Chapter 1

Photosynthesis: The Power Plant and the Chemical Factory of Life

Literally, photosynthesis means "synthesis with the help of light." This covers a variety of processes in organic and inorganic chemistry. However, the term is usually applied to one reaction only—the synthesis of organic matter by plants in light—a process also called "carbon assimilation." This is the basic process of life (at least as we know it on earth). It creates living matter out of inert inorganic materials, replenishes the reservoir of oxygen in the atmosphere, and stores the energy of sunlight to support the life activities of organisms. Its discovery is a thrilling chapter in the history of science.

About 1648, a Dutchman, *van Helmont,* grew a willow tree in a bucket of soil and found that the amount of soil did not diminish significantly, although a big tree was formed. He guessed that the material of the tree must have come from *water* used to wet the soil. In a book published in 1727 (called *Statical Essays, Containing Vegetable Statics, or, an Account of Some Statical Experiments on the Sap in Vegetation*), the great English minister-naturalist, *Stephan Hales,* surmised that plants drew a part of their nutrition from the *air*. Both views ran contrary to the long-accepted, Aristotelian view that plants feed on "humus" of the *soil.* Stephan Hales also suggested that *sunlight* may play a role in "ennobling the principles of vegetables."

Hales' and van Helmont's insights were remarkable. But before the advent of modern chemistry, they had to remain guesses, not provable by reliable experiment or by reference to well-established general laws.

THE AGE OF PNEUMOCHEMISTRY

Until the end of the eighteenth century, the different kinds of matter definitely known to man were *solids* or *liquids.* It was surmised that *air* also was something material, and that there existed different kinds of air, some "good" and some "bad," some able to support life, and some noxious or deadly. But not knowing how to weigh, transfer, mix, or separate the different kinds of air, chemists were baffled by reactions in which gases were formed or consumed. In fact, this was one of the weaknesses that made them alchemists rather than chemists! Metals rust. How would one explain it, not knowing that rusting is caused by the addition of oxygen from the air to the metal? Alchemists thought, not unnaturally, that in becoming rusty, and thus losing their value, metals must *lose* something, and they called this something *phlogiston.* Rusting, burning, and all other processes we now call oxidations were caused, according to them, by loss of phlogiston.

According to a law, first announced by Michael Lomonosov in Russia in 1748 and later by Antoine Lavoisier in France in 1770, the weight of the products of a reaction must be equal to that of the reactants. When Lavoisier found that rust weighs *more* than the metal from which it was formed, some adherents to the phlogiston theory, loath to abandon it, suggested that phlogiston must have negative weight! However, at about the same time, between 1770 and 1785, chemists in different countries of Europe, *Priestley* and *Cavendish* in England, *Scheele* in Germany, and *Lavoisier* in France, devised methods to catch gases, to transfer them from one container into another, and to determine their chemical and physical properties. The age of pneumochemistry (from the Greek word for breath) opened.

The air was found to consist of two main gaseous components. One was chemically reactive and was consumed in burning and respiration.

It became known as oxygen, the oxide-generating gas. The other was chemically inert, and became known as nitrogen, the niter-generating gas. It was also called azote, (from Greek word *azoē*), meaning "not sustaining life." Water was found to be a combination of oxygen with still another gas, which was called hydrogen, the water-generating gas. So-called fixed air, the asphyxiating gas produced by respiration of animals, burning wood, and heating of chalk, proved to be a combination of oxygen with carbon. It is now called carbon dioxide. Other gases, such as chlorine, carbon monoxide, and methane (swamp gas) were soon discovered. With these discoveries, the law of conservation of matter could be verified and the puzzle of phlogiston solved. Phlogiston was simply "minus oxygen." Chemistry began its transformation from a qualitative into a quantitative science.

IMPROVEMENT OF AIR BY PLANTS AND THE ROLE OF LIGHT

Joseph Priestley (1733–1804) was a nonconformist English minister. In 1791, his house in Birmingham was sacked by a mob because of his alleged sympathies with the French Revolution; in 1794, he emigrated to Pennsylvania. Early in the era of pneumochemistry, Priestley was engaged in pioneering experiments with gases, later described in two volumes called *Experiments and Observations on Different Kinds of Air*. The first volume, published in 1776, contains the discovery of the *improvement of air by plants:*

I have been so happy as by accident to hit upon a method of restoring air which has been injured by the burning of candles and to have discovered at least one of the restoratives which Nature employs for this purpose. It is vegetable as well as to animal life, both plants and animals had affected it vegetation. One might have imagined that since common air is necessary to in the same manner; and I own that I had that expectation when I first put a sprig of mint into a glass jar standing inverted in a vessel of water; but when it had continued growing there for some months, I found that the air would neither extinguish a candle, nor was it at all inconvenient to a mouse which I put into it.

Finding that candles would burn very well in air in which plants had grown a long time . . . I thought it was possible that plants might also restore the air which had been injured by the burning of candles. Accordingly, on the 17th of August, 1771, I put a sprig of mint into a quantity of air in which a wax candle had burned out and found that on the 27th of the same month another candle burnt perfectly well in it.

Two years later, in 1773, a court physician to the Austrian Empress Maria Theresa, a Dutchman, *Jan Ingenhousz* (1730–1799) visited London. He heard Sir John Pringle, then President of the Royal Society, describe in a lecture Priestley's experiments on the improvement of air by plants. Ingenhousz was so impressed that on the "earliest occasion" (which offered itself only six years later) he rented a villa near London, and spent there three summer months performing "over 500" experiments on the effects of plants on air. By October of the same year, he had not only completed a most momentous series of observations, but had also published a book, *Experiments Upon Vegetables, Discovering Their Great Power of Purifying the Common Air in Sunshine and Injuring It in the Shade and at Night*. Ingenhousz believed that he had made such important discoveries that immediate publication was needed to prevent somebody else from depriving him of priority. It was a hectic period in science, in which discoveries, made possible by experimentation with gases, crowded each other. The following is a quotation from Ingenhousz's summary of his findings on the action of sunlight on plants:

I observed that plants not only have a faculty to correct bad air in six or ten days, by growing in it, as the experiments of Dr. Priestley indicate, but that they perform this important office in a complete manner in a few hours; that this wonderful operation is by no means owing to the *vegetation* of the plant, but to the *influence of the light* of the sun upon the plant. I found that plants have, moreover, the most surprising faculty of elaborating the air which they contain, and undoubtedly absorb continually from the common atmosphere, into real and fine dephlogisticated air; that they pour down continually a shower of this depurated air, which . . . contributes to render the atmosphere more fit for animal life; that this operation . . . begins only after the sun has for some time made his appearance above the horizon . . . ; that this operation of the plants is more or less brisk in proportion to the clearness of the day and the exposition of the plants; that plants shaded by high buildings, or growing under a dark shade of other plants, do not perform this office, but on the contrary, throw out an air hurtful to animals; . . . that this operation of plants diminishes towards the close of the day, and ceases entirely at sunset; that this office is not performed by the whole plant, but only by the leaves and the green stalks; that even the most poisonous plants perform this office in common with the mildest and most salutary; that the most part of leaves pour out the greatest quantity of the dephlogisticated air from their under surface; . . . that all plants contaminate the surrounding air by night; . . . and by day; that roots and fruits have the same deleterious quality; . . . that that all flowers render the surrounding air highly noxious, equally by night the sun by itself has no power to mend the air without the concurrence of plants.

Priestley had been the first to observe the "improvement of air" by plants, but he had attributed this improvement to the slow process of "vegetation" of plants; while Ingenhousz noticed that it was due to a rapid chemical reaction that sunlight caused to occur in green leaves and stalks. In light, as well as in darkness, plants respire and consume oxygen similarly to animals. But when illumination becomes sufficiently strong, *liberation* of oxygen exceeds its uptake. Ingenhousz exaggerated when he described the gases produced by plant respiration as highly noxious; but at that time, no clear distinction was made between truly *poisonous* gases, such as carbon monoxide, and *inert* gases, which do not support life, like nitrogen or carbon dioxide.

THE PARTICIPATION OF CARBON DIOXIDE AND WATER

Ingenhousz's concern with priority proved to be justified. A Swiss pastor, *Jean Senebier* (1742–1809) published, in 1782, in Geneva, a rambling three-volume treatise, *Mémoires physicochimiques sur l'influence de la lumière solaire pour modifier les êtres de trois règnes, surtout ceux du règne végétal.* In this treatise, he described observations similar to those of Ingenhousz. Senebier, however, noted an important additional fact: the air-restoring activity of plants depends on the presence of "fixed air" (that is, carbon dioxide). He wrote:

I do not agree that common air of the atmosphere can be changed, in the leaves of vegetables, depositing there its phlogistic component, and leaving them after this cleansing as dephlogisticated air.

and the Renovation of Soils," published in 1796, translated the description of the whole phenomenon from the phlogiston language into the language of the new chemistry, founded by Lavoisier:

$$CO_2 + H_2O \xrightarrow[\text{green plant}]{\text{light}} O_2 + \text{organic matter} \tag{1.2}$$

Senebier's "fixed air" became carbon dioxide, CO_2, Priestley's "vital air" became oxygen, O_2, and "plant nourriture" became organic matter, that is, chemical compounds containing carbon, hydrogen, and oxygen, which form most of a living body.

The improvement of air by plants was thus recognized as "photosynthesis," or synthesis of organic matter in light. In addition to the change in terminology, the 1796 pamphlet by Ingenhousz was the first to describe clearly the role of photosynthesis in the nutrition of plants. In 1789, in the second volume of his "Experiments," Ingenhousz had ridiculed Senebier's suggestion that fixed air is taken up in photosynthesis and contributes, as suggested in Eq. 1.1, to the nutrition of plants. In 1796, he reversed himself and recognized this uptake as the *only* source of carbon contained in the organic matter of plants.

Photosynthesis is a remarkable example of great discovery to which several men, of different national origin (English, French, Swiss, and Dutch), and different background (two ministers, a physician and a professional chemist) have contributed. A bitter controversy over priority soon developed, particularly between the ambitious, worldly court physician, Jan Ingenhousz, a master of biting irony, and the plodding provincial pastor, Jean Senebier. This controversy was long kept alive by their biographers. Priestley, perhaps the greatest experimentalist of the three, also found his protagonists, who resented any credit given to either Ingenhousz or Senebier. In truth, each one of these men has made an invaluable contribution to the discovery, and there is fame enough to share among them.

ENERGY STORAGE IN PHOTOSYNTHESIS

One more name must be added to complete the history of the discovery of photosynthesis: that of a German doctor, *Julius Robert Mayer*

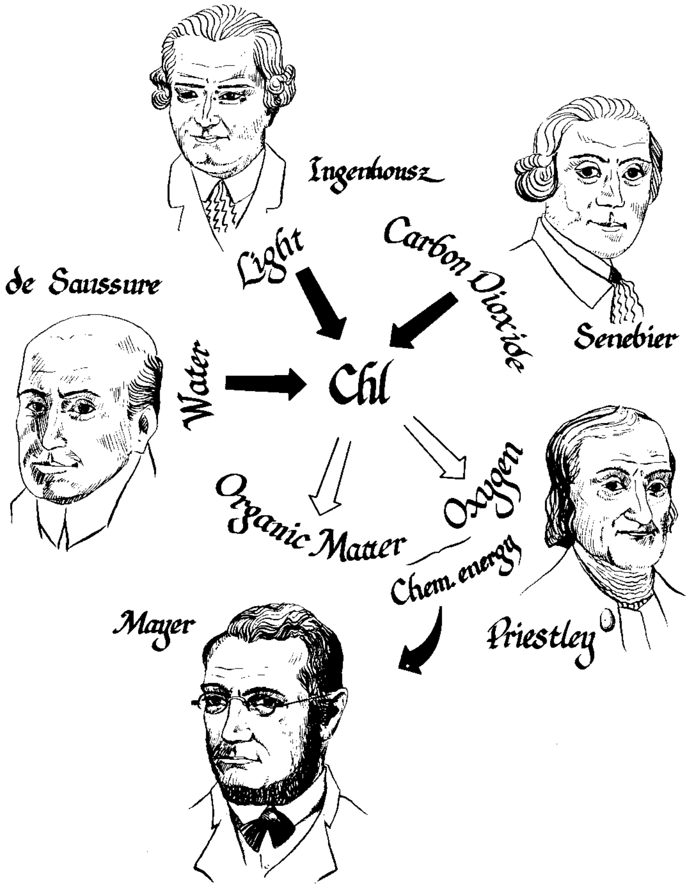

FIG. 1.1 The discoverers of photosynthesis.

(1814–1878), famous for his part in the formulation of the law of conservation of energy in 1842—sixty-six years after the discovery of photosynthesis (1776).

In carrying out photosynthesis, plants *store the energy of sunlight in the form of chemical energy.* Mayer saw in this conversion a particularly important illustration of the law of conservation of energy. In a pamphlet entitled, *The Organic Motion in its Relation to Metabolism,* published in 1845, he wrote:

Nature has put itself the problem how to catch in flight light streaming to the earth and to store the most elusive of all powers in rigid form. To achieve this aim, it has covered the crust of earth with organisms which in their life processes absorb the light of the sun and use this power to produce a continuously accumulating chemical difference.

These organisms are the plants; the plant kingdom forms a reservoir in which the fleeting sun rays are fixed and skillfully stored for future use; an economic provision to which the physical existence of mankind is inexorably bound.

The plants take in one form of power, light; and produce another power: chemical difference.

(Mayer used the term "power" where we would say energy, and "chemical difference" where we would say chemical energy.)

Before Mayer, only the chemical function of plants as *creators of organic matter* on earth, could be comprehended. After him, their physical function, that of *energy providers* for life, also became clear. The equation of photosynthesis could now be written as:

$$CO_2 + H_2O + \text{light} \xrightarrow{\text{green plant}} O_2 + \text{organic matter} + \text{chemical energy} \quad (1.3)$$

to represent not only the material balance, but also the energy balance of photosynthesis.

THE PRODUCTS OF PHOTOSYNTHESIS

Equations 1.1 to 1.3 are qualitative. They do not state the relative numbers of CO_2 molecules consumed and of O_2 molecules liberated by photosynthesis, and the composition of the organic matter produced is not specified. According to Avogadro's law (equal volumes of gases under the same pressure and temperature contain equal numbers of molecules) this question could be answered by measuring the ratio of the volume of CO_2 taken up ($-\Delta CO_2$) and the volume of O_2 liberated ($+\Delta O_2$). The first precise determinations of this ratio were carried out in 1864 by the French plant physiologist *T. B. Boussingault.* He worked with many different land plants, and found that the "photosynthetic ratios," $\Delta O_2/-\Delta CO_2$, were very close to unity for all of them.

As shown by Eq. 1.4, a photosynthetic quotient of 1 indicates that the organic matter produced by photosynthesis has the general composition of a carbohydrate, $C_n(H_2O)_m$:

$$n(CO_2) + mH_2O + \text{light} \xrightarrow[\text{plant}]{\text{green}} C_n(H_2O)_m + nO_2 + \text{chemical energy} \quad (1.4)$$

Equations similar to 1.4 can be written for the synthesis of organic products other than carbohydrates. However, those would require the volumes of oxygen evolved and of carbon dioxide consumed to be unequal. For example, fats are more strongly reduced (hydrogenated) than carbohydrates; consequently, in their formation the volume of oxygen released would be larger than that of carbon dioxide taken up.

For simple carbohydrates, such as glucose or fructose, $C_6H_{12}O_6$, $m = n$, so that Eq. 1.4 can be simplified to

$$CO_2 + H_2O + \text{light} \xrightarrow[\text{plant}]{\text{green}} (CH_2O) + O_2 + \text{chemical energy} \quad (1.5)$$

where (CH_2O) ($= \frac{1}{6}$ of $C_6H_{12}O_6$) signifies a unit of a carbohydrate molecule. That photosynthesis in green land plants leads to the synthesis of the carbohydrates, is illustrated by a simple experiment devised in 1864 by a leading German plant physiologist of the last century, *Julius Sachs*. He exposed one-half of a leaf attached to a plant to light and left the other in darkness. After some time, he placed the leaf in iodine vapor. The darkened half showed no change, but the illuminated half became dark-violet due to the formation of a starch-iodine complex. The American plant biochemist, *J. H. C. Smith,* demonstrated, in 1943, that in sunflower leaves, after one or two hours of photosynthesis, practically all the CO_2 taken up is found in newly synthesized carbohydrates, thus supporting Eq. 1.5 as representation of the overall process of photosynthesis.

In Chapter 17 we will see that compounds other than carbohydrates are also found among early products of photosynthesis. This must cause deviations of photosynthetic quotient from unity—which have been, in fact, observed. They are particularly strong in diatoms, which are known to store oil drops, as other plants store starch grains. It remains an open question whether the formation of fats (and of amino acids) occurs by side reactions competing with the completion of the main process (Eq. 1.5) or by rapid follow-up after its completion.