

The second law of thermodynamics, expressed by equations (4.8) and (4.10), integrated into the whole volume of the converter can be written, for the stationary case, as

$$\dot{S}_{\text{irr}} = \int_U \sigma_{\text{irr}} dU = \int_A \sum_i \mathbf{j}_{s,i} dA = \dot{S}_r - \dot{S}_s + \dot{S}_{mo} - \dot{S}_{mi} + \dot{S}_{\text{others}} \quad (4.41)$$

The irreversible rate of entropy production is obtained by the elimination of the terms with subscript *others* by multiplying equation (4.41) by  $T_a$ , subtracting equation (4.39) from the result and taking into account (4.40). In this way we obtain

$$T_a \dot{S}_{\text{irr}} = (\dot{E}_s - T_a \dot{S}_s) - (\dot{E}_r - T_a \dot{S}_r) + (\dot{E}_{mi} - T_a \dot{S}_{mi}) - (\dot{E}_{mo} - T_a \dot{S}_{mo}) \quad (4.42)$$

From equation I-4 (Table 4.1) and considering the annihilation of the grand canonical potential flow for electrons,  $(\dot{E}_{mi} - T_a \dot{S}_{mi}) = \varepsilon_{Fv} \dot{N}_{mi}$  and  $(\dot{E}_{mo} - T_a \dot{S}_{mo}) = \varepsilon_{Fc} \dot{N}_{mo}$ , so that we can write

$$T_a \dot{S}_{\text{irr}} = \varepsilon_{Fv} \dot{N}_{mi} - \varepsilon_{Fc} \dot{N}_{mo} + (\dot{E}_s - T_a \dot{S}_s) - (\dot{E}_r - T_a \dot{S}_r) \quad (4.43)$$

Taking into account that  $\dot{N}_{mi} = \dot{N}_{mo} = I/q$  and  $\varepsilon_{Fc} - \varepsilon_{Fv} = qV$ , equation (4.43) is now rewritten as

$$T_a \dot{S}_{\text{irr}} = -\dot{W} + (\dot{E}_s - T_a \dot{S}_s) - (\dot{E}_r - T_a \dot{S}_r) \quad (4.44)$$

Here, this equation has been derived from the *local* model. However, it can also be obtained with more generality from a classical formulation of the second law of thermodynamics [32]. It is valid for ideal as well as for non-ideal devices. The values of the thermodynamic variables to be used in equation (4.44) are given in Table 4.1. Power – which in other cases will be that of the converter under study – corresponds in this case to the power of an SQ ideal solar cell and is given by the product of equations (4.18) and (4.19).

We have already discussed the basic ambiguity for the thermodynamic description of any radiation concerning the choice of the temperature and the chemical potential. A useful corollary is derived from this fact [32]. If the power rate produced by a radiation converter depends on the radiation only through its rate of incident energy or number of photons, then any radiation received or emitted by the converter can be changed into a luminescent radiation at room temperature,  $T_a$ , and with chemical potential,  $\mu_x$ , without affecting the rate of power and of irreversible entropy produced. The chemical potential  $\mu_x$  of this equivalent luminescent radiation is linked to the thermodynamic parameters of the original radiation,  $T_{\text{rad}}$  and  $\mu_{\text{rad}}$ , through the equation

$$\frac{\varepsilon - \mu_{\text{rad}}}{kT_{\text{rad}}} = \frac{\varepsilon - \mu_x}{kT_a} \Rightarrow \mu_x = \varepsilon \left( 1 - \frac{T_a}{T_{\text{rad}}} \right) + \mu_{\text{rad}} \frac{T_a}{T_{\text{rad}}} \quad (4.45)$$

Note that, in general,  $\mu_x$  is a function of the photon energy,  $\varepsilon$ , as it may also be  $T_{\text{rad}}$  and  $\mu_{\text{rad}}$ .