Entropy consumption in primary photosynthesis

Robert C. Jennings [a,b,*], Erica Belgio [a], Anna Paola Casazza [a],
Flavio M. Garlaschi [a,b], Giuseppe Zucchelli [a,b]

[a] *Dipartimento di Biologia, Università degli Studi di Milano, via Celoria 26, 20133 Milano, Italy*
[b] *CNR Istituto di Biofisica-Sede di Milano, via Celoria 26, 20133 Milano, Italy*

Abstract

Knox and Parson have objected to our previous conclusion on possible negative entropy production during primary photochemistry, i.e., from photon absorption to primary charge separation, by considering a pigment system in which primary photochemistry is not specifically considered. This approach does not address our proposal. They suggest that when a pigment absorbs light and passes to an excited state, its entropy increases by $h\nu/T$. This point is discussed in two ways: (i) from considerations based on the energy gap law for excited state relaxation; (ii) using classical thermodynamics, in which free energy is introduced into the pigment (antenna) system by photon absorption. Both approaches lead us to conclude that the excited state and the ground state are isoentropic, in disagreement with Knox and Parson. A discussion on total entropy changes specifically during the charge separation process itself indicates that this process may be almost isoentropic and thus our conclusions on possible negentropy production associated with the sequence of reactions which go from light absorption to the first primary charge separation event, due to its very high thermodynamic efficiency, remain unchanged.
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1. Introduction

We have recently suggested that, contrary to the generally accepted view, primary photochemistry in plants can, in principle, proceed with negative entropy formation [1,2]. Based on straightforward entropy balance considerations for the total entropy change (ΔS_{total}; system plus environment) in a photoselected system, the following expression was presented

$$\Delta S_{\text{total}} = h\nu_0(T_{\text{r}} - \xi T_{\text{r}} - T)/TT_{\text{r}} + \Delta S_{\text{pc}} \qquad (1)$$

where $h\nu_0$ is the energy of a photon absorbed by a photosystem; T_{r} is the radiation temperature, i.e., the black body temperature which emits a certain, temperature dependent, photon density at frequency ν. Values in the literature for different energy flux densities considered are $1000\ \text{K} \leq T_{\text{r}} \leq 5800\ \text{K}$; ξ is the thermodynamic efficiency of primary photochemistry and contemplates all energy losses from photon absorption to primary charge separation, i.e., the Stokes shift, the quantum efficiency, the free energy changes during primary charge separation; T is the environmental bath temperature, in which the photosystems are embedded, and is taken as 300 K; ΔS_{pc} is the small entropy decrease associated with primary photochemical production of charge asymmetry. As already discussed in our earlier reply [2] to a paper by Lavergne [3], this conclusion refers to primary processes in a system of single photosystems each of which absorbs a photon or, in other words, to a system of photoselected photosystems in the excited state. At high values of ξ, $T_{\text{r}} - \xi T_{\text{r}}$ may be less than T and then ΔS_{total} has a negative value. This possibility is implicit in the earlier study by Yourgrau and van der Merwe [4] in their Eq. 13. In physical terms, this conclusion is largely based on the entropy loss by the light flux upon absorption ($-h\nu/T_{\text{r}}$) not being compensated by entropy release into the environmental bath at very high values of ξ. In our initial reasoning it was

* Corresponding author. CNR Istituto di Biofisica-Sede di Milano, via Celoria 26, 20133 Milano, Italy.
E-mail address: robert.jennings@unimi.it (R.C. Jennings).

suggested that under conditions of thermal equilibration in the excited state, for an "ideal" pigment such as chlorophyll, the entropy content of the excited and ground states is equal. This conclusion was based on the observation that the distribution functions over the vibrational levels of the ground and excited state (*) manifolds are equal, i.e., $g_i e^{E_{\mathrm{vib}_i}/k_{\mathrm{B}}T} = g_i^* e^{E_{\mathrm{vib}_i}^*/k_{\mathrm{B}}T}$ (for each ith level), where g is the degeneracy and E_{vib} is the energy levels of the vibrational states. Thus, the number of microstates is equal for the ground and the thermally relaxed excited states, which means that, in terms of statistical entropy, $\Delta S = 0$. Though this point of view is sometimes expressed for large chromophores due to the substantial equality of ground state and thermalised excited state partition functions (e.g., [5]), it has been criticised by Knox and Parson [6] who suggest that excited state generation leads to a positive value for $\Delta S = h\nu/T$, due to the energy difference between ground and excited states, and that our conclusions are flawed as Eq. (1) does not consider this term. In the present paper we specifically address the question of entropy changes associated with excited state generation. Several lines of reasoning are presented which lead us to confirm the view that $\Delta S = 0$.

2. Discussion

We wish to initially point out that the paper by Knox and Parson [6] does not address our proposal [1,2] that primary photochemistry, from photon absorption to primary charge separation, may occur with negative entropy production as primary charge separation is not considered by these authors. This has important consequences as discussed below. In addition, it should be emphasised that the above Eq. (1) refers to either a single photoactive particle which absorbs a photon, or a photoselected population of photoactive particles. This is not the case in the paper by Knox and Parson which, as in the earlier paper by Lavergne [3], deals with a system in which excited state molecules are created in a sea of ground state molecules. The two systems are not identical as in the second approach [3,6] an entropy "mixing" term is present which is not required in our photoselected case.

Point 1. A basic postulate of statistical mechanics is that each system microstate be accessible. If a microstate is for some reason inaccessible, it must be excluded from the statistical description. In the following we argue that if brief time lapses are considered, of the order of those in which primary photochemistry occurs, in a pigment the ground/excited states are effectively "isolated". Our reasoning is based on the "energy gap law" of Englman and Jortner [7] which provides an approximate description of non-radiative decay for a large unimolecular pigment, such as chlorophyll, in the weak coupling limit.

$$k_{\mathrm{r}} \approx K e^{-\gamma \Delta E/h\nu_{\mathrm{M}}} \qquad (2)$$

where K and γ are quasi-constants which have a weak temperature dependence; k_{r} is the non-radiative decay rate; ΔE is the energy gap between any two energy levels and ν_{M}

corresponds to the normal vibration of maximal frequency. This approximation is usually written

$$k_{\mathrm{r}} \propto e^{-\Delta E}. \qquad (3)$$

Due to the very high density of excited state vibrational levels, relaxation in the excited state manifold is extremely rapid, occurring on a sub-picosecond time scale. On the other hand, the large value of ΔE for the ground and excited states leads to a metastable excited state, thermalised with the environmental bath, which for solvated chlorophyll has a lifetime of around 5 ns. These kinetic considerations have important thermodynamic consequences. For the situation in which $k_{\mathrm{r}} \ll k_{\mathrm{obs}}$, where k_{obs} is the rate of data collection, the ground state/excited state population ratio in the $(k_{\mathrm{obs}})^{-1}$ time window is not obtained by the Boltzmann factor. The energy gap rule leads to a "quasi-isolation" of the excited state from the ground state and the excited state may be considered as a new thermodynamic entity. We mention a few photosystem (PS) trapping times to illustrate the importance of this point when primary photochemistry is considered. For the plant PSI core particle, the trapping time has been shown to occur with an approximately 17-ps lifetime [1] and that within the PSII core may be of the order of 50 ps [8]. Thus the "isolation" of the pigment excited and the ground states is virtually complete over the time span of primary photochemistry. This comment means that on the time scale of primary photochemistry almost no relaxation occurs and the excited state can be considered as effectively isolated from the ground state. As indicated above, thermodynamic considerations based on a ground/excited state partition function are not relevant during this time space. This suggests that the entropies of the excited state and that of the ground state are not thermodynamically or statistically interrelated. For the partition functions we therefore only consider the vibrational levels of the separate ground and excited states, which are therefore $(\sum g_i e^{-E_{\mathrm{vib}}/k_{\mathrm{B}}T})_g = (\sum g_i e^{-E_{\mathrm{vib}}/k_{\mathrm{B}}T})_e$. The subscripts refer to the ground and excited states. Thus, from a statistical point of view, the ground and excited state entropies may be considered to be equal ($\Delta S = 0$).

This reasoning may be expressed in another way. For a pigment system which transits reversibly to the excited state $P + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} P^*$, $h\nu$ is the energy absorbed. At thermal or radiation equilibrium, $k_1/k_{-1} = e^{-\Delta E/k_{\mathrm{B}}T}$ according to the Boltzmann equation and, thus, $k_{-1} = k_1 e^{\Delta E/k_{\mathrm{B}}T}$. On the other hand, according to the energy gap law $k_{-1} = K e^{-\gamma \Delta E/h\nu_{\mathrm{M}}}$. As $K e^{-\gamma \Delta E/h\nu_{\mathrm{M}}} \neq k_1 e^{\Delta E/k_{\mathrm{B}}T}$, it would seem that the Boltzmann equation is not applicable.

The above reasoning, based on the energy gap law, refers to excited state relaxation in a unimolecular system. It is quite different from that of Knox and Parson [6] who consider excited state/ground state population ratios in a pigment ensemble. In their study no restrictions on ground state accessibility from the excited state were considered or for the ground state/excited state population ratio (n_g/n_e). They argue that n_g/n_e for radiation and thermal equilibrium will be equal ($T_r = T$) and this is described by the Boltzmann distribution in their Eq. (6). The energy gap law suggests that such reasoning is incorrect for describing n_g/n_e ratios when very fast primary photochemistry occurs.

We wish also to point out that under conditions of photochemistry, the n_g/n_e ratio is not, in fact, an equilibrium ratio given by the Boltzmann factor but a steady-state ratio that has a different value. This comment applies to Eqs. (6) and (7) and the Appendix of the Knox and Parson paper [6] where equilibrium is assumed.

Point 2. We now consider a photosynthetic pigment system which is open to the environment and absorbs photons, in thermodynamic terms. For this system we may write the fundamental thermodynamic relationship for internal energy

$$dU = TdS - PdV + \mu N \qquad (4)$$

where U is the system internal energy, T is the temperature, S is the entropy, N is the absorbed photon particles, and μ is the chemical potential of the pigment excited state due to each photon absorption event. At constant volume this equation states that photon absorption increases the internal energy by the amount $\mu N = Nh\nu$ at constant S. We mention that the term μN introduces free energy into the photoactive particles. Thus one may write Eq. (4) in the form of the Gibbs equation, at constant volume

$$dU = TdS + dG. \qquad (5)$$

dG has a large positive and must be included for photochemistry. It is usually thought to approximately equal $h\nu$ for each photosynthetic pigment which absorbs a photon. As $U \equiv \Sigma \varepsilon_i n_i$, where ε and n are the quantum energy levels and n their populations, $dU = h\nu$. Therefore $dS \approx 0$ and is certainly less than $h\nu/T$.

We point out that if the Knox and Parson conclusion were correct, i.e., $dS = +h\nu/T$ and dG has a large positive value upon photon absorption, then $dU > h\nu$, which is unreasonable. Their conclusion in the thermodynamic section is based on the classical thermodynamic definition of temperature $1/T \equiv (dS/dU)_V$, which, as they state, is valid only for thermodynamic equilibrium, when T is the equilibrium temperature. However, as discussed above, the excited state/ground state ratio (n_g/n_e) never attains a thermodynamic equilibrium value for a photosystem particle and so this expression cannot be used. In addition, considering their Eqs. (4) and (5) it can be seen that Knox and Parson [6] take into account only the TdS term on the right hand side of the equations. Thus they seem to be thinking in terms of a closed system (equilibrium) which does not absorb photons ($N=0$) as the μN (dG) term is absent. This reasoning seems to preclude the creation of free energy upon photon absorption in a photosystem particle. We fail to appreciate their point as it is just this creation of free energy in the pigment excited state which is the thermodynamic basis for photosynthesis.

Point 3. From the above we conclude that both the classical thermodynamic entropy as well as statistical entropy do not change when the thermally equilibrated excited state is compared with the ground state in pigment systems, in agreement with others (e.g., [5,9]). Now, as stated above, we point out that Knox and Parson [6] only consider isolated pigment excited state generation whereas the proposal made in our paper [1], and Eq. (1), refers to the entire *primary*

photochemical process from light absorption to primary charge separation in photosystem particles. By primary charge separation we mean the formation of an initial charge separated complex and not the thermodynamically stabilised one. The term ΔS_{pc} in Eq. (1) refers to the entropy changes during this process. We have suggested [1] that this will have a small negative value due to the generation of charge distribution asymmetry. Hou et al. [10] were able to detect small negative entropy changes for charge separation even after some secondary transport in PSII. On the other hand recent high-resolution fluorescence decay studies [8] suggest that primary charge separation in PSII occurs with a very small decrease in the Gibbs free energy, and model studies suggest $\Delta G \approx -0.02 \ h\nu$. Similar results are obtained from model studies of the photosystem I reaction centre (Santabarbara, S. personal communications). Thus it would seem that the initial charge separation reaction almost entirely conserves the free energy of the chlorophyll excited state, which means that total entropy changes are negligible ($\Delta S_{total} = -\Delta G/T$). We may also consider these free energy changes in terms of ξ in Eq. (1). Once again these very small decreases in ξ associated with primary charge separation are insufficient to modify our previous conclusion.

Our proposal is that primary photochemistry, from photon absorption to the initial charge separation, may occur with entropy consumption when the thermodynamic efficiency is sufficiently high ($\xi \geq 0.9$). This process is, of course, coupled to other processes in the photosynthetic system which stabilises the charge separation and "displace" the electron. These processes occur with total entropy production. We wish to point out that this period of entropy consumption associated with primary photochemistry coincides with a period in which the dynamics of the system are in continuous non-equilibrium evolution. Under these conditions the use of statistical mechanics to describe the n_g/n_e ratio is not straightforward.

During the course of revision of this paper the study by Ford et al. [11] was pointed out to us by one of the reviewers. Ford et al. studied the thermodynamics of a quantum oscillator in a blackbody radiation field. This study, while certainly being of general interest to the present discussion, starts out from a situation in which the oscillator is at thermal equilibrium with the radiation field, and is thus not directly pertinent to our analysis.

Acknowledgments

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