

Rapid report

Reply to “Commentary on Photosynthesis and Negative Entropy Production by Jennings and coworkers” by J. Lavergne

R.C. Jennings^{a,b,*}, A.P. Casazza^a, E. Belgio^{a,b}, F.M. Garlaschi^{a,b}, G. Zucchelli^b

^a Dipartimento di Biologia dell'Università degli Studi di Milano, via Celoria 26, 20133 Milano, Italy

^b e Istituto di Biofisica del Consiglio Nazionale delle Ricerche-Sede di Milano, via Celoria 26, 20133 Milano, Italy

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Abstract

It is argued that the chemical potential analogy does not provide useful information on the thermodynamics of photosystems, as the thermodynamic efficiency of an absorbed quantum is not considered. Instead, the approach based on either entropy balance or entropy flux considerations does provide this information. At high thermodynamic efficiencies, primary photochemistry can, in principle, violate the Second Law of Thermodynamics.

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In his article entitled “Commentary on “Photosynthesis and Negative Entropy Production” by Jennings and coworkers,” Dr. J. Lavergne criticises our recently-published article [1], in which we conclude that primary charge separation in photosynthesis may violate the Second Law of thermodynamics by virtue of being, in principle, capable of negative entropy production. On the contrary, he presents the “chemical reaction analogy” view, in which photosynthetic primary reactions proceed with an overall efficiency which cannot exceed the Carnot cycle efficiency $(1 - T/T_r)$, where T is the ambient temperature and T_r is the radiation temperature, with a modification with respect to previous thoughts on the matter (e.g., [2]), in which the radiation “dilution factor” is recognised for the first time. Our reply to this article [4] is based on two main points. Firstly, we argue that the widely used “chemical reaction analogy”, while not being incorrect in itself, is unsuitable for a thermodynamic analysis of single photosystems. It is too macroscopic. Secondly, our “single photon-single photosystem approach” is correct for this microscopic level, as

can be demonstrated by the almost identical results obtained when using radiation flux parameters and specific intensity of entropy radiation.

We start out by discussing the “chemical reaction analogy”. The reaction considered is



where P is ground state chlorophyll and P^* is excited state chlorophyll. The forward reaction is promoted by photon absorption and the back reaction by excited state relaxation. The chemical potential equation is given in Eq. (2) (equivalent to Eq. (7) of [4])

$$\Delta\mu = h\nu + k_B T \ln([P^*]/[P]) \quad (2)$$

where μ is the chemical potential, ν is the photon frequency and the other symbols have their usual meaning. We note that the gas constant R and k_B are sometimes confused in this equation. With the notation “ $h\nu$ ” one must use $k_B (R/N)$, where N is Avogadro’s number). Also with the notation “ $h\nu$,” $\Delta\mu$ has the meaning $\Delta\mu/N$.

Starting off with Duysens [3], this expression has been used to conclude that

$$\Delta\mu = h\nu(l - T/T_r) \quad (3)$$

* Corresponding author. Dipartimento di Biologia dell'Università degli Studi di Milano, via Celoria 26, 20133 Milano, Italy.

E-mail address: robert.jennings@unimi.it (R.C. Jennings).

(where we add that $\Delta\mu = \Delta\mu/N$, T is the temperature of the P , P^* system under non-equilibrium conditions and T_r is the radiation temperature). Eq. (3), in this view, represents the maximum work which can be obtained from a photon, or the free energy of a photon. This is equivalent to Eq. (12) of [4]. Most recently this point of view was expressed in [2,5,6].

However, it is necessary to take into account the relation between radiation temperature and light “dilution factor” (α) [7,8], which is normally absent in this treatment. Not considering α leads to the determination of some kind of an “effective” temperature, different from that of the radiation temperature. Considering the “dilution factor”, Eq. (2) becomes

$$\Delta\mu = h\nu + k_B T \ln(\alpha[P^*]/[P]) \quad (4)$$

and Eq. (3) reads

$$\Delta\mu = h\nu(1 - T/T_r) + k_B T \ln\alpha \quad (5)$$

This “dilution factor” has, in fact, now been recognised in [4] (Eq. (15), similar to Eq. (5) above). We wish to point out that α is not a constant, but may be experimentally modulated by, for example, modifying the distance of a non-collimated light source from the P , P^* sample. Thus, according to Eq. (5), the maximum “amount of work that can be extracted per photon” changes with the light-source/sample distance. It is evident that this is not the case for the quantum efficiency or the thermodynamic efficiency of an absorbed quantum. In fact, $\Delta\mu$ contains information on the ratio of P^*/P , which is, however, of little use in analysing the thermodynamics of primary photochemistry within a photosystem. For this, it is necessary to have information on the quantum efficiency or the thermodynamic efficiency of an absorbed photon. Parson [9] reached a similar conclusion: “Evidently $\Delta\mu$ does not tell one anything about the reactions that are open to the excited molecule”.

From this brief discussion, we conclude that the Carnot cycle efficiency, even when the correct value of T_r is considered by virtue of contemplating the “dilution factor”, yields no information on the quantum efficiency or thermodynamic efficiency of an absorbed photon in a photosystem. The basic reason for this is that it is a macroscopic parameter which considers “concentration ratios” of excited photosystems and not what occurs within photosystems. The approach adopted in our paper [1] allows us to focus on this latter point.

We now discuss the approach which has been defined as the “single photon/single photosystem approach” [4]. In our paper [1], this approach, based on simple entropy balance considerations, led to equation

$$\Delta S_{\text{tot}} = [(1 - \xi)h\nu_0]/T - h\nu_0/T_r + \Delta S_{\text{pc}} \quad (6)$$

where ΔS_{tot} is the total entropy change in the photon bath and the photosystem upon absorption of a photon; and ξ is the thermodynamic efficiency of the absorbed photon. This term takes into account all energy changes from photon absorption to primary charge separation. ΔS_{pc} is the entropy decrease

associated with primary photosynthetic photochemistry. T is the environmental bath temperature, and T_r is the radiation temperature. This equation therefore contemplates *all* the entropy changes which occur during photon absorption and primary photochemistry in both the environmental bath and the photosystem. It can be rearranged to give

$$\Delta S_{\text{tot}} = [h\nu_0(T_r - \xi T_r - T)]/TT_r + \Delta S_{\text{pc}} \quad (7)$$

As ΔS_{pc} is negative, it is readily seen that for $T > (T_r - \xi T_r)$ the total entropy change will be negative. Now if we consider, by way of a numerical example, a tungsten lamp as an experimental light source, $T_r \approx 2800$ K. Then for $T = 300$ K, it is evident that positive entropy will be produced when $\xi < 0.89$. This value of ξ can be interpreted as the upper limit of the efficiency that can be reached by the physical system on the basis of the Second Law of Thermodynamics. For values of $\xi \geq 0.89$, entropy production will be negative. As we point out in [1], such high values of ξ may be contemplated for the “core” of photosystem I, and possibly also for that of photosystem II.

It has been stated that the “single photon-single photosystem” approach is “fallacious” [4], though we wish to underline that no attempt was made in [4] to demonstrate this. It is difficult to see just why our reasoning is not valid, as Eqs. (6) and (7) take into account *all* entropy changes. Moreover, our conclusion finds support in an article written in 1968 by two eminent physicists [10]. In this context we present equation 13 of Yourgrau and van der Merwe [10]

$$\eta \Delta S / nh\nu = 4/3(1 - \eta) / T - k_B / h\nu - 1/T_r \quad (8)$$

This equation shows that the global entropy change (ΔS , equivalent to our ΔS_{tot}) depends critically on the thermodynamic photosynthetic efficiency (equivalent to our ξ) and T_r , in agreement with Eqs. (6) and (7). In fact, these authors [10] state in their final conclusions, “We conclude that the Second Law will be valid, provided the efficiency is < 0.88 .” In other words, if the efficiency were greater than 0.88, then the Second Law would not be valid. For the above example of the tungsten light source ($T_r = 2800$ K, $T = 300$ K), the global entropy change using Eq. (8) is negative for $\eta \geq 0.88$, in very close agreement with our conclusion. Eq. (8) was derived by Yourgrau and van der Merwe [10] using the light flux parameters and specific intensity of entropy radiation, i.e. an approach which is very different from the entropy balance considerations which we used [1]. These two approaches are complementary: both set an equivalent upper limit on the efficiency, on the basis of the Second Law, and beyond which the Second Law is not obeyed. The “core” of PSI and PSII may reach and exceed this efficiency limit. Thus, our interpretation of the conclusions in [10] do not seem “incorrect” as stated in [4]. Moreover, in the summing up in [4], it is stated that “To conclude this review, aimed at showing that photosynthesis – unfortunately – does not decrease the entropy of this planet...”. We wish to point out that “photosynthesis and a possible entropy decrease of this planet” was not the subject of our paper. We dealt only with primary photochemistry. We write in [1] “of course, under normal photosynthetic conditions, where CO_2 is being fixed,

and both photosystems are required, the thermodynamic efficiency falls into the range of 0.02–0.1 and ΔS_{tot} has positive values”.

In addition, it is stated that “another precursor of second law violations in photosynthesis, according to Jennings et al., is Parson [4]”. We wish to clearly state that Parson [9] did *not* make the suggestion of Second Law violations (Parson does not discuss entropy) and we did *not* attribute it to him. He did, however, conclude that the recurrent use of Eq. (2) in the present context was mistaken.

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