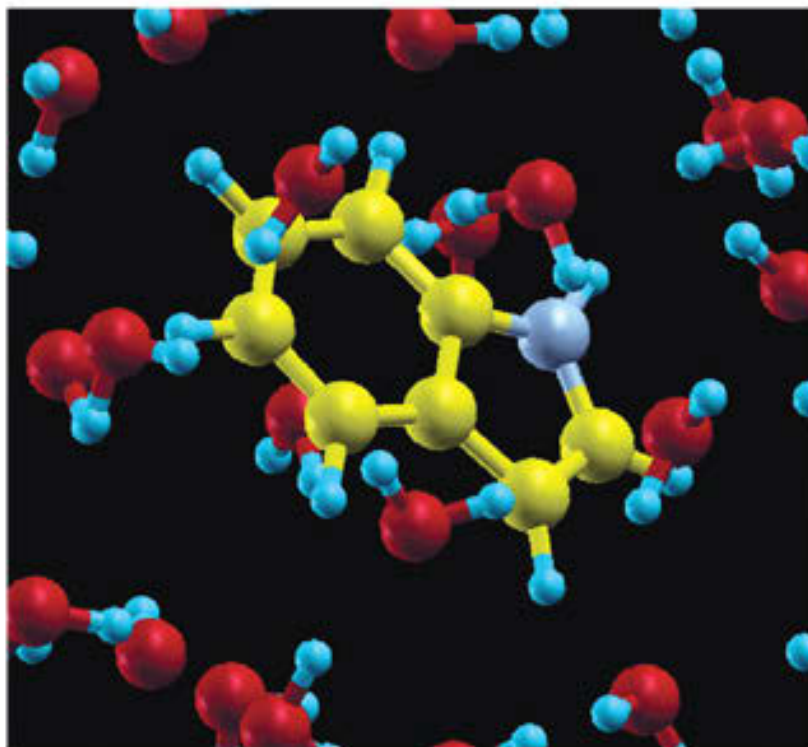


THE SCIENCE AND CULTURE SERIES — PHYSICS

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Proceedings of the 43rd Course of the
International School of Solid State Physics

EPIOPTICS-10



Editor
Antonio Cricenti

EPIOPTICS-10

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PREFACE

This special volume contains the Proceedings of the 10th Epioptics Workshop, held at the Ettore Majorana Foundation and Centre for Scientific Culture, Erice, Sicily, from June 19 to 26, 2008. This was the 10th Workshop in the Epioptics series and the 43rd of the International School of Solid State Physics. Antonio Cricenti from CNR Istituto di Struttura della Materia and Theo Rasing from the University of Nijmegen, were the Directors of the Workshop. The Advisory Committee of the Workshop included Y. Borensztein from U. Paris VII (F), R. Del Sole from U. Roma II Tor Vergata (I), D. Aspnes from NCSU (USA), O. Hunderi from U. Trondheim (N), J. McGilp from Trinity College Dublin (Eire), W. Richter from TU Berlin (D), N. Tolk from Vanderbilt University (USA), and P. Weightman from Liverpool University (UK). Fifty scientists from sixteen countries attended the Workshop.

The Workshop brought together researchers from universities and research institutes who work in the fields of (semiconductor) surface science, epitaxial growth, materials deposition and optical diagnostics relevant to (semiconductor) materials and structures of interest for present and anticipated (spin) electronic devices. The Workshop was aimed at assessing the capabilities of state-of-the-art optical techniques in elucidating the fundamental electronic and structural properties of semiconductor and metal surfaces, interfaces, thin layers, and layer structures, and assessing the usefulness of these techniques for optimization of high quality multilayer samples through feedback control during materials growth and processing. Particular emphasis was dedicated to the theory of non-linear optics and to dynamical processes through the use of pump-probe techniques together with the search for new optical sources. Some new applications of Scanning Probe Microscopy to Material science and biological samples, dried and in vivo, with the use of different laser sources were also presented. Materials of particular interest were silicon, semiconductor-metal interfaces, semiconductor and magnetic multi-layers and III-V compound semiconductors. As well as the notes collected in this Volume, the Workshop

combined tutorial aspects proper to a School with some of the most advanced topics in the field, which better characterized the Workshop.

I wish to thank Prof. A. Zichichi, President of the Ettore Majorana Foundation and Centre for Scientific Culture (EMFCSC), the Italian National Research Council (CNR) and the Sicilian Regional Government. I wish to thank Prof. G. Benedek, Director of the International School of Solid State Physics of the EMFCSC. Our thanks are also due to the Director for Administration and Organizational Affairs, Ms. F. Ruggiu and all the staff of the Centre for their excellent work.

Antonio Cricenti

Preface

To meet the entropy challenge, is probably more central than the issue of provision of sufficient power to the world. The entropy production, not the energy used, can measure our wastes and the efficiency of work, or the limit of our activity. This book introduces non-equilibrium thermodynamics to engineers, and discusses how the theory can be useful for typical engineering problems.

The book has been written on the basis of many years of teaching at the Norwegian University of Science and Technology, Trondheim, Norway, and the Technical University of Delft, Delft, The Netherlands. Early versions of the book have been used at short courses at the International Center of Thermodynamics, Istanbul, Chalmers Technical University, Gothenburg, Helsinki Technical University and Pennsylvania State University.

It can be used in the Bachelor or Master study programs after a basic course in thermodynamics, or for self study in the industry. The book requires knowledge of basic thermodynamics corresponding to that given by Smith, van Ness and Abbott, Introduction to chemical engineering, or Moran and Shapiro, Fundamentals of Engineering Thermodynamics.

To facilitate learning, exercises for the topics of the book and

solutions to these, are available on the NTNU homepage.¹ Eight DVD lectures are likewise available there or from The Technical University of Delft.²

Financial support from the Research Council of Norway is acknowledged. The authors are grateful to Statoil ASA for the cover picture from Mongstad.

The authors welcome comments and suggestions that can improve future editions.

Trondheim and Stuttgart, March 2010

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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

$$\sigma = \sum_i J_i X_i \geq 0 \quad (1.1)$$

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

$$J_i = \sum_j L_{ij} X_j \quad (1.2)$$

and the reciprocal relations

$$L_{ji} = L_{ij} \quad (1.3)$$

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 Weselingh [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 F rland, F rland 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.

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Chapter 2

Why non-equilibrium thermodynamics?

This chapter explains in more detail what non-equilibrium thermodynamics is, and how it adds to engineering fields.

The most common industrial and living systems are those that transport heat, mass, charge, and volume, in the presence or absence of a chemical reaction. The process industry, the electrochemical industry, biological systems, as well as laboratory experiments; all are systems that are out of equilibrium. Equilibrium thermodynamics is then not sufficient. There are six main reasons why non-equilibrium thermodynamics theory [12, 13, 18, 29] is needed. The theory

- gives an accurate description of coupled transport processes.
- gives the same systematic basis to all transport processes.
- can be used to define experiments.

- quantifies produced entropy, lost work or lost exergy.
- gives an entropy balance to use in thermodynamic modeling.
- can be used to optimize the energy efficiency.

These statements will be illustrated briefly in this Chapter, and more in-depth in the rest of the book.

The design of systems which waste less energy, is becoming increasingly more important [37]. We show in the end of this Chapter how entropy production of an industrial plant is related to the lost work in the plant. Non-equilibrium thermodynamics is the only theory that can be used to assess in detail the second law efficiency, or how valuable (energy) resources are exploited. It is the aim of this book to contribute especially to this issue. Chapter 10 develops rules for energy efficient designs in engineering practice.

2.1 Simple flux equations

Accurate expressions for the fluxes are required in engineering. In order to see immediately what non-equilibrium thermodynamics can add to the modeling of real systems, we compare simple flux equations to flux equations given by non-equilibrium thermodynamics in the following two sections.

The simplest descriptions of heat-, mass-, charge- and volume transport are the equations of Fourier, Fick, Ohm, Darcy and Newton. Fourier's law expresses the measurable heat flux in terms of the temperature gradient by:

$$J'_q = -\lambda \frac{dT}{dx} \quad (2.1)$$

where λ is the thermal conductivity, T is the absolute temperature, and x is the direction of transport. Fick's law gives the

mass flux of one of the components in terms of the gradient of its molar concentration c :

$$J = -D \frac{dc}{dx} \quad (2.2)$$

where D is the diffusion coefficient. Ohm's law gives the electric current in terms of the gradient of the electric potential:

$$j = -\kappa \frac{d\phi}{dx} \quad (2.3)$$

where κ is the electrical conductivity, and ϕ is the electric potential. Darcy's law says that the volume flow J_v in a tube is proportional to the pressure gradient dp/dx via the coefficient L_p :

$$J_v = -L_p \frac{dp}{dx} \quad (2.4)$$

And, a laminar flow in the x -direction with velocity $\mathbf{v} = (v_x, 0, 0)$ and velocity component $v_x = v_x(y)$ obeys Newton's law of friction:

$$\Pi_{xy} = -\eta \frac{\partial v_x}{\partial y} \quad (2.5)$$

where Π_{xy} is the viscous pressure tensor, and the proportionality constant, η , is the shear viscosity.

The fluxes in Eqs. (2.1)-(2.5) are all caused by one gradient, or one driving force (see next Section). Fick's law, for instance, says that there is no mass flux if there is no concentration gradient. We know from experiments that a temperature gradient and an electric potential gradient also can give rise to a mass flux. To neglect such effects can have severe consequences. When used at interfaces, such assumptions can even be in conflict with the laws of thermodynamics [29, 40].

Non-equilibrium thermodynamics generalizes equations (2.1)-(2.5) by taking all driving forces into account. The theory gives

a common basis to all simple transport equations, and show how they are connected. The basis is the second law of thermodynamics as expressed through (1.1)-(1.3). This means that the hydrodynamics of viscous fluids, the theory of diffusion, heat conduction, and chemical reaction, all have a common systematic basis [12]. One purpose of the book is to give this.

Exercise 2.1.1 *In a stationary state there is no accumulation of internal energy, mass or charge. This means that the heat, molar, and electric fluxes are independent of position. The derivative of the above equations with respect to x are then zero. For the first equation, we have:*

$$\frac{d}{dx} \lambda \frac{dT}{dx} = 0 \quad (2.6)$$

Equations like these can be used to calculate the temperature, concentration, electric potential and pressure as a function of the position, when their values on the boundaries of the system and λ , D , κ , L_p and η are known.

Calculate the temperature as a function of position between two walls separated by 10 cm. The walls are kept at constant temperature, 5 and 25 °C, respectively. Assume that the thermal conductivity is constant.

- **Solution:** According to Eq. (2.6) $d^2T/dx^2 = 0$. The general solution of this equation is $T(x) = a + bx$. The constants a and b follow from the boundary condition. We have $T(0) = 278$ K and $T(10) = 298$ K. It follows that $T(x) = (278 + 2x/\text{cm})$ K.

2.2 Flux equations in non-equilibrium thermodynamics

Many natural and man-made processes are not adequately described by the simple flux equations given above. There are, for instance, always large fluxes of mass and heat that accompany charge transport in batteries and electrolysis cells. The resulting local cooling in electrolysis cells may lead to unwanted freezing of electrolyte. Electrical energy is frequently used to transport mass in biological systems. Large temperature gradients across space ships have been used to supply electric power to the ships. Salt concentration differences between river water and sea water can be used to generate electric power. Pure water can be generated from salt water by application of pressure gradients. In all these more or less randomly chosen examples, one needs transport equations that describe coupling between various fluxes. The flux equations (2.1)-(2.5) become then too simple.

Non-equilibrium thermodynamics prescribes coupling among fluxes. Coupling means that transport of mass will take place in a system, not only when the gradient in the chemical potential is different from zero, but also when there are gradients in temperature or electric potential. Coupling between fluxes describes precisely the phenomena mentioned above.

For example, in a bulk system with transport of heat, mass, and electric charge, we shall learn in Chapters 3 and 4 that the linear relations for the fluxes (2.1)-(2.3) take the form

$$J'_q = L_{qq} \frac{d}{dx} \left(\frac{1}{T} \right) + L_{q\mu} \left(-\frac{1}{T} \frac{d\mu_T}{dx} \right) + L_{q\phi} \left(-\frac{1}{T} \frac{d\phi}{dx} \right) \quad (2.7)$$

$$J = L_{\mu q} \frac{d}{dx} \left(\frac{1}{T} \right) + L_{\mu\mu} \left(-\frac{1}{T} \frac{d\mu_T}{dx} \right) + L_{\mu\phi} \left(-\frac{1}{T} \frac{d\phi}{dx} \right) \quad (2.8)$$



$$j = L_{\phi q} \frac{d}{dx} \left(\frac{1}{T} \right) + L_{\phi \mu} \left(-\frac{1}{T} \frac{d\mu_T}{dx} \right) + L_{\phi \phi} \left(-\frac{1}{T} \frac{d\phi}{dx} \right) \quad (2.9)$$

The forces of transport conjugate to the fluxes J'_q , J and j are the thermal force $d(1/T)/dx$, the chemical force $[-(1/T)(d\mu_T/dx)]$, and the electrical force $[-(1/T)(d\phi/dx)]$, respectively. The subscript T of the chemical potential, μ_T , indicates that the derivative should be taken keeping the temperature constant. We return to this point in Section 3.2.

The L -coefficients are so-called phenomenological coefficients, or Onsager coefficients, as we shall call them. They must be measured. The Onsager coefficients on the diagonal of the matrix can be related to λ , D , and κ . They are called *main coefficients*. The off-diagonal L -coefficients describe the coupling between the fluxes. They are called *coupling coefficients*. Another common name is cross coefficients. According to Onsager, we have here three reciprocal relations or *Onsager relations* for the coupling coefficients:

$$L_{\mu q} = L_{q\mu}, \quad L_{q\phi} = L_{\phi q}, \quad L_{\phi\mu} = L_{\mu\phi} \quad (2.10)$$

The Onsager relations simplify the system. They reduce the number of independent coefficients from nine to six. Coupling coefficients are small in some cases but large in others. We shall see that large coupling coefficients lead to a small entropy production. If it is difficult to measure L_{ij} , we can rather measure L_{ji} . To measure both, gives a good control.

We shall see in Chapters 3, 6 and 7 how the conjugate forces can be found in a systematic manner. In Chapter 4 we shall learn how to write equations like the ones above. The importance of some coupling coefficients will be discussed. The exercise below show that knowledge of non-equilibrium thermodynamics is useful for interpreting experiments.

Exercise 2.2.1 Find the electric current in terms of the electric field $E = -d\phi/dx$, using Eqs. (2.7)-(2.9), in a system where there is no transport of heat and mass, $J'_q = 0$, $J = 0$.

Solution: It follows from Eqs. (2.7) and (2.8) that

$$\frac{L_{qq}}{T} \frac{dT}{dx} + L_{q\mu} \frac{d\mu_T}{dx} = L_{q\phi} E \quad \text{and} \quad \frac{L_{\mu q}}{T} \frac{dT}{dx} + L_{\mu\mu} \frac{d\mu_T}{dx} = L_{\mu\phi} E$$

Solving these equations, using the Onsager relations, one finds

$$\frac{1}{T} \frac{dT}{dx} = \frac{L_{q\phi} L_{\mu\mu} - L_{\mu\phi} L_{q\mu}}{L_{qq} L_{\mu\mu} - L_{q\mu}^2} E \quad \text{and} \quad \frac{d\mu_T}{dx} = \frac{L_{qq} L_{\mu\phi} - L_{\mu q} L_{q\phi}}{L_{qq} L_{\mu\mu} - L_{q\mu}^2} E$$

Substitution into Eq. (2.9) then gives

$$j = \frac{E}{T} \left[L_{\phi\phi} - L_{\phi q} \frac{L_{q\phi} L_{\mu\mu} - L_{\mu\phi} L_{q\mu}}{L_{qq} L_{\mu\mu} - L_{q\mu}^2} - L_{\phi\mu} \frac{L_{qq} L_{\mu\phi} - L_{\mu q} L_{q\phi}}{L_{qq} L_{\mu\mu} - L_{q\mu}^2} \right]$$

The exercise shows that the electric conductivity that is normally measured, as the ratio of measured values of j and E , is not given by $L_{\phi\phi}/T$ as one might have thought considering Eq. (2.9). The coupling coefficients lead to temperature and chemical potential gradients, which affect the electric current. The measured electric conductivity is the combination of the conductivity of a pure homogeneous conductor, found at zero chemical potential gradient and temperature gradients, minus additional terms. The combination of coefficients is an *effective* conductivity, or stationary state conductivity.

2.3 The lost work of an industrial plant

We shall see here why a second law analysis is important for the process industry. The industrial plant is a system, in which the materials undergo transformations. Materials are taken in and

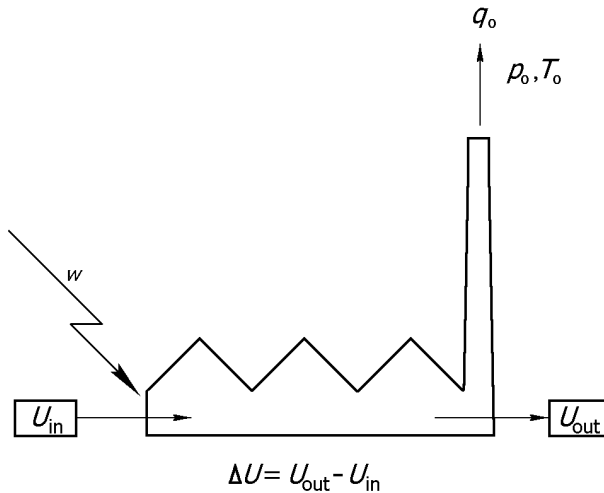


Figure 2.1: A schematic illustration of thermodynamic variables that are essential for the lost work in an industrial plant.

are leaving the plant at the conditions of the environment, see Fig. 2.1.

The environment is therefore the reference state for the thermodynamic analysis. It has constant pressure, p_0 (1 bar) and constant temperature, T_0 (for instance 298 K). We consider changes that take place during the time interval Δt . The first law of thermodynamics gives the change in internal energy of the process $\Delta U = U_{out} - U_{in}$:

$$\Delta U = q - p_0 \Delta V + w \quad (2.11)$$

Here q is the heat delivered to the materials. The total work delivered to the system is decomposed in two parts; with $-p_0 \Delta V$ as the work done on the system by volume expansion, ΔV , against the pressure of the environment, p_0 , and w as the additional work done on the materials.

We consider first processes for which work is needed, so that $w > 0$. The minimum work needed to perform a process, was defined as the least amount of energy that must be supplied, when at the conclusion of the process, the only parts which have undergone any change are the process materials and the environment [30]. To see that this is so, we first replace q by the heat delivered to the environment, $q_0 = -q$:

$$\Delta U = -q_0 - p_0 \Delta V + w \quad (2.12)$$

In the classical formulation of the second law, we have

$$\Delta S + \Delta S_0 \geq 0 \quad (2.13)$$

where ΔS is the entropy change of the process materials and ΔS_0 is the entropy change in the environment. The total entropy change is positive. For a completely reversible process the sum of the entropy changes is zero. For an irreversible process, the sum can be used to define the average total entropy production, dS_{irr}/dt , in the time interval Δt of a stationary process, as

$$\left(\frac{dS_{\text{irr}}}{dt} \right) \Delta t \equiv \Delta S + \Delta S_0 \quad (2.14)$$

Assuming always that the environment behaves reversibly, the entropy change in the surroundings is $\Delta S_0 = q_0/T_0$. By introducing q_0 into the expression for the entropy production, and combining the result with the first law, we obtain

$$w = T_0 \left(\frac{dS_{\text{irr}}}{dt} \right) \Delta t + \Delta U + p_0 \Delta V - T_0 \Delta S \quad (2.15)$$

The left hand side of this equation is the work that is needed to accomplish the process with a particular value of the entropy production, (dS_{irr}/dt) . Since $(dS_{\text{irr}}/dt) \geq 0$, the *least* work requirement is

$$w_{\text{ideal}} = \Delta U + p_0 \Delta V - T_0 \Delta S \equiv E \quad (2.16)$$



This is the work requirement for a completely reversible process. The equation defines the *exergy*, E , of the material [37,41]. The exergy of the environment at p_0, T_0 (the reference state) is set to zero. We see that exergy analysis uses the classical formulation of the second law. It calculates the ideal work and the lost work (see below) from values at the system boundaries. Another word for exergy is availability [42]. It is an important supplement to non-equilibrium thermodynamics.

For processes that produce work, w and w_{ideal} are negative as defined above. Correspondingly, the signs of $\Delta U, \Delta V$, and ΔS are such that the system can perform work. The ideal work w_{ideal} is minus the maximum work that can be obtained in the time interval Δt . This is the work performed by the system if the process is completely reversible. By comparing Eqs. (2.15) and (2.16), we see that $T_0 (dS_{\text{irr}}/dt) \Delta t$ is the additional quantity of work that must be used in the actual process, compared to the work in an ideal reversible process. Thus $T_0 (dS_{\text{irr}}/dt) \Delta t$ is the so-called non-compensated heat of Clausius. By comparing Eqs. (2.15) and (2.16), we see that $T_0 (dS_{\text{irr}}/dt) \Delta t$ is the work that is lost in the actual process, compared to the available work produced in an ideal (reversible) process. So, the lost work relative to the surroundings is:

$$w_{\text{lost}} = w - w_{\text{ideal}} = T_0 \left(\frac{dS_{\text{irr}}}{dt} \right) \Delta t \quad (2.17)$$

This is the Gouy-Stodola theorem [43]. Equations (2.16, 2.17) are central in the field that bears the name exergy analysis. In exergy analysis, the lost work is calculated from knowledge of w and w_{ideal} in Eq. (2.17).

In non-equilibrium thermodynamics we calculate the lost work from the entropy production. The entropy production is found by integrating the local entropy production, σ , over the

volume of the system

$$\frac{dS_{\text{irr}}}{dt} = \int \sigma dV \quad (2.18)$$

Non-equilibrium thermodynamics provide an explicit expression for σ of Eq. (1.1) from Eq. (1.2). The local resolution of dS_{irr}/dt in terms of σ is beyond the scope of exergy analysis, where only a balance around the outside of a process (unit) is conducted. The explicit expression of σ can be used to understand the origin of the entropy production or the lost work. At stationary state, the entropy production in a volume element is equal to the entropy flow into the surroundings of the element, see Section 2.5, and Chapter 3, Eq. (3.1). In Chapters 9 and 10 we show how the local resolution of irreversibilities can be used to optimize process units, by minimization of the entropy production.

Exercise 2.3.1 *A cylinder of a combustion engine contains 600 cm³ of air at a pressure of 10 bar and a temperature of 1200 K, just before the exhaust valve opens (before the expansion starts). Determine the maximum available work (the exergy) of the air. Assume that air consists of ideal gases. The molar weight of air is $M_{\text{air}} = 28$ g/mol. The temperature and pressure of the surroundings are $T_0 = 300$ K, $p_0 = 1$ bar.*

- **Solution:** The maximum available work per kg of gas is

$$\begin{aligned} |w_{\text{ideal}}| &= u(T, p) - u(T_0, p_0) + p_0 [v(T, p) - v(T_0, p_0)] \\ &\quad - T_0 [s(T, p) - s(T_0, p_0)] \end{aligned}$$

where the subscript 0 refers to values of the internal energy, the specific volume and the entropy of the air in the engine at the temperature and pressure of the surroundings. The thermodynamic functions were tabulated, see for instance

Table A.1, Table A.2, Table A.3

Moran and Shapiro [44]

$$\begin{aligned}
 u(T, p) - u(T_0, p_0) &= 719.3 \text{ kJ/kg} \\
 T_0 [s(T, p) - s(T_0, p_0)] &= \\
 T_0 \left[s(T, p_0) - s(T_0, p_0) + \frac{R}{M_{\text{air}}} \ln \frac{p_0}{p} \right] &= 237.9 \text{ kJ/kg} \\
 p_0 [v(T, p) - v(T_0, p_0)] &= \frac{R}{M_{\text{air}}} \left(\frac{T}{p} - \frac{T_0}{p_0} \right) = -53.5 \text{ kJ/kg}
 \end{aligned}$$

This results in

$$|w_{\text{ideal}}| = 427.9 \text{ kJ/kg}$$

for the maximum available work. Most of this work is normally not converted into useful work. The lost work is often significant in processes with chemical reactions, cf. Chapter 7.

Exercise 2.3.2 *A heat reservoir has a temperature-independent heat capacity at constant volume C_V . The temperature of the environment is $T_0 = 300 \text{ K}$. Determine the maximum available work (the exergy) of the heat reservoir when it has temperatures $T = 400, 4000$ and 40000 K . The volume of the reservoir is constant, $V = V_0$.*

- **Solution:** The maximum available work is

$$|w_{\text{ideal}}| = U(T, V_0) - U(T_0, V_0) - T_0 [S(T, V_0) - S(T_0, V_0)]$$

We have:

$$U(T, V_0) - U(T_0, V_0) = C_V (T - T_0)$$

and

$$S(T, V_0) - S(T_0, V_0) = C_V \ln \left(\frac{T}{T_0} \right)$$



This results in

$$|w_{\text{ideal}}| = C_V \left[(T - T_0) - T_0 \ln \left(\frac{T}{T_0} \right) \right]$$

for the maximum available work. By introducing $T = 400$, 4000 and 40000 K and $T_0 = 300$ K, $|w_{\text{ideal}}| = 13.7$ K C_V , 2923 K C_V and 38232 K C_V where C_V has unit J, respectively. The entropy contribution becomes negligible for $(T - T_0) \gg T_0$. The relative contribution of the entropy to the ideal work is larger, the lower is the temperature. We can thus expect larger losses of work at temperatures around T_0 .

2.4 The second law efficiency

In a work consuming process $w > w_{\text{ideal}}$, see Section 2.3. The second law efficiency is then:

$$\eta_{II} \equiv \frac{w_{\text{ideal}}}{w} = 1 - \frac{w_{\text{lost}}}{w} \quad (2.19)$$

This efficiency is also called the thermodynamic efficiency or the exergy efficiency. It includes w_{lost} . In a work producing process $w < w_{\text{ideal}}$ and

$$\eta_{II} \equiv \frac{|w|}{|w_{\text{ideal}}|} = 1 - \frac{w_{\text{lost}}}{|w_{\text{ideal}}|} \quad (2.20)$$

The exergy destruction coefficient is $\xi \equiv 1 - \eta_{II}$. The definitions of η_{II} in work (exergy) consuming or producing processes have values that vary between zero and one. An ideal reversible machine has $\eta_{II} = 1$, while a real machine has normally an efficiency far from one. A fuel cell, which is considered to be rather efficient, has typically $\eta_{II} = 0.6$. The efficiency refers to an unattainable reversible limit. An alternative practical limit is therefore proposed in Section 9.2; the state of minimum entropy production [45].

The Carnot-process played an important role in the definition of the entropy by Clausius. The process starts with a volume of gas at pressure p_A and temperature T_h . The system, in contact with a hot thermal reservoir with temperature T_h , is expanded isothermally to a pressure p_B . Subsequently it is expanded adiabatically ($q_{BC} = 0$) until it has the temperature T_c of a cold thermal reservoir. The pressure has then been changed to p_C . The next step is to compress the system in contact with the cold reservoir at constant temperature to a pressure p_D . Finally, the system is compressed adiabatically ($q_{DA} = 0$) to the original pressure p_A and temperature T_h . The system has now returned to its original state, but an amount of heat q_{AB} has been taken from the hot bath and converted into work w_{ideal} and heat $|q_{CD}|$ added to the cold bath.

In the reversible cycle of the Carnot process, the entropy production is zero, and the second law efficiency is unity. Stirling machines are examples of nearly reversible machines.

The first law efficiency [46] of a process is defined as

$$\eta_I = \frac{w}{q} \quad (2.21)$$

where q is the heat added to the process. For the Carnot process, this efficiency depends only on the temperatures of the two reservoirs

$$\eta_I \equiv \frac{w_{\text{ideal}}}{q_{AB}} = \frac{q_{AB} + q_{CD}}{q_{AB}} = \frac{T_h - T_c}{T_h} \quad (2.22)$$

where T_h and T_c are the temperatures of the hot and cold reservoirs, respectively. The first law efficiency is only close to unity if $T_h \gg T_c$.

In a combustion process, the heat available for work is the enthalpy of reaction, giving $q = \Delta_r H$ and $w = \eta_I \Delta_r H$. This is no measure of how well the machine operates in terms of frictional

and other losses. Such information can only be obtained from the second law efficiency, which measures how far the system is from reversible operation.

Exercise 2.4.1 *A saline power plant produces electric power from the mixing of sea water and river water to brackish water, at one bar and temperature $T_0 = 300$ K. One way to do this is by reverse electrodialysis, see Fig.4.3. Discuss the second law efficiency of this plant.*

- **Solution:** The ideal electric work obtainable from an electrochemical cell is given by Nernst's equation $w_{\text{ideal}} = FE = -\Delta G$ [46]. Here ΔG is the Gibbs energy difference of the mixing process, E is the ideal cell potential and F is Faraday's constant. We refer to one faraday of electrons transferred. The cell delivers in reality a smaller voltage, E' , due to its resistance and the concentration gradients inside the cell. The difference between E and E' is the lost work. The second law efficiency is

$$\eta_{II} = \frac{E'}{E}$$

The enthalpy of mixing ΔH is negligibly small for the mixing process. The ratio $-\Delta G/\Delta H$ obtained from η_I is therefore clearly not a good measure of the plant's performance.

2.5 Consistent thermodynamic models

We refer to a thermodynamic model as a set of thermodynamic and transport relations (equation of state, system variables etc., and flux-force equations) that are needed to solve the balance equations of the system. General balance equations are given in the Appendix A.1.

Non-equilibrium thermodynamics offers possibilities to test the model for consistency. We mentioned a first test in Section 2.2. Two independent experiments can be done to find the coefficients L_{ij} and L_{ji} . According to Onsager, these should be identical.

A second possibility is to use the entropy balance to evaluate the consistency of the thermodynamic model. The local entropy production can be calculated from Eq. (1.1) using the flux equations, Eq. (1.2), or alternatively, from the entropy balance 2.24. By integrating the local entropy production, σ , we obtain the total value:

$$\frac{dS_{\text{irr}}}{dt} = \int \sigma dV \quad (2.23)$$

At stationary state, we also have from Eq.(3.1):

$$\frac{dS_{\text{irr}}}{dt} = - (J_s^i - J_s^o) \Omega \quad (2.24)$$

where J_s^i is the entropy flux into the volume, J_s^o the entropy flux out of the volume and Ω is the surface area through which the fluxes enter or leave the volume. The entropy balance is a governing equation. Examples of entropy balances are given for heat exchangers, chemical reactors and distillation columns in Tables 9.1 and 10.3.

While dS_{irr}/dt depends on L_{ij} and the local values of the thermodynamic variables, the entropy fluxes J_s^i and J_s^o can be calculated without knowledge of L_{ij} . When the entropy production from Eq. (2.24) agrees with the one found from Eq. (2.23), the model is consistent with the second law of thermodynamics.

Through such analyses one may reveal inconsistencies in assumptions that are made, either in thermodynamic relations or in choice of parameters [47, 48]. Verification of assumptions is essential for model improvements. Examples of consistency controls are given in Chapter 9 and 10, Exercises 9.3.1 and 10.1.1.

Chapter 3

The entropy production of one-dimensional transport processes

We derive the entropy production for a volume element of a homogeneous phase where diffusion, conduction, and chemical reaction can take place along the x -axis. The system is in mechanical equilibrium. Equivalent pairs of conjugate fluxes and forces are derived.

The second law of thermodynamics, Eq. (2.13), says that the entropy change of a system plus its surroundings is positive for irreversible processes and zero for reversible processes. This formulation of the law gives the direction of a process; it does not give its rate. Non-equilibrium thermodynamics assumes that the Gibbs equation remains valid locally. We shall see that the second law, as expressed by Eq. (1.1), results from Gibbs equation. Rates of processes as introduced through Eq. (1.2) will then have a thermodynamic basis.

In this Chapter we shall consider systems where the transport processes are one-dimensional. They take place in the x -direction only. Such systems are essential in many industrial applications, where diffusion, conduction and chemical reaction take place.

The change in the entropy in a volume element is the result of a flow of entropy into and out of a volume element, and of the entropy production inside. The rate of change in the local entropy density is

$$\frac{\partial s}{\partial t} = -\frac{\partial}{\partial x} J_s + \sigma \quad (3.1)$$

where s is the entropy density per unit of volume, J_s is the entropy flux and σ the entropy production per unit of volume. By integrating Eq. (3.1) for stationary state conditions, we obtain Eq. (2.24). We shall now find an explicit expression for σ by combining:

- mass balances,
- the first law of thermodynamics,
- the local form of Gibbs' equation.

We shall see that σ can be written as the sum of the products of thermodynamic forces and fluxes in the system. These are the so-called *conjugate* fluxes and forces. The fluxes are used in subsequent Chapters to describe transports. The importance of σ for determination and minimization of lost work, see Eq. (2.17), shall be dealt with in Chapters 8, 9 and 10.

Consider a volume element between x and $x + dx$ of a container with an electroneutral homogeneous phase, see Fig. 3.1. The volume element does not move with respect to the walls of the container. It has a sufficient number of particles to give a statistical basis for thermodynamic calculations. We assume local equilibrium in the element. Its state is given by the temperature

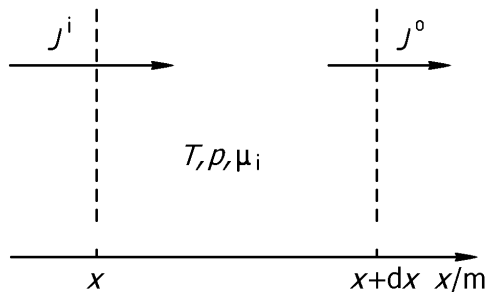


Figure 3.1: A volume element of a homogeneous phase with transport along the x -axis. J^i and J^o indicate fluxes that enter and leave the element. The element is in local equilibrium. indicates one of the fluxes.

$T(x)$, the pressure $p(x)$, and the chemical potentials $\mu_i(x)$. The system is in mechanical equilibrium. This means that the system has no acceleration. The pressure in a homogeneous phase is then constant.

The assumption of local equilibrium is basic to irreversible thermodynamics. It has been tested using non-equilibrium molecular dynamics and found valid for very large temperature gradients [49]. Our aim is to find σ in Eq. (3.1). The symbol list in the front of the book gives the dimensions in the equations that follow.

3.1 Balance equations

The balance equations for the components of the system in the volume element are

$$\frac{\partial c_j}{\partial t} = -\frac{\partial}{\partial x} J_j + \nu_j r \quad \text{for} \quad j = 1, \dots, n \quad (3.2)$$

where J_j are the component fluxes, all directed along the x -axis, ν_j are the stoichiometric constants in a chemical reaction, r is

its rate in the volume element. The reaction Gibbs energy¹ is

$$\Delta_r G = \sum_j \nu_j \mu_j \quad (3.3)$$

Exercise 3.1.1 *Derive Eq. (3.1) by considering changes in a fixed volume element.*

- **Solution:** The change of entropy is equal to the entropy flux into the volume element minus the flux out of the volume element, plus the increase in the entropy production. One has therefore

$$\frac{dS}{dt} = -\Omega[J_s(x+dx) - J_s(x)] + V\sigma$$

By using again that the cross section is equal to the volume divided by dx , we obtain in the limit of small dx

$$\frac{dS}{dt} = -V \frac{[J_s(x+dx) - J_s(x)]}{dx} + V\sigma = -V \frac{dJ_s(x)}{dx} + V\sigma$$

By dividing this equation left and right by the volume, one obtains Eq. (3.1).

The conservation equation for charge is

$$\frac{\partial z}{\partial t} = -\frac{\partial j}{\partial x} \quad (3.4)$$

where z is the charge density. The systems that we consider, can all be described as electroneutral. It follows that $\partial j / \partial x = 0$ so that the electric current, j , is constant throughout the system.

¹The driving force of the chemical reaction was called the affinity, A , by De Donder, with $A = -\Delta_r G$, see e.g. [21].

According to the first law of thermodynamics, the change in internal energy is the net heat plus the work added to the system. For a change in the internal energy density $u = U/V$ per unit of time, we have for a volume element:

$$\frac{\partial u}{\partial t} = -\frac{\partial}{\partial x} J_q + E j \quad (3.5)$$

where J_q is the energy flux. In most of the cases in the book we shall use the definition

$$J_q = J'_q + \sum_{j=1}^n H_j J_j \quad (3.6)$$

The energy flux is here the sum of the measurable heat flux $J'_q(x)$ and the enthalpy flux carried by the component fluxes, J_j , where H_j are the partial molar enthalpies. This definition has lead to the name “total heat flux” which we shall use for this quantity throughout the book. For other definitions, see Appendix A.1.

The product Ej in Eq. (3.5) is the electric power added to the volume element. The electric field is often replaced by minus the gradient of the electric potential:

$$E = -\frac{\partial \phi}{\partial x} \quad (3.7)$$

The first law is illustrated in Fig. 3.2. Appendix A.1 gives a discussion of the relation between Eq. (3.5), the first law and the definition of the total heat flux.

3.2 Entropy production

The balance equations shall be combined with the Gibbs equation

$$dU = TdS - pdV + \sum_{j=1}^n \mu_j dN_j \quad (3.8)$$

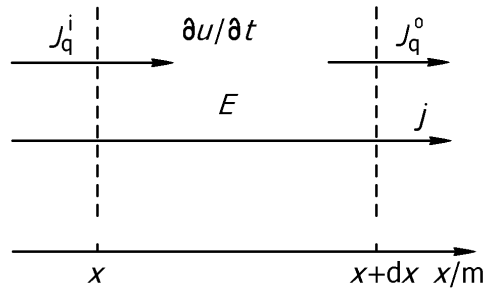


Figure 3.2: The internal energy change of a volume element with fluxes of total heat and charge across the boundaries.

in order to find σ . We replace the internal energy, U , entropy, S and the mole numbers, N_j , by densities of the same variables, $u = U/V$, $s = S/V$ and $c_j = N_j/V$. By using also the fundamental relation $U = TS - pV + \sum_j \mu_j N_j$, we obtain the local form of Gibbs' equation

$$du = Tds + \sum_{j=1}^n \mu_j dc_j \quad (3.9)$$

with μ_j as the chemical potential. The time derivative of the local entropy density is therefore

$$\frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \frac{1}{T} \sum_{j=1}^n \mu_j \frac{\partial c_j}{\partial t} \quad (3.10)$$

The use of partial derivatives indicates that the variables are also position dependent. By introducing the balance equations, Eqs. (3.2) and (3.5) into (3.10), using the rule for derivation of products, and solving for $\partial s/\partial t$, we obtain the balance equation

for the entropy

$$\begin{aligned} \frac{\partial s}{\partial t} = & -\frac{\partial}{\partial x} \left[\frac{1}{T} \left(J_q - \sum_{j=1}^n \mu_j J_j \right) \right] \\ & + J_q \frac{\partial}{\partial x} \left(\frac{1}{T} \right) + \sum_{j=1}^n J_j \frac{\partial}{\partial x} \left(-\frac{\mu_j}{T} \right) + j \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right) + r \left(-\frac{\Delta_r G}{T} \right) \end{aligned} \quad (3.11)$$

By comparing the above equations with the original Eq. (3.1), we can identify the entropy flux in the system

$$J_s = \frac{1}{T} \left(J_q - \sum_{j=1}^n \mu_j J_j \right) = \frac{1}{T} J'_q + \sum_{j=1}^n S_j J_j \quad (3.12)$$

and the entropy production

$$\sigma = J_q \left(\frac{\partial}{\partial x} \frac{1}{T} \right) + \sum_{j=1}^n J_j \left(-\frac{\partial}{\partial x} \frac{\mu_j}{T} \right) + j \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right) + r \left(-\frac{\Delta_r G}{T} \right) \quad (3.13)$$

By replacing the total heat flux, J_q , by the entropy flux, J_s , we obtain an alternative expression

$$\sigma = J_s \left(-\frac{1}{T} \frac{\partial T}{\partial x} \right) + \sum_{j=1}^n J_j \left(-\frac{1}{T} \frac{\partial \mu_j}{\partial x} \right) + j \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right) + r \left(-\frac{\Delta_r G}{T} \right) \quad (3.14)$$

We finally replace the total heat flux, J_q , by the more practical measurable heat flux, J'_q , by introducing Eq. (3.6) into Eq. (3.13). The result is yet an alternative expression:

$$\sigma = J'_q \left(\frac{\partial}{\partial x} \frac{1}{T} \right) + \sum_{j=1}^n J_j \left(-\frac{1}{T} \frac{\partial \mu_{j,T}}{\partial x} \right) + j \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right) + r \left(-\frac{\Delta_r G}{T} \right) \quad (3.15)$$

where $\partial \mu_{j,T} / \partial x = \partial H_i / \partial x - T \partial S_i / \partial x$. The result was derived for electroneutral, homogeneous phases, without any other assumption than that of local equilibrium. Local equilibrium does not imply local *chemical* equilibrium!

Remark 3.1 Equation (3.15) shall be the starting point for further considerations in this book.

Remark 3.2 Equation (3.15) was derived from the Gibbs equation and the balance equations and is valid whenever these equations are valid.

Remark 3.3 The difference between the total heat flux and the measurable heat flux can be illustrated by an example. Consider a liquid and its vapor in a box. A constant heat flux, J_q^l , is supplied to the liquid through the bottom of the box. A heat flux J_q^g is removed from the top of the vapor phase. From Eqs. (3.6) and (3.5) the energy flux is

$$J_q = J_q'^l + H_1^l J_1^l = J_q'^g + H_1^g J_1^g$$

In the stationary state, $J_1^l = J_1^g = J$, so

$$J_q'^l - J_q'^g = (H_1^g - H_1^l)J$$

The measurable heat fluxes in the liquid and the gas differ because of the source term at the interface. The total heat flux is constant. It cannot be measured in either of the phases, however, because H_1^g and H_1^l are not absolute.

The entropy production contains pairs of fluxes and forces. We call the corresponding pairs *conjugate fluxes and forces*. In Eq. (3.15) the measurable heat flux J_q' has the conjugate force $\partial(1/T)/\partial x$, the mass flux J_j has the conjugate force $-\partial\mu_{j,T}/T\partial x$, the electric current density j has the conjugate force $-\partial\phi/T\partial x$ and the reaction rate r has the conjugate force $-\Delta_r G/T$. The conjugate flux-force pairs in Eqs. (3.13), (3.14) and (3.15) are different. All these different choices are equivalent, however, and describe the same physical phenomena.

All force-flux pairs, except the last one, have a direction and are thus vectors. The reaction has a scalar flux-force pair, r and $-\Delta_r G/T$. We are dealing with one-dimensional problems in this Chapter and all vectorial fluxes and forces are directed along the x -axis. A divergence of a flux reduces to the derivative of the x -component with respect to x . A gradient is similarly directed along the x -direction, and is given by the derivative of a potential or a temperature with respect to x . As it is known that, for instance a heat flux or an electric field, is vectorial, we do not complicate the notation further by making this distinction explicit.

Introduction of different fluxes, or changing the frame of reference, does not change the value or the physical interpretation of σ . The entropy production is an absolute quantity, as is the entropy. The preference for one of the expressions for a particular system, is always motivated by the system itself. We can illustrate this by an example: If the system is such that the chemical potentials of all components are constant, Eq. (3.14) is appropriate. In that expression the second term, containing the sum over j , is zero. One can of course also use the other two forms of the entropy production and simplify them using the constant nature of the chemical potentials. It is then easy to verify that the first and the second term combine and reduce to the first term in Eq. (3.14). Thus it is the properties of the system that determine which form of the entropy production is useful. We will use the last one, Eq. (3.15) when we describe experiments. The three alternative expressions are given as a help to find the appropriate form quickly.

The separate products do not necessarily represent pure losses of work (cf. Section 2.3). For instance, the electric power per unit of volume, $-(j\partial\phi/\partial x)$, does not necessarily give only an ohmic contribution to the entropy production, there may also be electric work included in the product, as we shall see in detail

in Section 4.4. Each of the separate products normally contains work terms, and energy storage terms, see [18]. It is *their combination* which gives the entropy production and the work that is lost locally, $T_0 \sigma$. The temperature of the surroundings T_0 enter the formula for the lost work.

Dependent variables should be eliminated from σ . This simplifies the flux equations, and makes their solution easier. Such a simplification is one motivation for using electroneutral components in Eq. (3.2). Mass variables of this kind lead to straightforward reductions of Eq. (3.13). For instance, when the electric current density is zero, the electric power term disappears. The entropy production due to the chemical reaction disappears when the reaction rate vanishes, $r = 0$, or when the chemical reaction is in equilibrium, $\Delta_r G = 0$. Local chemical equilibrium introduces a relation between the remaining forces in the system. To see this, consider a reaction with $\Delta_r G = 0$. We can express the chemical potential μ_D of component D by the other chemical potentials contained in $\Delta_r G$. This can lead to a redefinition of the independent molar fluxes of the system. Gibbs-Duhem's equation (see also Exercise A.2.1 in Appendix A.2)

$$dp = s dT + \sum_{j=1}^n c_j d\mu_j \quad (3.16)$$

gives a further possibility for elimination of one of the chemical forces, $-(1/T)\partial\mu_j/\partial x$.

According to Prigogine's theorem [9] the expressions for σ , Eqs. (3.13)-(3.15), are valid in any frame of reference, which has a constant velocity v with respect to the laboratory frame of reference, provided that the system is in mechanical equilibrium. The mass fluxes change from J_j in the laboratory frame to $J_j - c_j v$ in a frame of reference with a constant velocity v , and the entropy flux changes from $J_s - sv$. The expression for the measurable heat flux remains the same. The transformation

formula for the energy and entropy fluxes follow from those of the mass and measurable heat fluxes. We consider only systems that are in mechanical equilibrium, so Prigogine's theorem is applicable. A discussion and proof of the theorem was given by de Groot and Mazur [12], see also Chapter 6.

Haase [14] defined the dissipation function in non-equilibrium thermodynamics, analogous to the Rayleigh dissipation function for hydrodynamic flow, by $\Psi = T\sigma$. The integral over this function may be called D . An integration with $T > T_0$, gives $w_{lost} < D$. The lost work was defined unambiguously in Chapter 2. It follows for cases with $T > T_0$, that parts of D can be extracted to do work. This means that D is ambiguous and leads to potentially incorrect results, when it comes to analysis of efficiencies in industrial processes. We shall avoid using Ψ for this reason (see also [29] Section 4.2.1).

3.3 Examples

The exercises below illustrate in more detail how the contributions to the entropy production arise. The exercises 3.3.1-3.3.5 are meant to illustrate the theory. Exercises 3.3.6, 3.3.7 give numerical insight and 3.3.8, 3.3.9 give physical insight.

Exercise 3.3.1 *Consider the special case that only component number j is transported. The densities of the other components, the internal energy, the molar volume and the polarization densities are all constant. Show that the entropy production is given by*

$$\sigma = -J_j \frac{\partial}{\partial x} \left(\frac{\mu_j}{T} \right)$$

- **Solution:** In this case the Gibbs equation, Eq. (3.10), reduces to

$$T \frac{\partial s}{\partial t} + \mu_j \frac{\partial c_j}{\partial t} = 0$$

The rate of change of the entropy is therefore given by

$$\frac{\partial s}{\partial t} = -\frac{\mu_j}{T} \frac{\partial c_j}{\partial t}$$

We use the balance equation for component j , Eq. (3.2), and obtain

$$\frac{\partial s}{\partial t} = \frac{\mu_j}{T} \frac{\partial}{\partial x} J_j = \frac{\partial}{\partial x} \left(\frac{\mu_j}{T} J_j \right) - J_j \frac{\partial}{\partial x} \frac{\mu_j}{T}$$

By comparing this equation with the entropy balance, Eq. (3.1), we may identify the entropy flux and the entropy production as

$$J_s = -\frac{\mu_j}{T} J_j \text{ and } \sigma = -J_j \frac{\partial}{\partial x} \left(\frac{\mu_j}{T} \right)$$

Exercise 3.3.2 *Consider the case that only heat is transported. The molar densities, the molar volume and the polarization densities are all constant. Show that the entropy production is given by*

$$\sigma = J'_q \frac{\partial}{\partial x} \left(\frac{1}{T} \right)$$

- **Solution:** In this case the Gibbs equation, Eq. (3.10), reduces to

$$\frac{\partial u}{\partial t} = T \frac{\partial s}{\partial t}$$

The rate of change of the entropy is therefore given by

$$\frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t}$$

The energy balance Eq. (3.5) reduces to

$$\frac{\partial u}{\partial t} = -\frac{\partial}{\partial x} J'_q$$

By substituting this into the equation above, we obtain

$$\frac{\partial s}{\partial t} = -\frac{1}{T} \frac{\partial}{\partial x} J'_q = -\frac{\partial}{\partial x} \left(\frac{1}{T} J'_q \right) + J'_q \frac{\partial}{\partial x} \left(\frac{1}{T} \right)$$

By comparing this equation with the entropy balance, Eq. (3.1), we can identify the entropy flux and the entropy production as

$$J_s = \frac{1}{T} J'_q \quad \text{and} \quad \sigma = J'_q \frac{\partial}{\partial x} \left(\frac{1}{T} \right)$$

Exercise 3.3.3 Consider a system with two components ($n = 2$), having $dT = 0$ and $dp = 0$. Show, using Gibbs-Duhem's equation, that one may reduce the description in terms of two components to one with only one component.

- **Solution:** Gibbs-Duhem's equation (3.16) gives

$$c_1 d\mu_{1,T} + c_2 d\mu_{2,T} = 0$$

The entropy production in Eq. (3.15) reduces for these conditions to

$$\sigma = -\frac{1}{T} \left(J_1 - \frac{c_1}{c_2} J_2 \right) \frac{\partial \mu_{1,T}}{\partial x}$$

The equation contains only one (independent) force. Energy is lost by interdiffusion of the two components. We can also write this entropy production as

$$\sigma = J_V \left(-\frac{c_1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right)$$

with $J_V \equiv J_1/c_1 - J_2/c_2$. This is the volumetric velocity flux of component 1 relative to the velocity, J_2/c_2 , of component 2. Note that J_V is independent of the frame of reference.

Exercise 3.3.4 Show how the chemical force in Eq. (3.15) can be derived from Eq. (3.13).

- **Solution:** The chemical force in Eq. (3.15) can be rewritten as

$$\begin{aligned}\frac{\partial}{\partial x} \left(\frac{\mu_i}{T} \right) &= \frac{1}{T} \frac{\partial}{\partial x} \mu_{i,T} + T S_i \left(\frac{1}{T^2} \frac{\partial T}{\partial x} \right) + \mu_i \frac{\partial \frac{1}{T}}{\partial x} \\ &= \frac{1}{T} \frac{\partial \mu_{i,T}}{\partial x} + H_i \frac{\partial \frac{1}{T}}{\partial x}\end{aligned}$$

By substituting this result into Eq. (3.13), we obtain

$$\begin{aligned}\sigma &= \left[J_q - \sum_{i=1}^n H_i J_i \right] \frac{\partial}{\partial x} \left(\frac{1}{T} \right) + \sum_{i=1}^n J_i \left(-\frac{1}{T} \frac{\partial}{\partial x} \mu_{i,T} \right) \\ &\quad + j \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right)\end{aligned}$$

By using $J_q = J'_q + \sum_{i=1}^n H_i J_i$, Eq. (3.15) follows. The new chemical force is related to the chemical potential by:

$$d\mu_{i,T} = d\mu_i - (\partial \mu_i / \partial T)_{p, \mu_j, j \neq i} dT = d\mu_i + S_i dT$$

Exercise 3.3.5 Derive the entropy production for an isothermal two-component system that does not transport charge. The solvent is the frame of reference for the fluxes.

- **Solution:** In an isothermal system $\partial(1/T)/\partial x = 0$. Furthermore there is no charge transport so that $j = 0$. Finally the solvent is the frame of reference, so $J_{\text{solvent}} = 0$. There remains only one force-flux pair, namely for transport of solute. Using Eq. (3.15) we then find

$$\sigma = -\frac{J}{T} \frac{\partial \mu_T}{\partial x}$$

for the entropy production. Knowing that $\sigma \geq 0$ it follows that the solute will move from a higher to a lower value of its chemical potential.

Exercise 3.3.6 Find the average entropy production due to the heat flux through a sidewalk pavement by a hot plate placed $d = 8$ cm under the pavement. The plate has a temperature of 343 K. The surface is in contact with melting ice (273 K). The Fourier type thermal conductivity of the pavement is 0.7 W/Km.

- Fourier's law for heat conduction is $J'_q = -\lambda(dT/dx)$. The entropy production per surface area is

$$\begin{aligned}\int_0^d \sigma dx &= \int_0^d J'_q \frac{\partial}{\partial x} \left(\frac{1}{T} \right) dx = -\lambda \frac{\Delta T}{d} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ &= -0.7 \frac{(-70)}{(0.08)} \left(\frac{1}{273} - \frac{1}{343} \right) = 0.46 \frac{W}{Km^2}\end{aligned}$$

The lost work $w_{lost} = T_0 \Omega \int_0^d \sigma dx$ per surface area Ω is $w_{lost}/\Omega = 275 \text{ K} \cdot 0.46 \frac{W}{Km^2} = 125 \frac{W}{m^2}$. It is typical for heat conduction around room temperature that the entropy production is large.

Exercise 3.3.7 In order to produce drinking water, one filters water through a 1 m thick sand layer with grain diameters around 0.1 mm. The height of the water column above the sand is $d = 1$ m, and the clean water outlet is at the top of the filter. Evaluate the entropy production for a water flux of $10^{-6} \text{ kg/m}^2 \text{ s}^1$ at 293 K. The density of water is $\rho = 1000 \text{ kg/m}^3$, and the process can be considered to be in mechanical equilibrium.

- The contribution to the chemical potential gradient is from the hydrostatic pressure gradient of the water column. The