Entropy production and the Second Law in photosynthesis

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Abstract

An assertion that the primary photochemistry of photosynthesis can violate the Second Law of thermodynamics in certain efficient systems has been put forward by Jennings et al., who maintain their position strongly despite an argument to the contrary by Lavergne. We identify a specific omission in the calculation of Jennings et al. and show that no violation of the Second Law occurs, regardless of the photosynthetic efficiency. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Application of thermodynamics to the determination of photosynthetic efficiency has a long history, whose description may be found in the many sources cited in references [1–11]. Its principal origin is the treatment by Duysens [1]. In a recent publication, Jennings et al. [4] claim that in certain circumstances the initial reaction of photosynthesis violates the Second Law of thermodynamics. This claim has been challenged by Lavergne [5], whose arguments are clearly not accepted by the former authors [6]. We point out here that Jennings et al. omitted a significant contribution to the entropy production, namely that which accompanies the initial photoexcitation. Restoring this term brings the process into accord with the Second Law.

2. Entropy changes associated with photoexcitation

The Second Law, in asserting that entropy production must be positive or zero, refers either to total entropy production within an isolated system or to internally-generated entropy production in an open system [12–14]. Consider the radiation (r), an ensemble of one or more pigments (p), and the surroundings (s) as an isolated system undergoing the process of absorption. We interpret "pigment" broadly to include whatever molecular components are involved in the initial photoexcitation prior to charge separation. The entropy change in the system when the pigment absorbs a photon is

$$\Delta S_{\text{total}} = \Delta S_{\text{r}} + \Delta S_{\text{p}} + \Delta S_{\text{s}}, \tag{1}$$

where the subscripts refer respectively to the three mentioned subsystems. Jennings et al. correctly evaluate ΔS_{r} as $-h v_0/T_{\text{r}}$, where $h v_0$ is the photon energy and T_{r} is the radiation temperature. They also evaluate ΔS_{s} as a positive contribution given by $(1-\xi)$ $h v_0/T$, where ξ is the fraction of the photon energy that goes into charge separation, i.e., does photochemical work, and T is the ambient temperature. We are left to evaluate the pigment contribution, ΔS_{p}, which can be separated temporally into two components, one accompanying the initial photoexcitation and the second accompanying dispersal of a fraction $1-\xi$ of the absorbed energy to the surroundings. We first treat the photoexcitation.

Consider an ensemble of N distinguishable pigments distributed among a set of eigenstates, the number of pigments in state i being n_i. The statistical entropy of such an ensemble is given by Boltzmann's expression,

$$S_{\text{p}} \equiv k_B \ln\left(\Omega_{\text{p}}\right) = k_B \ln\left(\frac{N!}{\prod_{\text{i}} n_i!}\right), \tag{2}$$

where k_B is Boltzmann's constant and Ω_p, the statistical weight or multiplicity of the distribution, is the number of ways of assigning the pigments to the microscopic states consistent with

the specified populations (see, e.g., [12–15]). Although Eq. (2) is used most commonly for systems at thermal equilibrium, it is generally accepted as a definition of entropy for a system with any given distribution. In particular, Eq. (2) could represent the entropy of an ensemble of pigments immediately following absorption of light, when n_e molecules are in an electronically excited state (e). If one of the excited molecules decays back to a ground state (g), releasing a photon, the population of state e will decrease from n_e to $n_e - 1$ while that of g increases from n_g to $n_g + 1$. The entropy of the ensemble then becomes

$$S_p = k_B \ln(\Omega_p) = k_B \ln \left(\frac{N!}{(\prod_i n_i!)\left(\frac{n_g+1}{n_e}\right)} \right). \tag{3}$$

The difference between the pigment entropy in the excited and ground states thus is

$$\Delta S_p = k_B \ln \left(\frac{N!}{\prod_i n_i!} \right) - k_B \ln \left(\frac{N!}{(\prod_i n_i!)\left(\frac{n_g+1}{n_e}\right)} \right)$$

$$= k_B \ln \left(\frac{n_g+1}{n_e} \right). \tag{4}$$

Since g is a ground state, we can assume that the ensemble is sufficiently large so that $n_g \gg 1$. Eq. (4) then simplifies to

$$\Delta S_p = k_B \ln(n_g/n_e). \tag{5}$$

This is our main expression for the entropy change associated with excitation of the pigment.

If the pigment ensemble is at thermal equilibrium at temperature T, the relative populations of the ground and excited states will conform to the Boltzmann distribution,

$$n_g/n_e \approx \exp(hv_0/k_B T). \tag{6}$$

In this limit, Eq. (5) evaluates to

$$\Delta S_p = k_B \ln(n_g/n_e) \approx \frac{hv_0}{T}. \tag{7}$$

If the pigments are in thermal equilibrium with radiation at the same temperature (i.e., if $T_r = T$), the entropy change of the radiation during absorption is $-hv_0/T$. The sum of the entropy changes in the pigment and radiation field is then zero, as one expects for a reversible process.

The fact that thermal excitation of a pigment at energies of interest to photosynthesis is an extremely unlikely event does not affect the evaluation of the entropy change. Presence of an activating radiation field with a higher effective temperature simply raises the probability of excitation to a functional level.

The result (7) can also be obtained by using the thermodynamic definition of temperature for a system at thermal equilibrium:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{V,N}, \tag{8}$$

where U is the internal energy of the system [12–14]. From Eq. (8),

$$\Delta S_P = \left(\frac{\partial S}{\partial U} \right)_{V,N} \Delta U + \cdots = \frac{1}{T} hv_0 + \cdots. \tag{9}$$

Higher terms in the expansion traditionally are neglected.

In the limit of high intensities, where the population ratio n_e/n_g is driven to unity, ΔS_p would become zero. If this is also an equilibrium situation, the net entropy change of radiation and pigment remains zero, because ΔS_r decreases in parallel with ΔS_p. A discussion of the dependence of ΔS_p on the light intensity for systems that are not in thermal equilibrium is provided in the Appendix.

It is instructive to compare the entropy change for exciting a single pigment molecule to that for exciting an ensemble of pigments. We assume that the individual pigment is connected to a thermal bath that does not absorb light directly, but serves to set the probabilities of finding the pigment in various states before the excitation. As a limiting case, let the pigment have only two states, ground (g) and excited (e), and let the energy gap between these states be much greater than the thermal energy of the bath. The pigment then is assured to be in g before the excitation ($n=1$, $n_e=0$) and in e afterward ($n_g=0$, $n_e=1$). Since the pigment distribution has a statistical multiplicity of unity both before and after excitation, Eqs. (2)–(4) give $\Delta S_p=0$. However, such a two-state pigment cannot realistically represent a molecule as large as chlorophyll, which has a vast number of rotational–vibrational sublevels of both the ground and excited electronic states. The excitation light will drive transitions between many different combinations of these microscopic states. Electronic excitation of an individual molecule thus has a configurational multiplicity that is formally equivalent to the multiplicity associated with exciting an ensemble of pigments. The entropy change is given by Eq. (5) with the population ratio n_g/n_e replaced by p_g/p_e, where p_i is the summed probability of finding the pigment in any of the rotational–vibrational sublevels of electronic state i. At low light intensity, we again obtain $\Delta S=hv_0/T$, with the provision that the electronic energy gap (hv_0) represents a thermally-weighted average over the rotational–vibrational sublevels of the ground state.

If excitation does not change the pigment's volume significantly, the increase in enthalpy when the pigment absorbs a photon is the same as the change in internal energy (hv_0). The pigment's increase in Gibbs free energy per photon absorbed ($\Delta G_p=hv_0 - T\Delta S_p$) then is zero at low light intensities where the enthalpic and entropic terms cancel, and increases to hv_0 at high intensities as n_e/n_g approaches 1 and the entropic term drops out.

For photosynthetic systems operating in continuous light, the effective radiation temperature T_r is typically in the vicinity of 1100 to 1300 K [1–3,9], so that $\Delta S_r \approx (1/4)hv_0/T$. However, the excited pigment molecules decay rapidly by electron-transfer reactions and other mechanisms in addition to fluorescence and stimulated emission. These decay paths decrease the n_e/n_g ratio, increasing ΔS_p and reducing ΔG_p as discussed in more detail in the Appendix.

3. Applicability of the Second Law

The first specification of the Second Law, given above, is that the entropy of an isolated system will not decrease. This applies to any time interval longer than the time scale of the thermal fluctuations of the system. Consider again the situation shortly after excitation of the pigment, when no energy has been dissipated to the environment, so that $\Delta S_s = 0$. At low light intensities such that $\Delta S_p \approx hv_0/T$, the total entropy change during excitation is

$$\Delta S_{total} = \Delta S_r + \Delta S_p = -\frac{hv_0}{T_r} + \frac{hv_0}{T}. \tag{10}$$

Since $T_r > T$, Eq. (10) shows clearly that the total entropy increases during the excitation. The magnitudes of ΔS_r and ΔS_p both decrease at higher light intensities, but the net entropy change remains positive in accord with the Second Law.

Following the initial excitation, vibrational relaxations of the pigment will transfer a fraction $1 - \xi$ of the excitation energy to the environment. The entropy changes associated with this process can be evaluated via Eq. (8). If the pigment and the environment are both at temperature T, the entropy of the surroundings increases by $\Delta S_s = (1-\xi)hv_0/T$, while the pigment entropy decreases by the same amount, so that the net change in entropy is zero. More generally, steady-state excitation may raise the pigment to a somewhat higher temperature (T_p), making the overall entropy change, $(1-\xi)hv_0(1/T-1/T_p)$, positive. Restricting ourselves again to low light intensities, and using temperature T_p for the pigment throughout, the total entropy change including both the initial excitation and vibrational relaxation will be

$$\Delta S_{total} = \Delta S_r + \Delta S_p + \Delta S_s = hv_0\left(\frac{1}{T_p} - \frac{1}{T_r}\right)$$
$$+ (1-\xi)hv_0\left(\frac{1}{T} - \frac{1}{T_p}\right). \tag{11}$$

This is greater than zero for any value of ξ between 0 and 1 since $T_r > T_p > T$. The Second Law thus continues to hold after vibrational relaxation of the pigment, as we would expect. Further, an entropy increase accompanying dissipation of vibrational energy to the environment could make the overall process of absorption and relaxation occur spontaneously even if there is no net change in entropy in the initial absorption.

The entropy changes up to the point where the photosystem is poised to perform work can be related to photosynthetic efficiencies as follows. Under the conditions for which Eq. (11) holds, the change in entropy of the photosystem per photon absorbed is $\Delta S = \xi hv_0/T_p$. In this case $T_p \leq T_r$, so we have $\Delta S_p \geq \xi hv_0/T_r$. The change in the internal energy of the photosystem (ΔU_p) is ξhv_0. We thus find that the change in Helmholtz free energy of the photosystem is limited by

$$\Delta F_p \leq \xi hv_0 - T_p(\xi hv_0/T_r) = \xi \cdot hv_0 \cdot (1 - T_p/T_r). \tag{12}$$

The last factor in parentheses reduces to the usual Carnot factor when $T_p = T$, which is the case usually assumed.

4. Discussion

To facilitate comparison with the expression used by Jennings et al. [4], Eq. (11) can be rearranged as

$$\Delta S_{total} = \xi hv_0/T_p - hv_0/T_r + (1-\xi)hv_0/T. \tag{13}$$

The critical equation of Jennings et al. is their Eq. (9):

$$\Delta S_{total} = -hv_0/T_r + (1-\xi)hv_0/T + \Delta S_{pc}, \tag{14}$$

where hv_0, T_r and ξ have the same meanings as here. (Jennings et al. [4] refer to ξ as the "thermodynamic efficiency" and identify the quantity $(1-\xi)hv_0$ as the Stokes shift of the absorbing pigment. More precisely, $(1-\xi)hv_0$ is the contribution to the Stokes shift from the reorganization energy of the excited state, as the contribution from the ground state is realized only when and if the excited pigment fluoresces.) Jennings et al. identify the term ΔS_{pc} as an entropy decrease associated with charge separation, which they estimate to be much smaller than the other terms. We will consider ΔS_{pc} to be negligible or to be included among the processes subsequent to vibrational relaxation of the photopigment.

When Eq. (13) is compared with Eq. (14), the term $\xi hv_0/T_p$ is seen to be missing in the latter. This omission is key to Jennings et al.'s claim of negative entropy production. It appears that the authors miscalculated the pigment entropy change on absorption at the outset. The error originates in the paragraph in the right column of page 252, where they state that during absorption ΔS_p (their ΔS)=0. They considered only the entropy changes associated with vibrational states, not observing that an increase in the pigment entropy occurs during electronic excitation.

In earlier days, the available work in a photochemical system occasionally was confused with the internal energies of the individual components of the system, a situation that was clarified by 1978 [2]. The work of Jennings et al. is partly a revisitation of this problem, in which the authors compare their analysis by what they call a "single photon/single photosystem approach" with a calculation of the available work by a "chemical reaction analogy." The latter refers to a process occurring in an ensemble of photosystems, where the concentrations of the molecules in the reactant and product states become pertinent. However, this distinction has little bearing on the point at issue here. As discussed above, the entropy change associated with electronic excitation of an individual pigment molecule is no different from the entropy change for an ensemble of molecules, as long as we consider the wealth of microscopic states that are available to any polyatomic molecule.

The statement by Jennings et al. [4,6] that their conclusions agree with those of Yourgrau and van der Merwe [7] appears to reflect a misunderstanding of the latter authors. Yourgrau and van der Merwe discussed the change in the entropy of the radiation field (ΔS_r) and, like Jennings et al., did not consider the entropy change in the absorber. However, their stated aim was to compare the change in the entropy of the radiation field with the entropy change for the chemical reaction $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$. The latter quantity had been

calculated independently from the entropies of formation of the reactants and products. Yourgrau and van der Merwe concluded that the overall entropy change would be positive if the process consumed 3 photons with an energy efficiency of less than 0.88; the entropy increase associated with dispersing the remaining fraction of the absorbed energy would outweigh the decrease in the radiation entropy and the decrease in chemical entropy associated with CO_2 fixation. Since the pigments return to their original states before the end of this process, the entropy change for the initial excitation is immaterial to the overall entropy change, as are the entropy changes in the other intermediate steps of the reaction. By contrast, Jennings et al. consider only part of the complete cycle, beginning at a stage when a photopigment is still in an excited electronic state, which, if treated correctly, must include the entropy increase associated with excitation.

As Lavergne [5] points out, Jennings et al. may also have been influenced unduly by the fact that the Second Law of thermodynamics does not necessarily hold on short time scales in small systems [16]. Such violations of the Second Law invariably disappear on averaging over macroscopic ensembles, longer time scales or larger numbers of states, and do not constitute a challenge to the conventional understanding or application of that Law [17].

Earlier discussions of the entropy of photosynthesis [1,3,8–10] included the entropy increase for absorption as $\Delta S_p = h\nu_0/T$, although this formulation was rarely justified in the detail offered above. Using a similar statistical treatment of the pigment entropy, Weinstein [15] showed that spontaneous fluorescence also obeys the Second Law. Several different expressions have been used for ΔS_r, and Yourgrau and van der Merwe [7] suggested still another treatment of this term. As indicated above, we consider the expression $\Delta S_r = -h\nu_0/T_r$ to be correct and have no disagreement with Jennings et al. here (see [3] for discussion of this point).

The name "thermodynamic efficiency" for the quantity ξ seems inappropriate. As used both here and by Jennings et al. [4], ξ is the ratio of two system parameters, ΔV_{pc} and $h\nu_0$, where ΔV_{pc} is the change in potential energy of the photosynthetic apparatus associated with charge separation. As we have seen above, this is not the same as the classical thermodynamic "Carnot efficiency," which refers to the quantity $(1 - T/T_r)$. Jennings et al. apparently prefer their definition of efficiency because the Carnot efficiency depends on geometric factors such as the degree of collimation of the light and is therefore not specific to the photosystem being considered. While this is only a matter of definition, using the term efficiency increases the likelihood of errors of interpretation. The factor ξ might be more appropriately called the energy yield.

In conclusion, the "efficiency horizon beyond which … the second law is not obeyed" [4] is non-existent, whereas the factor $(1 - T/T_r)$ represents a real limitation on the useful work of a photochemical system at low light intensities. The fraction of the photon energy that is captured on each excitation (ξ) can be higher than the Carnot factor, and in principle could exceed 1 if the system absorbs heat from the surroundings and undergoes an entropy increase during the relaxation. But regardless of the value of ξ, it is *not* the case that "... primary photochemistry

can, in principle, violate the Second Law of Thermodynamics" [6] on the basis of any physically realistic model of the photosynthetic apparatus.

Acknowledgments

Appendix A. The dependence of ΔS_p on light intensity

Consider an ensemble of pigment molecules that are exposed to radiation with energy density $\rho = \rho_0 + \rho_l$, where ρ_0 is the
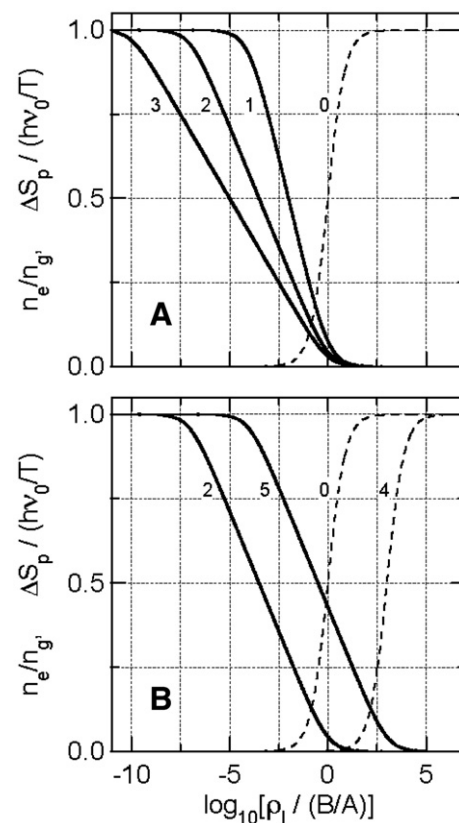

Fig. 1. Ratio of the populations of excited and ground states (n_e/n_g, dashed curves labeled 0 and 4), and the changes in the pigment's entropy accompanying absorption of a photon (ΔS_p, solid curves 1–3 and 5), as functions of the excitation light intensity during steady-state illumination of an ensemble of pigments. In panel A, the pigments are excited with rate constant $B\rho_0 + B\rho_l$ and decay with rate constant $B\rho_0 + B\rho_l + A$, where ρ_0 is the energy density of the ambient thermal radiation at temperature T and frequency ν_0, ρ_l is the energy density of any additional radiation at ν_0, B is the Einstein coefficient for absorption and stimulated emission, and A is the Einstein coefficient for fluorescence. Note that the abscissa is logarithmic. Curves 1–3 were obtained by Eqs. (5) and (A1) with $\phi = 10^{-4}$ (curve 1), 10^{-7} (curve 2) and 10^{-10} (curve 3). ΔS_p for each value of ϕ is scaled relative to the corresponding value of $h\nu_0/T$, which is related to ϕ through Eq. (A2). The plots of n_e/n_g for the three values of ϕ are superimposed (curve 0) on the ordinate scale used here. The curves labeled 0 and 2 in panel B are the same as those in A. For curves 4 and 5 in B, the excited pigment was given an additional non-radiative decay route with rate constant $\kappa = 10^3 A$, and n_e/n_g was obtained by Eq. (A3).

energy density of the diffuse thermal radiation at the excitation frequency (ν_0) and the ambient temperature (T), and ρ_l represents any additional radiation at ν_0 from a more directional source. If we neglect non-radiative decay pathways for the moment, the pigment will be converted to the excited state with rate constant $B\rho$ and return to the ground state with rate constant $B\rho+A$, where B is the Einstein coefficient for absorption and stimulated emission and A is the coefficient for spontaneous emission. The steady-state population ratio n_e/n_g will be

$$\frac{n_e}{n_g} = \frac{(\rho_l + \rho_0)B}{(\rho_l + \rho_0)B + A} = \left(\rho_l \frac{B}{A} + \phi\right) \Big/ \left(\rho_l \frac{B}{A} + 1 + \phi\right), \qquad (A1)$$

with

$$\phi = \frac{\exp(-h\nu_0/k_B T)}{1 - \exp(-h\nu_0/k_B T)}. \qquad (A2)$$

The substitution of ϕ for $\rho_0 B/A$ on the right-hand side of Eq. (A1) reflects the fact that n_e/n_g goes to $\exp(-h\nu_0/k_B T)$ at thermal equilibrium, when $\rho = \rho_0$.

Fig. 1A shows the dependence of n_e/n_g and ΔS_p on $\log(\rho_l)$, as given by Eqs. (5) and (A1) for $\phi = 10^{-4}$, 10^{-7} or 10^{-10}. Plots of $\Delta S_p/(h\nu_0/T)$ versus $\log[\rho_l/(B/A)]$ for different values of ϕ start at 1 when ρ_l is small and go to zero at high ρ_l, but have different slopes at intermediate intensities. The knees in the curves at low and high light intensities occur where $\rho_l \approx \phi B/A$ and $\rho_l \approx B/A$, respectively.

Electronically excited molecules generally decay by non-radiative pathways such as electron transfer and internal conversion as well as by fluorescence and stimulated emission, and in an efficient photochemical system the rate constant for a productive non-radiative route must be greater than A. In this situation,

$$\frac{n_e}{n_g} = \left(\rho_l \frac{B}{A} + \phi + \frac{\kappa \exp(-h\nu_0/k_B T)}{A}\right) \Big/ \left(\rho_l \frac{B}{A} + 1 + \phi + \frac{\kappa}{A}\right), \qquad (A3)$$

where κ is the sum of the rate constants for non-radiative routes. A non-radiative decay pathway shifts the curves for both n_e/n_g and ΔS_p to higher light intensities as shown in Fig. 1B. This increases ΔS_p at any value of ρ_l greater than zero, but most strongly in the region $\phi B/A < \rho_l$.

The energy density ρ_l in the above expressions is proportional to the irradiance of the excitation light, while coefficient B is proportional to the dipole strength of the absorption; A is the reciprocal of the radiative lifetime of the excited state. The proportionality constants can be found in [18] along with relationships between A and B and expressions for ρ_0 in terms of T and ν_0.

References

[1] L.N.M. Duysens, The path of light energy in photosynthesis, in: Photochemical Apparatus, Brookhaven Symp. Biol. 11 (1959) 10–25.

[2] W.W. Parson, Thermodynamics of the primary reactions of photosynthesis, Photochem. Photobiol. 28 (1978) 389–393.

[3] R.S. Knox, Conversion of light into free energy, in: H. Gerischer, J.J. Katz (Eds.), Light Induced Charge Separation at Interfaces in Biology and Chemistry, Verlag Chemie, Weinheim, 1979, pp. 45–59.

[4] R.C. Jennings, E. Engelmann, F. Garlaschi, A.P. Casazza, G. Zucchelli, Photosynthesis and negative entropy production, Biochim. Biophys. Acta 1709 (2005) 251–255.

[5] J. Lavergne, Commentary on photosynthesis and negative entropy production by Jennings and coworkers, Biochim. Biophys. Acta 1757 (2006) 1453–1459.

[6] R.C. Jennings, A.P. Casazza, E. Belgio, F.M. Garlaschi, G. Zucchelli, Reply to "Commentary on photosynthesis and negative entropy production by Jennings and coworkers" by J. Lavergne, Biochim. Biophys. Acta 1757 (2006) 1460–1462.

[7] W. Yourgrau, A. van der Merwe, Entropy balance in photosynthesis, Proc. Natl. Acad. Sci. U. S. A. 59 (1968) 734–737.

[8] W. Brittin, G. Gamow, Negative entropy and photosynthesis, Proc. Natl. Acad. Sci. U. S. A. 47 (1961) 724–727.

[9] R.T. Ross, Thermodynamic limitations on the conversion of radiant energy into work, J. Chem. Phys. 45 (1966) 1–7.

[10] R.S. Knox, Photosynthetic efficiency and excitation transfer and trapping, in: J. Barber (Ed.), Primary Processes of Photosynthesis, Elsevier-North Holland, Amsterdam, 1977, pp. 55–97.

[11] V.A. Shuvalov, Light Energy Conversion in the Primary Process of Charge Separation in Photosynthetic Reaction Centers, Nauka, Moscow, 2000, p. 13, (in Russian).

[12] W. Yourgrau, A. van der Merwe, G. Raw, Treatise on Irreversible and Statistical Thermophysics, Dover, New York, 1982 (Chapters 1, 2).

[13] C. Kittel, H. Kroemer, Thermal Physics, W.H. Freeman, San Francisco, 1980 (Chapter 2).

[14] T. Engel, P. Reid, Thermodynamics, Statistical Thermodynamics, and Kinetics, Benjamin Cummings, San Francisco, 2006 (Chapter 13).

[15] M.A. Weinstein, Thermodynamics of radiative emission processes, Phys. Rev. 119 (1960) 499–501.

[16] G.M. Wang, E.M. Sevick, D.J. Searles, D.J. Evans, Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales, Phys. Rev. Lett. 89 (2002) (050601-1-4).

[17] C. Bustamante, J. Liphardt, F. Ritort, The nonequilibrium thermodynamics of small systems, Phys. Today 58 (7) (2005) 43–48.

[18] W.W. Parson, Modern Optical Spectroscopy, Springer, Berlin, 2007 (Chapters 3 and 5).