then zero everywhere. If $f(T_s, 0) > f(T_a, qV)$, then $N_{\mathrm{ph}} > f(T_a, qV)$ and $\mu_{i-\mathrm{ph}} > qV$, so that both factors are positive and so is the product. If $f(T_s, 0) < f(T_a, qV)$, then $N_{\mathrm{ph}} < f(T_a, qV)$ and $\mu_{i-\mathrm{ph}} < qV$. In this case both factors are negative and the product is positive.

Thus, we have proven that every mode contributes non-negatively to the entropy. We can then state that the SQ cell produces non-negative entropy and, in this sense, it complies with the second law of thermodynamics.

For less idealised cases, as we have mentioned above, the existence of quasi-Fermi levels or temperature gradients generally produces additional positive entropy. Non-radiative net recombination of electrons from the conduction to the valence band also produces positive entropy. However, net generation would contribute to the production of negative entropy and, therefore, it may incur in violation of the second law of thermodynamics, if no other mechanism contributing to the creation of positive entropy exists. So the inclusion of imaginative carrier generation rates in novel device proposals, without counterparts, must be considered with some caution.

4.3.4 Entropy Production in the Whole Shockley–Queisser Solar Cell

The preceding approach is applicable to regions in which the physical properties of the system are continuous and differentiable, but not to abrupt interfaces. For testing the compliance with the second law, the continuity equations must be integrated in such cases by choosing volumes surrounding the suspected interfaces. This integral approach can also be extended to the whole converter to check for any violation of the second law and also to calculate the whole entropy production of a device. However, the integral approach, if not complemented with the local approach, is valid for proving thermodynamic inconsistency, but not for proving consistency that has to be proven at every point. An example of the use of such an integral approach is given here.

In the integral analysis we follow steps similar to those used in the local analysis. In particular, the first law of thermodynamics is applied by integrating equation (4.7) and using the first law expressed by equation (4.9). Then, we obtain, for the stationary case

$$0 = \int_A \sum_i \boldsymbol{j}_{e,i} \, \mathrm{d}A = +\dot{E}_r - \dot{E}_s + \dot{E}_{mo} - \dot{E}_{mi} + \dot{E}_{\mathrm{others}} \tag{4.39}$$

where $\dot{E}_s$ and $\dot{E}_r$ are the radiation energies entering or escaping from the converter, $\dot{E}_{mi}$ and $\dot{E}_{mo}$ are the energies of the electrons entering the VB and leaving the CB, respectively, and $\dot{E}_{\mathrm{others}}$ is the net flow of energy leaving the semiconductor as a result of other mechanisms.

Taking equation (4.5) into account, the fact that no chemical potential is associated with *other* particles and processes, and the annihilation of the grand canonical potential current density, the term corresponding to the other elements is more conventionally written as

$$\dot{E}_{\mathrm{others}} = T_a \dot{S}_{\mathrm{others}} \doteq \dot{Q} \tag{4.40}$$

where $\dot{Q}$ is defined as the rate of heat leaving the converter.