Comment on "Minimum entropy production in photosynthesis"

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The law of minimum entropy production [1] is an important result from nonequilibrium thermodynamics. Its validity requires that the phenomenological coefficients are independent of the state variables such as the particle density n and temperature T. In its very simple derivation for the case of two flows and corresponding forces, one must assume linear phenomenological relations between forces and flows and reciprocal relations for cross-coefficients [2] describing coupling between these two different irreversible processes. One process may be considered as the primary (driving), while the other may be secondary (driven by the primary process). Such a picture is appropriate for photosynthesis where everything is driven by the photon free energy [3]. The static head nonequilibrium steady state is established if the driving force is kept constant and the driven force left to adjust its value until the driven flux vanishes [4]. The entropy production is then minimal with respect to the optimal (maximal) value of the secondary (driven) force. It is important to notice that minimum entropy production state, as defined by Prigogine [1], is a nonequilibrium steady state with constant non-zero entropy production due to the action of constant non-zero driving force and corresponding flux. Continuous free-energy transduction serves only to maintain the maximal free-energy storage in the form of the secondary force in the static head state. In terms of efficiency in producing desired power (secondary flux and force) it is zero efficiency state due to vanishing secondary flux.

This introduction serves to highlight the difference between minimal entropy production as described in the Andriesse & Hollestelle paper [5] and standard derivation and application of that theorem [1,4]. In that paper, which is using the results of an earlier paper by the same author [6], only the assumption of linear relationships between forces and flows is maintained. We shall not discuss how realistic is that assumption or their choice of driving and driven forces and flows in photosynthesis.

We shall only show that minimal entropy production state, described in these two papers [5,6], is in reality an equilibrium state with zero entropy production. For assumed linear relationship between fluxes and forces entropy production becomes a quadratic function of both forces, and can be minimized with respect to each force. After such minimization in Dr. Andriessse papers two extremal conditions are obtained, which must be fulfilled simultaneously. If Onsager reciprocity relations [2] hold, one can easily recognize these conditions as requirement for both fluxes to vanish. The entropy production then vanishes too.

Authors are specific in their claim that Onsager reciprocity relations may be [5] or should be [6] violated ($C \neq \Gamma$ in their notation) and that both fluxes are different from zero when entropy production has reached its minimum. They apparently do not see that their flux ratio is then equal to negative force ratio (explicitly seen in earlier Dr. Andriesse paper [6] as equations (9) and (10)). They have obtained $J_2/J_1 = - X_1/X_2$, if primary force-flux couple is labeled with X_1, J_1 and secondary force-flux couple with X_2, J_2. Since the entropy production is proportional to $X_1J_1 + X_2J_2$, it must be equal to zero in their minimum entropy production state.

Therefore, it does not really matter whether Onsager relations are broken in the linear range near equilibrium or not. In both cases the minimal entropy production state described by the authors is the zero entropy production state of chemical or thermodynamic equilibrium. This is only to be expected. When all of present forces are used in the minimization process, then none of them is subject to a constraint and one is bound to obtain equilibrium as a steady state.

If we accept authors claim that fluxes (and forces) are different from zero in the state of minimal entropy production, as defined by them, then the efficiency of free energy transduction (of photon energy into glucose synthesis) must be 100%. This is seen when their $J_2/J_1 = - X_1/X_2$ result is inserted in the ratio $-X_2J_2/X_1J_1$, which is the efficiency of free-energy conversion [7].

It is worthy of note how authors avoided this obviously strange result (100% efficiency and zero entropy production) in the second part of their paper during efficiency estimations. There they do not see that force ratio can not be taken from literature as the factor 2.72 in the favor of the secondary force [5], but is fixed from the outset by their minimum entropy production requirement as being equal to negative flux ratio. With their best estimate for the flux ratio of 0.022, their secondary force would have to be 45 times higher than the primary force.

In conclusion, author's minimum entropy production requirement has nothing to do with the minimum entropy production law [1]. It simply describes the equilibrium state. Since in equilibrium all fluxes and forces vanish, free-energy transduction is impossible. It is the thermodynamic death of the system, as much opposed to bioenergetic processes maintaining life, such as the photosynthesis, as possible.

Even if the equilibrium state is a realistic picture of what is going on in stars [6], it is certainly not a good description of photosynthesis in which the driving force is considerably higher than the k_BT. The intensity of free-energy transduction in chloroplast, or in photosynthetic bacteria is at least 10^5 times more intensive than in the Sun, or in any other Sun-like star [8]. The input force in photosynthesis is both high and fixed at any given time and should not be used for the minimization of overall entropy production.

References:

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