

Solar cell as a heat engine: energy–entropy analysis of photovoltaic conversion

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A thermodynamic theory for the voltage or free energy generated by a quantum solar energy converter which has recently been proposed, is developed here in a more direct and simpler way. We consider separately the luminescence and conversion of a single photon of the incident radiation. The energy/entropy balance for the conversion process yields an expression for the voltage in a form familiar from the classical thermodynamics of the work carried out by the heat en-

gine. A similar balance for the absorption and emission of light gives an expression for the irreversible entropy generation which reduces the open circuit voltage generated by the solar cell. Detailed expressions for losses due to individual mechanisms, including non-radiative recombination, are obtained with the use of an approximation where photons in the incident and emitted beams are modelled as an ideal two-dimensional gas.

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1 Introduction The thermodynamics analysis of the conversion of light into useful work – be it electricity or photochemical energy – has attracted interest for many years (see, for example [1], for reviews of the subject). A new model has recently been proposed [2, 3] where the principal focus of analysis is the main energy term in photovoltaic conversion: the voltage generated by the solar cell, or the free energy produced by the photochemical system [4]. In keeping with other treatments of this subject, the methodology of [2, 3] uses the flows of photons, energy and entropy. These flows, however, are now defined in a manner consistent with irreversible thermodynamics [5], and applied to light as a stream of photons, rather than a continuous energy and entropy flow. The general thermodynamic framework that follows is based solely on the consideration of energy and entropy balance for photons transferred between the incident and emitted light beams.

The approach of [2, 3] is here revisited by deriving the results in a more direct way based on classical thermodynamics. The scheme that makes this possible is achieved by separating formally the two essential features of operation of the solar cell: light absorption followed by conversion of the photon into an electron–hole pair and useful work, or followed by photon emission as luminescence. The conversion part of this picture yields a result which

is familiar from textbooks dealing with the thermodynamics of the heat engine. The entropy balance in photon absorption and emission then furnishes the required result that determines the irreversible entropy generation and the ensuing losses in the conversion process. The use of an ideal gas model of [2, 3] for the incident and emitted photon beams yields a quantitative description of the four principal voltage losses in photovoltaic conversion:

- (i) Unavoidable entropy generation on account of kinetics of the conversion system,
- (ii) Losses due to étendue expansion between absorption and emission,
- (iii) Losses due to nonradiative recombination,
- (iv) Entropy generation due to photon cooling from temperature T_s of solar radiation to temperature T_o of the converter.

Losses under (ii) and (iii) above can, at least in principle, be eliminated. We have argued in [2, 3] that the photon cooling loss (iv) (which exists in all the present generation of solar cells) can also be avoided in a device based on hot carrier conversion. The present paper focuses on the thermodynamics of the conventional photovoltaic devices; a further discussion of hot carriers solar cell will be presented in a separate publication.

2 Solar cell as a heat engine The energy conversion process in solar cell is generally divided into two natural parts: the absorption and emission of the incident radiation, and conversion of the absorbed photons into useful work. A similar scheme can also be applied to the photochemical conversion apparatus in photosynthesis [4].

The energy scheme for each absorbed photon of the incident radiation which is converted into energy w , say, is shown in Fig. 1. The incident photon energy u_{in} is here pictured as heat which is absorbed by the cells from a high temperature reservoir at temperature T_s . During the conversion process, heat q_w is rejected into a low-temperature reservoir at temperature T_o of the solar cell, assumed here equal to temperature of the environment. The energy conservation law then gives

$$u_{\text{in}} = w + q_w. \quad (1)$$

The conversion process is also subject to entropy balance. Let us denote the entropy of the absorbed photon by s_{in} . The entropy emitted into the low temperature reservoir is q_w/T_o and since there is no entropy associated with the work w , the energy and entropy balance equations can be expressed in the simple form

$$s_{\text{in}} = q_w/T_o - \sigma_i, \quad (2)$$

where we denoted the entropy generated in the conversion process by σ_i . The second law of thermodynamics tells us that $\sigma_i \geq 0$.

The incident photons are pictured here as pure heat at temperature T_s so that $s_{\text{in}} = u_{\text{in}}/T_s$. A brief discussion of this statement is in order. Not everyone agrees that radiative transfer (where a factor of 4/3 is usually applied) can be treated as heat transfer. In the present treatment, the absorption and emission of photons is considered as removing or adding photons from or to the incident/emitted beams. This energy transfer is described, in a uniform fashion, by the expression $u = \mu + T_s$, where μ is the chemical potential. This expression is also consistent with the definition of fluxes which comply with the framework of irre-

versible thermodynamics [2, 3, 5]. As we consider here the incident flux in the form of the direct (beam) sunlight which is approximated well by black body radiation, we can set $\mu = 0$ and the above equation for equation for s_{in} follows. Clearly, work w carried out per photon is equal to qV , where q is the electron charge and V is the voltage generated by the solar cell.

Combining (2) with (1) now gives the photogenerated voltage as

$$qV = \left(1 - \frac{T_o}{T_s}\right) u_{\text{in}} - T_o \sigma_i. \quad (3)$$

Thus, the solar cell voltage can be written in a standard thermodynamic form for the amount of work that can be produced between two reservoirs at temperatures T_s and T_o by extracting energy u_{in} per photon from the high temperature reservoir. We have shown previously that, when written in terms of fluxes, Eq. (3) reduces to a form similar to Onsager's entropy generation in irreversible thermodynamics [3].

3 Entropy generation in terms of photon balance

Away from the short circuit, the solar cell not only absorbs photons but also emits them. We shall now consider the energy/entropy balance of the absorption/emission process (Fig. 2). The absorption of a photon contributes energy u_{in} that has already been defined in Section 2. Each emitted photon carries energy u_{out} , and each absorption/emission event results in the dissipation of heat q_{ph} into the low temperature reservoir. Noting that the absorbed and emitted photons carry entropy s_{in} and s_{out} , respectively, and that the entropy associated with the emission of heat q_{ph} is equal to q_{ph}/T_o , we arrive at the following energy and entropy balance for the absorption/emission process:

$$\begin{aligned} u_{\text{in}} &= u_{\text{out}} + q_{\text{ph}} \\ s_{\text{in}} &= s_{\text{out}} + q_{\text{ph}}/T_o - \sigma_i, \end{aligned} \quad (4)$$

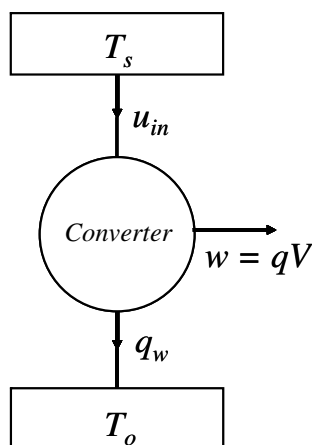


Figure 1 Energy balance for a photovoltaic converter.

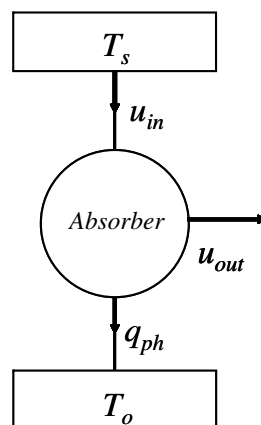


Figure 2 Energy balance for the absorption and emission of radiation.

which gives the entropy generation per photon in the form

$$T_o \sigma_i = (u_{\text{in}} - u_{\text{out}}) - T_o (s_{\text{in}} - s_{\text{out}}). \quad (5)$$

Thus, the entropy generation resembles the difference of availability between the incident and emitted photons for a process which takes place at constant volume [6].

A substitution of (5) into (3) immediately gives $qV = u_{\text{out}} - T_o s_{\text{out}} = \mu_{\text{out}}$: in other words, the work carried out by conversion of a photon into electrostatic or chemical energy is equal to the chemical potential of the emitted photons. This result is, of course, well known from the theory of p–n junction solar cell but is obtained here, quite generally, by an argument based purely on thermodynamics.

Equations (3) and (5) contain the essence of the thermodynamic description of the operation of the photovoltaic converter (solar cell). We note that no reference has been made to the material from which this converter is made: the voltage is given in terms of photon transfer between the incident and emitted beams.

4 Photon beam as an ideal two-dimensional gas Under modest illumination intensities, the photon statistics resembles the statistical mechanics of a two dimensional ideal gas. The number of dimensions comes from the two angular coordinates that are needed to specify the direction of the beam. It can be shown [3] that this ap-

proximation works well for solar radiation with concentration of up to about a hundred. In this transition from “photons in a box” to “photons in a beam” the number of particles in the volume is replaced by the photon flux, and the volume by the étendue \mathcal{E} of the beam [2, 3]. We assume that the solar cell is characterized by a material with energy gap E_g . Photons are incident from the Sun at rate \dot{N}_{in} , and are re-emitted at rate \dot{N}_{out} . The photon energy u and entropy s are then determined from

$$u = (\partial \dot{U} / \partial \dot{N})_{\mathcal{E}, T}, \quad s = (\partial \dot{S} / \partial \dot{N})_{\mathcal{E}, T}, \quad (6)$$

where \dot{U} and \dot{S} are the convective energy and entropy fluxes carried by the beam, defined in the usual fashion [7].

Using Eq. (6), the irreversible entropy generation rate σ_i given by Eq. (5) can be easily determined. Just as the energy per particle in an ideal gas is independent of the total number of particles in the volume, the energy per photon is independent of the photon flux, and is given by

$$u(T, \mathcal{E}, \dot{N}) = E_g + k_B T. \quad (7)$$

Using (6), the entropy per photon is obtained by differentiating the two-dimension analogue of the Sackur–Tetrode equation with respect to the number of particles. Since this is here replaced by the photon flux, we have

$$s(T, \mathcal{E}, \dot{N}) = k_B \left\{ \ln \left(\frac{\mathcal{E} T}{\dot{N}} \right) + 1 \right\} + \text{constant}. \quad (8)$$

Using (7) and (8) we then have

$$\begin{aligned} T_o \sigma_i &= \{u(T_s, \mathcal{E}_{\text{in}}, \dot{N}_{\text{in}}) - u(T_o, \mathcal{E}_{\text{out}}, \dot{N}_{\text{out}})\} - T_o \{s(T_s, \mathcal{E}_{\text{in}}, \dot{N}_{\text{in}}) - s(T_o, \mathcal{E}_{\text{out}}, \dot{N}_{\text{out}})\} \\ &= [\{u(T_s) - u(T_o)\} - T_o \{s(T_s, \mathcal{E}_{\text{in}}, \dot{N}_{\text{in}}) - s(T_o, \mathcal{E}_{\text{in}}, \dot{N}_{\text{in}})\}] + \{s(T_o, \mathcal{E}_{\text{in}}, \dot{N}_{\text{in}}) - s(T_o, \mathcal{E}_{\text{out}}, \dot{N}_{\text{out}})\} \\ &\quad + \{s(T_o, \mathcal{E}_{\text{out}}, \dot{N}_{\text{in}}) - s(T_o, \mathcal{E}_{\text{out}}, \dot{N}_{\text{out}})\}. \end{aligned} \quad (9)$$

Let us separate from (9) the last term in curly brackets, which we denote by σ_{kin} . This term corresponds to entropy generation due to finite current being extracted from the solar cell (a finite rate of turnover of the “engine”):

$$\sigma_{\text{kin}} = s(T_o, \mathcal{E}_{\text{out}}, \dot{N}_{\text{in}}) - s(T_o, \mathcal{E}_{\text{out}}, \dot{N}_{\text{out}}) = k_B \ln \left(\frac{\dot{N}_{\text{in}}}{\dot{N}_{\text{out}}} \right) \quad (10)$$

We consider, for the moment, an ideal solar cell where all absorbed photons are either emitted or converted into electrical current. Taking into account the equilibrium photon fluxes at temperature T_o of the converter – which we denote by \dot{N}_{in}^o and \dot{N}_{out}^o – the photon balance reads

$$\dot{N}_{\text{in}} - \dot{N}_{\text{out}} = \dot{N}_{\text{in}}^o - \dot{N}_{\text{out}}^o + I/q \cong I/q, \quad (11)$$

where I is the electrical current extracted from the solar cell. In the second part of (11) we have noted that the difference of the equilibrium fluxes can be safely neglected.

Thus

$$\sigma_{\text{kin}} = k_B \ln \left(\frac{I_\ell + I_o}{I_\ell + I_o - I} \right), \quad (12)$$

where $I_\ell = q(\dot{N}_{\text{in}} - \dot{N}_{\text{in}}^o)$ is the photogenerated current and $I_o = q\dot{N}_{\text{out}}^o$ is the dark diode saturation current.

We now return to (9). The first and second terms on the right hand side of the last expression have been discussed in detail in [2, 3] and need not therefore be discussed at great length. The second term arises as a results of étendue expansion between the incident and emitted beam, with étendues \mathcal{E}_{in} and \mathcal{E}_{out} :

$$\sigma_{\text{exp}} = k_B \ln \left(\frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \right). \quad (13)$$

By microscopic reversibility, $\mathcal{E}_{\text{in}} \leq \mathcal{E}_{\text{out}}$, and σ_{exp} is therefore always greater than or equal to zero.

Finally, the first term on the right hand side of (9) is the entropy generation by “photon cooling” from tempera-

ture T_s to temperature T_o ,

$$\sigma_c = k_B \left(\frac{T_s}{T_o} - 1 \right) - k_B \ln \left(\frac{T_s}{T_o} \right). \quad (14)$$

The sum of the last two terms (11) and (12) is denoted by $T_o \sigma_i(\text{oc})$. This is the entropy generation (5) at open circuit. We can then write

$$qV = qV_{\text{oc}} - k_B T_o \ln \left(\frac{I_\ell + I_o}{I_\ell + I_o - I} \right). \quad (15)$$

Equation (15) is the thermodynamic analogue of the Shockley ideal solar cell equation [8] to which it can be reduced by a straightforward algebra. Here, V_{oc} is the open circuit voltage, given by

$$qV_{\text{oc}} = \left(1 - \frac{T_o}{T_s} \right) u_{\text{in}} - T_o \sigma_i(\text{oc}). \quad (16)$$

Substituting from (13) and (14) then gives the following expression which has, in more restrictive form, been obtained in a number of occasions in the past:

$$qV_{\text{oc}} = \left(1 - \frac{T_o}{T_s} \right) E_g + k_B T_o \ln \left(\frac{T_s}{T_o} \right) - k_B T_o \ln \left(\frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \right). \quad (17)$$

5 Non-radiative losses The analysis so far has been restricted to ideal solar cells where the incident photon flux is equal to the combined emitted flux and the electrical current produced by the cell, expressed as a particle flux. In the presence of non-radiative transitions, the photon balance (11) becomes

$$\dot{N}_{\text{in}} = \dot{N}_{\text{out}} + \dot{N}_{\text{nr}} + I/q, \quad (18)$$

where \dot{N}_{nr} is the rate of non-radiative transitions in the system per unit time. Equation (10) for σ_{kin} can then be written as

$$\begin{aligned} \sigma_{\text{kin}} &= k_B \ln \left(\frac{\dot{N}_{\text{in}}}{\dot{N}_{\text{out}}} \right) \\ &= k_B \ln \left(\frac{\dot{N}_{\text{in}}}{\dot{N}_{\text{in}} - I/q} \right) + k_B \ln \left(\frac{\dot{N}_{\text{out}} + \dot{N}_{\text{nr}}}{\dot{N}_{\text{out}}} \right) \\ &= k_B \ln \left(\frac{I_\ell + I_o}{I_\ell + I_o - I} \right) - k_B \ln(\eta_{\text{em}}), \end{aligned} \quad (19)$$

where

$$\eta_{\text{em}} = \frac{\dot{N}_{\text{out}}}{\dot{N}_{\text{out}} + \dot{N}_{\text{nr}}}, \quad (20)$$

is the photon emission efficiency.

In the present approximation, the rate of photon emission by the converter is

$$\dot{N}_{\text{out}} = \mathcal{E}_{\text{out}} \frac{2E_g^2 k_B T_o}{h^3 c^2} e^{(\mu - E_g)/k_B T_o}. \quad (21)$$

The rate of non-radiative transitions depends on the material of the converter. For non-radiative transitions via defects in the bulk of a p-type semiconductor, for example,

$$\dot{N}_{\text{nr}} = \frac{V}{\tau_{\text{nr}}} n = \frac{V}{\tau_{\text{nr}}} \mathcal{N}_c e^{(\mu - E_g)/k_B T_o}, \quad (22)$$

where V is the volume, n is the electron density, τ_{nr} is the non-radiative (Shockley–Hall–Read) lifetime, and \mathcal{N}_c is the density of states in the conduction band, per unit volume. In a molecular converter, we have a similar expression

$$\dot{N}_{\text{nr}} = \frac{1}{\tau_{\text{nr}}} \left(\frac{N^*}{V} \right) V = \frac{1}{\tau_{\text{nr}}} \left(\frac{N_o}{V} \right) V e^{(\mu - E_g)/k_B T_o}, \quad (23)$$

where N^* and N_o are the numbers of molecules in the excited and ground states, respectively.

Substituting (21) and (23) into (20),

$$\eta_{\text{em}} = \frac{\gamma}{1 + \gamma}, \quad (24)$$

where $\gamma = 2E_g^2 k_B T_o \tau_{\text{nr}} \mathcal{E}_{\text{out}} / h^3 c^2 \mathcal{N}_c V$. For a molecular material, \mathcal{N}_c should be replaced by N_o/V .

We observe that, for a conventional planar solar cell structure, the second term in γ is inversely proportional to the cell thickness which we denote by d . In materials where non-radiative processes are dominant ($\gamma \ll 1$), the entropy generation on account of non-radiative losses σ_{nr} becomes

$$\sigma_{\text{nr}} = -k_B \ln(\eta_{\text{em}}) \cong -k_B \ln(\gamma) \propto k_B \ln(d). \quad (25)$$

Thus, the entropy generation σ_{nr} increases (and open circuit voltage decreases) with increasing cell thickness. This result is a consequence of the proportionality of the non-radiative recombination rate to the volume. A similar dependence of the voltage on non-radiative lifetime has been observed in [9, 10]. An explanation in terms of entropy generation has also been suggested in [11]. It is interesting to note that although the effect of non-radiative recombination through the photon emission efficiency (20) is to decrease the open circuit voltage, η_{em} does not enter the expression for the photogenerated current I_ℓ which remains equal to absorbed photon flux multiplied by the electron charge.

6 Conclusion We have shown that the Shockley solar cell equation can be obtained by a purely thermodynamic analysis of photon fluxes incident on and emitted from the solar cell. The voltage generated by the cell bears a close parallel to the work carried out by a classical heat engine, and is given by the Carnot efficiency less any irreversible losses. The three principal loss terms (plus an additional term if non-radiative recombination is present) which enter through entropy generation are then determined by a supplementary consideration based on the photon balance in the converter. We have previously shown [2, 3] that hot-

carrier conversion can be accommodated in the present analysis if work can be produced by photon cooling, removing the loss term (14) and increasing the solar cell efficiency.

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