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The thermodynamics of the conversion of radiation energy for photovoltaics

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Abstract. A standard thermodynamic theory of energy conversion is corrected by including the return fluxes from the sink to the converter and from the converter to the pump. By also allowing for the limited solid angle subtended by the pump at the converter and for general photon distributions (not only black-body), one obtains a better theory than has so far been available. It yields maximum conversion efficiencies as a function of solid angles and entropy generation rates. Comparison is made with earlier work where available.

1. Introduction

The thermodynamic efficiency of energy conversion of radiation into other forms of energy is of wide interest and has been much discussed. The work up to 1979 has been reviewed in [1]. In the 1980s these studies have continued in the area of photovoltaics, photochemistry and photobiology.

Here we shall consider a system consisting of two large reservoirs called pump (p) and sink (s) together with a converter (c). The last interacts with the pump by interchange of isotropic radiation and with the sink by isotropic radiation and possibly by other means so as to exchange work and heat. If the converter takes in black-body radiation at temperature T_p from the pump and rejects black-body radiation at a temperature marginally above the sink temperature T_s, then an upper limit to the conversion efficiency is [2, 3]

$$\eta_L = 1 - \tfrac{4}{3}(T_s/T_p) + \tfrac{1}{3}(T_s/T_p)^4 \qquad T_c \sim T_s. \tag{1.1}$$

This lies below the Carnot efficiency

$$\eta_C = 1 - T_s/T_p. \tag{1.2}$$

Throughout our work we shall assume

$$T_p \geqslant T_c \geqslant T_s. \tag{1.3}$$

The expression (1.1) assumes that the pump surrounds the converter completely (the so-called 4π-geometry) and that the entropy generation rate can be neglected, assumptions which will both be discarded here. For example, the validity of (1.1), even when the pump does not completely surround the converter, is established in (3.7), below. The expressions (1.1) and (1.2) are still very much higher than observed efficiencies.

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The question has recently been raised [4] as to how (1.1) has to be amended to allow for the fact that the pump normally subtends a limited solid angle at the absorber, and how to allow for the cut-off energy E_g below which an absorber such as a photovoltaic cell cannot absorb. Here E_g is the semiconductor energy gap. These effects change the efficiency. If one limits the solid angle at $E_g=0$ the efficiency is lowered; if one introduces a band gap at the full solid angle of 4π one also lowers the efficiency. If, however, a band gap is introduced at a solid angle less than 4π the efficiency as a function of E_g goes through a maximum (see for example [5]). Our appreciation of [4] is in no way diminished by the fact that we believe the answers obtained in [4] are in need of correction. For when all of the fluxes in the problem are correctly taken into account, as in (2.3) below, a strange result of [4]

$$\eta'_L = 1 - \tfrac{4}{3}(T_s/T_p) + (1/3g)(T_s/T_p)^4 \tag{1.4}$$

is removed. Here g is a geometrical factor which goes to zero if the pump subtends zero solid angle at the absorber. One would want (1.4) to remain finite as $g \to 0$.

In this paper we give a rather general formulation (§ 2) of energy conversion theory which applies in principle to all incident spectra and all angles subtended by the pump and sink. In this way one can recover many of the results in the literature in a novel way, and obtain new results as well. The theory is then specialised to the case when all radiation involved is black-body (§ 3) or monochromatic (§ 4). We show that the results obtained through our general thermodynamic formulation are consistent with those obtained in special cases through a kinetic rate process approach (e.g. [6]).

2. General theory

2.1. *The balance equations*

Including the entropy generation $\dot{S}_g$ per unit area in the converter, the net energy and entropy fluxes received by the converter are respectively (figure 1)

$$\phi_c^{(r)} = \phi_{pc} - \dot{Q} - \phi_{cs} - \dot{W} + \phi_{sc} - \phi_{cp} \tag{2.1}$$

$$T_s\psi_c^{(r)} = T_s\psi_{pc} - \dot{Q} - T_s\psi_{cs} + T_s\dot{S}_g + T_s\psi_{sc} - T_s\psi_{cp}. \tag{2.2}$$

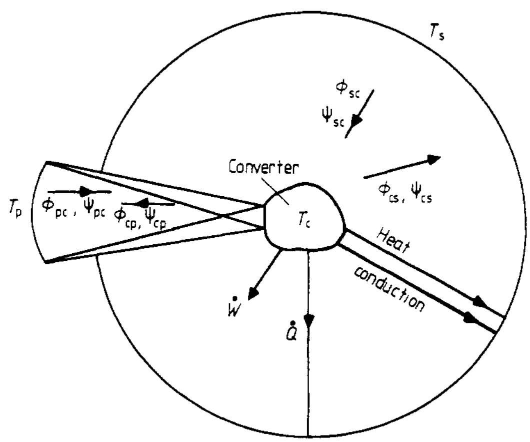

Figure 1. The system considered here, showing converter, pump and sink. Our analysis neglects the heat conduction which is shown for completeness.

Here T_s is the temperature of the ambient and of the surface of the converter so that the entropy flux emitted by the converter in the form of a heat flux is Q/T_s. We call T_s the sink temperature. The suffix pc denotes fluxes from the pump to the converter and cs fluxes from the converter to the sink. These terms and the work flux $\dot{W}$ are the usual ones. However, one also has to consider the return fluxes from sink to converter (sc) and from the converter to the pump (cp). These are not normally considered. Apart from $\dot{Q}$, $\dot{W}$ and $\dot{S}_g$, which can incorporate heat conduction, all of the terms on the right of (2.1) and (2.2) are radiative terms. Taking the difference between these equations,

$$\begin{aligned}\dot{W} = \phi_{pc} - T_s\psi_{pc} - (\phi_{cs} - T_s\psi_{cs})\\ + \phi_{sc} - T_s\psi_{sc} - (\phi_{cp} - T_s\psi_{cp})\\ - (\phi_c^{(r)} - T_s\psi_c^{(r)}) - T\dot{S}_g.\end{aligned} \tag{2.3}$$

The main (normal) terms are in the first line; the (new) return fluxes are in the second line. Terms in the third line to be denoted collectively by A are often neglected.

2.2. Geometrical considerations

The total emitted fluxes by component $j (j = \text{p, c, s})$ are

$$\phi_j = \iint K_{\nu j} \cos\theta_j \, \mathrm{d}\nu \, \mathrm{d}\Omega_j \qquad K_{\nu j} \equiv \frac{l_j h \nu^3}{c^2} n_{\nu j} \tag{2.4}$$

$$\begin{aligned}\psi_j &= \iint L_{\nu j} \cos\theta_j \, \mathrm{d}\nu \, \mathrm{d}\Omega\\ L_{\nu j} &\equiv \frac{l_j k \nu^2}{c^2}[(1+n_{\nu j})\ln(1+n_{\nu j}) - n_{\nu j}\ln n_{\nu j}].\end{aligned} \tag{2.5}$$

Here $l_j = 1$ or 2 is a polarisation factor for polarised and unpolarised radiation respectively. The spectral energy and entropy radiances are denoted by $K_{\nu j}$ and $L_{\nu j}$ respectively. The $n_{\nu j}$ are the photon numbers of frequency ν present in component j. Planck's constant (h) and the velocity of light (c) also occur. The approach and notation is that of [1].

Assume now that all elementary areas of the radiating part of the surface of component j have the same properties and that the surface is Lambertian so that the radiances are independent of direction within the solid angle Ω_j. This latter assumption is rather stringent and fails for lasers. The subsequent work therefore holds only for Lambertian devices although the photon distributions $n_{\nu j}$ are otherwise arbitrary. Hence for any surface element of the radiating surface of component j the fluxes emitted are

$$\phi_j = B_j \int K_{\nu j} \, \mathrm{d}\nu \qquad \psi_j = B_j \int L_{\nu j} \, \mathrm{d}\nu \tag{2.6}$$

where

$$B_j \equiv \int_{\Omega_j} \cos\theta_j \, \mathrm{d}\Omega_j$$

and Ω_j is the solid angle for which emission is possible.

Without loss of generality we can assume that $n_{\nu j}$ depends on the parameter $x_j = h\nu/kT_j$ where kT_j is a normalising constant for component j. Temperatures T_j are arbitrary, but if $n_{\nu j}$ is a black-body distribution, then T_j has to be interpreted as the black-body temperature. We shall put for simplicity $n_{\nu j}(x_j) \equiv n_j$. Substituting (2.4) and (2.5) into (2.6) we obtain

$$\phi_j = B_j l_j \int \frac{h\nu^3}{c^2} n_{\nu j}\, \mathrm{d}\nu = \frac{15\sigma}{2\pi^5} B_j l_j T_j^4 I(n_j) \tag{2.7}$$

$$\psi_j = \frac{15\sigma}{2\pi^5} B_j l_j T_j^3 J(n_j) \tag{2.8}$$

where Stefan's constant $\sigma \equiv 2\pi^5 k^4/15h^3c^2$ and the dimensionless integrals $(x \equiv h\nu/kT)$

$$I(n_j) \equiv \int x^3 n_j\, \mathrm{d}x \qquad J(n_j) \equiv \int x^2[ln(1+n_j) + n_j \ln(1+n_j^{-1})]\, \mathrm{d}x \tag{2.9}$$

have been introduced.

2.3. *Balance equations including geometric effects*

In applying the above results to the fluxes ϕ_{ij}, ψ_{ij} between components i and j of the device, one must replace the B_j by B_{ij}. Also, the total solid angle accessible for emission from the converter is now split into two parts according to whether the individual 'rays' reach the pump or the sink. Using also the reversibility of the rays

$$B_{ck} = B_{kc} \qquad k = \mathrm{s, p} \tag{2.10a}$$

$$B_\mathrm{T} = B_{cp} + B_{cs}. \tag{2.10b}$$

(2.10a) is called the reciprocity relation, and is discussed in books on heat transfer and optics and goes back to Helmholtz [7]. Here B_T corresponds to the total solid angle accessible to the converter. For a flat surface it is 2π. For a flat plate with both sides radiating it is 4π. For a simply connected closed radiating surface it is again 4π.

2.4. *Results for the steady state*

In this case (2.1) and (2.2) vanish and we can use (2.3) and (2.7)-(2.10) to give the work flux delivered by the converter. Two equivalent expressions are given:

$$\begin{aligned}\frac{2\pi^5}{15\sigma}\dot{W} &= B_{pc}[l_p T_p^4 I(n_p) - l_p T_p^3 T_s J(n_p)] + B_{cs}[l_s T_s^4 I(n_s) - l_s T_s^4 J(n_s)] \\ &\quad - B_\mathrm{T}[l_c T_c^4 I(n_c) - l_c T_c^3 T_s J(n_c)] - \frac{2\pi^5}{15\sigma} T_s \dot{S}_g \qquad (2.11)\\ &= B_{pc}[l_p T_p^4 I(n_p) - l_p T_p^3 T_s J(n_p) - l_s T_s^4 I(n_s) + l_s T_s^4 J(n_s)] \\ &\quad - B_\mathrm{T}[l_c T_c^4 I(n_c) - l_c T_c^3 T_s J(n_c) - l_s T_s^4 I(n_s) + l_s T_s^4 J(n_s)] - \frac{2\pi^5}{15\sigma} T_s \dot{S}_g.\end{aligned} \tag{2.12}$$

Relation (2.11) is more symmetrical between B_{pc} and B_{cs} and shows that by virtue of the second row of terms in (2.3) the sink acts as a (usually weaker) extra pump. Complete symmetry in these expressions is not expected since the heat flux $\dot{Q}$ is preferentially associated with the sink temperature T_s. The coefficients B_{ps} and B_{sp} refer to direct radiative exchanges between pump and sink without affecting the converter, and they are therefore not needed here.

We now use an earlier idea [8] which is also useful in the analysis of a solar cell as a Carnot engine [9]. Regard the entropy generation as taking place in a Lambertian converter coupled to a reversibly acting Carnot engine, and make the device equivalent to the one considered so far (figure 2). The rate of working of the Carnot engine is determined by the net radiative input:

$$\dot{W} = [1 - (T_s/T_c)][\phi_{pc} - \phi_{cp} - (\phi_{cs} - \phi_{sc})]$$

i.e.

$$\frac{2\pi^5}{15\sigma}\dot{W} = [1 - (T_s/T_c)][B_{pc} l_p T_p^4 I(n_p) + B_{cs} l_s T_s^4 I(n_s) - B_T l_c T_c^4 I(n_c)]. \tag{2.13}$$

The entropy generation flux in the absorber is now found by equating (2.11) and (2.13), a procedure introduced in [8],

$$\begin{aligned}\frac{2\pi^5}{15\sigma}\dot{S}_g = {} & [B_{pc} l_p T_p^4 I(n_p) + B_{cs} l_s T_s^4 I(n_s) - B_T l_c T_c^4 I(n_c)](1/T_c) \\ & - B_{pc} l_p T_p^3 J(n_p) - B_{cs} l_s T_s^3 J(n_s) + B_T l_c T_c^3 J(n_c).\end{aligned} \tag{2.14}$$

The efficiency of work production is best defined by

$$\eta \equiv \dot{W}/\phi_{pc} \tag{2.15}$$

which is the ratio of two fluxes. Use of (2.7) and (2.11) yields

$$\begin{aligned}\eta = 1 - \left(\frac{T_s}{T_p}\right)\frac{J(n_p)}{I(n_p)} - \frac{l_s}{l_p}\left(\frac{T_s}{T_p}\right)^4 \frac{I(n_s) - J(n_s)}{I(n_p)} - \frac{B_T}{l_p B_{pc} T_p^4 I(n_p)} \\ \times [l_c T_c^4 I(n_c) - l_c T_c^3 T_s J(n_c) - l_s T_s^4 I(n_s) + l_s T_s^4 J(n_s)] - \frac{2\pi^5 T_s \dot{S}_g}{15 B_{pc} l_p T_p^4 I(n_p)}.\end{aligned} \tag{2.16}$$

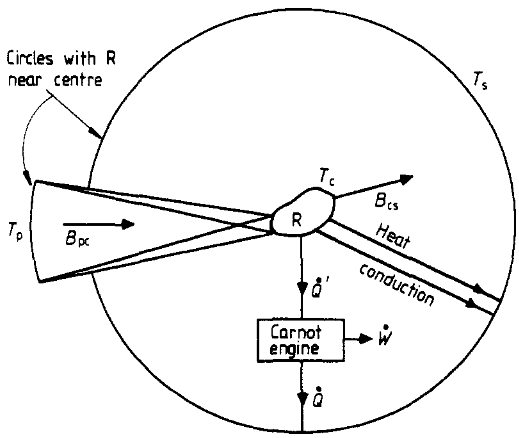

Figure 2. A model of the converter conceived as consisting of a radiator R and a Carnot engine.

The result (2.16) is based on figure 1. If figure 2 is used, one has from (2.13)

$$\eta=\left(1-\frac{T_s}{T_c}\right)\left(1+\frac{B_{cs}l_s}{B_{pc}l_p}\left(\frac{T_s}{T_p}\right)^4\frac{I(n_s)}{I(n_p)}-\frac{B_T l_c}{B_{pc}l_p}\left(\frac{T_c}{T_p}\right)^4\frac{I(n_c)}{I(n_p)}\right). \tag{2.17}$$

The difference between (2.12) and (2.13) and between (2.15) and (2.16) will be seen to be important in § 3.

Lastly, observe that the current-voltage (j, V)-relation of the device can be obtained from (2.13) by replacing W by $j(V)$:

$$j(V)=\frac{15\sigma}{2\pi^5}\left(1-\frac{T_s}{T_c}\right)\frac{1}{V}[B_{pc}l_pT_p^4I(n_p)+B_{cs}l_sT_s^4I(n_s)-B_Tl_cT_c^4I(n_c)]. \tag{2.18}$$

For solar cells, even if completely surrounded by the pump, we shall see in (4.7) that

$$qV=E_g(1-T_s/T_c) \tag{2.19}$$

so that the voltage dependence on the right-hand side of (2.18) is then determined by the voltage dependence of the photon distribution.

2.5. Special cases

As a first example of the preceding results, consider the case where pump, converter and sink are in *equilibrium*. Then the three T_j become one and the same real temperature of black-body distributions. The l_j all have the value 2 and the integrals (2.9) do not depend on j. Hence the entropy generation rate per unit area, (2.14), vanishes by virtue of (2.10*b*). Also, $\dot W$ vanishes, as is to be expected.

A less stringent constraint is that of *zero power output* (open circuit). While $\dot W=0$ as before in that case, the integrals (2.9) still depend on j and non-zero entropy generation is expected since the incident photons are converted into emitted photons. Given the three B_j and the three normalising temperatures T_j, the zero-work condition is a constraint on the non-equilibrium steady-state photon distribution in the converter. By (2.13) and using figure 1, n_c must satisfy

$$\frac{l_cT_c^4I(n_c)}{l_pT_p^4I(n_p)}=r^4+(1-r^4)\frac{l_sT_s^4I(n_s)}{l_pT_p^4I(n_p)} \qquad r^4\equiv\frac{B_{pc}}{B_t}. \tag{2.20}$$

Since $\dot Q$ and $\dot W$ do not appear, this is a condition for a purely radiative steady state in which the three distributions n_j and parameters T_j are linked by (2.20).

The coefficient of B_{pc} in (2.12) is normally positive (since $T_p \gg T_s$). The power output of the device then increases with the transfer coefficient B_{pc} (other things being equal), as would be expected. On the other hand, B_{pc} cannot be decreased indefinitely since $\dot W \geqslant 0$ is a constraint for an engine (as contrasted with a heat pump). This imposes a least value for B_{pc} and it ensures that the efficiencies (2.15)-(2.17) cannot diverge. From (2.12) and (2.13) one finds

$$B_{pc}\left[l_pT_p^4I(n_p)\left(1-\frac{T_s}{T_p}\frac{J(n_p)}{I(n_p)}\right)-l_cT_c^4I(n_c)\left(1-\frac{T_s}{T_c}\frac{J(n_c)}{I(n_c)}\right)\right]$$
$$\geqslant B_{cs}\left[l_cT_c^4I(n_c)\left(1-\frac{T_s}{T_c}\frac{J(n_c)}{I(n_c)}\right)-l_sT_s^4I(n_s)\left(1-\frac{J(n_s)}{I(n_s)}\right)\right]+\frac{2\pi^5}{15\sigma}T_s\dot S_g \tag{2.21}$$

or

$$B_{pc}\geqslant B_{cs}l_cT_c^4I(n_c)\left[1-\frac{l_s}{l_c}\left(\frac{T_s}{T_c}\right)^4\frac{I(n_s)}{I(n_c)}\right]\left\{l_pT_p^4I(n_p)\left[1-\frac{l_c}{l_p}\left(\frac{T_c}{T_p}\right)^4\frac{I(n_c)}{I(n_p)}\right]\right\}^{-1}. \tag{2.22}$$

Assuming black-body radiation, (2.22) gives as a condition for operation as a heat engine

$$(B_{\mathrm{pc}})_{\min} = B_{\mathrm{cs}} \frac{T_{\mathrm{c}}^4 - T_{\mathrm{s}}^4}{T_{\mathrm{p}}^4 - T_{\mathrm{c}}^4}. \tag{2.23}$$

Thus the minimum permitted value of B_{pc} depends on the thermal details of the device and is zero in the case of black-body radiation when the converter temperature becomes identical with that of the sink.

3. The case of black-body radiation

3.1. General

In this section the radiation in the three components (pump, converter and sink) of the device will be assumed to be black-body. Because of the extra terms in (2.3), this will give generalisations of results already in the literature. In this section we shall use: (i) the same polarisation factor (l) for all components; (ii)

$$I(n_j) = \pi^4/15 \qquad J(n_j) = 4\pi^4/45 \tag{3.1}$$

and (iii)

$$a \equiv T_{\mathrm{s}}/T_{\mathrm{p}} \qquad b \equiv T_{\mathrm{c}}/T_{\mathrm{p}} \qquad T_{\mathrm{s}} \leqslant T_{\mathrm{c}} \leqslant T_{\mathrm{p}} \tag{3.2}$$

so that

$$0 \leqslant a \leqslant b \leqslant 1 \qquad 0 \leqslant r \leqslant 1. \tag{3.3}$$

The last condition follows from (2.10).

3.2. Use of figure 1 only

From (2.12) and (2.16) we have

$$\dot{W} = \frac{l_\sigma B_{\mathrm{T}} T_{\mathrm{p}}^4}{2\pi}[(1 - \tfrac{4}{3}a + \tfrac{1}{3}a^4)r^4 - (b^4 - \tfrac{4}{3}ab^3 + \tfrac{1}{3}a^4)] - T_{\mathrm{s}}\dot{S}_{\mathrm{g}} \tag{3.4}$$

$$\eta = (1 - \tfrac{4}{3}a + \tfrac{1}{3}a^4) - r^{-4}(b^4 - \tfrac{4}{3}ab^3 + \tfrac{1}{3}a^4) - \frac{2\pi^5 T_{\mathrm{s}}\dot{S}_{\mathrm{g}}}{15 B_{\mathrm{pc}} l_{\mathrm{p}} T_{\mathrm{p}}^4 I(n_{\mathrm{p}})}. \tag{3.5}$$

If the converter is completely surrounded by pump radiation, then $r = 1$ and (3.5) is equation (7) or [10] on which the inequalities

$$\eta \leqslant 1 - b^4 - \tfrac{4}{3}a(1 - b^3) \equiv \eta^* \leqslant 1 - \tfrac{4}{3}a + \tfrac{1}{3}a^4 \equiv \eta_{\mathrm{L}} \tag{3.6}$$

were based. The last form is found in the limiting case $b \to a$, i.e. $T_{\mathrm{c}} \to T_{\mathrm{s}}$. In the other limiting case of no pump radiation ($r \to 0$), the steady state enforces $T_{\mathrm{s}} = T_{\mathrm{c}}$ ($a = b$), and this means that a divergence is avoided in (3.5).

The 'Landsberg efficiency' η_{L} [4, 11] can be obtained in a novel manner by factorising the first two expressions in (3.5). In order to achieve an inequality we neglect $\dot{S}_{\mathrm{g}}$:

$$\eta \leqslant \tfrac{1}{3}(a-1)^2(a^2 + 2a + 3) - \frac{1}{3r^4}(b - a)^2(3b^2 + 2ba + a^2) \leqslant \eta_{\mathrm{L}}. \tag{3.7}$$

The last step is obtained by maximising the central expression by putting $b = a$. Thus η_L is a valid upper limit of the efficiency as based on figure 1 even if the pump does not completely surround the converter.

It must be appreciated that T_c and also the voltage V across the cell depend on the work flux W extracted from it. We shall put $T_c = T_c(\dot{W})$ and later $V = V(\dot{W})$. In the open-circuit case, equation (2.20), which is based on figure 2, shows that for black-body radiation

$$b \to b(0) \equiv T_c(0)/T_p \tag{3.8}$$

where

$$b(0)^4 = r^4 + (1 - r^4)a^4.$$

Thus if the converter communicates only with the pump, then $r = 1$ and $T_c(0) = T_p$. If it communicates only with the sink, then $r = 0$ and $T_c(0) = T_s$, cf equation (2.23). A similar argument based on figure 1, i.e. on (3.4), should give the same result if the entropy generation rate (2.14) is used. The present procedure can therefore be regarded as based on either figure 1 or figure 2. From (3.8)

$$b(0)^4 = a^4 + (1 - a^4)r^4 \to a^4 \qquad \text{if } r = 0. \tag{3.9}$$

For simplicity we shall write b_0 instead of $b(0)$ below.

Note that (2.23) gives as a condition for operation of the device as a heat engine that

$$b^4 \leqslant a^4 + (1 - a^4)r^4 = b_0^4. \tag{3.10}$$

3.2. *The model of figure 2*

For unpolarised black-body radiation, using (2.13), (2.17) and (3.8),

$$\dot{W} = \frac{\sigma}{\pi} B_{pc} T_p^4 \left(1 - \frac{a}{b}\right) \frac{b_0^4 - b^4}{r^4}$$

$$\eta = \left(1 - \frac{a}{b}\right) \frac{b_0^4 - b^4}{r^4} = \left(1 - \frac{a}{b}\right) \frac{b_0^4 - b^4}{b_0^4 - a^4}(1 - a^4). \tag{3.11}$$

From (3.9) and (3.11) one sees that $b_0 \geqslant b$. The efficiency vanishes in three different situations.

(i) If $T_p = T_s$, which implies via (3.8) that all three temperatures are equal; the system is then in thermal equilibrium.

(ii) If $T_c = T_s$, which means that the Carnot engine in figure 2 cannot produce work.

(iii) If $T_c = T_c(0)$, which corresponds to the open-circuit, purely radiative, non-equilibrium steady state (2.20).

Starting with open circuit, as one draws work from the device T_c drops from $T_c(0)$ and η rises from zero. Eventually, T_c reaches $T_s(a = b)$ from above T_s and η reaches zero again, as illustrated in figures 3 and 4. Between its zeros η reaches its maximum with respect to b, at $b = b_m \equiv T_{cm}/T_p$, say. This is given by (figure 5)

$$\frac{4b_m^5}{b_0^4 + 3b_m^4} = a. \tag{3.12}$$

The changes in efficiency as $b = T_c/T_p$ rises from its lowest value, a, to its highest value, b_0, are illustrated in figures 3 and 4. One sees

$$T_c(0) \geqslant T_{cm} \qquad \text{i.e. } b_0 \geqslant b_m. \tag{3.13}$$

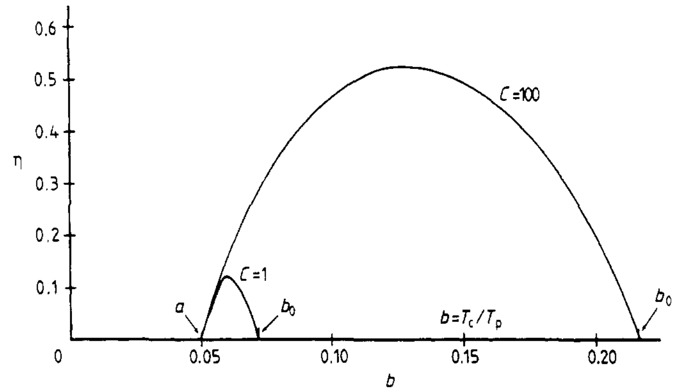

Figure 3. The efficiency as a function of b, assuming $a=300/6000=0.05$, $r^4 \equiv B_{pc}/B_T = 2.17\times10^{-5}\ C$ (see equations (A3) and (A5)), where the concentration ratio C is taken to be 1 and 100. This yields $b_0=0.0726$ and 0.216 via (3.8) and hence η by (3.11). The maximum efficiencies are 0.12 and 0.54.

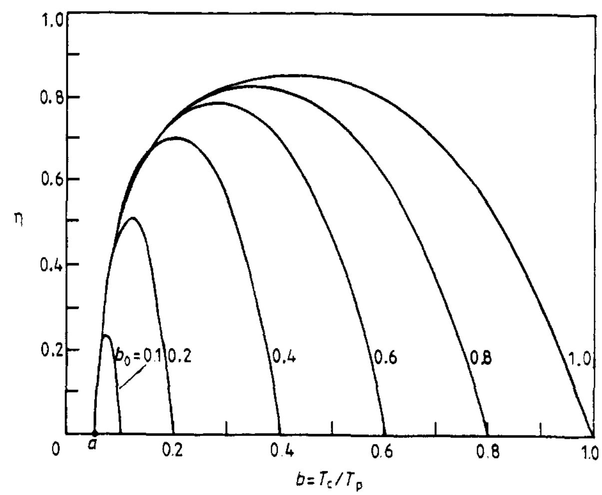

Figure 4. A family of curves η against b for $a=0.05$ according to (3.11). All curves rise from ($\eta=0$, $b=a$) and end at ($\eta=0$, $b=b_0$). From (A3) and (A5) the concentration ratios are, in order of increasing b_0, 4.33, 73.9, 1182, 5983, 18 909 and 46 164.

A key point, noted already in connection with (1.4), is that the maximum conversion efficiency is expected to increase with the pump-converter transfer coefficient, i.e. with the solid angle entering B_{pc} (see equation (2.6)). This is confirmed by figure 5 where increases in b_0 represent increases in $r^4 \equiv B_{pc}/B_T$. This clears up some confusion in the literature [4, 12].

Both the η_L curve and the ($b_0=1$) curve of figure 6 correspond to the converter being surrounded by the pump radiation. They differ because η_L is based on figure 1 and is an upper limit to the efficiency owing to the neglect of $\dot{S}_g$. The ($b_0=1$) curve, on the other hand, is based on figure 2. Here $\dot{S}_g$ has been incorporated in the action of the radiator R and so does not have to be neglected. Since it incorporates the effect of $\dot{S}_g$ on the efficiency, it lies lower.

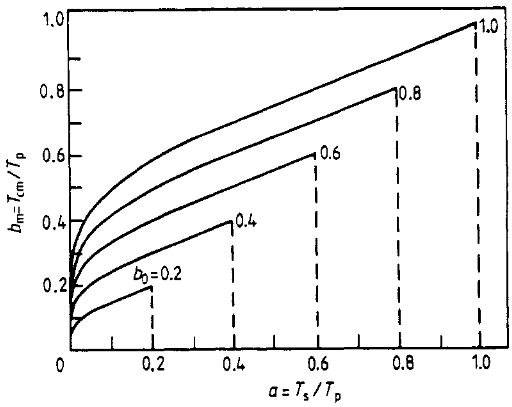

Figure 5. Curves showing how b_m rises from zero to b_0 as a is increased, plotted for various values of b_0 using (3.12). At the end points of the curves $b_m = b_0 = a$. The values of b_0 are marked on the curves.

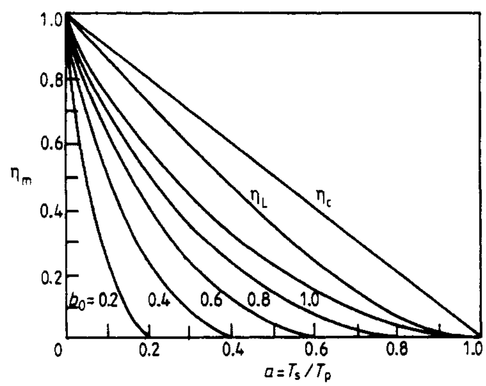

Figure 6. Maximum conversion efficiencies η_m as a function of a; η_c, η_L are the efficiencies (1.1) and (1.2). The remaining five curves give our new efficiency (3.11) with the value $b = b_m$ given by (3.12) and shown in figure 5. The values of b_0 used are marked on the curves.

We do not show η of (3.11) as a function of a by a diagram for the case when the pump surrounds the converter ($b_0 = 1$ by (3.8)). In that case

$$\eta = (1 - a/b)(1 - b^4) \tag{3.14}$$

and one finds the falling straight lines, denoted η_2 in [8]. Relation (3.14) was given early on and its history has been briefly reviewed [13]. It has been championed by Jeter [11] and Castañs [14], and it has also been used in [8] and elsewhere. In the present paper this much discussed result appears in the generalised form (3.11). If the assumption of black-body radiation is dropped, it appears in the even more general form (2.17). A controversy concerning various efficiency formulae in [11, 13] may be of interest in this context.

One should also recognise (3.12) as a generalisation to $b_0 \neq 1$ of the well known quintic equation [10, 14] for the value T_{cm}, say, of T_c:

$$4T_{cm}^5 - 3T_sT_{cm}^4 - T_sT_p^4 = 0 \tag{3.15}$$

which maximises (3.14) with respect to b.

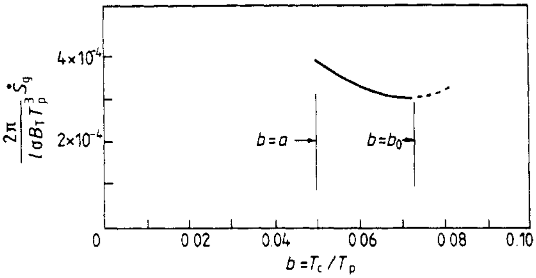

Figure 7. The minimum entropy generation flux for $C = 1$, $a = 0.05$, $r^4 = 2.17 \times 10^{-5}$ as a function of b using (3.8) and (3.20). Heat engine operation extends from $b = a$ to $b = b_0$.

3.3. *The entropy-generation rate*

The entropy generation flux is by (2.14), using the notation (3.2),

$$\frac{2\pi}{l\sigma B_T T_p^3}\dot{S}_g = \frac{r^4}{b} + \frac{(1-r^4)a^4}{b} - \tfrac{4}{3}[r^4 + a^3(1-r^4)] + \tfrac{1}{3}b^3 \tag{3.16}$$

$$= \frac{b_0^4}{b} + \tfrac{1}{3}b^3 - \frac{4}{3}\frac{(1+a+a^2)b_0^4 + a^3}{(1+a)(1+a^2)}. \tag{3.17}$$

For $r = 1$ ($B_T = \pi$, $l = 2$), one obtains the familiar result of [10] which was derived in a more general form as equation (12) of [8]:

$$\frac{1}{\sigma T_p^3}\dot{S}_g = \frac{1}{b} - \frac{4}{3} + \frac{b^3}{3}. \tag{3.18}$$

The entropy generation rate in the converter is then independent of the sink. On the other hand, if $r = 0$ and the sink is the only pump, then one finds by virtue of the extra terms in (2.3) that

$$\frac{1}{\sigma T_s^3}\dot{S}_g = \frac{a}{b} - \frac{4}{3} + \frac{1}{3}\left(\frac{b}{a}\right)^3. \tag{3.19}$$

In thermal equilibrium ($a = b = 1$) the expressions (3.16)–(3.19) vanish, as they should.

The entropy generation rate (3.17) can be minimised with respect to b (i.e. T_c). The minimum rate occurs, as expected, for the open-circuit condition $b = b_0$ of (3.8). The minimum rate is given by

$$\frac{3\pi}{2l\sigma B_T T_p^3}(\dot{S}_g)_{\min} = (1-b_0)\left(b_0^3 + \frac{1+b_0+b_0^2+b_0^3}{1+a+a^2+a^3}a^3\right). \tag{3.20}$$

It vanishes when the pump radiation surrounds the converter ($r = 1$, i.e. $b_0 = 1$), but is positive in other cases, as seen in figure 7. Note that the device operates as a heat engine only for $b \leqslant b_0$, by virtue of (3.10).

4. Black-body radiation: the monochromatic case

If the converter is surrounded by filters which pass only black-body photons in a narrow frequency range $(\nu, \nu+\Delta\nu)$, then the integrals (2.9) become

$$I(n_j) \to I(x_j) = \frac{x_j^3 \Delta x_j}{\exp(x_j)-1} \qquad x_j \equiv \frac{h\nu}{kT_j} \tag{4.1}$$

$$J(n_j) \to J(x_j) = \frac{4}{3}\frac{x_j^3 \Delta x_j}{\exp(x_j)-1} + \frac{x_j}{3}\ln[1-\exp(-x_j)]. \tag{4.2}$$

Using the model of figure 2, (2.13) or (2.18) specialise to

$$jV = \dot{W} = \frac{15\sigma l}{2\pi^5}\left(1-\frac{T_s}{T_c}\right)\left(\frac{r^4}{\exp(x_p)-1} + \frac{1-r^4}{\exp(x_s)-1} - \frac{1}{\exp(x_c)-1}\right)\left(\frac{h\nu}{k}\right)^4 B_T\Delta(h\nu). \tag{4.3}$$

The energy and entropy exchanges are made only through photons of energy $h\nu$ so that the system is monochromatic. The interesting point is that its behaviour can be shown to be identical to that of a two-level quantum system as described by both of us in different ways as models for a solar cell [15, 16].

If in (4.3) $\dot{W}=0$ (open circuit), then the temperatures T_p, T_s, $T_c(0)$ are related by $[x_{c0} \equiv h\nu/kT_c(0)]$

$$\frac{1}{\exp(x_{c0})-1} = \frac{r^4}{\exp(x_p)-1} + \frac{1-r^4}{\exp(x_s)-1} \tag{4.4}$$

where T_p and T_s are taken as fixed, while T_c is a function of $\dot{W}$. As in (3.3), the suffix 0 refers to open-circuit conditions. T_c, as given by (4.4), is the steady-state temperature which a monochromatic absorber with the configuration of figure 2 would attain if only radiative exchanges occur. If the sink term is neglected in (4.4), one finds

$$\frac{1}{T_c(0)} \simeq \frac{1}{T_p} - \frac{k}{h\nu}\ln(r^4). \tag{4.5}$$

This equation has been used in the context of photosynthesis [17].

For the application to photovoltaic conversion one models the converter as a semiconductor with an energy gap $E_g = h\nu$ illuminated through monochromatic filters. Such a converter is equivalent to a two-level quantum system with the lattice at the sink temperature T_s. The semiconductor emits radiation with a broad spectrum by virtue of electron-hole pair radiative recombination. This spectrum is roughly black-body with a cutoff at $h\nu = E_g$, defined by a generalised Kirchhoff law [18]. The three terms in large brackets in (4.3) represent respectively the current induced by the pump, the current induced by radiation from the sink and the current loss due to re-radiation from the converter.

If μ_e, μ_h are the quasi-Fermi levels of electrons and holes (assumed flat) and $qV(\dot{W}) = \mu_e - \mu_h$ is the terminal voltage of the device, the re-radiated spectrum can be related to the sink temperature:

$$(E_g - qV(\dot{W}))/kT_s = h\nu/kT_c(\dot{W}) \tag{4.6}$$

which has been justified elsewhere, for example in [8, 10, 15, 19, 20]. It leads to a Carnot efficiency of type (1.2) for the Carnot engine of figure 2

$$\frac{qV(\dot{W})}{E_g} = 1 - \frac{T_s}{T_c(\dot{W})}. \tag{4.7}$$

In fact, it can be shown [9] that the operation of an ideal photovoltaic converter can be described in terms of a Carnot cycle of an electron-hole plasma between T_c and T_s.

In the case of open circuit (4.4) with (4.6) is equivalent to

$$\frac{1}{\exp[(E_g - qV_{0c})/kT_s] - 1} = \frac{r^4}{\exp(E_g/kT_p) - 1} + \frac{1 - r^4}{\exp(E_g/kT_s) - 1}. \tag{4.8}$$

This enables one to determine V_{0c} in terms of T_p and T_s. An approximate solution of (4.8) (which involves the same approximation as (4.5)) is

$$\frac{qV_{0c}}{E_g} \simeq 1 - \frac{T_s}{T_p} + \frac{kT_s}{E_g} \ln r^4. \tag{4.9}$$

These equations have been obtained in [15] by a detailed balance argument. The two approaches are therefore in agreement.

The current density-voltage relation of the device can be obtained from (4.3) and (4.7), with A an appropriate factor, as

$$j(V) = \frac{\dot{W}}{V} = A\left(\frac{r^4}{\exp(E_g/kT_p) - 1} + \frac{1 - r^4}{\exp(E_g/kT_s)} - \frac{1}{\exp[(E_g - qV)/kT_s] - 1}\right). \tag{4.10}$$

Similar equations have been obtained in a different way and for $r = 1$ by other authors, for example [21, 22]. By (4.4) and (4.6) we have

$$j(V) = A\left\{\left[\exp\left(\frac{E_g - qV_{0c}}{kT_s}\right) - 1\right]^{-1} - \left[\exp\left(\frac{E_g - qV}{kT_s}\right) - 1\right]^{-1}\right\}. \tag{4.11}$$

If the electron-hole gas is non-degenerate, $(E_g - qV)/kT_s \gg 1$, then a good approximation to (4.11) is

$$j(V) = A \exp\left(-\frac{E_g}{kT_s}\right)\left[\exp\left(\frac{qV_{0c}}{kT_s}\right) - \exp\left(\frac{qV}{kT_s}\right)\right] \tag{4.12}$$

which is equivalent to the standard ideal diode characteristic. The usual short circuit and dark current can readily be obtained from (4.12).

The discussion in this section shows that a largely thermodynamic derivation of the two-level photovoltaic converter gives the same results as an approach based on transition rates and detailed balance. However, the two-level case studied here is not the normal semiconductor situation which involves a two-band system and interband transitions. Still, one of us [23] has shown that one can go from the two-level to the two-band case: an assembly of an infinite number of two-level system is equivalent to a two-band system, and the complete diode equation can be retrieved in this way.

5. Conclusion

In this paper the solar-cell theory of efficiency and current–voltage relations has been generalised by including effects which are not normally considered and integrating them into a single formalism. These effects are: (i) the return fluxes from the sink to the converter and from the converter to the pump; (ii) the limited solid angle normally subtended by the pump (e.g. the sun) at the converter; and (iii) the possibility of an arbitrary distribution function n_ν over frequency. As a result many well known results of conventional solar-cell theory appear here in generalised, and more widely applicable, form. Special attention may be drawn to the following three points.

(a) The conversion efficiency (3.14), based on figure 2,

$$\eta = (1 - T_s/T_c)[1 - (T_c/T_p)^4]$$

is generalised for converters which are incompletely surrounded by the pump to (3.11) and (2.17). Based on figure 1 the upper limit (1.1)

$$\eta_L = 1 - \tfrac{4}{3}T_s/T_p + \tfrac{1}{3}(T_s/T_p)^4$$

is similarly generalised to (3.5). It appears in (2.16) for general photon distributions.

(b) The entropy generation flux (3.18) in the converter

$$\dot{S}_g \propto \frac{T_p}{T_c} - \frac{4}{3} + \frac{1}{3}\left(\frac{T_c}{T_p}\right)^3$$

is generalised similarly in (3.16) and, for general photon distributions, in (2.14).

(c) The familiar current density-voltage characteristic, which can be written in the form (4.12), is generalised in (4.11) and (4.3) for solid angle effects, and additionally in (2.18) for arbitrary photon distributions.

Lastly, we mention the generalised open-circuit conditions (2.20), (3.13) and (4.4).

Some of the considerations of this paper, e.g. equation (3.12), are relevant for thermophotovoltaic conversion, see [27] and references cited therein. In fact, the simplified version,

$$\eta \sim (1 - a/b)[1 - (b/b_0)^4]$$

obtained on neglecting the a^4 terms, has been used in the design of solar thermal engines. This formula has the merit that it still displays the two non-trivial zeros of (3.11).

Appendix. The solar concentration factor C and the coefficient B_{pc}

When considering the pump-converter system each point on the surface of the converter implies a value of $B_j \to B_{pc}$ in (2.6), which value also depends on the concentration ratio, C. Here C is the energy input rate $p \to c$ with the concentrator, divided by its value without it. For an ideal concentrator this definition is equivalent to the ratio of the exit aperture area to the input aperture area, which is a standard definition. With the concentrator in position the normal semi-vertical angle $\theta_\odot$ subtended by the solar disc at the earth is enlarged to θ_c say, where the subscript c indicates the presence of a concentrator. Integrating over all elements dA of converter area,

$$C = \frac{\int B_{pc}(C)\mathrm{d}A}{\int B_{pc}(1)\mathrm{d}A} \sim \frac{B_{pc}(C)}{B_{pc}(1)}. \tag{A1}$$

This follows from (2.6), assuming the concentration optics is not selective and delivers uniform illumination to the cell. This is a simplifying assumption which would be violated by shadowing, etc. For realistic geometries the integrals in (A1) can be quite complicated [24].

For a maximal C, C_m say, (2.10b) shows that

$$B_{pc}(C_m) = B_T. \tag{A2}$$

It follows from the definition (2.20) that

$$r^4 \equiv \frac{B_{pc}}{B_T} = \frac{B_{pc}(C)}{B_{pc}(C_m)} = \frac{C}{C_m} \tag{A3}$$

where (A1) has been used.

To obtain a numerical estimate of C_m, take a simple hemispherical geometry with the converter cell mounted on a mirror so that it does not radiate from the back. This corresponds to the usual geometry for a photovoltaic cell. Then by (2.6)

$$B_{pc}(C) = \int \cos\theta \, d\Omega = 2\pi \int_0^{\theta_c} \cos\theta \sin\theta \, d\theta = \pi \sin^2\theta_c. \tag{A4}$$

Using (A4) in (A1) with $\theta_\odot \sim 16$ minutes of arc, i.e. 4.654×10^{-3} steradians

$$C = \frac{\sin^2\theta_c}{\sin^2\theta_\odot} \qquad \text{i.e. } C_m = \frac{1}{\sin^2\theta_\odot} = 46165. \tag{A5}$$

From (3.8)

$$b_0^4 = \frac{C}{C_m}(1 - a^4) + a^4 \qquad \text{i.e. } C = \frac{b_0^4 - a^4}{1 - a^4} C_m.$$

These relations, including (A5), have been used for the numerical values given in the captions of figures 3–7.

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