter 18). Its most common form is that present in adenosine triphosphate, abbreviated ATP. This molecule releases about 8–10 Kcal/mole upon hydrolysis into adenosine diphosphate, ADP and inorganic phosphate, Pi.



The "phosphate bond energy" is less than 10 percent of the energy accumulated in the elementary process of photosynthesis. The energy bank of life takes in energy in 100 Kcal bills and spends it in 10 Kcal coins (Fig. 3.2b).

It is worth pointing out here that a natural process exists which is, physically speaking, closer to the true reversal of photosynthesis than respiration. This is bioluminescence. Many animals (fishes, crustaceans, worms), and some plants (dinoflagellates, fungi, bacteria) emit light, the energy of which is supplied by a special form of oxidative metabolism. In these organisms, a certain part of the "energy capital," originally accumulated by photosynthesis, is prevented from being broken up into the "small change" of phosphate quanta, and liberated in bulk, in the form of visible light quanta of 40–60 Kcal/einstein each. (An einstein is a mole of quanta.) Since these organisms do not absorb visible light, it is not the case of absorbed quanta being reemitted as such, as in fluorescence (see Chapters 10 and 15). Rather, the light quantum becomes available by following a special pathway of oxidation—rather like a ski jump built on the down slope of a hill (Fig. 3.4).

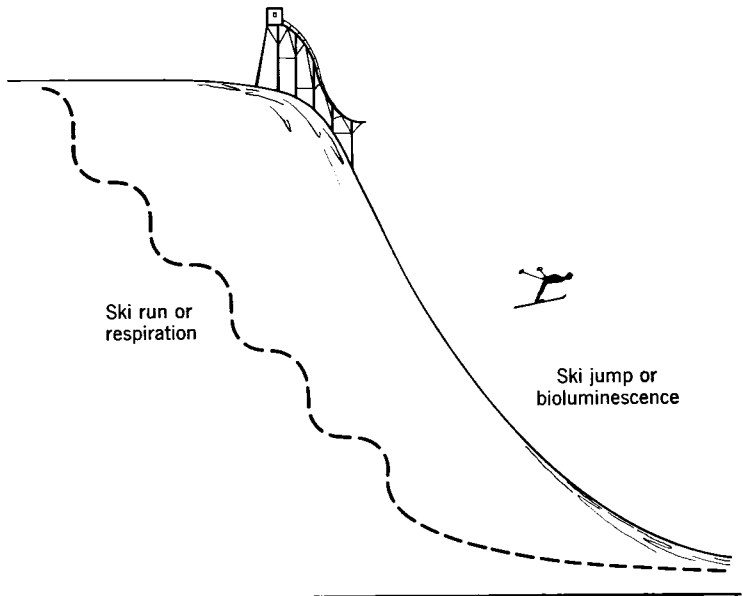
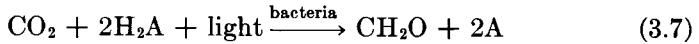


FIG. 3.4 Ski run and ski jump; respiration and bioluminescence.

ENERGETICS OF BACTERIAL PHOTOSYNTHESIS

Bacterial photosynthesis is represented by Van Niel's equation (see Eq. 2.2):



In this equation, the amount of energy stored depends on the nature of A. We saw it to be 112 Kcal when A is oxygen, that is, in green plant photosynthesis. In the case of A being sulfur, the energy storage is about 7 Kcal, if sulfur is oxidized to sulfate. With some reductants, no energy storage occurs at all. For example, if H_2S is oxidized only to elemental sulfur, 5 Kcal of chemical energy are *lost*. In the oxidation of H_2 to H_2O (in "hydrogen" bacteria), as much as 25 Kcal are dissipated. (However, ΔF , the free energy change, is even in this case slightly positive.)