Chapter 2

Overall Chemistry of Photosynthesis; Autotrophic and the Heterotrophic Ways of Life

Photosynthesizing plants on earth are an immense organic-chemical factory and a giant energy transformer station. Let us estimate their overall annual performance.

TOTAL YIELD OF ORGANIC SYNTHESIS AND ENERGY STORAGE ON EARTH

Estimates of the total yield of photosynthesis on earth are by necessity only approximate. They start with measurements carried out, by a variety of methods, on limited areas of vegetation, for example, a grass plot, or a forest area, or a certain volume of water in a lake or ocean. Then, each result is multiplied by the total area or volume inhabited by this type of vegetation, and the products are added (see Table 2.1).

Unfortunately, the largest item is the one of which we know least. This is the production of organic matter in the ocean. The smaller figures

TABLE 2.1   Yield of Photosynthesis on Earth in Tons of Carbon Incorporated Annually into Organic Matter

Type of Vegetation	Area in Millions of Km²	Annual Yield in Tons of C per Km²	Total Yield in Billions (10^9) of Tons of C per year
Forests	44	250	11.0
Grassland	31	35	1.1
Farmland	27	150	4.0
Desert	47	5	0.2
Total on land	149[a]	—	16.3
Ocean	361	375[b] 62[c]	135[b] 22[c] 19[d]
Total	510	—	151[b] 38[c] 35[d]
Total, corrected for respiration[e]	—	—	173[b] 44[c] 40[d]

[a] Figures for land productivity in this table are from Schroeder, *Naturwissenschaften*, *7*, 8, 976 (1919). Since then, farm production must have increased considerably to provide for about doubled population!

[b] G. A. Riley, *J. Marine Research (Sears Found.)*, *1*, 335 (1938); *2*, 145 (1939).

[c] A. Steemann-Nielsen, *Ann. Rev. Plant Physiol.*, *11*, 341 (1960).

[d] S. T. Pike and A. Spilhaus, *Marine Resources*, NAS/NRC Publ. 100 E (1962).

[e] A correction of $+15\%$ is applied to account for losses of carbon by respiration. This is a very uncertain figure (Steemann-Nielsen used $+40\%$ for the plankton).

given in Table 2.1 for the rate of oceanic synthesis have been derived from ^{14}C-tracer incorporation measurements, mainly by Steeman-Nielsen in Denmark; the higher ones, from measurements of oxygen production, mainly by Riley in the United States. A discrepancy of an order of magnitude exists between them. The newest estimates, included in Table 2.1, are "in between," but closer to Steeman-Nielsen's low figures.

In recent years, new interest in the ocean as a potential source of food for the growing world population has led to extensive oceanographic studies, covering physics, chemistry, and biology of the ocean. These studies have shown that the biological productivity of the waters in the ocean is far from uniform. According to a recent Russian review

(1966), based on oceanographic expeditions of Soviet ships, the photosynthetic production varies, in different parts of the ocean, by a factor of 16 (as compared to a factor of 50 on land, according to Table 2.1). The average value of oceanic photosynthesis is, however, closer to the lower limit than it is on land. (In other words, "deserts" include a greater proportion of the oceans than of the continents.)

The reason for wide differences in biological productivity of the oceans lies in variations in the supply of certain nutrient elements, such as nitrogen, phosphorus, iron, and manganese. This distribution depends strongly on vertical and horizontal water currents. Therefore, it is impossible to estimate reliably the total production of organic matter in the ocean from local measurements, and this may be the reason for the discrepancies in Table 2.1 Precise calculations must await the outcome of wide-range surveys, some of which are already under way, such as the international survey of the Indian Ocean. A committee of The International Biological Program (IBP) is planning a survey of all the world oceans.

As noted already by Ingenhousz, photosynthesis in plants is superimposed on the reverse process—respiration, that is, slow combustion of organic matter to water and carbon dioxide. A considerable part of the chemical energy stored by photosynthesis is converted in respiration into a special form—that of energy-rich phosphate. In this form, it can be used for various energy-consuming biological processes: production of mechanical work, chemical synthesis, osmotic work, and transmission of electric signals (Fig. 2.1).

An excess of photosynthesis over respiration is what permits growth of plants and storage of food reserves (starch, oil, fat) in them. In estimating the true yield of photosynthesis, the observed net yield must be corrected for plant respiration. With a crude corrrection of 15%, the total in Table 2.1 becomes 32–146 billion tons.[1]

These values of the total annual production of organic *matter* on

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[1] The reader may ask: How can the amount of living matter on earth be approximately constant, if plant respiration takes care of less than ¼ of the products of photosynthesis? The answer is that *animal respiration* accounts for a significant part of the remaining ¾, particularly in the ocean, where animal life (zooplankton) is much more abundant than plant life (phytoplankton); the rest is destroyed by bacteria in the rotting of organic material on land and on the bottom of the sea.
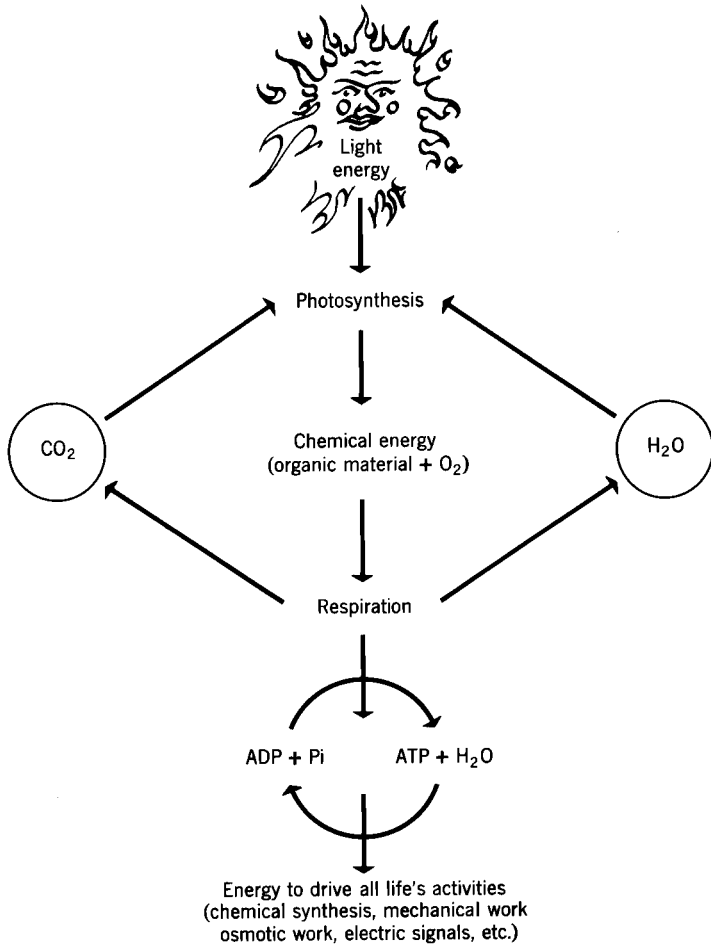
FIG. 2.1 Energy flow diagram showing conversion of light energy into chemical energy in photosynthesis, the formation of energy-rich phosphate in respiration and its use in energy-consuming biological processes. (ADP, adenosine diphosphate; ATP, adenosine triphosphate; Pi, inorganic phosphate; (P)OH has also been used for Pi, see Chapter 18.)

earth can be used to calculate the total *energy* storage by photosynthesis. A simple ratio exists between the chemical turnover and the storage of energy, determined by the amount of chemical energy stored in a unit mass of synthesized organic matter (not to forget the equivalent

volume of oxygen!). Organic matter varies considerably in composition and energy content. However, its *average* composition is close to that of a carbohydrate $C_n(H_2O)_m$. Cellulose and starch are high-polymeric forms $(C_6H_{10}O_5)_n$, of the most common sugars, hexoses (obtained by elimination of one molecule of H_2O from each $C_{16}H_{12}O_6$ molecule), and much of the total weight of living organisms on earth is represented by cellulose, the structural material of trees. Carbohydrates are widespread also as food reserves in plants (starch) and in the liver of animals (glycogen). As an approximation, it is permissible to attribute to living matter on earth the average composition and average energy content of a carbohydrate.

All carbohydrates have approximately the same energy content of about 112 Kcal per gram atom (12g) of carbon contained in them. (One calorie is the amount of heat needed to heat one gram water by 1° centigrade; one kilocalorie is 1000 calories.)

Now, Eq. 1.5 can be rewritten by inserting the specific value of 112 Kcal for the term "chemical energy."

$$CO_2 + H_2O + \text{light} \xrightarrow[\text{plant}]{\text{green}} O_2 + (CH_2O) + 112 \text{ Kcal} \qquad (2.1)$$
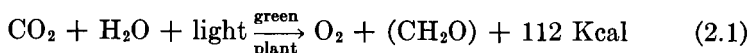
where the brackets suggest that the equation refers to the formation of a (CH_2O) group in a carbohydrate molecule $(CH_2O)_n$.

Equation 2.1 indicates that storage of 112 Kcal is associated with the transfer of 12 grams (one gram-atom) of carbon into organic matter. This means a storage of about 9.6×10^6 Kcal in the formation of one ton (10^6 grams) of organic carbon. A total annual yield of 19 to 135×10^9 tons of organic carbon (Table 2.1) thus corresponds to storage of 1.8 to 13×10^{12} Kcal of chemical energy.

THE CARBON AND OXYGEN CYCLES ON EARTH

The total reserves of fossil coal on earth have been estimated as of the order of 10^{13} (ten trillion) tons. Photosynthesis adds annually something like one percent to the organic carbon now stored underground. Under today's climatic conditions, only a negligible part of this production is stored, while the overwhelming proportion is returned into the

atmosphere and the ocean by respiration of plants and animals, by the burning of straw, wood, and dung, and by the activity of bacteria destroying dead plants and animals (Fig. 2.2).
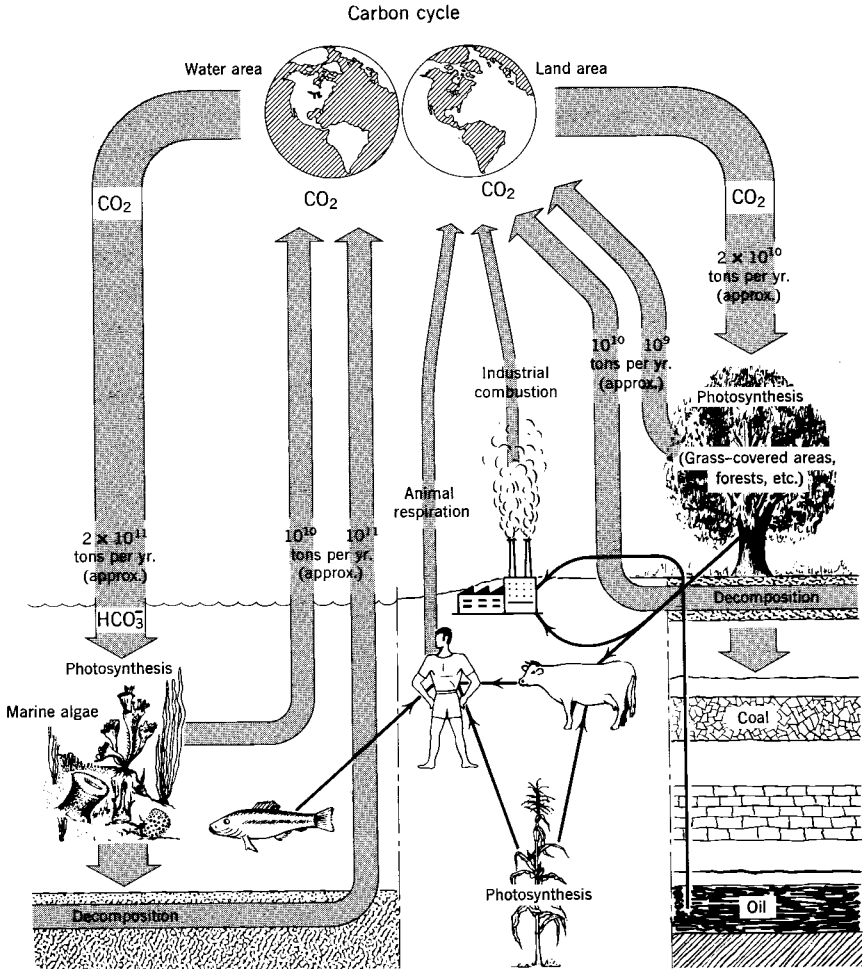

Carbon cycle

FIG. 2.2   The carbon dioxide cycle in nature. Zooplankton is missing in the figure between marine algae and fish. It accounts for a greater mass of marine life than the phytoplankton, and contributes largely to total respiration in the ocean. The figures for oceanic photosynthesis (and CO_2 liberation) used in this figure, were those of Riley, not the (almost ten times smaller) more recent figures of Steemann-Nielsen or Pike and Spilhaus. The CO_2 supply to the cereals feeding man and cattle is not shown.

An annual synthesis of about 5×10^{10} tons of organic carbon means liberation of about 13×10^{10} tons of oxygen into the air and fixation of about 20×10^{11} tons of carbon dioxide from the air and the oceans.[2] The amount of oxygen liberated is equivalent to about 0.05 percent of the atmospheric and oceanic store of free oxygen. Respiration and rotting of organic matter reverse this process. Together they create a more or less steady state distribution of carbon and oxygen between the free and the fixed state. Industrial combustion of fossil fuels makes a small, but not negligible addition to the natural cycle. At present, man makes annually about 3×10^9 tons of carbon dioxide by combustion. This is about one percent of the annual carbon dioxide consumption by photosynthesis (or of annual carbon dioxide liberation by respiration of plants and animals, and bacterial fermentation).

Because of photosynthesis and respiration, the elements carbon and oxygen go through closed natural cycles on earth (Fig. 2.3). Carbon passes by photosynthesis from gaseous or dissolved CO_2, into organic matter and thence by respiration back into the air or the ocean. Oxygen is consumed by the respiration of plants and animals and released again into air or water by photosynthesis. Since the total amount of oxygen in the air and in the ocean is ten times larger than that of carbon, the oxygen cycle turns around ten times slower than the carbon cycle. Every atom of available carbon on earth passes once every one (or a few) hundred years from the inorganic into the organic state. The same thing happens to every atom of oxygen present as O_2 in the air or in the water only about once every one or a few thousand years.

Actually, the situation is more complex. The carbon and oxygen cycles in the ocean revolve largely independently from the carbon and oxygen cycles on land, because the exchange of the gases CO_2 and O_2 between the air and ocean is slow.

There is, however, no doubt that all carbon in the organic matter now present on earth, and all oxygen now present in the air and in water, have passed several times through the organic cycle.

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[2] Carbon dioxide is present in the oceans mainly as dissolved bicarbonate. It is considered half "free" and half "bound," because bicarbonate ion can give off one-half molecule of carbon dioxide:

$$HCO_3^- \rightarrow \tfrac{1}{2}CO_2 + \tfrac{1}{2}CO_3^{2-}$$

The other half becomes bound in the ion CO_3^{2-}, and usually made unavailable for photosynthesis by precipitation as an insoluble carbonate.
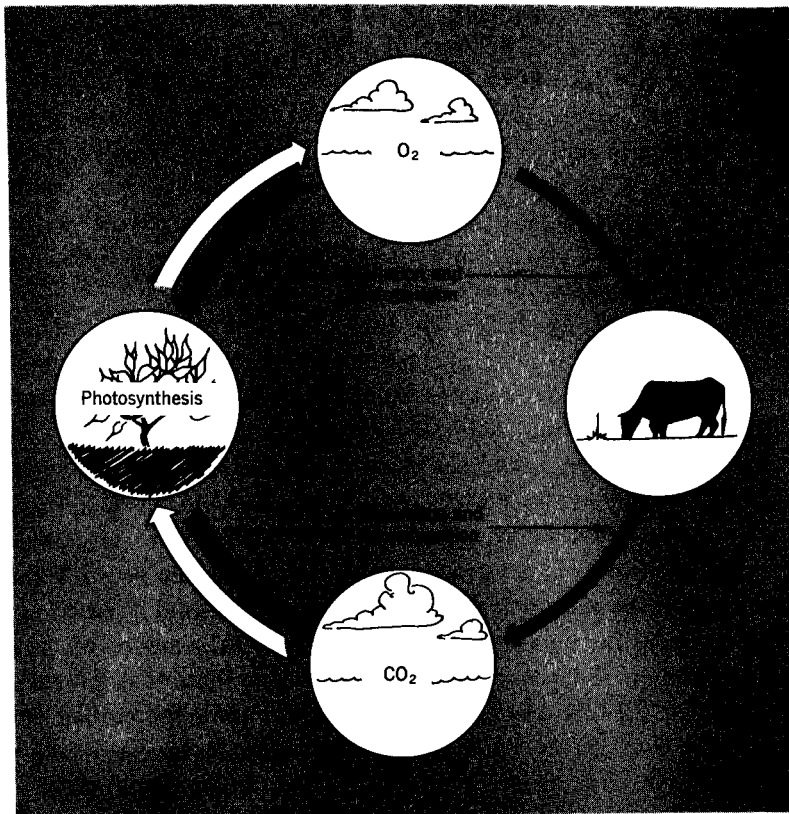
FIG. 2.3   The oxygen and carbon cycles on earth. (White arrows = photochemical reactions; black arrows = dark reactions.)

PHOTOAUTOTROPHIC, CHEMOAUTOTROPHIC, AND HETEROTROPHIC WAY OF LIFE

In certain locations on the earth's surface, there exist chemical energy sources of terrestrial origin, independent of sunlight. In regions of volcanic activity, hot water or hot gases escape from the earth. They often contain hydrogen sulfide, elementary sulfur, or hydrocarbons. Methane gas escapes from coal layers. (This is what creates the danger of mine explosions.) Free hydrogen is found in the soil, where it is formed by

the activity of soil bacteria. The ultimate origin of these chemically unstable, combustible products (that is, products that contain free chemical energy when in contact with oxygen), may be either the heat of the interior of the earth (heat of volcanoes or hot springs), or the activity of now existing organisms, or the activity of organisms that have existed on earth in the past, and whose remains have been preserved underground in the form of coal, peat, or oil. Whatever its origin, this energy could be used—and in fact, is used—to support life in the form of so-called autotrophic, that is, self-nourishing bacteria. These bacteria are of two types: one kind merely substitutes a reducing chemical compound for the water used in photosynthesis of higher plants, in a process called *bacterial photosynthesis*. These organisms, which do not require *oxygen* but do require *light*, were discovered by the Russian microbiologist *S. Vinogradsky* in 1889. *C. B. Van Niel*, in a series of articles published in 1930 and later, proposed the following generalized equation for their photosynthesis:

$$CO_2 + 2H_2A + \xrightarrow[\text{light}]{\text{bacteria}} (CH_2O) + 2A \text{ (or } A_2) + H_2O \qquad (2.2)$$
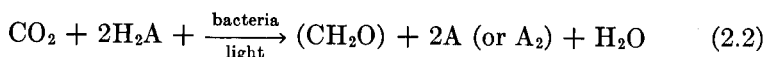
where A can be sulfur, or an organic radical. One particularly interesting case is "A equals nothing"—bacterial photosynthesis with molecular hydrogen as reductant. (Higher plant photosynthesis is a special case of Eq. 2.2 in which A is oxygen.)

The second type of autotrophic bacteria catalyze the oxidation of various compounds (usually by oxygen, but occasionally by nitrate, sulphate, or even carbonate) and utilize the energy of oxidation for the reduction of carbon dioxide to organic compounds. This process is called *chemosynthesis*. These organisms require *no light* for their growth, but they do require *oxygen* (or another oxidizing agent).

We call organisms capable of living by means of photosynthesis, *photoautotrophic* (or self-supporting with the help of light). Organisms capable of living by means of nonphotochemical energy—releasing chemical processes are called *chemoautotrophic,* whereas organisms able to live only by consuming other live or dead organisms, or organic food, are *heterotrophic*. All animals, including man, as well as the fungi, most bacteria, and all viruses, belong to this latter, fundamentally parasitic kind. They cannot synthesize their own food, but rely on autotrophic organisms to prepare it for them.

ORIGIN AND EVOLUTION OF LIFE

The present picture of the evolution of life on earth, originating with *J. Haldane* in England and *A. I. Oparin* in Russia, assumes that in the early history of the earth, when life was absent, the earth's atmosphere contained no oxygen and had reducing properties. Hydrogen, ammonia, hydrogen sulfide, and simple hydrocarbons abounded in this atmosphere. Under the influence of electric discharges (during thunderstorms) and of ultraviolet light from the sun, increasingly more complicated organic compounds, such as amino acids, peptides, and porphyrin derivatives were synthesized. The ocean became a primeval "broth" filled with a great variety of organic compounds. At a certain stage of this chemical evolution, complex molecules arose with a capacity of assimilating simpler molecules and arranging them into copies of themselves. This is still done now by one kind of molecules only—the nucleic acids. When the nucleic acid molecule of a virus is injected into a living cell, whose interior takes the place of the primeval soup, the virus picks up simpler building stones, nucleotides and amino acids. and builds up complete new viruses, thus exhausting and soon destroying the cell. Recently, such self-replication of nucleic acids was achieved also in vitro. The original living molecules must have similarly scavenged organic material in the primeval broth. Theirs was a heterotrophic way of life; it could not last forever, since the broth had to become thinner and thinner. Some kind of "mutation" must have interfered to prevent the end of all life; it converted heterotrophic into autotrophic organisms, able to build organic molecules from inorganic building stones. At first, perhaps, this energy-consuming process utilized the chemical energy of simple inorganic reactions—that is, the organisms were chemoautotrophs. Later, they found a way to utilize the energy of light, and photoautotrophs evolved.

It seems plausible that, at first, hydrogen for the reduction of CO_2 was derived from the then still abundantly available reducing gases, such as H_2S or H_2; that is, the earliest photoautotrophic organisms may have been *photosynthetic bacteria*. However, the availability of such reductants also decreased with time. Another mutation must have intervened, leading to a new kind of organism, the true plant, capable of using the practically unlimited supply of water as a source of hydrogen.

In this new era, the atmosphere began to fill up with oxygen, and a new type of heterotrophic existence became possible, based on aerobic respiration, rather than on simple ingestion of ready-made organic compounds. Animals and fungi were added to viruses in the world of heterotrophs, and plants themselves began to depend on respiration as source of biological energy.