# Reply to "Ideal Solar Cell Efficiencies":

# A brief guide to the thermodynamics of the Shockley-Queisser model

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We wrote our comment[1] as a brief and concise guide to the SQ model,[2] chiefly aiming to explain how *real-world* solar cells (non-concentrating, single-junction) must be related to the efficiency limits that result from the SQ-model. The need for such a comment arises, especially in the context of a widened portfolio of new very efficient solar cell materials and a rapidly growing community. As obvious from the title[1], we target *non-specialist* readers. Such approach[3] has the risk that the resulting text is unsatisfactory for *specialist* readers. The author of the 'comment on our comment' (CoC)[4] is certainly such specialist reader. Thus, to reply to the CoC we need to leave the level at which we presented the topic in our comment, to make clear that while there can be differences of opinion as how to explain the issue to the "perplexed", *what is written in our comment is a valid description of the SQ model.*

The most important issue brought up in the CoC, and the one we concentrate on in our reply, is the role of étendue expansion as a main loss, especially in the case were all recombination is radiative. In Ref. 1, we introduced the term 'isothermal losses' for the actual heat generation (loss of *total,* i.e. internal, energy per incoming photon) that occurs in the device in addition to the initial non-absorption and thermalization losses. Étendue losses, in contrast, refer specifically to the entropy increase associated to photon exchange between the sun, the device and the environment. Étendue expansion refers to the fact that the étendue $\varepsilon_{in}$ of the incoming solar radiation differs by a factor of ~46000 from that of the outgoing radiation (emitted by the solar cell), $\varepsilon_{out}$, if no additional measures are in place to either concentrate the light or limit the solid angle of the emitted radiation.

To put our explanation of the SQ model into its thermodynamic context requires splitting the total energy into the Helmholtz free energy and an entropic term resulting in a simple refinement to Fig. 2c of Ref.1 as shown in Fig. 1. To focus the discussion, we consider the available power *after* thermalization losses and non-absorption losses have been discounted in the solar cell. This can be represented as the area of a rectangle (Fig. 1) where one side is the photogenerated current $J_{SC}$ and the other is the maximum open circuit voltage $V_{OC}^{\max}$, obtained with full concentration of the sunlight (or matching étendues, i.e. $\varepsilon_{in} = \varepsilon_{out}$). Note that $J_{SC} = q\dot{\nu}_{in}$ is defined by the total incoming photon flux $\dot{\nu}_{in}$ and the elementary charge $q$. Also included in Fig. 1 is the current vs. voltage characteristics of the solar cell as calculated from the balance of incoming and outgoing radiation (see suppl. information). Each working point (the maximum power point is used in the figure) defines a horizontal line that separates the emitted *photon* flux $\dot{\nu}_{out}$, from the collected *electron* current $J = q(\dot{\nu}_{in} - \dot{\nu}_{out})$ and a vertical line at the voltage $V_{mpp}$ that separates the free energy (work) carried by each particle on the left from the dissipative processes (heat) incurred by each particle on the right.

These two lines separate the initial rectangle $J_{SC} \times V_{OC}^{\max}$ into four subareas, each representing a power with a tangible physical meaning. The light red area is the chemical potential $F_{eh}$ (per particle) of the electron/hole pairs multiplied by the collected electrical current *J, divided by q (i.e., the net electron flux)* and corresponds to the electrical output power. The dark red area then stands for the entropy production in the electronic system (referred to as isothermal losses in Ref. 1). The light blue area corresponds to the power radiated by the cell at the chemical potential $F_\gamma$ of photons emitted from the solar cell multiplied by the number $\dot{\nu}_{out}$ of emitted photons per unit time. Finally, the dark blue area represents the entropy flow in the photonic system and includes the étendue change. As pointed out by the CoC author,[5,6] the entropy production $\sigma$ per incident photon is the sum $\sigma = \sigma_{et} + \sigma_{kin}$ of a contribution of étendue expansion (controlled by the way *photons* enter and leave the cell) and a "kinetic" term associated with charge carrier collection (controlled by the amount of particles leaving the cell in the form of *electron-hole pairs,* see also suppl. information). This entropy term defines the shift between the maximum open circuit voltage and the voltage of the actual working point at maximum power according to $V_{mpp} = V_{OC}^{\max} - T(\sigma_{et} + \sigma_{kin})/q$, with the absolute cell temperature *T*, and defines the *width* of both the dark red and the dark blue area, as well as by default the width of the light areas as well.

The entropy generation *per particle,* measured in the photon system (by $\sigma_{et}$ and $\sigma_{kin}$), defines simultaneously the entropy generation per particle in the electronic system. This follows from an important implication of the SQ model, namely that both systems mirror each other exactly: The free energy $F_{eh}$ of the electron/hole pairs equals $F_\gamma$, the free energy of the emitted photons,[7] and both equal $qV_{mpp}$. All three quantities are defined by the same vertical line shown in Fig.1. In turn, the horizontal line reflects the conservation of particles *across* both systems, namely that the incoming photons *must* leave the cell *either* in the form of an emitted photon *or* as electron-hole pairs at the cell's terminals. Considering the power loss, i.e. energy multiplied with particle flow, we see that although the largest power loss, the isothermal loss (dark red area) carries the same dissipation per particle as the power loss in the photon system, the dissipation actually *occurs* within the solar cell.

Thus, while the undisputed elegance of the SQ model results from describing the solar cell only via its input and output balance, the model contains strong implications on what happens inside the cell as discussed above and in [1]. Furthermore, a closer look into the solar cell becomes mandatory as soon as further loss channels that actually happen *inside* the cell, like non-radiative recombination or resistive ones, are added. To relate these additional losses to the losses and the assumptions implied by the SQ model was one aim of Ref.1.

The second criticism in the CoC concerns the way how we treat the departure of the photovoltaic quantum efficiency of a real-world solar cell from an ideal step-function. There is admittedly not a unique solution for this problem and any proposition has pros and cons. In Ref. 1 we use a specific approach[8] that has been successfully used to analyze and compare solar cells across all technologies.[9,10]

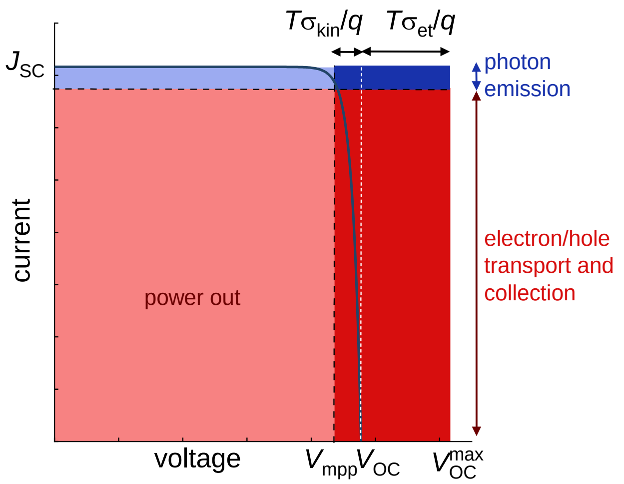


**Figure 1: Power losses in the SQ model including the effect of étendue expansion.** Current-voltage curve of a solar cell in the SQ model without concentration (i.e., with étendue expansion). The maximum open circuit voltage $V_{OC}^{max}$ is reduced by two entropy terms $T\sigma_{et}/q$ towards the actual open circuit voltage $V_{OC}$ and by $T\sigma_{kin}/q$ towards the voltage $V_{mpp}$ at the maximum power point. The power losses due to photon emission are indicated as blue rectangles (dark blue losses associated with entropy generation $T(\sigma_{et}+\sigma_{kin})/q$, light blue losses at the free energy $F_\gamma = qV_{mpp}$ of the emitted photons). The electrical output power is defined by the number of extracted hole pairs multiplied with their free energy $F_{eh} = F_\gamma = qV_{mpp}$ (light red area). The largest loss channel (dark red) is that of the entropy losses in the electron/hole system. On the energy axis this loss equals the entropic losses in the photonic system. However, the height on the current axis is much larger than the contribution from the emitted photons because the number of collected electron/hole pairs at the maximum power point, fortunately, exceeds the number of emitted photons by far. With suitable units, the vertical axis represents a particle flux and the horizontal axis an energy per particle, so that the product is still a power.

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