Thermodynamic Analysis of Photosynthesis

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A classical example of thermodynamic analysis of a biological process has been given about 1940 by E. Schrödinger in his famous treatise "What is life" [PH1]. The process considered is photosynthesis which is an endergonic system of chemical reactions occurring in phototrophs (plants etc.) during which carbohydrates are formed from carbon dioxide (CO_2) and water (H_2O) by using the exergy of solar radiation [PH2]. A schematics of this process is sketched in Fig. PH1 below.
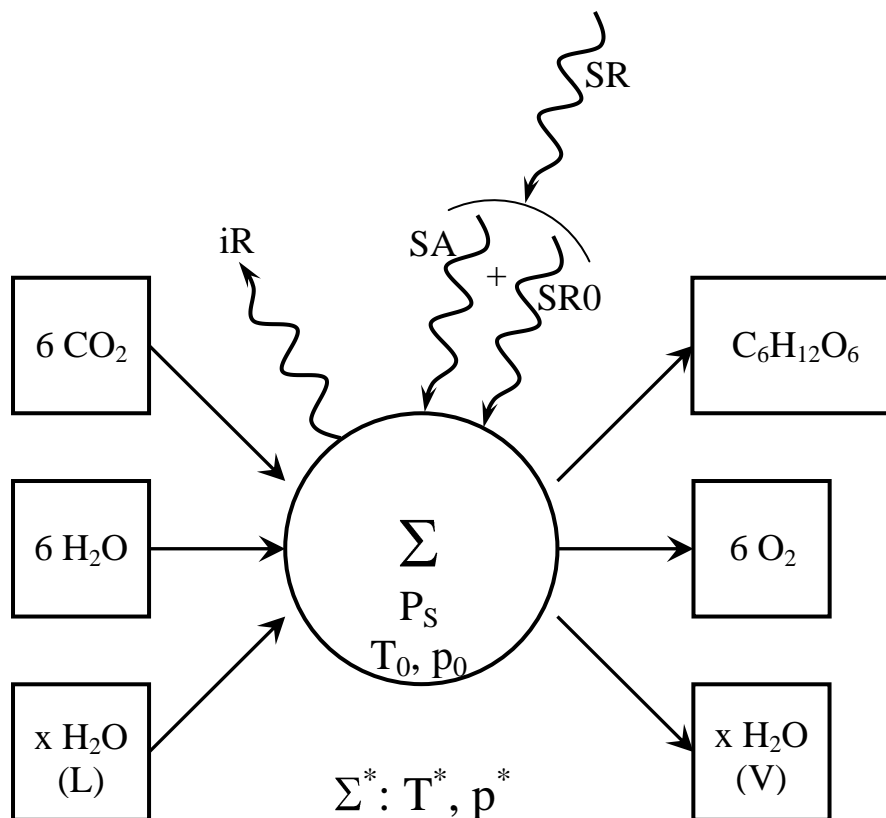

Fig. PH1. Ideal phototrophic system Σ (leaves of a tree) converting carbon dioxide (CO_2) from air and liquid water (H_2O) to carbohydrates – for example – D-glucose ($C_6H_{12}O_6$) and oxygen (O_2) by using the exergy of solar radiation (SR). In addition, solar radiation may be absorbed in the leaves to evaporate water or to be reemitted as infrared radiation (IR), both processes serving to export entropy produced during the photosynthesis process. Environmental system: Σ* with temperature T*. The incoming solar radiation is split into two parts:
 SR = SR0 + SA, this partition to be explained later on.

The photosynthesis system Σ represents mainly the leaves of a tree. Carbon dioxide is extracted from the ambient air and together with water provided by osmotic effects to the leaves and sun light or solar radiation (SR) to form – for example – D-glucose ($C_6H_{12}O_6$) and oxygen (O_2) which is emitted to the air. The glucose actually is a transient product which afterwards is transformed to more complex molecules like starch, cellulose, lignocellulose etc. by polymerisation etc.

The solar radiation absorbed in the system is used in different ways, namely

a. to perform the photosynthesis process itself via adenosine-triphosphate (ATP) as energy carier and the enzyme RUBISCO;

b. to evaporate water ($H_2O(L) \rightarrow H_2O(V)$) and

c. to be reemitted as infrared radiation (IR).

Processes (b, c) serve to export entropy from the system being produced during photosynthesis. In principle this entropy export also could be performed by heat transfer from the system (leaves) to its surroundings (air). Actually this does not happen in phototrophs as mechanisms (b, c) are much more effective. But heat transfer is essential in thermotrophs as they exist in the (dark) deep sea in the surroundings of so-called black chimneys [PH3]. For sake of simplicity we assume the system Σ and its surroundings Σ^* to be at standard temperature ($T_0 = T^* = 298.15$ K) and pressure $p_0 = p^* = 1$ atm.

In a rough and highly lumped manner the photosynthesis process can be described by the stochiometric equation

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \tag{PH1}$$

The reverse (exergonic) process, respiration, normally does not occur in plants, but is essential for aerobic living systems, taking place in their muscles etc., the oxygen being provided by air.

The energy balance related to reaction (PH1) in stationary states of the open system Σ is

$$6\Delta H_{CO2} + 6\Delta H_{H2O} - \Delta H_{GLU} - 6\Delta H_{O2} + E_{SR} - E_{IR} = 0. \tag{PH2}$$

Here ΔH_{XYZ} indicates the molar enthalpy of formation of the chemical component (XYZ) and (E_{SR}) is the energy of the highly exergetic solar radiation absorbed by the system Σ during synthesis of one mole of D-glucose. E_{IR} is the energy of the infrared radiation emitted to the ambient during this process.

The molar enthalpies and entropies in equation (PH2) refer to the formation reactions of the respective pure substances ($C_{XYZ} = H_2O, CO_2, C_6H_{12}O_6, O_2$) from their chemical elements ($E^{(1)} = C, E^{(2)} = H, E^{(3)} = O$) in (well defined) standard states [PH4], [PH5]. Given the stochiometric equation

$$xE^{(1)} + yE^{(2)} + zE^{(3)} \rightarrow C_{xyz}, \tag{PH3}$$

we have from the 1st Law

$$\Delta H_{xyz} = H_{xyz} - xH^{(1)} - yH^{(2)} - zH^{(3)} = Q_{xyz}. \tag{PH4}$$

Here ($H^{(i)}$, i = 1, 2, 3) are the molar enthalpies of the pure chemical elements ($E^{(i)}$, i = 1, 2, 3) and $Q_{xyz} \gtrless 0$ is the heat to be supplied (>)for or gained (<) by performing the reaction (PH3), ecucts and products assumed to be in standard reference states. The respective reaction scheme is sketched in Figure PH2
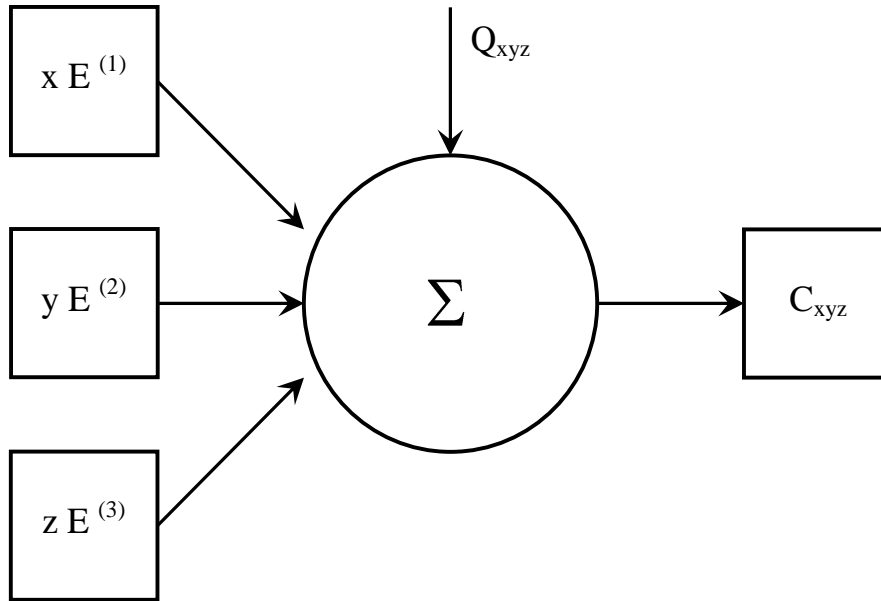
Fig. PH2. Ideal chemical reactor (Σ) in which pure component (C_{xyz}) is formed from pure chemical elements ($E^{(1)}$, $E^{(2)}$, $E^{(3)}$) all substances being at standard states [PH4].

Similarly to the 1st Law of Thermodynamics, i. e. the energy balance (PH2) of the reaction (PH1), we can formulate from the 2nd Law of Thermodynamics the entropy balance of the phototrophic system in stationary states as

$$6\Delta S_{CO2} + 6\Delta S_{H2O} + S_{SR} - \Delta S_{GLU} - 6\Delta S_{O2} - S_{IR} + P_S = 0 \qquad \text{(PH5)}$$

The symbol ΔS_{XYZ} is the molar entropy of formation of the component (C_{XYZ}), S_{SR} is the entropy content of the solar radiation with energy (E_{SR}); similarly S_{IR} is the entropy content of the infrared radiation with energy E_{IR} and P_S in units (kJ / mol Glucose K) is the entropy production of reaction (PH1) per mole of glucose produced. This quantity must be non-negative, i. e. we have

$$P_S \geq 0 \qquad \text{(PH6)}$$

in all real photosynthesis processes according to the 2nd Law of Thermodynamics [PH6].

The radiation entropies S_{SR} and S_{IR} are approximated by their black body radiation values via the Boltzmann relations [PH7]

$$S_{SR} = \frac{4}{3} \frac{E_{SR}}{T_{SR}}, \qquad S_{IR} = \frac{4}{3} \frac{E_{IR}}{T_0} \qquad\qquad (PH7)$$

Here $T_{SR} = 5,800$ K is the temperature of the photosphere of the sun and $T_0 = 298.15$ K the temperature of the system Σ chosen to be the standard reference temperature of chemical thermodynamics.

For numerical calculations the molar masses and some thermodynamic data of the educts (CO_2, H_2O) and the products ($C_6H_{12}O_6$, O_2) of the photosynthesis reaction (PH1) are given in Tab. PH1 below [PH8, p. 271].

	M	**ΔH**	**ΔS**	**ΔG = ΔH - T ΔS**
	g/mol	kJ/mol	kJ/molK	kJ/mol, T = 298 K
CO_2	44	-394.1	0.0009	-394.36
H_2O	18	-286	-0.1638	-237.18
$C_6H_{12}O_6$	180	-1,264	-0.1637	-917.22
O_2	32	0	0	0

Tab. PH1. Thermodynamic data of reactants in Eq. (PH1), [PH8].

Using the ΔH-data, the net radiation energy E_{SR0} needed to synthesize one mole of D-glucose without any infrared radiation to be reflected from the system can be calculated from the energy balance (PH2) of the process. Indeed, assuming $E_{IR} = 0$ we have

$$E_{SR0} = \Delta H_{GLU} + 6\ \Delta H_{O2} - 6\ \Delta H_{CO2} - 6\ \Delta H_{H2O} \qquad\qquad (PH8)$$

Using the data of Tab. PH1 we get

$$E_{SR0} = 2,816 \text{ kJ / mol glucose} \qquad\qquad (PH8a)$$

leading formally to an energetic efficiency of

$$\mu_0 = \frac{\text{enthalpy of formation of 1 mol glucose}}{\text{expenditure of radiation energy to produce 1 mol glukose}} = \tag{PH9}$$

$$= \frac{\Delta H_{GLU}}{E_{SR0}} = \frac{1,264}{2,816} = 45\%$$

Note that the radiation energy E_{SR0} has to be absorbed by the leaves, that is in reality much more radiation is needed as neither reflection nor emission of radiation by the leaves has been taken into account in this hypothetical reference process.

Considering the entropy production per mole glucose produced (P_{S0}) in this process we get from equation (PH5) with $S_{IR} \simeq E_{IR} = 0$ and (PH7), i. e. $S_{SR0} = 4\,E_{SR0}/(3T_{SR})$ using the data of Tab. PH1 and (PH7), (PH8a)

$$P_{S0} = \Delta S_{GLU} + 6\,\Delta S_{O2} - 6\,\Delta S_{CO2} - 6\,\Delta S_{H2O} - S_{SR0} \tag{PH10}$$

$$= -0.8337 \text{ kJ/Kmol glucose} < 0 \tag{PH10A}$$

This numerical result clearly violates the 2nd Law of Thermodynamics, i. e. inequality (PH6). Hence, a photosynthesis process of this type, i. e. with $E_{IR} = 0$ cannot exist. To overcome this difficulty we assume that in addition to the solar radiation SR with energy E_{SR0}, entropy $S_{SR0} = 4\,E_{SR0}/(3T_{SR})$, radiation SA with energy E_{SA} and entropy $S_{SA} = 4\,E_{SA}/(3\,T_{SR})$ is absorbed in the system Σ and reemitted as infrared radiation with energy $E_{IR} = E_{SA}$ and entropy $S_{IR} = 4\,E_{IR}/(3T_0)$. Hence we get from the entropy balance (PH5) with

$$S_{SR} = S_{SR0} + S_{SA} \tag{PH11}$$

$$= \frac{4}{3T_{SR}}(E_{SR0} + E_{SA}),$$

$$S_{IR} = \frac{4}{3T_0} E_{IR} \tag{PH12}$$

$$E_{SA} = E_{IR} \tag{PH13}$$

the relation

$$-P_{S0} + \frac{4}{3}\left(\frac{1}{T_{SR}} - \frac{1}{T_0}\right)E_{SA} + P_S = 0 \tag{PH14}$$

with P_{S0} being defined by eq. (PH10). From it we can calculate for reversible processes, i. e. $P_S = 0$, the radiation energy E_{SA0} which additionally to E_{SR0} at least must be absorbed by the system Σ (leaves) to realize the photosynthesis process as

$$E_{SA0} = -\frac{3}{4}P_{S0} / \left(\frac{1}{T_0} - \frac{1}{T_{SR}}\right) \tag{PH15}$$

$$= 196.5 \text{ kJ / mol glucose} \tag{PH15a}$$

The total radiation energy needed for this process is

$$E_{SR} = E_{SR0} + E_{SA0} \tag{PH16}$$

$$= 3{,}012.5 \text{ kJ / mol glucose} \tag{PH16a}$$

leading to an upper bound of the energetic efficiency of photosynthesis as

$$\mu_S = \frac{\Delta H_{GLU}}{E_{SR}} = \frac{1{,}264}{3{,}012.5} = 42\% \tag{PH17}$$

Note that this maximum efficiency only holds if infrared radiation is used to export entropy from the photosystem.

Another possibility to overcome the prohibitive result (PH10a) is to use extra solar radiation being absorbed in the photosystem to evaporate water available in the system. Actually, this process serves in nature as a very effective means to balance the 2nd Law as has been demonstrated by E. Schrödinger already in the 1940s. The stochiometric reaction (PH1) is complemented by the "evaporation reaction" of water

$$x(H_2O)_L \rightarrow x(H_2O)_V \tag{PH18}$$

where x is the number of moles of water which is evaporated, that is transferred from the liquid state (L) to the vapor state (V) at $T_0 = 289.15$ K per mole of glucose produced in reaction (PH1). The radiation energy needed to realize processes (PH1) and (PH18) is

$$E_{SR} = E_{SR0} + x r^{LV}_{mH_2O} \qquad \text{(PH19)}$$

with $r^{LV}_{mH_2O} = 43.2$ kJ / mol water being the molar latent heat of water at $T_0 = 298.15$ K.

The entropy of this radiation is in the "black body approximation"

$$S_{SR} = S_{SR0} + \frac{4 r^{LV}_{mH_2O}}{3 T_{SR}} x \qquad \text{(PH20)}$$

with $S_{SR0} = 4 E_{SR0} / (3 T_{SR})$, cp. (PH10). Assuming also that no infrared radiation is emitted in this case, i. e.

$$E_{SA} = E_{IR} = 0 \qquad \text{(PH21)}$$

and hence

$$S_{SA} = S_{IR} = 0, \qquad \text{(PH22)}$$

the entropy balance (PH5) for the combined processes (PH1), (PH18) can be written as

$$-P_{S0} + x(\Delta S^L_{H_2O} - \Delta S^V_{H_2O}) + \frac{4 r^{LV}_{mH_2O}}{3 T_{SR}} x + P_S = 0 \qquad \text{(PH23)}$$

with P_{S0} being defined by (PH10). For reversible processes, i. e. $P_S = 0$, the minimum mole number x_{rev} of water to be evaporated for entropy export can be calculated from eq. (PH23) as

$$x_{rev} = P_{S0} / (\Delta S^L_{H_2O} - \Delta S^V_{H_2O} + \frac{4 r^{LV}_{mH_2O}}{3 T_{SR}}) \qquad \text{(PH24)}$$

The entropies of formation of water in the liquid state $\Delta S_{H_2O}^L$, and isothermal gaseous state $\Delta S_{H_2O}^V$ are related by the equation

$$-\Delta S_{H_2O}^L + \Delta S_{H_2O}^V = \frac{r_{mH_2O}^{LV}}{T_0} \tag{PH25}$$

Hence we get with $r_{mH_2O}^{LV} = 43.2$ kJ/mol water, T = 298.15 K in view of (PH10a) from (PH24)

$$x_{rev} == 6.18 \frac{\text{mol water}}{\text{mol glucose}} \tag{PH24a}$$

This is the minimum number of moles of water which must be evaporated per mole of glucose produced in the system if all the entropy produced during photosynthesis is exported by evaporation of water only, i. e. without any radiative entropy export, cp. (PH15).

The radiation energy needed for processes (PH1) and (PH18) is according to (PH19) and (PH8a)

$$\begin{aligned} E_{SR} &= (2,816 + 6.18 \cdot 43,2) \text{ kJ/mol} \\ &= 3,083 \text{ kJ/mol glucose} \end{aligned} \tag{PH19a}$$

This leads to an upper bound of the energetic efficiency

$$\mu_E = \frac{\Delta H_{GLU}}{E_{SR}} = \frac{1,264}{3,083} = 41\% \tag{PH17a}$$

being slightly smaller than the radiation related efficiency $\mu_S = 42$ %, cp. (PH17).

In nature both mechanisms for entropy export, namely by transfer of solar radiation to infrared radiation and by evaporation of water, are used depending mainly on the availability of water to the plant. In any case, water supply is very important for all botanical growth processes and evaporation of water is – beside radiation absorption and emission – a very effective process for a phototropic organism to get rid of the entropy produced.

This simple example clearly demonstrates that in biosystems it is very important, if not decisive to choose the appropriate scheme of chemical and physical reaction processes underlying the thermodynamic analysis. Otherwise one may run into difficulties as shown for example by eq. (PH10a). Similar discrepancies also have been discussed in the analysis of glycolysis in literature [PH9].

To elucidate the overall energetic situation of a real phototrophic system we will present basic data of the photosynthesis process of an oak tree (fagus sylvatica) in central Europe. The tree at age 100 years typically is 20 m in height and its branches and leaves are limited by a sphere with diameter 12 m. The leaves cover an area of 1,600 m^2 producing during a summer day with 10 hours of sunshine $p_{GLU} = 7.5$ g / (m^2 day) D-glucose ($C_6H_{12}O_6$). The average power density of direct sunshine is assumed to be $\sigma = 0.8$ kW/m^2. This tree produces 12 kg / day glucose and 12.8 kg / day oxygen (O_2) taking 17.6 kg / day carbon dioxide (CO2) from air and 7.2 kg/day water from the leaves . The radiation energy needed for this process is 205 MJ /day which is 6.3 % of the total radiation energy available per day, namely $E_{sd}^* = 3.26$ GJ / day. These data hold under the assumption that the photosynthesis process is reversible and all the entropy produced is exported by evaporation of water only. The enthalpy stored in the glucose produced per day is 84.3 MJ /day which is 2.6 % of the total radiation energy E_{sd}^* available per day. If this energy were only used to evaporate water at 25 °C, the mass $m_{w0} = 1,360$ kg /d could be steamed. However, in evaluating this figure one should take into account that water in the leaves of a tree is in a kind of sorbed state and not in the ordinary liquid state. That is, it first has to be transported from micro-channels within the leaves to its surface and only then can be transferred to the gaseous state. Hence, the evaporation energy of water $r_{H_2O}^{LV} = 2,400$ kJ / kg has to be replaced by its desorption energy which typically is twice as large as $r_{H_2O}^{LV}$, thus reducing the amount of water evaporated to half of its value namely $m_{w1} \cong 700$ kg / day. Taking also reflection of approximately 30 % of sunlight from the leaves into account this amount is again reduced to 70 % of its value namely $m_{w2} \cong 490$ kg / day which is near measured data of $m_w \simeq 400$ kg / day, [PH10].

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