

Understanding Non-equilibrium Thermodynamics

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Foundations, Applications, Frontiers

 Springer

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Preface

Our time is characterized by an explosion of information and by an acceleration of knowledge. A book cannot compete with the huge amount of data available on the Web. However, to assimilate all this information, it is necessary to structure our knowledge in a useful conceptual framework. The purpose of the present work is to provide such a structure for students and researchers interested by the current state of the art of non-equilibrium thermodynamics. The main features of the book are a concise and critical presentation of the basic ideas, illustrated by a series of examples, selected not only for their pedagogical value but also for the perspectives offered by recent technological advances. This book is aimed at students and researchers in physics, chemistry, engineering, material sciences, and biology.

We have been guided by two apparently antagonistic objectives: generality and simplicity. To make the book accessible to a large audience of non-specialists, we have decided about a simplified but rigorous presentation. Emphasis is put on the underlying physical background without sacrificing mathematical rigour, the several formalisms being illustrated by a list of examples and problems. All over this work, we have been guided by the formula: “Get the more from the less”, with the purpose to make a maximum of people aware of a maximum of knowledge from a minimum of basic tools.

Besides being an introductory text, our objective is to present an overview, as general as possible, of the more recent developments in non-equilibrium thermodynamics, especially beyond the local equilibrium description. This is partially a *terra incognita*, an unknown land, because basic concepts as temperature, entropy, and the validity of the second law become problematic beyond the local equilibrium hypothesis. The answers provided up to now must be considered as partial and provisional, but are nevertheless worth to be examined.

Chapters 1 and 2 are introductory chapters in which the main concepts underlying equilibrium thermodynamics and classical non-equilibrium thermodynamics are stated. The basic notions are discussed with special emphasis on these needed later in this book.

Several applications of classical non-equilibrium thermodynamics are presented in Chaps. 3 and 4. These illustrations have not been chosen arbitrarily, but keeping in mind the perspectives opened by recent technological advancements. For instance, advances in material sciences have led to promising possibilities for thermoelectric devices; localized intense laser heating used to make easier the separation of molecules has contributed to a revival of interest in thermodiffusion; chemical reactions are of special interest in biology, in relation with their coupling with active transport across membranes and recent developments of molecular motors.

The purpose of Chaps. 5 and 6 is to discuss two particular aspects of classical non-equilibrium thermodynamics which have been the subject of active research during the last decades. Chapter 5 is devoted to finite-time thermodynamics whose main concern is the competition between maximum efficiency and maximum power and its impact on economy and ecology. This classical subject is treated here in an updated form, taking into account the last technological possibilities and challenges, as well as some social concerns. Chapter 6 deals with instabilities and pattern formation; organized structures occur in closed and open systems as a consequence of fluctuations growing far from equilibrium under the action of external forces. Patterns are observed in a multitude of our daily life experiences, like in hydrodynamics, biology, chemistry, electricity, material sciences, or geology. After introducing the mathematical theory of stability, several examples of ordered structures are analysed with a special attention to the celebrated Bénard cells.

Chapters 1–6 may provide a self-consistent basis for a graduate introductory course in non-equilibrium thermodynamics.

In the remainder of the book, we go beyond the framework of the classical description and spend some time to address and compare the most recent developments in non-equilibrium thermodynamics. Chapters 7–11 will be of interest for students and researchers, who feel attracted by new scientific projects wherein they may be involved. This second part of the book may provide the basis for an advanced graduate or even postgraduate course on the several trends in contemporary thermodynamics.

The coexistence of several schools in non-equilibrium thermodynamics is a reality; it is not a surprise in view of the complexity of most macroscopic systems and the fact that some basic notions as temperature and entropy are not univocally defined outside equilibrium. To appreciate this form of multiculturalism in a positive sense, it is obviously necessary to know what are the foundations of these theories and to which extent they are related. A superficial inspection reveals that some viewpoints are overlapping but none of them is rigorously equivalent to the other. A detailed and complete understanding of the relationship among the diverse schools turns out to be not an easy task. The first difficulty stems from the fact that each approach is associated with a certain insight, we may even say an intuition or feeling that is sometimes rather difficult to apprehend. Also some unavoidable differences in the terminology and the notation do not facilitate the communication. Another

factor that contributes to the difficulty to reaching a mutual comprehension is that the schools are not frozen in time: they evolve as a consequence of internal dynamics and by contact with others. Our goal is to contribute to a better understanding among the different schools by discussing their main concepts, results, advantages, and limitations. Comparison of different viewpoints may be helpful for a deeper comprehension and a possible synthesis of the many faces of the theory. Such a comparative study is not found in other textbooks.

One problem was the selection of the main representative ones among the wealth of thermodynamic formalisms. Here we have focused our attention on five of them: extended thermodynamics (Chap. 7), theories with internal variables (Chap. 8), rational thermodynamics (Chap. 9), Hamiltonian formulation (Chap. 10), and mesoscopic approaches (Chap. 11). In each of them, we have tried to save the particular spirit of each theory.

It is clear that our choice is subjective: we have nevertheless been guided not only by the pedagogical aspect and/or the impact and universality of the different formalisms, but also by the fact that we had to restrict ourselves. Moreover, it is our belief that a good comprehension of these different versions allows for a better and more understandable comprehension of theories whose opportunity was not offered to be discussed here. The common points shared by the theories presented in Chaps. 7–11 are not only to get rid of the local equilibrium hypothesis, which is the pillar of the classical theory, but also to propose new phenomenological approaches involving non-linearities, memory and non-local effects, with the purpose to account for the technological requirements of faster processes and more miniaturized devices.

It could be surprising that the book is completely devoted to macroscopic and mesoscopic aspects and that microscopic theories have been widely omitted. The reasons are that many excellent treatises have been written on microscopic theories and that we decided to keep the volume of the book to a reasonable ratio. Although statistical mechanics appears to be more fashionable than thermodynamics in the eyes of some people and the developments of microscopic methods are challenging, we hope to convince the reader that macroscopic approaches, like thermodynamics, deserve a careful attention and are the seeds of the progress of knowledge. Notwithstanding, we remain convinced that, within the perspectives of improvement and unification, it is highly desirable to include as many microscopic results as possible into the macroscopic framework.

Chapters 7–11 are autonomous and self-consistent, they have been structured in such a way that they can be read independently of each other and in arbitrary order. However, it is highly recommended to browse through all the chapters to better apprehend the essence and the complementarity of the diverse theories.

At the end of each chapter is given a list of problems. The aim is not only to allow the reader to check his understanding, but also to stimulate his interest to solve concrete situations. Some of these problems have been

inspired by recent papers, which are mentioned, and which may be consulted for further investigation. More technical and advanced parts are confined in boxes and can be omitted during a first reading.

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Chapter 1

Equilibrium Thermodynamics: A Review

Equilibrium States, Reversible Processes, Energy Conversion

Equilibrium or classical thermodynamics deals essentially with the study of macroscopic properties of matter at *equilibrium*. A comprehensive definition of equilibrium will be given later; here it is sufficient to characterize it as a time-independent state, like a column of air at rest in absence of any flux of matter, energy, charge, or momentum. By extension, equilibrium thermodynamics has also been applied to the description of *reversible processes*: they represent a special class of idealized processes considered as a continuum sequence of equilibrium states.

Since time does not appear explicitly in the formalism, it would be more appropriate to call it *thermostatistics* and to reserve the name *thermodynamics* to the study of processes taking place in the course of time outside equilibrium. However, for historical reasons, the name “thermodynamics” is widely utilized nowadays, even when referring to equilibrium situations. We shall here follow the attitude dictated by the majority but, to avoid any confusion, we shall speak about *equilibrium thermodynamics* and designate beyond-equilibrium theories under the name of *non-equilibrium thermodynamics*.

The reader is assumed to be already acquainted with equilibrium thermodynamics but, for the sake of completeness, we briefly recall here the essential concepts needed along this book. This chapter will run as follows. After a short historical introduction and a brief recall of basic definitions, we present the fundamental laws underlying equilibrium thermodynamics. We shall put emphasis on Gibbs’ equation and its consequences. After having established the criteria of stability of equilibrium, a last section, will be devoted to an introduction to chemical thermodynamics.

1.1 The Early History

Equilibrium thermodynamics is the natural extension of the older science, Mechanics. The latter, which rests on Newton’s law, is essentially concerned with the study of motions of idealized systems as mass-particles and rigid

solids. Two important notions, heat and temperature, which are absent in mechanics, constitute the pillars of the establishment of equilibrium thermodynamics as a branch of science. The need to develop a science beyond the abstract approach of Newton's law to cope with the reality of engineer's activities was born in the beginning of nineteenth century. The first steps and concepts of thermodynamics were established by Fourier, Carnot, Kelvin, Clausius, and Gibbs among others. Thermodynamics began in 1822 with Fourier's publication of the *Théorie analytique de la chaleur* wherein is derived the partial differential equation for the temperature distribution in a rigid body. Two years later, in 1824, Sadi Carnot (1796–1832) put down further the foundations of thermodynamics with his renowned memoir *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*. Carnot perceived that steam power was a motor of industrial revolution that would prompt economical and social life. Although a cornerstone in the formulation of thermodynamics, Carnot's work is based on several misconceptions, as for instance the identification of heat with a hypothetical indestructible weightless substance, the caloric, a notion introduced by Lavoisier. Significant progresses towards a better comprehension of the subject can be attributed to a generation of outstanding scientists as James P. Joule (1818–1889) who identified heat as a form of energy transfer by showing experimentally that heat and work are mutually convertible. This was the birth of the concept of energy and the basis of the formulation of the first law of thermodynamics. At the same period, William Thomson (1824–1907), who later matured into Lord Kelvin, realized that the work of Carnot was not contradicting the ideas of Joule. One of his main contributions remains a particular scale of absolute temperature. In his paper "On the dynamical theory of heat" appeared in 1851, Kelvin developed the point of view that the mechanical action of heat could be interpreted by appealing to two laws, later known as the first and second laws. In this respect, Rudolf Clausius (1822–1888), a contemporary of Joule and Kelvin, accomplished substantial advancements. Clausius was the first to introduce the words "internal energy" and "entropy", one of the most subtle notions of thermodynamics. Clausius got definitively rid of the notion of caloric, reformulated Kelvin's statement of the second law, and tried to explain heat in terms of the behaviour of the individual particles composing matter. It was the merit of Carnot, Joule, Kelvin, and Clausius to thrust thermodynamics towards the level of an undisputed scientific discipline. Another generation of scientists was needed to unify this new formalism and to link it with other currents of science. One of them was Ludwig Boltzmann (1844–1906) who put forward a decisive "mechanistic" interpretation of heat transport; his major contribution was to link the behaviour of the particles at the microscopic level to their consequences on the macroscopic level. Another prominent scientist, Josiah Williard Gibbs (1839–1903), deserves the credit to have converted thermodynamics into a deductive science. In fact he recognized soon that thermodynamics of the nineteenth century is a pure static science wherein time does not play any

role. Among his main contributions, let us point out the theory of stability based on the use of the properties of convex (or concave) functions, the potential bearing his name, and the well-known Gibbs' ensembles. Gibbs' paper "On the equilibrium of the heterogeneous substances" ranks among the most decisive impacts in the developments of modern chemical thermodynamics.

Other leading scientists have contributed to the development of equilibrium thermodynamics as a well structured, universal, and undisputed science since the pioneers laid down its first steps. Although the list is far from being exhaustive, let us mention the names of Caratheodory, Cauchy, Clapeyron, Duhem, Einstein, Helmholtz, Maxwell, Nernst, and Planck.

1.2 Scope and Definitions

Equilibrium thermodynamics is a section of macroscopic physics whose original objective is to describe the transformations of energy in all its forms. It is a generalization of mechanics by introducing three new concepts:

1. The concept of *state*, i.e. an ensemble of quantities, called state variables, whose knowledge allows us to identify any property of the system under study. It is desirable that the state variables are independent and easily accessible to experiments. For example, a motionless fluid may be described by its mass m , volume V , and temperature T .
2. The notion of *internal energy*, complementing the notion of kinetic energy, which is of pure mechanical origin. Answering the question "what is internal energy?" is a difficult task. Internal energy is not a directly measurable quantity: there exist no "energymeters". For the moment, let us be rather evasive and say that it is presumed to be some function of the measurable properties of a system like mass, volume, and temperature. Considering a macroscopic system as agglomerate of individual particles, the internal energy can be viewed as the mean value of the sum of the kinetic and interacting energies of the particles. The notion of internal energy is also related to these temperature and heat, which are absent from the vocabulary of mechanics.
3. The notion of *entropy*. Like internal energy, it is a characteristic of the system but we cannot measure it directly, we will merely have a way to measure its changes. From a microscopic point of view, the notion of entropy is related to disorder: the higher the entropy, the larger the disorder inside the system. There are also connections between entropy and information in the sense that entropy can be considered as a measure of our lack of information on the state of the system. The link between entropy and information is widely exploited into the so-called information theory.

Energy and entropy are obeying two major laws: the first law stating that *the energy of the universe is a constant*, and the second law stating that *the entropy of the universe never decreases*.

At this stage, it is useful to recall some definitions. By *system* is understood a portion of matter with a given mass, volume, and surface. An *open system* is able to exchange matter and energy through its boundaries, a *closed system* exchanges energy but not matter with the outside while an *isolated system* does exchange neither energy nor matter with its surroundings. It is admitted that the universe (the union of system and surroundings) acts as an isolated system. In this chapter, we will deal essentially with *homogeneous* systems, whose properties are independent of the position.

As mentioned earlier, the *state* of a system is defined by an ensemble of quantities, called state variables, characterizing the system. Considering a system evolving between two equilibrium states, A and B , it is important to realize that, by definition, the state variables will not depend on the particular way taken to go from A to B . The selection of the state variables is not a trivial task, and both theoretical and experimental observations constitute a suitable guide. It is to a certain extent arbitrary and non-unique, depending on the level of description, either microscopic or macroscopic, and the degree of accuracy that is required. A delicate notion is that of *equilibrium* state which turns out to be a state, which is time independent and generally spatially homogeneous. It is associated with the absence of fluxes of matter and energy. On the contrary, a non-equilibrium state needs for its description time- and space-dependent state variables, because of exchanges of mass and energy between the system and its surroundings. However, the above definition of equilibrium is not complete; as shown in Sect. 1.3.3, equilibrium of an isolated system is characterized by a maximum of entropy. Notice that the concept of equilibrium is to some extent subjective; it is itself an idealization and remains a little bit indefinite because of the presence of fluctuations inherent to each equilibrium state. It depends also widely on the available data and the degree of accuracy of our observations.

One distinguishes *extensive* and *intensive* state variables; extensive variables like mass, volume, and energy have values in a composite system equal to the sum of the values in each subsystem; intensive variables as temperature or chemical potential take the same values everywhere in a system at equilibrium. As a variable like temperature can only be rigorously defined at equilibrium, one may expect difficulties when dealing with situations beyond equilibrium.

Classical thermodynamics is not firmly restricted to equilibrium states but also includes the study of some classes of processes, namely those that may be considered as a sequence of neighbouring equilibrium states. Such processes are called *quasi-static* and are obtained by modifying the state variables very slowly and by a small amount. A quasi-static process is either *reversible* or *irreversible*. A reversible process $1 \rightarrow 2 \rightarrow 3$ may be viewed as a continuum sequence of equilibrium states and will take place infinitesimally slowly. When undergoing a reverse transformation $3 \rightarrow 2 \rightarrow 1$, the state variables take the same values as in the direct way and the exchanges of matter and energy with the outside world are of opposite sign; needless to

say that reversible processes are pure idealizations. An irreversible process is a non-reversible one. It takes place at finite velocity, may be mimicked by a discrete series of equilibrium states and in a reverse transformation, input of external energy from the outside is required to go back to its initial state. Irreversible processes are generally associated with friction, shocks, explosions, chemical reactions, viscous fluid flows, etc.

1.3 The Fundamental Laws

The first law, also popularly known as the law of conservation of energy, was not formulated first but second after the second law, which was recognized first. Paradoxically, the zeroth law was formulated the latest, by Fowler during the 1930s and quoted for the first time in Fowler and Guggenheim's book published in 1939.

1.3.1 The Zeroth Law

It refers to the introduction of the idea of empirical temperature, which is one of the most fundamental concepts of thermodynamics. When a system 1 is put in contact with a system 2 but no net flow of energy occurs, both systems are said to be in thermal equilibrium. As sketched in Fig. 1.1a, we take two systems 1 and 2, characterized by appropriate parameters, separated by an adiabatic wall, but in contact (a thermal contact) with the system 3 through a diathermal wall, which allows for energy transfer in opposition with an adiabatic wall. If the systems 1 and 2 are put in contact (see Fig. 1.1b), they will change the values of their parameters in such a way that they reach a state of thermal equilibrium, in which there is no net heat transfer between them.

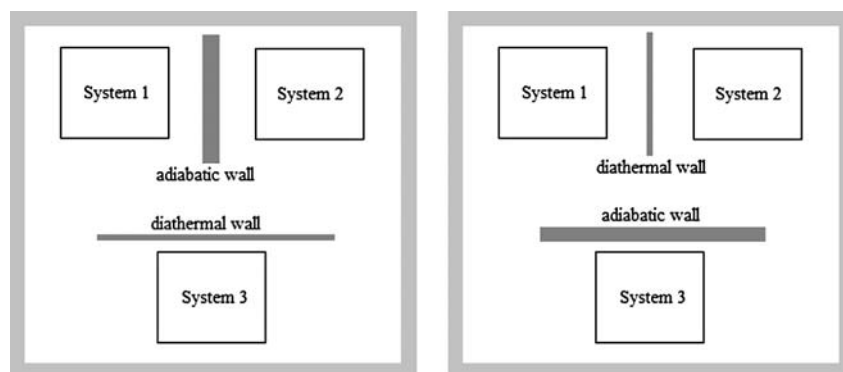


Fig. 1.1 Steps for introducing the empirical temperature concept

The zeroth law of thermodynamics states that *if the systems 1 and 2 are separately in thermal equilibrium with 3, then 1 and 2 are in thermal equilibrium with one another*. The property of transitivity of thermal equilibrium allows one to classify the space of thermodynamic states in classes of equivalence, each of which constituted by states in mutual thermal equilibrium. Every class may be assigned a label, called *empirical temperature*, and the mathematical relation describing a class in terms of its state variables and the empirical temperature is known as *the thermal equation of state* of the system. For one mole of a simple fluid this equation has the general form $\phi(p, V, \theta) = 0$ where p is the pressure, V the volume, and θ the empirical temperature.

1.3.2 The First Law or Energy Balance

The first law introduces the notion of energy, which emerges as a unifying concept, and the notion of heat, related to the transfer of energy. Here, we examine the formulation of the first law for closed systems.

Consider first a system enclosed by a thermally isolated (adiabatic), impermeable wall, so that the sole interaction with the external world will appear under the form of a mechanical work W , for instance by expansion of its volume or by stirring. Referring to the famous experience of Joule, the work can be measured by the decrease in potential energy of a slowly falling weight and is given by $W = mgh$, where h is the displacement and g the acceleration of gravity. During the evolution of the system between the two given equilibrium states A and B , it is checked experimentally that the work W is determined exclusively by the initial and the final states A and B , independently of the transformation paths. This observation allows us to identify W with the difference $\Delta U = U(B) - U(A)$ of a state variable U which will be given the name of *internal energy*

$$W = \Delta U. \quad (1.1)$$

The above result provides a mean to measure the internal energy of a system, whatever be its nature. Assume now that we remove the adiabatic wall enclosing the system, which again proceeds from state A to state B . When this is accomplished, it is observed that in general $W \neq \Delta U$, and calling Q the difference between these two quantities, one obtains

$$\Delta U - W = Q, \quad (1.2)$$

where Q is referred to as the heat exchanged between the system and its surroundings. Expression (1.2) is the first law of thermodynamics and is usually written under the more familiar form

$$\Delta U = Q + W, \quad (1.3a)$$

or, in terms of differentials,

$$dU = \bar{d}Q + \bar{d}W, \quad (1.3b)$$

where the stroke through the symbol “d” means that $\bar{d}Q$ and $\bar{d}W$ are inexact differentials, i.e. that they depend on the path and not only on the initial and final states. From now on, we adopt the sign convention that $Q > 0$, $W > 0$ when heat and work are supplied to the system, $Q < 0$, $W < 0$ when heat and work are delivered by the system. Some authors use other conventions resulting in a minus sign in front of $\bar{d}W$.

It is important to stress that the domain of applicability of the first law is not limited to reversible processes between equilibrium states. The first law remains valid whatever the nature of the process, either reversible or irreversible and the status of the states A and B , either equilibrium or non-equilibrium. Designating by $E = U + K + E_{\text{pot}}$ the total energy of the system (i.e. the sum of the internal U , kinetic K , and potential energy E_{pot}), (1.3b) will be cast in the more general form

$$dE = \bar{d}Q + \bar{d}W. \quad (1.4)$$

At this point, it should be observed that with respect to the law of energy $\Delta K = W$ as known in mechanics, we have introduced two new notions: internal energy U and heat Q . The internal energy can be modified either by heating the body or by acting mechanically, for instance by expansion or compression, or by coupling both mechanisms. The quantity U consists of a stored energy in the body while Q and W represent two different means to transfer energy through its boundaries. The internal energy U is a state function whose variation is completely determined by the knowledge of the initial and final states of the process; in contrast, Q and W are not state functions as they depend on the particular path followed by the process. It would therefore be incorrect to speak about the heat or the work of a system. The difference between heat and work is that the second is associated with a change of the boundaries of the system or of the field acting on it, like a membrane deformation or a piston displacement. Microscopically, mechanical work is related to coherent correlated motions of the particles while heat represents that part of motion, which is uncorrelated, say incoherent.

In equilibrium thermodynamics, the processes are reversible from which follows that the energy balance equation (1.4) will take the form:

$$dU = \bar{d}Q_{\text{rev}} - p dV, \quad (1.5)$$

wherein use is made of the classical result that the reversible work performed by a piston that compresses a gas of volume V and pressure p trapped in a cylinder is given by $\bar{d}W_{\text{rev}} = -p dV$ (see Problem 1.1). In engineering applications, it is customary to work with the enthalpy H defined by $H = U + pV$. In terms of H , expression (1.5) of the first law reads as

$$dH = \bar{d}Q_{\text{rev}} + V dp. \quad (1.6)$$

For an isolated system, one has simply

$$dU = 0 \quad (1.7)$$

expressing that its energy remains constant.

Note that, when applied to *open systems* with n different constituents, (1.5) will contain an additional contribution due to the exchange of matter with the environment and takes the form (Prigogine 1947)

$$dU = d^iQ - p dV + \sum_{k=1}^n h_k d^e m_k; \quad (1.8)$$

note that d^iQ is not the total amount of heat but only that portion associated to the variations of the thermomechanical properties, T and p , and the last term in (1.8), which is the extra contribution caused by the exchange of matter $d^e m_k$ with the surroundings, depends on the specific enthalpy $h_k = H/m_k$ of the various constituents.

1.3.3 The Second Law

The first law does not establish any preferred direction for the evolution of the system. For instance, it does not forbid that heat could pass spontaneously from a body of lower temperature to a body of higher temperature, nor the possibility to convert completely heat into work or that the huge energy contained in oceans can be transformed in available work to propel a boat without consuming fuel. More generally, the first law establishes the equivalence between heat and work but is silent about the restrictions on the transformation of one into the other. The role of the second law of thermodynamics is to place such limitations and to reflect the property that natural processes evolve spontaneously in one direction only. The first formulations of the second law were proposed by Clausius (1850, 1851) and Kelvin (1851) and were stated in terms of the impossibility of some processes to be performed. Clausius' statement of the second law is enunciated as follows: *No process is possible whose sole effect is to transfer heat from a cold body to a hot body.* Kelvin's statement considers another facet: *it is impossible to construct an engine which can take heat from a single reservoir, and convert it entirely to work in a cyclic process.* In this book we will examine in detail, the formulations of the second law out of equilibrium. Here, we shall concentrate on some elements that are essential to a good understanding of the forthcoming chapters. We will split the presentation of the second law in two parts. In the first one, we are going to build-up a formal definition of a new quantity, the entropy – so named by Clausius from the Greek words *en* (in) and *tropē* (turning) for representing “capacity of change or transformation” – which is as fundamental and universal (for equilibrium systems) as the notion of

energy. In the second part, which constitutes truly the essence of the second law, we shall enounce the principle of entropy increase during an irreversible process.

1.3.3.1 The Concept of Entropy

Consider a homogeneous system of constant mass undergoing a reversible transformation between two equilibrium states A and B . The quantity of heat $\int_A^B dQ_{\text{rev}}$ depends on the path followed between states A and B (in mathematical terms, it is an imperfect differential) and therefore cannot be selected as a state variable. However, experimental observations have indicated that by dividing dQ_{rev} by a uniform and continuous function $T(\theta)$ of an empirical temperature θ , one obtains an integral which is independent of the path and may therefore be identified with a state function, called entropy and denoted S

$$\int_A^B \frac{dQ_{\text{rev}}}{T(\theta)} = \Delta S = S_B - S_A. \quad (1.9)$$

Since in reversible processes, quantities of heat are additive, entropy is also additive and is thus an extensive quantity. A function like $T(\theta)$ which transforms an imperfect differential into a perfect one is called an integrating factor. The empirical temperature is that indicated by a mercury or an alcohol thermometer or a thermocouple and its value depends of course on the nature of the thermometer; the same remark is true for the entropy, as it depends on $T(\theta)$. It was the great merit of Kelvin to propose a temperature scale for T , the absolute temperature, independently of any thermodynamic system (see Box 1.1). In differential terms, (1.9) takes the form

$$dS = \frac{dQ_{\text{rev}}}{T}. \quad (1.10)$$

This is a very important result as it introduces two new concepts, absolute temperature and entropy. The latter can be viewed as the quantity of heat exchanged by the system during a reversible process taking place at the equilibrium temperature T . Note that only differences in entropy can be measured. Given two equilibrium states A and B , it is always possible to determine their entropy difference regardless of whether the process between A and B is reversible or irreversible. Indeed, it suffices to select or imagine a reversible path joining these initial and final equilibrium states. The question is how to realize a reversible heat transfer. Practically, the driving force for heat transfer is a temperature difference and for reversible transfer, we need only imagine that this temperature difference is infinitesimally small so that $dQ_{\text{rev}} = \lim_{\Delta T \rightarrow 0} dQ$. Nevertheless, when the process takes place between non-equilibrium states, the problem of the definition of entropy is open, and actually not yet definitively solved.

Box 1.1 Absolute Temperature

Heat engines take heat from some hot reservoir, deliver heat to some cold reservoir, and perform an amount of work, i.e. they partially transform heat into work. Consider a Carnot's reversible engine (see Fig. 1.2a) operating between a single hot reservoir at the unknown empirical temperature θ_1 and a single cold reservoir at temperature θ_2 . The Carnot cycle is accomplished in four steps consisting in two isothermal and two adiabatic transformations (Fig. 1.2b).

During the first isothermal process, the Carnot's engine absorbs an amount of heat Q_1 at temperature θ_1 . In the second step, the system undergoes an adiabatic expansion decreasing the temperature from θ_1 to θ_2 . Afterwards, the system goes through an isothermal compression at temperature θ_2 (step 3) and finally (step 4), an adiabatic compression which brings the system back to its initial state. After one cycle, the engine has performed a quantity of work W but its total variation of entropy is zero

$$\Delta S_{\text{engine}} = \frac{|Q_1|}{T(\theta_1)} - \frac{|Q_2|}{T(\theta_2)} = 0. \quad (1.1.1)$$

Selecting the reference temperature as $T(\theta_2) = 273.16$, the triple point temperature of water, it follows from (1.1.1)

$$T(\theta_1) = 273.16 \frac{|Q_1|}{|Q_2|}. \quad (1.1.2)$$

The ratio $|Q_1|/|Q_2|$ is universal in the sense that it is independent of the working substance. Therefore, Carnot cycles offer the opportunity to reduce temperature measurements to measurements of quantities of heat and to define an absolute scale of positive temperatures, independently of the measurement of temperature on any empirical temperature scale, which depends on thermometric substance.

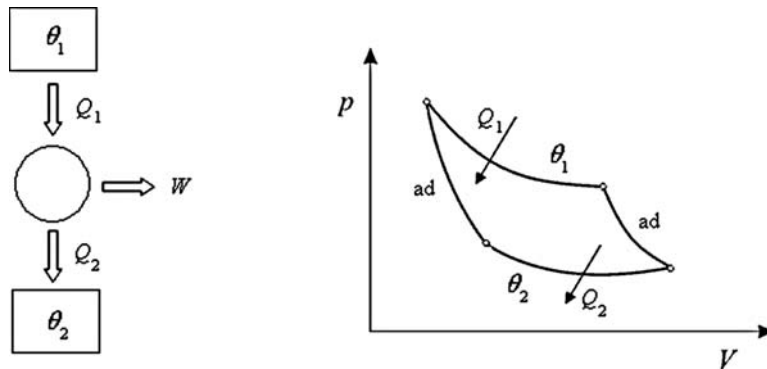


Fig. 1.2 (a) Heat engine and (b) Carnot diagram

The *efficiency* of a heat engine, in particular that of Carnot, is defined by the ratio of the work produced to the heat supplied

$$\eta = \frac{W}{Q_1} \quad (1.11)$$

for a cycle one has, in virtue of the first law, $W = Q_1 - Q_2$, so that

$$\eta = 1 - \frac{Q_2}{Q_1}. \quad (1.12)$$

Finally, making use of (1.1.2), it is found that the efficiency of a reversible cycle is

$$\eta = 1 - \frac{T_2}{T_1}. \quad (1.13)$$

As it will be seen, this is the maximum value for the efficiency of any heat engine working between the selected heat reservoirs. More considerations about the efficiency of reversible and irreversible cycles are developed in Chap. 5.

1.3.3.2 The Principle of Increase of Entropy

The second law was formulated by Clausius (1865) for isolated systems in terms of the change of the entropy in the form

$$\Delta S \geq 0. \quad (1.14)$$

To illustrate the principle of entropy increase, imagine an arbitrary number of subsystems, for instance three different gases A , B , and C at equilibrium, enclosed in a common *isolated* container and separated each other by adiabatic and rigid walls (Fig. 1.3). Let S_{ini} be the entropy in this initial configuration. Remove then the internal wall separating A and B which are diffusing into each other until a new state of equilibrium characterized by an entropy S_{int} , corresponding to the intermediate configuration, which is larger than S_{ini} is reached. By eliminating finally the last internal constraint between $A \cup B$ and C , and after the final state of equilibrium, corresponding to complete mixing, is reached, it is noted that entropy S_{fin} is still increased: $S_{\text{fin}} > S_{\text{int}} > S_{\text{ini}}$. Figure 1.3 reflects also that disorder is increased by passing from the initial

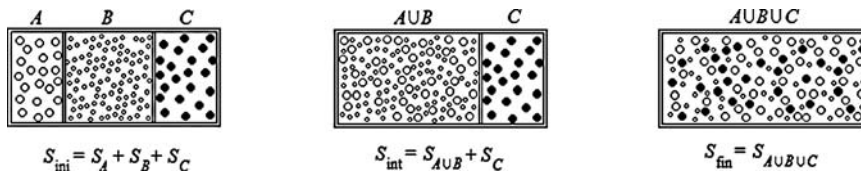


Fig. 1.3 Increase of entropy after removal of internal constraints

to the final configuration, which suggests the use of entropy as a measure of disorder: larger the disorder larger the entropy (Bridgman 1941).

It is therefore concluded that entropy is increased as internal constraints are removed and that entropy reaches a maximum in the final state of equilibrium, i.e. the state of maximum “disorder”. In other terms, in isolated systems, one has

$$\Delta S = S_{\text{fin}} - S_{\text{in}} \geq 0 \quad (\text{isolated system}). \quad (1.15)$$

Thus, entropy is continuously increasing when irreversible processes take place until it reaches a state of maximum value, the equilibrium state, which in mathematical terms is characterized by $dS = 0, d^2S < 0$. This statement constitutes the celebrated principle of entropy increase and is often referred to as the *Second Law* of thermodynamics. It follows that a decrease in entropy $dS < 0$ corresponds to an impossible process. Another consequence is that the entropy of an isolated system remains constant when reversible processes occur in it.

An illustration of the entropy increase principle is found in Box 1.2. When the system is not isolated, as in the case of *closed and open systems*, the entropy change in the system consists in two parts: $d^e S$ due to exchanges of energy and matter with the outside, which may be positive or negative, and $d^i S$ due to internal irreversible processes

$$dS = d^e S + d^i S. \quad (1.16)$$

The second law asserts that the entropy production $d^i S$ can only be greater than or equal to zero

$$d^i S \geq 0 \quad (\text{closed and open systems}), \quad (1.17)$$

the equality sign referring to reversible or equilibrium situations. Expression (1.17) is the statement of the second law in its more general form. In the particular case of isolated systems, there is no exchange of energy and matter so that $d^e S = 0$ and one recovers (1.15) of the second law, namely $dS = d^i S \geq 0$. For closed systems, for which $d^e S = \bar{d}Q/T$, one has

$$dS \geq \bar{d}Q/T \quad (\text{closed system}). \quad (1.18)$$

In the particular case of a cyclic process for which $dS = 0$, one has $\bar{d}Q/T \leq 0$, which is usually identified as the Clausius’ inequality.

Box 1.2 Entropy Increase

Consider two different gases *A* and *B* at equilibrium, enclosed in a common isolated container and separated each other by an adiabatic and fixed wall (Fig. 1.4). Both gases are characterized by their internal energy *U* and volume *V*.

In the initial configuration, entropy $S^{(i)}$ is a function of the initial values of internal energy $U_A^{(i)}$ and volume $V_A^{(i)}$ corresponding to subsystem A , and similarly of $U_B^{(i)}$ and $V_B^{(i)}$ for subsystem B , in such a way that $S^{(i)} = S_A(U_A^{(i)}, V_A^{(i)}) + S_B(U_B^{(i)}, V_B^{(i)})$. If the adiabatic and fixed wall separating both subsystems A and B is replaced by a diathermal and movable wall, a new configuration is attained whose entropy $S^{(f)}$ may be expressed as $S^{(f)} = S_A(U_A^{(f)}, V_A^{(f)}) + S_B(U_B^{(f)}, V_B^{(f)})$; superscript (f) denotes the final values of energy and volume submitted to the closure relations $U_A^{(i)} + U_B^{(i)} = U_A^{(f)} + U_B^{(f)} = U_{\text{total}}$ and $V_A^{(i)} + V_B^{(i)} = V_A^{(f)} + V_B^{(f)} = V_{\text{total}}$ reflecting conservation of these quantities for the composite system $A + B$. The removal of internal constraints that prevent the exchange of internal energy and volume leads to the establishment of a new equilibrium state of entropy $S^{(f)} > S^{(i)}$. The values taken by the (extensive) variables, in the absence of internal constraints, in this case $U_A^{(f)}$, $V_A^{(f)}$ and $U_B^{(f)}$, $V_B^{(f)}$, are those that maximize the entropy over the manifold of equilibrium states (Callen 1985).

In Fig. 1.4 is represented $S^{(f)}/S^{(i)}$ in terms of $x \equiv U_A/U_{\text{total}}$ and $y \equiv V_A/V_{\text{total}}$ using an ideal gas model; the final values of x and y are those corresponding to the maximum of $S^{(f)}/S^{(i)}$. The arbitrary curve drawn on the surface between the initial “i” and final “f” states stands for an idealized process defined as a succession of equilibrium states, quite distinct from a real physical process formed by a temporal succession of equilibrium and non-equilibrium states.

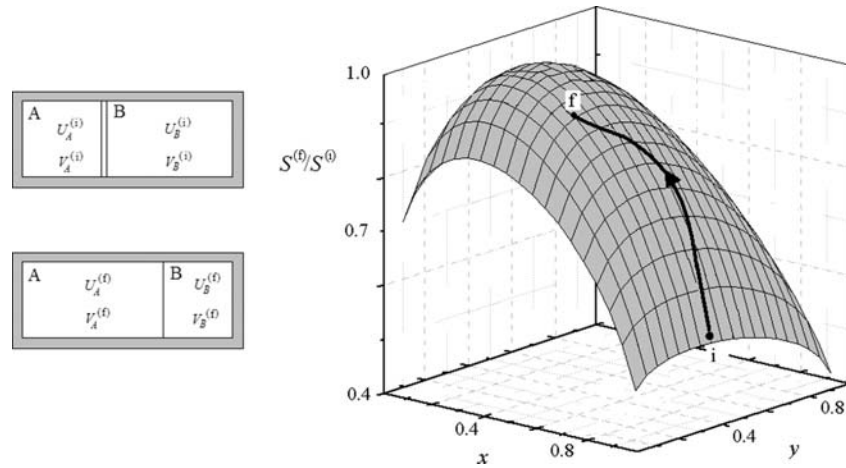


Fig. 1.4 Illustration of the entropy increase principle in the case of two gases initially separated by an adiabatic and fixed wall

1.3.4 The Third Law

The roots of this law appear in the study of thermodynamic quantities as the absolute temperature tends to zero. In 1909, Nernst formulated his heat theorem, later known as the third law of thermodynamics, to better understand the nature of chemical equilibrium. Nernst's formulation was that *the entropy change in any isothermal process approaches zero as the temperature at which the process occurs approaches zero*, i.e.

$$(\Delta S)_{T \rightarrow 0} \rightarrow 0. \quad (1.19)$$

This statement is sufficient for any thermodynamic development, but sometimes the stronger Planck's statement ($S \rightarrow 0$ as $T \rightarrow 0$) is preferred. Since the third law is more of quantum statistical essence, it is not of the same nature as the other laws and no further reference will be made to it in this book.

1.4 Gibbs' Equation

Let us now gather the results obtained for the first and second laws. Consider a reversible transformation, taking place in a closed system, for which the first law takes the form

$$dU = dQ_{\text{rev}} - p dV, \quad (1.20)$$

and combine it with the definition of entropy $dQ_{\text{rev}} = T dS$, resulting in

$$dU = T dS - p dV. \quad (1.21)$$

Expression (1.21) is known as Gibbs' equation; it is, however, not complete when there are matter exchanges as in open systems, or variations in composition as in chemical reactions. To calculate the reversible work corresponding to a chemical reaction involving n species, it is necessary to devise a reversible process of mixing. This is achieved thanks to van't Hoff's box (Kestin 1968), accordingly the reversible chemical work is given by

$$dW_{\text{rev}}^{\text{ch}} = \sum_{k=1}^n \bar{\mu}_k dm_k, \quad (1.22)$$

where $\bar{\mu}_k$ is defined as the chemical potential of substance k . The properties of the chemical potential will be explicitly examined below. With this additional term, one is led to the generalized Gibbs' equations

$$dU = T dS - p dV + \sum_{k=1}^n \bar{\mu}_k dm_k, \quad (1.23a)$$

or equivalently,

$$dS = T^{-1}dU + pT^{-1}dV - \sum_{k=1}^n T^{-1}\bar{\mu}_k dm_k. \quad (1.23b)$$

As discussed in the forthcoming sections, the Gibbs' equation plays a fundamental role in equilibrium thermodynamics. We should also mention that Gibbs' equation is one of the pillars of the Classical Theory of Irreversible Processes, as shown in Chap. 2. Let us now examine the main consequences of Gibbs' equation.

1.4.1 Fundamental Relations and State Equations

It follows directly from Gibbs' equation (1.23a) that

$$U = U(S, V, m_1, m_2, \dots, m_n), \quad (1.24)$$

or, solving with respect to S ,

$$S = S(U, V, m_1, m_2, \dots, m_n). \quad (1.25)$$

Relations like (1.24) or (1.25) expressing that U or S are single-valued functions of extensive state variables are called *fundamental relations* because they contain all thermodynamic information about the system. When U (respectively, S) is expressed as a function of the variables, we are speaking of the “energy representation” (respectively, “entropy representation”).

Another consequence of Gibbs' equation (1.23a) is that the intensive variables, represented by temperature, pressure and chemical potentials, can be defined as partial derivatives of U :

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, \{m_k\}} \quad (\text{a}), \quad p = - \left(\frac{\partial U}{\partial V} \right)_{S, \{m_k\}} \quad (\text{b}), \quad \bar{\mu}_k = \left(\frac{\partial U}{\partial m_k} \right)_{V, S, \{m_{i \neq k}\}} \quad (\text{c}), \quad (1.26)$$

where $\{m_k\}$ stands for all m_k constant. Since U is a function of S , V , m_k , the same remains true for T , p , and μ_k so that

$$T = T(S, V, m_1, m_2, \dots, m_n), \quad (1.27a)$$

$$p = p(S, V, m_1, m_2, \dots, m_n), \quad (1.27b)$$

$$\bar{\mu}_k = \bar{\mu}_k(S, V, m_1, m_2, \dots, m_n). \quad (1.27c)$$

Such relationships between intensive and extensive variables are called *state equations*. Elimination of S between (1.27a) and (1.27b) leads to the thermal equation of state $p = p(T, V, m_1, m_2, \dots, m_n)$; similarly by combining

(1.24) and (1.27a), one obtains the so-called caloric equation $U = U(T, V, m_1, m_2, \dots, m_n)$. The knowledge of one single state equation is not sufficient to describe the state of a system, which requires the knowledge of *all* the equations of state. For instance in the case of a monatomic perfect gas, $pV = NRT$ does not constitute the complete knowledge of the system but must be complemented by $U = \frac{3}{2}NRT$, R being the gas constant and N the mole number.

1.4.2 Euler's Relation

The extensive property of U implies that, from the mathematical point of view, it is a first-order homogeneous function of the extensive variables:

$$U(\lambda S, \lambda V, \lambda m_1, \dots, \lambda m_n) = \lambda U(S, V, m_1, \dots, m_n), \quad (1.28)$$

where λ is an arbitrary scalar. Differentiation of the fundamental relation (1.28) with respect to λ and setting $\lambda = 1$, leads to

$$\left(\frac{\partial U}{\partial S}\right)_{V, \{m_k\}} S + \left(\frac{\partial U}{\partial V}\right)_{S, \{m_k\}} V + \sum_k \left(\frac{\partial U}{\partial m_k}\right)_{V, S, \{m_j \neq k\}} m_k = U, \quad (1.29)$$

and, after making use of (1.26), one obtains *Euler's relation*

$$U = TS - pV + \sum_k \bar{\mu}_k m_k. \quad (1.30)$$

1.4.3 Gibbs–Duhem's Relation

A differential equation among the intensive variables can be derived directly from Euler's relation. Indeed, after differentiating (1.30), it is found that

$$dU = T dS - p dV + \sum_{k=1}^n \bar{\mu}_k dm_k + S dT - V dp + \sum_{k=1}^n m_k d\bar{\mu}_k, \quad (1.31)$$

which, after using Gibbs' equation (1.23a), yields Gibbs–Duhem's relation

$$S dT - V dp + \sum_{k=1}^n m_k d\bar{\mu}_k = 0. \quad (1.32)$$

It follows that the $n + 2$ intensive variables are not independent but related through the Gibbs–Duhem's relation. For a n -component mixture, the number of independent intensive state variables, called *thermodynamic degrees of freedom*, is equal to $n + 1$: for instance, the $n - 1$ chemical potentials plus temperature and pressure. In the case of a one-component fluid, the thermodynamic description of the system requires the knowledge of two independent intensive quantities, generally selected as the temperature T and the pressure p .

1.4.4 Some Definitions

In view of further developments, it is useful to introduce the following definitions of well-known experimental quantities:

- *Coefficient of thermal expansion:*

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p, \{m_k\}}. \quad (1.33)$$

- *Isothermal compressibility:*

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, \{m_k\}}. \quad (1.34)$$

- *Heat capacity at constant volume:*

$$c_V = \left(\frac{\partial U}{\partial T} \right)_{V, \{m_k\}} = \left(\frac{dQ_{\text{rev}}}{dT} \right)_{V, \{m_k\}}. \quad (1.35)$$

- *Heat capacity at constant pressure:*

$$c_p = \left(\frac{\partial H}{\partial T} \right)_{p, \{m_k\}} = \left(\frac{dQ_{\text{rev}}}{dT} \right)_{p, \{m_k\}}. \quad (1.36)$$

Other partial derivatives may be introduced but generally, they do not have a specific practical usefulness. Relations between these partial derivatives may be derived by equating mixed second-order partial derivatives of U and S . Such expressions have been identified as *Maxwell's relations*.

As a last remark, let us mention that the results established so far in homogeneous systems of total mass m and volume V are still valid when referred per unit mass and unit volume. Analogous to (1.24), the fundamental relation per unit mass is

$$u = u(s, v, \dots, c_k, \dots) \quad (1.37)$$

with $u = U/m$, $s = S/m$, $v = V/m$, $c_k = m_k/m$, and $\sum_k c_k = 1$. After differentiation, (1.37) reads as

$$du = T ds - p dv + \sum_{k=1}^{n-1} (\bar{\mu}_k - \bar{\mu}_n) dc_k \quad (1.38)$$

with $T = (\partial u / \partial s)_{v, \{c_k\}}$, $p = -(\partial u / \partial v)_{s, \{c_k\}}$, $\bar{\mu}_k = (\partial u / \partial c_k)_{s, v, \{c_{j \neq k}\}}$. Similarly, the Euler and Gibbs–Duhem's relations (1.30) and (1.32) take the form

$$u = Ts - pv + \sum_{k=1}^n \bar{\mu}_k c_k, \quad S dT - v dp + \sum_{k=1}^n c_k d\bar{\mu}_k = 0. \quad (1.39)$$

1.4.5 The Basic Problem of Equilibrium Thermodynamics

To maintain a system in an equilibrium state, one needs the presence of constraints; if some of them are removed, the system will move towards a new equilibrium state. The basic problem is to determine the final equilibrium state when the initial equilibrium state and the nature of the constraints are specified. As illustration, we have considered in Box 1.3 the problem of thermo-diffusion. The system consists of two gases filling two containers separated by a rigid, impermeable and adiabatic wall: the whole system is isolated. If we now replace the original wall by a semi-permeable, diathermal one, there will be heat exchange coupled with a flow of matter between the two subsystems until a new state of equilibrium is reached; the problem is the calculation of the state parameters in the final equilibrium state.

Box 1.3 Thermodiffusion

Let us suppose that an isolated system consists of two separated containers I and II, each of fixed volume, and separated by an impermeable, rigid and adiabatic wall (see Fig.1.5). Container I is filled with a gas *A* and container II with a mixture of two non-reacting gases *A* and *B*. Substitute now the original wall by a diathermal, non-deformable but semi-permeable membrane, permeable to substance *A*. The latter will diffuse through the membrane until the system comes to a new equilibrium, of which we want to know the properties. The volumes of each container and the mass of substance *B* are fixed:

$$V_I = \text{constant}, \quad V_{II} = \text{constant}, \quad m_{II}^B = \text{constant}, \quad (1.3.1)$$

but the energies in both containers as well as the mass of substance *A* are free to change, subject to the constraints

$$U_I + U_{II} = \text{constant}, \quad m_I^A + m_{II}^A = \text{constant}. \quad (1.3.2)$$

In virtue of the second law, the values of $U_I, U_{II}, m_I^A, m_{II}^A$ in the new equilibrium state are such as to maximize the entropy, i.e. $dS = 0$ and, from the additivity of the entropy in the two subsystems

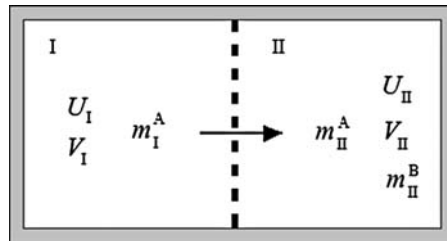


Fig. 1.5 Equilibrium conditions for thermodiffusion