

IRREVERSIBLE THERMODYNAMICS

Theory and Applications

K. S. Førland, T. Førland and S. K. Røtjke

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K. S. Fjørland, T. Fjørland and S. K. Ratkje

*The University of Trondheim
The Norwegian Institute of Technology
Department of Chemistry*

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PREFACE

Irreversible thermodynamics is an extension of classical thermodynamics to give a unified method of treating transport processes. It is particularly useful when several interacting transport processes occur simultaneously. Simultaneous transport processes, e.g. transport by diffusion and electric current or the transport of heat coupled to transport of mass or electric charge, are encountered in many fields of science. These are common phenomena in different fields such as electrochemistry, chemical engineering, biochemistry and biophysics, metallurgy and geology.

The book is intended for senior level students, but may also be useful to others who intend to apply the principles of irreversible thermodynamics to their problems. To facilitate understanding, the basic equations are derived in a simple way using a minimum of mathematics. Equations of transport are therefore derived for transport in one direction only. Furthermore, the derivations are first carried out for very simple systems and then extended to more complex cases. In order to develop a physical understanding of the mathematical operations, the quantities used are operationally defined, i.e. experimental determinations of the quantities are described or outlined.

The symbols are in agreement with the IUPAC recommendations and SI units are used. We have made efforts to keep the language simple, avoiding — as far as possible — specialized terminology in the different fields.

In Part I of the book the theoretical fundamentals are developed and related to reality by examples. In Part II the theories are applied to solve some important problems within varied fields of science and technology. The chapters of Part II can be read independently of one another.

Many colleagues from several countries have been helpful to us with suggestions and advice leading to improvements in the text. They are too numerous to be mentioned by name, but we are grateful to them all for the keen interest they have shown. We are also indebted to our students who have scrutinized the manuscript for mistakes and obscurities.

Katrine Seip Førland Tormod Førland Signe Kjelstrup Ratkje

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PART I
Theory



CHAPTER 1

Introduction

Classical thermodynamics deals with the driving forces for reactions and with *equilibrium*. It is well established as one of the pillars of the natural sciences. The theory of equilibrium, however, is limited to systems that can be regarded as isolated from the environment. It is not applicable where there is transport of heat, electricity or matter across the borders of the system. Open systems with transport across the borders are very familiar. The steady influx of energy from the sun to the earth counteracts the formation of equilibrium. Changes and movements are more common than situations of equilibrium where no macroscopic change takes place. *Irreversible thermodynamics* was developed to take care of *non-equilibrium* situations. Irreversible thermodynamics also has its limitations, and the treatment in this book is limited to near-equilibrium situations with *microscopic reversibility*, that is *local equilibrium*, and *linear transport processes*.

It is customary to date the beginning of irreversible thermodynamics back to Thomson's work in 1854 on the thermoelectric effect, interacting transports of heat and electric charge.¹ The consecutive studies of phenomena and development of theory were undertaken by some of the world's most famous scientists: Helmholtz, Boltzmann, Nernst, Einstein, to mention just a few. The papers by Onsager^{2, 3} on *Reciprocal Relations in Irreversible Processes*, Parts I and II, in 1931 constituted an important milestone in the development of the theory. In the following decades the theory was further developed, and the assumptions behind the theory were scrutinized. Some leading names in these studies are Meixner, Prigogine, and de Groot and Mazur.

The main objective of irreversible thermodynamics is to describe completely and quantitatively interacting transport processes.

Simpler problems of interacting transports can be treated without the use of irreversible thermodynamics, but the unifying theory is an important tool for organizing more complex problems. Irreversible thermodynamics gives the set of equations needed to deal with simultaneous transport processes in a systematic way. The conditions of a system often imply relations that can reduce the number of parameters needed to describe the process. The systematics of irreversible thermodynamics helps to analyse these relations. Thus the number of independent experiments needed to study the system can be reduced. Alternatively a consistency check can be made by determining the same quantity by different methods.

The theory of irreversible thermodynamics is well suited for the study of transports in electrolyte systems (see Chapter 4). It adapts itself to electrolyte solutions and to fused salts. The theory is almost indispensable for transport processes through membranes (see Chapter 5). The use of the theory for studying biological phenomena is steadily increasing. With the increasing use of membranes in technological processes, the characterization of transport parameters and their interrelation is of interest. Transport of heat coupled to transport of matter and electric charge (Chapter 6) and the influence of gravity on transport phenomena (Chapter 7) are generally better understood by the use of irreversible thermodynamics.

To demonstrate the applicability of irreversible thermodynamics to a variety of practical problems, some examples are given in Chapters 8–11. The reader who works with transport problems may find other applications of the theory.

1.1. *The Dynamic Equilibrium*

The second law of thermodynamics gives the fundamental equilibrium criterion, the sum of all entropy changes for the system and the surroundings is equal to zero, $dS = 0$. For an irreversible process this sum has a positive value, $dS > 0$. The equilibrium state is a *dynamic state*, where the rates of processes in opposite directions are equal. When a system is slightly out of equilibrium, and it approaches equilibrium, processes in opposite directions are taking place continuously. The rate in one direction is slightly higher than the rate in the opposite direction until equilibrium is

attained and the rates become equal. This description is valid both for chemical reactions without any coordinates in space and for directed transport processes.

The transport processes can be illustrated with an example. Consider the electrochemical cell:



The charge carriers in the solid electrolyte are Ag^+ ions moving over interstitial positions. When the cell is open, or the emf of the cell is balanced by an outer emf, there is no net current. With no net current the electric potential over the electrolyte is zero. The charge carriers are still in motion, but an equal number of steps are taken in each direction, and they cancel. The movements of interstitial Ag^+ ions can be pictured as going from one interstitial position to another over an energy barrier, E_a (see Fig. 1.1(a)). No direction is preferred.

Due to vibrations an Ag^+ ion in an interstitial position will have a probability of reaching the top of the barrier proportional to an exponential function, $\exp(-E_a/kT)$, where E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. There is no net transport in any direction. The rate of transport to the right, v_{\rightarrow} , is equal to the rate of transport to the left, v_{\leftarrow} . At equilibrium $v_{\rightarrow} = v_{\leftarrow} = v_0$, where v_0 can be expressed as

$$v_0 = k_1 \exp(-E_a/kT) \quad (1.1)$$

where k_1 is a constant.

Figure 1.1(b) shows the situation when the emf of the cell is not balanced, i.e. a net current passes from left to right. There is now an electric potential, $\Delta\phi$, between adjacent interstitial positions, and the height of the barrier is reduced to $E_a - \frac{1}{2}e\Delta\phi$ for movements to the right, while the barrier is increased to $E_a + \frac{1}{2}e\Delta\phi$ for movements to the left, where e is the charge of an electron. The net rate of movement from left to right is

$$v = v_{\rightarrow} - v_{\leftarrow} = k_1 \exp(-E_a/kT) [\exp(\frac{1}{2}e\Delta\phi/kT) - \exp(-\frac{1}{2}e\Delta\phi/kT)] \quad (1.2)$$

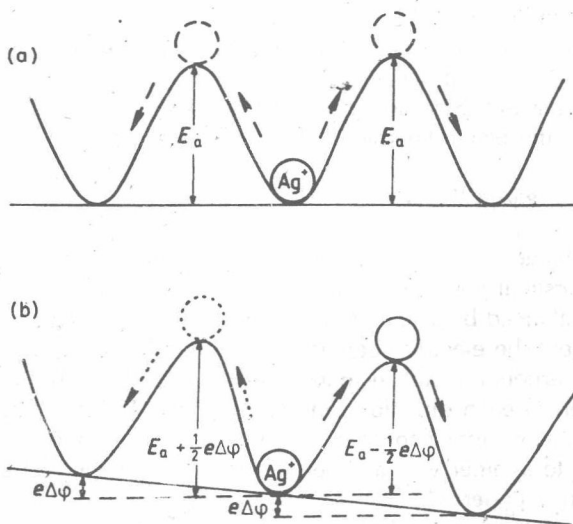


Figure 1.1. Motion of an ion from one position to a neighbouring position over an energy barrier. (a) No electric field. The energy barrier, E_a , is equal in both directions. (b) With an electric field. The energy barrier is decreased by an amount $\frac{1}{2}e\Delta\phi$ in the direction of the field and increased by the same amount in the opposite direction.

1.2 The Linear Range of Transport Processes

Equation (1.2) is an exponential equation, and it does not easily lend itself to treatment by irreversible thermodynamics. For small electric potentials, however, where $\frac{1}{2}e\Delta\phi \ll kT$, the approximation $e^x \approx 1 + x$ can be used; v_0 can also be introduced from eq. (1.1), and from eq. (1.2) a simplified expression is obtained for the net rate of movement:

$$v = v_0 (e/kT)\Delta\phi \quad (1.3)$$

The exponential rate equation is thus reduced to a linear relation between the rate, v , and the force, $\Delta\phi$. The force is expressed as the electrical potential over a distance Δx of molecular dimensions. This may also be expressed as the ratio $\Delta\phi/\Delta x$ or $d\phi/dx$. Forces can be of different kinds. An example is a change in chemical