THERMODYNAMICS AND THE PRIMARY PROCESSES OF PHOTOSYNTHESIS

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ABSTRACT Numerous discussions of the relationship of the thermodynamics of radiation to photosynthesis have been published, but the results are often in disagreement or at best difficult to compare with one another. The recent treatment of maximal photosynthetic efficiencies by Ross and Calvin is here shown to be directly related to the thermodynamic method of Duysens. A smooth connection between the light and dark conditions is derived, the case of polarized light is considered briefly, and a critique of some other thermodynamic treatments is presented.

INTRODUCTION

Interest in the calculation of a theoretical upper limit to the efficiency of the photosynthetic process has continued ever since the appearance of the thermodynamic argument of Duysens (1958). Some workers (Mortimer and Mazo, 1961; Bell, 1964) have been primarily concerned with the assignment of an effective temperature to the radiation field, with results differing little from those of Duysens. Others (Brittin and Gamow, 1961; Spanner, 1964; Yourgrau and van der Merwe, 1968) have focused on the question of whether the entropy balance in photosynthesis is consistent with the second law of thermodynamics. Most recently Ross (1966; 1967) and particularly Ross and Calvin (1967) have introduced a thermodynamic and kinetic approach to the problem which provides a new upper limit to the efficiency (lower than Duysens's 73%). In the present article a connection between the kinetic calculation and Duysens's is demonstrated; this had not been explicitly recognized before. The kinetics are extended to a point where a smooth connection between light and dark conditions is obtained, and the choice of fluorescence yield to be used in the theory is clarified. Finally, we comment on other thermodynamic approaches and attempt to reconcile them with the Duysens result.

KINETIC MODEL

We consider first a "two-level" model in which energy is interchanged among the four systems sketched in Fig. 1. A radiation field of intensity I at a photon energy E

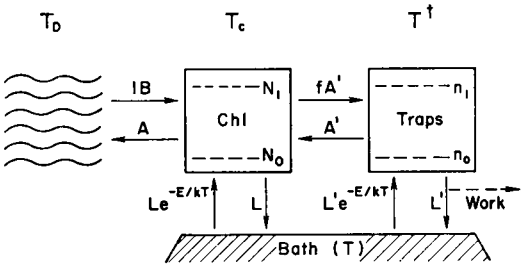

FIGURE 1 Rate constants and schematic diagram of a two-level adaptation of the Ross-Calvin kinetic model for the primary photosynthetic process. Symbols are defined in the text. The wavy lines represent a radiation field.

is coupled to a chlorophyll system whose ground and excited state populations, at energies 0 and E, are N_0 and N_1, respectively. A and B are the Einstein coefficients; induced emission and depopulation of the ground state are neglected throughout. The excited chlorophyll system is further coupled to the environment at temperature T, losing energy with a rate constant L and regaining it with a rate constant $Le^{-E/kT}$, where k is Boltzmann's constant.[1] Finally, the excited chlorophyll system is coupled to a trapping system, interchanging energy at rates CN_1n_0 (out) and CN_0n_1 (in). Here n_0 and n_1 are the ground and excited state populations of another two-level system (energy 0 and E, respectively) about which the same kinetic assumptions are made. The path with a loss rate L' is the one from which work is eventually extracted from the system. As long as the ground states of the two subsystems are not depleted significantly, n_0 and N_0 may be regarded as constants whose ratio will be called $f = n_0/N_0$. Then the rates CN_1n_0 and CN_0n_1 become $A'fN_1$ and $A'n_1$, respectively, where $A' = CN_0$. The resulting first-order constants $A'f$ and A' are shown in Fig. 1, and the connection between our notation and some others' is given in Appendix A.

The quantities n_0 and C may be thought of for convenience as a number of "traps" and as a second-order coupling constant for transfer from the bulk chlorophylls into these traps, respectively. However, this must be done with caution because the kinetics of excitation transfer to actual trapping centers may be described quantitatively only after the assumption of specific models for the dynamical structure of the pigment system has been made (for a discussion, see Clayton, 1967). Our model is restricted to steady-state predictions and cannot be used unmodified to interpret experiments involving variable trapping conditions—not because it is necessarily incorrect, but because no relationship between n_0 and the details of the trapping system has been postulated here.

For the steady state the following conditions are imposed on the various populations:

$$dN_1/dt = IBN_0 - AN_1 - LN_1 + LN_0e^{-E/kT} - fA'N_1 + A'n_1 = 0 \qquad (1)$$

$$dn_1/dt = fA'N_1 - A'n_1 - L'n_1 + L'n_0e^{-E/kT} = 0. \qquad (2)$$

[1] The use of an effective rate constant of this type is particularly convenient for establishing a smooth connection with the case of thermal equilibrium (see Kittel, 1958).

At thermal equilibrium, which will be denoted by a superscript 0, equations 1 and 2 are solved identically by $n_1^0/n_0 = N_1^0/N_0 = e^{-E/kT}$, provided that $I = I_{BB} = (A/B)e^{-E/kT}$, which is the condition that the radiation field also be in equilibrium with the surroundings at temperature T. Under these equilibrium conditions terms adjacent in pairs on the right in equations 1 and 2 cancel individually. For example, the terms in L' cancel and it is thus seen in detail why no net work can be extracted from the system as I approaches I_{BB}.

More generally, when $I \geqq I_{BB}$ the solutions of equations 1 and 2 may be written compactly as follows:

$$N_1/N_0 = \phi_F e^{-E/kT_D} + (1 - \phi_F)e^{-E/kT} \tag{3}$$

$$n_1/n_0 = \phi_R\phi_F e^{-E/kT_D} + (1 - \phi_R\phi_F)e^{-E/kT}. \tag{4}$$

Three parameters of physical significance have been introduced. The first is T_D, defined implicitly by

$$e^{-E/kT_D} = IB/A. \tag{5}$$

T_D is essentially the source temperature T_2 defined by Duysens, since equation 5 is a rearrangement of the blackbody radiation formula with stimulated emission neglected. The second parameter is

$$\phi_F = \frac{A}{A + L + fL'[A'/(A' + L')]}, \tag{6}$$

which resembles a fluorescence yield, and which indeed happens to be equal to the fluorescence yield on our model when one is considering intensities of interest to photosynthesis (see below). The third new parameter is

$$\phi_R = \frac{A'}{A' + L'}, \tag{7}$$

a "reversibility yield" for the trap. The solutions given by equations 3 and 4 are *exact* for the steady state described by equations 1 and 2, and they are seen to approach the proper equilibrium values as T_D approaches T, which means reducing the intensity to the dark level.

Before leaving the two-level kinetic model, let us verify that the parameter ϕ_F is indeed the usual fluorescence yield. In terms of fluxes, we can write

$$\text{(Fluorescence yield)} = \frac{AN_1}{(A + L)N_1 + fAN_1 - A'n_1}. \tag{8}$$

If the "thermal" terms, i.e. the second terms on the right in equations 3 and 4, are omitted, one finds upon substitution that the yield in equation 8 is exactly equal to

ϕ_F as given by equation 6. Since our applications will deal with this nonequilibrium case, we shall henceforth regard ϕ_F as being precisely equal to the actual yield, although at extremely low intensities the latter formally approaches the value $A/(A + L)$.

A slight generalization of the two-level model can be made which establishes a direct connection with Ross's (1967) broad-band formalism. Let the chlorophyll be represented by a many level system with excited-state energies E_1 , $E_2 \cdots$, E_n , and let the radiation field contain photons of corresponding energies at relative intensities I_1 , I_2 , $\cdots$, I_n . Furthermore, let only the lowest state of the chlorophyll be coupled to the trap, and let the population in the excited states be "in thermal equilibrium," i.e. canonically distributed with respect to the lowest excited state,[2] whose energy E_1 we shall take to be equal to E of the two-level model. One may then show that the results obtained for the two-level system apply directly to the many level system with the substitutions $IB \rightarrow \Sigma_\nu I_\nu B_\nu$, $A \rightarrow \Sigma_\nu A_\nu e^{-(E_\nu - E)/kT}$, and

$$(A + L) \rightarrow \Sigma_\nu (A_\nu + L_\nu) e^{-(E_\nu - E)/kT},$$

where B_ν , A_ν , and L_ν are the Einstein and loss coefficients for the νth excited state. N_1 is still the population of the lowest excited state and T_D must now be defined by

$$e^{-\bar{E}/kT_D} = \Sigma_\nu I_\nu B_\nu / \Sigma_\nu A_\nu e^{-(E_\nu - E)/kT}, \tag{9}$$

where $\bar{E}$ is some average photon energy, also taken to be equal to E for simplicity. The selection of this average and the selection of the range over which to sum on the right hand side of equation 9 constitute the only arbitrariness in the definition of T_D . Since T_D is introduced only for convenience, this arbitrariness is tolerable and leads to no problems in principle. (The most important consideration is that both sums in equation 9 run over the same set of states.) Finally, by making use of the blackbody radiation distribution, $(I_{BB})_\nu B_\nu = A_\nu e^{-E_\nu/kT}$, and by converting the summations in equation 9 to spectral integrals, we have

$$e^{-E/kT_D} = \frac{\int I(\nu) B(\nu)\, d\nu}{\int I_{BB}(\nu) B(\nu)\, d\nu} e^{-E/kT}. \tag{10}$$

The ratio of the two integrals is just the one appearing in the theory of Ross and Calvin.

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[2] The latter assumption is also made explicitly by Ross and Calvin, and its validity is discussed by them. The former assumption is necessary for the use of a single kinetic pathway into the trap. If any higher states are coupled to the trap, even further assumptions about rates of relaxation to thermal equilibrium will be required.

CONNECTION WITH THERMODYNAMICS

Ross and Calvin begin by noting that the steady-state concentration of excited chlorophyll molecules is raised by external irradiation, so that this energy-donating species attains an excess free energy

$$\Delta F_{\max} = kT \ln (N_1/N_1^0) \tag{11}$$

above the free energy of thermally excited chlorophylls. Since there exist numerous possibilities for irreversible loss between these excitations and the final chemical energy storage, $\Delta F_{\max}$ is the largest possible free energy available to the system due to irradiation; hence the subscript max. In three separate cases Ross and Calvin's computed values lie very close to those of Duysens, i.e. $\Delta F_{\max}$ is about 70% of the representative photon energy. Duysens obtained this result by actually computing a thermodynamic fraction of the photon energy. Since equation 11 does not contain the photon energy explicitly, one might be led to regard these facts as coincidental, but this is not the case. To bring out the connection, it is convenient to introduce the "absorber temperature" (Ross, 1966) for the chlorophyll. This temperature, T_c is the temperature which would be necessary to maintain the excited chlorophyll, molecules at the same population as that which is created when the system is illuminated; it is defined by

$$N_1/N_1^0 = e^{-E/kT_c}. \tag{12}$$

Observing again that, in the dark, the relative population of excitations is given by $N_1^0/N_0 = e^{-E/kT}$, we may combine equations 11 and 12 to show that the maximum free energy is given simply by

$$\Delta F_{\max} = \left(1 - \frac{T}{T_c}\right) E. \tag{13}$$

Next we find, by combining equations 3, 12, and 13, that

$$\Delta F_{\max} = \left(1 - \frac{T}{T_D}\right) E + kT \ln [\phi_F + e^{-E/kT} e^{E/kT_D}(1 - \phi_F)]. \tag{14}$$

This expression is valid for all intensities from normal down to dark conditions (i.e. for T_D approaching T). In practice the exponential term in the logarithm is completely negligible ($\approx e^{-80}$) and we have the working result

$$\Delta F_{\max} = \left(1 - \frac{T}{T_D}\right) E - kT \ln \frac{1}{\phi_F}. \tag{15}$$

In the same approximation the following expression for the absorber temperature

may be obtained:

$$T_c = T_D/[1 + (kT_D/E) \ln (1/\phi_F)]. \quad (16)$$

Duysens assumed a unit fluorescence yield in order to maintain a reversible model and find a very safe upper limit to the efficiency. In that case $T_c = T_D$, as may be seen from the foregoing equations, and the two calculations are seen to coincide precisely. Ross and Calvin have generalized Duysens's result to account for fluorescent quantum yields less than unity; we have further provided a smooth connection with the case of complete equilibrium, via equation 14. It should be noted that the fluorescence yield appearing in equations 15 and 16 is the true yield at any rate of transfer of energy to the trap. This point is discussed further in the next section.

Although we have emphasized the formal connection between the two theories, it remains to show that their authors have chosen equivalent values of T_D. In both cases the smallest radiation intensity required for photosynthetic activity was chosen, or, in our terms, the smallest T_D. We need not retrace the arguments for the choices of bandwidths and intensities, which may be found in the papers of Duysens and of Ross and Calvin. Rather, we can simply compare the radiation temperatures ultimately used (Table I). To find the equivalent temperatures used by Ross and Calvin, we have worked backward from their quoted values of ΔF_{max}, taking $E = 1.83$ ev in the case of spinach and 1.39 ev in *Chromatium*. Also shown in the table are the corresponding chlorophyll temperatures. Physically the chlorophyll is at a lower temperature when $\phi_F < 1$ because it is in thermal contact with the bath and trap.

TABLE I

TEMPERATURE PARAMETERS AND RELATED QUANTITIES IN THE CALCULATION OF MAXIMUM FREE ENERGIES AVAILABLE FOR PHOTOSYNTHESIS

Symbols are defined and discussed in the text. The ambient temperature is taken to be $T = 295°K$.

System	T_D	ϕF^*	$\Delta F_{max}/E$	T_c
	°K		%	°K
Green plant ($E = 1.83$ ev)				
(Alga)	1100‡	1	73.2	1100
Spinach, sys. I	1080§	⅛	69.4	971
Spinach, sys. II	1148§	⅓	72.8	1085
Spinach, sys. II	1148§	0.03‖	69.5	968
Bacteria ($E = 1.39$ ev)				
(Purple bacteria)	950‡	1	69.0	950
Chromatium	839§	⅛	62.8	794
Chromatium	839§	0.01§	56.5	678

* Representative values assumed by the respective authors.

‡ Estimated by Duysens (1958).

§ Calculated from the ΔF_{max} values of Ross and Calvin (1967); see text.

‖ Observed value; see discussion above in Optimal Efficiencies and Fluorescence Yield.

In Duysens's case the chlorophyll is in complete thermal contact with the radiation field and shares its temperature. Table I shows remarkably good agreement between the two calculations, and the results may be regarded as a kinetic confirmation of Duysens's thermodynamic approach.

Since the thermodynamic limitation on efficiency may be phrased in terms of the "negentropy of the absorbed radiation," we have considered the case of incident polarized light, which contains more negentropy. It is found (see Appendix B) that the maximum efficiency can be boosted by at most 1 % in a system capable of recognizing this possibility.

OPTIMAL EFFICIENCIES AND FLUORESCENCE YIELD

A fluorescence yield less than 1 lowers the kinetic temperature of the chlorophyll and, consequently, the maximum available free energy (see equation 15). It would appear that $\phi_F = 1$ represents the most favorable situation, but at the same time no energy is being transferred to the trap, since each quantum absorbed gives rise to one of fluorescence. (In the presence of primary radiationless loss L, the apparent maximum appears when $\phi_F = \phi_F^0 = A/(A + L)$.) Recognizing this, Ross and Calvin introduced an optimum free energy, one for which the product of ΔF_{max} and ϕ_T, the fraction of quanta transferred, is largest. On our model this fraction is given by (see, e.g. Kamen, 1963)

$$\phi_T = 1 - (\phi_F/\phi_F^0). \tag{17}$$

Since ΔF_{max} and ϕ_T are simple functions of ϕ_F, the maximization can be carried out most easily in terms of variation with respect to ϕ_F, and in so doing, we handle Ross and Calvin's "reversible" and "irreversible" cases simultaneously. The result is that $\phi_T \Delta F_{max}$ is largest when

$$\frac{\phi_F^0}{\phi_F} = (1 - T/T_D)\frac{E}{kT} + 1 - \ln\frac{1}{\phi_F}. \tag{18}$$

This equation can be solved numerically in any given situation, but the order of magnitude of the resulting value of ϕ_F is firmly fixed by the first term on the right, which is the photon energy in units of kT multiplied by the Duysens efficiency factor, or (0.73) (1.83/0.0254) = 53. For any reasonable photosynthetic system we should therefore expect $\phi_F \approx 0.02\ \phi^0_F$ (and consequently $\phi_T \approx 0.98$) at the optimum. This is borne out in Ross and Calvin's finding that "2 per cent of the quanta are lost for thermodynamic reasons in the systems studied," a statement which refers only to steps up to and including transfer into the trap. In the case of purple bacteria, the analogous loss at the optimum is 3 %.

A much more useful maximal and optimal free energy could be obtained if more information were available about the trap and its kinetics. Indeed, we may state

that another (lower) absolute upper limit to the free energy available is

$$\Delta F'_{\max} = (1 - T/T^t)E, \tag{19}$$

where T^t is the trap kinetic temperature, defined by $n_1/n_0 = e^{-E/kT^t}$. Unfortunately, T^t involves ϕ_R, about which we have no independent information. To a given optimal ϕ_F there can be assigned any trap temperature, since L' may be adjusted to produce the required value of ϕ_R (see equation 8).

APPLICATIONS TO SPECIFIC SYSTEMS

In applying the equivalent of equation 15 to spinach chloroplasts and *Chromatium*, Ross and Calvin used values of ϕ_F corresponding to two particular situations, namely, that in which the maximum trap potential is developed (highest ϕ_F) and that associated with the optimum situation described above. For a direct assessment of the situation in vivo, one may use the observed fluorescence yield under weak illumination, which is known to be of the order of 0.02–0.03 in alga (Latimer et al. 1956) and 0.01 in *Chromatium* (Duysens, 1952). The resulting maximum free energy in *Chromatium*, $\Delta F_{\max} = 0.78$ ev, corresponds to a potential below the redox potential difference for the P890-ferrodoxin couple (estimated to be 0.80 v in the acceptor states by Ross and Calvin), and is not far above that of the P890-flavoprotein or cytochrome *c*–flavoprotein potential difference. One may conclude that in *Chromatium*, P890 and ferrodoxin must operate at potentials much closer to one another than indicated by the standard potentials, or even Ross and Calvin's corrected potentials, and that if the standard cytochrome and pyridine nucleotide potentials are appropriate, the system must be operating very close to the thermodynamically limited potential. This provides an additional reason to prefer a two-electron or two-photoreaction scheme in bacteria (e.g. Sybesma, 1969), although it does not rigorously preclude a one-electron photoreaction involving P890 and an acceptor at a potential of 0.0 v.

The total intensity from background radiation at $T = 300°K$ in the wavelength interval 665–675 nm is 0.4×10^{-24} nE cm^{-2} sec^{-1}. In their experiments with spinach chloroplast fragments, Sauer and Park (1965) worked in this wavelength range at an intensity of 0.04 nE cm^{-2} sec^{-1}, or 10^{23} times as great. Therefore, the Duysens temperature under these conditions would be determined by

$$e^{-E/kT_D} = 10^{23}e^{-E/kT}$$

or $T_D = 626°K$. The largest free energy available per photon at 1.85 ev would therefore be (see equation 15)

$$\Delta F_{\max} = (1 - 300/626)(1.85) - 0.025 \ln 33 = 0.88 \text{ ev}$$

which is very close to the energy requirement for a series scheme of photosyn-

thesis. One might conclude that in the experiment at 0.04 nE cm^{-2} sec^{-1}, the primary photochemistry was being performed barely at the thermodynamic limit of efficiency, and this is borne out by the sharp drop in activity which Rosenberg (1969) finds at just slightly lower intensities.

OTHER THERMODYNAMIC TREATMENTS

We shall briefly discuss Spanner's (1964) approach and then the related treatments of Brittin and Gamow (1961) and of Yourgrau and van der Merwe (1968). Spanner obtains an expression

$$\eta_{max} = 1 - \frac{4}{3}\frac{T_l}{T_r}, \tag{20}$$

where η_{max} is the largest fraction of photon energy which may ultimately be used for work, T_l is the temperature of the leaf (our T), and T_r the radiation temperature. The latter is roughly equal in magnitude to T_D, but in Spanner's treatment it is 1350°K, the effective temperature of solar radiation which has been scattered into a solid angle of 4π. One obvious deficiency of this result is that it becomes negative when T_r is reduced to T_l, but this may be remedied by reintroducing the terms Spanner neglects in arriving at equation 23. The result is (Spanner, 1964)

$$\eta_{max} = 1 - \frac{4}{3}\frac{T_l}{T_r} + \frac{1}{3}\frac{U_l}{U_r}, \tag{21}$$

where the new quantities U_l and U_r are the energies of the radiation created and absorbed, respectively. As T_r approaches T_l, U_r approaches U_l and the efficiency goes properly to zero. Since, during the derivation, Spanner has distinguished between energy wasted by heat loss to the surroundings (Q) and heat radiated (U_l), but has given no prescription for doing so, it is impossible to evaluate U_l/U_r in a nonequilibrium situation. He ignores U_l/U_r on the grounds that it is proportional to (T_l/T_r),[4] which is incorrect because the Stefan-Boltzmann law refers to a rate of radiation, not an energy increment during an absorption process. Even granting this point, we must reconcile the presence of the $\frac{4}{3}$ in equation 23 with the corresponding 1 in the Duysens formula.

The ultimate source of Spanner's $\frac{4}{3}$ is an expression for radiation entropy, $S_r = \frac{4}{3}(U_r/T)$. This expression is a result of equilibrium thermodynamics; as Spanner himself shows, U_r/T comes from the usual isovolumic entropy change of a photon gas at temperature T when radiation of energy U_r is added. The other $U_r/3T$ comes from the work done in expanding the volume to accommodate the new radiation at the original temperature. As we show in a different way in Appendix B, the correct expression for the entropy change when a photon is simply added to or removed from a radiation field is $\pm U_r/T$; the contribution from work done on the environment simply should not be included, because equilibrium is *not* maintained,

and in particular the sun's radiation field and that of a leaf are far from equilibrium. This point has been emphasized by Yourgrau and van der Merwe (see below) in a different context.

The approaches of Brittin and Gamow and of Yourgrau and van der Merwe will not be discussed here in detail. The principal quantitative difference in their work is the use of $T_D = 5800°K$, the sun's temperature, in the Carnot efficiency factor. Certainly this usage will produce an absolute upper limit on the efficiency, but it implicitly assumes that every molecular absorber utilizes the unscattered radiation field of the sun. Under normal conditions, this is not the case in algae, bacteria, and in all but possibly those cells at the nearest surface of the leaves of higher plants. The use of a radiation temperature corresponding to scattered sunlight takes into account the ensemble averaging of incident radiation directions which is provided by the atmosphere and the biological structure itself.

APPENDIX A

The kinetic parameters used by Ross and Calvin are related to ours as follows: $K_{\text{tran}} = A'f$, $K_{\text{rad}} = A$, $\alpha K_{\text{rad}} = A + L$, and $\delta = A'(A + L)[(A' + L') + A'L'f]^{-1}$. Their case of "finite rate of transfer from the trap" corresponds to $L' > 0$. The quantity ϕ_T in our theory indeed factors into a "kinetic" and "thermodynamic" part as follows: from equations 17 and 6

$$\phi_T = 1 - \frac{(A + L)\phi_F}{A} = \frac{fA'L'}{(A + L)(A' + L') + fA'L'}$$

$$= \frac{A'f}{A + L + A'f}\left[1 - \frac{(A + L)A'}{(A + L)(A' + L') + A'L'f}\right]$$

to be compared directly with Ross and Calvin's equation 13. Thus our L' represents their "thermodynamics," but it may be seen from the above expression that the separation into kinetics and thermodynamics is somewhat artificial. All of the kinetic parameters also appear in δ.

Our kinetic parameters also closely parallel those used by Clayton in a recent review (1966) as follows: $A + L = k$, $A' = \beta N$, $f = \alpha/\beta$, $L' \approx k + Q$. The correspondence is not precise because Clayton does not distinguish between radiative and nonradiative losses (their sum is k), and we do not separate any of the losses in the trap (their sum is L').

APPENDIX B

The effect of polarization on thermodynamic efficiencies appears not to have been assessed. One may imagine a system designed to absorb and utilize polarized light more efficiently than unpolarized light of the same intensity. It is shown here that the gain in maximum efficiency when the system makes full use of such a mechanism is of the order of 1%.

The entropy of a monochromatic beam of one polarization is (see, e.g., Yourgrau and van der Merwe, 1968)

$$S_p = -k[N \ln N - (N + 1) \ln (N + 1)],$$

where N is the number of photons of frequency $h\nu$ present and k is the Boltzmann constant. Entropies associated with independent polarization states are additive, so we may compare S_p with the entropy S_u of a completely unpolarized beam of the same intensity by observing that S_u is twice the entropy of a beam with half as many photons;

$$S_u = -2k\left[\frac{N}{2}\ln\frac{N}{2} - \left(\frac{N}{2}+1\right)\ln\left(\frac{N}{2}+1\right)\right].$$

Since we are interested in entropy changes when photons are added to or subtracted from the beam, the quantities of interest are

$$\frac{\partial S_p}{\partial N} = k\ln\left(\frac{N+1}{N}\right)$$

and

$$\frac{\partial S_u}{\partial N} = k\ln\left(\frac{N+2}{N}\right).$$

For small N, as in normal physiological growth conditions, we have

$$\partial S_p/\partial N \approx -k\ln N = h\nu/T_D$$

$$\partial S_u/\partial N \approx -k(\ln N - \ln 2) \approx h\nu/T_D + k\ln 2.$$

Here T_D has been used, as defined in the text, simply as an alternative means of describing an intensity. The factor $k\ln 2$ per photon is recognized as a common entropy of mixing, as expected for the case of low intensities where the photons are behaving as classical particles, as far as statistics are concerned.

For the case $h_\nu = 1.83$ ev and $T_D = 1100°K$, in may be seen from the foregoing that a polarized beam contains 3.5% less entropy than unpolarized beam of the same intensity. If the system can "recognize" a polarized beam, it may therefore regain 3.5% of the $T\Delta S$ which it would normally lose because of the decrease of entropy of the photon beam. Under optimal conditions we have seen that this is at least $\approx$33% of the photon energy. The net gain in efficiency is therefore $\approx$1%.

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