## Thermodynamic lessons of the detailed-balance principle of the photovoltaic effect

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For the most part, since their invention more than 60 years ago, photovoltaic (PV) solar cells were a niche product with marginalized applications, primarily efficient but costly power source for outer space missions or a cheap less than 10% efficient source for low-end electronic devices. Large-scale power production, at that time, was at the hand of thermo-solar plants that boasted an impressive efficiency of about 20% or more. In the past 30 years, all that changed as cells became cheaper and more efficient. Today's cells are 20% efficient and produce electricity at less than 50 cents per kWh. It is not surprising, thus, to find that the bulk of today's renewable energy production is at the hands of photovoltaic cells. What made this impressive forward leap possible was the combined understanding of the optoelectronics of semiconductors and the fundamental limits of a PV process in the form of the Shockley and Queisser (SQ) approach. Advancement in these two aspects is a prerequisite for any further progress in the field.

The SQ approach is based on the principle of detailed balance (DB), which is the equality of electronhole generation and depletion rates. The general consent among experts today is that DB is somehow immanent to thermodynamics. Despite that, attempts to settle the two succeeded only at open circuit conditions, namely when the cell is not working, which is thermodynamics' prime objective.

In the talk, we will show that DB and thermodynamics' first law are, in fact, distinct requirements. As a result, there are circumstances where a PV process cannot uphold the two for a given temperature and potential. This fact points to a significant limitation in our understanding of the PV effect. We will also discuss what must become for a PV process to follow the DB and thermodynamics' first law. As a result, we conceptualize a process controlled by a third parameter and the temperature and potential, which is the sub-bandgap emission/absorption that any semiconductor material possesses, albeit in a small amount at standard conditions. As a result, we can fix the ultimate thermodynamic efficiency limit for the first time by minimizing the generated entropy of the PV process. This SQ-thermo unified approach shows us why the SQ approach is accurate at terrestrial conditions and when it fails.

From a more applied perspective, having a unified DB-thermodynamic approach allows us to base our calculations not on the unknown cell temperature but the known temperature of the cell's surroundings and the corresponding heat conduction. In other words, unlike the SQ approach that calculates the potential based on the temperature, we calculate the temperature, potential, and more (sub-bandgap emissivity) based on the heat conduction coefficient of the cell to its environment. As a result, we are the first to consider the mutual effect of heat conduction and the PV effect. Such an approach is essential once the radiative heat supply to the cell is immense, as in CPV and thermo-PV, when the heat conduction is low as in outer space solar cells, or when both occur as in concentrated space solar cells.