Relating Surface Energy Budgets to the Biochemistry of Photosynthesis: A Review for Non-Biologists

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Abstract

Transpiration from plant canopies is an important determinant of surface energy budgets at the vegetated land surface. A recent parameterization of plant transpiration and stomatal conductance (Sellers *et al*., 1992*a*) is based on enzyme kinetics in plant chloroplasts. This paper presents background concepts in plant physiology and biochemistry needed to understand and evaluate the parameterization. Photosynthesis is the process by which plants store solar energy in chemical bonds, thereby providing the source of all energy in the biosphere. Atmospheric carbon dioxide (CO_2) is reduced to organic compounds in specialized plant organelles called chloroplasts. The process involves an energy generation mechanism (the "light reactions") and a carbon fixation mechanism (the "dark reactions"). In the light-driven part, chlorophyll pigment is excited by visible radiation in two distinct wavelength intervals, producing an oxidation-reduction couple and resulting in a strong gradient of pH within leaf cells. The pH gradient is used to produce adenosine triphosphate (ATP), and a strong reductant known as $NADPH_2$. These products are used to drive the "dark phase" of photosynthesis by coupling strongly exergonic reactions with slightly endergonic ones, resulting in the reduction of atmospherically derived CO_2 and the formation of six carbon sugars such as fructose or glucose. The carbon fixation step is regulated by an enzyme known as "Rubisco," and by the regeneration of key reagents in a series of reactions collectively known as the Calvin Cycle. The net carbon assimilation rate is parameterized in terms of three possible rate limits: Rubisco activity, reagent regeneration, and end-product inhibition. Net assimilation of carbon is then used to calculate the stomatal conductance, which is related to evapotranspiration from the plant canopy using an integration scheme based on nutrient and light economy.

1. Introduction

Radiant energy absorbed by land surfaces is partitioned into latent and sensible heat fluxes (*e.g.* Rosenberg *et al.*, 1983). The relative fraction of latent and sensible heating in the planetary boundary layer (PBL) can have a huge effect on surface temperature, humidity, and the evolution of PBL structure, and inhomogeneities in surface types can lead to large horizontal gradients in these variables and induce significant mesoscale circulations (*e.g.* Pielke and Avissar, 1990). The processes which control this partitioning of the surface energy budget operate essentially at the scale of plants or small groups of plants and are generally unresolvable at the scale of atmospheric models. Parameterizations have therefore been developed to represent these predominantly biological processes in atmospheric models (see the recent reviews by Dickinson *et al.*, 1991 and Lee *et al.*, 1993).

True evaporation from the land surface is limited by the availability of water substance, because diffusion of water vapor in soil pores is very slow, and radiative heating does not penetrate very deeply into the ground. Most water vapor flux from vegetated surfaces is through the plants themselves, whose roots are able to reach deeper water in the soil than can evaporate directly. Moist plant tissues lose water to the atmosphere through microscopic openings in their leaves called *stomata* (see Fig. 10 in section 3.1). Plants have a physiological mechanism which opens and closes the stomata to regulate the rate of water loss to the surrounding air (*e.g.*, Nobel, 1974).

The regulatory action of the stomata has been modeled in analogy to electrical circuits as a *resistance* to the flux of water vapor at least since the 1940s (Penman, 1948). In such models, the flux of vapor is calculated as the ratio of a concentration gradient and a resistance,

$$\mathrm{E} = \frac{e_{\mathrm{a}} - e_{\mathrm{sat}}}{r_{\mathrm{s}}} \qquad \textbf{(1)}$$

where e_a is the vapor pressure outside the leaf, e_{sat} is the saturation vapor pressure at the temperature of the leaf, and r_s is the stomatal resistance. This is also frequently represented as a *conductance*, $g_s = 1/r_s$. In any case, expression (1) is simply a *definition* of the stomatal resistance, rather than a mechanistic representation.

Until very recently, parameterizations of stomatal conductance used in atmospheric

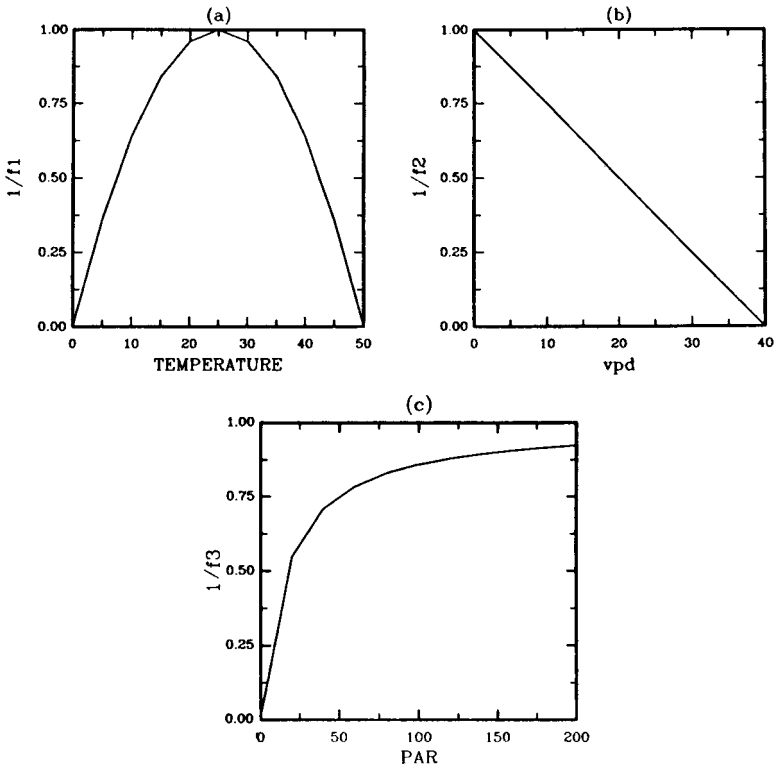

FIGURE 1: Environmental dependencies of the inverse of stomatal resistance (*i.e.* conductance) in BATS model on: (a) Temperature; (b) vapor pressure deficit; (c) photosynthetically active radiation. Scanned without permission from Dickinson *et al.* (1991).

models represented it in terms of various environmental parameters such as temperature, incident radiation, and the vapor pressure deficit of the ambient air. In the Biosphere-Atmosphere Transfer Scheme (BATS, Dickinson *et al.*, 1986) for example, stomatal resistance is represented as

$$r_s = r_{smin} f_1(T) f_2(D) f_3(\mathrm{PAR}) \quad \textbf{(2)}$$

where r_{smin} is a minimum stomatal resistance, T is leaf temperature, D is the difference in water vapor pressure across the stomatal opening, and PAR is the intensity of photosynthetically-active radiation (Dickinson *et al.*, 1991; see Fig. 1). The scaling factors f_1, f_2, and f_3, are empirically-derived parameters. These are typically determined by measuring leaf gas exchange rates in a carefully controlled apparatus and varying one parameter at a time.

In reality, of course, environmental factors affecting stomatal conductance may vary simultaneously, complicating the response considerably as compared to the simple curves shown in Fig. 1. Also, because of the sensitive dependence of saturation vapor pressure on temperature, there is considerable interaction between the T and D terms in equation (2). Collatz *et al.* (1991) have reported that the response curve of g_s as a function of vapor pressure deficit (f_2 in the notation of Dickinson) varies with temperature; they claim that stomatal response to relative humidity is a more linear relationship. Such nonlinear responses to environmental conditions have spawned recent research which seeks to parameterize the physiological mechanism responsible for regulating transpiration in a more biologically realistic way.

Water loss by transpiration is, for plants, an unfortunate consequence of the necessity of opening their tissues to allow CO_2 to diffuse in (Fig. 2). The water vapor pressure gradient across the stomatal opening is generally much greater than the gradient of CO_2 partial pressure, so that several hundred molecules of water are lost for

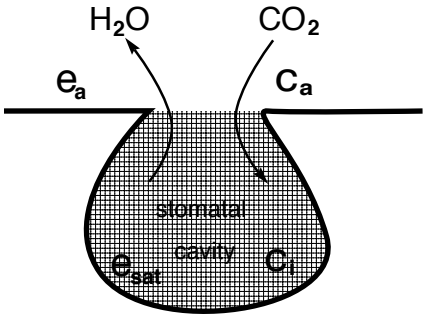

FIGURE 2: Gas exchange through a stoma.

each molecule of CO_2 that enters the leaf (Bazzaz and Fajer, 1992). Collatz *et al.* (1991) have written

> [S]tomata serve the conflicting roles of permitting CO_2 to diffuse into the leaf to support photosynthesis and restricting the diffusion of water vapor out of the leaf. To succeed fully in one role must necessarily lead to total failure in the other role … the regulatory system must strike an appropriate compromise between permitting photosynthesis and restricting water loss.

The regulation of stomatal conductance by plants can be seen as an optimization problem: they seek to maximize their ability to import atmospheric CO_2 while at the same time minimizing water losses. This concept is the basis for a new parameterization of stomatal function (Ball, 1987; Ball, 1988; Collatz *et al.*, 1991; Sellers *et al*., 1992*a*). Rather than the scaling factors used in equation (1), Sellers *et al.* (1992*a*) calculate the stomatal conductance from

$$g_s = m \frac{A_n h_s}{c_s} p + b \qquad (3)$$

where A_n is the net assimilation rate of CO_2 by the plant (μmol m^{-2} s^{-1}), h_s is the relative humidity at the leaf surface (outside the stomatal aperture), c_s is the partial pressure of CO_2 concentration at the leaf surface (Pa), and p is the atmospheric pressure (Pa). The coefficients m and b are empirically-derived slope and intercept of the (assumed linear) relationship between $\frac{A_n h_s}{c_s} p$ and g_s. The intercept b represents the resistance when the stomata are completely closed (also called the *cuticle resistance*). In these units, g_s is in μmol m^{-2} s^{-1}, as is b. The slope m is nondimensional.

Although still empirical, equation (3) is more mechanistically based than equation (2). Recognizing the optimization strategy of the physiological regulation of g_s from the plants' point of view, the equation is easy to interpret. Conductance increases as the assimilation

rate of CO_2 increases, and also as the relative humidity outside the leaves increases. Conductance decreases for increasing partial pressure of CO_2 outside the stomata because since the rate of diffusion of the gas into the leaf is directly proportional to its concentration. Other environmental conditions such as temperature and light intensity are implicitly included in the assimilation rate.

The difficult part of the new parameterization is of course the calculation of the assimilation rate A_n. This is done following a biochemical model first developed by Farquhar *et al.* (1980). Assimilation (essentially the rate of CO_2 fixation by photosynthesis) is seen as limited by the kinetics of an enzyme called ***r**ib**u**lose **bis**phosphate **c**arboxylase **o**xygenase (Rubisco*) and by *electron transport*, which is a series of reactions that take place when green plant cells are illuminated with visible radiation. Farquhar *et al.* (1980) used a simple minimum of the three limits to calculate the assimilation rate

$$A_n = \min(A_R, A_L, A_E) - R_d \qquad \textbf{(4)}$$

where A_R is the Rubisco-limited rate of photosynthesis, A_L is the light-limited rate, A_E is the end product-limited rate, and R_d is the rate of carbon loss due to "dark" respiration. Sellers *et al.* (1992*a*) use a smoothed function to avoid abrupt transitions from one limitation to another, but the essence of their method is also captured by equation (4).

Sellers *et al.* (1992*a*) present simple equations for the calculation of each term in (4). Unfortunately, it is not at all easy to understand how these equations are derived without a solid background in biochemistry. Most atmospheric scientists lack such a background, and so will find it difficult if not impossible to evaluate this new parameterization. In this paper, I will attempt to impart such a background to the reader. I assume a rudimentary knowledge of college-level chemistry, and will present the relevant concepts of biochemistry, plant

physiology, and biophysics in sections 2 and 3. In section 4, I will return to equation (4), and will explain its various terms more fully.

2. Basic Biochemical Concepts

In this section I will review certain basic concepts of biochemistry to clarify the more focused discussion of photosynthesis which follows. Some of the terminology discussed in this section will be used in later sections. In section 2.1, I will define enzymes and discuss their importance in biochemical reactions. Section 2.2 introduces the role of adenosine triphosphate (ATP), which is the "currency" for energy exchange in biological systems. Finally, section 2.3 discusses oxidation and reduction reactions in terms of their role in biological energetics. The review in this section is derived from a basic biochemistry textbook (Stryer, 1981) except where noted otherwise.

2.1 Enzymes

Enzymes are specialized proteins which act as catalysts for biochemical reactions. All proteins are composed of amino acids, linked together in long chains. Amino acids are molecules with a structure like that shown in Fig. 3. The *R* in the figure refers to any functional group of atoms bound to the central carbon atom. In the simplest amino acid, called *Glycine*, this *R* group is just a hydrogen atom. There are twenty different amino acids, with "side chains" or *R* groups of varying complexity, that are linked together in chains of almost unlimited size and shape, to form all of the proteins in the biosphere. Many proteins are formed from hundreds of these amino acid building blocks, combined in complex three-dimensional structures that coil and twist back on themselves and having molecular weights in the hundreds of thousands. Some proteins serve as catalysts in biochemical re-

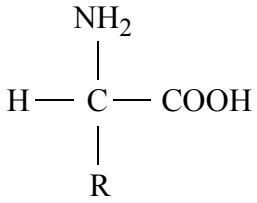

FIGURE 3: Structure of a generic amino acid

actions. These specialized compounds generally only catalyze a single reaction, and are called enzymes. Note that all proteins contain nitrogen, which is often a limiting nutrient in plants. This fact has important implications for photosynthesis, as will be discussed in section 4.

2.1.1 Enzyme Catalysis

Catalysts are compounds which reduce the activation energy of a reaction (Fig. 4). The

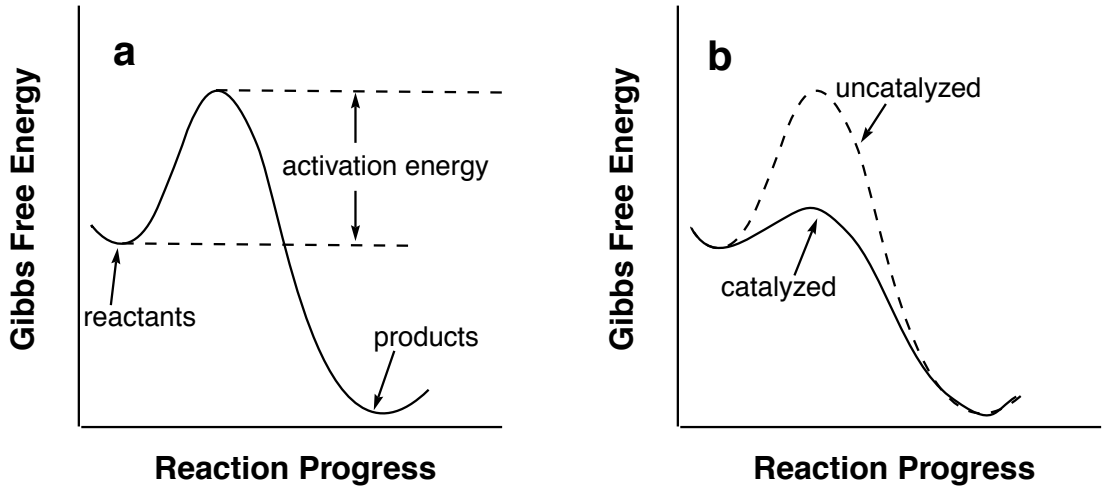

FIGURE 4: Effect of a catalyst on a chemical reaction. **a**) The overall reaction results in a reduction of the Gibbs free energy, but some energy must be supplied to start the reaction. **b**) This activation energy is reduced by introducing a catalyst, although the overall change in the free energy of the system is the same in both cases. Modified from Stryer (1981, p107).

tendency of a reaction $A + B \rightleftharpoons C + D$ to proceed in the forward direction is given by the difference in the Gibbs free energy between the products and the reactants. The *rate* at which the reaction proceeds is limited by the energy barrier in the formation of an intermediate complex (the "activation energy," Fig. 4a). The activation energy is essentially a measure of threshold energy of molecular collisions above which the reaction occurs. The presence of a catalyst reduces the activation energy, but since the overall change in Gibbs free energy between reactants and products is the same for both the catalyzed and uncata-

lyzed reactions (Fig. 4b), the equilibrium concentrations of reactants and products are the same in both cases.

An example of a common reaction which is catalyzed by an enzyme is the hydration of CO_2. The solubility of CO_2 in water is determined by the temperature, pressure, pH, and the presence of other solutes. The *rate* of hydration of the gas is limited by kinetic effects, however. This rate is more than ten million times faster in the presence of an enzyme called carbonic anhydrase than without the catalyst (Stryer, 1981, p. 103). When catalyzed by the enzyme, the gaseous and dissolved phases reach equilibrium almost instantly, which allows the efficient transfer of the gas across biological interfaces in our lungs and in plants.

The catalytic properties of enzymes are extremely specific. That is, their molecular

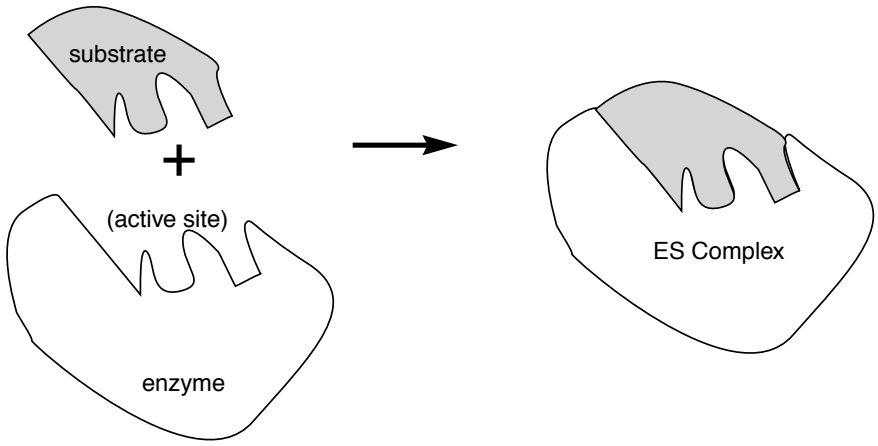

FIGURE 5: "Lock-and-key" model of enzyme-substrate interaction. Adapted from Stryer (1981, p. 110)

structure is such that the catalytic effect is restricted to a certain set of reagents. In enzyme kinetics, the molecule to which the enzyme bonds is referred to as the *substrate*. The enzyme and substrate molecules combine to form an *enzyme-substrate complex*. The relevant interactions between the two molecules takes place at an *active site* where the geometries of the chemical bonds of the two species "fit" each other like pieces of a puzzle (Fig. 5).

2.1.2 Michaelis-Menten Kinetics

A simple model of enzyme kinetics was proposed in 1913 by Michaelis and Menten (Stryer, 1981, p. 110-114). Their model describes the properties of many enzyme systems remarkably well. Consider an enzyme-catalyzed reaction of the form

$$\mathrm{E} + \mathrm{S} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_3} \mathrm{E} + \mathrm{P} \tag{5}$$

where E represents the enzyme, S the substrate (or reactant) and P the product, and k_1, k_2, and k_3 are rate constants for the formation and dissociation of the enzyme-substrate complex and the formation of the products, respectively. The rate of formation of products is given by

$$V = k_3[\mathrm{ES}] \, . \tag{6}$$

Once formed, the ES complex can either go on to form the product or revert back to E + S. Therefore the concentration of ES evolves according to

$$\frac{\mathrm{d}}{\mathrm{dt}}[\mathrm{ES}] = k_1[\mathrm{E}][\mathrm{S}] - (k_2 + k_3)[\mathrm{ES}] . \tag{7}$$

At steady state, the concentration of the ES complex is assumed to be constant, so from (7), $k_1[\mathrm{E}][\mathrm{S}] = (k_2 + k_3)[\mathrm{ES}]$, or

$$[\mathrm{ES}] = \frac{[\mathrm{E}][\mathrm{S}]}{(k_2 + k_3)/k_1} = \frac{[\mathrm{E}][\mathrm{S}]}{K_\mathrm{M}} \tag{8}$$

where $K_\mathrm{M} \equiv (k_2 + k_3)/k_1$ is called the *Michaelis constant*.

The concentration of uncombined enzyme, [E], is just the total concentration of the enzyme $[E_T]$, minus the concentration of the ES complex. Making this substitution into (8),

$$[ES] = ([E_T] - [ES])[S]/K_M . \quad (9)$$

Solving (9) for [ES],

$$[ES] = [E_T]\frac{[S]}{[S] + K_M}. \quad (10)$$

Substituting equation (10) into (6), the rate of formation of products is given by

$$V = k_3[E_T]\frac{[S]}{[S] + K_M}. \quad (11)$$

In equation (11), the reaction rate V reaches a maximum when the system is saturated with S, *i.e.* when $[S] \gg K_M$. In that case, all the active sites on the enzyme molecules are occupied by molecules of substrate and the reaction rate is limited only by the rate of "turnover" of the enzyme. This maximum reaction rate is given by $V_{max} = k_3[E_T]$. Using this definition, the overall reaction rate can be written more simply as

$$V = V_{max}\frac{[S]}{[S] + K_M}, \quad (12)$$

which is known as the *Michaelis-Menten equation*.

A reaction which proceeds according to equation (12) responds to increasing concentration of the reactants as shown in Fig. 6. At low concentrations, when $[S] \ll K_M$, $V \approx (V_{max}/K_M)[S]$. In other words, the rate is approximately proportional to the substrate concentration. At very high substrate concentrations when $[S] \gg K_M$, and the active sites

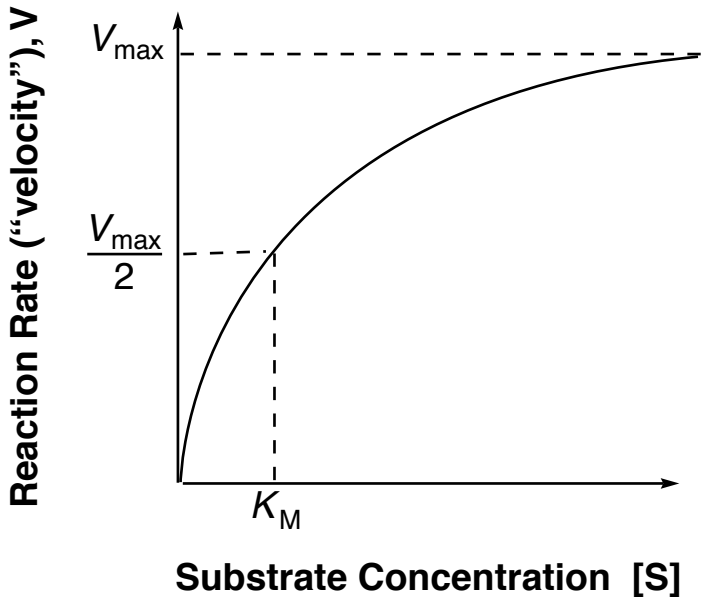

FIGURE 6: Michaelis-Menten model of enzyme kinetics. Adapted from Stryer (1981, p. 111).

are saturated, $V \approx V_{max}$ and the reaction proceeds at its (constant) enzyme-limited rate. When the substrate concentration is equal to K_M, the reaction rate is exactly half of V_{max}. The parameter V_{max} is proportional to the total concentration $[E_T]$ of the enzyme.

The above analysis holds only for "standard" environmental conditions, *i.e.* standard temperature, pressure, ionic strength, etc. In biological systems, environmental variables are generally constant over the time periods relevant to enzyme kinetics. Temperature effects generally introduce the most important environmental correction which must be applied to the Michaelis-Menten model.

2.2 Energetics and ATP

Many biochemical reactions are "driven uphill" away from chemical equilibrium. Such reactions require the expenditure of stored energy; the maintenance of disequilibrium conditions is one of the most fundamental properties of life itself. The most basic of these re-

actions is the formation of reduced organic compounds such as sugars and starches from inorganic CO_2 in photosynthesis. These reactions do not proceed spontaneously because they involve an increase in the Gibbs free energy of the system; that is, they are *endergonic*. Recall that enzyme catalysis can only increase the rate at which reactions achieve equilibrium; they can never alter the final equilibrium state. What then, is the source of the energy expended in biological systems to drive endergonic reactions?

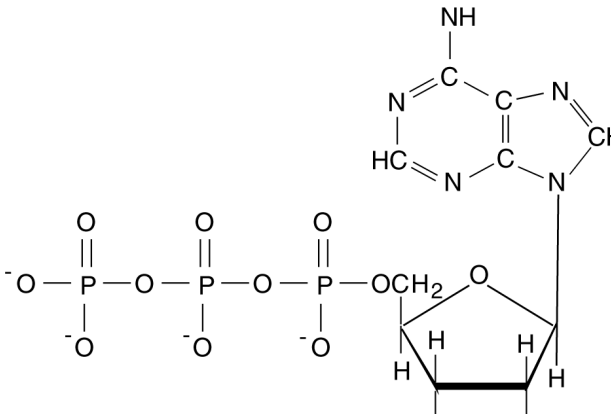

Figure 7: Molecular structure of ATP

Reactions which raise the Gibbs free energy of the reagents can be driven forward when they are coupled to reactions which have the opposite effect. The primary mechanism by which endergonic reactions are driven in biological systems is by coupling them to the breakage of high-energy phosphate bonds in a special molecule called *adenosine triphosphate* (ATP, Fig. 7). When one of the phosphate groups in the ATP molecule is stripped off in a hydrolysis reaction, 7.3 kcal of energy is released per mole of ATP (1 kcal = 4186 Joules). The resulting product is *adenosine diphosphate* (ADP). When this reaction is coupled to a mildly endergonic reaction, the resulting system becomes exergonic (the system is able to reduce its free energy). Coupling the ATP hydrolysis to another reaction increases the equilibrium constant (the ratio of products to reactants) by a factor of 10^8!

Exergonic reactions such as the consumption of fuel molecules like sugars are used to restore the high energy phosphate group and transform ADP back to ATP. The reaction

$$ADP + HPO_4^{2-} + H^+ \rightleftharpoons ATP + H_2O \qquad (13)$$

is called *phosphorylation* when it is driven (endergonically) in the forward direction, and ATP hydrolysis when it is allowed to spontaneously proceed in the backward direction by the action of an enzyme catalyst. The interconversion of ATP and ADP by consuming fuel and to perform biological functions is called *metabolism*. The particular suitability of the phosphorus atom for this crucial role in bioenergetics is based on properties of its electron orbitals and its limited solubility (Westheimer, 1987).

Although the hydrolysis of ATP to ADP is strongly favored thermodynamically, the reaction is extremely slow except when it is catalyzed by a special enzyme called *myokinase*. This means that both ATP and ADP are kinetically stable enough to be stored and transported by living systems. The production of the catalytic enzyme is a means of regulating the flow of energy, and can be used to drive thermodynamically unfavorable reactions.

2.3 Oxidation and Reduction

Oxidation refers to a chemical reaction in which one chemical species "donates" electrons to another, acquiring a positive charge or a higher "oxidation state." Reduction is just the opposite process. In order that the system maintain electrical neutrality, these reactions occur in pairs or "redox couples." A generalized redox pair can be written as

$$\begin{aligned} D &\rightleftharpoons D^{+} + e^{-} \\ A^{+} + e^{-} &\longrightarrow A \end{aligned} \qquad \textbf{(14)}$$

where D plays the role of an electron donor (a reduced compound which becomes oxidized) and A plays the role of an electron acceptor (an oxidized compound which becomes reduced). A simple apparatus can be constructed (Chang, 1981) by separating the oxidation and reduction reactions in different containers ("half cells") connected by a wire through

which electrons flow from the donor to the acceptor and a "salt bridge" to allow return flow of anions for electroneutrality. This is the basis for chemical batteries such as car batteries, and the voltage which can be sustained across such a circuit is called the "redox potential."

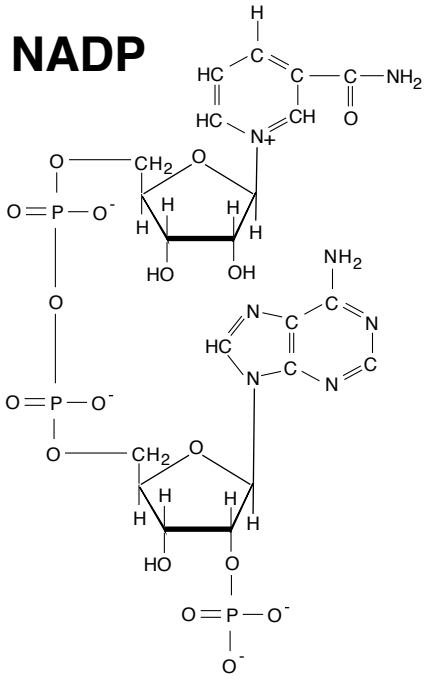

FIGURE 8: Molecular structure of the oxidized form of NADP. Adapted from Curtis (1979).

The flow of electrons up a gradient in electrical potential results in the release of free energy, and is therefore a spontaneous process. This means that redox couples can also serve as energy storage and exchange compounds in biological systems. One compound that plays this role in photosynthesis is called *nicotinamide adenine dinucleotide phosphate* (NADP, Fig. 8). This molecule is kinetically stable in both the oxidized form as shown in the figure, and in the reduced form with two hydrogen atoms attached, in which case it is referred to as $NADPH_2$. Just as ATP can be used to store and transport energy against thermodynamic gradients, $NADPH_2$ can be used to store and transport *reducing power* from a reducing environment to an oxidizing one. This process is again made possible by a catalytic enzyme without which the oxidation-reduction reactions are extremely slow, allowing the molecule to exist in thermodynamically unfavorable conditions. This property is crucial to the biochemistry of photosynthesis, as will be discussed in the next section.

3. Photosynthesis

The overall process of photosynthesis can be divided into three parts: photochemistry, electrochemistry, and biochemistry (Nobel, 1974). In the photochemical step, eight photons are absorbed in two distinct wavelength bands, giving rise to pigment molecules with two

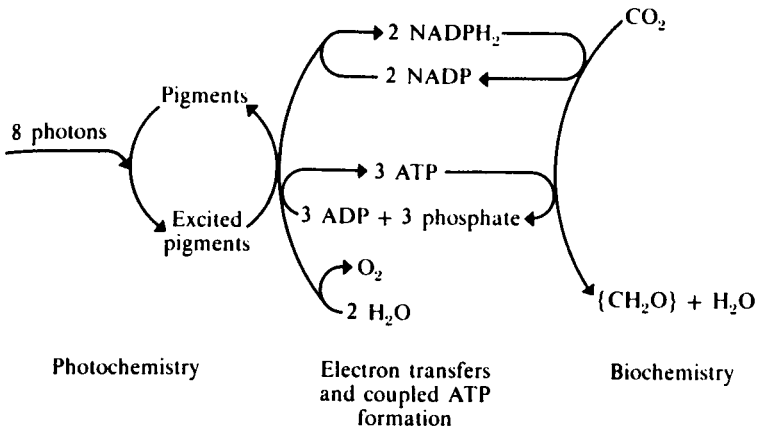

FIGURE 9: Schematic representation of the three stages of photosynthesis. Scanned without permission from Nobel (1974).

types of excited electrons in molecular orbitals. These excited electrons are then passed on in a series of redox couples leading to the splitting (oxidation) of two water molecules and the reduction of two molecules of NADP to $NADPH_2$. These "electron transport" reactions concurrently lead to the phosphorylation of three molecules of ADP into ATP. Finally, in the biochemical step, the energy and reducing power produced in the first two stages is used to reduce a molecule of CO_2 into a carbohydrate like glucose, and to regenerate the necessary reagents so that the process is self-sustaining.

A brief review of the physiology of leaves and plant cells is presented in section 3.1, followed by consideration of the biochemical and biophysical details of energy capture and carbon fixation in sections 3.2 and 3.3. The material in this section follows the discussion of Nobel (1974, pp. 214-259) and of Stryer (1981, pp. 430-453), except as indicated.

3.1 Physiology

Leaves are the primary photosynthetic organs of most plants. Most leaves are several hundred micrometers thick (Fig. 10), with specialized cells on the upper and lower surfaces covered by a waxy cuticle that resists water loss (Nobel, 1974). Between these surfaces, the interior of the leaf is composed of *mesophyll* cells containing *chloroplasts*, the specialized

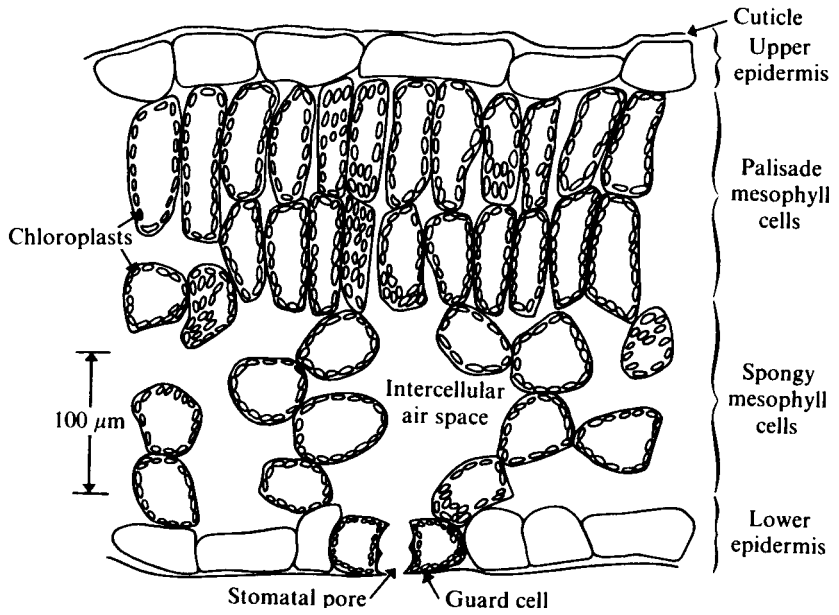

FIGURE 10: Generalized structure of a plant leaf. Scanned without permission from Nobel (1974).

cell parts in which photosynthesis is carried out. The structural integrity of the leaf is maintained by layers of closely-packed *palisade* mesophyll cells near the upper surface. Near the lower leaf surface, the mesophyll cells are further apart, with abundant intercellular air space to facilitate gas exchange. This region is referred to as the *spongy mesophyll*. Along the lower surface of the leaf are small openings called *stomata* or *stomates (*singular *stoma* or *stomate*, respectively). It is through these openings that atmospheric CO_2 enters the leaf, and water vapor is lost. Stomatal openings are regulated by specialized *guard cells*, which can seal the opening to prevent excessive water loss. Guard cells also contain chloroplasts, and it is believed that photosynthetic reactions in the guard cells play an important role in stomatal response to environmental conditions (Joseph A. Berry, personal communication).

Most of the volume of each plant cell is occupied by water in the *central vacuole* of the cell (Fig. 11). Water pressure in the vacuoles is responsible for the rigidity or *turgor* of the plant. The vacuole is surrounded by a membrane which separates it from the *cytoplasm*, or living material of the cell. Within the cytoplasm are many specialized parts, also separated

by membranes. These *organelles* each perform specific functions, and are analogous to organs in animals. The cytoplasm is surrounded by yet another membrane, and the entire cell is enclosed in a *cell wall,* which adds structural strength to the plant.

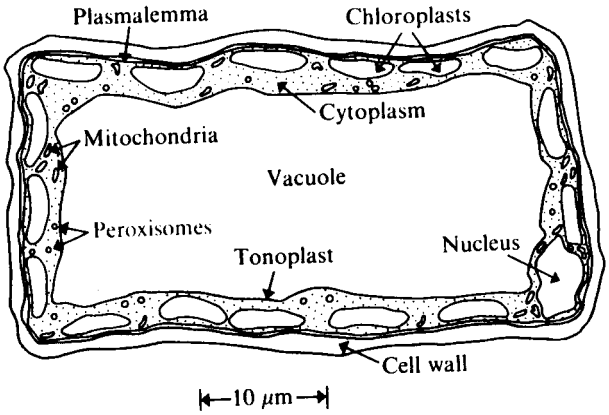

FIGURE 11: Structure of a mature mesophyll cell. Scanned without permission from Nobel (1974).

Photosynthesis takes place entirely within the chloroplasts. The *inner limiting membrane* (Fig. 12) in a chloroplast is deeply folded and convoluted in the interior of the organelle, forming a specialized membrane called the *thylakoid membrane*. The space contained within this membrane is known as the *thylakoid space*. These units are organized in "stacks" called *grana* (singular *granum*), which are connected to each other by thin strands of membrane called *stromal lamellae*. The interior material in the chloroplast which is not contained by the thylakoid membrane is called the *stroma*. Photosynthesis involves reactions which take place in both the grana and the stroma. Radiant energy is converted into chemical energy and reducing power by photochemical reactions in the grana, and the energy produced in this manner is used to reduce atmospherically-derived CO_2 into simple sugars in the stroma.

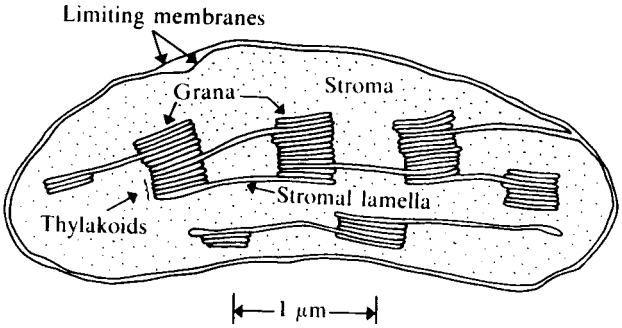

FIGURE 12: Generalized chloroplast from a leaf mesophyll cell. Scanned without permission from Nobel (1974).

3.2 Energy Capture in the "Light Reactions"

3.2.1 Chlorophyll and Other Pigments

Bound to protein molecules on the interior of the thylakoid membranes in chloroplasts are molecules of various photochemically-active pigments. The most abundant pigment (and the most im-

portant for the understanding of photosynthesis) is called chlorophyll-*a* (chl-*a*). Chlorophyll comprises about 0.1% of the weight of green leaves, and is entirely responsible for their green color. Other important plant pigments are chl-*b*, β-carotene, and lutein.

Chlorophyll-*a* has a molecular weight of 893.5 g mol^{-1}. Its molecular structure consists of a "head" about 1.5 nm across and a "tail" about 2 nm long (Fig. 13). The head contains five ring structures (labeled I through V in the figure) with double bonds that can be "shared" among all the atoms in each ring. It is the electrons in these shared double bonds which interact strongly with visible light, giving chlorophyll its unique energy-gathering properties.

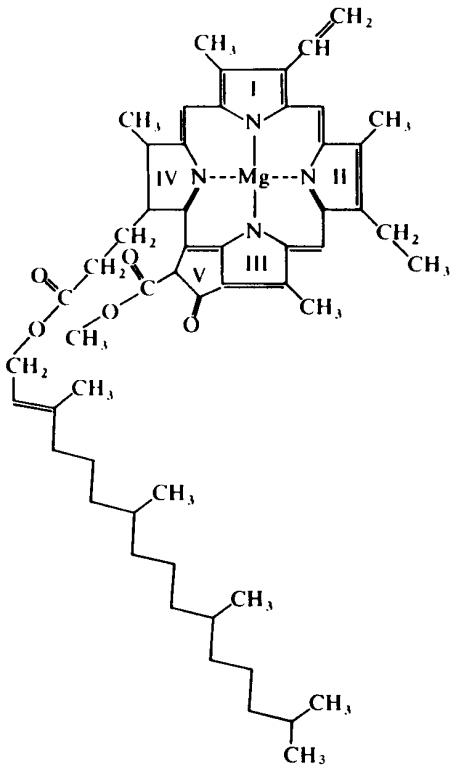

FIGURE 13: Molecular structure of chlorophyll-*a*. Scanned without permission from Nobel (1974).

3.2.2 Excitation and Energy Transfer

When a photon of appropriate energy (wavelength) encounters the head of a chl molecule (or a molecule of another photosynthetic pigment), molecular orbitals are distorted or "excited" into a higher energy level. The excited molecule can pass the energy on to adjacent molecules with the same orbital configurations and thus return to the ground state in a process called "resonance transfer." This process is extremely rapid, taking only about 10^{-12} s. By contrast, the loss of the excitation energy to a by reradiating another photon (fluorescence) takes about 10^{-8} s. After a photon is absorbed by a pigment molecule, the energy is rapidly transferred among many pigment molecules until it reaches a special chlorophyll molecule known as a *trap chl* (Fig. 14). These molecules are not different in composition or structure from other chl molecules, but interactions with neighboring molecules cause them to absorb energy at somewhat higher wavelengths (lower energy). For this reason,

once the excitation has passed to a trap chl molecule (and the excess energy has been dissipated through vibration), it is too weak to pass back to the "normal" pigment molecules. About one in every 450 chl molecules posses this unique property. The "normal" pigment molecules are also referred to as "antenna" molecules, and include other pigments as well as chlorophyll.

The lower-energy trap chl molecules are unable to excite neighboring chl molecules. Instead they are *photo-oxidized*, passing an electron from the excited orbital to a neighboring molecule (an electron acceptor). The trap chl is then deactivated, and cannot accept excitation from another molecule until it has been "reset" by being reduced by (receiving an electron from) a neighboring electron donor molecule.

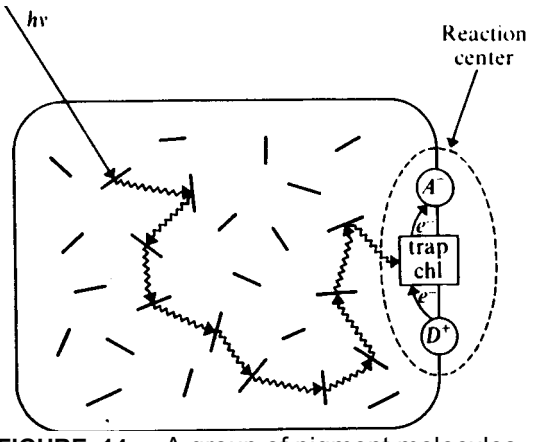

FIGURE 14: A group of pigment molecules act as a photosynthetic unit, passing the energy of an absorbed photon to a reaction center. Scanned without permission from Nobel (1974).

Taken together, the trap chl and its neighboring electron donor and acceptor molecules are called a *reaction center*. The entire collection of chl and accessory pigment molecules that feed excitation energy into such a reaction center are referred to as a *photosynthetic unit*. Two different types of photosynthetic units (photosystems) are required for the energy capturing mechanism to be complete. These involve trap chl molecules which absorb slightly different wavelengths of energy. *Photosystem I* has a molecule called P_{700} (for pigment-700) at its reaction center. This is a trap chl molecule with an absorption peak at about 700 nm. The trap chl of *Photosystem II*, on the other hand, has its maximum absorption at about 680 nm. The electron donor and acceptor molecules in the reaction centers of the two photosystems are different compounds. It is the flow of electrons ("electron transport") through a series of redox reactions from Photosystem II to Photosystem I which drives the production of ATP and reducing power in photosynthesis.

3.2.3 Electron Transport

When a molecule of special P_{700} chl is photo-oxidized at the reaction center of Photosystem I, it reduces a neighboring molecule, as discussed above. This reduced intermediate compound then passes an electron to a molecule of NADP (see section 2.3) with the aid of a catalytic enzyme. This reaction is performed twice, resulting in the reduction of NADP to $NADPH_2$. The oxidized trap chl in the reaction center of Photosystem II leads (through an intermediate) to the oxidation of a water molecule. Two cycles of this reaction produce a molecule of O_2 and four hydrogen ions, reducing the pH of the solution inside the thylakoid space. This water-splitting reaction is the source of the oxygen evolved by photosynthesis. The pH gradient across the thylakoid membrane may reach about 3 units (*i.e.*, the interior is 1000 times as acid as the exterior). In the presence of such a strong gradient, special protein molecules which make up the membrane perform a phosphorylation reaction; that is, they convert a molecule of ADP into the higher-energy ATP. This process is known as *photophosphorylation*. Both the ATP and $NADPH_2$ produced by the electron transport reactions are released into the stromal space, where they are used in the "dark" carbon-fixation reactions as discussed in the next section.

A weak reductant produced at the reaction center of Photosystem II passes its "extra" electron through a series of at least three intermediate compounds to a P_{700} molecule at the reaction center of Photosystem I. In this way both reaction centers are "regenerated" and ready to accept another energy quantum.

The overall results of the "light reactions" is summarized in Fig. 15. Energy is absorbed by antenna chl molecules and passed to two distinct types of reaction centers, where a high-energy electron is passed to an acceptor molecule. In Photosystem I, the electrons are then passed to NADP, reducing it to $NADPH_2$ in an oxidizing environment. The electron mobilized at the reaction center in Photosystem II is passed down an "electron transport" chain of redox reactions to the donor molecule in a Photosystem I reaction center, where it "re-

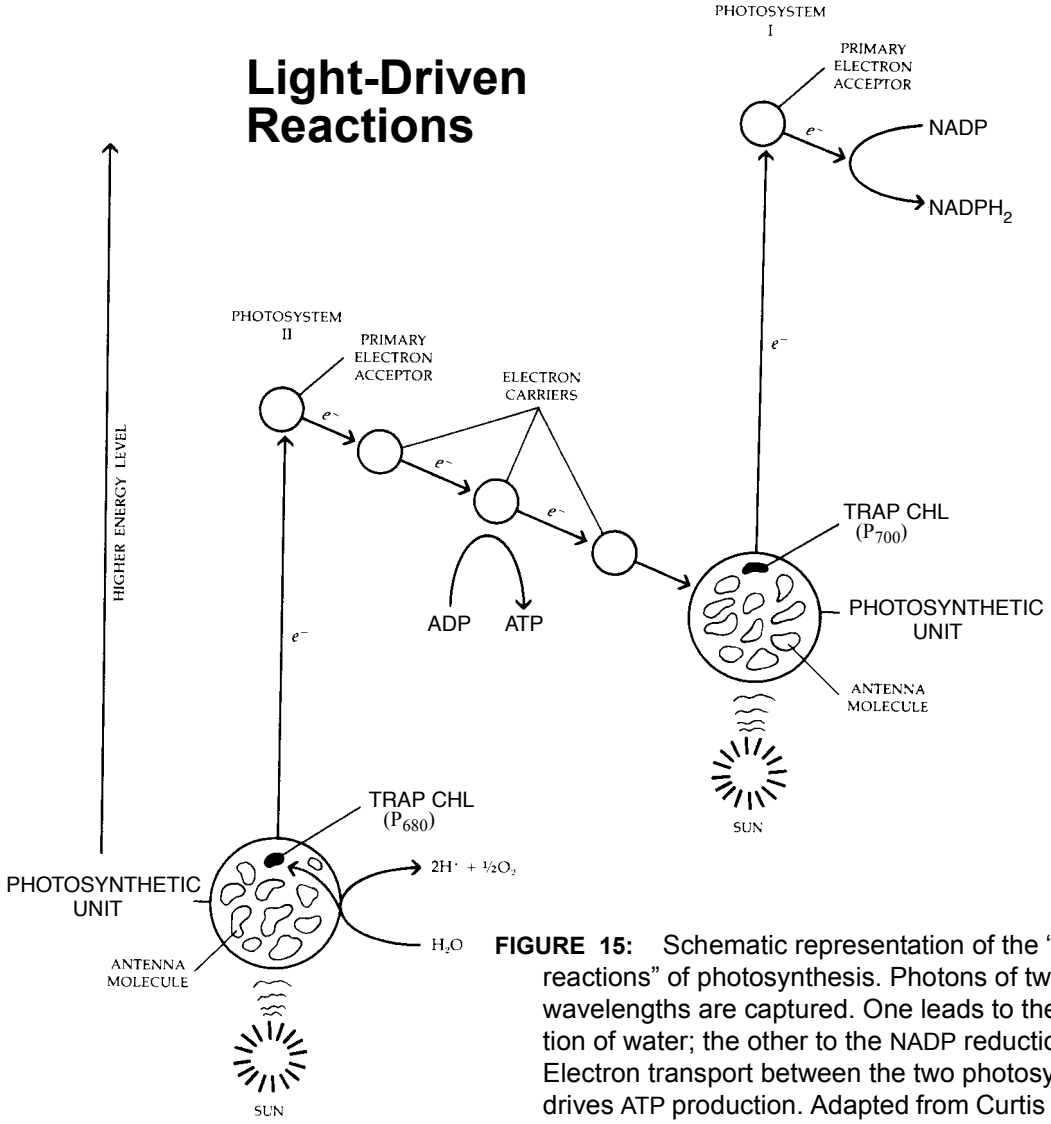

FIGURE 15: Schematic representation of the "light reactions" of photosynthesis. Photons of two wavelengths are captured. One leads to the oxidation of water; the other to the NADP reduction. Electron transport between the two photosystems drives ATP production. Adapted from Curtis (1979).

sets" the trap chl in preparation for another cycle. The reaction center of Photosystem II is reduced (reset) by splitting a water molecule, which evolves oxygen gas. The electron transport reactions and water splitting result in a strong pH gradient across the thylakoid membranes, which is used by specialized proteins on their surface to convert an ADP molecule to ATP.

3.3 Carbon Fixation – The "Dark Reactions"

The actual carbon fixation reactions which lead to the formation of carbohydrate molecules in plants are not directly dependent on light. Rather, they are driven by energy and reducing power stored in the ATP and $NADPH_2$ molecules synthesized in the photochemical and electrochemical steps described in the previous sections. In this section, the fixation of carbon into organic molecules is reviewed. The material is again derived from similar discussions by Nobel (1974) and Stryer (1981).

3.3.1 Primary Carbon Fixation – The Importance of Rubisco

The primary reaction in which atmospherically-derived CO_2 is fixed in an organic compound is illustrated schematically in Fig. 16. This reaction takes place in the stromal space

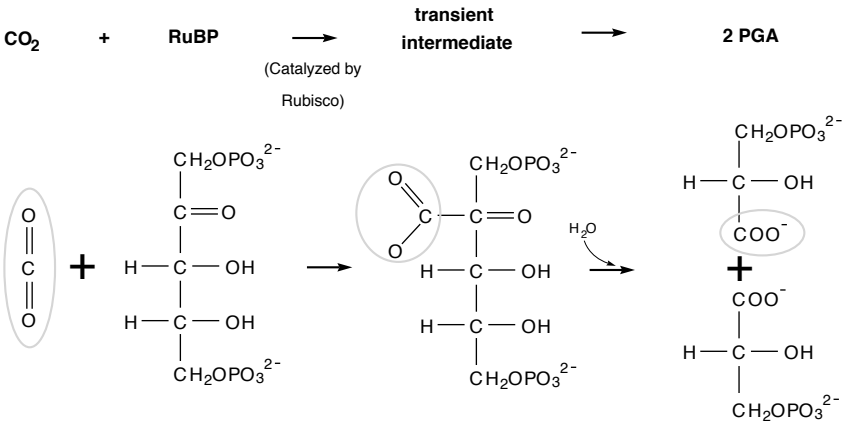

FIGURE 16: The primary carbon fixation reaction in photosynthesis. The dotted ovals indicate the atmospherically-derived CO_2. Adapted from Stryer (1981).

outside the thylakoid membranes. A molecule of CO_2 reacts with a five-carbon compound called *ribulose bisphosphate* (RuBP) in a process called *carboxylation*. This reaction is catalyzed by the enzyme ***rib****u****lose*** ***bis****phosphate* ***c****arboxylase-****o****xygenase* (Rubisco). The reaction between CO_2 and the primary carbon acceptor molecule RuBP is the *rate limiting step* in photosynthetic carbon reduction.

The enzyme Rubisco a very large molecule, about 10 nm across (Stryer, 1981, p. 446), with a molecular weight of about 250,000 g mol^{-1}. It is probably the most abundant protein on Earth, comprising about 20% by weight of the soluble protein in leaves (Sharkey, 1985). Besides the carboxylation reaction, Rubisco also catalyzes a competing reaction in which oxygen breaks up a molecule of RuBP into a three-carbon sugar and a two-carbon compound (this dual action of Rubisco is reflected in its characterization as both a carboxylase and an oxygenase). The competing reaction is known as *photorespiration*, which is regarded as a wasteful process in which the energy reserves of the cell are depleted without any apparent gain.

The six-carbon compound formed from CO_2 and RuBP in primary carboxylation is unstable, and breaks up (Fig. 16) into two three-carbon molecules called *3-phosphoglycerate* (PGA). This three-carbon compound is the first detectable product of photosynthesis when radiocarbon-labeled CO_2 is added to chloroplasts in the laboratory, which gives rise to the term C_3 photosynthesis, which is by far the most common photosynthetic carbon reduction process on Earth. An alternative pathway for carbon fixation involves the formation of a four-carbon compound. This C_4 pathway will be described briefly in section 3.3.3.

3.3.2 Carbon Reduction and RuBP Regeneration – The Calvin Cycle

Having fixed a molecule of atmospherically-derived CO_2 at the expense of a molecule of RuBP, two tasks remain in the photosynthetic process. These are: 1) to convert the organically-bound carbon just acquired into a form which can be used by the plant, and 2) to regenerate the carbon acceptor molecule RuBP. These tasks are accomplished by a series of reactions collectively known as the Calvin Cycle (Fig. 17). The details of the individual reactions in the Calvin Cycle are beyond the scope of this review, but it should be noted that three molecules of ATP and two of $NADPH_2$ are consumed by each round of the cycle. The two molecules of PGA produced by the reaction shown in Fig. 16 are rearranged into a six carbon sugar (fructose in the figure, but glucose is an alternative structure (Sharkey, 1985)).

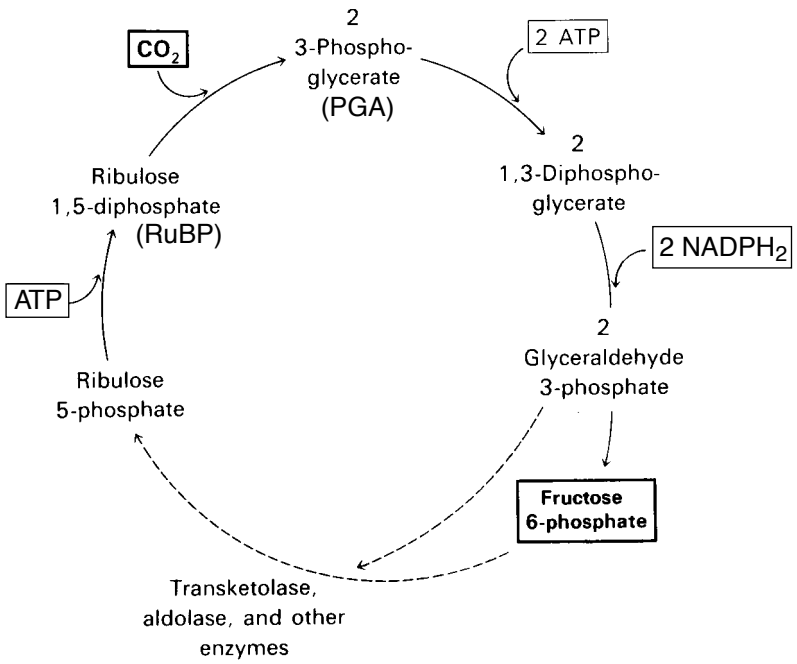

FIGURE 17: The Calvin Cycle. Six rounds of the cycle are required to form one six-carbon sugar. Scanned without permission from Stryer (1981).

This endergonic process requires the coupled hydrolysis of two molecules of ATP into ADP (equation (13)), and the oxidation of two molecules of $NADPH_2$ to NADP (section 2.3, Fig. 8). Some of the sugar is broken down into a five-carbon phosphate compound, which is then phosphorylated by the hydrolysis of a third molecule of ATP to reform RuBP. At this point the system is able to capture another CO_2 molecule. Since the end product is a six-carbon carbohydrate molecule, six rounds of the Calvin Cycle are required per molecule of sugar formed. The overall reaction can be written as

$$6\ CO_2 + 18\ ATP + 12\ NADPH_2 + 12\ H_2O \longrightarrow$$

$$C_6H_{12}O_6 + 18\ ADP + 18\ HPO_4^{2-} + 12\ NADP + 6\ H^+ \quad \text{(15)}$$

(glucose or fructose)

The energetics of this process are summarized by Stryer (1981, p. 448). The reduction of CO_2 to a six-carbon sugar requires 114 kcal per mole of CO_2 consumed. This energy

comes from the hydrolysis of ATP. Reduction in an oxidizing environment requires the enzyme-catalyzed oxidation of $NADPH_2$ to NADP, which releases two electrons per molecule of $NADPH_2$. The two moles of $NADPH_2$ oxidized per mole of CO_2 reduced require four moles of electrons provided by the capture of four moles of photons in Photosystem I. Each of these electrons is replenished from Photosystem II, requiring the capture of an additional four moles of photons. Eight moles of photons in the red part of the visible spectrum carry at least 380 kcal. This gives an overall energetic efficiency of photosynthesis of 114/380 or 30%, which is remarkable high given the number of steps in which energy is dissipated.

3.3.3 C_3 and C_4 Plants

As mentioned in section 3.3.1, some of the energy fixed in photosynthesis can be lost to photorespiration when oxygen competes with CO_2 for the active sites of the Rubisco enzyme. This process is more effective at higher temperatures, because the oxygenase activity of Rubisco increases with temperature faster than does the carboxylase activity. Tropical plants, and some temperate ones as well, have evolved a biochemical mechanism which minimizes this energy loss. The mechanism uses a different primary CO_2 acceptor compound than the C_3 pathway, which results in the formation of a four-carbon compound (*oxaloacetate*) as the first measurable product of photosynthesis. It is therefore called C_4 photosynthesis.

The four-carbon compound is transported in solution to a specialized cell (a *bundle-sheath* cell) where the CO_2 is extracted again and the normal Calvin Cycle operates. This process essentially "pumps" CO_2 up a concentration gradient so that it reaches very high concentrations in the vicinity of the RuBP molecules. It is therefore able to out-compete oxygen for the active sites of the Rubisco enzyme and reduce photorespiration losses. As with the C_3 mechanism, the primary CO_2 acceptor molecule must be regenerated before more CO_2 can be fixed. Both the up-gradient transport and the reagent regeneration require

energy in the form of the hydrolysis of high-energy phosphate bonds from ATP. The net C_4 reaction can be written (Stryer, 1981, p. 450)

$$\begin{aligned} &6\ CO_2 + 30\ ATP + 12\ NADPH_2 + 12\ H_2O \longrightarrow \\ &C_6H_{12}O_6 + 30\ ADP + 30\ HPO_4^{2-} + 12\ NADP + 6\ H^+ \end{aligned} \tag{16}$$

The extra energy required in the form of ATP for C_4 photosynthesis is justified by the reduced losses to photorespiration only if the temperature is high enough that the oxygenase activity of Rubisco is significantly greater than its carboxylase activity. Also, since the ATP is produced by photophosphorylation in the electron transport chain, abundant light must be available to allow the C_4 pathway to "pay for itself." Since more CO_2 is fixed for the same amount of gas exchange (and therefore water loss) through the stomata than in C_3 photosynthesis, C_4 plants tend to be more drought tolerant (Bazzaz and Fajer, 1992). They are therefore found in hot, dry climates such as tropical savannas and dry temperate grasslands.

4. The Transpiration Connection – Limits to Photosynthesis and Stomatal Conductance

We are now ready at last to return to the calculation of stomatal conductance, having acquired a knowledge of the biological process of photosynthesis. Recall from section 1 that a new parameterization (Sellers *et al*., 1992*a*) represents stomatal conductance according to equation (3), repeated here for convenience

$$g_s = m \frac{A_n h_s}{c_s} p + b, \tag{3}$$

where A_n is the net assimilation rate, h_s is the relative humidity, and c_s is the partial pressure of CO_2. Further recall that A_n is represented by Sellers *et al.* according to a smoothed version of equation (4), again repeated here for convenience:

$$A_n = \min(A_R, A_L, A_E) - R_d . \quad \textbf{(4)}$$

In this expression, A_R is the Rubisco-limited rate of photosynthesis, A_L is the light-limited rate, A_E is the end product-limited rate, and R_d is the rate of "dark" respiration.

Sharkey (1985) has written that the "limitations to the rate of photosynthesis can be divided among three general classes: (1) the supply or utilization of CO_2, (2) the supply or utilization of light, and (3) the supply or utilization of phosphate." Utilization of CO_2 is of course regulated by the kinetics of the reaction shown in Fig. 16, which is catalyzed by Rubisco. This system is well described by Michaelis-Menten kinetics, as described in section 2.1.2 (Fig. 6), once allowance is made for the competing effects of oxygen at the enzyme's active sites (photorespiration, see page 23). Light utilization refers to the production of ATP and $NADPH_2$ by the photochemical and electrochemical processes described in section 3.2. Phosphate utilization refers to the ability of the photosynthetic apparatus to process the various compounds involved in the Calvin Cycle (see section 3.3.2). Sharkey (1985) has shown that "end product inhibition" as described in the Sellers *et al.* (1992*a*) model is actually the result of phosphate limitation.

The Rubisco limited assimilation rate is given by Sellers *et al.* (1992*a*) as

$$w_C = V_m\left[\frac{c_i - \Gamma}{c_i + K_C(1 + O_2/K_O)}\right] \quad \textbf{(17)}$$

where

$$V_{\mathrm{m}} = V_{\max} Q_{10}^{(T-25)/10} \tag{18}$$

is the maximum carboxylation rate (proportional to the Rubisco concentration) for the reaction shown in Fig. 16, adjusted for temperature ($V_{\max}$ is the rate at 25° C and $Q_{10} = 2.4$ expresses the sensitivity of the reaction rate to a 10° difference in temperature). The parameter $\Gamma = \frac{[\mathrm{O}_2]}{2\tau}$ is called the "CO_2 *compensation point"*. This indicates the concentration of CO_2 below which carboxylation is slower than the competing oxygenation reaction, and reflects the fact that one CO_2 is released for every two oxygenations of RuBP. The parameter τ is the ratio of kinetic rate constants for carboxylation and oxygenation, and is determined from laboratory measurements of Rubisco kinetics. The factor $K_{\mathrm{C}}(1 + [\mathrm{O}_2]/K_{\mathrm{O}})$ in the denominator of (17) is simply the Michaelis constant for the carboxylation reaction, adjusted to reflect the competitive inhibition by photorespiration (see section 2.1.2). With these modifications in mind, equation (17) is just the Michaelis-Menten equation (12). Equation (17) was first derived by Farquhar (1979).

The light-limited assimilation rate is given by Sellers *et al.* (1992*a*) as

$$w_{\mathrm{e}} = (\mathbf{F} \bullet \mathbf{n})\varepsilon(1 - \omega_{\mathrm{v}})\left[\frac{c_{\mathrm{i}} - \Gamma}{c_{\mathrm{i}} + 2\Gamma}\right] \tag{19}$$

where $\mathbf{F} \bullet \mathbf{n}$ is the intensity of the incident photosynthetically-active radiation normal to the leaf surface, ε is the quantum efficiency for CO_2 uptake (essentially a measure of the photochemical efficiency of the photosynthetic apparatus), and ω_{v} is the shortwave albedo of the leaf. The factor $\left[\frac{c_{\mathrm{i}} - \Gamma}{c_{\mathrm{i}} + 2\Gamma}\right]$ reflects the stoichiometry of the production of ATP and $NADPH_2$ in the photochemical reactions described in section 3.2.3. This expression comes

from the Appendix of Collatz *et al.* (1991), and can be derived from a consideration of ATP and $NADPH_2$ photochemistry as presented by Farquhar *et al.* (1980). Specifically, the expression $c_i - \Gamma$ in the numerator reflects net CO_2 fixation, corrected for CO_2 release by photorespiration. The term $c_i + 2\Gamma$ in the denominator is the net cost of CO_2 fixation in terms of the $NADPH_2$ required under light-limited conditions (Joseph A. Berry, personal communication).

Finally, the end product inhibition limited assimilation rate is given by Sellers *et al.* (1992*a*) as simply

$$w_s = V_m / 2 \, . \tag{20}$$

This is an extremely simplified parameterization of the complicated phosphate limitation chemistry described by Sharkey (1985). Conceptually, this means that the capacity to utilize the immediate products of photosynthesis scales linearly with the Rubisco concentration in the leaf (which is not unreasonable since both represent leaf nitrogen allocation). This is just a "seat of the pants" guess, but it appears to work reasonably well.

The net assimilation must also reflect the loss of CO_2 due to plant respiration, R_d. This is not to be confused with the wasteful photorespiration which results from competitive inhibition of the carboxylation activity of Rubisco, but is a necessary part of plant metabolism. Most of the energy released by respiration is used by the plant to generate more Rubisco. Sellers *et al.* (1992*a*) follow Collatz *et al.* (1991) in simply setting

$$R_d = 0.015 V_m \, . \tag{21}$$

Collatz *et al.* (1991), also corrected V_m and R_d for temperature according to

$$R_d = \frac{0.015\ V_m}{1 + \exp[1.3(T - 55)]}$$

$$V_m = V_m^0 \left[1 + \exp \frac{-a + b(T + 273)}{R(T + 273)}\right]^{-1} \quad \textbf{(22)}$$

so that both assimilation and respiration collapse near 55°C as observed.

The analysis presented here is based on considerations of local conditions (internal CO_2 concentration, Rubisco activity, light intensity, *etc.*) at the scale of a single chloroplast or at most a single leaf. Sellers *et al.* (1992*a*) extend the applicability of this model by performing an integration through a full plant canopy. This is made possible by a remarkable simplifying assumption, namely, that the distribution of Rubisco activity (*i.e.* V_{max}) in the canopy reflects the time-mean distribution of PAR. This assumption is justified based on studies of the economics of nitrogen allocation in plants (e.g. Field and Mooney, 1986; Cowan, 1986; Givnish, 1986), which suggest exactly such a partition to maximize the return in energy for a given investment in scarce nitrogen. Sellers *et al.* (1992*a*) apply Beer's Law for interception and absorption of PAR to express the net assimilation and stomatal conductance for the entire canopy as closed-form integrals which are solved analytically. This allows the parameterization of stomatal conductance based on environmental parameters which are already predicted in most atmospheric models (*e.g.*, temperature, vapor pressure, radiation), or observable from aircraft or satellites (spectral vegetation indices).

Initial experiments with the new parameterization (Sellers *et al.*, 1992*b*) indicate that simulated evapotranspiration rates agree well with field measurements over tallgrass prairie at scales from 100 m × 100 m to 15 km × 15 km. Significantly, the results appear to be nearly scale-invariant, although field experiments have not yet been conducted at scales large enough to include mesoscale fluxes. Multi-year simulations at the global scale are currently underway (Randall *et al.*, 1993).

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