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The Thermodynamic and Kinetic Limits on the Process of Free Energy Storage by Photosynthetic Systems*

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The kinetic limits for light energy transduction are explored by using one simple model for the light activated proton pump. In the far from equilibrium steady state of biological interest the efficiency of free energy transfer and entropy production can be simultaneously maximized with respect to kinetic constants for excited state relaxation.

The limits on the power produced by light action and on the amount of free energy stored are both thermodynamic and kinetic. The thermodynamics puts an upper limit on the Gibbs free energy supplied by photons:¹

$$\Delta G_L^m = h\nu(1 - T/T_R) \quad (1)$$

where $T_R(\nu)$ is the radiation temperature introduced by Planck² in order to describe the nonequilibrium radiation, and T is the working system temperature. The kinetic arrangements for free energy storage are completely ignored in (1).

The simplest known photosynthetic mechanism developed by nature is based on the action of protein bacteriorhodopsin, which was isolated from purple membrane patches of *Halobacterium halobium*.³ Upon illumination the light absorbing pigment: retinal, goes through the cycle of conformational changes concomitant with such changes of the opsin part of bacteriorhodopsin, with net result that protons are ejected from archaebacteria. Since proton electrochemical gradient is created at the expense of photon free energy bacteriorhodopsin acts as free energy converter rather than quantum detector like his cousin rhodopsin which is involved in the process of vision.

The kinetic limits are explored by using one simple model (Figure 1) for the bacteriorhodopsin light activated proton pump action. We consider N equivalent and independent macromolecular units each of which may exist in any one of N_i ($i = 1, 2 \dots n$) discrete states. The states are represented by points in a diagram, and transition between states by lines. In our simplified model there is only one light activated transition i. e. the one from state 0 to 1. The rate of light absorption x is proportional to the radiation energy density

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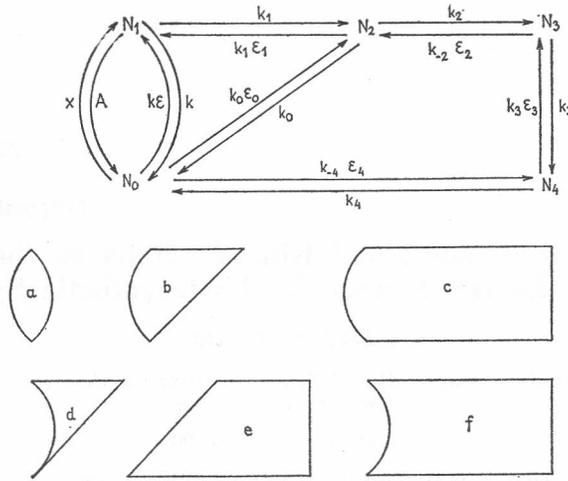


Figure 1. The state diagram for light-activated proton pump cycle of bacteriorhodopsin. The thermodynamic forces are associated with 6 cycles of the basic graph. The dominant cycles a, b and c involve ΔG_L . Free energy transduction into proton electrochemical gradient is possible in the cycle c.

ρ and to the Einstein coefficient $B_{01} : x = \rho B_{01}$. Stimulated emission B_{10} is usually negligible with respect to the rate of spontaneous emission A . The proton release steps 2 — 3 and 0 — 4 and reassociation steps 3 — 2 and 4 — 0 depend on an association constant k_a , dissociation constant k_d , proton concentration in the cell H_1 , external proton concentration H_2 , and membrane potential developed by proton pump action that enters via a specific model into constant α_0 :

$$k_2 = k_d \alpha_0, \quad k_4 = k_a H_1 \alpha_0 \tag{2}$$

$$k_{-2} = k_a H_2 / \alpha_0, \quad k_{-4} = k_d / \alpha_0$$

The second pathway between ground state 0 and excited state 1 consists of a nonradiative relaxation rate constant k and a reverse thermal transition, $k \epsilon$, of very low probability. The light absorption process is further simplified in our model by assuming that:

i) We have a narrow band absorber that absorbs only photons of frequency ν .

ii) The excited state 1 is above ground state just for the photon energy $h \nu$. Following Luger⁴ whose 5 state proton pump model is essentially the same as ours, we can assume that spectroscopic states⁵ bR₅₇₀, K₆₁₀, L₅₅₀, M₄₁₂ and O₆₄₀ correspond to our states 0, 1, 2, 3 and 4 respectively. This identification of states in our model is only tentative. For instance our excited state 1 may be too short living to be clearly detected.

It is well known from network thermodynamics⁶ that thermodynamic forces can be associated with the cycles of the basic graph (Figure 1). It is true that the diagram representation of nonequilibrium thermodynamics⁷ breaks down for the light absorption process. In our case Gibbs canonical

ensemble can not be applied to the light absorption step 0 — 1, which is not isothermal and certainly is very far from thermodynamic equilibrium. However, this step can be omitted when »light force« is calculated as a sum over all free energy changes in the cycle 0 — 1 — 0. In accordance with assumption iii) the free energy drop because of photon absorption is just compensated by the free energy increase associated with system transition into excited state 1. Therefore, the thermodynamic drive, for any such light cycle is:

$$\Delta G_L = h\nu + KT \ln(\bar{p}_1/\bar{p}_0) \quad (3)$$

where \bar{p}_i are stationary nonequilibrium values of occupational probabilities: $\bar{p}_i = N_i/N$, and K is the Boltzmann's constant.

If we neglect all terms containing reverse rate constants ε_i :

$$\Delta G_L = \Delta G_L^m + KT \ln \Phi_F \quad (4)$$

with quantum yield for spontaneous emission:

$$\Phi_F = A/(A + k + k_1) \quad (5)$$

In the same approximation light cycle ($N_0 \rightleftharpoons N_1$) current J_{01}^L is

$$J_{01}^L/xN = (k + k_1)/(A + k + k_1) \quad (6)$$

The corresponding entropy production is

$$TP = \Delta G_L J_{01}^L \quad (7)$$

The efficiency of energy transfer can be defined as

$$\eta_1 = \frac{\Delta G_L J_{01}^L}{\Delta G_L^m xN} \quad (8)$$

The denominator can be considered as the maximal power injected into the system. For constant light intensity it is independent of rate constants. In our case:

$$\eta_1 = [1 - \frac{1}{X_L} \ln \frac{1}{\Phi_F}] (1 - \Phi_F) \quad (9)$$

where

$$X_L \equiv \Delta G_L^m / KT$$

Maximal energy transfer with respect to k , A , k_1 or Φ_F is achieved when

$$X_L = \frac{1}{\Phi_F} + \ln \frac{1}{\Phi_F} - 1 \quad (10)$$

Static head state is characterized with zero net proton current J_{23} and maximal proton electrochemical gradient:

$$X_2^m = -KT \ln(1 + \frac{x \Phi_T}{\varepsilon_0 k_0}) \quad (11)$$

where $\Phi_T = k_1/(A + k + k_1)$ is the transfer factor.

Static head state can be established easily and quickly by bacteria, although proton back pathways are most probably not going through the bacteriorhodopsin. Since such stationary states capable of efficient free energy storage might have also played important role during early evolution, it is of interest to find if they can be selected with the help of some optimization principle from thermodynamics. As a first step we realize that total entropy production of our model system can be expressed as

$$TP = \Delta G_L J_{01}^L + X_2 J_{23} \tag{12}$$

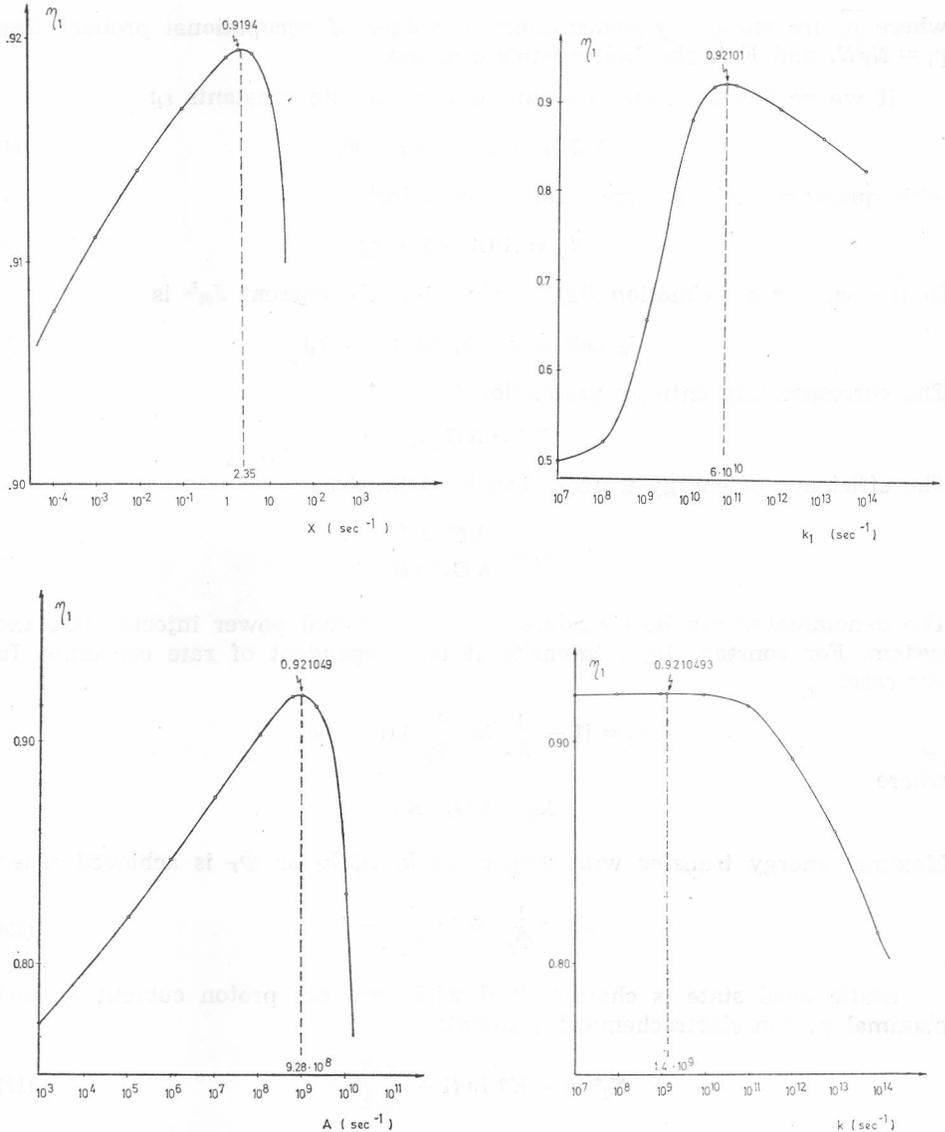


Figure 2. The efficiency of free energy transfer as a function of rate constants x , k_1 , A and k respectively.

where secondary force X_2 is acting in the cycle c, e and f (Figure 1). Since J_{23} vanishes in the static head state, such state can be characterized with (7) as a total entropy production, which, as we have seen, assumes maximal value together with the efficiency of energy transfer (8) with respect to the rate constants.

Optimal rate constants giving maximal μ_1 can be easily found in our model system. For bacteriorhodopsin at room temperature $E_1/KT = 85.56$, assuming that only the radiation of wavelength 570 nm is absorbed. Using this value and trial values for other rate constants (in s^{-1}):

$$k_1 = 10^{11}, \quad k_0 = k_2 = k = A = 10^9,$$

$$k_3 = 10^8, \quad k_4 = 10^8$$

optimal $T_R = 1270$ and $x_{opt} = 2.35 s^{-1}$ as well as the optimal values of some other rate constants can be calculated (Figure 2):

$$k_1 = 6 \cdot 10^{10} s^{-1}, \quad A = 9.3 \cdot 10^8 s^{-1}, \quad k = 1.4 \cdot 10^9 s^{-1}$$

In conclusion in this work we have proposed new expression (8) for the efficiency of free energy transfer in light absorption process. By multiplication of (8) with Carnot's thermodynamic factor $\eta_c = 1 - T/T_R$ a new theoretical upper limit is obtained for that process efficiency. In the future work, by using more elaborate model systems, one can try to answer the question are optimal values of kinetic constants close to the measured values. It is really the question of what is the best strategy for life to maintain the structures of low probability. The point of this paper is that high efficiency of free energy transfer and storage and high entropy production are not contradictory goals in the far from equilibrium steady states.

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SAŽETAK

Termodinamička i kinetička ograničenja u procesu pohranjivanja slobodne energije kod fotosintetskih sistema

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Upotrijebljen je jednostavan model za rad protonske crpke aktivirane svjetlom, da bi se istražila kinetička ograničenja prilikom pretvorbe slobodne energije svjetla. U neravnnotežnom stacionarnom stanju, koje je od biološkog interesa, moguće je simultano maksimizirati efikasnost prijenosa slobodne energije i nastajanje entropije, i to s obzirom na kinetičke konstante za relaksaciju pobuđenog stanja.