Chapter 1

Scope

The aim of this book is to present the essence of non-equilibrium thermodynamics for engineers. The field was established in 1931 and developed during the forties and fifties for transport in homogeneous phases. Applications of the theory are now increasing. Some perspectives on the applications are given after a brief introduction.

Non-equilibrium thermodynamics describes transport processes in systems that are not in global equilibrium. The field resulted from efforts of many scientists to find a more explicit formulation of the second law of thermodynamics. This started already in 1856 with Thomson's studies of thermoelectricity, see [1]. Onsager is, however, counted as the founder of the field with his papers from 1931 [2, 3], see also [4], because these put earlier research by Thomson, Boltzmann, Nernst, Duhem, Jauman and Einstein into a systematic framework. Onsager was given the Nobel prize in chemistry in 1968 for this work.

The second law is reformulated in terms of the entropy production σ. In Onsager's formulation, the entropy production is given by the product sum of so-called conjugate fluxes, J_i, and forces, X_i, in the system. The second law then becomes

$$\sigma = \sum_i J_i X_i \geq 0 \tag{1.1}$$

where σ is larger than or equal to zero. Each flux is taken to be a linear combination of all forces,

$$J_i = \sum_j L_{ij} X_j \tag{1.2}$$

and the reciprocal relations

$$L_{ji} = L_{ij} \tag{1.3}$$

apply. They now bear Onsager's name.

In order to use the theory, one first has to identify a complete set of extensive *independent* variables, α_i. The resulting conjugate fluxes and forces are $J_i = d\alpha_i/dt$ and $X_i = (\partial S/\partial \alpha_i)_{\alpha_{j \neq i}}$, respectively. Here t is the time and S is the entropy of the system. The three equations above contain then all information on the non-equilibrium behavior of the system.

Following Onsager, a consistent theory of non-equilibrium processes in continuous systems was set up in the forties by Meixner [5–8] and Prigogine [9]. They calculated the entropy production for a number of physical problems. Prigogine received the Nobel price for his work on dissipative structures in systems that are not in equilibrium in 1977, and Mitchell the year after for his application of the driving force concept to transport processes in biology [10].

The most general description of non-equilibrium thermodynamics is still the 1962 monograph of de Groot and Mazur [11] reprinted in 1985 [12]. Haase's book [13] also reprinted [14], contains many results for electrochemical systems and systems with temperature gradients. Katchalsky and Curran developed the theory for biophysical systems [15]. Their analysis was carried further by Caplan and Essig [16]. Førland and coworkers gave various applications in electrochemistry and biology, and they treated frost heave [17,18]. Their book presented the theory in a way suitable for chemists. Newer books on equilibrium thermodynamics or statistical thermodynamics often include chapters on non-equilibrium thermodynamics, see e.g. [19]. In 1998, Kondepudi and Prigogine [20] presented an integrated approach of basic equilibrium and non-equilibrium thermodynamics. Jou et al. [21] published the second edition of their book on extended non-equilibrium thermodynamics and Öttinger gave a non-equilibrium description of the nonlinear regime [22].

Non-equilibrium thermodynamics is constantly being applied in new contexts. Fitts gave an early presentation of viscous phenomena [23]. Kuiken [24] has written the most general treatment of multicomponent diffusion and rheology of colloidal systems. Rubi and coworkers [25–27] used the internal molecular degrees of freedom to explore the development within a system. We are now able to deal with chemical reactions within the framework of non-equilibrium thermodynamics [12] and shall do so in Chapter 7. Bedeaux and Mazur [28] extended the theory to quantum mechanical systems. Kjelstrup and Bedeaux [29] wrote a book dealing with transports into and across surfaces. All these efforts broaden the scope of the theory.

Chemical and mechanical engineering needs theories of transport in systems with gradients in pressure, concentration, and temperature, see Denbigh [30, 31]. In isotropic systems there is no coupling between tensorial (viscous) and vectorial (diffusional) phenomena, so the two classes can usually be dealt with separately [12]. We concentrate on isotropic systems here.

Simple vectorial transport laws have long worked well in engineering, but there is now an increased effort to be more precise. The need for more accurate flux equations in modeling [32] increases the need for non-equilibrium thermodynamics. The books by Taylor and Krishna [32], Cussler [33] and Demirel [34], which present Maxwell-Stefan's formulation of the flux equations, are important books in this context. Krishna and Wesselingh [35] and Kuiken [24] have shown that the coefficients in the Maxwell-Stefan equations are relatively well-behaved, by analyzing an impressive amount of experimental data.

Non-equilibrium thermodynamics is necessary for a precise description of all systems that exchange heat, mass and charge. There is a need in mechanical and chemical engineering to design systems that waste less work [36–38]. Fossil energy sources, as long as they last, lead to waste that may harm the environment. Better and more efficient use of energy resources is therefore central. It is then not good enough to only optimize the first law efficiency. The second law has to be taken into account. The entropy production σ can be seen as a measure for the non-sustainability of a technical process. Through non-equilibrium thermodynamics, one can develop methods to improve the second law efficiency. One purpose of the book is to present such methods.

The process industry may, in a not too distant future, have to give annual reports not only on the products that they produce, but also on their annual lost exergy or entropy production. Some energy companies are making an effort in this direction already. The public sector can enhance this development, by giving benefits to those who limit their entropy production, or increase their energy efficiency. And the engineering community can develop tools to accomplish the task. The present book should be seen in this context. Efforts in other fields, like control theory [39], are also made. This book as well as the references cited above, gives instruments that are needed to understand the nature of the entropy production and can therefore help to avoid it.

We give in Chapter 2 the *characteristics of non-equilibrium thermodynamics* and explain why it is an important field. In Chapter 3, we show how to derive *the entropy production* for systems with diffusion and conduction. The derivations follow de Groot and Mazur [12] and Førland, Førland and Kjelstrup [18]. Chapter 4 presents examples of *flux equations* for coupled transport of heat, mass and charge. Chapter 6 deals with shear flow and 7 with chemical reactions. Examples are used to show how the different processes are coupled. In Chapter 8 we estimate the lost work in an industrial process, the Hall-Heroult process for aluminum electrolysis. The entropy production by charge transfer and by heat transfer are both large. In Chapter 9, we describe a method to minimize the entropy production in process equipment. The method is described in detail for ideal gas expansion and energy efficient heat exchange in this Chapter. Its application to chemical reactors and distillation columns is illustrated in Chapter 10.