



Ideal Efficiencies

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1. INTRODUCTION

In this chapter we deal with the simplest ideas that have been used in the past to attain an understanding of solar cell efficiencies from a theoretical point of view. The first and most obvious attack on this problem is to use thermodynamics, and we offer four such estimates in Section 2. Only the first of these is the famous Carnot efficiency. The other three demonstrate that one has more possibilities even within the framework of thermodynamics. To make progress, however, one has to introduce at least one solid-state characteristic, and the obvious one is the energy gap, E_g . That this represents an advance in the direction of a more realistic model is obvious, but it is also indicated by the fact that the efficiency now calculated is lower than the (unrealistically high) thermodynamic efficiencies (Section 3). In order to get closer to reality, we introduce in Section 4 the fact that the radiation is effectively reduced from the normal blackbody value (Equation (6)) owing to the finite size of the solar disc. This still leaves important special design features such as the number of series-connected tandem cells and higher-order impact ionisation, and these are noted in Section 5.



2. THERMODYNAMIC EFFICIENCIES

The formulae for ideal efficiencies of solar cells are simplest when based on purely thermodynamic arguments. We here offer four of these: they involve only (absolute) temperatures:

- T_a , temperature of the surroundings (or the ambient),
- T_s , temperature of the pump (i.e., the sun),
- T_c , temperature of the actual cell that converts the incoming radiation into electricity.

From these temperatures, we form the following efficiencies [1]:

$$\eta_C \equiv 1 - T_a/T_s, \text{ the Carnot efficiency} \quad (1)$$

$$\eta_{CA} \equiv 1 - (T_a/T_s)^{\frac{1}{2}}, \text{ the Curzon–Ahlborn efficiency} \quad (2)$$

$$\eta_L \equiv 1 - (4/3)(T_a/T_s) + (1/3)(T_a/T_s)^4, \text{ the Landsberg efficiency} \quad (3)$$

$$\eta_{PT} = [1 - (T_c/T_s)^4][1 - T_a/T_c], \text{ the photo–thermal efficiency} \quad (4)$$

due to Müser

In the latter efficiency, the cell temperature is determined by the quintic equation

$$4T_C^5 - 3T_aT_c^4 - T_aT_s^4 = 0 \quad (5)$$

The names associated with these efficiencies are not historically strictly correct: for example, in Equations (2) and (3) other authors have played a significant part.

Figure 1 [1] shows curves of the four efficiencies, which all start at unity when $T_a/T_s \equiv 0$, and they all end at zero when $T_a = T_s$. No efficiency ever beats the Carnot efficiency, of course, in accordance with the rules of thermodynamics. Values near $T_s = 5760\text{--}5770$ K seem to give the best agreement with the observed solar spectrum and the total energy received on Earth, but a less accurate but more convenient value of $T_s = 6000$ K is also commonly used. Using the latter value of T_s and $T_a = 300$ K as the temperature for Earth, one finds

$$\eta_C = 95\%, \eta_{CA} = 77.6\%, \eta_L = 93.3\%, \eta_{PT} = 85\%$$

If $T_s = T_a = T_c$ one has in effect an equilibrium situation, so that the theoretical efficiencies are expected to vanish.

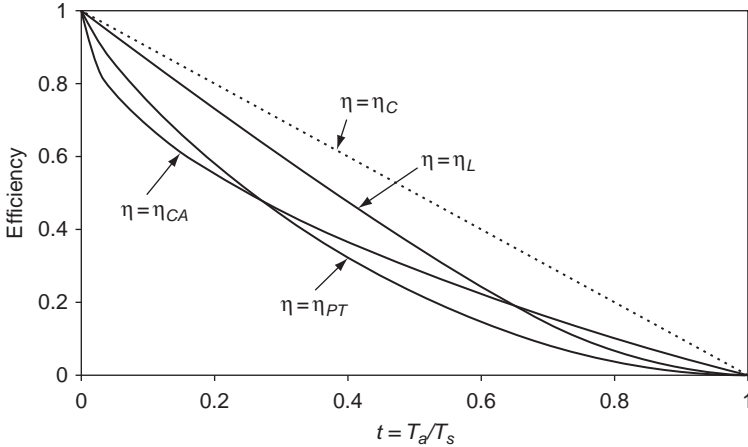


Figure 1 The efficiencies (1)–(4) as functions of T_d/T_s .

The above thermodynamic efficiencies utilise merely temperatures, and they lie well above experimental results. One needs an energy gap (E_g) as well to take us from pure thermodynamics to solid-state physics. Incident photons can excite electrons across this gap, thus enabling the solar cell to produce an electric current as the electrons drop back again. The thermodynamic results presented earlier, on the other hand, are obtained simply by considering energy and entropy fluxes.



3. EFFICIENCIES IN TERMS OF ENERGIES

In order to proceed, we need next an expression for the number of photons in blackbody radiation with an energy in excess of the energy gap, E_g say, so that they can excite electrons across the gap. At blackbody temperature T_s the number of photons incident on unit area in unit time is given by standard theory as an integral over the photon energy [2]:

$$\Phi(E_g, T_s) = \frac{2\pi k^3}{h^3 c^2} T_s^3 \int_{E_g/kT_s}^{\infty} \frac{x^2 dx}{e^x - 1} \tag{6}$$

Now suppose that each of these photons contributes only an energy equal to the energy gap to the output of the device, i.e., a quantity proportional to

$$x_g \int_{x_g}^{\infty} \frac{x^2 dx}{e^x - 1} \quad (x_g \equiv E_g/kTs) \quad (7)$$

To obtain the efficiency η of energy conversion, we must divide this quantity by the whole energy that is, in principle, available from the radiation:

$$\eta = x_g \int_{x_g}^{\infty} \frac{x^2 dx}{e^x - 1} / \int_0^{\infty} \frac{x^2 dx}{e^x - 1} \quad (8)$$

Equation (8) gives the first of the Shockley–Queisser estimates for the limiting efficiency of a solar cell, the *ultimate efficiency* (see Figure 5). The argument neglects recombination in the semiconductor device, even radiative recombination, which is always present (a substance that absorbs radiation can always emit it!). It is also based on the blackbody photon flux (Equation (6)) rather than on a more realistic spectrum incident on Earth.

We shall return to these points in Section 4, but first a brief discussion of Equation (8) is in order. There is a maximum value of η for some energy gap that may be seen by noting that $\eta = 0$ for both $x_g = 0$ and for x_g very large. So there is a maximum efficiency between these values. Differentiating η with respect to x_g and equating to zero, the condition for a maximum is

$$x_g = x_{gopt} = 2.17$$

corresponding to $\eta = 44\%$.

This is still higher than most experimental efficiencies, but the beauty of it is that it is a rather general result that assumes merely properties of blackbody radiation.

Let $f(x)$ be a generalised photon distribution function; then a generalised efficiency can be defined by

$$\eta = \frac{x_g \int_{x_g}^{\infty} f(x) dx}{\int_0^{\infty} x f(x) dx} \quad (9)$$

The maximum efficiency with respect to x_g is then given by

$$x_{gopt} f(x_{gopt}) = \int_{x_{gopt}}^{\infty} f(x) dx \quad (10)$$

This is rather general and will serve also when the photon distribution departs from the blackbody forms and even for radiation in different numbers of dimensions.



4. EFFICIENCIES USING THE SHOCKLEY SOLAR CELL EQUATION

A further step in finding the appropriate efficiency limits for single-junction solar cells can be made by estimating the relevant terms in the Shockley ideal solar cell equation (Equation (1) in Chapter Ia-1). To this end, further remarks must be made about the solar spectrum and solar energy incident on Earth's surface. The ultimate efficiency, discussed in Section 3, was based on the blackbody photon flux (Equation (6)), a rigorous thermodynamic quantity but not a very good estimate of the solar spectrum as seen on Earth. By virtue of the large distance between the Sun and Earth, the radiative energy incident on Earth's surface is less than that of Equation (6) by a factor f_ω , which describes the size of the solar disk (of solid angle ω_s) as perceived from Earth:

$$f_\omega = \left(\frac{R_s}{R_{SE}} \right)^2 = \frac{\omega_s}{\pi} \quad (11)$$

where R_s is the radius of the Sun (696×10^3 km), and R_{SE} is the mean distance between the Sun and Earth (149.6×10^6 km), giving $\omega_s = 6.85 \times 10^{-5}$ sterad and $f_\omega = 2.18 \times 10^{-5}$. The resulting spectrum is shown in Figure 2 alongside the standard terrestrial AM1.5 spectrum (a further discussion of the

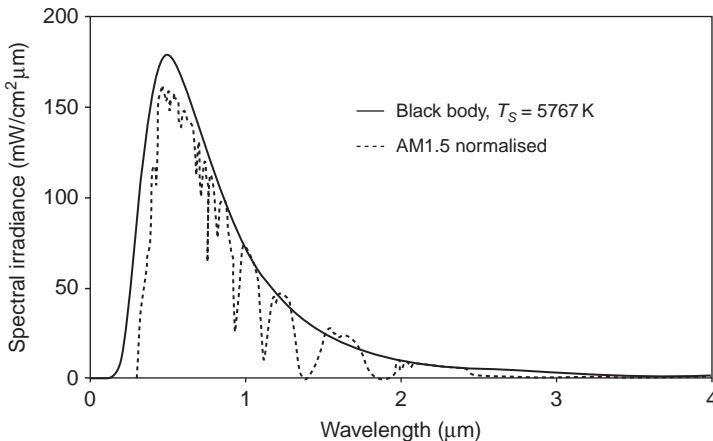


Figure 2 The blackbody spectrum of solar radiation and the AM1.5 spectrum, normalised to total irradiance 1 kW/m^2 , which is used for the calibration of terrestrial cells and modules.

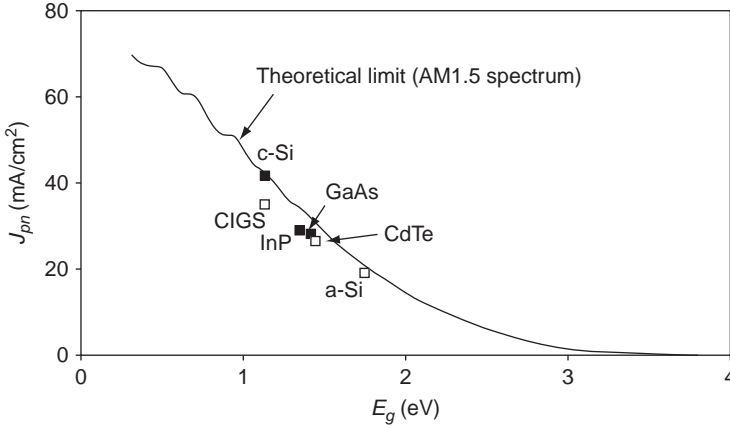


Figure 3 The theoretical limit on photogenerated current, compared with the best measured values. The curve is obtained by replacing the product $f_{\omega}\Phi(E_g, T_s)$ in Equation (12) by the appropriate AM1.5 photon flux. Full symbols correspond to crystalline materials, open symbols to thin films.

spectra that are used for solar cell measurements in practice can be found in Chapter III-2, which also shows the extraterrestrial spectrum AMO).

The maximum value of the photogenerated current I_{ph} now follows if we assume that one absorbed photon contributes exactly one electron to the current in the external circuit:

$$I_{ph} = Aqf\omega\Phi(E_g, T_s) \quad (12)$$

where A is the illuminated area of the solar cell and q is the electron charge. The maximum photogenerated current density $J_{ph} = I_{ph}/A$ that can be produced by a solar cell with band gap E_g is shown in Figure 3. To allow a comparison with photocurrents measured in actual devices, Figure 3 is plotted for the AM1.5 solar spectrum, which is used for calibration of terrestrial solar cells, rather than for the blackbody spectrum used in Section 3.

The open-circuit voltage V_{oc} can now be obtained using the photogenerated current I_{ph} (Equation (12)) and the (dark) saturation current I_0 that appears in the ideal solar cell equation:

$$V_{oc} = \frac{kT}{q} \ln \left(1 + \frac{I_{ph}}{I_0} \right) \quad (13)$$

The current I_0 can be obtained by a similar argument as the photogenerated current I_{ph} , since, as argued by Shockley and Queisser, it can

be equated to the blackbody photon flux at the cell temperature T_c (in what follows, the cell temperature T_c will be assumed to be equal to the ambient temperature T_a):

$$I_0 = Aqf_0\Phi(E_g, T_a) \quad (14)$$

where the coefficient f_0 has been inserted to describe correctly the total area f_0A exposed to the ambient photon flux. Various values of f_0 (some dependent on the refractive index \mathbf{n} of the cell material) can be found, appropriate for different device structures and geometries. The usual value is $f_0 = 2$, as suggested by Shockley and Queisser [2], since this radiation is incident through the two (front and rear) surfaces of the cell. A similar argument for a spherical solar cell yields an effective value $f_0 = 4$ [3]. Henry [4] gives $f_0 = 1 + \mathbf{n}^2$ for a cell grown on a semiconductor substrate, but the value $f_0 = 1$ is also sometimes used (see, for example, [5]). Green [6] gives a semi-empirical expression for the dark saturation current density $J_0 = I_0/A$:

$$J_0(\text{in Amps}/\text{cm}^2) = 1.5 \times 10^5 \exp\left(-\frac{E_g}{kT_a}\right) \quad (15)$$

An approximate analytical method for estimating V_{oc} can also be useful, particularly as it stresses the thermodynamic origin of V_{oc} . Indeed, it can be shown [7] that, near the open circuit, the solar cell behaves as an ideal thermodynamic engine with Carnot efficiency $(1 - T_c/T_s)$. Ruppel and Würfel [3] and Araújo [8] show that V_{oc} can be approximated to a reasonable accuracy by the expression

$$V_{oc} \frac{E_g}{q} \left(1 - \frac{T_c}{T_s}\right) + \frac{kT}{q} \ln \frac{f_\omega}{f_0} + \frac{kT_c}{q} \ln \frac{T_s}{T_c} \quad (16)$$

which depicts the dependence of V_{oc} on the band gap E_g and on the cell temperature T_c . Figure 4 compares this theoretical values for the open-circuit voltage with data for the best solar cells to date from different materials.

Using now an expression for the fill factor (defined by Equation (3) in Chapter Ia-1), one readily obtains a theoretical estimate for the efficiency. Slightly different results may be encountered, principally by virtue of the different ways one can estimate the current and the voltage. Figure 5 shows the best-known result, the celebrated Shockley–Queisser ideal efficiency limit [2]. Shockley and Queisser call this limit the *nominal*

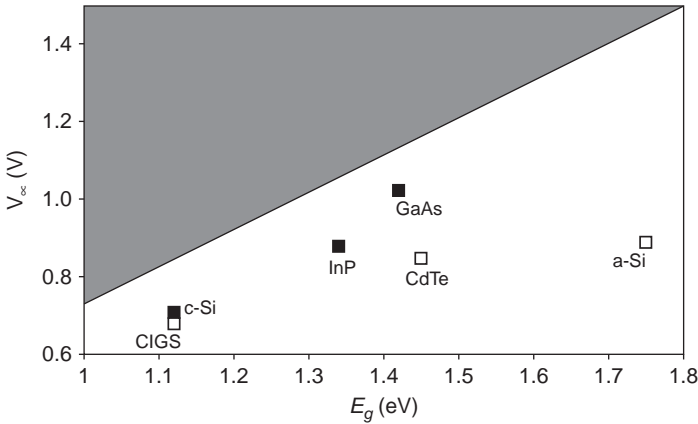


Figure 4 The theoretical Shockley–Queisser limit on open-circuit voltage: values exceeding this limit lie in the shaded area of the graph. Line corresponding to Equation (16) appears as identical to within the accuracy of this graph. Full symbols correspond to crystalline materials, open symbols to thin films.

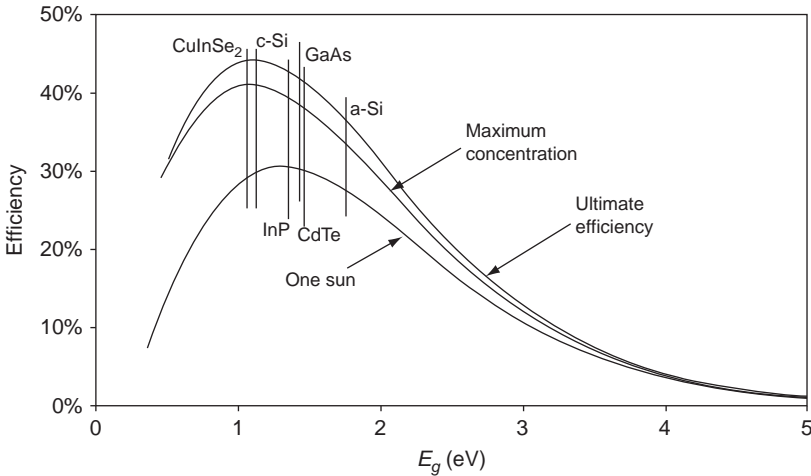


Figure 5 The ‘ultimate’ and two ‘nominal’ Shockley–Queisser efficiencies. Note that the blackbody radiation with temperature $T_s = 6000$ K has been used here, in keeping with the Shockley–Queisser work [2].

efficiency, to be compared with the *ultimate efficiency*, which is discussed in Section 3. Figure 5 shows two such curves: one labelled ‘one-sun’ corresponds to the AMO solar intensity, as observed outside Earth’s atmosphere. A second curve, labelled ‘maximum concentration’ corresponds

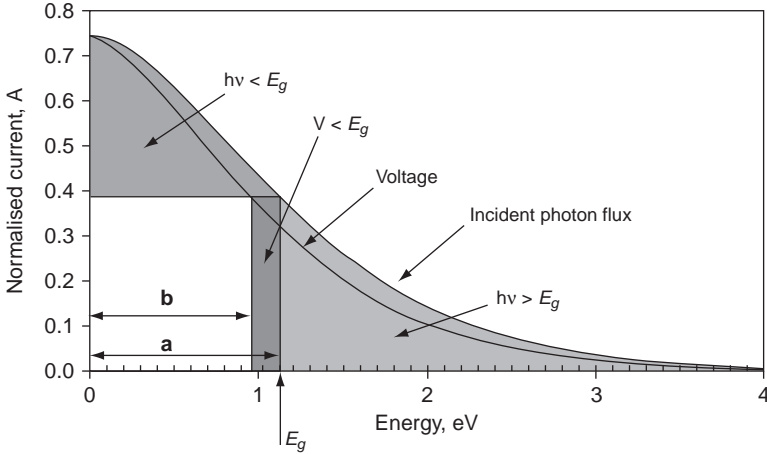


Figure 6 Henry's construction.

to light focused on the cell, by a mirror or a lens, at the maximum concentration ratio of $1/f_\omega = 45,872$ [9].

The various unavoidable losses in photovoltaic energy conversion by single-junction solar cells can be depicted in a graph constructed by Henry [4] and analogous to Figure 6. There are two curves in this graph:

- The photogenerated current density J_{ph} from Equation (12) as a function of photon energy. J_{ph} is divided here by the total irradiance, making the area under this curve equal to unity by construction.
- The maximum voltage that can be extracted from the cell at the maximum power point. This curve is drawn in such a way that the ratio of lengths of the two arrows b/a is equal to V_m/E_g .

The three shaded areas then depict the three fundamental losses in a single junction solar cell (shown here for silicon with band gap E_g equal to 1.12 eV):

- Shaded area marked $h\nu < E_g$ is equal to the loss of current due to the inability of the semiconductor to absorb below-band-gap light.
- Shaded area marked $h\nu > E_g$ represents energy losses due to the thermalization of electron–hole pairs to the band-gap energy.
- Hatched area marked $V < E_g$ corresponds to the combined thermodynamic losses due to V_{oc} being less than E_g and losses represented by the fill factor FF.

The area of the blank rectangle then represents the maximum efficiency that can be obtained for a single junction cell made from a

semiconductor with band gap E_g . The graph is drawn here for light with maximum possible concentration. A different ‘voltage curve’ would result if light with one-sun intensity were used.



5. GENERAL COMMENTS ON EFFICIENCIES

The ideal solar cell efficiencies discussed above refer to single-junction semiconductor devices. The limitations considered in the ultimate efficiency of Section 3 are due to the fact that the simplest semiconductor (i.e., one whose defects and impurities can be ignored) cannot absorb below-band-gap photons. Furthermore, it is also due to the fact that the part of the energy of the absorbed photons in excess of the band gap is lost as heat. Radiative recombination at the necessary fundamental level was taken into account in the treatment of Section 4. It is sometimes argued that there are other ‘unavoidable’ losses due to electronic energy transfer to other electrons by the Auger effect (electron–electron collisions) [10–12]. There is also the effect of band-gap shrinkage, discussed in Chapter Ia-2, and light trapping may also play a part [11]. None of these effects are discussed here, and the reader is referred to the relevant literature.

It is clear that it is most beneficial if one can improve the effect of a typical photon on the electron and hole density. This can be achieved, for example, if the photon is energetic enough to produce two or more electron–hole pairs. This is called *impact ionisation* and has been studied quite extensively. A very energetic photon can also project an electron high enough into the conduction band so that it can, by collision, excite a second electron from the valence band. This also improves the performance of the cell. On the other hand, an electron can combine with a hole, and the energy release can be used to excite a conduction-band electron higher into the band. In this case, energy is uselessly dissipated with a loss of useful carriers and hence of conversion efficiency. This is one type of Auger effect. For a survey of these and related effects, see [12]. These phenomena suggest a number of interesting design problems. For example, is there a way of limiting the deleterious results of Auger recombination [13]? One way is to try to ‘tune’ the split-off and the fundamental band gaps appropriately. If one is dealing with parabolic bands,

Table 1 The maximum efficiencies of tandem cells as a function of the number of cells in the stack for different concentration ratios [17]. Note that de Vos [17] uses a slightly smaller value of f_{ω} than Shockley and Queisser, resulting in a marginally different maximum concentration ratio than used in Figure 5

Concentration ratio	Number of cells in the stack	Maximum efficiency (%)
1	1	31.0
	2	49.9
	3	49.3
	...	
	∞	68.2
46.300	1	40.8
	2	55.7
	3	63.9
	...	
	∞	86.8

then the obvious way is to examine the threshold energies that an electron has to have in order to jump across the gap and make these large so as to make this jump difficult.

Then there is the possibility of placing impurities on the energy band scale in such a way as to help better use to be made of low-energy photons, so that they can now increase the density of electrons in the system. This is sometimes referred to as the *impurity photovoltaic effect*. So one can make use of it [14].

One can also utilise excitons to improve the efficiencies of solar cells. There may be as many as 10^{17} cm^{-3} excitons in silicon at room temperature. If they are split up in the field of a p–n junction, this will increase the concentration of current carriers and so increase the light generated current, which is of course beneficial.

We have here indicated some useful ideas for improving solar cells, There are of course many others, some of which are discussed in Chapters Ib-2 and Id-2 as well as elsewhere [15]. Note, in particular, the idea of developing tandem cells in which photons hit a large band-gap material first and then proceed gradually to smaller band-gap materials. Tandem cells are now available with three or more stages. Solar cells with efficiency of order 20% are predicted to be produced on a large scale in the near future [16]. Table 2 shows the best laboratory efficiencies at the present time for different materials.

Table 2 The best reported efficiencies, at time of writing, for different types of solar cells [18]

	Efficiency (%)	J_{se} (mA/cm ²)	V_{oc} (V)	FF (%)
Crystalline: single junction				
c-Si	24.7	42.2	0.706	82.8
GaAs	25.1	28.2	1.022	87.1
InP	21.9	29.3	0.878	85.4
Crystalline: multijunction				
GaNIP/GaAs/Ge tandem	31.0	14.11	2.548	86.2
Thin-film: single junction				
CdTe	16.5	25.9	0.845	75.5
CIGS	18.9	34.8	0.696	78.0
Thin-film: multijunction				
a-Si/a-SiGe tandem	13.5	7.72	2.375	74.4
Photoelectrochemical				
Dye-sensitised TiO ₂	11.0	19.4	0.795	71.0

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