

# 13 The Free-Energy Transduction and Entropy Production in Initial Photosynthetic Reactions

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**Summary.** Initial photosynthetic reactions in bacterial photosynthesis are modeled in this chapter as transitions among discrete states of integral membrane proteins performing these reactions. The steady state entropy production is then associated with each transition starting from photon absorption. The assumption of maximum entropy production in all irreversible non-slip transitions leads to high free energy transfer efficiency (high quantum yield) and to optimal values of kinetic constants that are comparable to experimentally determined values. Optimal overall efficiency of close to 20% is similar to measured values for the efficiency of producing the protonmotive power in reconstituted systems. We conclude that photosynthetic proton pumps operate close to maximum entropy production regime and use the advantage of nonlinear flux-force relationships to transfer power with around 90% efficiency instead of 50% as prescribed by the maximal power transfer theorem in the linear regime. Finally, the evolution-coupling hypothesis is suggested, according to which photoconverters couple their own evolution to thermodynamic evolution in a positive feedback loop accelerating both evolutions.

## 13.1 Introduction

The optimization and dissipation in initial photosynthetic reactions is very challenging problem, because even the most basic questions are still in dispute, such as can thermodynamics be applied at all (Hill 1977), and if it can, are equilibrium or near-equilibrium thermodynamics appropriate tools (Meszéna and Westerhoff 1999). Attempts to apply thermodynamics to photosynthesis mainly belong to two categories. In the first and earlier class are attempts to divine what was evolution's goal in photosynthesis. It is immediately obvious that maximal free-energy transduction efficiency was never evolution's goal, because of measured low efficiency values. More promising was the assumption that maximal output power must have been evolution's goal from the very start (Knox 1977; Lavergne and Joliot 2000). This idea worked only for very simple two-state photosynthetic models, when the requirement of maximal output power produced high optimal quantum yield in accord with spectroscopic measurements. For more complex models that allow for charge separation and the creation of a electrochemical proton gradient as the output force, it is far from clear that evolution tried to maximize the output power as the product of proton flux and protonmotive force.

Instead of guessing what evolution's goal is, some researchers speculated that photosynthesis must be governed by known principles from the thermodynamics of irreversible processes (Andriessse and Hollestelle 2001). Such an approach has the advantage of avoiding the artificial separation between the living and nonliving world, between the cell's environmental evolution in accord with thermodynamic laws and the apparently purposeful evolution of biological macromolecules. It is only natural to try to apply the well known minimal entropy production theorem associated with Prigogine's name (Prigogine 1967; see also Kleidon and Lorenz, this volume). Unfortunately, when applied to photosynthesis, authors missed the main point of that theorem that it describes a very special non-equilibrium state (the static head state), and performed their calculations assuming equilibrium (Andriessse 2000; Andriessse and Hollestelle 2001; Juretić 2002). The correct application of Prigogine's theorem in photosynthesis would not help, however, because the static head state is associated with zero net proton flux and accordingly vanishing free-energy transduction efficiency. Such a state can serve as the blockage to free-energy transduction, and is unlikely to describe the essence of photosynthesis. We shall also see that in the absence of leak the static head state of zero proton flux can never be reached in photosynthesis. No less serious is the objection to the application of Prigogine's theorem that this theorem is valid only for linear flux-force relationships close to equilibrium (Hunt and Hunt 1987). Measured flux-force relationships are nonlinear and both, input and output forces, are large keeping the system assuredly far from equilibrium (Cotton et al. 1984; Gräber et al. 1984; Wanders and Westerhoff 1988).

What is an alternative to minimum entropy production as the optimization principle? Is there any other "thermodynamic criterion" that would provide causal explanation for efficient free-energy transfer and conversion in bioenergetics? We propose in this work that the maximum entropy production principle (Dewar 2003; also Dewar, this volume) is relevant for photosynthesis. The maximum entropy production principle (MEP) has extremely wide applications (this volume). We applied it recently to standard electrical circuits, photovoltaic cells, biochemical circuits and photosynthetic free-energy conversions (Juretić and Županović 2003; Županović and Juretić 2004). The MEP principle can be applied both for linear and nonlinear flux-force relationships (Onsager 1931; Kohler 1948; Paltridge 1979; Juretić 1983,1984). In the linear range it is equivalent to Kirchhoff's laws for current distributions in the steady state for fixed parameters (Jeans 1923; Županović et al. 2004).

### 13.2 The Two-State Kinetic Model

The system at temperature  $T$ , illuminated with radiation at higher effective temperature  $T_R$ , can absorb maximal free energy  $A_{oc}$ , which is equal to the chemical potential of a photon (Meszéna and Westerhoff, 1999):

$$A_{oc} = h\nu(1 - T/T_R) \quad (13.1)$$

where  $h\nu$  is the photon energy.

The steady state affinity  $A$  of a pigment  $P$  is (Lavergne and Joliot 1996):

$$A = h\nu + k_B T \ln([P^*]/[P]) \quad (13.2)$$

where  $k_B$  is the Boltzmann constant, and  $[P]$  and  $[P^*]$  are fractions of ground and excited chlorophyll states respectively. Energy utilization is possible only if a branched pathway exists through which part of photon energy can be invested into charge separation and stored into an electrochemical form. Assuming no branched pathway, which would decrease the  $[P^*]$ ,  $A$  is equal to  $A_{oc}$ . The efficiency of free energy transduction then vanishes.

Fortunately, nature has designed photosynthesis so that charge separation through a branched pathway takes place with very high efficiency when other chlorophyll molecules are close by and a special chlorophyll molecule is strategically located close to an electron acceptor and an electron donor. As in an electrical circuit, when net electron current  $J$  flows, dissipation occurs and steady state affinity or photocell voltage (13.1) will be decreased. We know that the large majority of absorbed photons are converted into photoelectrons, which implies that a photosynthetic system works far from the chemical equilibrium state for absorbed and emitted photons.

A convenient quantity to measure the distance from the chemical equilibrium state ( $A = A_{oc}$ ) is the thermodynamic force for light reactions (Mesz ena and Westerhoff 1999):

$$X_L = A_{oc} - A \geq 0 \quad (13.3)$$

The affinity transfer efficiency can then be defined as  $A/A_{oc}$ .

The entropy production  $P$  per the unit volume in the branched productive pathway due to transmitted free energy  $A$  and electron flux  $J$  is:

$$TP = AJ \quad (13.4)$$

where the electron flux  $J$  is proportional to the flux  $I$  of absorbed photons, but is an exponential function of the force  $X_L$ :

$$J = I(1 - \exp(-X_L/k_B T)) \quad (13.5)$$

where we assumed that the photon flux is approximately equal to the rate constant for photon absorption, because  $[P^*] \ll [P]$ .

For an optimal thermodynamic force for light transitions, or for corresponding optimal photochemical yield  $\Phi = J/I$ , entropy production is maximal. Maximal entropy production does not lead to poor affinity transfer efficiency or poor photochemical yield. In fact, due to the strongly nonlinear relationship (13.5) and the convexity of the graph of the current versus transmitted free-energy, maximum entropy production must occur both for high affinity transfer efficiency and for high photochemical yield. For assumed photon wavelength of 870 nm, an environment temperature of 25  C, non-radiative relaxation constant  $k_d = 10^8 \text{ s}^{-1}$ , and light absorption rate  $I = 100 \text{ s}^{-1}$ , maximal entropy production  $P_{\max} = 29.5 \text{ kJ mol}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  is obtained for an optimal thermodynamic force for light transitions of  $X_L = 9 \text{ kJ/mol}$  (0.093 V),

for an optimal photochemical yield  $\Phi = 0.97$  and an optimal affinity transfer efficiency  $A/A_{oc} = 0.91$ . The experimentally observed photochemical yield values are indeed close to one (Cho et al. 1984; Lavergne and Joliot 1996). With optimal quantum yield close to one, only about 10% of available power is dissipated in the pathway  $P \rightarrow P^*$  where energy utilisation cannot occur. In other words, the entropy production expression (13.4), which is associated with a potentially productive electron transfer pathway, is the major part of the total entropy production. Maximizing entropy production, in the case of a nonlinear current-force relationship, ensures that most of the absorbed power is channelled in the charge-separation pathway. Minimum entropy production would require working in the linear regime, when  $\Phi \ll 1$  and  $X_L \ll k_B T$ , and having either zero affinity transfer efficiency, or zero photochemical yield. In the linear regime, in terms of the theory of electrical circuits,  $A_{oc}$  can be identified as the electromotive force,  $A$  as the voltage drop on a load, and  $X_L$  as the voltage drop through internal resistance. The entropy production (13.4) can be recognized then as the dissipation on the external resistor. It is maximal for the impedance matching requirement:

$$A_{optimal} = (X_L)_{optimal} = A_{oc}/2 \quad (13.6)$$

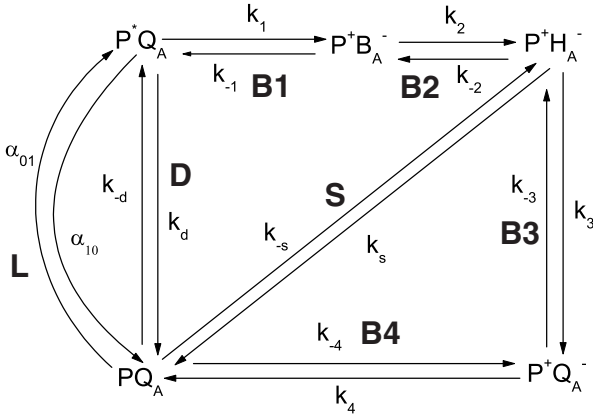
which is also known as the maximum power transfer theorem (Boylestad 1999). This requirement ensures that an optimal external resistance is equal to the internal resistance, so that 50% of the available source power is dissipated on the load.

### 13.3 The Five State Model for Chlorophyll Based Photoconversion

The scheme shown in Fig. 13.1 is a simplified five-state model for an-oxygenic chlorophyll-based bacterial photosynthesis (Van Rotterdam 1998; Lavergne and Joliot 1996). The five states are the chlorophyll ground state  $P$  and the chlorophyll excited states  $P^*$ ,  $B \equiv P^+B^-_A$ ,  $H \equiv P^+H^-_A$  and  $Q \equiv P^+Q^-_A$ . The electron transport is assumed to be coupled to proton pumping in the recovery  $B4$  transition. The photochemistry quantum yield  $\Phi$  is the ratio of the  $J(B4)$  flux and the flux of absorbed photons  $J(L)$ .

The application of Kirchhoff's junction rule leads to relationships among currents:

$$\begin{aligned} J(L) &= J(D) + J(B1) \\ J(B1) &= J(B2) \\ J(B2) &= J(S) + J(B3) \\ J(B3) &= J(B4) \end{aligned} \quad (13.7)$$



**Fig. 13.1.** The five-state kinetic model with a slip for the chlorophyll-based bacterial photosynthesis. The  $Q_A$  is ubiquinone electron acceptor, the  $B_A$  is accessory bacteriochlorophyll, while the  $H_A$  is pheophytin. Each transition is associated with forward and reverse rate constant. The excited state  $P^*$  is reached through a light-activated transition  $L$  between the chlorophyll ground ( $P$ ) and the excited state, and depopulated through a non-radiative transition  $D$  back to ground state, and through relaxation  $B1$  from the excited state with electron transfer and charge separation. Productive transitions leading to charge separation are  $B1$ ,  $B2$ ,  $B3$  and  $B4$

The affinity  $A_{PP^*}(L)$  is the thermodynamic force  $X_L$  introduced in (13.3) for the light-activated transition  $L$ . Kirchoff’s loop rule gives the connection between affinities and forces in each loop:

$$A_P * P (D) = A_{oc} - X_L$$

$$A_P * B (B1) + A_{BH}(B2) + A_{HP}(S) - A_P * P (D) = 0 \tag{13.8}$$

$$A_{HQ}(B3) + A_{QP}(B4) - A_{HP}(S) = X_{out}$$

where input force  $A_{oc}$  and output force  $X_{out}$  can be derived by forming the clockwise and counterclockwise products of rate constants in cycles  $L-D$  and  $S-B3-B4$  where these forces are respectively operational (Hill 1977).

The  $K_4$  equilibrium constant for the  $B4$  transition is a function of electron donor and acceptor concentrations and of the proton-motive force  $X_{out}$ :

$$K_4 = k_4/k_{-4} = \exp(u + X_{out}/k_B T) \tag{13.9}$$

where the donor/acceptor ratio is equal to  $\exp(u)$ . Relationships (13.8) are used to find the equilibrium constants  $K(B3)$  and  $K(S)$ . Using the diagram technique (Hill 1977) one can derive the dependence of the transition and the operational fluxes and affinities on rate constants.

In terms of transition affinities and fluxes, total free-energy dissipation associated with our five-state diagram is:

$$\begin{aligned}
 PT = & A_{PP} * (L) J(L) + A_P * _P (D) J(D) + A_P * _B (B1) J(B1) \\
 & + A_{BH}(B2) J(B2) + A_{HQ}(B3) J(B3) + A_{QP}(B4) J(B4) + A_{HP}(S) J(S)
 \end{aligned}
 \tag{13.10}$$

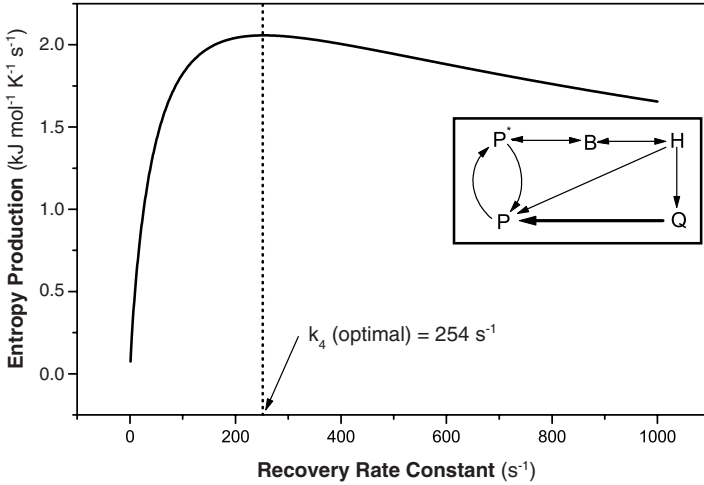
De Donder's Theorem (De Donder and Van Rysseberghe 1936) requires that the product of each affinity with corresponding flux is positive definite. Each term from the right hand side of (13.10) can be interpreted as the free-energy dissipation associated with corresponding transitions. Another way to consider total free-energy dissipation is to realise that it is equal to free-energy change of the input and output sources (Hill 1977):

$$PT = A_{oc}J(L) + X_{out}J(B4) \tag{13.11}$$

The corresponding efficiency expression is:

$$\eta = -X_{out} J(B4)/A_{oc} J(L) \tag{13.12}$$

Both initial transitions  $B1$  and  $B2$  are regarded as close to equilibrium, with equilibrium constants  $K_1 = 4.8$  and  $K_2 = 7.1$ , respectively (Van Rotterdam 1998). One can ask if entropy production in irreversible transitions associated with productive pathway can always be maximized? Extensive modelling convinced us that connected maximums in the productive pathway will always occur, if we take care to perform free-energy transduction in the normal operating regime far from the static head state (Juretić and Županović 2003). We performed such optimization with respect to the rate constants in transitions  $B3$  and  $B4$  with the other rate and equilibrium constants taken as fixed, using observed values (Van Rotterdam 1998). Optimal final values of forward kinetic constants were stable with respect to the choice of initial values from  $10^{-30}$  to  $10^{30}$  and the iteration to the optimum was very fast, usually taking place during the first 10 steps. With a choice of  $u = 12$ ,  $K_4 = 100$ ,  $\alpha_{01} = 100 \text{ s}^{-1}$ ,  $X_{out} = -18.55 \text{ kJ/mol}$ , an overall optimal efficiency of 17.7% is obtained (which is quite high compared to the maximal efficiency of 18.4% ) and optimal forward rate constants are:  $k_3(\text{optimal}) = 2.15 \times 10^9 \text{ s}^{-1}$ ,  $k_4(\text{optimal}) = 254 \text{ s}^{-1}$ . As an example, entropy production in the recovery transition ( $B4$ ) is depicted in the Fig. 13.2, as the function of recovery rate constant  $k_4$ . The total entropy production of  $19.78 \text{ kJ mol}^{-1} \text{ K}^{-1} \text{ s}^{-1}$  is distributed among transitions  $L, D, S, B1, B2, B3, B4$  (Fig. 13.1) as 2.92, 0.33, 0.80, 0.10, 0.02, 13.55 and  $2.06 \text{ kJ mol}^{-1} \text{ K}^{-1} \text{ s}^{-1}$  respectively. Notice the high contribution of irreversible transitions  $B3$  and  $B4$  (78.8% ) to the total entropy production. The thermodynamic force for light reactions is  $X_L(\text{optimal}) = 12.08 \text{ kJ/mol}$ , the affinity transfer efficiency is  $(A_{oc} - X_L)/A_{oc}(\text{optimal}) = 87.8\%$  , and the photochemical yield is  $\Phi(\text{optimal}) = 94.6\%$  . Optimal values for these performance parameters are nearly constant over wide range of light intensities, while the optimal proton current  $J(B4)$  is proportional to the photon absorption rate. These optimized performance parameters are in the rough accord with experimental data (Juretić and Županović 2003).



**Fig. 13.2.** The five-state kinetic model for chlorophyll-based photosynthesis has been optimized in the self-consistent manner so that entropy production in the chlorophyll recovery step is maximal in all non-slip irreversible dark transitions ( $B3$  and  $B4$  in Fig. 13.1). Insert: The bold line in the kinetic model specifies the recovery irreversible transition  $B4$  for which the entropy production dependence on the forward rate constant  $k_4$  is shown in the graph

### 13.4 Slip Coefficients and Forward Static Head State

The “forward” static head state (zero output flux) and corresponding slip coefficients have been defined for the nonlinear free-energy transduction as well (Juretić and Westerhoff 1987). We increased the secondary force by increasing the reverse recovery constant  $k_{-4}$  (Fig. 13.1). Total entropy production is low ( $P = 2.3 \times 10^{-12} \text{ kJ mol}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ ) in the state with vanishing proton flux, but it is still not minimal. The efficiency  $\eta$  is increased on approaching vanishing net proton flux, passes through maximum of almost 83% efficiency, and decreases to zero value.

The general expression for the static head output force is:

$$(X^{SH})_{out} = k_B T \ln((s_0 + 1)/(s_0 + \exp(X_{in}/k_B T))) \quad (13.13)$$

In the case of photosynthesis  $X_{in} = A_{oc}$ , where  $A_{oc}$  is given with (13.1). The forward slip coefficient  $s_0$  is for the five-state chlorophyll based model:

$$s_0 = (k_d k_{-2} k_{-1} + k_s(k_1 k_2 + (\alpha_{10} + k_d)(k_{-1} + k_2)))/(\alpha_{10} k_{-2} k_{-1}) \quad (13.14)$$

With rate constants and equilibrium constants for chlorophyll based photosynthesis taken from Van Rotterdam (1998) and as applied in our simplified kinetic model (Fig. 13.1), the secondary force high enough to cause vanishing

flux  $J(B4)$  is indeed very high (94.6 kJ/mol or 980 mV for  $A_{oc} = 99$  kJ/mol and  $s_0 = 5.7$ ). The static head state is actually very similar to an equilibrium state, because photon-activated cycling essentially stops and practically all chlorophyll is accumulated in the  $Q$  state due to a very low recovery equilibrium constant  $K_4 = 8 \times 10^{-14}$ . Of course, more complete kinetic models, e.g., including leak, can reach the steady state of zero net transmembrane proton current for much lower (and more realistic) values of the proton-motive force.

### 13.5 Conclusions

When life learned how to use the photon free energy to perform charge separation, that major accomplishment steered all subsequent biological evolution. Charge separation leads, for instance, to the creation of the protonmotive force as the output force, which can be maintained only by continuous destruction of free energy packages. Maximal protonmotive force is associated with minimal (in the linear range) or very small entropy production (as demonstrated in this work for nonlinear flux-force relationships). However, net proton flux then vanishes, and ATP is not synthesized, so that uphill biosynthetic reactions, requiring ATP hydrolysis, cease to work. Since biological macromolecules are all more or less unstable and need to be constantly replaced, the cell is effectively dead in seconds after the ATP synthesis stops. Such a scenario never materializes due to the simple reason that the static head state with maximal protonmotive force cannot be reached. As soon as the membrane potential (the major part of the protonmotive force) reaches about 300 mV, the dielectric breakdown of the membrane occurs and the cell dies. Regulatory mechanisms maintaining the protonmotive force at a safe upper limit of around 200 mV must have been developed very early during life's evolution. Our point is that only a small percentage of photon free energy suffices to create such a protonmotive force, while the major part of incoming free energy packages must be dissipated. In other words the biochemical composition of cells is such that life is possible only far from thermodynamic equilibrium and far from the static head state. Then, entropy production is closer to maximal than minimal values (it is higher from the static head value by more than 12 orders of magnitude in our kinetic model for bacterial photosynthesis).

When all external forces are fixed (the photon free energy and protonmotive force) the conditions in the cell are analogous to an electrical network with all electromotive forces fixed. Then, Kirchhoff's laws and the condition of energy conservation requires that entropy production of the network is maximal (Jeans 1923; Ziman 1956; Županović et al. 2004). The analogues of Kirchhoff's laws and energy conservation condition holds for biochemical circuits as well (Županović and Juretić 2004). However, this theorem cannot be applied directly to biochemical circuits, because flux-force relationships in biochemistry are generally nonlinear and because biochemical circuits are not fixed in time, but rate constants and macromolecular states can change during



evolution and even during the operation of the circuit. Taking advantage of the greater flexibility of biochemical networks we propose that all irreversible transitions involved in the power transfer are optimized with respect to rate constants so that the associated rates of entropy production are maximal. This proposal led to stable steady state with performance parameters, such as the efficiency of free energy transduction, close to experimentally measured values (Van Rotterdam et al. 2001). Using different kinetic models or different macromolecules for performing initial photosynthetic reactions (e.g., bacteriorhodopsin) does not change this conclusion (Juretić and Županović 2003). In addition, non-linearity turned out to be crucial, because optimal power transfer of around 90% is considerably higher than maximal power transfer of 50% in linear circuits. Due to the practically infinite source of free energy from the Sun, the advantage of the nonlinear mode in its superior capability to transfer, dissipate and store large amounts of free-energy is more important during evolution than its disadvantage in terms of limited overall efficiency, which is usually below 20% (Juretić 1992 and this work).

The proposed entropy production principle reverses the usual picture of what is important for a photosynthetic cell in its interaction with the environment. Its overall efficiency must be low enough to support a high level of entropy production associated with a rich pattern of metabolic fluxes. This may be quite general, because for most living cells, with photosynthetic ability or not, the major thermodynamic process is a large outflow of entropy, and less than 10% of available energy is incorporated into biomass (Bermudez and Wagensberg 1986). Notice that the steady state of exponential growth in a continuous culture experiments is preferred by microorganisms when all restrictions on growth factors have been removed (Forrest and Walker 1964). In such a steady state entropy change per unit mass of cells vanishes, but entropy production, entropy outflow and internal organization reaches its highest constant level. Living entities tend to increase the entropy production in the universe while active metabolically, so that life serves as a catalytic agent speeding entropy production in its environment (Ulanowicz and Hannon 1987; also Chaisson, this volume; Lineweaver, this volume). This observation brings biological evolution in synergy with the thermodynamic evolution. By operating close to maximal entropy production, photoconverters couple their own (biological) evolution to thermodynamic evolution in a positive feedback loop which speeds up both evolutions. This “evolution coupling” hypothesis postulates that biosphere evolution is intimately connected with the evolution of life’s physical environment as suggested by the Gaia hypothesis (Lovelock and Margulis 1974; Pujol 2002; see also Kleidon and Fraedrich, this volume; Toniazzo et al., this volume). In this picture biological evolution is just a clever way nature found to accelerate its thermodynamic evolution. Life’s particular goal seems to be to channel the input power into those dissipative pathways where electrochemical rather than only thermal free-energy conversions can occur.

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