Detailed balance method for thin photovoltaic converters

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Thermodynamics and detailed balance arguments have provided the basic ideas for the understanding of solar cell efficiencies from a theoretical point of view. The general thermodynamic theories (see, for example,[1]) are usually not specific to details of the solar energy converter and hence give the most general and unrealistically high estimates. The Shockley-Queisser theory[2] is based on the detailed balance between the incident and emitted photon fluxes. The incident flux - assumed to be completely absorbed by the cell - is approximated by a black-body distribution at temperature T_s of the sun. The emitted photon flux is often written in the form of a modified Planck distribution at the ambient temperature T_o. The resulting efficiency contains only one parameter of the semiconductor: the energy gap E_g. In the limit $E_g >> kT_s$, the open circuit voltage can be approximated by[3]

$$qV_{oc} = E_g\left(1 - \frac{T_o}{T_s}\right) + kT_o\, ln\left(\frac{T_o}{T_s}\right) + T_o\, ln\left(\frac{\omega_s}{4\pi}\right) \tag{1}$$

where ω_s is the size of the solar disk in steradians.

This paper considers the ideal efficiency of thin semiconductor converters which do not comply with the Shockley-Queisser framework. The interest in such converters extends beyond the purely academic arena: the aim of going to thinner cells made from, for example, crystalline silicon, with the resulting saving of material is one of the principal research goals of photovoltaic technology today.

We shall therefore consider the opposite limit to that discussed by Shockley and Queisser and assume that the thickness of the converter is sufficiently small that only a fraction of the above-bandgap solar flux is absorbed by the solar cell. The photon absorption rate then depends on the absorption coefficient. The solar black body radiation incident on an area A of the cell is absorbed at the rate

$$n^2 \omega_s'\, Adx \int_{\nu_g}^{\infty} \alpha(\nu)\, F(\nu, T_s)\, d\nu \tag{2}$$

where ω_s' is the solid angle corresponding to ω_s inside the cell subtended by the refracted radiation, $\alpha(\nu)$ is the absorption coefficient, n is the refractive index of the cell material, dx is the thickness of the cell, ν is the frequency, $\nu_g = E_g/h$ and $F(\nu, T)$ is the black body photon flux of per unit area, per unit time, and per unit frequency interval:

$$F(\nu, T) = \frac{2\nu^2}{c^2}\, \frac{1}{e^{h\nu/kT} - 1} \tag{3}$$

The rate of photon emission inside the cell can be calculated using the van Roosbroeck-Shockley detailed balance[4] as

$$R = 4\pi n^2 e^{\Delta\mu/kT_o} \int_{\nu_g}^{\infty} \alpha(\nu)\, F(\nu, T_o)\, d\nu\; Adx \tag{4}$$

[1] P.T. Landsberg and T. Markvart, Ideal Efficiencies, in: T. Markvart and L. Castañer (eds), *Practical Handbook of Photovoltaics: From Fundamentals to Applications*, Elsevier, Oxford (2003), p. 123.
[2] W. Shockley and H J Queisser, Detailed balance limit of efficiency of pn junction solar cells, *J. Appl. Phys.* **32** 510 (1961).
[3] W. Ruppel and P. Würfel, Upper limit for the conversion of solar energy, *IEEE Trans. Electron Devices* ED-27, 877 (1980).
[4] W. van Roosbroeck and W. Shockley, Photon-radiative recombination of electrons and holes in germanium, *Phys. Rev.* 94, 1558 (1954)

Equating (2) to (4) one obtains the splitting of the quasi-Fermi levels $\Delta\mu$ (or qV_{oc})

$$\Delta\mu = kT_o \, ln\left\{\frac{K(T_s)}{K(T_o)}\right\} + kT_o \, ln\left(\frac{\omega_s'}{4\pi}\right) \tag{5}$$

where

$$K(T) = \int\limits_{\nu_g}^{\infty} \alpha(\nu)\,F(\nu,T)\,d\nu \tag{6}$$

Actually, the last term in (5) is not quite correct as only the photons within a solid angle $2\omega_c$ limited by total internal reflection will be emitted from the cell; the rest will be trapped. Hence, the full solid angle 4π in the last term has to be replaced by $2\omega_c$, giving

$$kT_o \, ln\left\{\frac{\omega_s'}{2\omega_c}\right\} = kT_o \, ln\left\{\frac{\omega_s}{4\pi}\left(1 + cos\theta_c\right)\right\} \tag{7}$$

where θ_c is one half of the (linear) critical apex angle corresponding to ω_c and we have also approximated ω_s' *by* ω_s/n^2 for one-sun solar radiation.

To obtain a clearer picture of the voltage (5), we write the absorption coefficient in the form $\alpha(\nu) = \alpha_o(\nu - \nu_g)^g$, where $g = \frac{1}{2}$ or 2 for direct and indirect bandgap semiconductors. This is a standard expression for α if we neglect the energy of the photons participating in the optical transition of the latter. It is interesting to note that $g = d/2 - 1$, where d is the number of degrees of freedom of the photogenerated electron hole pair (assumed to be 3 and 6 for direct- and indirect-gap semiconductors, respectively). Adopting a rather crude approximation for the integral $K(T)$, similar to (1) and valid in the limit $E_g >> kT$:

$$K(T) \cong C(kT)^{g+1} e^{-E_g/kT} \tag{8}$$

where C is a temperature-independent constant, we obtain

$$\Delta\mu = E_g\left(1 - \frac{T_o}{T_s}\right) + \frac{d}{2} kT_o \, ln\left(\frac{T_o}{T_s}\right) + kT_o \, ln\left\{\frac{\omega_s}{4\pi}\left(1 + cos\theta_c\right)\right\} \tag{9}$$

Equation (9) can be discussed in thermodynamic terms. One can show, for example, that the factor $d/2$ in the second term of (9) is due to the entropy of photogenerated electron-hole pairs. Indeed, the first two terms on the left-hand side of equation (9) can be written as

$$T_o\left\{\frac{F(T_s)}{T_s} - \frac{F(T_o)}{T_o}\right\} = T_o\left\{\frac{U(T_s)}{T_s} - \frac{U(T_o)}{T_o}\right\} - T_o\left\{S(T_S) - S(T_o)\right\} \tag{10}$$

where $F(T)$, $U(T)$ and $S(T)$ are the free energy, internal energy and entropy of a (fictitious) gas of electron-hole pairs of dimension d. Standard thermodynamics then gives for the two terms in the open circuit voltage

$$\Delta\mu = kT_o \int\limits_{T_o}^{T_s} \frac{U(T)}{T^2}\,dT + T_o\Delta S \tag{11}$$

where ΔS denotes the logarithmic part of the last terms in (9) which can be interpreted as an angular contribution to the entropy of absorption or emission. An additional term can be added to (1) and (9) to improve the accuracy of this approximation which, even in the present form, is quite good. An expression similar to (9) has been discussed already in[5].

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[5] T. Markvart and P.T. Landsberg, Everyman's guide to third generation efficiencies, *Proc. 3rd World Conf. On Photovoltaic Solar Energy Conversion*, Osaka, 2003, in the press.