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Theoretical Limits of Photovoltaic Conversion

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4.1 INTRODUCTION

Efficiency is an important matter in the photovoltaic (PV) conversion of solar energy because the sun is a source of power whose density is not very low, so it gives some expectations on the feasibility of its generalised cost-effective use in electric power production. However, this density is not so high as to render this task easy. After a quarter of a century of attempting it, cost still does not allow a generalised use of this conversion technology.

Efficiency forecasts have been carried out from the very beginning of PV conversion to guide the research activity. In solar cells the efficiency is strongly related to the generation of electron–hole pairs caused by the light, and their recombination before being delivered to the external circuit at a certain voltage. This recombination is due to a large variety of mechanisms and cannot be easily linked to the material used to make the cell. Nevertheless, already in 1975 Lofersky [1] had established an empirical link that allowed him to predict which materials were most promising for solar cell fabrication.

In 1960, Shockley and Queisser [2] pointed out that the ultimate recombination mechanisms – impossible to avoid – was just the detailed balance counterpart of the generation mechanisms. This allowed them to determine the maximum efficiency to be expected from a solar cell. This efficiency limit (40.7% for the photon spectrum approximated by a black body at 6000 K) is not too high because solar cells make rather ineffective use of the sun's photons. Many of them are not absorbed, and the energy of many of the absorbed ones is only poorly exploited.

Revisiting the topic of efficiency limits is pertinent because today there are renewed attempts to invent and develop novel concepts in solar cells – sometimes known as

third-generation cells [3] – aimed towards obtaining a higher efficiency. The oldest of them, and well established today, is the use of multijunction solar cells, to be studied in detail in Chapter 9 of this book. However, novel attempts are favoured by the general advancement of science and technology that puts new tools in the inventor's hands, such as nanotechnology, not available just a decade ago.

Conventional solar cells are semiconductor devices in which an interaction between electrons and holes is produced by absorption of light photons in order to produce electric work. Unlike solar thermal converters, they can operate at room temperature.¹ In this chapter we shall start by presenting some of the irreversible thermodynamic background regarding the photon–electron interaction. Special attention is paid to the conditions for complying with the second law of the thermodynamics as a guide for new device inventors.

This thermodynamic approach will give us the efficiency that a certain solar converter can obtain under certain ideal conditions. This will be applied not only to the present solar cells but also to a number of proposed new converters, some of them actually tried experimentally and some not.

The solar converter theory developed in this chapter looks very different from the one presented in Chapter 3 and is complementary to it. There the solar cell will be analysed in a solid-state physics context, on the basis of electric carrier transport and recombination, taking into account the subtleties that a given material may impose. In this chapter all materials will be considered ideal, entropy-producing mechanisms will be reduced to those inherent to the concept being studied and all other mechanisms will be ignored. In this way, the efficiencies given in this chapter are to be considered as upper bounds of the solar cells studied both in Chapter 3 and the remaining chapters of this book. The lower values found there are not necessarily due to poor technology. They may be fundamental when linked to the actual materials and processes used to manufacture real solar cells. However, they are not fundamental in the sense that other materials and processes could, in principle, be found where different materials or process limitations will apply, which perhaps might be less restrictive.

4.2 THERMODYNAMIC BACKGROUND

4.2.1 Basic Relationships

Thermodynamics defines a state function for a system in equilibrium. This function can be the entropy, the internal energy, the canonical grand potential, the enthalpy and so on, all of them mutually equivalent, containing the same information of the system and related to each other through the Legendre's transformation [4]. The variables used to describe the macroscopic state of a system are divided into *extensive* (volume U , number of particles N , entropy S , internal energy E , etc.) and *intensive* (pressure P , electrochemical potential μ , temperature T , etc.) variables. A number of relationships may be written with them. For instance,

$$dE = T dS - P dU + \mu dN \quad (4.1)$$

¹ Solar cells usually operate at some 40 to 60°C, but there is nothing theoretical against improving cooling to reach a cell temperature as close to the ambient one as desired.

For our purposes it is convenient to choose the grand potential Ω as our preferred state function. It is the state function that describes the state of a system when the electrochemical potential, the volume and the temperature are chosen as independent variables. It is also the Legendre transform of the energy with respect to the temperature and the electrochemical potential:

$$\Omega \doteq E - TS - \mu N = -PU \quad (4.2)$$

Its definition is given by the equal-by-definition sign (\doteq). The right-hand equality represents a property proven with generality [5].

Other thermodynamic variables that characterise the system in equilibrium can be obtained from the grand potential as derivatives. Hence, the number of particles, entropy and pressure of the system under consideration can be obtained as

$$N = - \left. \frac{\partial \Omega}{\partial \mu} \right|_{U,T}; \quad S = - \left. \frac{\partial \Omega}{\partial T} \right|_{U,\mu}; \quad P = - \left. \frac{\partial \Omega}{\partial U} \right|_{\mu,T} \quad (4.3)$$

For describing systems in non-equilibrium, the system under study is assumed to be subdivided into small subsystems each one comprising an elementary volume in the space-of-phases² (x, y, z, v_x, v_y, v_z) and having a size sufficient to allow the definition of thermodynamic magnitudes in it. Within such volumes, the subsystems are assumed to be in equilibrium. Thus, thermodynamic magnitudes are dependent on the position $\mathbf{r} \doteq (x, y, z)$ of the elementary volume and the velocity of motion $\mathbf{v} \doteq (v_x, v_y, v_z)$ of the elementary bodies or particles in it.

For describing the system in non-equilibrium, it is necessary to introduce the concept of *thermodynamic current densities* [6], \mathbf{j}_x . They are related to the extensive variables X and are defined for those elementary bodies with velocity \mathbf{v} at the point \mathbf{r} as follows:

$$\mathbf{j}_x(\mathbf{r}, \mathbf{v}) = x(\mathbf{r}, \mathbf{v}) \mathbf{v} \quad (4.4)$$

where $x = X/U$ is the contribution to the extensive variable X , per unit of volume U at the point \mathbf{r} of the elementary bodies with velocity \mathbf{v} .

Equation (4.2) can be applied to the thermodynamic current densities allowing us to write

$$\mathbf{j}_\omega = \mathbf{j}_e - T(\mathbf{r}, \mathbf{v}) \mathbf{j}_s - \mu(\mathbf{r}, \mathbf{v}) \mathbf{j}_n = -P(\mathbf{r}, \mathbf{v}) \mathbf{v} \quad (4.5)$$

For the thermodynamic current densities, we can write the following continuity equations [7]:

$$\mathbf{g} \doteq \frac{\partial n}{\partial t} + \nabla \cdot \mathbf{j}_n \quad (4.6)$$

$$\mathbf{v} \doteq \frac{\partial e}{\partial t} + \nabla \cdot \mathbf{j}_e \quad (4.7)$$

$$\sigma \doteq \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{j}_s \quad (4.8)$$

² x, y and z are the spatial co-ordinates giving the position of the particle and v_x, v_y and v_z are the co-ordinates of its velocity.

where g , ν and σ are formally defined as the number of particles, energy and entropy generation rates per unity of volume. The symbol “ $\nabla \cdot$ ” is the divergence operator.³

4.2.2 The Two Laws of Thermodynamics

Equations (4.7) and (4.8) have close links with the laws of thermodynamics. A certain elementary subsystem or body can draw energy from or release energy to another body close to it, but the first law of thermodynamics states that the sum of the energies generated at all the i elementary bodies at a given position \mathbf{r} must be zero, that is,

$$\sum_i \nu(\mathbf{r}, \mathbf{v}_i) = 0 \quad (4.9)$$

In the same way, the entropy generated by an elementary body can possibly be negative, but the second law of thermodynamics, as stated by Prigogine [7], determines that the sum of all the entropy generated by all the bodies, σ_{irr} , must be non-negative everywhere.

$$\sum_i \sigma(\mathbf{r}, \mathbf{v}_i) = \sigma_{\text{irr}}(\mathbf{r}) \geq 0 \quad (4.10)$$

4.2.3 Local Entropy Production

It is illustrative to have a look at the sources for entropy production. Using equation (4.2) in the basic thermodynamic relationship of equation (4.1), we obtain an interesting relationship between thermodynamic variables per unity of volume:

$$ds = \frac{1}{T} de - \frac{\mu}{T} dn \quad (4.11)$$

If this relationship and equation (4.5) are substituted in equation (4.8), we find that

$$\sigma = \frac{1}{T} \frac{\partial e}{\partial t} - \frac{\mu}{T} \frac{\partial n}{\partial t} + \nabla \cdot \left(\frac{1}{T} \mathbf{j}_e - \frac{1}{T} \mathbf{j}_w - \frac{\mu}{T} \mathbf{j}_n \right) \quad (4.12)$$

Introducing equations (4.6) and (4.7) in (4.12) and after some mathematical handling we obtain that [8]

$$\sigma = \frac{1}{T} \nu + \mathbf{j}_e \nabla \frac{1}{T} - \frac{\mu}{T} g - \mathbf{j}_n \nabla \frac{\mu}{T} + \nabla \cdot \left(-\frac{1}{T} \mathbf{j}_\omega \right) \quad (4.13)$$

where “ ∇ ” is the gradient operator.⁴ This is an important equation allowing us to identify the possible sources of entropy generation in a given subsystem. It contains terms involving energy generation (from another subsystem: ν) and transfer (from the surroundings:

³ The linear unbounded operator “ $\nabla \cdot$ ” applied to the vector $\mathbf{A} \doteq (A_x, A_y, A_z)$ is defined as $\nabla \cdot \mathbf{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$.

⁴ The gradient operator, “ ∇ ,” (without being followed by a dot) is a linear unbounded operator whose actuation on a scalar field $f(x, y, z)$ is defined as $\nabla f = \frac{\partial f}{\partial x} \mathbf{e}_1 + \frac{\partial f}{\partial y} \mathbf{e}_2 + \frac{\partial f}{\partial z} \mathbf{e}_3$ where $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ are the orthonormal basis vectors of the Cartesian framework being used as reference.

$j_e \nabla 1/T$), free energy (μg) generation, Joule effect ($j_n \nabla \mu$) and expansion of the volume that contains the particles ($\nabla j_\omega / T$). This equation is very important and will be used to prove the thermodynamic consistence of solar cells.

4.2.4 An Integral View

Fluxes, \dot{X} , of the thermodynamic currents, j_x , will be frequently used in this paper. In this text, they will be also called *thermodynamic variable rates*. By definition, the following relationship exists:

$$\dot{X} \doteq \int_A \sum_i j_x dA \quad (4.14)$$

where the sum refers to the different subsystems with different velocities to be found at a given position. A is the surface through which the flux is calculated. Actually, $j_x dA$ represents the scalar product of the current density vector j_x and the oriented surface element dA (orientation is arbitrary and if a relevant volume exists the orientation selected leads to the definition of *escaping* or *entering* rates).

4.2.5 Thermodynamic Functions of Radiation

The number of photons in a given mode of radiation is given [9] by the well-known Bose–Einstein factor $f_{BE} = \{\exp[(\varepsilon - \mu)/kT] - 1\}^{-1}$, which through equation (4.3) is related to the grand canonical potential $\Omega = kT \ln\{\exp[(\mu - \varepsilon)/kT] - 1\}$. In these equations, most of the symbols have been defined earlier: ε is the photon energy in the mode and k is the Boltzman constant. The corresponding thermodynamic current densities for these photons are

$$j_n = f_{BE} \mathbf{c} / (Un_r); \quad j_e = \varepsilon j_n f_{BE} \mathbf{c} / (Un_r); \quad j_\omega = \Omega \mathbf{c} / (Un_r) \quad (4.15)$$

where \mathbf{c} is the light velocity (a vector since it includes its direction) in the vacuum and n_r is the index of refraction of the medium in which the photons propagate, which is assumed to be independent of the direction of propagation. Thus, \mathbf{c}/n_r is the velocity of the photons in the medium.

The number of photon modes with energy between ε and $\varepsilon + d\varepsilon$ is $8\pi Un_r^3 \varepsilon^2 / (h^3 \mathbf{c}^2) d\varepsilon$. When the modes with energies $\varepsilon_m < \varepsilon < \varepsilon_M$ are taken into account, the total grand canonical potential of the photons, Ω_{ph} , associated with these modes is the sum of the contributions from each mode and can be written as

$$\Omega_{ph}(U, T, \mu) = \frac{8\pi Un_r^3}{h^3 \mathbf{c}^3} \int_{\varepsilon_m}^{\varepsilon_M} \varepsilon^2 kT \ln(1 - e^{(\mu - \varepsilon)/kT}) d\varepsilon \quad (4.16)$$

where h is the Planck's constant.

Photons do not interact among themselves, such that temperatures and chemical potentials can be different for each mode. This means that they can be a function of the energy and of the direction of propagation. In the non-equilibrium case they can also be a

function of the position. If we only take into account the photons' propagation in a small solid angle $d\varpi$, the grand potential in equation (4.16) must be multiplied by $d\varpi/4\pi$. The same coefficient affects other thermodynamic variables of the radiation.

The flux of a thermodynamic variable X of the radiation through a surface A with a solid angle ϖ is then given by

$$\dot{X} = \int_A \sum_i j_x dA = \int_{A,\varpi} \frac{1}{4\pi} \frac{X}{U} \frac{\mathbf{c}}{n_r} \cos \theta d\varpi dA = \int_H \frac{1}{4\pi} \frac{X}{U} \frac{\mathbf{c}}{n_r^3} dH \quad (4.17)$$

where the angle θ is defined in Figure 4.1. In this case, the sum of equation (4.14) has been substituted by the integration on solid angles. In many cases the integration will be extended to a restricted domain of solid angles. It is, in particular, the case of the photons when they come from a remote source such as the sun.

The differential variable $dH = n_r^2 \cos \theta d\varpi dA$, or its integral on a certain domain (at each position of A it must include the solid angle ϖ containing photons), is the so-called multilinear Lagrange invariant [10]. It is invariant for any optical system [11]. For instance, at the entry aperture of a solar concentrator (think of a simple lens), the bundle of rays has a narrow angular dispersion at its entry since all the rays come from the sun within a narrow cone. Then, they are collected across the whole entry aperture. The invariance for H indicates that it must take the same value at the entry aperture and at the receiver, or even at any intermediate surface that the bundle may cross. If no ray is turned back, all the rays will be present at the receiver. However, if this receiver is smaller than the entry aperture, the angular spread with which the rays illuminate the receiver has to be bigger than the angular spread that they have at the entry. In this way, H becomes a sort of measure of a bundle of rays, similar to its four-dimensional area with two spatial dimensions (in dA) and two angular dimensions (in $d\varpi$). Thus, we may talk of the H_{sr} of a certain bundle of rays linking the sun with a certain receiver.

Besides *Lagrange invariant*, this invariant receives other names. In treatises of thermal transfer it is called *vision* or *view factor*, but Welford and Winston [12] have recovered for this invariant the old name given by Poincaré that in our opinion accurately reflects its properties. He refers to it as *étendue* (extension) of a bundle of rays. We shall adopt in this chapter this name as a shortened denomination for this *multilinear Lagrange invariant*.

When the solid angle of illumination consists of the total hemisphere, $H = n_r^2 \pi A$, where A is the area of the surface traversed by the photons. However, in the absence of optical elements, the photons from the sun reach the converter located on the Earth within

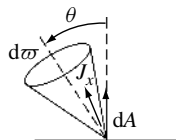


Figure 4.1 Drawing used to show the flux of a thermodynamic variable across a surface element dA

Table 4.1 Several thermodynamic fluxes for photons with energies between ε_m and ε_M distributed according to a black body law determined by a temperature T and chemical potential μ . The last line involves the calculations for a full-energy spectrum ($\varepsilon_m = 0$ and $\varepsilon_M = \infty$). One of the results (the one containing T^4) constitutes the Stefan–Boltzman law

$$\dot{\Omega}(T, \mu, \varepsilon_m, \varepsilon_M, H) = kT \frac{2H}{h^3 c^2} \int_{\varepsilon_m}^{\varepsilon_M} \ln(1 - e^{(\mu - \varepsilon)/kT}) \varepsilon^2 d\varepsilon = \int_{\varepsilon_m}^{\varepsilon_M} \dot{\omega}(T, \mu, \varepsilon, H) d\varepsilon \quad (\text{I-1})$$

$$\dot{N}(T, \mu, \varepsilon_m, \varepsilon_M, H) = \frac{2H}{h^3 c^2} \int_{\varepsilon_m}^{\varepsilon_M} \frac{\varepsilon^2 d\varepsilon}{e^{(\varepsilon - \mu)/kT}} - 1 = \int_{\varepsilon_m}^{\varepsilon_M} \dot{n}(T, \mu, \varepsilon, H) d\varepsilon \quad (\text{I-2})$$

$$\dot{E}(T, \mu, \varepsilon_m, \varepsilon_M, H) = \frac{2H}{h^3 c^2} \int_{\varepsilon_m}^{\varepsilon_M} \frac{\varepsilon^3 d\varepsilon}{e^{(\varepsilon - \mu)/kT}} - 1 = \int_{\varepsilon_m}^{\varepsilon_M} \dot{e}(T, \mu, \varepsilon, H) d\varepsilon \quad (\text{I-3})$$

$$\dot{S} = \frac{\dot{E} - \mu \dot{N} - \dot{\Omega}}{T}; \quad \dot{F} \doteq \dot{E} - T \dot{S} = \mu \dot{N} + \dot{\Omega} \quad (\text{I-4})$$

$$\begin{aligned} \dot{E}(T, 0, 0, \infty, H) &= (H/\pi) \sigma_{\text{SB}} T^4; \quad \dot{S}(T, 0, 0, \infty, H) = (4H/3\pi) \sigma_{\text{SB}} T^3; \\ \sigma_{\text{SB}} &= 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \end{aligned} \quad (\text{I-5})$$

a narrow cone of rays. In this case, $H = \pi A \sin^2 \theta_s$, where θ_s is the sun's semi-angle of vision (taking into account the sun's radius and its distance to Earth), which is equal [13] to 0.267° . No index of refraction is used in this case because the photons come from the vacuum.

Fluxes of some thermodynamic variables and some formulas of interest, which can be obtained from the above principles, are collected in Table 4.1.

4.2.6 Thermodynamic Functions of Electrons

For electrons, the number of particles in a quantum state with energy ε is given by the Fermi–Dirac function $f_{\text{FD}} = \{\exp[(\varepsilon - \varepsilon_F)/kT] + 1\}^{-1}$ where the electrochemical potential (the chemical potential including the potential energy due to electric fields) of the electrons is usually called *Fermi level*, ε_F . Unlike photons, electrons are in continuous interaction among themselves, so that finding different temperatures for electrons is rather difficult. In fact, once a monochromatic light pulse is shined on the semiconductor, the electrons or holes thermalise to an internal electron temperature in less than 100 fs. Cooling to the network temperature will take approximately 10 to 20 ps [14]. However, electrons in semiconductors are found in two bands separated by a large energy gap in which electron states cannot be found. The consequence of this is that, in non-equilibrium, different electrochemical potentials, ε_{Fc} and ε_{Fv} (also called *quasi-Fermi levels*), can exist for the electrons in the conduction band (CB) and the valence band (VB), respectively. Sometimes we prefer to refer to the electrochemical potential of the holes (empty states at the VB), which is then equal to $-\varepsilon_{Fv}$. Once the excitation is suppressed, it can even take milliseconds before the two quasi-Fermi levels become a single one, as it is in the case of silicon.

4.3 PHOTOVOLTAIC CONVERTERS

4.3.1 The Balance Equation of a PV Converter

In 1960, Shockley and Queisser (SQ) published an important paper [2] in which the efficiency upper limit of a solar cell was presented. In this article it was pointed out, for the first time in solar cells, that the generation due to light absorption has a detailed balance counterpart, which is the radiative recombination. This SQ efficiency limit, detailed below, occurs in ideal solar cells that are the archetype of the current solar cells. Such cells (Figure 4.2) are made up of a semiconductor with a VB and a CB, more energetic and separated from the VB by the band gap, ε_g . Each band is able to develop separate quasi-Fermi levels, ε_{Fc} for the CB and ε_{Fv} for the VB, to describe the carrier concentration in the respective bands. In the ideal SQ cell the mobility of the carriers is infinite, and since the electron and hole currents are proportional to the quasi-Fermi level gradients, it follows that the quasi-Fermi levels are constant. Contact to the CB is made by depositing a metal on an n^+ -doped semiconductor. The carriers going through this contact are mainly electrons due to the small hole density. The few holes passing through this contact are accounted for as surface recombination, assumed zero in the ideal case. Similarly, contact with the VB is made with a metal deposited on a p -doped semiconductor. The metal Fermi levels ε_{F+} and ε_{F-} are levelled, respectively, to the hole and the electron quasi-Fermi levels ε_{Fv} and ε_{Fc} at each interface. In equilibrium, the two quasi-Fermi levels become just one.

The voltage V appearing between the two electrodes is given by the splitting of the quasi-Fermi levels, or, more precisely, by the difference in the quasi-Fermi levels of majority carriers at the ohmic contact interfaces. With constant quasi-Fermi levels and ideal contacts, the split is simply

$$qV = \varepsilon_{Fc} - \varepsilon_{Fv} \quad (4.18)$$

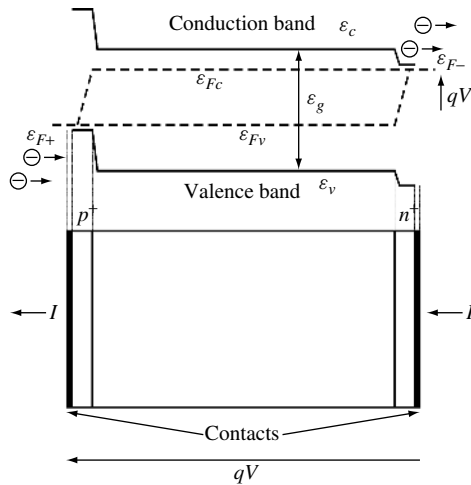


Figure 4.2 Band diagram of a solar cell with its contacts

Photons are absorbed by pumping electrons from the VB to the CB through the process known as electron–hole pair generation. However, as required by the detailed balance, the opposite mechanism is also produced so that a CB electron can decay to the VB and emit a photon, leading to what is called a *radiative recombination process*, responsible for luminescent light emission. In fact, many of such luminescent photons whose energy is slightly above the band gap are reabsorbed, leading to new electron–hole pair generations and balancing out the recombinations. Only the recombination processes leading to the effective emission of a photon out of the semiconductor produce a net recombination. Taking into account that the luminescent photons are emitted isotropically, only those photons emitted near the cell faces, at distances in the range of or smaller than the inverse of the absorption coefficient, and directed towards the cell faces with small angles (those reaching the surface with angles higher than the limit angle will be reflected back) have chances to actually leave the semiconductor, and thus to contribute to the net radiative recombination. The rare device analyses that account for this re-absorption – not yet very common as they are rather involved and the radiative recombination is small in silicon and in many thin-film cells – are said to include photon recycling [15].

In the ideal SQ cell any non-radiative recombination mechanism, which is an entropy-producing mechanism, is assumed to be absent.

The difference between the electrons pumped to the CB by external photon absorption and those falling again into the VB and effectively emitting a luminescent photon equals the current extracted from the cell. This can be presented in an equation form as

$$I/q = \dot{N}_s - \dot{N}_r = \int_{\varepsilon_g}^{\infty} (\dot{n}_s - \dot{n}_r) d\varepsilon \quad (4.19)$$

where $\varepsilon_g = \varepsilon_c - \varepsilon_v$ is the semiconductor band gap and \dot{N}_s and \dot{N}_r are the photon fluxes entering or leaving the solar cell, respectively, through any surface. When the cell is properly contacted, this current is constituted by the electrons that leave the CB through the highly doped n -contact. In a similar balance, in the VB, I/q are also the electrons that enter the VB through the highly doped p -contact. Note that the sign of the current is the opposite to that of the flow of the electrons.

Using the nomenclature in Table 4.1, the terms in equation (4.19) for unit-area cells are $\dot{N}_s = a\dot{N}(T_s, 0, \varepsilon_g, \infty, \pi \sin^2 \theta_s)$ for the cell facing the sun directly or $\dot{N}_s = a\dot{N}(T_s, 0, \varepsilon_g, \infty, \pi)$ for the cell under full concentration and $\dot{N}_r = \xi\dot{N}(T_a, qV, \varepsilon_g, \infty, \pi)$ where a and ξ are the absorptivity and emissivity of the cell. T_s is the sun temperature and T_a is the room temperature. Full concentration means using a concentrator without losses that is able to provide isotropic illumination; this is the highest illuminating power flux from a given source. The conservation of the étendue requires this concentrator to have a concentration C fulfilling the equation $C\pi \sin^2 \theta_s = \pi n_r^2$, that is, $C = 46050n_r^2$. This concentration is indeed unrealistic, but it does lead to the highest efficiency. Furthermore, it can be proven [16] that when the quasi-Fermi level split is uniform in the semiconductor bulk, then $a = \xi$. We shall assume – from now on in this chapter – that the solar cell is thick enough and perfectly coated with antireflection layers so as to fully absorb any photon with energy above the band gap energy so that $a = \xi = 1$ for these photons.

The assumption $\dot{N}_r = \dot{N}(T_a, qV, \varepsilon_g, \infty, \pi)$ states that the temperature associated with the emitted photons is the room temperature T_a . This is natural because the cell is at this temperature. However, it also states that the chemical potential of the radiation emitted, μ_{ph} , is not zero but

$$\mu_{\text{ph}} = \varepsilon_{Fc} - \varepsilon_{Fv} = qV \quad (4.20)$$

This is so because the radiation is due to the recombination of electron–hole pairs, each one with a different electrochemical potential or quasi-Fermi level. A plausibility argument for admitting $\mu_{\text{ph}} = \varepsilon_{Fc} - \varepsilon_{Fv}$ is to consider that photons and electron–hole pairs are produced through the reversible (i.e. not producing entropy) equation electron + hole \leftrightarrow photon. Equation (4.20) would then result as a consequence of equalling the chemical potentials before and after the reaction. Equation (4.20) can be also proven by solving the continuity equation for photons within the cell bulk [16, 17].

When the exponential of the Bose–Einstein function is much higher than one, the recombination term in equation (4.19) for full concentration can be written as

$$\begin{aligned} \dot{N}_r &= \frac{2\pi}{h^3 c^2} \int_{\varepsilon_g}^{\infty} \varepsilon^2 \exp\left(\frac{\varepsilon - qV}{kT_a}\right) d\varepsilon \\ &= \frac{2\pi kT}{h^3 c^2} [4(kT)^2 + 2\varepsilon_g kT + \varepsilon_g^2] \exp\left(\frac{qV - \varepsilon_g}{kT_a}\right) \end{aligned} \quad (4.21)$$

This equation is therefore valid for $\varepsilon_g - qV \gg kT_a$. Within this approximation, the current–voltage characteristic of the solar cell takes its conventional *single* exponential appearance. In fact, this equation, with the appropriate factor $\sin^2 \theta_s$, is accurate in all the ranges of interest of the current–voltage characteristic of ideal cells under unconcentrated sunlight.

The SQ solar cell can reach an efficiency limit given by

$$\eta = \frac{\{qV[\dot{N}_s - \dot{N}_r(qV)]\}_{\max}}{\sigma_{\text{SB}} T_s^4} \quad (4.22)$$

where the maximum is calculated by optimising V . This efficiency limit was first obtained by Shockley and Queisser [2] (for unconcentrated light) and is plotted in Figure 4.3 for several illumination spectra as a function of the band gap.

Outside the atmosphere the sun is seen quite accurately as a black body whose spectrum corresponds to a temperature of 5758 K [19]. To stress the idealistic approach of this chapter, we do not take this value in most of our calculations but rather 6000 K for the sun temperature and 300 K for the room temperature.

It must be pointed out that the limiting efficiency obtained for full concentration can be obtained also at lower concentrations if the étendue of the escaping photons is made equal to that of the incoming photons [16]. This can be achieved by locating the cell in a cavity [20] that limits the angle of the escaping photons.

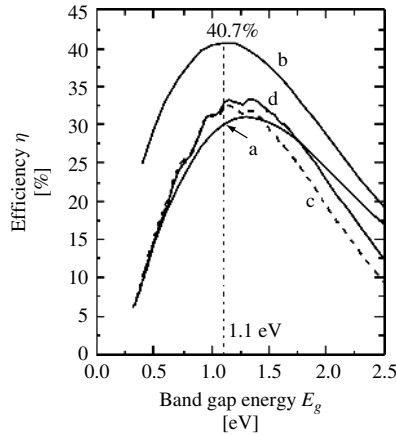


Figure 4.3 SQ efficiency limit for an ideal solar cell versus band gap energy for unconcentrated black body illumination, for full concentrated illumination and for illumination under the terrestrial sun spectrum: (a) unconcentrated 6000 K black body radiation (1595.9 Wm^{-2}); (b) full concentrated 6000 K black body radiation ($7349.0 \times 10^4 \text{ Wm}^{-2}$); (c) unconcentrated AM1.5-Direct [18] (767.2 Wm^{-2}) and (d) AM1.5 Global [18] (962.5 Wm^{-2})

It is interesting to note that the SQ analysis limit does not make any reference to semiconductor *pn* junctions. William Shockley, who first devised the *pn*-junction operation [21], was also the first in implicitly recognising [2] its secondary role in solar cells. In fact, a *pn* junction is not a fundamental constituent of a solar cell. What seems to be fundamental in a solar cell is the existence of two gases of electrons with different quasi-Fermi levels (electrochemical potentials) and the existence of selective contacts [22] that are traversed by each one of these two gases. The importance of the role of the existence of these selective contacts has not been sufficiently recognised. This is achieved today with *n*- and *p*-doped semiconductor regions, not necessarily forming layers, as in the point contact solar cell [23], but in the future it might be achieved otherwise, maybe leading to substantial advancements in PV technology. The role of the semiconductor, of which the cell is made, is to provide the two gases of electrons that may have different quasi-Fermi levels owing to the gap energy separation that makes the recombination difficult.

So far, for non-concentrated light, the most efficient single-junction solar cell, made of GaAs, has achieved an efficiency of 25.1% [24] of AM1.5G spectrum. This is only 23% below the highest theoretical efficiency of 32.8% for the GaAs band gap, of 1.42 eV, for this spectrum [25]. The theoretical maximum almost corresponds to the GaAs band gap. However, most cells are manufactured so that the radiation is also emitted towards the cell substrate located in the rear face of the cell, and little radiation, if any, turns back to the active cell. The consequence of this is that the étendue of the emitted radiation, which is π for a single face radiating to the air, is enlarged. The étendue is then $\pi + \pi n_r^2$. The term πn_r^2 proceeds from the emission of photons towards the substrate of the cell, which has a refraction index n_r . This reduces the limiting efficiency of the GaAs solar cell from 32.8 to 30.7%. Taking this into account, the efficiency of this best experimental cell is only 18.2% below the achievable efficiency of this cell, only on the basis of radiative recombination. Some substantial increase in efficiency might then be achieved by putting a reflector at the rear side of the active layers

of the cells [26] (not behind the substrate!). This would require the use of thin GaAs solar cells [27] or the fabrication of Bragg reflectors [28] (a stack of thin semiconductor layers of alternating refraction indices) underneath the active layers. Bragg reflectors have been investigated for enhancing the absorption of the incoming light in very thin cells, but the reduction of the luminescent emission towards the substrate might be an additional motivation.

4.3.2 The Monochromatic Cell

It is very instructive to consider an ideal cell under monochromatic illumination. When speaking of monochromatic illumination, we mean that, in fact, the cell is illuminated by photons within a narrow interval of energy $\Delta\varepsilon$ around the central energy ε . The monochromatic cell must also prevent the luminescent radiation of energy outside the range $\Delta\varepsilon$ from escaping from the converter.

For building this device an ideal concentrator [29] can be used that collects the rays from the solar disc, with an angular acceptance of just θ_s , with a filter on the entry aperture, letting the aforementioned monochromatic illumination to pass through. This concentrator is able to produce isotropic illumination at the receiver. By a reversal of the ray directions, the rays issuing from the cell in any direction are to be found also at the entry aperture with directions within the cone of semi-angle θ_s . Those with the proper energy will escape and be emitted towards the sun. The rest will be reflected back into the cell where they will be recycled. Thus, under ideal conditions no photon will escape with energy outside the filter energy and, furthermore, the photons escaping will be sent directly back to the sun with the same étendue of the incoming bundle H_{sr} .

The current in the monochromatic cell, ΔI , will then be given by

$$\begin{aligned} \Delta I/q &\equiv i(\varepsilon, V)\Delta\varepsilon/q = (\dot{n}_s - \dot{n}_r)\Delta\varepsilon \\ &= \frac{2H_{sr}}{h^3 c^2} \left[\frac{\varepsilon^2 \Delta\varepsilon}{\exp\left(\frac{\varepsilon}{kT_s}\right) - 1} - \frac{\varepsilon^2 \Delta\varepsilon}{\exp\left(\frac{\varepsilon - qV}{kT_a}\right) - 1} \right] \end{aligned} \quad (4.23)$$

This equation allows for defining an equivalent cell temperature T_r ,

$$\frac{\varepsilon}{kT_r} = \frac{\varepsilon - qV}{kT_a} \Rightarrow qV = \varepsilon \left(1 - \frac{T_a}{T_r}\right) \quad (4.24)$$

so that the power produced by this cell, $\Delta\dot{W}$, is

$$\begin{aligned} \Delta\dot{W} &= \frac{2H_{sr}}{h^3 c^2} \left[\frac{\varepsilon^3 \Delta\varepsilon}{\exp\left(\frac{\varepsilon}{kT_s}\right) - 1} - \frac{\varepsilon^3 \Delta\varepsilon}{\exp\left(\frac{\varepsilon}{kT_r}\right) - 1} \right] \left(1 - \frac{T_a}{T_r}\right) \\ &= (\dot{e}_s - \dot{e}_r)\Delta\varepsilon \left(1 - \frac{T_a}{T_r}\right) \end{aligned} \quad (4.25)$$

We realise that the work extracted from the monochromatic cell is the same as that extracted from a Carnot engine fed with a heat rate from the hot reservoir $\Delta\dot{q} = (\dot{e}_s - \dot{e}_r)\Delta\varepsilon$. However, this similarity does not hold under a non-monochromatic illumination because, for a given voltage, the cell equivalent temperature would depend on the photon energy ε being unable to define a single equivalent temperature for the whole spectrum. Note that the equivalent cell temperatures corresponding to short-circuit and open-circuit conditions are T_a and T_s , respectively.

To calculate the efficiency, $\Delta\dot{W}$ in equation (4.25) must be divided by the appropriate denominator. We could divide by the black body incident energy $\sigma_{\text{SB}}T_s^4$, but this would be unfair because the unused energy that is reflected by the entry aperture could be deflected with an optical device and used in other solar converters. We can divide by $\dot{e}_s\Delta\varepsilon$, the rate of power received at the cell, thus obtaining the *monochromatic* efficiency, η_{mc} , given by

$$\eta_{\text{mc}} = \left. \frac{q(\dot{n}_s - \dot{n}_r)V}{\dot{e}_s} \right|_{\text{max}} = \left(1 - \frac{\dot{e}_r}{\dot{e}_s} \right) \left(1 - \frac{T_a}{T_r} \right) \Big|_{\text{max}} \quad (4.26)$$

that is represented in Figure 4.4 as a function of the energy ε .

Alternatively, we could have used the standard definition of efficiency used in thermodynamics [30, 31] to compute the efficiency of the monochromatic cell. In this context, we put in the denominator the energy really wasted in the conversion process, that is, $(\dot{e}_s - \dot{e}_r)\Delta\varepsilon$. Actually, the energy $\dot{e}_r\Delta\varepsilon$ is returned to the sun, perhaps for later use (slowing down, for example, the sun's energy loss process!). This leads to the *thermodynamic* efficiency:

$$\eta_{\text{th}} = \left(1 - \frac{T_a}{T_r} \right) \quad (4.27)$$

This efficiency is the same as the Carnot efficiency obtained by a reversible engine operating between an absorber at temperature T_r and the ambient temperature and suggests that an ideal solar cell may work reversibly, without entropy generation. Its maximum,

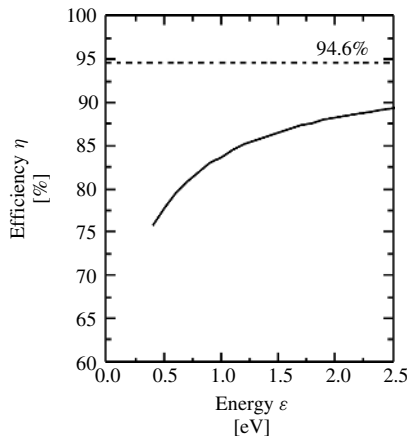


Figure 4.4 Monochromatic cell efficiency versus photon energy

for $\Delta\dot{w} \geq 0$, is obtained for $T_r = T_s$, although unfortunately it occurs when $\Delta\dot{w} = 0$, that is, when negligible (actually, none) work is done by the cell. However, this is a general characteristic of reversible engines, which yield the Carnot efficiency only at the expense of producing negligible power.

4.3.3 Thermodynamic Consistence of the Shockley–Queisser Photovoltaic Cell

Electrons and photons are the main particles interacting in a solar cell [8]. However, other interactions occur as well. In general, looking at equation (4.13), the generation of entropy for each kind of particle (electrons, photons and others) is written as

$$\sigma = \sum_i \left[\frac{1}{T} v + \mathbf{j}_e \nabla \frac{1}{T} - \frac{\mu}{T} g - \mathbf{j}_n \nabla \frac{\mu}{T} + \nabla \cdot \left(-\frac{1}{T} \mathbf{j}_\omega \right) \right] \quad (4.28)$$

where the summation extends to the different states of the particle.

First we analyse the generation of entropy by electrons, σ_{ele} . Except for the case of ballistic electrons, the pressure – appearing inside \mathbf{j}_ω as shown in equation (4.5) – is very quickly equilibrated; it is the same for $+\mathbf{v}$ and for $-\mathbf{v}$ as a result of the frequent elastic collisions. Thus, the term in \mathbf{j}_ω for electrons disappears when the sum is extended to all the states in each energy. These collisions also cause the temperature and the free energy to become the same for all the directions, at least for a given energy. Furthermore, in conventional solar cells, the temperature of the electrons is the same for any energy and is equal to the lattice temperature T_a . Also, the electrochemical potential is the same for all the electrons within the same band at a given \mathbf{r} .

In a real cell, the energy flow \mathbf{j}_e goes from the high-temperature regions towards the low-temperature ones [$\nabla(1/T) \geq 0$] so that the term in (4.28) involving \mathbf{j}_e produces positive entropy. The electron flow, \mathbf{j}_n , opposes the gradient of electrochemical potential, thus also producing positive entropy for constant temperature. However, in the ideal cell, the lattice temperature, which is also that of the electrons, is constant and the term involving $\nabla(1/T)$ disappears. Furthermore, in the SQ [2] ideal cell, mobility is infinite and, therefore, its conduction and valence band electrochemical potentials or quasi-Fermi levels (ε_{Fc} , ε_{Fv}) are constant throughout the whole solar cell and their gradients are also zero. Therefore, all the gradients in equation (4.28) disappear and the electron contribution to entropy generation, σ_{ele} , is given by

$$\sigma_{\text{ele}} = \sum_{i-\text{ele}} \left[\frac{1}{T_a} v_{i-\text{ele}} - \frac{\varepsilon_{Fc(v)}}{T_a} g_{i-\text{ele}} \right] \quad (4.29)$$

The quasi-Fermi level to be used in this case is ε_{Fc} or ε_{Fv} depending on the band to which the electronic state i -ele belongs. This is represented by $\varepsilon_{Fc(v)}$.

Other interactions may occur in the cell involving other particles besides the electrons and the photons. We shall assume that in these interactions the bodies involved (labelled as *others*) also have a direction-independent pressure and that they are also at

the lattice temperature. Furthermore, if these particles exist, they are assumed to have zero chemical potential (as it is the case, for example, of the phonons). Using these assumptions, the contribution to the irreversible entropy generation rate from these *other* particles becomes

$$\sigma_{\text{others}} = \sum_{i-\text{others}} \left[\frac{1}{T_a} v_{i-\text{others}} \right] \quad (4.30)$$

For the case of the photons, the situation is rather different. As said before, photons do not interact with each other and, therefore, they are essentially ballistic. Their thermodynamic intensive variables may experience variations with the photon energy and also with their direction of propagation. In fact, they come from the sun in a few directions only, and only in these directions do they exert a pressure. The direct consequence is that a non-vanishing current of grand potential exists for the photons. (It vanishes in gases of photons that are confined and in thermal equilibrium with the confining walls. Using this condition for photon beams from the sun is not correct.)

N_{ph} being the number of photons in a mode corresponding to a certain ray moving inside the semiconductor, their evolution along a given ray path corresponding to a radiation mode is given by [17]

$$N_{\text{ph}}(\varsigma) = f_{\text{BE}}(T, qV)[1 - e^{-\alpha\varsigma}] + N_{\text{ph}}(0)e^{-\alpha\varsigma} \quad (4.31)$$

where ς is the length of the ray, f_{BE} is the Bose–Einstein factor for luminescent photons whose chemical potential is the separation between the conduction and the valence band electron quasi-Fermi levels – in this case equalling the cell voltage V (times q) – and α is the absorption coefficient. Equation (4.31) shows a non-homogeneous profile for N_{ph} contributed to by luminescent photons that increase with ς (first term on the right-hand side) and externally fed photons that decrease when the ray proceeds across the semiconductor (second term), and these photons are absorbed. $N_{\text{ph}}(0) = f_{\text{BE}}(T_s, 0)$ is usually taken in solar cells that correspond to illumination by free (i.e. with zero chemical potential) radiation at the sun temperature T_s .

In general, the photons in a mode of energy ε are considered as a macroscopic body [9] for which temperature and chemical potential can be defined. However, thermodynamically, they can be arbitrarily characterised by a chemical potential μ and a temperature T as long as $(\varepsilon - \mu)/T$ takes the same value. For example, the incident solar photons may be considered at the solar temperature T_s with zero chemical potential or, alternatively, at room temperature T_a with an energy variable chemical potential $\mu_s = \varepsilon(1 - T_a/T_s)$. This property has already been used in the study of the monochromatic cell.

Indeed, this arbitrary choice of T and μ does not affect the entropy production. This becomes evident if we rewrite equation (4.28) in the case of photons as

$$\sigma_{\text{ph}} = \sum_{i-\text{ph}} \left[\frac{\varepsilon - \mu}{T} g + \mathbf{j}_n \cdot \nabla \left(\frac{\varepsilon - \mu}{T} \right) + \nabla \cdot \left(-\frac{1}{T} \mathbf{j}_\omega \right) \right] \quad (4.32)$$

where we have made use of equation (4.15) and of the fact that $v = \varepsilon g$. This equation depends explicitly only on $(\varepsilon - \mu)/T$. This is less evident in the term in \mathbf{j}_ω/T , but as

discussed in the context of equation (4.15), j_ω is proportional to T and thus j_ω/T only depends on $(\varepsilon - \mu)/T$. Note, however, that j_ω is affected by the specific choice of T .

For simplicity, we shall consider the photons at room temperature and we shall calculate their chemical potential, μ_{ph} , from setting the equality

$$N_{\text{ph}}(\zeta, \varepsilon) = \frac{\varepsilon^2}{\exp\left[\frac{\varepsilon - \mu_{\text{ph}}(\zeta, \varepsilon)}{kT_a}\right] - 1} \quad (4.33)$$

However, we might have chosen to leave $\mu_{\text{ph}} = 0$, and then the effect of the absorption of light when passing through the semiconductor could have been described as a cooling down of the photons (if N_{ph} actually decreases with ζ).

With the room-temperature luminescent photon description, the production of entropy by photons is given by

$$\sigma_{\text{ph}} = \sum_{i-\text{ph}} \left[\frac{v_{i-\text{ph}}}{T_a} - \frac{\mu_{i-\text{ph}} g_{i-\text{ph}}}{T_a} - \frac{j_{n,i-\text{ph}} \nabla \mu_{i-\text{ph}}}{T_a} - \frac{\nabla j_{\omega,i-\text{ph}}}{T_a} \right] \quad (4.34)$$

However, using equations (4.15) and (4.3),

$$\nabla j_\omega = \frac{c}{Un_r} \frac{d\Omega}{d\mu} \nabla \mu = -\frac{c}{Un_r} f_{\text{BE}} \nabla \mu = -j_n \nabla \mu \quad (4.35)$$

and

$$\sigma_{\text{ph}} = \sum_{i-\text{ph}} \left[-\frac{v_{i-\text{ph}}}{T_a} + \frac{\mu_{i-\text{ph}} g_{i-\text{ph}}}{T_a} \right] \quad (4.36)$$

where

$$g = (c/Un_r) \alpha f_{\text{BE}}(T_a, qV) e^{-\alpha \zeta} - (c/Un_r) \alpha f_{\text{BE}}(T_s, 0) e^{-\alpha \zeta}; \quad v = \varepsilon g \quad (4.37)$$

The total irreversible entropy production is obtained by adding equations (4.29), (4.30) and (4.36), taking into account equation (4.37). Now, the terms in energy generation, all at the same temperature, must balance out by the first principle of thermodynamics. The net absorption of photons corresponds to an electron transfer (positive and negative generations) between states gaining an electrochemical potential qV , so the terms $\mu g/T$ corresponding to electrons and photons subtract each other. No additional generations are assumed to take place. Thus the total irreversible entropy generation rate can be written as

$$\sigma_{\text{irr}} = \frac{c\alpha}{Un_r} \sum_{i-\text{ph}} \frac{(\mu_{i-\text{ph}} - qV) [f_{\text{BE}}(T_s, 0) e^{-\alpha \zeta} - f_{\text{BE}}(T_a, qV) e^{-\alpha \zeta}]}{T_a} \quad (4.38)$$

For a given mode the second factor balances out when $f_{\text{BE}}(T_s, 0) = f_{\text{BE}}(T_a, qV)$, and so does the irreversible entropy generation. In this case, $N_{\text{ph}} = f_{\text{BE}}(T_a, qV)$ is constant along the ray and $\mu_{i-\text{ph}} = qV$ is constant at all points. The irreversible entropy generation rate is

then zero everywhere. If $f(T_s, 0) > f(T_a, qV)$, then $N_{ph} > f(T_a, qV)$ and $\mu_{i-ph} > qV$, so that both factors are positive and so is the product. If $f(T_s, 0) < f(T_a, qV)$, then $N_{ph} < f(T_a, qV)$ and $\mu_{i-ph} < qV$. In this case both factors are negative and the product is positive.

Thus, we have proven that every mode contributes non-negatively to the entropy. We can then state that the SQ cell produces non-negative entropy and, in this sense, it complies with the second law of thermodynamics.

For less idealised cases, as we have mentioned above, the existence of quasi-Fermi levels or temperature gradients generally produces additional positive entropy. Non-radiative net recombination of electrons from the conduction to the valence band also produces positive entropy. However, net generation would contribute to the production of negative entropy and, therefore, it may incur in violation of the second law of thermodynamics, if no other mechanism contributing to the creation of positive entropy exists. So the inclusion of imaginative carrier generation rates in novel device proposals, without counterparts, must be considered with some caution.

4.3.4 Entropy Production in the Whole Shockley–Queisser Solar Cell

The preceding approach is applicable to regions in which the physical properties of the system are continuous and differentiable, but not to abrupt interfaces. For testing the compliance with the second law, the continuity equations must be integrated in such cases by choosing volumes surrounding the suspected interfaces. This integral approach can also be extended to the whole converter to check for any violation of the second law and also to calculate the whole entropy production of a device. However, the integral approach, if not complemented with the local approach, is valid for proving thermodynamic inconsistency, but not for proving consistency that has to be proven at every point. An example of the use of such an integral approach is given here.

In the integral analysis we follow steps similar to those used in the local analysis. In particular, the first law of thermodynamics is applied by integrating equation (4.7) and using the first law expressed by equation (4.9). Then, we obtain, for the stationary case

$$0 = \int_A \sum_i \mathbf{j}_{e,i} dA = +\dot{E}_r - \dot{E}_s + \dot{E}_{mo} - \dot{E}_{mi} + \dot{E}_{others} \quad (4.39)$$

where \dot{E}_s and \dot{E}_r are the radiation energies entering or escaping from the converter, \dot{E}_{mi} and \dot{E}_{mo} are the energies of the electrons entering the VB and leaving the CB, respectively, and \dot{E}_{others} is the net flow of energy leaving the semiconductor as a result of other mechanisms.

Taking equation (4.5) into account, the fact that no chemical potential is associated with *other* particles and processes, and the annihilation of the grand canonical potential current density, the term corresponding to the other elements is more conventionally written as

$$\dot{E}_{others} = T_a \dot{S}_{others} \doteq \dot{Q} \quad (4.40)$$

where \dot{Q} is defined as the rate of heat leaving the converter.

The second law of thermodynamics, expressed by equations (4.8) and (4.10), integrated into the whole volume of the converter can be written, for the stationary case, as

$$\dot{S}_{\text{irr}} = \int_U \sigma_{\text{irr}} dU = \int_A \sum_i \mathbf{j}_{s,i} dA = \dot{S}_r - \dot{S}_s + \dot{S}_{mo} - \dot{S}_{mi} + \dot{S}_{\text{others}} \quad (4.41)$$

The irreversible rate of entropy production is obtained by the elimination of the terms with subscript *others* by multiplying equation (4.41) by T_a , subtracting equation (4.39) from the result and taking into account (4.40). In this way we obtain

$$T_a \dot{S}_{\text{irr}} = (\dot{E}_s - T_a \dot{S}_s) - (\dot{E}_r - T_a \dot{S}_r) + (\dot{E}_{mi} - T_a \dot{S}_{mi}) - (\dot{E}_{mo} - T_a \dot{S}_{mo}) \quad (4.42)$$

From equation I-4 (Table 4.1) and considering the annihilation of the grand canonical potential flow for electrons, $(\dot{E}_{mi} - T_a \dot{S}_{mi}) = \varepsilon_{Fv} \dot{N}_{mi}$ and $(\dot{E}_{mo} - T_a \dot{S}_{mo}) = \varepsilon_{Fc} \dot{N}_{mo}$, so that we can write

$$T_a \dot{S}_{\text{irr}} = \varepsilon_{Fv} \dot{N}_{mi} - \varepsilon_{Fc} \dot{N}_{mo} + (\dot{E}_s - T_a \dot{S}_s) - (\dot{E}_r - T_a \dot{S}_r) \quad (4.43)$$

Taking into account that $\dot{N}_{mi} = \dot{N}_{mo} = I/q$ and $\varepsilon_{Fc} - \varepsilon_{Fv} = qV$, equation (4.43) is now rewritten as

$$T_a \dot{S}_{\text{irr}} = -\dot{W} + (\dot{E}_s - T_a \dot{S}_s) - (\dot{E}_r - T_a \dot{S}_r) \quad (4.44)$$

Here, this equation has been derived from the *local* model. However, it can also be obtained with more generality from a classical formulation of the second law of thermodynamics [32]. It is valid for ideal as well as for non-ideal devices. The values of the thermodynamic variables to be used in equation (4.44) are given in Table 4.1. Power – which in other cases will be that of the converter under study – corresponds in this case to the power of an SQ ideal solar cell and is given by the product of equations (4.18) and (4.19).

We have already discussed the basic ambiguity for the thermodynamic description of any radiation concerning the choice of the temperature and the chemical potential. A useful corollary is derived from this fact [32]. If the power rate produced by a radiation converter depends on the radiation only through its rate of incident energy or number of photons, then any radiation received or emitted by the converter can be changed into a luminescent radiation at room temperature, T_a , and with chemical potential, μ_x , without affecting the rate of power and of irreversible entropy produced. The chemical potential μ_x of this equivalent luminescent radiation is linked to the thermodynamic parameters of the original radiation, T_{rad} and μ_{rad} , through the equation

$$\frac{\varepsilon - \mu_{\text{rad}}}{kT_{\text{rad}}} = \frac{\varepsilon - \mu_x}{kT_a} \Rightarrow \mu_x = \varepsilon \left(1 - \frac{T_a}{T_{\text{rad}}} \right) + \mu_{\text{rad}} \frac{T_a}{T_{\text{rad}}} \quad (4.45)$$

Note that, in general, μ_x is a function of the photon energy, ε , as it may also be T_{rad} and μ_{rad} .

The proof of the theorem is rather simple and is brought in here because it uses relationships of instrumental value. It is straightforward to see that

$$\dot{n}_x = \dot{n}_{\text{rad}}; \quad \dot{e}_x = \varepsilon \dot{n}_x = \dot{e}_{\text{rad}}; \quad \dot{\omega}_x / T_a = \dot{\omega}_{\text{rad}} / T_{\text{rad}}; \quad \dot{e}_{\text{rad}} - T \dot{s}_{\text{rad}} = \mu_x \dot{n}_x + \dot{\omega}_x \quad (4.46)$$

where, again, the suffix *rad* labels the thermodynamic variables of the original radiation.

The equality of the energy and the number of photons of the original and equivalent radiation proves that the power production is unchanged. Furthermore, the last relationship can be introduced in equation (4.44) to prove that the calculation of the entropy production rate also remains unchanged.

Taking all this into account, the application of equation (4.44) to the SQ solar cell is rather simple. Using the SQ cell model for the power and using the room-temperature equivalent radiation (of chemical potential μ_s) of the solar radiation, we obtain

$$\begin{aligned} T_a \dot{S}_{\text{irr}} &= - \int_{\varepsilon_g}^{\infty} qV [\dot{n}(T_a, \mu_s) - \dot{n}(T_a, qV)] d\varepsilon + \int_{\varepsilon_g}^{\infty} [\mu_s \dot{n}(T_a, \mu_s) + \dot{\omega}(T_a, \mu_s)] d\varepsilon \\ &\quad - \int_{\varepsilon_g}^{\infty} [qV \dot{n}(T_a, qV) + \dot{\omega}(T_a, qV)] d\varepsilon \\ &= \int_{\varepsilon_g}^{\infty} [\dot{\omega}(T_a, \mu_s) - \dot{\omega}(T_a, qV)] d\varepsilon + \int_{\varepsilon_g}^{\infty} [(\mu_s - qV) \dot{n}(T_a, \mu_s)] d\varepsilon \end{aligned} \quad (4.47)$$

The integrand is zero for $qV = \mu_s$, but as μ_s varies with ε it is not zero simultaneously for all ε . To prove that it is positive, we differentiate with respect to qV . Using $d\dot{\omega}/d\mu = -\dot{n}$,

$$\frac{d(T_a \dot{S}_{\text{irr}})}{dqV} = - \int_{\varepsilon_g}^{\infty} [\dot{n}(T_a, \mu_s) - \dot{n}(T_a, qV)] d\varepsilon = I/q \quad (4.48)$$

Thus, for each energy, the minimum of the integrand also appears for $qV = \mu_s(\varepsilon)$. Since this minimum is zero, the integrand is non-negative for any ε and so is the integral, proving also the thermodynamic consistence of this cell from the integral perspective. Furthermore, the minimum of the entropy, which for the non-monochromatic cell is not zero, occurs for open-circuit conditions. However, the ideal monochromatic cell reaches zero entropy production, and therefore reversible operation, under open-circuit conditions, and this is why this cell may reach the Carnot efficiency, as discussed in a preceding section.

4.4 THE TECHNICAL EFFICIENCY LIMIT FOR SOLAR CONVERTERS

We have seen that with the technical definition of efficiency – in whose denominator the radiation returned to the sun is not considered – the Carnot efficiency cannot be reached with a PV converter. What then is the technical efficiency upper limit for solar converters?

We can consider that this limit would be achieved if we could build a converter producing zero entropy [33]. In this case, the power that this converter can produce,

\dot{W}_{lim} , can be obtained from equation (4.44) by setting the irreversible entropy-generation term to zero. Substituting the terms involving emitted radiation by their room-temperature luminescent equivalent, equation (4.44) becomes

$$\dot{W}_{\text{lim}} = \int_{\varepsilon_g}^{\infty} \{[\dot{e}_s - T_a \dot{s}_s] - [\mu_x(\varepsilon) \dot{n}_x + \dot{\omega}_x]\} d\varepsilon = \int_{\varepsilon_g}^{\infty} \dot{w}_{\text{lim}}(\varepsilon, \mu_x) d\varepsilon \quad (4.49)$$

The integrand should now be maximised [32] with respect to μ_x . For this, we calculate the derivative

$$\frac{d\dot{w}_{\text{lim}}}{d\mu_x} = -\dot{n}_x - \frac{d\dot{\omega}_x}{d\mu_x} - \mu_x \frac{d\dot{n}_x}{d\mu_x} = -\mu_x \frac{d\dot{n}_x}{d\mu_x} \quad (4.50)$$

where we have used that the derivative of the grand potential with respect to the chemical potential is the number of particles with a change of sign. This equation shows that the maximum is achieved if $\mu_x = 0$ for any ε , or, in other words, if the radiation emitted is a room-temperature thermal radiation. This is the radiation emitted by all the bodies in thermal equilibrium with the ambient. However, the same result will be also achieved if the emitted radiation is any radiation whose room-temperature luminescent equivalent is a room-temperature thermal radiation.

Now, we can determine this efficiency, according to Landsberg [33], as

$$\begin{aligned} \eta &= \frac{\left(\frac{H_{sr}}{\pi}\right) \left[\left(\sigma T_s^4 - \frac{4}{3} \sigma T_a T_s^3 \right) - \left(\sigma T_a^4 - \frac{4}{3} \sigma T_a^3 \right) \right]}{(H_{sr}/\pi) \sigma T_s^4} \\ &= 1 - \frac{4}{3} \left(\frac{T_a}{T_s} \right) + \frac{1}{3} \left(\frac{T_a}{T_s} \right)^4 \end{aligned} \quad (4.51)$$

which for $T_s = 6000$ K and $T = 300$ K gives 93.33% instead of 95% of the Carnot efficiency.

No ideal device is known that is able to reach this efficiency. Ideal solar thermal converters, not considered in this chapter, have a limiting efficiency of 85.4% [34, 35] and therefore do not reach this limit. Other high-efficiency ideal devices considered in this chapter do not reach it either. We do not know whether the Landsberg efficiency is out of reach. At least it is certainly an upper limit of the technical efficiency of any solar converter.

4.5 VERY HIGH EFFICIENCY CONCEPTS

4.5.1 Multijunction Solar Cells

A conceptually straightforward way of overcoming the fundamental limitation of the SQ cell, already pointed out by SQ, is the use of several solar cells of different band gaps to convert photons of different energies. A simple configuration to achieve it is by just stacking the cells so that the upper cell has the highest band gap and lets the photons pass through towards the inner cells (Figure 4.5). The last cell in the stack is the one with the narrowest band gap. Between cells we put low-energy pass filters so that the

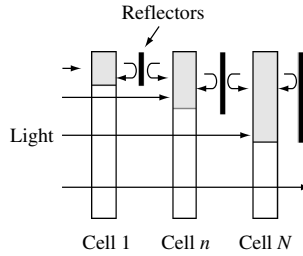


Figure 4.5 Stack of solar cells ordered from left to right in decreasing band gap ($E_{g1} > E_{g2} > E_{g3}$). (Reprinted from *Solar Energy Materials and Solar Cells* V. 43, N. 2, Martí A. and Araújo G. L, *Limiting Efficiencies for Photovoltaic Energy Conversion in Multigap Systems*, 203–222, © 1996 with permission from Elsevier Science)

reflection threshold of each filter is the band gap of the cell situated above. This prevents the luminescent photons from being emitted for energies different to those with which the photons from the sun are received in each cell. In this configuration, every cell has its own load circuit, and therefore, is biased at a different voltage. It has been shown [31] that a configuration without back reflectors leads to a lower efficiency if the number of cells is finite. For the case of a stack with an infinite number of cells, the limiting efficiency is found to be independent of whether reflectors are placed or not.

For example, for the case of a stack with two cells, the power generated is

$$W = qV_l[\dot{N}(T_s, 0, \varepsilon_{gl}, \varepsilon_{gh}, H_s) - \dot{N}(T_a, qV_l, \varepsilon_{gl}, \varepsilon_{gh}, H_r)] + qV_h[\dot{N}(T_s, 0, \varepsilon_{gh}, \infty, H_s) - \dot{N}(T_a, qV_h, \varepsilon_{gh}, \infty, H_r)] \quad (4.52)$$

where the suffixes l and h (low and high) refer to the band gap and the voltage of the two cells involved. The maximum power is obtained by optimising this function with respect to the variables V_l , V_h , ε_{gl} and ε_{gh} . We present in Figure 4.6 the efficiency of

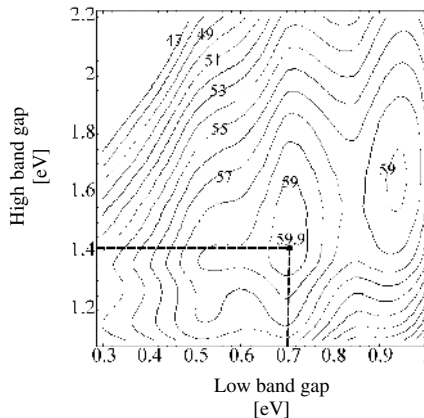


Figure 4.6 Efficiency of a tandem of two ideal cells under AM1.5D illumination as a function of the two cells' band gap ε_l and ε_h

two ideal cells as a function of the two cells' band gaps, which is optimised only with respect to V_l and V_h . The generation term is in this case not the one in equation (4.52) but the one corresponding to a standard spectrum AM1.5D [18]. Power is converted into efficiency by dividing by 767.2 Wm^{-2} , which is the power flux carried by the photons in this spectrum. In the figure, we can observe that the efficiency maximum is very broad, allowing for a wide combination of materials.

A lot of experimental work has been done on this subject. To our knowledge, the highest efficiency so far achieved, 34% (AM1.5 Global), has been obtained by Spectrolab [24, 36], in 2001, using a monolithic (made on the same chip) two-terminal tandem InGaP/GaAs stuck on a Ge cell and operating at a concentration factor of 210, that is, at 21 Wcm^{-2} .

The maximum efficiency is obtained with an infinite number of solar cells, each one biased at its own voltage $V(\varepsilon)$ and illuminated with monochromatic radiation. The efficiency of this cell is given by

$$\eta = \frac{\int_0^\infty \eta_{mc}(\varepsilon) \dot{\varepsilon}_s d\varepsilon}{\int_0^\infty \dot{\varepsilon}_s d\varepsilon} = \frac{1}{\sigma_{SB} T_s^4} \int_0^\infty \eta_{mc}(\varepsilon) \dot{\varepsilon}_s d\varepsilon = \frac{1}{\sigma_{SB} T_s^4} \int_0^\infty i(\varepsilon, V) V|_{\max} d\varepsilon \quad (4.53)$$

where $\eta_{mc}(\varepsilon)$ is the monochromatic cell efficiency given by equation (4.26) and $i(\varepsilon, V)$ was defined in equation (4.23). For $T_s = 6000 \text{ K}$ and $T_a = 300 \text{ K}$, the sun and ambient temperature, respectively, this efficiency is [34] 86.8%. This is the highest efficiency limit of known ideal converter.

Tandem cells emit room-temperature luminescent radiation. This radiation presents, however, a variable chemical potential $\mu(\varepsilon) = qV(\varepsilon)$ and therefore it is not a radiation with zero chemical potential (free radiation). In addition, the entropy produced by this array is positive since the entropy produced by each one of the monochromatic cells forming the stack is positive. None of the conditions for reaching the Landsberg efficiency (zero entropy generation rate and emission of free radiation at room temperature) is then fulfilled and, therefore, tandem cells do not reach this upper bound.

It is highly desirable to obtain monolithic stacks of solar cells, that is, on the same chip. In this case, the series connection of all the cells in the stack is the most compact solution. Chapter 9 will deal with this case extensively. If the cells are series-connected, a limitation appears that the same current must go through all the cells. For the case of two cells studied above, this limitation is expressed by the equation

$$\begin{aligned} I &= q [\dot{N}(T_s, 0, \varepsilon_{gl}, \varepsilon_{gh}, H_s) - \dot{N}(T_a, qV_l, \varepsilon_{gl}, \varepsilon_{gh}, H_r)] \\ &= q [\dot{N}(T_s, 0, \varepsilon_{gh}, \infty, H_s) - \dot{N}(T_a, qV_h, \varepsilon_{gh}, \infty, H_r)] \end{aligned} \quad (4.54)$$

This equation establishes a link between V_l and V_h (for each couple $\varepsilon_l, \varepsilon_h$), which reduces the value of the maximum achievable efficiency. The total voltage obtained from the stack is $V = V_l + V_h$.

Our interest now is to determine the top efficiency achievable in this case when the number of cells is increased to infinity. Surprisingly enough, it is found [37, 38] that

the solution is also given by equation (4.53) and therefore, the limiting efficiency of a set of cells that is series-connected is also 86.8%.

4.5.2 Thermophotovoltaic Converters

Thermophotovoltaic (TPV) converters are devices in which a solar cell converts the radiation emitted by a heated body into electricity. This emitter may be heated, for example, by the ignition of a fuel. However, in our context, we are more interested in solar TPV converters in which the sun is the source of energy that heats an absorber at temperature T_r , which then emits radiation towards the PV converter. Figure 4.7 draws the ideal converter for this situation.

An interesting feature of the TPV converter is that the radiation emitted by the solar cells is sent back to the absorber assisting in keeping it hot. To make the cell area different from the radiator area (so far cells in this chapter have all been considered to be of area unity), the absorber in Figure 4.7 radiates into a reflecting cavity containing the cell. The reflective surfaces in the cavity and the mirrors in the concentrator are assumed to be free of light absorption.

In the ideal case [39], the radiator emits two bundles of rays, one of étendue H_{rc} (emitted by the right side of the absorber in the Figure 4.7a), which is sent to the cell after reflections in the cavity walls, with energy \dot{E}'_r without losses, and another (unavoidable) one H_{rs} , with energy \dot{E}_r , which is sent back to the sun (by the left face of the absorber) after suffering reflections in the left-side concentrator. Ideally, the radiator illuminates no other absorbing element or dark part of the sky: all the light emitted by the radiator's left side is sent back to the sun by the concentrator. Rays emitted by the radiator into the cavity may return to the radiator again without touching the cell, but since no energy is transferred, such rays are not taken into account.

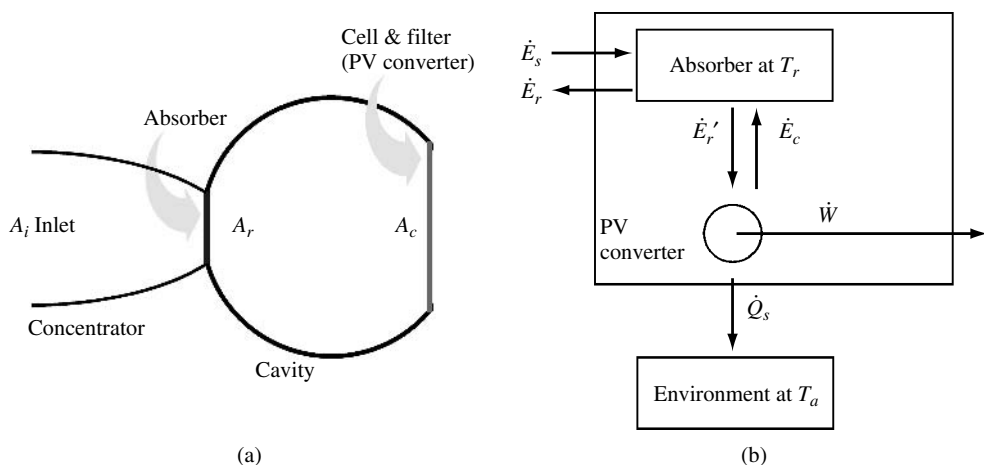


Figure 4.7 (a) Schematic of an ideal TPV converter with the elements inserted in loss-free reflecting cavities and (b) illustration of the thermodynamic fluxes involved. In the monochromatic case, $\dot{E}_s \equiv \dot{E}(T_s, 0, 0, \infty, H_{rs})$, $\dot{E}_r \equiv \dot{E}(T_r, 0, 0, \infty, H_{rs})$, $\dot{E}'_r \equiv \dot{e}(\varepsilon, T_r, 0, H_{rc})\Delta\varepsilon$, $\dot{E}_c \equiv \dot{e}(\varepsilon, T_a, qV, H_{rc})\Delta\varepsilon$

On the other hand, the radiator is illuminated by a bundle of rays, coming from the sun, of étendue $H_{sr} = H_{rs}$ and by the radiation emitted by the cell itself, of étendue $H_{cr} = H_{rc}$. Also, the cell may emit some radiation into the cavity, which returns to the cell again. This radiation is therefore not accounted for as an energy loss in the cell. In addition, we shall assume that the cell is coated with an ideal filter that allows only photons with energy ε and within a bandwidth $\Delta\varepsilon$ to pass through, while the others are totally reflected. In this situation the energy balance in the radiator becomes

$$\dot{E}(T_s, 0, 0, \infty, H_{rs}) + \dot{e}(\varepsilon, T_a, qV, H_{rc})\Delta\varepsilon = \dot{e}(\varepsilon, T_r, 0, H_{rc})\Delta\varepsilon + \dot{E}(T_r, 0, 0, \infty, H_{rs}) \quad (4.55)$$

where the first equation member is the net rate of energy received by the radiator and the second member is the energy emitted.

Using $\dot{e}(\varepsilon, T_r, 0, H_{rc})\Delta\varepsilon - \dot{e}(\varepsilon, T_a, qV, H_{rc})\Delta\varepsilon = \varepsilon\Delta i/q = \varepsilon\Delta\dot{w}/(qV)$, where Δi is the current extracted from the monochromatic cell and $\Delta\dot{w}$ is the electric power delivered, it is obtained that

$$\frac{\varepsilon\Delta\dot{w}}{qV} = \frac{H_{rs}\sigma_{SB}}{\pi}(T_s^4 - T_r^4) \Leftrightarrow \frac{\varepsilon^2\Delta i}{qH_{rc}\Delta\varepsilon} = \frac{H_{rs}\varepsilon}{H_{rc}\Delta\varepsilon} \frac{\sigma_{SB}}{\pi}(T_s^4 - T_r^4) \quad (4.56)$$

This equation can be used to determine the operation temperature of the radiator, T_r , as a function of the voltage V , the sun temperature T_s , the energy ε and the dimensionless parameter $H_{rc}\Delta\varepsilon/H_{rs}\varepsilon$. Notice that the left-hand side of equation (4.56) is independent of the cell étendue and of the filter bandwidth (notice that $\Delta i \propto H_{rc}\Delta\varepsilon$).

Dividing by $H_{rs}\sigma_{SB}T_s^4/\pi$, the solar input power, allows expressing the efficiency of the TPV converter as

$$\eta = \left(1 - \frac{T_r^4}{T_s^4}\right) \left(\frac{qV}{\varepsilon}\right) = \left(1 - \frac{T_r^4}{T_s^4}\right) \left(1 - \frac{T_a}{T_c}\right) \quad (4.57)$$

where T_c is the equivalent cell temperature as defined by equation (4.24). As presented in Figure 4.8, this efficiency is a monotonically increasing function of $H_{rc}\Delta\varepsilon/H_{rs}\varepsilon$. For $(H_{rc}\Delta\varepsilon/H_{rs}\varepsilon) \rightarrow \infty$, $\Delta i \rightarrow 0$ and $T_r \rightarrow T_c$. In this case an optimal efficiency [40] for $T_s = 6000$ K and $T_a = 300$ K is found to be 85.4% and is obtained for a temperature $T_c = T_r = 2544$ K. This is exactly the same as the optimum temperature of an ideal solar thermal converter feeding a Carnot engine. In reality, the ideal monochromatic solar cell is a way of constructing the Carnot engine. This efficiency is below the Landsberg efficiency (93.33%) and slightly below the one of an infinite stack of solar cells (86.8%).

It is worth noting that the condition $(H_{rc}\Delta\varepsilon/H_{rs}\varepsilon) \rightarrow \infty$ requires that $H_{rc} \gg H_{rs}$, and for this condition to be achieved, the cell area must be very large compared to the radiator area. This compensates the narrow energy range in which the cell absorbs. This is why a mirrored cavity must be used in this case.

4.5.3 Thermophotonic Converters

A recent concept for solar conversion has been proposed [3] with the name of thermophotonic (TPH) converter. In this concept, a solar cell converts the luminescent radiation

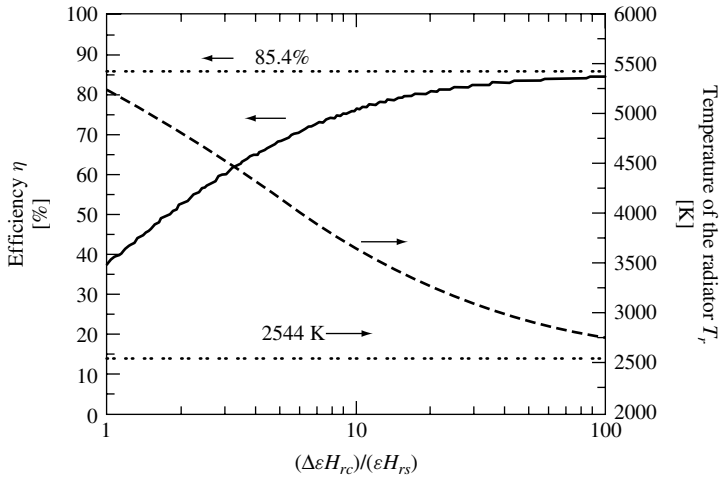


Figure 4.8 TPV ideal converter efficiency versus $H_{rc} \Delta \varepsilon / H_{rs} \varepsilon$. The energy ε and the cell voltage V are optimised

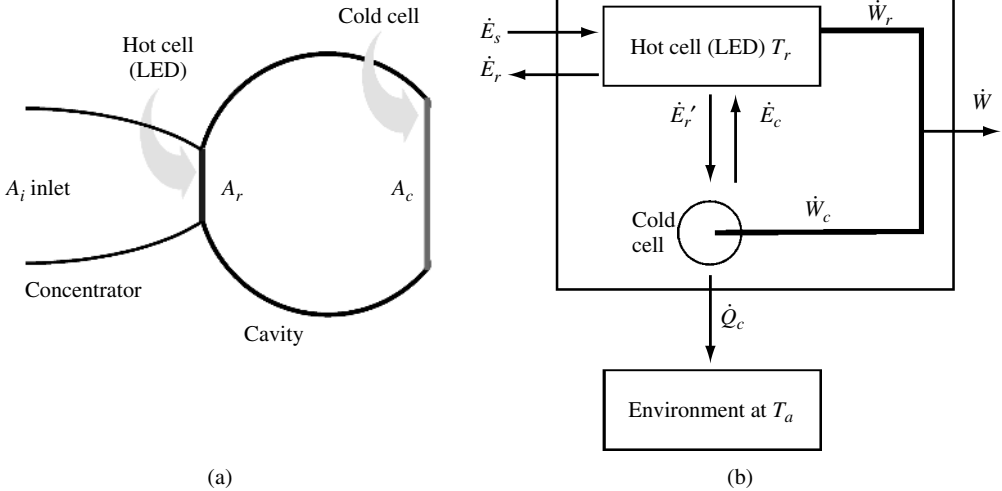


Figure 4.9 Diagram of the TPH converter with cavity. In (b), the energy fluxes are given by $\dot{E}_s \equiv E(T_s, 0, 0, \infty, H_{rs})$, $\dot{E}_r \equiv E(T_r, qV_r, 0, \infty, H_{rs})$, $\dot{Q}_c = \dot{E}_s - \dot{E}_r$, $\dot{E}'_r \equiv E(T_r, qV_r, 0, \infty, H_{rc})$, $\dot{E}'_c \equiv E(T_a, qV_c, \varepsilon_g, \infty, H_{rc})$

emitted by a heated light emitting diode (LED) into electricity. A diagram of this device is found in Figure 4.9. As in the TPV device, the LED can be heated with a fuel, but in our context it is heated as well with radiation absorbed from the sun. To emit luminescent radiation, the LED absorbs electric power, \dot{W}_r , in addition to the power delivered from the photons that illuminate the absorber. This power is to be subtracted from the electric power converted by the solar cell \dot{W}_c .

As a matter of fact, this converter is a generalisation of the TPV converter. If the LED is in short circuit, the TPH converter is exactly the same as the TPV converter. The application of a voltage to the LED changes the converter properties.

Ideal LEDs are like solar cells. Thus, to describe the ideal TPH converter, we shall refer to the LED as the hot cell, as opposed to the electric power generator, which is the cold cell. When they are considered as ideal devices, the current–voltage characteristics of both, the LED and the solar cell, are the same. This causes the current passing by the cold cell to be faithfully replicated (with the sign changed) by the hot cell, owing to the reciprocal illumination of both devices, as expressed by the two following equations:

$$I_c/q = \dot{N}(T_r, qV_r, \varepsilon_g, \infty, H_{rc}) - \dot{N}(T_a, qV_c, \varepsilon_g, \infty, H_{rc}) \quad (4.58)$$

$$I_r/q = \dot{N}(T_a, qV_c, \varepsilon_g, \infty, H_{rc}) - \dot{N}(T_r, qV_r, \varepsilon_g, \infty, H_{rc}) \quad (4.59)$$

We shall use the subindex c for the cold solar cell current and voltage and r for the hot solar cell. The power generated by each cell is $\dot{W}_c = I_c V_c$ and $\dot{W}_r = I_r V_r$. In a normal operation, I_r is negative and the power generated by the hot cell is negative.

The application of the first law of thermodynamics to the cold and the hot cell, respectively, leads to

$$\dot{E}(T_r, qV_r, \varepsilon_g, \infty, H_{rc}) = \dot{E}(T_c, qV_c, \varepsilon_g, \infty, H_{rc}) + \dot{W}_c + \dot{Q}_c \quad (4.60)$$

$$\dot{Q}_r + \dot{E}(T_c, qV_c, \varepsilon_g, \infty, H_{rc}) = \dot{E}(T_r, qV_r, \varepsilon_g, \infty, H_{rc}) + \dot{W}_r \quad (4.61)$$

where \dot{Q}_c is the heat rate delivered by the cold cell in the heat sink, while

$$\dot{Q}_r = \dot{E}(T_s, 0, 0, \infty, H_{rs}) - \dot{E}(T_r, 0, 0, \infty, H_{rs}) = \frac{H_{sr}\sigma_{SB}}{\pi}(T_s^4 - T_r^4) \quad (4.62)$$

is the heat injected by the sun into the hot cell. The sum of equations (4.60) and (4.61) leads to

$$\dot{Q}_r - \dot{Q}_c = \dot{W}_r + \dot{W}_c = I_r(V_r - V_c) = I_c(V_c - V_r) = \dot{W} \quad (4.63)$$

where \dot{W} is the algebraic sum of the powers produced by both cells (usually the hot cell will be absorbing, not producing, power).

In the case of monochromatic cell and LED operation, a proper filter of bandwidth $\Delta\varepsilon$ and centred at the energy ε is to be located somewhere in the optical system to allow for an interchange of photons only within the filter bandwidth. The preceding equations can be easily particularised in this case. An interesting relationship holding in this case, $\dot{e}\Delta\varepsilon = \varepsilon\dot{n}\Delta\varepsilon \equiv \dot{E}$, allows for a simple expression of the heat rate in both cells,

$$\dot{Q}_r = (V_r - \varepsilon/q)I_r \quad (4.64)$$

$$\dot{Q}_c = (\varepsilon/q - V_c)I_c \quad (4.65)$$

and this allows for writing the efficiency, using the equations (4.63) to (4.65) as

$$\eta = \frac{\dot{Q}_r}{H_{sr} \sigma_{SB} T_s^4 / \pi} \frac{\dot{W}}{\dot{Q}_r} = \left(1 - \frac{T_r^4}{T_s^4}\right) \left(1 - \frac{\dot{Q}_c}{\dot{Q}_r}\right) = \left(1 - \frac{T_r^4}{T_s^4}\right) \left(\frac{q V_c / \varepsilon - q V_r / \varepsilon}{1 - q V_r / \varepsilon}\right) \quad (4.66)$$

As said before, the TPH converter has an extra degree of freedom in the design, as compared to the TPV. It is the hot cell voltage V_r . The hot cell temperature in the monochromatic case depends on the same parameter $H_{rc} \Delta \varepsilon / H_{rs} \varepsilon$ as in the TPV case. When this parameter tends to infinity, the cold cell tends to be in open circuit, V_{coc} , given by

$$\frac{(\varepsilon - q V_{coc})}{k T_a} = \frac{(\varepsilon - q V_r)}{k T_r} \Rightarrow q V_{coc} = \varepsilon \left(1 - \frac{T_a}{T_r}\right) + q V_r \frac{T_a}{T_r} \quad (4.67)$$

Using this equation in equation (4.66), we obtain the same limit equation for the efficiency as the one for the TPV converter (equation 4.57):

$$\eta = \left(1 - \frac{T_r^4}{T_s^4}\right) \left(1 - \frac{T_a}{T_r}\right) \quad (4.68)$$

An interesting feature of this formula is that it holds for any value of V_r . Thus the TPH converter has the same upper limit as the TPV one. Furthermore, T_r is the same as in the TPV.

To our knowledge, this novel concept has not yet been fully explored. However, we present in Figure 4.10 the efficiency versus the cold cell voltage V_c (usually, in other contexts, we call efficiency to the maximum of this curve) for V_r in forward bias, zero bias (TPV mode) and reverse bias. In Figure 4.11, we present the hot cell temperature. We can

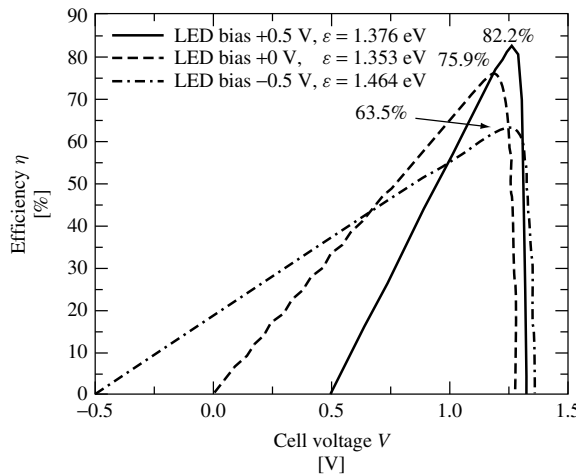


Figure 4.10 TPH efficiency versus V_c for three values of V_r for $H_{rc} \Delta \varepsilon / H_{rs} \varepsilon = 10/\pi$. The energy ε has been optimised

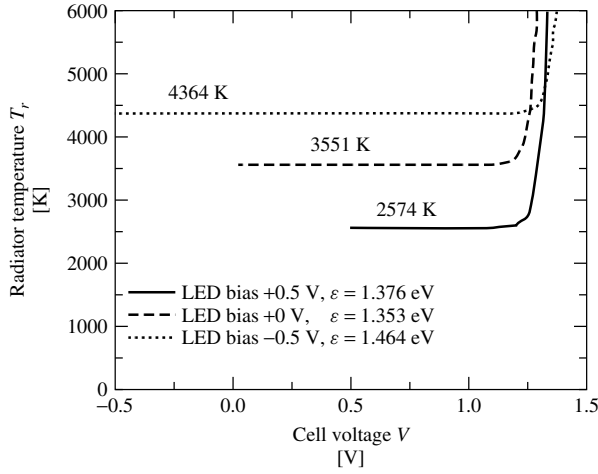


Figure 4.11 Hot cell temperature as a function of the cold cell voltage for several biasing voltages of the hot cell (LED) and for the energy that leads to maximum efficiency ($H_{rc} \Delta \varepsilon / H_{rs} \varepsilon = 10/\pi$). The energy ε has been optimised

see that higher efficiencies at lower temperatures can be obtained using the TPH concept under direct bias. This is not in contradiction to the fact that the limiting efficiency and the temperature for it is the same in both cases.

4.5.4 Higher-than-one Quantum Efficiency Solar Cells

One of the drawbacks that limit the efficiency of single-junction solar cells is the energy wasted from each photon that is absorbed because it is not converted into electrical power. Werner, Kolodinski, Brendel and Queisser [41, 42] have proposed a cell in which each photon may generate more than one electron–hole pair, thus leading to higher-than-one quantum efficiency solar cells. Without discussing which physical mechanisms may allow for this behaviour, let us examine its implications. Admitting that every photon may create $m(\varepsilon)$ electron–hole pairs, the current extracted from the device would be given by

$$I/q = \int_{\varepsilon_g}^{\infty} [m(\varepsilon) \dot{n}_s - m(\varepsilon) \dot{n}_r(T, \mu)] d\varepsilon \quad (4.69)$$

In this equation, ε_g is the energy threshold for photon absorption and the factor m in the generation term is our initial assumption. The same term must appear in the recombination term to reach the detailed balance: if the sun temperature is brought to the ambient temperature, the current will be zero when $\mu = 0$, only if the factor m also appears in the recombination term. For the moment we are saying nothing about the chemical potential μ of the photons emitted.

The power delivered, \dot{W} , is given by

$$\dot{W} = \int_{\varepsilon_g}^{\infty} qV [m \dot{n}_s - m \dot{n}_r(T, \mu)] d\varepsilon \quad (4.70)$$

Let us consider a monochromatic cell and calculate the irreversible entropy generation rate \dot{S}_{irr} in the whole device. With the aid of the general equation (4.44) and equation I-4 in Table 4.1, it is given by

$$T_a \dot{S}_{\text{irr}} / \Delta \varepsilon = (\mu_x \dot{n}_x + \dot{\omega}_x) - (\mu \dot{n}_r + \dot{\omega}_r) - qV(m\dot{n}_x - m\dot{n}_r) \quad (4.71)$$

where the source of photons has been substituted by its equivalent room-temperature luminescent radiation characterised by the chemical potential μ_x and the ambient temperature T_a . The open-circuit conditions are achieved when $\mu_{\text{OC}} = \mu_x$. For this value the entropy rate is zero since then $\dot{n}_x = \dot{n}_r$ and $\dot{\omega}_x = \dot{\omega}_r$.

Let us calculate the derivative of the irreversible entropy generation rate (equation 4.71) with respect to μ and particularise it for the open-circuit value of μ . Considering what follows V as only an unknown function of μ and independent of the way of obtaining the excitation (which is the case for infinite mobility) and using the fundamental relationship $\partial \dot{\omega}_r / \partial \mu = -\dot{n}_r$, the result is

$$\left[\frac{d(T_a \dot{S}_{\text{irr}} / \Delta \varepsilon)}{d\mu} \right]_{\mu_{\text{OC}}} = (qmV_{\text{OC}} - \mu_{\text{OC}}) \left[\frac{d\dot{n}_r}{d\mu} \right]_{\mu_{\text{OC}}} \quad (4.72)$$

This derivative is only zero if $qmV_{\text{OC}} = \mu_{\text{OC}}$. Since $\mu_{\text{OC}} = \mu_x$ can take any value by changing the source adequately, we obtain the result $qmV = \mu$. Any other value would produce a negative rate of entropy generation in the vicinity of the open circuit, against the second law of thermodynamics. This is a demonstration, based on the second law of thermodynamics, of the relationship between the chemical potential of the photons and the voltage (or electron and hole quasi-Fermi level split).

If we could choose m freely, the maximum power is achieved if we can maximise the integrand of equation (4.70) for each value of the energy [43, 44]. Once this is done, the reduction in ε_g so that it tends towards zero increases the power output. For the limit of $\varepsilon_g \rightarrow 0$, the maximum efficiency is the same as in equation (4.53), where a stack of an infinite number of cells was studied. Here $qVm(\varepsilon)$ is the variable that plays the same role as $qV(\varepsilon)$ earlier, although here V is the same for all the terms. In consequence, the upper efficiency is the same as for the tandem cell stack, 86.8%.

The higher-than-one quantum efficiency behaviour has been actually found [45, 46], although very close to one, for visible photons of high-energy and UV photons. The effect is attributed to impact ionisation, a mechanism in which the electron or the hole created by the high-energy photon, instead of thermalising by scattering with phonons, by means of impact processes transfers its high energy to a valence-band electron that gets pumped into the conduction band. This mechanism has a detailed balance counterpart that is the Auger recombination, in which the energy recovered in the recombination is transferred to an electron or a hole, which thus acquires a high kinetic energy.

4.5.5 Hot Electron Solar Cells

Wurfel [47] has studied the impact ionisation cells from another perspective and has shown that they become identical to the hot carrier solar cells proposed by Ross and Nozik [48]

pointing out also in this respect the necessity of providing the cell with special contacts as will be explained below.

In the hot carrier solar cell, the electron gas (semiconductor properties exhibiting a band gap does not seem to be essential for its operation) is in equilibrium at the lattice temperature T_a despite the absence of phonon interaction. This equilibrium is reached through other interactions as, for example, the interaction with thermal photons. Out of the equilibrium, electrons are thermalised by elastic scattering between them that allows a set of energy-dependent chemical potentials, one for the electrons of each energy. Furthermore, transference of energy between electrons exists through mechanisms that include impact ionisation and Auger recombination (this terminology is used in the context of semiconductors, which, as mentioned, we think is not necessary for this cell) according to reactions like $e_1^- + e_2^- \leftrightarrow e_3^- + e_4^-$. Actually in this equation transference of energy between electrons is produced by couples so that $\hat{\varepsilon}_1 + \hat{\varepsilon}_2 = \hat{\varepsilon}_3 + \hat{\varepsilon}_4$ where $\hat{\varepsilon}$ is electron (not photon) energy. However, the equilibrium of the reaction also establishes that the electrochemical potentials of the electrons (that we still call ε_F) are related by $\varepsilon_F(\hat{\varepsilon}_1) + \varepsilon_F(\hat{\varepsilon}_2) = \varepsilon_F(\hat{\varepsilon}_3) + \varepsilon_F(\hat{\varepsilon}_4)$. Therefore, the electrochemical potential of the electrons is a linear function of the energy in the form

$$\varepsilon_F(\hat{\varepsilon}) = \beta \hat{\varepsilon} + \varepsilon_{F0} \quad (4.73)$$

where the Fermi energy reference ε_{F0} becomes the same for both electrons and holes.

Since the Fermi function for electrons is written as

$$\frac{1}{\exp\left[\frac{\hat{\varepsilon} - \beta \hat{\varepsilon} - \varepsilon_{F0}}{kT_a}\right] + 1} = \frac{1}{\exp\left[\frac{\hat{\varepsilon} - \varepsilon_{F0}/(1 - \beta)}{kT_a/(1 - \beta)}\right] + 1} \quad (4.74)$$

the electron distribution can be regarded equivalently as a distribution at the lattice temperature T_a but characterised by a varying electrochemical potential given by equation (4.73) or as a hot carrier distribution with a constant electrochemical potential given by $\mu_{hc} = \varepsilon_{F0}/(1 - \beta)$ and a *hot carrier* temperature $T_{hc} = T_a/(1 - \beta)$.

If the interaction with phonons is introduced, through the reaction $e_1^- + \text{phonon} \leftrightarrow e_2^-$, where $e_{1(2)}^-$ represents an electron with energy $\hat{\varepsilon}_{1(2)}$, the fact that the phonon chemical potential is zero leads to $\varepsilon_F(\hat{\varepsilon}_1) = \varepsilon_F(\hat{\varepsilon}_2)$. However, $\hat{\varepsilon}_1 \neq \hat{\varepsilon}_2$ but $\hat{\varepsilon}_2 = \hat{\varepsilon}_1 + \varepsilon$, where ε is the phonon energy and, therefore, $\varepsilon_F(\hat{\varepsilon}_1) = \varepsilon_F(\hat{\varepsilon}_2)$ is only fulfilled if $\beta = 0$ and consequently all the electrons have the same electrochemical potential ε_{F0} and are at the lattice temperature. Phonon interaction is not considered to occur in what follows.

If the interaction with photons is considered now, $e_1^- + \text{photon} \leftrightarrow e_2^-$, the equilibrium of the reaction is represented by $\varepsilon_F(\hat{\varepsilon}_1) + \mu_{ph} = \varepsilon_F(\hat{\varepsilon}_2)$ where μ_{ph} is the photon chemical potential. Taking into account equation (4.73), it is obtained that $\mu_{ph} = \beta(\hat{\varepsilon}_1 - \hat{\varepsilon}_2) = \beta\varepsilon$ where ε is the energy of the photon involved. The result is that we have an energy-dependent photon chemical potential μ_{ph} . The Bose function that describes the occupation probability of the photon energy level ε becomes

$$\frac{1}{\exp\left[\frac{\varepsilon - \beta\varepsilon}{kT_a}\right] - 1} = \frac{1}{\exp\left[\frac{\varepsilon}{kT_a/(1 - \beta)}\right] - 1} \quad (4.75)$$

which can be seen as free radiation (zero chemical potential) at the hot carrier temperature.

Würfel also points out that, provided we can find a material in which a weak phonon coupling is produced in order to manufacture a solar cell, we still should be careful with the contacts because they do not allow for the maintenance of hot carriers inside the absorbing material. These special contacts must be able to cool the electrons from the hot temperature T_{hc} to the contact temperature T_a reversibly by changing their electrochemical potential from ε_{F0} to the electron electrochemical potential at the contacts (Fermi level at the metals) ε_{F+} and ε_{F-} . In Würfel's Reference [47], these special contacts are devised as selective membranes (Figure 4.12) that only allow electrons with energy centred around ε_e (left contact) and ε_h (right contact) to pass through. The reversible change in temperature and electrochemical potential of the electrons at the membranes is obtained by setting

$$\begin{aligned}\frac{\hat{\varepsilon}_e - \mu_{hc}}{kT_{hc}} &= \frac{\hat{\varepsilon}_e - \varepsilon_{F-}}{kT_a} \Leftrightarrow \varepsilon_{F-} = \hat{\varepsilon}_e \left(1 - \frac{T_a}{T_{hc}}\right) + \mu_{hc} \frac{T_a}{T_{hc}} \\ \frac{\hat{\varepsilon}_h - \mu_{hc}}{kT_{hc}} &= \frac{\hat{\varepsilon}_h - \varepsilon_{F+}}{kT_a} \Leftrightarrow \varepsilon_{F+} = \hat{\varepsilon}_h \left(1 - \frac{T_a}{T_{hc}}\right) + \mu_{hc} \frac{T_a}{T_{hc}}\end{aligned}\quad (4.76)$$

where $T_{hc} = T_a/(1 - \beta)$. The cell voltage will therefore be given by

$$qV = \varepsilon_{F-} - \varepsilon_{F+} = (\hat{\varepsilon}_e - \hat{\varepsilon}_h) \left(1 - \frac{T_a}{T_{hc}}\right) \quad (4.77)$$

The current extracted from the cell is determined by the rate at which electron-hole pairs of energy $\hat{\varepsilon}_e - \hat{\varepsilon}_h$ can be withdrawn from the cell. Since no energy is lost as heat, the energy balance equation (first principle) leads to

$$I(\hat{\varepsilon}_e - \hat{\varepsilon}_h)/q = \dot{E}(T_s, 0, \varepsilon_g, \infty, H_s) - \dot{E}(T_{hc}, 0, \varepsilon_g, \infty, H_r) \quad (4.78)$$

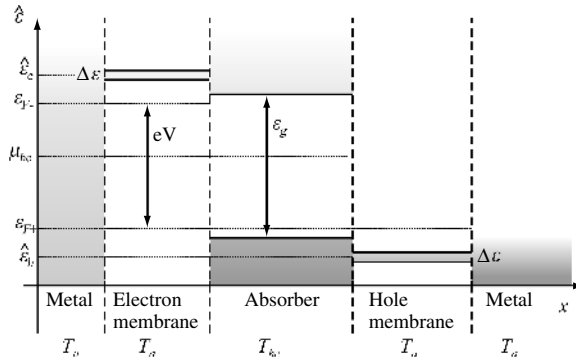


Figure 4.12 Band structure of a hot electron solar cell showing contacting scheme by means of selective membranes. (Reprinted from *Solar Energy Materials and Solar Cells* V. 46, N. 1, Würfel P., *Solar Energy Conversion with Hot Electrons from Impact Ionisation*, 43–52, © 1997 with permission from Elsevier Science)

and the power extracted from the cell can be finally computed as

$$\dot{W} = IV = [\dot{E}(T_s, 0, \varepsilon_g, \infty, H_s) - \dot{E}(T_{hc}, 0, \varepsilon_g, \infty, H_r)] \left(1 - \frac{T_a}{T_{hc}}\right) \quad (4.79)$$

which is independent of the carrier-extracting energies of the contacts. In other words, a large separation of the extracting energies leads to high voltage and low current and *vice versa*. Note that T_{hc} is a parameter for equation (4.79) and for equation (4.77). By elimination, we obtain the $W(V)$ and from it the derived IV curve. The cell efficiency is obtained from the maximum of $W(V)$ or $W(T_{hc})$.

For $\varepsilon_g \rightarrow 0$ the limit efficiency becomes

$$\eta = \left(1 - \frac{T_{hc}^4}{T_s^4}\right) \left(1 - \frac{T_a}{T_{hc}}\right) \quad (4.80)$$

just as in the TPV converters, leading to a limiting efficiency of 85.4%.

The monoenergetic membrane for electron and hole transfer to the contacting metals might perhaps be an insulator with an impurity band, but the nature of the phonon-insulated absorber is totally unknown. Ross and Nozik [48, 49] who have developed concepts close to those expressed here are investigating the poorer coupling of the electrons with the photons in materials with quantum dots with the idea of favouring this hot electron type of cell or the impact ionisation one that we have described in the preceding section.

4.5.6 Intermediate Band Solar Cell

One of the causes of efficiency reduction in single-junction solar cells is the transparency of the semiconductor to sub-band gap photons [50]. The inclusion of an intermediate band (IB) may greatly increase the efficiency. We show in Figure 4.13 a band diagram of the photon absorption and emission in this intermediate band material. Photons are absorbed not only by pumping electrons from the VB to the CB as in a traditional solar cell (photons with energy $h\nu_3$) but also by transitions from the VB to the IB (photons with energy $h\nu_2$) and from the IB to the CB (photons with energy $h\nu_1$). In total, two low-energy photons are used to pump an electron from the valence band to the conduction band, passing through the intermediate band. This certainly increases the cell current.

The three absorption mechanisms detailed above are effective if the IB is a band partially filled with electrons. In this way, there are empty states in it to accommodate the electrons from the VB and there are electrons to sustain a strong pumping to the CB. The detailed balance imposes photon emissions that are opposite to each one of the three absorption mechanisms.

The cell is contacted as shown in Figure 4.14. The electrons are extracted from the VB and returned to the CB using two layers of n and p ordinary semiconductors. A high voltage is produced as the sum of the two semiconductor junction voltages occurring at both sides of the IB material.

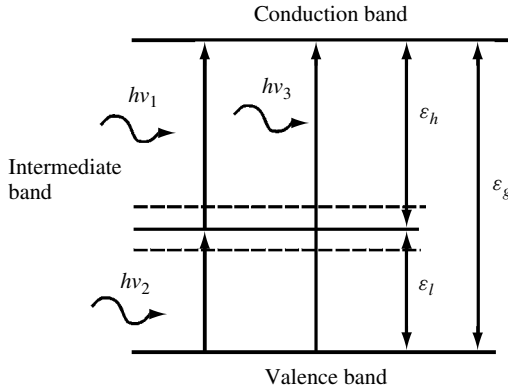


Figure 4.13 The band diagram of an intermediate band solar cell

In this IB material we admit that there are three quasi-Fermi levels, one for each band. The cell voltage is q times the splitting of the CB and VB quasi-Fermi levels.

In general, there is an energy threshold for each one of the absorption mechanisms described earlier. However, the ideal structure is the one in which the upper energy (lintel) of a photon that can be absorbed in certain mechanisms – involving, for example, transitions from the VB to the IB – is the threshold of the next one – for example, transitions from the IB to the CB. More specifically, calling ϵ_g the energy interval between the conduction and the valence band, ϵ_l the interval between the Fermi level in the intermediate band and the valence band and $\epsilon_h = \epsilon_g - \epsilon_l$, and assuming that $\epsilon_l < \epsilon_h$, we consider that all the photons in the interval (ϵ_l, ϵ_h) are absorbed by transitions from the VB to the IB, all the photons in the interval (ϵ_h, ϵ_g) are absorbed by transitions from the IB to the CB and all the photons in the interval (ϵ_g, ∞) are absorbed by transitions from the VB to the CB.

Under such conditions the equations that rule the current–voltage characteristic of the cell are

$$I/q = [\dot{N}(T_s, 0, \epsilon_g, \infty, \pi) - \dot{N}(T, \mu_{CV}, \epsilon_g, \infty, \pi)] + [\dot{N}(T_s, 0, \epsilon_h, \epsilon_g, \pi) - \dot{N}(T, \mu_{CI}, \epsilon_h, \epsilon_g, \pi)] \quad (4.81)$$

$$\dot{N}(T_s, 0, \epsilon_l, \epsilon_h, \pi) - \dot{N}(T, \mu_{IV}, \epsilon_l, \epsilon_h, \pi) = \dot{N}(T_s, 0, \epsilon_h, \epsilon_g, \pi) - \dot{N}(T, \mu_{CI}, \epsilon_h, \epsilon_g, \pi) \quad (4.82)$$

with μ_{XY} being the photon chemical potentials equal to the separation of quasi-Fermi levels between band X and band Y . Equation (4.81) states the balance of electrons in the CB (addition of those that are pumped from the IB and the VB by means of the absorption of the corresponding photon less those that radiatively recombine). Equation (4.82) states a similar balance equation for the electrons in the IB and takes into account that no current is extracted from the IB. In addition,

$$qV = \mu_{CV} = \mu_{CI} + \mu_{IV} \quad (4.83)$$

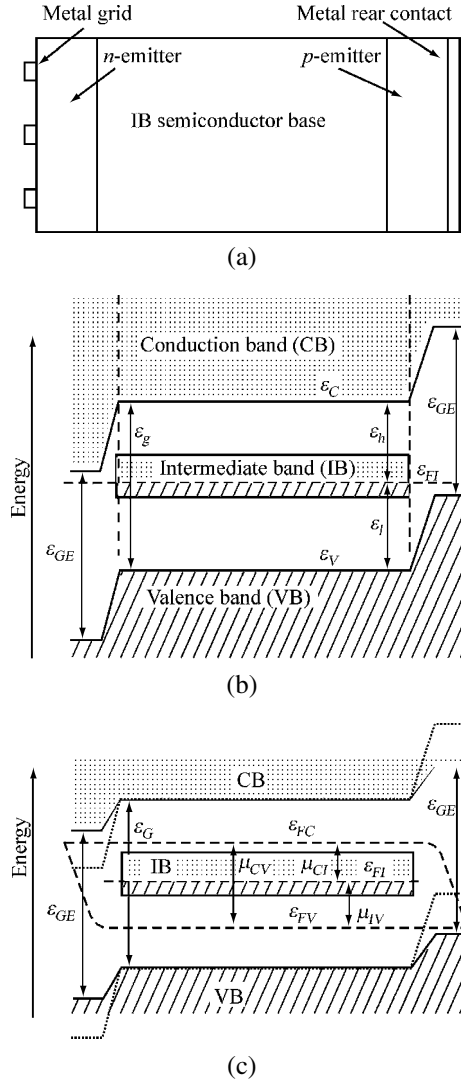


Figure 4.14 (a) Structure of the IB solar cell; (b) band diagram in equilibrium and (c) band diagram of forward bias conditions. (Reproduced from *A Metallic Intermediate Band High Efficiency Solar Cell*, Luque A. and Martí A., by permission of John Wiley & Sons Limited © 2001)

By eliminating μ_{CI} and μ_{IV} from the last three equations, we obtain the current–voltage characteristic of the cell. Efficiencies for different values of ϵ_l and ϵ_g are plotted in Figure 4.15.

The maximum efficiency of 63.2% is achieved for a cell of gap 1.95 eV with the IB Fermi level located at 0.71 eV from one of the bands. This efficiency is higher than the one corresponding to two series-connected ideal cells in tandem, of 54.5% (for band gaps of 0.8 and 1.54 eV). A detailed analysis of this cell operation can be found in the References [50–52]. The generalisation of the concept to more than two intermediate

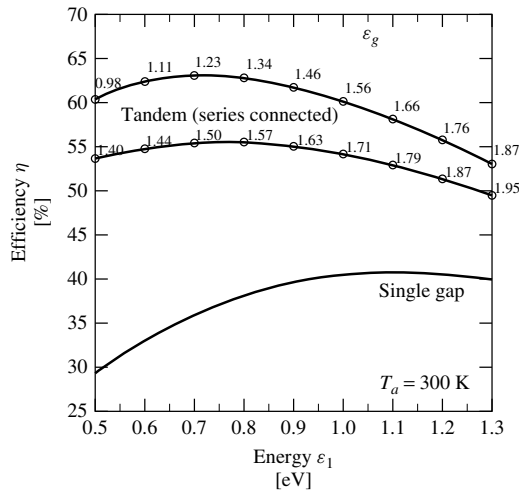


Figure 4.15 Limiting efficiency for the IB solar cell under maximum concentrated sunlight. For comparison, the limiting efficiency of single-gap solar cells (in this case, $\epsilon_l \equiv \epsilon_g$) and a tandem of two cells that are series-connected are also shown (in this case, ϵ_l labels the lowest band gap of the cells and the figures on the curve correspond to the highest of the band gaps). (Reproduced from *Increasing the Efficiency of Ideal Solar Cells by Photon Induced Transitions at Intermediate Levels*, Luque A. and Martí A., Physical Review Letters V. 78 N. 34, 5014–5017, by permission of American Physical Society © 1997)

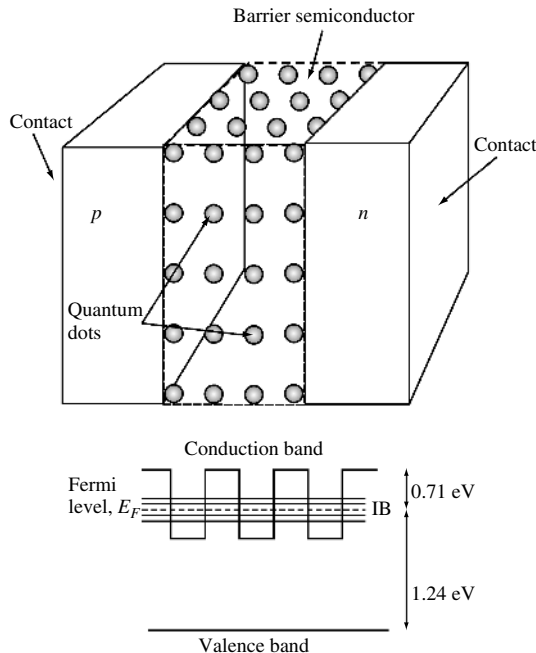


Figure 4.16 IB formation in QD arrays

band gaps (multiband solar cells) has been studied in [53, 54]. Some related concepts are that of an impurity band, in which the IB is made up of impurities [55], and the use of intermediate band materials as up- and down-converters [56, 57].

Suitable materials for a metallic IB are not very common. Accurate theoretical calculations establish that some alloys of the type $\text{III}_3\text{-V}_4\text{-IVb}$ (with four electrons in the outer shell) present the required band [58]. No experiment has been carried out so far for implementing these materials, and therefore it is not certain whether the required metallic IB is actually formed or if the corresponding alloys are thermodynamically stable or separate into phases.

Another proposal [59] for forming the required IB is the use of nanotechnology. In particular, closely spaced quantum dot arrays might produce the desired band Figure 4.16. $\text{In}_{0.58}\text{Ga}_{0.42}\text{As}$ dots (of band gap 0.87 eV) of a radius of 39 nm in a barrier material of $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ of band gap 1.95 eV could produce an IB centred at 0.71 eV from the CB (if strain effects could be avoided and the offset in the VB could be suppressed [60]). The half filling of the IB can be achieved by barrier material doping [61, 62]. Experiments to prove the principle of operation of this type of cell have not yet been carried out.

4.6 CONCLUSIONS

In this chapter we have provided a thermodynamic basis that allows evaluating the thermodynamic consistency of classical and newly proposed solar cells. Also, we have assessed the efficiency limit of several PV concepts.

As deduced by Shockley and Queisser, the upper limit reachable with a single-junction solar cell is 40.7% for the cell illuminated by a black body source of photons at 6000 K and assuming the cell temperature at 300 K. This value is rather low if we take into account that the Carnot limiting efficiency for a reversible engine operating between hot and cold heat reservoirs at 6000 K and 300 K, respectively, is 95%. High-efficiency devices that can ideally surpass the Shockley–Queisser efficiency have been called *third generation PV converters*. Thus, the following question arises: could we invent a solar converter that exhibits this Carnot efficiency?

The answer is negative and the reason for it lies in the definition of efficiency. In the definition of the Carnot efficiency, the term entering in the denominator is the power *consumed*, that is, the power *arriving* at the converter less the power *leaving* the converter owing to the radiation that is emitted. In the conventional definition of the efficiency for solar converters, the term entering in the denominator is the power *arriving* at the converter and because it is higher than the *consumed* power this leads to a lower efficiency. With this definition, the higher achievable efficiency is the Landsberg efficiency of 93.33%. However, this efficiency, if reachable, cannot be reached with any known ideal solar converter.

A very high efficiency of 85.4% can ideally be reached with several devices such as the TPV converter, constituted by one ideal solar cell and one absorber and the TPH converter, conceived with one ideal solar cell and one LED that also plays the role of an absorber, or even a hot carrier solar cell. To reach this efficiency they all must emit radiation with zero chemical potential (free radiation) at 2544 K. This efficiency is also the limit for solar thermal devices.

However, this is not the highest efficiency that can be reached in solar converters. Efficiencies of up to 86.8% can be achieved using an array of solar cells of different band gap, either series-connected or independently connected.

Except for the TPH case, all solar cells operate at ambient temperature. This is a highly desirable feature. The TPH concept, which allows for higher efficiencies at lower temperatures than the TPV concept, may bring some advances. However, such devices to be practical require an almost ideal external quantum efficiency of the LED and the ability of working at high temperatures, both requirements being very difficult to acquire.

Experimental work on IB solar cells – whose upper limit efficiency is 63.2% – is now starting. It is conceivable that IBs may substitute two junction materials with perhaps less complexity. They may also be combined in tandem with more ordinary or IB cells.

Finally, it seems unlikely to us that a semiconductor can be found where the electrons are uncoupled enough from the phonons as to allow effective impact ionisation cells. However, a multilevel organic dye may be found or an array of quantum dots may be engineered where this coupling is reduced. In any case, the operation principles of this cell, and not only that of the usual solar cells, should be taken into account by those trying to bring other technologies into the manufacture of PV converters.

From the preceding statements it is clear that very high efficiencies are possible in a device operating in the PV mode. But what is possible in practice? This is a very difficult question. Certainly, stimulated by space research, there is a trend towards the development of multijunction cells. We stress again here that efficiencies of 34% (Global AM1.5) with a monolithic tandem of InGaP/GaAs, stuck on a Ge cell operating at 212 suns have been achieved. It can be asked whether such solutions are not too expensive for terrestrial use. However, we disagree. The use of very high concentration elements, in the range of 1000 or more, may make very expensive cells [63] usable. Wide acceptance angle concentrators with this concentration factor have already been developed that seem very suitable for mounting in low-cost tracking structures [64].

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