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Photosynthesis and negative entropy production

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Abstract

The widely held view that the maximum efficiency of a photosynthetic pigment system is given by the Carnot cycle expression $(1-T/T_r)$ for energy transfer from a hot bath (radiation at temperature T_r) to a cold bath (pigment system at temperature T) is critically examined and demonstrated to be inaccurate when the entropy changes associated with the microscopic process of photon absorption and photochemistry at the level of single photosystems are considered. This is because entropy losses due to excited state generation and relaxation are extremely small ($\Delta S \ll T/T_r$) and are essentially associated with the absorption-fluorescence Stokes shift. Total entropy changes associated with primary photochemistry for single photosystems are shown to depend critically on the thermodynamic efficiency of the process. This principle is applied to the case of primary photochemistry of the isolated core of higher plant photosystem I and photosystem II, which are demonstrated to have maximal thermodynamic efficiencies of $\xi > 0.98$ and $\xi > 0.92$ respectively, and which, in principle, function with negative entropy production. It is demonstrated that for the case of $\xi > (1-T/T_r)$ entropy production is always negative and only becomes positive when $\xi < (1-T/T_r)$.

Keywords: Carnot cycle; Entropy; Fluorescence lifetime; Photosynthesis; Photosystem I core; Photosystem II core

1. Introduction

Over the past five decades, a considerable literature has accumulated on thermodynamic aspects of primary photosynthetic processes, and quite widely contrasting views have been published. Following the initial suggestion by Duysens [1] many people have accepted the view that the photosynthetic conversion of electromagnetic energy, which is the internal energy of the photons (U), into the free energy of chlorophyll excited states (G) is described by the Carnot cycle equation $G = Q(1-T/T_r)$, where $Q = h\nu_0$, the purely electronic transition of the lowest excited singlet state (Q_y), and T and T_r are the temperatures of the chlorophyll system (approximately 300 K) and the radiant energy, respectively (e.g. [2–4]). This point is interesting for two main reasons.

Firstly, in the interpretation of the above cited authors, this is understood to place an upper limit on the maximal photochemical work obtainable from an *absorbed photon*. For values of $T_r \approx 1100$ K, as suggested by Duysens [1], the Carnot cycle efficiency $1-T/T_r = 0.73$ and thus according to this point of view the Gibbs free energy of a chlorophyll molecule in the first singlet excited state could not exceed this value. Thus, the maximum chemical work associated with charge separation was not expected to exceed 1.3 eV, even though $h\nu_0 = 1.8$ eV. However, this point of view was criticized by Parson [5], who pointed out that this misunderstanding arose from the incorrect application of the concept of chemical potential to photosynthetic systems Eq. (1).

$$\mu = h\nu_0 + \mathrm{kTlnZ} \quad (1)$$

μ is the chemical potential associated with chlorophyll in the excited state; $h\nu_0$ is the photon energy for frequency ν_0 which is taken as that of the Q_y purely electronic transition. Z is some factor related to the relative concentrations of chl and chl*, T is the temperature of the chlorophyll system. This author pointed out that the concept of chemical potential was applicable only to molecular ensembles and not to single chlorophyll molecules, or single molecular complexes, which absorb photons and perform photochemistry within single photosystems. Thus, Eq. (1) is applicable to "systems containing large numbers of

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molecules" and not to "individual molecules or photons" [5]. In the case of photosynthesis, Parson [5] concluded that the free energy available for primary photochemistry was probably not much less than that of the photon energy, hv_0 and that the chemical potential concept "does not tell anything about the reactions that are open to the excited molecules". Surprisingly, these words of caution of Parson [5] seem to have been little heeded in photosynthetic studies as one finds that hv_0 $(1-T/T_r)$ is still often interpreted as being the "free energy delivered to the chlorophyll molecule by absorbing a photon" [3] or "the maximal free energy that chlorophyll can absorb when in chemical equilibrium with radiation of higher effective temperature T_r" [4].

Secondly, and more importantly, the Carnot cycle concept for photosynthetic energy conversion is based on the assumption that the second law of thermodynamics is necessarily applicable to photosystem function. This point is not trivial as arguments have been presented in recent years that on a microscopic level entropy production may not always be positive [6,7]. In fact, for photosynthesis, this point was discussed in the 1960s [8,9]. Though their final conclusion was that the overall photosynthetic process, due to its low quantum efficiency in vivo, does not seem to constitute an exception to the second law, this can not be assumed a priori. One obvious reason for this is the decrease in molecular entropy associated with glucose production. If the overall quantum efficiency is high enough, negative or zero entropy changes are able to be contemplated. These papers are rarely, or not at all, cited in thermodynamic studies on photosynthesis. In the present study, we examine the entropy changes associated with the microscopic process of photon absorption and photochemistry at the level of single photosystems. Using a straightforward approach, it is demonstrated that the core particle of both plant photosystems is able to achieve primary charge separation with an accompanying increase in negative entropy.

2. Materials and methods

The core complex of photosystem I was prepared from maize plants as previously described [10]. This complex, which binds approximately 96 antenna chla a molecules and the reaction center cofactors, has an absorption maximum at room temperature near 680 nm. For fluorescence lifetime measurements it was resuspended in a Tricine (5 mM) buffer, pH 7.8, with 0.015% n-dodecy-β-D-maltoside. Time resolved fluorescence lifetime measurements were performed as previously described [11]. After deconvolution of the measurements with the instrument response function, the time resolution was 10–20 ps. The emissions were recorded at 10 nm intervals between 680 and 750 nm and analyzed globally with a Frontline Systems Premium Solver Plus algorithm.

3. Results and discussion

When a photosystem absorbs a photon, as pointed out by Knox [2], the internal energy ($U=hv_0$) of the photon is converted into the free energy of the chlorophyll excited state (ΔG) and some part of the energy is expected to be converted into entropy (ΔS), which becomes unavailable for performing chemical work Eq. (2). This is the case for heat machines for negligible pressure–volume changes. T is the temperature of the chlorophyll system.

$$\Delta G = \Delta U - T\Delta S = hv_0 - T\Delta S \tag{2}$$

We now address the question of what the entropy change (ΔS) of the chlorophyll photosystem is upon light absorption. The statistical mechanics description of entropy is given by:

$$S = kln\Omega, \tag{3}$$

where k is the Boltzmann constant and Ω is the thermodynamic probability. As can be seen in textbooks on thermodynamics, this latter term expresses the probability distribution of the system in a unit volume. If we now consider the case of an ideal pigment in which electronic rearrangements in the excited state do not occur and excited state interactions with the host solvent are absent, the initially excited state rapidly relaxes to a metastable excited state equilibrated with the thermal bath at temperature T. In this case, it is apparent that the distribution function over the vibrational levels of the ground and excited states (*) are equal, i.e., $g_i e^{E_{vib_i}/kT} = g_i^* e^{E^*_{vib_i}/kT}$, where g is the degeneracy and the E_{vib} are the energy gaps of the vibrational states. Thus, $\Omega_g = \Omega_{eq}{}^*$ is equal for the ground and the thermally relaxed excited states and $\Delta S = 0$. From Eq. (2) it may be concluded that $\Delta G = hv_0$. However the situation is more complex as $\Omega_{eq}{}^*$ is not exactly equal to that of the *initially* excited state $\Omega_{pe}{}^*$ when the pre-equilibrium excited state vibrational population, E^*_{pe} is considered, as this is energetically greater than $E^*_{vib_i}$ $(E^*_{pe} > E^*_{vib_i})$ and the molecular temperature may be thought of as being higher, i.e., $T^*_{pe} > T$ [12]. Relaxation between E^*_{pe} and $E^*_{vib_i}$ gives rise to the Stokes shift which, in thermodynamic terms, may be considered as heat (Δq) being released into the thermal bath at temperature T. Thus, the entropy decrease of the pigment, associated with the Stokes shift, is $-\Delta q/T^*_{pe}$ while that of the environment is $+\Delta q/T$. This enables us to rewrite Eq. (2) in the following form for the thermalised excited state:

$$\Delta G_{eq} = hv_0 - \Delta q\left(1 - T/T^*_{pe}\right); \tag{4}$$

ΔG_{eq} is the free energy gap of the thermally equilibrated excited state with respect to the ground state. This interesting formulation of the free energy equation for a thermally equilibrated excited state means that the free energy available for photochemistry is that of the absorbed photon *minus* the heat lost during thermal equilibration modulated by the Carnot cycle efficiency of this process. For most pigments the Stokes shift energy $\Delta q(1 - T/T^*_{pe}) << 0.01 \times hv_0$. We therefore conclude that the free energy transferred to an ideal pigment upon the absorption of a photon is essentially the internal energy of the photon. Energy "loss" by entropy production need hardly be considered.

The question thus presents itself as to whether chlorophyll bound to pigment–protein complexes may be thought of as an ideal pigment. The thermodynamics of an ideal pigment have been studied by Kennard [13] and Stepanov [14] who demonstrated that, for such a case, there is a precise relationship between the electronic absorption spectrum and the spontaneous

fluorescence emission spectrum. This unique relationship is expressed in the so-called Stepanov relation Eq. (5)

$$F_\nu/A_\nu = \mathrm{D}(T)8\pi h\nu^2/c^2 \quad e^{-h\nu/kT}, \tag{5}$$

where F_ν and A_ν are the absorption and emission spectra, $D(T)$ is a temperature dependent term, T is the Stepanov temperature which in the case of an ideal pigment is equal to that of the heat bath in which the pigment is embedded after thermalisation. This equivalence for a chlorophyll–protein complex was first demonstrated by Knox and van Metter [15], and subsequently by others, for a considerable number of pigment–protein complexes [16–18]. We therefore conclude that chlorophyll bound to photosynthetic pigment–protein complexes behaves, to a close approximation, as an ideal pigment.

If our conclusion that the temperature and entropy differences between the thermally equilibrated metastable first singlet excited state and the ground state is zero, the heat flow analogy, explicit in the Carnot cycle efficiency for a photosynthetic photosystem, is inapplicable. Thus, the maximum photochemical work (W_{max}) attainable from photon electronic absorption is $W_{max} > 0.99h\nu_0$. The maximum free energy difference for primary charge separation in chl-based plant photosystems is therefore of the order of 1.8 eV, in agreement with Parson [5].

In the context of W_{max}, it is interesting to consider the case of a real photosystem. In this case, excitation energy is lost to photochemistry by virtue of the so-called trivial decay processes (thermal and fluorescence relaxation) and this reduces the photochemical quantum yield (φ). The extent of this decrease is related to the effective photosystem trapping time (τ_{eff}), which represents the lifetime of the excited state prior to reaction centre trapping. For a recent discussion of τ_{eff}, see Engelmann et al. [11]. Here, we briefly examine the case of the PSI and PSII cores from plants, as these particles have a high quantum efficiency for primary photochemical trapping. In Fig. 1, we present the fluorescence decay associated spectrum for higher plant PSI core as this has not previously been published. The decay is dominated by a single component with a lifetime of 20±5 ps. The longer lifetime decays, with very low amplitudes, are interpreted as contaminants in the preparation. In order to determine the quantum efficiency, we have also measured the decay of the external antenna of PSI, i.e., LHCI, which is PSI antenna without photochemical traps [19]. The mean lifetime for LHCI has the value of 2.4 ns. This decay is entirely due to the trivial decay process. The quantum efficiency of the PSI core may be then calculated using Eq. (6):

$$\varphi = (\tau_{\mathrm{LHCI}} - \tau_{\mathrm{core}})/\tau_{\mathrm{LHCI}}. \tag{6}$$

This yields the value of $\varphi = 0.99$. Of course, it would have been more appropriate to use the mean lifetime of the core antenna rather than that of LHCI for quantum efficiency determination. This however is not possible, as the PSI reaction center is an integral part of the core antenna/reaction center complex. However, we feel that the present approach is probably fairly accurate as all isolated chlorophyll/antenna complexes have mean lifetime values in the 2–3.5 ns range.

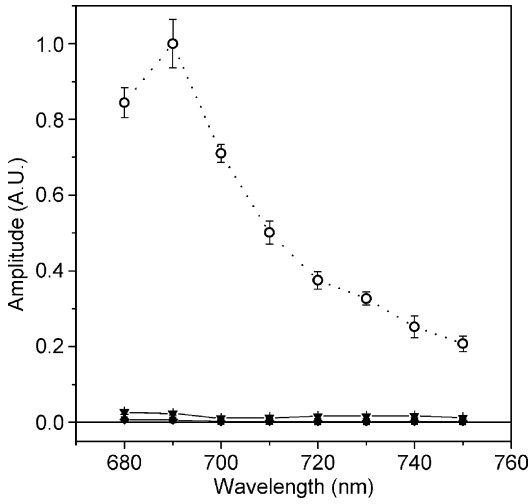

Fig. 1. Decay associated emission spectra of the purified core of maize photosystem I. Open symbols, 20±5 ps component. The minor 125 ps decay (solid triangles) is thought to represent a small contamination of PSI-LHCI while the 3900 ps component (solid squares) is due to a small amount of solubilised chlorophyll. The data are the average of three separate measurements and the vertical bars are the standard deviations from the mean.

Thus, a chlorophyll-based photosystem is capable of generating a quantum efficiency for primary charge separation of at least 0.99. It is worth commenting that this very high efficiency for PSI core is in part due to the low levels of red forms in its antenna (see DAS bandshape of Fig. 1), which is not the case for the frequently investigated cyanobacteria PSI core particles. By means of Eq. (4) it is therefore possible to conclude that a chlorophyll based photosystem may function with a maximal thermodynamic efficiency (ξ) of $\xi \geq 0.99$ ($h\nu_0 - \Delta q(1 - T/T^*)$) or $0.98 \leq \xi < 1.0$.

This conclusion regarding the maximal thermodynamic efficiency of a chlorophyll based photosynthetic system is extremely interesting from the point of view of the so-called "principle of entropy" in the second law of thermodynamics. To illustrate this, we now determine the total entropy change ($\Delta S_{\mathrm{total}}$), during primary photosynthetic charge separation. This is simply achieved by establishing the entropy balance of a photosynthetic system associated with light absorption and primary charge separation.

As pointed out by Knox [2], when a photon is removed from a light system, this undergoes an entropy change, $\Delta S_r = -h\nu_0/T_r$, where T_r is the equilibrium radiation temperature and is given by the well known Planck equation, where $u_\nu(T_r)$ is the spectral energy density

$$u_\nu(T_r) = \left(8\pi h\nu^3/c^3\right)\left(e^{h\nu/\mathrm{kTr}} - 1\right)^{-1} \tag{7}$$

and the flux density (J_ν)

$$J_\nu = u_\nu(c/4\pi). \tag{8}$$

It should be mentioned that the concept of radiant temperature, T_r, is based on the idea of $u_\nu(T)$ in equilibrium with a blackbody of temperature $T = T_r$. From Eqs. (7) and (8) it is seen to be a (weak) function of J_ν and thus varies with the source light flux. Values given for T_r in the literature vary from

around 1100 to 1300 K (e.g. [1,20]) or 5700 K [9]. On the basis of the measured energy density of the 670 nm laser pulses used in our experimental set up, we estimate that T_r=2600 K. It is therefore clear that $\Delta S_r = -h\nu_0/T_r$ also depends on the light source.

For conditions of maximal photosynthetic thermodynamic efficiency (ξ), the entropy released to the environmental bath by the photosynthetic system will be minimal and its value cannot exceed $\Delta S_{min} = +[(1-\xi)\ h\nu_0]/T$, where T is the temperature of the environmental thermal bath, usually around 300 K. For this situation, the total entropy change, $\Delta S_{total,}$ for maximal photosynthetic efficiency is given by Eq. (9)

$$\Delta S_{total} = [(1-\xi)h\nu_0]/T - h\nu_0/T_r + \Delta S_{pc}, \quad (9)$$

ΔS_{pc} is the (small) entropy decrease associated with photosynthetic photochemistry. Under the assumption that the approximately 40 π electrons of the primary donor and acceptor may be approximated as an ideal gas, one estimates $\Delta S_{pc} \approx k\ \ln(40/41) = -1.2 \times 10^{-6}\ h\nu_0\ K^{-1}$, which is approximately two orders of magnitude less than the other terms. In this simplifying assumption, we do not take into account entropy changes associated with possible environmental relaxation around the primary charge separation state. However, there is experimental evidence, at least for the PSII reaction center, that such changes are not sufficient to modify the fluorescence Stokes shift [21], as would be expected [22]. Eq. (9) may be rearranged to give

$$\Delta S_{total} = [h\nu_0(T_r - \xi T_r - T)]/TT_r + \Delta S_{pc}. \quad (10)$$

It is therefore clear that when $(T_r - \xi T_r) < T$, Eq. (10) will have a negative value. This is the case for the above mentioned values of T and T_r considering $(0.98 \leq \xi < 1.0)$. Thus, in principle, primary PSI photochemistry may function with negative entropy production. Of course, the ΔS_{pc} term, possibly underestimated here, as discussed above, would further contribute to this negative entropy production.

We now briefly examine the PSII core in the same way. This is the particle which binds the chlorophyll/protein complexes CP43, CP47 and the D1/D2/cytb559 complex of the reaction center. Several laboratories have measured fluorescence decay times which indicate that the effective photochemical trapping time (τ_{core}) is around 160 ps [11,23]. While this value is considerably slower than that for the PSI core, the quantum efficiency (φ), as calculated by Eq. (6), is 0.93 and $0.92 \leq \xi < 0.93$. Thus, for the value of T_r=2600 K of our experimental set-up, and of course for all lower values, this thermodynamic efficiency (ξ) also sustains a negative value for ΔS_{total}.

The above considerations demonstrate that the second law is violated by the core particles of both plant photosystems for primary charge separation. This conclusion is also valid for the isolated and intact PSI preparation (PSI-LHCI) in which the core binds the external antenna complexes (LHCI) and for which $0.96 \leq \varphi \leq 0.97$ ([24] and Eq. (6)). It is not however the case for the intact photosystem II particle in which the outer antenna lowers φ to values of around 0.83 [11,25,26]. Of course, under normal photosynthetic conditions, where CO_2 is being fixed, and both photosystems are required, ξ falls in the range 0.02–0.10 and ΔS_{total} has a positive value. However, we conclude that, in principle, a chlorophyll-based photochemical process may function with negative entropy production.

It should be mentioned that in the early thermodynamic literature on photosynthesis the suggestion that the fixation of CO_2 might be a negative entropy process was made [8]. This point was however subsequently further investigated by Yourgrau and van der Merwe [9] who concluded that this was not the case. It is interesting however to note that these latter authors derived an expression in which the production of negative entropy is in fact possible at very high thermodynamic efficiencies. Our present conclusions are in agreement with this result of Yourgrau and van der Merwe [9].

The free energy change corresponding to ΔS_{total} is given by $T\Delta S_{total}$. Thus, for free energy changes associated with entropy and maximal thermodynamic efficiency, we rewrite Eq. (10):

$$T\Delta S_{total} = [h\nu_0 T(T_r - \xi T_r - T)]/TT_r + T\Delta S_{pc}$$
$$= h\nu_0(1 - T/T_r) - h\nu_0\xi + T\Delta S_{pc}. \quad (11)$$

For ΔS_{total}=0, Eq. (11) becomes:

$$(1 - T/T_r) = \xi - T\Delta S_{pc}/h\nu_0. \quad (12)$$

Thus, the Carnot cycle efficiency term $(1-T/T_r)$, often discussed in the photosynthetic literature (e.g. [1,3,20]) does, in fact, have a precise physical meaning, quite different from what one might expect, and which is given by the right hand side of Eq. (12) for the condition of ΔS_{total}=0. As $T\Delta S_{pc}/h\nu_0 << \xi$, we may conclude that $(1-T/T_r)$ yields the maximal thermodynamic efficiency ($\xi = \varphi(h\nu_0 - \Delta q(1-T/T^*))$, which is not the Carnot cycle efficiency, under conditions of zero entropy change. For $\xi > (1-T/T_r)$, ΔS_{total} is negative and for $\xi < (1-T/T_r)$, ΔS_{total} is positive. Thus, $(1-T/T_r)$ represents a kind of efficiency horizon beyond which negative entropy is produced and the second law is not obeyed. As this is impossible for a heat machine, it serves to underline the difference between photosynthetic photochemistry and a heat machine.

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