third-generation cells [3] – aimed towards obtaining a higher efficiency. The oldest of them, and well established today, is the use of multijunction solar cells, to be studied in detail in Chapter 9 of this book. However, novel attempts are favoured by the general advancement of science and technology that puts new tools in the inventor's hands, such as nanotechnology, not available just a decade ago.

Conventional solar cells are semiconductor devices in which an interaction between electrons and holes is produced by absorption of light photons in order to produce electric work. Unlike solar thermal converters, they can operate at room temperature.[1] In this chapter we shall start by presenting some of the irreversible thermodynamic background regarding the photon–electron interaction. Special attention is paid to the conditions for complying with the second law of the thermodynamics as a guide for new device inventors.

This thermodynamic approach will give us the efficiency that a certain solar converter can obtain under certain ideal conditions. This will be applied not only to the present solar cells but also to a number of proposed new converters, some of them actually tried experimentally and some not.

The solar converter theory developed in this chapter looks very different from the one presented in Chapter 3 and is complementary to it. There the solar cell will be analysed in a solid-state physics context, on the basis of electric carrier transport and recombination, taking into account the subtleties that a given material may impose. In this chapter all materials will be considered ideal, entropy-producing mechanisms will be reduced to those inherent to the concept being studied and all other mechanisms will be ignored. In this way, the efficiencies given in this chapter are to be considered as upper bounds of the solar cells studied both in Chapter 3 and the remaining chapters of this book. The lower values found there are not necessarily due to poor technology. They may be fundamental when linked to the actual materials and processes used to manufacture real solar cells. However, they are not fundamental in the sense that other materials and processes could, in principle, be found where different materials or process limitations will apply, which perhaps might be less restrictive.

4.2 THERMODYNAMIC BACKGROUND

4.2.1 Basic Relationships

Thermodynamics defines a state function for a system in equilibrium. This function can be the entropy, the internal energy, the canonical grand potential, the enthalpy and so on, all of them mutually equivalent, containing the same information of the system and related to each other through the Legendre's transformation [4]. The variables used to describe the macroscopic state of a system are divided into *extensive* (volume U, number of particles N, entropy S, internal energy E, etc.) and *intensive* (pressure P, electrochemical potential μ, temperature T, etc.) variables. A number of relationships may be written with them. For instance,

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}U + \mu\,\mathrm{d}N \tag{4.1}$$

[1] Solar cells usually operate at some 40 to 60°C, but there is nothing theoretical against improving cooling to reach a cell temperature as close to the ambient one as desired.