

Entropy production in photovoltaic conversion

Antonio Luque and Antonio Martí

Instituto de Energía Solar, Universidad Politécnica de Madrid, Madrid, Spain

(Received 3 September 1996; revised manuscript received 13 November 1996)

Recent experiments have shown that more than one electron-hole generation per photon in solar cells is possible. A number of modeling works to appraise the theoretical potential of cells with high quantum efficiency have been carried out by several authors, and in some of them violations of the thermodynamic principles have occurred. A procedure to test the thermodynamic coherence of ideal models is developed in this paper, and applied to the most convincing model so far presented, proving that it is thermodynamically coherent. For the purpose of demonstration, the procedure is applied to an alternative credible model that violates thermodynamics. Also in this paper the absolute thermodynamic limit of work production in light converters, beyond the reference to specific devices—so far studied for blackbody radiation—is proven for any kind of radiation. [S0163-1829(97)08311-2]

I. INTRODUCTION

Today it is widely believed that every photon absorbed in a solar cell produces at most one electron-hole pair. Recent accurate measurements have shown quantum efficiencies higher than 1 in the short-wavelength range.¹ This can be explained as an optically induced Auger mechanism: the energy in excess of the band gap that one of the carriers receives from a high-energy photon is used in a second electron-hole generation.

This has led to the revision of the Shockley-Queisser (SQ) model² of the ideal solar cell, so far widely accepted as the physical limit of the photovoltaic conversion. Several attempts have been made to present modifications to this model,^{3,4} and in general are very enlightening in certain aspects. However, they have not respected the detailed balance, thus violating the second law of thermodynamics, as has already been pointed out (Refs. 4 and 5, respectively). But even if the detailed balance is respected, it would be easy to make generalizations of the SQ model that violated the thermodynamic laws. A deeper thermodynamic analysis is necessary to prevent these mistakes and, to some extent, to validate the proposed models. This deeper thermodynamic analysis consists of checking that the rate of entropy production is never negative.

This paper describes this analysis, which is applied to the model presented by Werner, Brendel, and Queisser⁵ (we call it WKBQ model after these three scientists and S. Kodolinski, who also worked on it). We find that this model complies with the condition of not producing negative entropy.

In addition to the introduction the paper is organized into five additional sections plus one more for conclusions. Section II introduces an expression to calculate the rate of entropy production of any device converting radiation into work, also applicable to solar cells. Section III presents a method for converting any radiation into an *equivalent* luminescent radiation. This is interesting because the behavior of an ideal solar cell under luminescent radiation can be analyzed more easily. The *equivalent radiation* concept allows us to assure the occurrence of positive entropy production under arbitrary illumination in the WKBQ model. It is also

used to obtain the highest possible conversion efficiency in any radiation-to-work converter under arbitrary radiation. In Sec. IV the proof of the thermodynamic coherence of the WKBQ model is given. To underline the interest of the entropy analysis, in Sec. V we present a credible model for ideal cells with quantum efficiency above 1, that fulfills the detailed balance but at the same time produces a negative entropy. Obviously this leads us to conclude that this model is wrong. Finally, in Sec. VI, by stressing the correctness of the WKBQ model that leads to efficiencies much higher than the SQ model, we minimize the importance of models for determining the efficiency limit of photovoltaic devices. As an alternative we present the real efficiency limit, perhaps not achievable, based on the production of zero entropy; that is, based on full reversibility. This limit was already found by other authors, but proven only in the framework of solar thermal devices. In this paper it is generalized with the use of the equivalent radiation concept.

II. ENTROPY PRODUCTION EQUATION

In Sec. II A, we derive the fundamental equation of the rate of entropy production [Eq. (3)], valid for photovoltaic converters but also for any kind of radiation-to-work converter. In Sec. II B, the expressions for several thermodynamic features, of use throughout the paper, are collected or derived.

A. Fundamental equation

A photovoltaic converter is a device, made of a semiconductor, that receives radiation and converts it into useful work in form of electricity. In this process some heat is also produced at the crystal network temperature T_a (the ambient temperature). In turn the photovoltaic converter (solar cell) must emit back some radiation, because if there is a path for the luminous rays to enter into the cell some rays can also leave it through this path by time reversal. In photovoltaic conversion such radiation is a luminescent radiation at room temperature, coupled with the excited gases of electrons and holes in the cell. In the SQ model this radiation has a single

chemical potential $\mu \neq 0$. In the WKBJ (Ref. 5) model it presents several chemical potentials. Conversely, in solar thermal converters the emitted radiation is free radiation (that is, with $\mu=0$), not at room temperature.

The first law of thermodynamics is written as follows:

$$\dot{E}_s = \dot{E}_r + \dot{W} + \dot{Q} \quad (1)$$

where \dot{E}_s and \dot{E}_r are the internal energy fluxes for the incoming photons and the escaping photons, respectively. The rate of production of useful work (useful power) \dot{W} and the rate of heat supplied to the ambient \dot{Q} are also accounted for.

Notice that no radiation from outside the source (the solar disk) is assumed to reach the receiver. This might be an approximation, or may be exact if no ray in our optical system links the solar cell with the dark region of the sky (where a weak radiation can still be found).

With analogous nomenclature and arguments, the S 's being entropies, the second law of thermodynamics leads to

$$\dot{S}_{\text{irr}} + \dot{S}_s = \dot{S}_r + \frac{\dot{Q}}{T_a}. \quad (2)$$

Here we have used the non-negative \dot{S}_{irr} to express the inequality of the second law that states that the entropy at the right of the sign equal, being the effect of the source excitation, must be higher than the entropy incoming from the source.

The *fundamental equation of entropy production* is obtained by eliminating \dot{Q} between the two preceding equations. The result is

$$\dot{E}_s - T_a \dot{S}_s = (\dot{E}_r - T_a \dot{S}_r) + \dot{W} + T \dot{S}_{\text{irr}}. \quad (3)$$

In its derivation no assumption has been made about the temperatures of the incoming and escaping radiations. As mentioned above, the escaping radiation is at room temperature in the photovoltaic case (not in solar thermal converters). As a consequence the term in parentheses constitutes a flux of Helmholtz free energy $\dot{F} = \dot{E} - T \dot{S}$.

B. Expressions for some thermodynamic variables

To avoid unnecessary complexity, let us assume that the cell is illuminated isotropically by the source radiation, using an ideal concentrator of zero absorptance (emittance). This leads to the highest efficiency but is not the only way; for instance, the use of light-confining cavities may lead to the same result.⁶ In the receiver we assume area and absorptance (emittance) unity.

Among the thermodynamic variables appearing in the preceding formulas we find the photon \dot{N} and energy \dot{E} fluxes, given by⁷

$$\begin{aligned} \dot{N} &= \frac{2}{h^3 c^2} \int_{\epsilon_m}^{\epsilon_M} \frac{\epsilon^2 d\epsilon}{e^{(\epsilon-\mu)/kT} - 1} \doteq \int_{\epsilon_m}^{\epsilon_M} \dot{n}(\epsilon, T, \mu) d\epsilon, \\ \dot{E} &= \frac{2}{h^3 c^2} \int_{\epsilon_m}^{\epsilon_M} \frac{\epsilon^3 d\epsilon}{e^{(\epsilon-\mu)/kT} - 1} \doteq \int_{\epsilon_m}^{\epsilon_M} \dot{e}(\epsilon, T, \mu) d\epsilon. \end{aligned} \quad (4)$$

In this equation c , h , and k , are, respectively, the speed of the light *in vacuo*, and the Planck and Boltzmann constants; T is the radiation temperature, μ its chemical potential, and ϵ

the photon energy. The integration is done between two limits for the sake of generality. In normal cases the lower limit is the semiconductor band gap ϵ_g , and the upper limit is infinite, but other cases will also be analyzed. Spectral photon $\dot{n}(\epsilon, T, \mu)$ and energy $\dot{e}(\epsilon, T, \mu)$ fluxes as defined with the equal-by-definition sign (\doteq) are also presented. It is important to point out that for a gas of photons (that cannot interact among themselves) every monochromatic component can be considered as a separate thermodynamic body with all thermodynamic variables, functions, and potentials. In other words, radiation beams with variable $T(\epsilon)$ and $\mu(\epsilon)$ can be found.

These expressions are to be used for the source radiation (subindex s) or for the emitted radiation (subindex r) by providing the proper temperature and chemical potential.

From very general arguments,⁸ regarding its extensive character, the Gibbs free energy can be written as $G = \mu N$. It is related to the Helmholtz free energy by $F = G - PV$, but $-PV = \Omega$, Ω being the grand potential, so that $F = \mu N + \Omega$. Therefore,

$$\begin{aligned} \dot{F} &= \mu \dot{N} + \dot{\Omega}, \\ \dot{S} &= \frac{\dot{E} - \mu \dot{N} - \dot{\Omega}}{T}, \end{aligned} \quad (5)$$

using

$$\dot{\Omega} = \frac{2kT}{h^3 c^2} \int_{\epsilon_m}^{\epsilon_M} \ln(1 - e^{(\mu-\epsilon)/kT}) \epsilon^2 d\epsilon \doteq \int_{\epsilon_m}^{\epsilon_M} \dot{\omega}(\epsilon, T, \mu) d\epsilon \quad (6)$$

as the grand potential flux.⁹ In many cases of interest, when $\epsilon_m - \mu \gg kT$, $\dot{\Omega} = -kT \dot{N}$.

III. ROOM-TEMPERATURE EQUIVALENT RADIATION FLUX

Any radiation flux, characterized in the most general case by the energy-dependent temperature $T(\epsilon)$ and chemical potential $\mu(\epsilon)$, can be represented by an *equivalent* luminescent flux *at room temperature* T_a with a chemical potential $\mu_x(\epsilon)$ related, for each energy, by

$$\frac{\epsilon - \mu}{kT} = \frac{\epsilon - \mu_x}{kT_a} \Rightarrow \mu_x = \epsilon \left(1 - \frac{T_a}{T} \right) + \mu \frac{T_a}{T}. \quad (7)$$

The thermodynamic functions of the equivalent source can be calculated by means of Eqs. (4) and (6) by substitution of T_a and μ_x ,

$$\dot{n}_x = \dot{n}; \quad \dot{e}_x = \epsilon \dot{n}_x = \dot{e}; \quad \dot{\omega}_x / T_a = \dot{\omega} / T, \quad (8)$$

so that [see also Eq. (5)]

$$\dot{e} - T_a \dot{s} = \epsilon \left(1 - \frac{T_a}{T} \right) \dot{n} + \mu \frac{T_a}{T} \dot{n} + \dot{\omega} \frac{T_a}{T} = \mu_x \dot{n}_x + \dot{\omega}_x. \quad (9)$$

Notice that the last equation is the spectral flux of Helmholtz free energy of the equivalent radiation, $\dot{e}_x - T_a \dot{s}_x$.

In these equations subindices s and r must be added to T and μ when they refer to radiation emitted by the source (and received by the converter) or emitted by the converter,

respectively. For the source radiation, which is often a thermal radiation, the most common case is that $\mu_s=0$, but exceptions occur, for instance when the converter is illuminated with a luminescent source. For the radiation emitted by the converter the temperature $T_r=T_a$ if it is photovoltaic, and in this case $\mu_x=\mu_r$, but this is not the case if the converter is, for instance, solar thermal.

Notice that the radiation flux and the *equivalent* radiation flux are not exactly the same, but they have the same fluxes of energy and photons and the same value for the function $\dot{e}-T_a\dot{s}$; as a consequence they also have the same entropy flux. That is why they can be replaced in the fundamental equation of entropy production [Eq. (3), written in terms of spectral sources] where the only radiation parameters to use explicitly are $\dot{e}_s-T_a\dot{s}_s$ and $\dot{e}_r-T_a\dot{s}_r$. They can also be replaced in the power equation of solar cell models—like those described in Sec. IV—as long as they only use the above functions. This is often the case with photovoltaic converters, most of them using only photon fluxes.

IV. THERMODYNAMIC COHERENCE OF THE WKBQ MODEL

In the first two subsections, the SQ and WKBQ solar cell models are described, and their power-voltage equations are introduced. In Sec. IV C these equations are applied to the fundamental equation of entropy production [Eq. (3)] and its rate is obtained being found that this entropy production rate is minimum at open circuit. In Sec. IV D, it is proven that this minimum is zero for monochromatic cells. For that purpose we use the concept of equivalent radiation. Based on the monochromatic cell we can then verify, in Sec. IV E, that the entropy production is never negative. Finally in Sec. IV F, the implications of zero being the minimum entropy production rate are discussed.

A. SQ model

The SQ model²—which presents an ideal device where any nonavoidable entropy production is prevented—states that an ideal solar cell is made of a semiconductor with a conduction band and a valence band separated by a band gap ϵ_g . In this cell, the photons from the source (the sun) are absorbed at a rate \dot{N}_s generating electron-hole pairs, one per absorbed photon. Electrons and holes may recombine again, but only by emission of luminescent photons that may be absorbed again; nonradiative recombination, a process producing irreversible entropy, is absent. The resulting recombination equals the rate of escaping photons \dot{N}_r . By a balance of particles the extracted current is q times the difference of generation less recombination rates, that is, $I/q=\dot{N}_s-\dot{N}_r(qV)$.

Shockley and Queisser also considered that the semiconductor presents infinite mobility (finite mobility also produces irreversible entropy), so that the quasi-Fermi levels are constant throughout the whole cell. However, as these are out of the thermal equilibrium they are different, with values ϵ_{Fn} and ϵ_{Fp} , and the cell voltage is $qV=\epsilon_{Fn}-\epsilon_{Fp}=\Delta\epsilon_F$. In addition these authors considered the ideal situation in which the electron and hole gases are in equilibrium with the radiation, so that the photons are emitted at room temperature with a chemical potential $\mu_r=\Delta\epsilon_F=qV$.

B. WKBQ model

In the WKBQ model,⁵ the current equation is the sum of a number—finite or infinite—in terms, each one corresponding to the energy interval $\{m\epsilon_g, (m+1)\epsilon_g\}$ (the last interval extends to ∞), in which the photons have enough energy as to produce m generations of electron-hole pairs. The power equation is

$$\dot{W}=(qV)(I/q)=qV\sum_{m=1}^{\infty}m\dot{N}_{s,m}-m\dot{N}_{r,m}(mqV), \quad (10)$$

In each interval the chemical potential of the emitted radiation is $\mu_r=mqV$.

The interest of this model lies in the fact that it predicts a limiting efficiency (sun temperature 5760 K, room temperature 300 K) of 85.4%, well above the one associated with the classical SQ model (40.6%). It is important to verify its thermodynamic consistency because, in a first version, this model was published⁴ lacking this consistency. In addition, while in the present form⁵ it is convincing, there are a number of intuitively stated thermodynamic arguments that probably allow for a more rigorous presentation.

It is possible to generalize the WKBQ model as follows:

$$\dot{W}=(qV)(I/q)=qV\int_{\epsilon_g}^{\infty}[m(\epsilon)\dot{n}_s(\epsilon,T_s,\mu_s)-m(\epsilon)\dot{n}_r(\epsilon,T_a,mqV)]d\epsilon. \quad (11)$$

Here we have assumed a noninteger $m(\epsilon)$. The preceding model occurs for a stepwise $m(\epsilon)$ that takes constant integer values in the intervals $\{m\epsilon_g, (m+1)\epsilon_g\}$. The chemical potential of the emitted radiation is $m(\epsilon)qV$. For the sake of generality the source has been considered with arbitrary temperature T_s and chemical potential μ_s (both variable with the photon energy), the latter being zero for thermal sources. Notice that the chemical potential must be lower than ϵ (otherwise the thermodynamic functions become ∞), that is, $m(\epsilon)qV<\epsilon$.

C. Determination of the minimum rate of entropy production

The production of entropy is calculated by putting the power of the preceding equation into Eq. (3). We use a spectral development of the thermodynamic variables as well as the free energy expression of Eq. (5) for the emitter radiation, thus obtaining

$$\begin{aligned} T_a\dot{S}_{\text{int}} &= \int_{\epsilon_g}^{\infty} \{(\dot{e}_s-T_a\dot{s}_s)-[mqV\dot{n}_r+\dot{\omega}_r] \\ &\quad -qV[m\dot{n}_s-m\dot{n}_r]\}d\epsilon \\ &= \int_{\epsilon_g}^{\infty} [(\dot{e}_s-T_a\dot{s}_s)-mqV\dot{n}_s-\dot{\omega}_r]d\epsilon. \end{aligned} \quad (12)$$

If we consider $T_a \dot{S}_{\text{irr}}$ as a function of qV , its derivative is given by

$$\begin{aligned} \frac{d(T_a \dot{S}_{\text{irr}})}{d(qV)} &= \int_{\epsilon_g}^{\infty} \left(-m\dot{n}_s - m \frac{d\omega_r}{d(mqV)} \right) d\epsilon \\ &= \int_{\epsilon_g}^{\infty} (-m\dot{n}_s + m\dot{n}_r) d\epsilon = -I/q, \end{aligned} \quad (13)$$

where we have used the basic thermodynamic relationship that states that the grand potential flux derivative with respect to μ ($=mqV$), with the sign changed, is just the particle flux.

The derivative in Eq. (13) is zero for open circuit conditions, showing that the production of entropy is minimum under such conditions.

D. Value of the minimum rate of entropy production in monochromatic cells

In this subsection our aim is to prove that this minimum is not negative. This will insure that the entropy production is always positive.

Let us consider the case of a cell covered by a narrow filter of bandwidth $\Delta\epsilon$ around the energy ϵ_f . Only monochromatic photons can enter or escape from this cell (the luminescent photons generated at energies unable to leave the cell are absorbed again thus reducing the net recombination). Equation (12) becomes

$$T_a \dot{S}_{\text{irr}} = [(\dot{\epsilon}_s - T_a \dot{s}_s) - mqV \dot{n}_s - \dot{\omega}_r] \Delta\epsilon. \quad (14)$$

As in the previous case (and using the same arguments) the function $T_a \dot{S}_{\text{irr}}(qV)$ presents a minimum for open circuit ($\dot{n}_s = \dot{n}_r$), of value

$$\begin{aligned} T_a \dot{S}_{\text{irr},\text{min}} / \Delta\epsilon &= (\dot{\epsilon}_s - T_a \dot{s}_s) - [mqV_{\text{oc}} \dot{n}_r(mqV_{\text{oc}}) \\ &\quad + \dot{\omega}_r(mqV_{\text{oc}})], \end{aligned} \quad (15)$$

but using the concept of equivalent radiation of Eq. (9) we can write

$$\begin{aligned} T_a \dot{S}_{\text{irr},\text{min}} / \Delta\epsilon &= [\mu_x \dot{n}_x(\mu_x) + \dot{\omega}_x(\mu_x)] - [mqV_{\text{oc}} \dot{n}_r(mqV_{\text{oc}}) \\ &\quad + \dot{\omega}_r(mqV_{\text{oc}})]. \end{aligned} \quad (16)$$

The open-circuit voltage of this cell—obtained when $\dot{n}_s = \dot{n}_x = \dot{n}_r$ —occurs for $mqV_{\text{oc}} = \mu_x$, and therefore $T_a \dot{S}_{\text{irr},\text{min}} / \Delta\epsilon$ is zero for open-circuit conditions and so $\dot{S}_{\text{irr},\text{min}} = 0$; that is, it is not negative, as we wanted to prove. The aspect of the curve of equation $T_a \dot{S}_{\text{irr}} / \Delta\epsilon$, as resulting from Eq. (14), is presented in Fig. 1, normalized to $\dot{\epsilon}_s$.

E. Non-negative value of the rate or entropy production in a general case

In Sec. IV D, the proof was limited to cells for monochromatic operation. In fact, we have shown that the entropy of Eq. (14) is never negative, but in this equation the integrand of Eq. (12) appears, and implies that this integrand is non-negative as well. In consequence the entropy represented by Eq. (12) must also be non-negative. It has to be emphasized that this entropy refers to a totally arbitrary incoming radi-

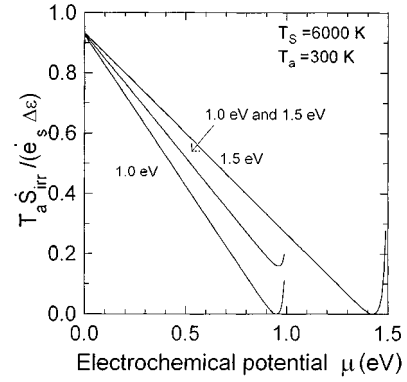


FIG. 1. Function $T_a \dot{S}_{\text{irr}}$ for cells covered by a monochromatic filter, normalized to the energy flux through the filter $\dot{\epsilon}_s \Delta\epsilon$ vs the chemical potential $\mu = mqV$, for two values of ϵ_f . Also for the case of a cell operating at both energies with equal $\Delta\epsilon$ at each energy.

tion. No limiting filter is now located at the cell either. Thus the general proof announced by this subsection heading is provided.

With the purpose of gaining some insight into the behavior under full spectrum, the case of a cell operating at two energies is presented in Fig. 1 (together with the monochromatic cases already discussed). In this case the entropy is always positive, having a minimum (as shown above, at open circuit), but this minimum is also positive and not zero.

F. Concluding remarks

It has been shown that the generalized WKBQ model does not violate the laws of thermodynamics, and the same occurs with the WKBQ model *stricto sensu* (that is, with the stepwise m function). Under any arbitrary radiation no negative entropy production takes place.

The fact that the WKBQ model predicts a reversible operation (zero entropy production) at an open circuit for monochromatic cells, though not a mathematical (logically irreproachable) proof, constitutes a strong indication that this model refers to a cell that is really ideal, and by this we mean that any nonunavoidable source of entropy production has been removed and that the entropy production of the cell described by this model is actually unavoidable and inherent to this type of converters in their most perfected form.

What has just been said can also be applied to the SQ model, which is a particularization of the WKBQ model for $m=1$. In Fig. 2 the entropy production minima vs the cell band gap for several thermal sources is given, which are of course always positive.

IV. AN INTUITIVELY REASONABLE MODEL NOT PASSING THE NON-NEGATIVE ENTROPY CHECK

It is easy to make mistakes in thermodynamics when proposing a model. Besides those already mentioned in Sec. I, see, for instance, Refs. 10 and 11, as discussed in Ref. 12; and Ref. 13, as discussed in Ref. 14.

To stress the interest of our non-negative entropy check we also provide in this section an example of a plausible model for the more-than-1 quantum efficiency cell. We shall prove that this fulfills the detailed balance, but we shall also

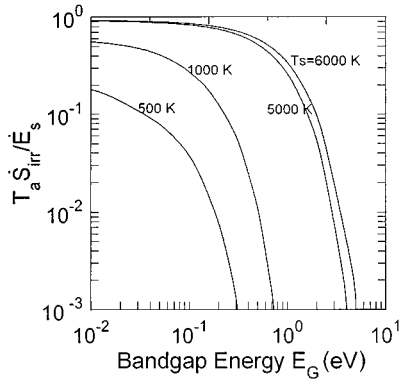


FIG. 2. Entropy production minima in the SQ model (normalized to the incident energy) vs the cell band gap for blackbody sources at different temperatures. The cell is at 300 K.

prove that it may produce negative entropy under certain circumstances—which tells us that our plausible model has to be wrong.

For the sake of argument let us state, in the WKBQ model, that the chemical potential of the emitted radiation is qV as in the SQ model, instead of $m qV$, so that for the filter covered cell power we set

$$\dot{W} = (qV) \cdot (I/q) = qV[m(\epsilon)\dot{n}_s(\epsilon, T_s, \mu_s) - m(\epsilon)\dot{n}_r(\epsilon, T_a, qV)]\Delta\epsilon \quad (17)$$

instead of the original equation derived from Eq. (11).

The intuitively reasonable nature of this model is as follows. In the current factor the generation term $m\dot{n}_s$ accounts in a straightforward manner for the higher-than-1 (actually m) quantum efficiency. The m in the recombination term $m\dot{n}_r$ means that m electron-hole pairs are required to recombine cooperatively to radiate one single photon. This m is necessary for the fulfillment of the detailed balance because in this way the recombination is the reverse mechanism of the generation of multiple pairs with one photon. On the other hand, its omission (as in Ref. 4) would give rise to an obvious violation of the second law of thermodynamics, detected by the usual detailed balance check.

In effect, in thermal equilibrium the cell is illuminated by a thermal radiation at room temperature, that is by $\dot{n}_s = \dot{n}(\epsilon, T_a, 0)$, but if $V=0$ (placing the cell terminals in short circuit) then the emitted radiation is $\dot{n}_r = \dot{n}(\epsilon, T_a, 0)$. Both radiations are equal and, because of the m in the emitted radiation term, the current delivered is zero. With this check this model is said to have fulfilled the detailed balance.

However, our plausible model does not pass the non-negative entropy check. In effect, using the concept of equivalent source, the entropy production is

$$T_a \dot{S}_{irr} / \Delta\epsilon = (\mu_x \dot{n}_x + \dot{\omega}_x) - (qV \dot{n}_r + \dot{\omega}_r) - qV(m\dot{n}_x - m\dot{n}_r). \quad (18)$$

In an open circuit (obtained when $\dot{n}_s = \dot{n}_x = \dot{n}_r$, and occurring for $qV_{oc} = \mu_x$) $T_a \dot{S}_{irr} / \Delta\epsilon$ is zero and so is \dot{S}_{irr} . However, the derivative with respect to qV , now the chemical potential of the emitted radiation, is

$$\left[\frac{d(T_a \dot{S}_{irr} / \Delta\epsilon)}{d(qV)} \right]_{V_{oc}} = -qV_{oc} \left[\frac{d[(m-1)\dot{n}_r]}{d(qV)} \right]_{V_{oc}}, \quad (19)$$

which is zero only if $m=1$ (the case of the SQ model). In any other case, for a voltage either a bit smaller or higher than V_{oc} , the entropy production is negative, in violation of the second law of the thermodynamics.

This flaw is produced when we adopt without any criticism the same chemical potential qV for the radiated current as in the SQ model. This flaw is, however, detected with our non-negative entropy test. Furthermore, our test might have been active in determining—with the help of the derivative—the factor m to apply to qV to obtain the chemical potential able to give a zero derivative under short circuit.

Intuitively speaking, the value $m qV$ of the emitted radiation chemical potential tells us that, in the multiple electron-hole-pair recombination occurring in this model, a free energy is transferred to the photon produced that equals the one lost by the material particles in the recombination. This is what is cleverly stated by WKBQ in Ref. 5.

Thus, in summary, in Eq. (17) we present a model for the more-than-1 quantum efficiency ideal solar cell, being rather reasonable from an intuitive point of view. As it passes the detailed balance check, it leaves its user untroubled. However, as we have just seen, it does not pass the most definitive non-negative entropy check, and therefore it can be said without a shadow of a doubt that this model is wrong (while the WKBQ model is right). This is a clear verification of the usefulness of the negative entropy check.

V. POWER CONVERSION LIMIT

The present situation, in which the SQ efficiency limit has been surpassed by the WKBQ model, clearly teaches us that models are only valid in their framework. By this we mean that we cannot use an ideal cell model to state that its efficiency limit is the efficiency limit of the photovoltaic conversion. A different photovoltaic device—by this we mean a radiation to electricity converter using solid-state matter-radiation interaction at the crystal network temperature—might be invented or discovered, which would overcome some limitations of the preceding devices. The WKBQ model of a solar cell is an example of how the SQ model has been surpassed.

What, then, is the power conversion limit of any solar device? The answer is to be found in Eq. (3), when the irreversible production of entropy is set at zero. From this equation the power limit is obtained.

This limit depends on the type of radiation emitted by the converter. We can apply the concept of an equivalent source to analyze the emitted radiation. Thus such radiation becomes the superposition of a number of monochromatic components, each one representing a luminescent radiation at room temperature—and this occurs even if the converter is not photovoltaic. The temperature and the chemical potential of these components are variable with the energy of the emitted photons in the most general case. Therefore this power limit is

$$\begin{aligned} \dot{W}_{lim} &= \int_{e_g}^{\infty} \{ [\dot{e}_s - T_a \dot{s}_s] - [\mu_x(\epsilon)\dot{n}_r(\epsilon, \mu_x) + \dot{\omega}_r(\epsilon, \mu_x)] \} d\epsilon \\ &= \int_{e_g}^{\infty} \dot{w}_{lim}(\epsilon, \mu_x) d\epsilon. \end{aligned} \quad (20)$$

The optimization for a given photon energy is achieved if the derivative

$$\frac{d\dot{w}_{\text{lim}}}{d\mu_x} = -\dot{n}_r - \frac{d\dot{w}_r}{d\mu_x} - \mu_x \frac{d\dot{n}_r}{d\mu_x} = -\mu_x \frac{d\dot{n}_r}{d\mu_x} \quad (21)$$

is zero, but this only happens if $\mu_x=0$, and this for any photon energy. Consequently the limit power is achieved for a device that emits thermal radiation ($\mu_x=0$) at room temperature for the entire spectrum concerned.

This result generalizes the one presented by Landsberg and Tonge¹⁵ for the case of solar thermal converters, that is, the case restricted to devices radiating a thermal radiation at any temperature. Our result is applicable to any converter that fulfills the reversal of time, regardless of the type of radiation emitted. Furthermore, this limiting condition is found not only for devices emitting thermal radiation at room temperature, but also for devices emitting any equivalent radiation as defined by Eq. (7). For the sun-room temperatures used above (5760 K/300 K) this efficiency limit is 93.1%.¹⁵

We do not know how to build such a device, or even if it can be built. The endoreversible thermodynamics suggests that some irreversibility will be produced in the transport of the heat from the sun to the converter,¹⁶ or, more precisely, in its absorption/reemission mechanism if some power is to be extracted.

VI. CONCLUSIONS

A method has been presented in this paper to check the thermodynamic consistency of solar cell models. It has been used to prove the thermodynamic consistency of the WKBQ model for multiple electron-hole pair generation [see Eqs. (13) and (16)]. The thermodynamic consistency of the classic SQ model—not in question—has also been proven.

The method is based on a determination of the rate of

entropy production—using Eq. (3) jointly with the power provided by the model under study—and the verification that this rate is always positive. It is sufficient to prove this under any monochromatic luminescent illumination at room temperature, once we have assured ourselves that only radiation in this monochromatic range will be emitted by covering the cell with the proper filter. The completeness of the proof, for any incoming radiation, results from the transformation of such incoming radiation into its luminescent equivalent.

This procedure is more conclusive than a simple check of the fulfillment of the detailed balance in the particle balance equations leading to the photovoltaic current, because this procedure—as it is presently being applied—says nothing about the chemical potential of the emitted radiation. A clear example of this has been presented [see Eq. (17)].

As regards the monochromatic ideal WKBQ cell, a reversible operation occurs under open-circuit conditions, but this zero entropy production is at a minimum. This assures us that the entropy production as presented in this paper is fundamental in the sense of being unavoidable in the framework of the model. Actual devices attempting to reproduce the ideal device will produce more entropy (but never less).

It is important to stress that ideal devices do not represent real fundamental limitations. The WKBQ model shows that some cells may behave better than the ideal cells described by the SQ model. Thus it is not unthinkable that a cell may behave better than was predicted by the WKBQ model, if some unexpected physical principles become operative. The only true limitation (according to the laws of thermodynamics) is the one found when the entropy production is zero [see Eqs. (20) and (21)]. In this case it has been found that the conditions set by Landsberg and Tonge for solar thermal devices can be applied with the greatest generality to any radiation-to-work converter, indeed including photovoltaic converters.

¹S. Kodolinski, J. H. Werner, T. Wittchen, and H. J. Queisser, *Appl. Phys. Lett.* **63**, 2405 (1993).

²W. Shockley and H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).

³P. T. Landsberg, N. Nussbaumer, and G. Willeke, *J. Appl. Phys.* **74**, 1441 (1993).

⁴J. H. Werner, S. Kodolinski, and H. J. Queisser, *Phys. Rev. Lett.* **72**, 3851 (1994).

⁵J. H. Werner, R. Brendel, and K. J. Queisser, in *Proceedings of the 1st World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1994), p. 1742.

⁶A. Luque, in *Physical Limitations to Photovoltaic Energy Conversion*, edited by A. Luque and G. L. Araújo (Adam Hilger, Bristol, 1990), p. 1.

⁷L. D. Landau and E. M. Lifchitz, *Physique Statistique* (MIR, Moscow, 1967), p. 206.

⁸L. D. Landau and E. M. Lifchitz, *Physique Statistique* (Ref. 7), p. 88.

⁹L. D. Landau and E. M. Lifchitz, *Physique Statistique* (Ref. 7), p. 186.

¹⁰K. W. J. Barnham and G. Duggan, *J. Appl. Phys.* **67**, 3490 (1990).

¹¹R. Corkish and M. Green, in *Proceedings of the 23rd Photovoltaic Specialists Conference* (IEEE, New York, 1993), p. 675.

¹²G. L. Araújo, A. Martí, F. W. Ragay, and J. H. Wolter, in *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, edited by R. Hill, W. Palz, and P. Helm (Stephen, Belford, 1994), p. 1481.

¹³Jianming Li, Ming Chong, Jiancheng Zhu, Yuanjin Li, Jiadong Xu, Peida Wang, Zuogi Shang, Zhankun Yang, Ronghua Zhu, and Xiolan Cao, *Appl. Phys. Lett.* **60**, 2240 (1990).

¹⁴A. Luque, *Appl. Phys. Lett.* **63**, 848 (1993).

¹⁵P. T. Landsberg and G. Tonge, *J. Appl. Phys.* **51**, R1 (1980).

¹⁶A. de Vos, *Endoreversible Thermodynamics of Solar Energy Conversion* (Oxford University Press, Oxford, 1992).