



Chapter 2

Thermodynamics of the Excited States of Photosynthesis

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2.1 INTRODUCTION

In this chapter, we shall discuss the energetic aspects involved in the photosynthetic conversion of light into biochemically usable free energy. Let us start with a rapid overview of the main steps.

1 . A photon of frequency ν is absorbed by a pigment (say, a chlorophyll) belonging to a light-harvesting chlorophyll-containing protein ("antenna"). This results in an excited molecule, i.e. an electron from a HOMO (Highest Occupied Molecular Orbital) jumps to an unoccupied orbital of higher energy. "Higher" means the electron is less tightly bound. Very rapidly (in the sub-ps domain), the excited molecule loses part of its vibrational and electronic energy (it dissipates heat) and reaches the lowest of the excited orbitals (Lowest Unoccupied Molecular Orbital; LUMO). The electron spin is conserved in the process, hence both the HOMO and LUMO are singlet states, denoted S_0 and S_1 , respectively. The energy difference between LUMO and HOMO is defined as $h\nu_0$ (the energy of a photon corresponding to this transition). If left alone, the excited molecule will decay back to the ground state, re-emitting light (and also some heat). We assign k_d as the rate constant for this process (k_d^{-1} is the lifetime of the excited state).

2 . Due to the presence of other chlorophylls at appropriately short distances and orientations, there is a high probability that the excitation "hops" to a neighbor during its lifetime. In this manner, it will drift randomly among the antenna chlorophylls.

3 . This goes on until the excitation either decays or visits a special chlorophyll "*P*" called the primary electron donor of the reaction center (RC). *P* becomes thus excited (denoted P^*). The special aspect of *P* is that it is located close to both an electron acceptor (*A*) and an electron donor (*D*). The following electron transfer reactions can then take place: $DP^*A \rightarrow DP^+A^- \rightarrow D^+PA^-$. Subsequent reactions transfer the charges further away, regenerating the initial active state of the trap (*DPA*). The overall result is that we have converted part of the energy of the impinging photon ($h\nu$) to an electrochemical form (the redox potential difference between the oxidized donor chain and reduced acceptor chain).

One main concern of this chapter is to discuss the efficiency of this energy conversion: on the one hand, what is the maximum value for an ideal system? On the other hand, what are the constraints that directed the evolution of the biological system? Concerning the first question (the efficiency of an ideal system), one might be enticed by the following reasoning: "If the reaction center

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chlorophyll P absorbs N photons of frequency ν_0 per second, then one should be able to retrieve the whole energy $N h\nu_0$ every second". That this is actually wrong for basic thermodynamic reasons (Second Law) is a major point of emphasis in the following.

2. 2 THERMODYNAMIC BACKGROUND

Chemical Potential and Affinity

Consider some chemical reaction $X \rightleftharpoons Y$. The chemical potentials of X and Y are:

$$\mathbf{m}^X = \mathbf{m}_0^X + k_B T \ln[X] \quad 2-1$$

$$\mathbf{m}^Y = \mathbf{m}_0^Y + k_B T \ln[Y] \quad 2-2$$

We adopt the molecular rather than molar scale, hence the Boltzmann constant k_B instead of gas constant R . The bracketed quantities are molecular fractions, proportional to the concentration of each species. In such expressions, the second term involving the \ln of the molecular fraction is purely entropic ("entropy of mixing", related to the probability to encounter X or Y). The first term (standard potential with subscript '0') reflects molecular properties of X or Y (their intrinsic molecular free energy). In general it contains both an enthalpy (i.e. internal energy + PV) and an entropic term. At equilibrium, the concentrations of A and B adjust so that the chemical potentials are equal:

$$\frac{[X]}{[Y]} = \exp\left(-\frac{\mathbf{m}_0^X - \mathbf{m}_0^Y}{k_B T}\right) \quad 2-3$$

If X and Y are *not* at equilibrium (say, an excess of X), free energy can be retrieved (at best) or wasted (at worst) by converting X into Y . We consider a small extent ($d\mathbf{x}$) of the reaction so that $[X]$ and $[Y]$ are not appreciably changed. The free energy change is then:

$$A d\mathbf{x} = (\mathbf{m}^X - \mathbf{m}^Y) d\mathbf{x} = \left(\mathbf{m}_0^X - \mathbf{m}_0^Y + k_B T \ln\left(\frac{[X]}{[Y]}\right) \right) d\mathbf{x} \quad 2-4$$

The quantity $A = \mathbf{m}^X - \mathbf{m}^Y$ is called the affinity, meaning the free energy involved (to be retrieved or dissipated) when converting a molecule of X into Y : a very simple formula of non-equilibrium thermodynamics indeed! At equilibrium, the affinity is zero. In all respects, A can be thought of as the potential difference driving the reaction.

The above expressions apply to the case of a photochemical pigment with ground and excited states noted P and P^* . If, under steady-state illumination, one has fractions $[P]$ and $[P^*]$ of these states, the affinity of the system is:

$$A = \mathbf{m}^{ex} - \mathbf{m}^g = \mathbf{m}_0^{ex} - \mathbf{m}_0^g + k_B T \ln\left(\frac{[P^*]}{[P]}\right) \quad 2-5$$

where superscripts g and ex stand for, respectively, the ground and excited states. If we assume that there is negligible volume and entropy change between both states, the difference in standard potentials is just the energy of the electronic transition, i.e. $h\nu_0$. Thus:

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$$A = h\nu_0 + k_B T \ln\left(\frac{[P^*]}{[P]}\right) \quad 2-6$$

Eq. 2-6 shows that, in general, $A \neq h\nu_0$ and depends through the \ln term on the steady-state fraction of P^* that can be sustained.

The Electrochemical Approach

As explained in the Introduction, the primary donor of the RC is involved in electron transfer reactions with an acceptor and a donor. Two redox couples (both involving the same oxidized state P^+) are involved, P^+/P^* for the excited state (midpoint potential E_m^{ex}), and P^+/P for the ground state (midpoint potential E_m^g). Given the steady-state fractions $[P]$, $[P^*]$, $[P^+]$, one may imagine a coupling of the $P^* \rightleftharpoons P^+ + e^-$ reaction with some specific "acceptor side" electrode and, similarly, a coupling of the $P \rightleftharpoons P^+ + e^-$ reaction with a "donor side" electrode. These electrodes would equilibrate at respective potentials of:

$$E_{acceptor} = E_m^{ex} + \frac{RT}{F} \ln \frac{[P^+]}{[P^*]} \quad 2-7$$

$$E_{donor} = E_m^g + \frac{RT}{F} \ln \frac{[P^+]}{[P]} \quad 2-8$$

Where F is the Faraday (N_{Av} times the absolute value of the electronic charge - which we note $|e|$). Thus, the RT/F factor may be equivalently written $k_B T/|e|$. It is useful to remember that if one uses a decimal \log instead of the \ln , the numerical value of this factor is about 60 mV at 300 K (increasing the ratio $[ox]/[red]$ by a factor of 10 means increasing the potential by 60 mV). The E_m term is again a standard ("midpoint") potential expressing intrinsic molecular properties. It reflects the binding energy of the electron to the reduced species (the more tightly bound the electron, the higher the E_m). Using Eqs. 2-7 and 2-8, the potential difference between the two electrodes is:

$$E_{donor} - E_{acceptor} = E_m^g - E_m^{ex} + \frac{RT}{F} \ln \frac{[P^*]}{[P]} \quad 2-9$$

where the $[P^+]$ cancels out. If we express the energy in eV (multiplying Eq. 2-9 by $|e|$), we obtain the same expression as in Eq. 2-6. Indeed the term $|e|(E_m^g - E_m^{ex})$ is the energy difference between the excited and ground states, i.e. $h\nu_0$.

2.3 RADIATION EQUILIBRIUM

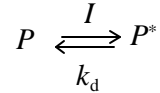
So far, we have learnt that the free energy available from our photochemical converter P is not just $h\nu_0$ but also depends on the term $k_B T \ln([P^*]/[P])$. We have made clear that this is by no means a specific feature of photochemical converters, but a general rule in chemical thermodynamics (see Eq. 2-4). It is in general wrong to estimate the energy involved in a given process by considering only the difference in standard potentials between reactants and products: the actual

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concentrations intervene through the ln term. Admittedly, under many circumstances, the error made by forgetting this term may be tolerable - because the ln dependence is weak. In the case of the photochemical converter, however, the ratio $[P^*]/[P]$ is very small, say less than 10^{-10} (see below), so that the second term is far from negligible (i.e. more than -600 meV). We will now examine more closely what controls the actual value of this ratio.

Absorption / Deactivation Equilibrium

We consider the equilibrium:



We assume a monochromatic illumination at frequency ν_0 . I is the rate constant for light absorption by P and k_d the rate constant for deactivation of P^* back to P . There is actually another deactivation term, equal to I , that we omit here. This is the process of stimulated emission (essential to the laser effect) which is negligible under physiological illumination intensities. One has:

$$I = \int \mathbf{j}(\mathbf{n}) \mathbf{s}(\mathbf{n}) d\mathbf{n} \quad 2-10$$

where $\mathbf{j}(\mathbf{n})$ is the photon flux (number of photons per area unit per second), and $\mathbf{s}(\mathbf{n})$ is the absorption cross-section of P (its extinction coefficient). Since the absorption of P is assumed to be a narrow band centered around \mathbf{n}_0 , we may treat it as a Dirac function of area \mathbf{s}_0 and write $I = \mathbf{j}(\mathbf{n}_0) \mathbf{s}_0$. At steady-state:

$$\frac{[P^*]}{[P]} = \frac{I}{k_d} = \frac{\mathbf{j}(\mathbf{n}_0) \mathbf{s}_0}{k_d} \quad 2-11$$

So that, substituting into Eq. 2-6,

$$A = h\mathbf{n}_0 + k_B T \ln\left(\frac{I}{k_d}\right) \quad 2-12$$

The ratio $[P^*]/[P]$ thus depends on the intensity of the illumination (through \mathbf{j}) and on properties (extinction coefficient, deactivation rate) of P . One should now recall that these properties (\mathbf{s} and k_d) are not mutually independent. This is easily realized by considering that the photon flux \mathbf{j} at frequency \mathbf{n}_0 could be radiated by a black body at a definite temperature T_{bb} . In the spectral domain which is relevant here, $h\mathbf{n}_0 \gg k_B T$ and Planck's formula for the blackbody emission approximates to:

$$\mathbf{j}(\mathbf{n}_0) \approx \frac{4\mathbf{n}_0^2}{c^2} \exp\left(-\frac{h\mathbf{n}_0}{k_B T_{BB}}\right) \quad 2-13$$

Now, it must be equivalent to establish *radiation* equilibrium between P and the black body or to establish *thermal* equilibrium. Thus we can apply the Boltzmann formula:

$$\frac{[P^*]}{[P]} = \exp\left(-\frac{h\mathbf{n}_0}{k_B T_{bb}}\right) \quad 2-14$$

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From Eqs. 2-11, 2-13, and 2-14, it turns out that $k_d / s_0 = 4n_0^2 / c^2$, independent of any specific property of the particular absorber (except n_0). The absorption cross section and the deactivation rate constant of any molecule are linked: "A good absorber is a good emitter." Given n_0 and j , there is nothing we can do to enhance the $[P^*]/[P]$ term: if we increase s_0 , we also increase k_d .

Inserting Eq. 2-14 into 2-6, we get:

$$A = hn_0 \left(1 - \frac{T}{T_{bb}}\right) \quad 2-15$$

The factor between brackets is a Carnot yield for some "machine" working reversibly with hot source at T_{bb} and cold source at T (Duysens, 1958; Knox, 1969). To visualize such a machine, one may think of locating a dilute solution of P in a container enclosed within the black body. The walls of the container are assumed to ensure perfect thermal insulation so that the inside temperature is kept at T . They are, however, transparent to radiation at frequency n_0 so that photons can be freely exchanged between P/P^* and the black body.

Numerical Estimates

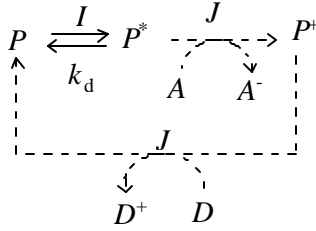
An order of magnitude for the excitation rate I of chlorophyll under bright daylight illumination is 1 s^{-1} . The "natural lifetime" of chlorophyll is $1/k_d = 18 \text{ ns}$. The value of hn_0 (close to the peak of the red absorption band) is approximately 1800 meV. Thus, the affinity that can be sustained by an ideal chlorophyll-based photoconverter is, using Eq. 2-12: $1800 - 445 = 1355 \text{ meV}$. The Carnot yield is thus $1355/1800 = 0.75$. For a bacteriochlorophyll-based converter ($hn_0 \approx 1400 \text{ meV}$), the Carnot yield is about 0.68.

Notice that, *in vivo*, chlorophyll is not in a gas, but attached to membrane proteins, thus interacting with amino acid residues and with neighboring chlorophylls. These interactions result in a *ca.* 20-fold decrease of the excited state lifetime (i.e. about 1 ns). Furthermore, real photosynthesis is close to saturation for $I = 1 \text{ s}^{-1}$ and is more efficient at lower intensity, say 0.1 s^{-1} . With these new figures, the "Carnot yields" become 0.67 and 0.57 for chlorophyll and bacteriochlorophyll, respectively.

2.4 EXTRACTING WORK

At this stage, we have established that the potential of a photochemical converter submitted to a photon flux F at frequency n_0 is given by Eq. 2-12. But the kinetic scheme we have used offers no pathway for energy utilization. This is why the Carnot yield applies: a Carnot machine has no significant work output in order to ensure its reversible functioning. In other words, we determined the voltage of our photocell under open circuit conditions. When the circuit is under load, the voltage will drop to some extent, because of an effective "internal resistance". This is what we will discuss now. Let us consider the scheme:

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The dotted arrows are meant to indicate a net flux of J electrons per second, from P^* to A and from P^+ to D (we do not bother with detailed rate constants, just consider the net flux). At steady-state, one has:

$$\frac{d[P^*]}{dt} = I[P] - k_d[P^*] - J = 0 \quad 2-16$$

Hence,

$$\frac{[P^*]}{[P]} = \frac{I}{k_d} - \frac{J}{k_d [P]} \quad 2-17$$

and, as $[P] = 1 - [P^*] - [P^+] \leq 1$, one has the inequality:

$$\frac{[P^*]}{[P]} \leq \frac{I}{k_d} - \frac{J}{k_d} = \frac{I}{k_d} \left(1 - \frac{J}{I}\right) = \frac{I}{k_d} (1 - f) \quad 2-18$$

where $f = J/I$ is the quantum yield of photochemistry (flux of utilized electrons over flux of absorbed photons). The equal sign applies when $[P] \approx 1$ (small steady-state fractions of P^* and P^+) and we assume that such is the case. Substituting into Eq. 2-6, we thus obtain for the affinity:

$$A = h\nu_0 + k_B T \ln\left(\frac{I}{k_d}\right) + k_B T \ln(1 - f) = A_C + k_B T \ln(1 - f) \quad 2-19$$

where A_C denotes the open circuit affinity (Eq. 2-12) with maximal energetic (Carnot) yield. This shows that the higher the quantum yield f , the lower the thermodynamic potential. Obviously, some compromise has to be found between the two extremes: no flux at high potential or high flux at low potential. What makes sense is to maximize the product, a power, of both (Ross and Calvin, 1967; Knox, 1969):

$$JA = If (A_C + k_B T \ln(1 - f)) \quad 2-20$$

In this expression, the factor I depends on the illumination intensity. This parameter fluctuates quite a lot. In a temperate region, solar illumination around midday during the summer may vary by as much as 20. Instead of the power JA , the energetic performance of the converter may thus be more appropriately described by the power yield JA/I , i.e. the available free energy per absorbed photon. This quantity still depends on I , although weakly (through the $\ln(I)$ term in A_C , Eq. 2-19). When Eq. 2-20 is plotted as a function of f , it displays a maximum which is actually located close to $f = 1$. For chlorophyll, the maximum power yield is about 1230 meV ($= 0.68 h\nu_0$) corresponding to $f = 0.98$. For bacteriochlorophyll, the maximum power yield is 840 meV ($= 0.60 h\nu_0$) for $f = 0.97$. Hence, the optimization of the available power occurs when the system works far from radiation

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equilibrium (98 % of the absorbed photons converted to photoelectrons) and implies an additional drop of the affinity with respect to the Carnot yield (by 7-8 %).

If we ignore any possible limitation on the donor side, the photochemical yield of a reaction center is equal to the ratio $k_{PA}/(k_d + k_{PA})$, where k_{PA} is the rate constant for the electron transfer $P^*A \rightarrow P^+A^-$. In photosynthetic reaction centers, this ratio is large (k_{PA} is typically $(3 \text{ ps})^{-1}$ and $k_d \approx (1 \text{ ns})^{-1}$), so that the F of the *isolated RC* is close to 1. We shall, however, put forward an important qualification when discussing below the role of the antenna.

It should be stressed that the standard redox potentials (E_m) of the primary donor and acceptor play no role in the above derivations. For instance, if the maximum power yield is $0.68 h\nu_0$, this does not mean at all that one should have $E_m(P^+/P) - E_m(A/A^-) = 0.68 h\nu_0$ (as pointed out by Parson, 1978). Nevertheless, these midpoint potentials are relevant to the energetic efficiency because of kinetic constraints and, above all, because of their relation with the quantum yield (Lavergne and Joliot, 1996). The RC is photochemically competent only when its primary donor is reduced and its primary acceptors are oxidized. Therefore, in order to keep most centers in the open state under steady-state conditions, the E_m of the primary donor must be sufficiently high and the E_m of the acceptors sufficiently low.

2. 5 THE ENERGETIC PICTURE IN "REAL" PHOTOSYNTHESIS

We will now attempt to leave the enchanted realm of ideal photoconverters and focus on those features of real photosynthesis which are the most relevant to our subject.

Absorption Spectra

The solar radiation reaching the earth is obviously not a monochromatic source of frequency ν_0 but consists of a broad spectrum extending from the near UV to the near IR (for a discussion of the spectral and optical factors determining the efficiency of oxygenic photosynthesis under "field-conditions", see Bolton and Hall, 1991). The magnitude of the energy gap between ground and first excited singlet states ($h\nu_0$) of the primary donor will be again some compromise between extremes. The absorption spectrum of the antenna pigment may be rather broad, so that photons with $\nu > \nu_0$ can be efficiently absorbed, but, eventually, the excitation energy will decay to $h\nu_0$. Thus, if you adopt a short wavelength (large ν_0), you get high energy photons, but a low flux (because the photons with $\nu < \nu_0$ are not absorbed). On the other hand, if you want to collect a large fraction of the illuminating light you have to set ν_0 more to the infrared and accept accordingly a lower potential energy. Plants and cyanobacteria (both using chlorophyll) have "chosen" a ν_0 corresponding to wavelengths close to 700 nm. Most bacteria (using bacteriochlorophyll) have a much smaller ν_0 (corresponding to wavelengths close to 900 nm or longer). This is related to another strategic choice: oxygenic photosynthesis could not work (unless very differently designed) with such weak photons that suffice for the cyclic ATP-producing pathway used by bacteria. Another important

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aspect is the "spectral niche", that is the evolutionary pressure that will favor the adoption of an absorption spectrum in regions where competitors do not absorb.

Role of the Antenna

So far, we only discussed the energetics of an idealized isolated RC possessing one pigment P . Let us consider a "photosynthetic unit" consisting of a reaction center surrounded by N chlorophylls, located so that that the excitonic transfer between all pigments is efficient. We first assume that all pigments (RC included) have the same n_0 . We also assume that the transfers are fast enough so that the excitation is evenly distributed on each of the $N+1$ pigments (N antenna chlorophylls + P), even if the RC is an efficient trap (for simplicity, we count P as one pigment, even though in reality it is a "special pair" of two coupled chlorophylls). Under such conditions, nothing has to be changed in our calculations for A or for power maximization, since for each individual pigment the $[excited]/[ground]$ ratio is the same. The value of F that maximizes the power is also the same for the photosynthetic unit as a whole as for an equivalent array of $N+1$ isolated reaction centers. To comply with this, however, the *intrinsic* photochemical yield of the RC should be $(N+1)$ times larger in the photosynthetic unit compared to the case of isolated RCs. Indeed, the overall absorption rate is $(N+1)I$, the overall deactivation rate is $(N+1)k_d$, so that in order to keep F the same, J must be also multiplied by $(N+1)$. This could only be done by enhancing the rate constant for charge separation, k_{PA} by the same factor. This rate constant in real reaction centers, however, is probably close to the physically attainable limit, with a value of about $(10 \text{ ps})^{-1}$. It is an activationless reaction, limited by the electronic wavefunction overlap between P^* and the primary acceptor. This overlap can hardly be increased without enhancing also the efficiency of the wasteful back reaction ($P^+A^- \rightarrow PA$). Thus, if k_{PA} is held fixed, the quantum yield of the photosynthetic unit is a decreasing function of N :

$$f = \frac{k_{PA}}{k_{PA} + (N+1)k_d} \quad 2-21$$

If we accept the constraint that k_{PA} cannot be improved, the consequence is that the presence of a large antenna will degrade the power yield, by imposing a lower than optimal overall quantum yield. It is true, of course, that if we consider an individual reaction center, it is better to surround it with antenna pigments (rather than with non-absorbing material) because this will increase the overall light-absorption. What we actually discuss, though, is the advantage of tiling some membrane surface entirely with reaction centers or to substitute part of them by antenna pigments, so that the light absorption is the same. Under such conditions, the antenna can only diminish the power output. There is, however, an important factor that must be taken into account. Whereas an antenna protein is stuffed with closely arranged (bacterio-) chlorophylls, a reaction center has to carry a number of redox cofactors which do not participate in the light-harvesting process. Furthermore, the electron transfer chain also includes another membrane protein (the b6-f or b-c complex; the ATP-synthase should also be taken into account) which carries no light-harvesting pigments (or almost so: it has been recently reported that one chlorophyll is attached to the b6-f). Therefore, our idealization of

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tiling the membrane surface entirely with pigments is obviously not correct. The larger the antenna size N (i.e. the ratio of chlorophylls to non-absorbing material), the larger is the actual collection of light by a unit of membrane surface. We can make this quantitative by assuming that the non-absorbing material associated with one reaction center occupies a surface equivalent to that occupied by X antenna chlorophylls. The surface of our photosynthetic unit is thus proportional to $(N+1+X)$, while its light absorption is proportional to $(N+1)$. The power per unit surface is thus:

$$\frac{(N+1)I}{(N+1+X)} \mathbf{f} A = \frac{(N+1)I}{(N+1+X)} \mathbf{f} (A_C + k_B T \ln(1 - \mathbf{f})) \quad 2-22$$

where \mathbf{f} is given by Eq. 2-20. This function of N has a maximum which predicts an optimal antenna size, representing the best compromise between quantum yield (diminished by N) and light harvesting efficiency (increased by N).

The absorption spectra of the antenna and of P may be different. In general, P absorbs at longer wavelengths than the antenna. This has the effect of concentrating the excitation towards P , thus increasing the quantum yield to the expense of the $h\nu_0$ (and of A). For some bacteria, such as *R. viridis*, which have adopted a spectral niche far in the infrared (about 1020 nm), it is the other way around. The P of the reaction center absorbs at a shorter wavelength (around 960 nm), so that the exciton has to go up an energy barrier (of about 75 meV) which diminishes the probability of presence of the excitation on P about 15-fold. This decreases the quantum yield by the same factor and the antenna has to be diminished accordingly. *R. viridis* has an antenna size of 24 bacteriochlorophylls per RC, to be compared with $N = 100$ for *R. sphaeroides* (where the antenna absorbs at slightly shorter wavelengths than P : the excitation probability of P is increased by a factor of about 2), or heliobacteria with $N = 1000-2000$ (where the antenna absorbs about 90 nm below P : the excitation probability of P is increased by a factor of about 800).

Potential vs. Quantum Yield

From the engineer's viewpoint, it makes no difference in general to trade a decrease of potential against a quantum yield (or current) increase: what really matters is the available power which can be adapted at a later stage to the particular requirement of the utilization device by, say, a transformer. In biology, things may be different, because evolution proceeds by gradual tinkering and cannot at once change drastically the channels under use. For instance, once a choice has been made concerning stoichiometries at crucial energy conserving steps (e.g. the H^+ per ATP ratio of the ATP-synthase), it may not be easily modified. It is interesting in this respect to discuss the case of *R. viridis*. As mentioned above, this species has evolved by adopting a long-wavelength spectral niche (around 1020 nm), taking an advantage in the competition with other organisms for the collection of light. The penalty, however, is the weak potential available from $h\nu_0 \approx 1200$ meV. This may not be sufficient to drive the utilization reactions, given the conversion stoichiometries inherited from other organisms. This explains why the P in *R. viridis* absorbs uphill with respect to the antenna. A diminished quantum yield has been traded off for an increase in potential. The quantum yield of *R. viridis* is indeed much lower than that of other bacteria (about 45 % compared with 90-99 %).

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Nevertheless, given the n_0 's of the antenna and *P. R. viridis* has adapted its antenna size so as to maximize the available power (Eq. 2-21 with $X \approx 20$).

A most important case is the organization of oxygenic photosynthesis, using two photosystems (PS I and PS II) in series. From a purely thermodynamic standpoint, the available power is the same whether one uses one type of reaction center or two. For instance, one could imagine a cyclic electron transfer (such as in bacteria, see below), converting the photochemical power into ATP production and then an ATP-driven metabolic system oxidizing water and reducing NADP^+ and eventually CO_2 . Another option has been selected in oxygenic photosynthesis, coupling more directly the reduction of NADP^+ to the light-driven electron flow. A non-cyclic pathway is used where the photochemical electron flow abstracts electrons from water and drives them into NADP^+ with a one-to-one stoichiometry. Part of the electronic energy is taken during the process to produce the ATP required to drive the Calvin cycle (reduction of CO_2 by NADPH). Once this stoichiometry is fixed, it is clear on thermodynamic grounds that this cannot be done with a single photosystem (in spite of contradictory reports appearing from time to time). The reduction of NADP^+ from water requires a standard potential of $815+320 = 1135$ meV per electron. The Calvin cycle requires 0.75 ATP per electron (standard energy 310 meV). Thus, a total of 1365 meV per electron. On the other hand, using Eqs. (12) and (19), with $I = 0.1 \text{ s}^{-1}$, $k_d = 10^9 \text{ s}^{-1}$, $h n_0 = 1800$ meV and $F = 0.9$, one computes $A = 1140$ meV. This is 200 meV below the standard energy of the process (i.e. it could only sustain the very poor equilibrium constant of 10^3 between products and reactants). On the other hand, if we sum up the A 's for two photochemical reaction in series we get 2280 meV, thus plenty of potential to accumulate energy-rich products. Of course, by doing so, the electronic flux is halved: the linear chain with two photosystems in series acts like a transformer raising the potential by decreasing the current.

It is of course possible to achieve CO_2 reduction using a single photosystem, but then a different type of "transformer" has to be designed. This is occurring in photosynthetic bacteria (where the electron source is not water, but lower potential compounds such as H_2S). In this case, most of the electron flow occurs in a cyclic pathway, generating a protonmotive force and ATP. Part of the protonmotive force is used to drive a non-cyclic flow from the electron source to NAD^+ . There is no thermodynamic impossibility in this scheme, because of the low stoichiometry between the non-cyclic flux and the light-driven, cyclic pathway.

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