Lectures on Thermodynamics

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Preface

In the introductory courses on Physics it is customary to present the laws of Thermodynamics and the connected physical quantities: temperature, interna energy and entropy. Examples and exercises are generally limited to very simple systems, such as mono- and bi-atomic ideal gases. To the majority of students Thermodynamics reduces to the science of thermal engines and entropy remains a vague concept. The widespread areas of applications of Thermodynamics, the formal elegance of its mathematical apparatus as well as the statistical interpretation of its basic concepts are thus generally ignored.

The present lectures address university students already acquainted with the rudiments of Thermodynamics. Their aim is to go deeper into the basic concepts as well as to open a perspective on the many possible applications of Thermodynamics.

The first three parts are devoted to the introduction of the basic concepts according to three different approaches: the classical approach based on cyclic transformations, the axiomatic approach based on the coordinates and on the maximum entropy principle, and the statistical approach.

The fourth and fifth parts are devoted to applications that are particularly important from both the scientific and technical points of view: magnetic systems, low temperatures and phase transitions.

The sixth part is an introduction to the Thermodynamics of irreversible processes.

The seventh part contains a collection of different applications, such as the kinetic model and the statistics of ideal gases and the Thermodynamics of crystals.

In the Appendices the reader can find some notes on the historical development of Thermodynamics, short biographical notes on relevant scientists as well as a number of useful tables.

Contents

Part I

The laws of Thermodynamics

This Part I is dedicate to the basic laws of Thermodynamics: zeroth law, first law and second law (the third law will be considered later on, Part IV, Chapter 20). Correpondingly, the three thermodynamical quantities temperature, internal energy and entropy are introduced.

The reader is supposed to be already familiar with the basics of Thermodynamics. This Part I contains a critical revision and some extensions of concepts supposed already known, and represents the phenomenological base for the axiomatic treatment of the Part II.

Chapter 1

Basic concepts

In this introductory chapter, we define the field of study of Thermodynamics, clarify the concept of *thermodynamic system* and attempt a general classification of thermodynamic systems.
We emphasise the main differences between Mechanics and Thermodynamics in terms of systems considered, methods of approach and physical quantities quantities

1.1 Thermodynamic systems and phenomena

The first question to be answered is: which physical systems are studied by Thermodynamics?
Historically, Thermodynamics was developed, in the first half of the XIX century, to give a conceptual framework to the processes in which mechanical work is obtained from heat; hence the very name Thermo-dynamics. In these applications, the thermodynamic system is typically a fluid that, within a thermal engine, undergoes a series of cyclic transformations which allow the partial conversion of heat into mechanical work.
Subsequently, the principles and methods of Thermodynamics were extended to a number of other systems and phenomena, such as chemical reactions, phase transformations, diffusion phenomena, magnetisation and electrical polarisation, and so on.
All these phenomena cannot be described, at least from a macroscopic point of view, in purely mechanical terms. New quantities (such as temperature, internal energy, heat, entropy) and new laws, the laws of Thermodynamics, have to be introduced, to which this Part**??** is dedicated.

In the second half of the XIX century, the atomic structure of matter becomes more and more evident. Correspondingly, one attempts at explaining thermodynamic phenomena in mechanical terms, starting from the atomic structure of matter and the interactions between the atoms. The microscopic approach, initiated with the kinetic model of ideal gases, finds its highest expression with the general theory of statistical mechanics (which will be considered in Part III).

The knowledge of the atomic structure of matter allows us to answer the initial question: what is a thermodynamic system?
Thermodynamics deals with the description of macroscopic systems containing a very large number of elementary entities, like atoms or molecules, and of their transformations. The very presence of a huge number of elementary constituents gives rise to the emergence of some properties that cannot be described in purely mechanical terms at the macroscopic level (typically, the thermal properties, which demand the introduction of a non-mechanical quantity, the temperature).
Statistical Thermodynamics explains how the thermodynamical properties are the average effect of the mechanical behaviour of a large number of elementary constituents. The larger the number of elementary constituents, the smaller are the fluctuations of some quantities with respect to their average values. When the fluctuations are sufficiently small, the average macroscopic behaviour can be conveniently described in terms of macroscopic Thermodynamics.

Example 1: Let us consider a nitrogen molecule N_2 belonging to the air mass of a given room.
Our molecule continuously interacts with other molecules, so that its kinetic energy is con-

tinuously changing. The instantaneous values of the kinetic energy are well defined , but the fluctuations with respect to the average value due to the collisions are very large. There is no thermodynamic description of the state of a molecule and we cannot speak of the temperature of a molecule. A molecule *is not* a thermodynamic system.

Example 2: Let us now consider a copper block lying in the same room. The copper block continuously exchange energy with the air, as a consequence of the collisions of air molecules. However, due to the huge number of copper atoms constituting the block, the fluctuations with respect to the average value of the energy are extremely small, practically negligible. One can thus give a thermodynamic description of the copper block, with a well defined value of internal energy and temperature. The copper block *is* a thermodynamic system.

The larger is the number of atoms in the system, the more significant is its thermodynamic description. There is no neat border between thermodynamic systems and non-thermodynamic systems. Statistical thermodynamics allows one to quantitatively study the extent of the fluctuations as a function of the number of atoms. As a rule of thumb, one can consider as thermodynamic systems the systems composed by a number of atoms of the order of the Avogadro number, say $\sim 10^{23}$.

Classification of thermodynamic systems

A thermodynamic system can interact with other systems, globally called its *surroundings*, exchanging matter and/or energy.

According to these properties, thermodynamic systems can be classified into three main categories.

(a) *Isolated systems* cannot exchange nor matter nor energy with their surroundings.
A gas enclosed in an impermeable vessel, with rigid and insulating walls (e.g. a Dewar flask) is an example of isolated system.

(b) *Closed systems* can only exchange energy with their surroundings.
A gas enclosed in an impermeable metal cylinder with a movable piston is an example of a closed non isolated system.

(c) *Open systems* can exchange both matter and energy with their surroundings.
A flux chemical reactor and a biological cell are examples of open systems.

A further classification can be done according to the system homogeneity. A multicomponent system is

(a) *Homogeneous* if it contains only one phase, such as a gas within a bottle or a copper block.

(b) *Inhomogeneous* if it contains more than one phase, such as a liquid in equilibrium with its vapour or an ice block in equilibrium with liquid water at zero degrees Celsius.

In this Chapter we try to better define the thermodynamic systems and their purely thermodynamic properties by analyzing some relevant differences between the thermodynamic approach and the macroscopic mechanical approach.

1.2 Thermodynamic state and thermodynamic coordinates

A first step to understand the peculiarities of Thermodynamics consists in studying the difference between mechanical and thermodynamical states as well as between purely mechanical coordinates and thermodynamical coordinates. Only classical Mechanics is here considered; the differences between classical and quantum Mechanics are irrelevant for the present discussion.

As already stated, we are interested in systems composed of a very large number of atoms, of the order of Avogadro number.

1.2.1 Inadequacy of mechanical description

In classical mechanics, the dynamical state of a macroscopic system composed of a large number of atoms is described by a small number of parameters (macroscopic mechanical coordinates).

Example 1a: The dynamical state of a rigid body is defined by the position of the center of mass $\vec{r}_{\rm cm}$, by the three Euler angles α, β, γ that give the spatial orientation, by the center of mass velocity $\vec{v}_{\rm cm}$ and by a vectorial angular velocity $\vec{\omega}$. In total 12 scalar quantities. The volume V of the rigid body is constant.

Example 2a: Let us consider a homogeneous gas contained in a rigid metal vessel. The macroscopic dynamical state is defined by position and velocity of the center of mass, by the spatial orientation of the vessel as well as by a possible angula velocity vector. The volume V is constant.

According to common experience, many phenomena exist that cannot be simply described by the dynamical coordinates.

Example 1b: Let us consider a solid body, such as a metal block. In some cases the solid can be considered as a rigid body and its dynamical state can be described by the 12 scalar quantities considered in the Example 1a. In other cases, however, the solid doesn't behave as a rigid body and undergoes modifications that cannot be described by the 12 scalar quantities of the Example 1a. For example, the volume V can be varied if the solid is in contact with a heat source or if the hydrostatic pressure p of the surrounding air is modified. One can also observe that the relation between pressure p and volume V can be modified if the solid is put in contact with different heat sources.

Example 2b: Let us consider again, as in the Example 2a, a gas contained in a rigid metal vessel (constant V) and rub the external walls of the vessel for a sufficiently long time. Notwithstanding the position and velocity of the center of mass are unaltered, and no macroscopic rotation with respect to the center of mass is present, the state of the system undergoes a modification. The change escapes a description in terms of macroscopic dynamical coordinates, but can be described by considering the variations of the pressure p of the gas. If we now consider as a vessel a cylinder with a movable piston, say a vessel with variable volume, one can observe that the rubbing can give rise to variations of both the volume V and the pressure p.

The properties that have been described in Examples 1b and 2b can be connected to the microscopic structure of systems at the atomic level. In principle, one could think of resorting to a purely mechanical description, based on the dynamical coordinates of each microscopic entity. Such a description, however, in view of the large number of microscopic consituents (of the order of 10^{23}) is practically impossible, and, even if possible, would be devoid of any real usefulness.

Example: A cubic centimeter of air at $T = 300\,\mathrm{K}$ and $p = 1\,\mathrm{bar}$ contains about 2.7×10^{19} molecules, with average velocity $\langle v \rangle \simeq 500\,\mathrm{m\,s^{-1}}$ and mean free path $\lambda \simeq 10^{-7}$ m; each molecule undergoes about 5×10^{9} collisions per second.

1.2.2 Thermodynamical description

Thermodynamics specifically deals with phenomena that depend on the very large number of elementary constituents of a system and cannot be described in terms of macroscopic mechanical coordinates.
The motion of the center of mass has no relevance for Thermodynamics. The thermodynamic behaviour of a system is thus studied within the reference frame of the center of mass. Also the motion of the whole system with respect to the center of mass, like the rotation of a rigid body, has no thermodynamic relevance.

The thermodynamic state of a system is described by a limited number of quantities, called thermodynamic coordinates. The simplest systems can be described by two independent thermodynamical coordinates; for example, the thermodynamical state of a simple substance, such as those considered in the examples 1b and 2b, can be described by the values of pressure p and volume V.

The choice of thermodynamical coordinates for a given system is not univocal; different choices can be best suited to different situations fo the same system. Different choices can give rise to different approaches of Thermodynamics (§ 1.4).
It is convenient to distinguish two types of thermodynamic coordinates:

(a) Extensive coordinates, whose value depends on the system size (a typical example is volume); more precisely, te value of extensive coordinates is proportional to the mass of the system;
(b) Intensive coordinates, whose value does not depend on the system size (a typical example is pressure)

If a system is divided in two equal parts, the values of the extensive coordinates of each part are one half of the value of the entire system, while the values of the intensive coordinates of the two parts are equal to the value of the entire system.
Extensive and intensive coordinates can be grouped into pairs of *conjugate variables.*

Example: For a gas, volume V and pressure p are conjugate variables; for an elastic spring, length ℓ and tension τ are conjugate variables; for a magnet, magnetization M and magnetic field $\mathcal{H}$ are conjugate variables.

Note: It is worth noting that a set of solely intensive coordinates in insufficient to describe the thermodynamic state of a system, since it does contain information on the system size.

1.2.3 Micro-macro connection

The thermodynamic coordinates of a system depend on the microscopic structure at the atomic and subatomic levels. As already noted, one cannot establish a rigorous quantitative connection between the macroscopic thermodynamic coordinates and all the dynamic coordinates of microscopic constituents.
However, just because of the very large number of microscopic constituents ($\simeq 10^{23}$), one can obtain an effective quantitative connection through a probabilistic approach. To this effect, the microscopic behaviour is considered perfectly random, provided some constraints are taken into account, such as the conservation of energy or of the number of particles. Because of the very large number of constituents, the mean value of some quantities is particularly stable, and can be connected to the macroscopic thermodynamic coordinates.
The kinetic model of ideal gases allows one to express the pressure and temperature as a function of the mean kinetic energy of the molecular translational motion. Statistical thermodynamics, to be considered in Part III, is a more general approach, that allows one to connect the macroscopic coordinates to the energy distribution of the microscopic constituents for any system.

The larger the system, the more precise is its description and the less significnt are the details neglected by limiting the number of coordinates (thermodynamic limit).

Note 1: The kinetic model of ideal gases is charactrised by the proportionality of temperature to average kinetic energy, so that the two quantities are equivalent. The equivalence is not true for other systems.

Note 2: The term “microscopic” is here conventionally used to indicate objects and phenomena at atomic or molecular scale. Elsewhere, “microscopic” refers to objects of micro-meter size and “nanoscopic” to objects of nano-meter size.

1.2.4 Energy

The law of Physics are assumed to be invariant with respect to time, say they are not modified by the flow of time. As a consequence of this symmetry with respect to time translations, one can demonstrate that the four fundamental interaction forces (gravitational, electromagnetic, strong nuclear and weak nuclear) are conservative.

In a *mechanical microscopic* description, the interactions between the atoms of a system are due to conservative forces (it is generally sufficient to consider electromagnetic forces). In a transformation of a given system from an initial to a final state the conservation law holds:

(a) if the system is isolated: $\Delta E_k + \Delta E_p = 0$
(b) if the system is not isolated: $\Delta E_k + \Delta E_p = W$

where the symbol Δ means variation, E_k is the sum of the kinetic energies of the atoms, E_p are the total potential energy due to all the interatios within the system of the system, and W is the total work made on the system by the environment.
It should be anyway noted that it is generally very difficult, if not impossible, to take rigorously into account all the interactions present in a system.

Let us now consider the *mechanical macrosopic* description of system composed by a large number of atoms. The kinetic and potential energies are now expressed as a function of the macroscopic coordinates (position and velocity of the center of mass and so on). When the system undergoes a transformation from an initial to a final state, macroscopic nonconservative forces, like friction, have always to be taken into account. The conservation of mechanical energy has to be considered only as an approximation, valid in the absence of friction. Strictly speaking, for macroscopic systems:

(a) For an isolated system $\Delta E_k + \Delta E_p \neq 0$
(b) For a non-isolated system, $\Delta E_k + \Delta E_p \neq W$

Example: Let us consider a spring within a perfectly isolated vessel. Initially the spring is elongated beyond its equilibrium length. Once left free, the spring oscillates, but the amplitude of oscillations is progressively reduced to zero. Notwithstanding that the system is isolated, the macroscopic mechanical energy is not conserved due to the presence fo non-conservative friction forces.

In the *thermodynamic* description, the concepts of macroscopic energy of a system and of energy transport are somewhat enlarged with respect to a purely mechanical description, in order to allow the assumption of conservation of energy for any transformation of a macroscopic isolated system (first law of thermodynamics, Chapter 3).

The conservation of energy in Thermodynamics is anyway depending on the conservative character of the fundamental interaction forces at the microscopic level.

1.3 Equilibrium

1.3.1 Mechanical equilibrium

For a conservative mechanical system, the conditions of mechanical equilibrium and its stability are related to the shape of the hypersurface $E_p(q_i)$ of the potential energy as a function of the generalized coordinates q_i. For the sake of simplicity, let us refer here to a system depending on one coordinate x (for example, think of the rail of a roller-coaster, where x is the distance along the projection on the horizontal plane, and $E_p = mgh$).
One gets mechanical equilibrium when $dE_p/dx = 0$, so that the force is zero. If the body is at rest, one has the condition of static equilibrium.
The equilibrium is said to be *stable* if the function $E_p(x)$ has a minimum, total or local; a displacement from the position of stable equilibrium gives rise to a force that tends to restore the equilibrium situation. For the points of local minimum one often speaks of *metastable* equilibrium.
The equilibrium is said to be *unstable* in the points of maximum or of inflection of the function $E_p(x)$; a displacement from the position of unstable equilibrium gives rise to a force that tends to further increase the displacement.

For a system out of mechanical equilibrium, the laws of dynamics allow one to describe the mechanical behaviour of the system. The laws of mechanics represent a deterministic criterion of evolution.

One finds experimentally that a system, in spite of being in a state of mechanical equilibrium, can undergo modifications related to a change of its thermodynamic coordinates. Let us consider here some examples.

Example 1: A cylinder is divided in two parts by a movable piston. Initially the iston is fixed and the two parts of the cylinder contain a gas at different pressures. When the piston is left free to move, the system undergoes a transformation towards a final stte where the two pressures are equal. The state of mechanical macroscopic equilibrium is not altered.

Example 2: A metal block placed on a heating surface maintains its mechanical equilibrium, but undergoes a modification of its state because of the heat exchange.

Example 3: A volume of water into which an ink drop is poured maintains its mechanical equilibrium, but undergoes a modification of its state, because of the ink diffusion, corresponding to a microscopic transport of matter.

Example 4: During a chemical reaction, a system can maintain its mechanical equilibrium, but its state is somewhat modified

1.3.2 Thermodynamical equilibrium

A state of thermodynamic equilibrium is a state where three different types of equilibrium are contemporarily present:

1. *Mechanical equilibrium*, say equilibrium with respect to the forces that can modify the thermodynamic coordinates.
   Let us stress the difference between the mechanical equilibrium here defined in relation to the thermodynamical coordinates and the mechanical equilibrium considered above and related to the function $E_p(q_i)$. See also the Note below.
   Two thermodynamical systems connected by a movable wall are in mechanical equilibrium when characterised by the same pressure p.
2. *Thermal equilibrium*, say equilibrium with respect to the heat exchanges; the concept will be better specified in Chapter 2, together with the introduction of the zeroth law of thermodynamics.
   As we will see, two thermodynamical systems connected by a heat-conducting wall are in thermal equilibrium when characterised by the same temperature.
3. *Chemical equilibrium*, say equilibrium with respect to chemical reactions and microscopic transport of matter.
   A new quantity will be introduced in Part II, the chemical potential μ, that has the same role in chemical equilibrium as pressure and temperature have in mechanical and thermal equilibrium, respectively.
   Two thermodynamical systems connected by a wall permeable to the exchange of matter are in thermal equilibrium when characterised by the same chemical potential.

In order that a system be in thermodynamic equilibrium, all three forms of equilibrium (mechanical, thermal and chemical) have to be present between the system and its surroundings as well as between the different parts of the system.

Note: It is important to pay attention to the meaning of mechanical equilibrium in thermodynamics. A free-falling gas bottle, although not in equilibrium from a mechanical point of view, is in thermodynamic equilibrium, because the motion of the center of mass is thermodynamically irrelevant. If the gas is instead contained in a cylinder closed by a moving piston, and the pressure is different on the two sides of the piston, then the lack of mechanical equilibrium has thermodynamic relevance, because it can cause a modification of the volume, which is a thermodynamic coordinate.

Even if there are no external stresses, a system in thermodynamic equilibrium continuously undergoes spontaneous breakdowns of the equilibrium conditions, due to local fluctuations of pressure, temperature, concentration of components. Such fluctuations represent a spontaneous local breaking of equilibrium, from which however the system spontaneously recovers. Thermodynamic equilibrium is necessarily stable. The conditions for the stability of thermodynamic equilibrium are studied in Part II, at § 9.6.

Classical thermodynamics only considers systems in thermodynamic equilibrium. For a system out of equilibrium, the thermodynamic coordinates are generally not defined, and the state of the system cannot be described. There is no evolution criterion for thermodynamic systems similar to the evolution criterion of purely mechanical systems, able to describe deterministically and step by step the variation of the system coordinates. It is nevertheless possible to introduce an evolution criterion that establishes a relation between two equilibrium states, an initial one and a final one (the law of increase of entropy for isolated systems, Cap **??**).
A thermodynamics of irreversible processes has been developed, that describes the behavior of systems not too far from equilibrium by means of specific techniques (Part VI).

A far from trivial problem, which will be considered later on, is the operative definition of thermodynamic equilibrium: how can we experimentally determine whether a system is in equilibrium?

1.3.3 Transformations

When the conditions under which a given system is in thermodynamic equilibrium are modified, the system undergoes a transformation at the end of which the system is in a new equilibrium state, characterised by new values of the thermodynamic coordinates.
Let us label by i and f the initial and final equilibrium states, respectively. The intermediate states of transformation $i \to f$ are non-equilibrium states and thus, in principle, not suitable for a thermodynamic description.

Example: A copper block, initially in equilibrium at room temperature, is immersed in boiling water. The block leaves its initial equilibrium state i and undergoes a transformation during which its temperature is progressively raised and finally it finishes in a new final equilibrium state f.

1.3.4 Quasi-static transformations

A thermodynamic transformation can be described, even if only approximately, when the intermediate states differ very little (in principle infinitesimally) from equilibrium states. One such transfrmation is said to be *quasi-static*. A quasi-static transformation can be conceived as a succession of equilibrium states and can be thus graphically represented in a state diagram.
In order for a transformation to be considered quasi-static, it is necessary that the system progressively undergo infinitesimal imbalances of pressure, temperature, chemical potential or other possible thermodynamical coordinates.

Example: Let us again consider the example of the copper block. To approximate a quasi-static $i \to f$ transformation, the block should be put in contact with different systems of progressively increasing temperature.

1.3.5 System and environment

When a system s undergoes a transformation from an initial state i_s to a final state f_s, its environment generally undergoes a transformation from an initial state i_e to a final state f_e too. In some cases in can happen that $f_a = i_e$, say the environment doesn't undergo anu modification as a consequence of the system transformation.

1.3.6 Reversibility and Irreversibility

The notion of reversibility of a transformation plays a fundamental role in Thermodynamics.
Le us stress that the meaning of reversibility in Thermodynamics shouldn't be mistaken for its meaning in the common language; reversibility and irreversibility are explicitly and rigorously defined in Thermodynamics.

Even if the restrict our attention to the purely scientific field, one can single out at least three different meanings of the term “reversibility”.

1) A first meaning of reversibility concerns systems in thermodynamic equilibrium (mechnical, thermal, chemical) for which a suitable variation of an external parameter can give rise to a variation of the state in one direction or in the opposite direction.
   For example, a chemical reaction $A + B \rightleftharpoons C + D$ is said to be reversible if there is an equilibrium between the reagents A, B and the products C, D. The equilibrium can be modified towards left or towards right by suitably modifying one of the external parameters, such as the temperature
   This kind of reversibility is different from the thermodynamic reversibility we are here interested in.
2) A second meaning of reversibility concerns the dependence on time of the physical laws. A physical process is said to be reversible if it is described by a law invariant with respect to the inversion of the time axis, say with respect to the substitution of t with $-t$.
   The fundamental interactions are reversible in this sense (with the exception of some processes of weak nuclear interaction).
   In particular, the processes at the atomic level in whichever thermodynamic system are reversible. One generally speaks of “microscopic reversibility”. Also the mechanics of celestial bodies is reversible with very good approximation.
3) Thermodynamic reversibility is defined as follows. The transformation of a system s from an initial state i_s to a final state f_s is said to be reversible if one can bring back the system to the initial state i_s contemporarily bringing its environment e to its initial state i_e.

As we will se in Chapter 4, the Second Law of Thermodynamics assumes the irreversibility of two well defined processes and, as a consequence that can be demonstrated, the irreversibility of all spontaneous macroscopic processes.

In macroscopic systems also the purely mechanical reversibility is not verified, due to the unavoidable friction forces that depend on velocity and are thus not invariant with respect to the direction of time. In general, all real transformations of macroscopic systems (characterised by friction forces, heat conduction, diffusion phenomena and so on) are thermodynamically irreversible.
As a simple example, we can consider a ball that is left to fall from a given height and is bounced on the ground. If at a given time the direction of velocity is inverted, the ball will not retrace the same previous dynamical states.

The connection between microscopic reversibility and macroscopic reversibility is still a problem of scientific and epistemological relevance.

Although it is impossible to completely eliminate the irreversibility in real macroscopic processes, equilibrium Thermodynamics largely resorts to reversible transformations, o be considered as limiting transformations..
In order that a transformation could be considered as reversible, it shoud contemporarily be

- quasi-static,
- free from dissipative effects (friction).

1.3.7 Evolution criteria

As we will se in Chapter 4, the Second Law of Thermodynamics establishes evolution criteria of general validity for natural phenomena. For example, for an isolated system the evolution criterion is connected to the variation of a state function, the entropy S: an isolated system, initially in equilibrium in an equilibrium state i_s, can spontaneously evolve towards a final equilibrium state f_s only if the entropy of the final state is not inferior to the entropy of the initial state. Fo non isolated systems equivalent evolution criteria have been developed, which will be introduced in Part II.

Such evolution criteria allow one only to decide whether a system can spontaneously go from an initial equilibrium state i_s to a final equilibrium state f_s. Contrary to Mechanics, equilibrium Thermodynamics cannot follow step by step the evolution of a system through its non-equilibrium states.

Let us anyway mention that a *Thermodynamic of irreversible processes* also exists, which can describe the systems evolution provided the deviation from equilibrium is sufficiently small.To an introduction to the Thermodynamic of irreversible processes Part is devoted.

1.4 Classifications of Thermodynamics

To conclude this introductory chapter, let us attempt a schematic classification of the different phenomena studied by Thermodynamics and of the different possible approaches.

Equilibrium Thermodynamics

Thermodynamics has achieved a very high degree of accuracy in describing systems at equilibrium. Two different main approaches to equilibrium Thermodynamics can be single out:

1. Macroscopic thermodynamics (sometimes referred to as classical Thermodynamics), which can in turn be treated according to two different approaches:
   - 1a. an empirical approach, based on the empirical laws of thermodynamics (Part I of this book)
   - 1b. an axiomatic approach, based on the variational principle of maximum entropy (Part II of this book)
2. Statistical thermodynamics (of which an introductory account will be given in Part III of this book)

1.4.1 Non-equilibrium Thermodynamics

Two different approaches can be used also for a thermodynamic description of systems out of equilibrium.

1. Macroscopic approach, also referred to as Thermodynamics of irreversible processes (Part VI of this book)
2. Macroscopic approach, also referred to as hpysical kinetics (not considered in this book)

Chapter 2

The Zeroth Law of Thermodynamics: Temperature

Temperature is one of the physical quantities that characterise the thermodynamic behaviour of a macroscopic system. The intuitive idea of temperature dates bak to ancient Greece and ancient Rome, where itv was connected to the human body physiology by the physicians Hippocrates and Galen.
The temperature ceases to be a subjectively evaluated quantity and becomes a measurable physical quantity at the beginning of 1600, with the invention of the first thermometer by Galileo Galilei.
The definition of temperature is nowadays base on the properties of thermal equilibrium between different systems, which have been proposed as a postulate by the british physicist R.H. Fowler around 1930. Since at that time the First and Second Laws were already well established, the new postulate, which is logically precedent, was called Zeroth Law. La definizione di temperatura è oggi basata sulle proprietà dell'equilibrio termico tra sistemi, che sono state proposte come assioma da parte del fisico inglese R. H. Fowler intorno al 1930. Poiché in quell'epoca il Primo e il Secondo Principio erano già ben consolidati, il nuovo assioma, che dal punto di vista logico li precede, è stato chiamato Principio Zero.

2.1 Thermal equilibrium and its properties

The thermodynamic coordinates describe the state of a system only with reference to its properties of thermodynamic interest, say the properties depending on the presence and behaviour of a large number of elementary constituents. In what follows we consider, for simplicity, a system that can be described by only two independent thermodynamic coordinates, that will be labeled as X, Y (they could be, for example, pressure and volume, p, V.)
As previously stated, the thermodynamic equilibrium is a synthesis of mechanical, thermal and chemical equilibria. Our aim now is to give a rigorous definition of thermal equilibrium.

To this aim, let us consider two thermodynamic systems A and B, which can be described by the two sets of coordinates X_A, Y_A and X_B, Y_B, respectively. Let the two systems be separated by a wall in mechanical equilibrium and impermeable to matter trasport (Fig. 2.1).
The wall is said to be

- *adiabatic* if the values of the X, Y coordinates of the system A are in no way affected by any variation of the coordinates X', Y' of the system B, and viceversa;
- *diathermal* if the variation of the coordinates of one of the two systems can influence the coordinates of the other system.

Two systems separated by a diathermal wall are said to be in thermal equilibrium when their thermodynamic coordinates are invariant with time.

Note 1: A perfectly adiabatic wall cannot be realised in practice. From an operative point of view,

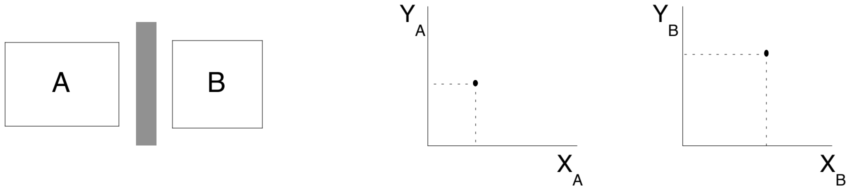


Figure 2.1: Left: two systems separated by a wall fixed and impermeable to matter transport. Right: the stat of each system is represented by a point in the XY plane.

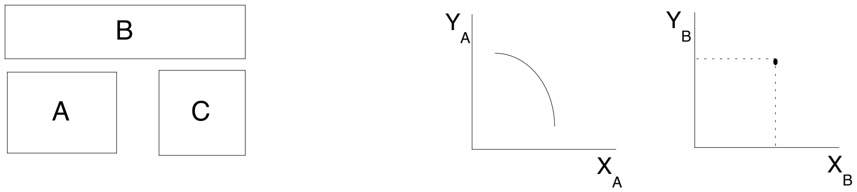


Figure 2.2: Left: three systems in thermal equilibrium. Right: there are many states of the system A (line) in thermal equilibrium with a given state of the system B (point).

the distinction of an adiabatic wall from a diathermal wall is based on the ratio between the typical time of variation of the coordinates of systems separated by a wall (relaxation time τ) and the observation time $t_{\rm obs}$. A real wall can be considered adiabatic to a good approximation if the relaxation time is much larger than the observation time, $\tau \gg t_{\rm os}$.

Note 2: the process leading two systems to thermal equilibrium ha asymptotic character and requires, in principle, an infinite time. However, if the relaxation time is sufficiently short with respect to the typical observation times, the difference between the actual state and the thermodynamic equilibrium state is generally negligible with respect to the measurement uncertainties, so that one can speak of thermal equilibrium with very good approximation.

Note 3: The above considerations on the thermal equilibrium between two systems also hold for two or more parts of the same system. A single system is in thermal equilibrium if all its different parts are in thermal equilibrium.

Note 4: In some cases the relaxation time can be much longer than the observation time (one important case ir represented by substance in the glassy state); in such cases the system can appear to be in equilibrium without actually being. We will come to this subject after the introduction of the Third Law of Thermodynamics in Chapter 20.

The **Zeroth Law of Thermodynamics** asserts the transitivity of the relation “to be in thermal equilibrium”:

> *Given three systems A, B and C* (Fig. 2.2, left)*, if A is in thermal equilibrium with B and B is in thermal equilibrium with C, then A is in thermal equilibrium with C.*

The relation “to be in thermal equilibrium” is thus an equivalence relation, since it is reflexive, symmetric and transitive. As a consequence, the set of all possible thermodynamic systems can be partitioned into disjoint equivalence classes. All systems belonging to a given class are in thermal equilibrium. Systems belonging to different classes are not in thermal equilibrium.

One can then introduce a new physical quantity, the *temperature*, that univocally labels the different classes of systems in thermal equilibrium. At each class of systems in thermal equilibrium one can associate a different temperature.

Note: The procedure for defining the temperature is formally similar tothe procedure by which the length is defined in Geometry: one verifies that the congruence relation of segments is an equivalence relation and one associates a different length to each different class of equivalence.

A thermodynamic system A can assume different values of the coordinates X_A, Y_A maintaining the same temperature (say staying in thermal equilibrium with another system B whose coordinates X_B, Y_B remain constant). The corresponding values of the X_A, Y_A coordinates define a curve called *isotherm* (Fig. 2.2, right).

2.2 Empirical temperature

An *operative* definition of temperature requires that an empirical methodology of measurement is established, say a criterion for univocally associating a value of temperature to every class of system in thermal equilibrium.

As for the length (or for the mass or the time interval), also for the temperature one can establish a comparative criterion that allows one to decide whether a system A has temperature lower, equal or higher than a system B. To this aim one can use different types of thermoscopes. Thanks to this possibility, the temperature can be considered a physical quantity.

However, contrary to the length (or the mass or the time interval), the temperature is not an additive quantity. It is impossible to define ad addition of temperatures and it is thus impossible to define a direct measurement method based on the comparison with a standard unit.

The temperature can be only indirectly measured. Many different methods have been devised to measure the temperature, based on the direct measurement of a *thermometric property* of a given *termometric substance*. The choice of a particular measurement method corresponds to the choice of a *thermometer*.

Example 1: In an electric resistance thermometer, the thermometric substance is a metal, the thermometric property is the electrical resistivity.

Example 2: In a mercury thermometer, the thermometric substance is mercury, the thermometric property is the height of the mercury column in the glass capillary.

A *temperature scale* is generally established by assigning arbitrary values of temperature to some easily reproducible phenomena, which are called “fixed points”; for example, the Celsius scale assigns the values 0°C and 100°C to the fusion and boiling points of water at atmospheric pressure, respectively; other examples are listed in table 32.3 of Appendix 32.

Once a given scale has been chosen, thermometers based on different thermometric substances and properties can anyway give different values of temperature outside the fixed points. The readings of different thermometers have thus to be made compatible by suitable clibration procedures.

In the next § 2.3 we will introduce a particularly relevant temperature scale, base on the ideal gas thermometer

We will see later on, in Chapter 4, that the Second Law of Thermodynamics allows the introduction of an absolute temperature scale, independent of any thermometric substance and in agreement with the ideal gas scale.

2.3 The gas thermometer

In the gas thermometers, the thermometric property is the pressure p measured at constant volume. Different gases have different behaviours; however the differences progressively reduce when the rarefaction increases (say when the density decreases) This experimental observation led to introduce the abstract idea of *ideal gas* , conceived as the limit towards which all gases tend when sufficiently rarefied.

To obtain a temperature value independent of the type of gas, the pressure p of a given gas is measured for different decreasing values of density (say for different decreasing values of the pressure p_0 measured at a fixed point of temperature); the p value is then extrapolated for $p_0 \rightarrow 0$. The extrapolation for different gases converges to the same value p/p_0, which is said to be the ideal gas value. (Fig. 2.3, left).

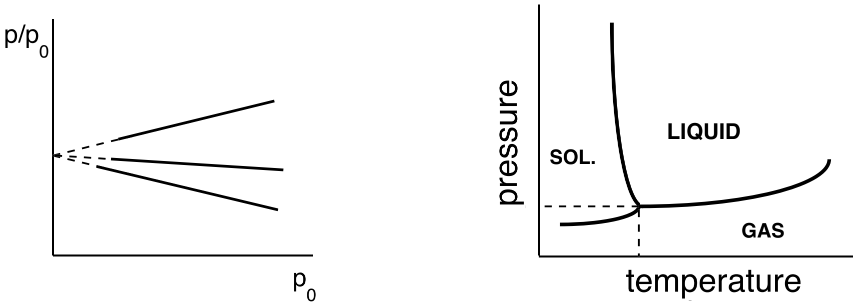


Figure 2.3: The gas thermometer. Left: the ratio p/p_0 of three different gases tends to the same value when $p_0 \to 0$, say when the gases become more and more rarefied. Right: state diagram of water: the triple point ($T = 273.16\,\mathrm{K}$, $p = 611.73\,\mathrm{Pa}$) corresponds to the coexistence of the two phases solid, liquid and gaseous.

The temperature of the ideal gas thermometer is defined as

$$\theta = 273.16 \lim_{p_0 \to 0} \frac{p}{p_0} \tag{2.1}$$

where p_0 is, by convention, the pressure measured when the thermometer is thermal in equilibrium with water at its triple point (Fig. 2.3, right). The triple point of a substance is defined as the thermodynamic state in which the three phases solid, liquid and gaseous are in equilibrium (Chapter 22). The ideal gas temperature scale is thus based on a single fixed point.

Note 1: The gas thermometer cannot measure all possible temperatures. Actually, at sufficiently low temperatures all gases transforms to liquids and at sufficiently high temperatures become ionised. In particular, for the gas thermometers it makes no sense to speak of zero temperature.

Note 2: The ideal gas temperature θ coincides, within the range of possible superposition, with the absolute temperature T to be introduced as a consequence of the Second Law of Thermodynamics (Chapter 4). As we will see, the fundamental relations of equilibrium Thermodynamics, such as $dU = TdS - pdV$, are based on the use of absolute temperature.
The unit of absolute temperature, and also of the gas thermometer temperature, is the kelvin (symbol K).

Note 3: The fusion and boiling points of water at room pressure (1 bar) are 273.15 and 373.15 K, respectively. The Celsius scale corresponds to the kelvin scale to within a constant 273.15: $\theta(^\circ\mathrm{C}) = \theta\,(\mathrm{K})$-273.15.

Note 4: The scales of thermometers different from the gas thermometer (thermocouples, thermistors, resistance thermometers, etc.) are not linear with respect to the absolute scale, and have to be calibrated with reference to the gas thermometer.

2.4 Thermal equation of state

According to experience, the thermodynamic coordinates necessary to define the state of a system are linked to the temperature by a functional relation.
For a simple substance, whose state is described by the two values of pressure an volume (p, V), the thermal equation of state is a function like the following

$$f(p, V, \theta) = 0\,. \tag{2.2}$$

For an ideal gas the thermal equation of state is

$$pV = nR\theta \quad \text{or more generally} \quad pV = nRT\,, \tag{2.3}$$

where
n is the number of moles,
$R \simeq 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is the gas constant
, θ is the ideal gas temperature defined by (2.1) and measured in kelvin
T is the absolute temperature, to be introduced in Chapter 4.

For other simple substances (real gases, solids, liquids) the thermal equation of state assumes different forms and is generally less simple.
If other thermodynamic coordinates are necessary to describe the state of the system (for example to describe magnetic or electric properties), the thermal equation of state will include also these new coordinates.

2.5 Microscopic interpretation of temperature

The temperature has been above defined in relation to the equilibrium properties of thermodynamic systems and some operative criteria for its measurements have been given. This purely macroscopic approach will be further improved with the introduction of the absolute temperature in Chapter 4 and is fundamental for both this Part I and the following Part II.

Since the first acceptance of the atomic theory a microscopic interpretation of temperature has been sought for. The first result was obtained by J.K. Maxwell in the middle of the XIX Century with the kinetic model of the ideal gas (see Chapter 30). In the model, the temperature is proportional to the average kinetic energy of the translational motion of the gas molecules; the temperature is thus interpreted as the quantity that measures the microscopic "degree of thermal motion".
Within the model, Maxwell calculated also the distributions of the velocities and of the kinetic energies of the ideal gases and found that when the temperature increases the distributions become broader.

The interpretation of the temperature based on the ideal gas kinetic model is intuitive but somewhat limited. How can the interpretation in terms of thermal motion be extended to solid or liquid atomic aggregates ? And which is the meaning of temperature when the thermal motion becomes negligible and other types of energy become significant, as for magnetic systems at low temperatures (to be considered in Chapter 19) ?

An exhaustive answer to the problem is given by the statistica theory developed by L. Boltzmann and J.W. Gibbs at the end of the XIX Century, which will be considered in Part III.
To grasp the basic idea, let us consider a thermodynamic system maintained in contact with a reservoir at constant temperature; the energy of the system is not constant but fluctuates around an average value (corresponding to the macroscopic internal energy) according to a distribution law which is called *canonical* (Capters 14 and**??**). The temperature measures the dispersion of the distribution of the system energy: the higher the system temperature, the broader the distribution.
As we will see in Chapter 16, the mathematical formalism of the canonical distribution can be applied also to the statistic of particles (atoms and molecules), confirming the Maxwell distribution of velocities and energies of the ideal gas (Fig. 16.3).

Chapter 3

The First Law of Thermodynamics

For a long time, up to the middle of the XIX Century, thermal phenomena were interpreted by considering heat as an indestructible substance. The work production in thermal engines was explained in terms of the transfer of heat from a hot to a cold body, by analogy with the production of work in hydraulic machines due to the transfer of water from a higher to a lower level.

Th possibility of converting heat into work and viceversa was hypothesised by Rumford at the end of the XVIII Century. In the first half of the XIX Century the intuitions of the german physician Mayer, the many experiments of the non-professional scientist Joule and the systematic work of Helmholtz led to conceiving heat as a form of energy, like mechanical work, and to define the mechanical equivalent of the heat unit.

The introduction of the concept of intern energy by Clausius in the middle of the XIX Century led to the expression of the First Law of Thermodynamics in its definitive form.

The parallel evolution of Thermodynamics and Electromagnetism in the first half of the XIX Century greatly contributed to the enlargement of the fields of application of the concept of energy, which had been already well established in Mechanics.

3.1 Internal energy, work and heat

To introduce the First Law of Thermodynamics we will neglect the historical development and will rely on a modern approach.

3.1.1 Adiabatic work

Let us consider a system enclosed by adiabatic walls (defined in § 2.1) and let the state of the system be defined by a given number of thermodynamical coordinates (in the simplest cases by the pair pressure-volume p, V).

The First Law of Thermodynamics states:

> *When an adiabatic system undergoes a transformation from an initial equilibrium state i to a final equilibrium state f, the work W_{ad} performed on the system only depends on the initial and final states and not on the intermediate states.*

Example: Let us consider, within a thermally insulated vessel, a system s consisting in a fluid, a mechanical stirrer and an electric resistor (reproducing one of the Joule experiments). The transformation of the system from an initial state i to a final state f can be obtained in different ways, for example varying the velocity of the stirrer or the intensity of the electrical current. One can see that, within the accuracy of the experiment, the work performed on the system is independent of the procedure of the transformation.

Note: It is not always possible to perform a transformation from a state i to a state f adiabatically, say by the only exchange of work between the system and its ambient. However, if the adiabatic transformation i to f is impossible, the experience shows that the inverse adiabatic transformation f to i is possible.

It is wort remembering that the validity of the First Law of Thermodynamics depends, more than on its direct experimental verification, on the verification of all the laws that are derived from it.

3.1.2 Internal energy

Since the adiabatic work is independent on the details of the transformation connecting the i and f equilibrium states, a state function U (called *internal energy*) can be defined such that its variation ΔU is equal to the adiabatic work:

$$W_{\mathrm{ad}} \;=\; U_f - U_i \;=\; \Delta U\,. \tag{3.1}$$

Eq. (3.1) shows that the variation ΔU can be obtained by measuring the adiabatic work W; the absolute value of the internal energy U can thus only be known to within an arbitrary additive constant.

The dependence of U on the thermodynamical coordinates cannot be inferred form the Laws of Thermodynamics; it can be only obtained from experiment or from theoretical models.

Note 1: Eq. (3.1) holds independently of whether the adiabatic transformation $i \to f$ be reversible or irreversible. The expression of the adiabatic work as a function of the thermodynamic coordinates can be different, or even impossible, for different transformations connecting the same i and f states.

Note 2: Given two equilibrium states i and f of a system, not always are both adiabatic transformations $i \to f$ and $f \to i$ possible. Always possible are anyway the adiabatic transformations in which the internal energy u increases.

Note 3: The term "energy" comes from the ancient greek *enèrgheia* = force, effectiveness.

3.1.3 Heat

Let us again consider two equilibrium states i and f of a given system. The difference of internal energy $\Delta U = U_f - U_i$ can be measured by means of (3.1) say by means of an adiabatic transform. Let us now remove the thermal insulation of the walls and perform the $i \to f$ transformation avoiding any exchange of work between the system and its ambient, so that $W = 0$.

The *quantity of heat* Q absorbed by the system is defined as the energy absorbed when the work is zero, and is equal to the variation of interna energy:

$$Q = \Delta U \qquad (W = 0). \tag{3.2}$$

Note 1: Also (3.2), like (3.1), holds independently of whether the adiabatic transformation $i \to f$ be reversible or irreversible.

Note 2: The notion of quantity of heat precedes historically the statement of the First Law. The definition (3.2) is based on the well known esperiments of Joule on the equivalence between heat and work.

3.1.4 Caloric equation of state

In § 2.4 we introduced the *thermal equation of state* that establishes a connection between the thermodynamic coordinates of a system. For a simple system, the thermal equation of state has the form

$$f(p, V, \theta) = 0. \tag{3.3}$$

One can now introduce a second equation, the *caloric equation of state*, which consists in expressing the interna energy as a function of the independent thermodynamic coordinates. For a simple system, the caloric equation of state has the form

$$U = U(p, V, \theta). \tag{3.4}$$

The knowledge of both equations of state, thermal and caloric, of a given system corresponds to the knowledge of all its thermodynamical properties.

Example: Let us consider an ideal gas, . Its thermal equation of state $pV = nR\theta$, based on experiment, has been introduced in § 2.4.

The properties of an ideal gas can be reproduced by the kinetic model, according to which at sufficiently low density one can neglect the forces of interaction between the molecules and the corresponding potential energy is null. For a monatomic ideal gas, in particular, the internal energy is the sum of the translational kinetic energies of single atoms; one can demonstrate that the internal energy is proportional to the temperature and that the caloric equation fo state of a monatomic ideal gas can be written as

$$U = \frac{3}{2} nR\theta = \frac{3}{2} N k_B \theta \,, \tag{3.5}$$

where n is the number of moles, $R \simeq 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is the gas constant, N isthe number of atoms, $k_B \simeq 1.381 \cdot 10^{-23}$ J K^{-1} is the Boltzmann constant and θ is the temperature measured in kelvin.

It is worth noting the peculiarity of the ideal gas model, where the internal energy is only of kinetic nature, and is then absolutely defined, without arbitrary additive constants.

3.2 Conservation of energy

For every transformation, reversible or irreversible, of whichever thermodynamical system, the First Law can be written as

$$\boxed{\Delta U = W + Q} \tag{3.6}$$

and corresponds to the energy balance of the system: the energy of a system can be exchanged as heat or work or both; it cannot never be created nor destroyed.

Note: Here and in the following we consider as positive the amounts of energy (heat or work) absorbed by a system and negative the amounts o energy (heat or work) emitted by the system. This choice is motivated mainly by symmetry reasons. Be careful that elsewhere different conventions can be adopted; in elementary introductions the work is often positive when performed *by* the system; in Chemistry the heat produced by a reaction is often considered as positive.

3.2.1 Isolated systems

If a system is isolated and cannot exchange nor heat nor work with its ambient, eq. (3.6) bocomes

$$\boxed{\Delta U = 0} \qquad \text{(sistema isolato)}. \tag{3.7}$$

Eq. (3.7) states the principle of *conservation of energy* for isolated systems.

Note: In an isolated system the total internal energy is conserved independently of whether the system undergoes reversible or irreversible transformations (contrary to what happens in Mechanics, where macroscopic mechanical energy can be reduced as a consequence of dissipative forces). As we will see in Chapter ch:pr2, as a consequence of the Second Law of thermodynamics a further function of state can be defined, the entropy, which is conserved only in reversible transformation on isolated systems.

3.2.2 Differential form

The internal energy U is by definition a function of state and can thus be formally expressed as a function of the thermodynamical coordinates of the system, e.g. $U(p, V)$, even if the explicit form of the caloric equation of state $U(p, V)$ cannot be deduced from the laws of Thermodynamics.

Since the interna energy is a function of the thermodynamical coordinates, its differential dU exists.

The heat Q and the work W, on the contrary, arn't functions of the state of the system; they are different forms of energy transferred between a system and its ambient, and their amount depends on the type of transformation between the initial and final equilibrium states. A sa consequence, exact differentials dQ and dW *don't exist* !

The differential form of (3.6) is generally expressed as

$$\boxed{dU = đW + đQ} \tag{3.8}$$

where by the symbol đ one conventionally indicates an infinitesimal quantity that is not a differential. It is worth noting anyway that, even if the infinitesimal quantities $đW$ and $đQ$ are not exact differentials, their sum dU always is.

As (3.6), also (3.8) holds for whichever transformation, reversible or irreversible.

Note: As the differentials dW and dQ are meaningless, also the use of ΔW and ΔQ for finite quantities should be avoided, since the Δ symbol is used to indicate finite variations of a function..

3.2.3 Work in qusi-static transformations

The intermediate states of *quasi-static transformations* approximate equilibrium states, for which one can attribute definite values to the thermodynamic coordinates. Therefore in a quasi-static transformation the work W can be expressed as a function of the system coordinates; as a general expression

$$đW = \sum\nolimits_i Y_i dX_i\,, \qquad \text{(only for quasi-static transformations !)} \tag{3.9}$$

where Y_i and X_i are conjugate coordinates, intensive and extensive, respectively. As an example, for the quasi-static expansion of a gas $đW = -p\,dV$.
A more detailed discussion of work will be made in § 3.4.

Note: As we will see in Chapter 4, as a consequence of the Second Law a new extensive coordinate, the entropy S, will be introduced, which will allow one to express also the infinitesimal heat exchanged in a quasi-static transformation as the product of two thermodynamic coordinates, $đQ = T\,dS$.

3.3 Microscopic intrpretation

In the previous sections, the internal energy and the principle of its conservation in isolated systems have been introduced according to the classical approach developed in the middle of the XIX century. This approach is simple and elegant and doesn't require any details on the nature of the system considered.
However, the atomic structure of matter is well known since a long time, so that it is useful to try to establish a connection between the thermodynamical internal energy and the various forms of energy present in matter at the microscopic level.
To this aim, in this § 3.3 we will begin from the Mechanics of macroscopic systems, where one can define an internal energy too, to transfer the the same formalism to system formed by a very large number of atoms. By this procedure il will be possible not only to give an interpretation of the thermodynamical internal energy, but also of the difference between heat and work.

3.3.1 Internal energy in Mechanics

In macroscopic Mechanics, if all the forces acting on the diverse parts of a system, both internal and external, are *conservative*, from the Principles of Dynamics one can derivate the law of conservation of mechanical energy, $E_{\text{tot}} = \text{cost}$.
It is convenient to express the total mechanical energy of a system as the sum of four terms:

$$E_{\text{tot}} = E_{k,0} + E_{k,cm} + E_{p,i} + E_{p,e} = \text{const} \tag{3.10}$$

where:

- $E_{k,0}$ is the kinetic energy *of the* center of mass (cm) of the system;
- $E_{k,cm}$ is the total kinetic energy of the motion of the different parts of the system *relative to* the center of mass;
- $E_{p,i}$ is the total potential energy of the forces internal to the system;
- $E_{p,e}$ is the total potential energy of the force fields external to the system.

In Mechanics, one can define the *internal energy* of a system as the sum of the kinetic energy relative to the center of mass and the potential energy of the internal forces:

$$E_{\text{int}} = E_{k,cm} + E_{p,i}\,. \tag{3.11}$$

In the reference system of the center of mass, the mechanical work W performed on the system by the external forces is equal to the variation of the internal energy:

$$W = \Delta E_{\text{int}}. \tag{3.12}$$

Example: Let us consider a macroscopic mechanical system formed by two bodies connected by a perfectly elastic spring. The internal energy is $E_{\text{int}} = E_{k,cm} + E_{p,el}$, where $E_{k,cm} = \mu v^2/2$ and $E_{p,el} = kx^2/2$: μ is the reduced mss, v the relative velocity of the two bodies, k the elastic constant and x the spring elongation. The work W of (3.12) is the work performed on the spring.

If the forces internal to the system are not conservative, it is impossible to define a potential energy $E_{p,i}$ and it is impossible to define an internal energy E_{int}. In this case, the work performed on the system doesn't depend solely on the initial end final states of the system.

Example: Let us consider the compression work performed on a real spring (not perfectly elastic). The work cannot be completely recovered when the spring expands to the initial state. The amount of mechanical energy sissipated depends on the conditions under which the compression is mad (for example on the temperature).

The transformations of conservative systems are reversible; the transformations of dissipative systems are irreversible. One can associate the mechanical reversibility to the conservation of mechanical energy.

3.3.2 Microscopic interpretation of internal energy, heat and work

A thermodynamical system is formed by a huge number of elementary constituents. It is natural to seek for an interpretation of internal energy, heat and work in terms of the microscopic properties of the system.

Internal energy

The mechanical internal energy (3.11) corresponds to the thermodynamical internal energy U:

$$E_{\text{int}} = E_{k,cm} + E_{p,i} = U\,. \tag{3.13}$$

Let us rewrite (3.10) enlightening the relation between the total energy E_{tot} and the thermodynamic internal energy U:

$$E_{\text{tot}} \;=\; E_{k,0} \;+\; U \;+\; E_{\text{p,ext}}\,. \tag{3.14}$$

The potential energy of external fields $E_{\text{p,ext}}$ doesn't refer solely to the gravitational field; examples concerning the magnetic and electric fields will be considered in § 3.6 and 3.7.

The conservation of energy in isolated systems expressed by the First Law of Thermodynamics can be traced back to the conservation of energy in the fundamental interactions (gravitational, electromagnetic, weak nuclear, strong nuclear) between the elementary constituents of matter, which in turn can be deduced from the invariance of the physical law with respect to the time translations.

Heat and work

The difference between heat and work can be traced back to a microscopic interpretation too. At the microscopic level, the exchange on energy between a system and its ambient is always due to interactions between atoms or molecules of the system and atoms and molecules of the ambient. Microscopic forces perform microscopic work on single atoms or molecules.

At the macroscopic level one distinguishes heat and work as two different forms of energy transfer. The *work* W corresponds to an energy transfer macroscopically ordered, that can be expressed as the product of a macroscopic force by a macroscopic displacement.
The *heat* Q corresponds to an energy transfer macroscopically disordered, that cannot be expressed in terms of macroscopic forces and displacements.

The difference between heat and work is further clarified by statistical considerations (see Chapter 15): the work is connected to variations of the energy levels of the system, the work is connected to variations of the populations of the energy levels.

3.4 Thermodynamic work

In introductory treatments of Thermodynamics, one generally considers only the compression or expansion work of a substance, whose properties are summarised in the next § 3.4.1.
To allow for a thermodynamical treatment of all possible systems, it is necessary to extend the expression of work; for example, one should consider the magnetisation work or the work of polarisation of a dieletric or the work of surface tension and so on. In the § 3.4.2 the concept of *generalised work* will be introducd.

3.4.1 Compression and expansion work

For a thermodynamic system immersed in an ambient at a pressure p_{ext}, the compression work done by the ambient on the system is

$$đW = -p_{\text{ext}}\, dV\,, \qquad W = -\int_i^f p_{\text{ext}}\, dV\,, \tag{3.15}$$

where V is the volume of the system, i and f are te initial and final states, respectively. The infinitesimal work $đW$ done on the system is positive when the volume of the system is reduced, $dV < 0$.

If the transformation is quasi-static, the pressure p of the system is equal to the external pressure $p = p_{\text{ext}}$, so that the compression work done by the ambient on the system can be expressed as a function of the system pressure p

$$đW = -p\, dV\,, \qquad W = -\int_i^f p\, dV\,. \tag{3.16}$$

The quasi-static work done by the system on its ambient is

$$đW_{\text{sys}} = -đW = p\, dV\,, \qquad W_{\text{sys}} = -W = \int_i^f p\, dV\,. \tag{3.17}$$

To calculate the integrals of (3.16) and (3.17), it is necessary to know the dependence of p on V along the transformation connecting the i and f states. The thermodynamical equilibrium state of a simple system is identified by the values of two variables, for example (V, θ). It is thusnecessary to knowthe values of the two coordinates (V, θ) in the initial and final states $i \equiv (V_i, \theta_i)$ and $f \equiv (V_f, \theta_f)$, respectively, as well as along the transformation, in order to calculate the integral

$$W = -\int_i^f p(V, \theta)\, dV\,. \tag{3.18}$$

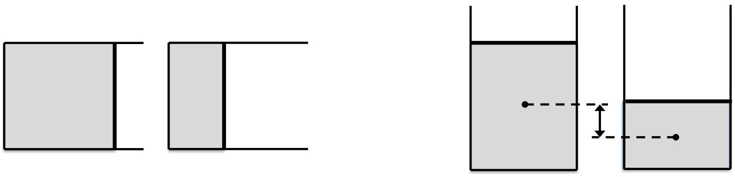


Figure 3.1: Compression of a gas enclosed in a cylinder with a piston. Left: the piston slides horizontally. Right: The piston slides vertically..

(?) Calculate the integral (3.18) for an ideal monatomic gas for different reversible transformations (isothermal, isobar, adiabatic), choosing suitable initial and final states for each transformation.

(?) Consider again an ideal gas, choose two initial and final states $i \equiv (V_i, \theta_i)$ and $f \equiv (V_f, \theta_f)$, respectively, and calculate the integral (3.18) along different reversible transformations connecting the two states.

3.4.2 Generalised work

The expression of work can be generalised in the form

$$đW = \xi \, dX \tag{3.19}$$

where

ξ is the *generalised force*, and is generally an intensive quantity;
X is the *generalised coordinate*, and is generally an extensive quanity.

For the compression work considered above, $\xi = -p_{\text{ext}}$ and $X = V$; for quasi-static transformations, $\xi = -p_{\text{ext}} = -p$ (pressure of the system).

In many cases, it can be necessary to consider contemporarily different forms of work, in addition to the compression work. The quasi-static work is thus expressd as

$$\begin{aligned} đW = \sum_i \xi_i \, dX_i &= -p \, dV + đW^* \\ &= -p \, dV + \sum_i \xi_i^* \, dX_i^* \, , \end{aligned} \tag{3.20}$$

where the star * labels the work forms different from the compression work.

To conclude Capter 3, let us consider some particularly interesting cases. In § 3.5 we study the energy balance for the compression of an ideal gas performed in different ways. We consider then two cases of generalised work: the magnetisation work (§ 3.6) and the polarisation work of a dielectric substance (§ 3.7).

3.5 Transformations of an ideal gas

Let us consider a particularly simple system: a gas contained in a cylinder with a piston (Fig. 3.1). The thermodynamic system here considered is the gas, while the container (cylinder plus piston) is considered as part of the ambient. The equilibrium thermodynamic state of the gas is identified by two coordinates, pressure p and volume V. To simplify the calculations, let the gas by approximated by a monatomic ideal gas, for which the two state equations hold, the thermal one (2.3) and the caloric one (3.5)

$$pV = nR\theta \, , \qquad U = \frac{3}{2} nR\theta \, , \tag{3.21}$$

where the temperature θ is measured in kelvin.
We want now to check the conservation of energy expressed by (3.6) and (3.8). To this aim, let us consider a compression that reduces the volume of the gas from an initial value V_i to a final value $V_f = V_i/2$ (Fig. 3.1, left) and let us examine different possible types of tranforrmation.

3.5.1 Reversible compression

In order to be reversible, a transformation has to be quasi-static and free from friction. This is obviously ad ideal situation. To approximate a quasi-static transformation, the difference between the pressure of the gas and of its ambient should be infinitesimal; in practice, one should slowly and progressively modify the external pressure in order to accompany the variation of the internal pressure of the gas.

The reversible compression work is given by (3.18)

$$W = -\int_{V_i}^{V_f} p(V,\theta)\, dV\,. \tag{3.22}$$

The evaluation of the integral depends on the form of the $p(V,\theta)$ function, that in turn depends on the modality of the transformation. Let us consider a particularly simple case.

If the compression is isothermal, say if the gas has a good thermal contact with the ambient at constant temperature θ, using the thermal equation of state $pV = nR\theta$ one easily calculates the compression work

$$W = -nR\theta\, \ln(V_f/V_i) = nR\theta\, \ln 2\,. \tag{3.23}$$

From the caloric equation of state for the monatomic ideal gas $U = 3nR\theta/2$ one gets that if $\Delta\theta = 0$ also $\Delta U = 0$. As a consequence, from (3.6) one gets $Q = -W$. The energy entering the system as work outgoes entirely as heat.

If the reversible transformation is reversed, the gas expands and the compression work is completely recovered as expansion work done by the system on its ambient.

3.5.2 Quasi-static compression with friction

Let us now suppose that in the quasi-static compression from V_i to $V_f = V_i/2$ friction forces cannot be neglected. To the compression work W considered above the work W_a against the friction forces has to be added, so that the total work done on the system is

$$W_{\text{tot}} = W + W_a = nR\theta\, \ln 2 + W_a\,. \tag{3.24}$$

For an isothermal transformation of the ideal gas $\Delta U = 0$: the entire energy entering the system as work $W + W_a$ (positive) outgoes as heat $Q + Q_a$ (negative) where $Q = -W$ and $Q_a = -W_a$ is the heat dissipated by the system in the ambient due to friction.
Viceversa, for the ambient the work done on the system is $-W - W_a$ (negative) and the absorbed heat is $-Q - Q_a$ (positive). See Fig. 3.2, left.

Let us now reverse the transformation, so that the gas expands quasi-statically from V_f to $V_i = 2V_f$. The system (the gas) recovers its initial state, the expansion work $W' = -W = nR\theta\, \ln(V_f/V_i) = -nR\theta\, \ln 2$ done on the ambient is negative and the heat absorbed $Q' = -Q = -W'$ is positive. However, due to the friction, the system has to do a further work $W'_a = -W_a$ (negative) absorbing the corresponding heat $Q'_a = -Q_a$ (positive) from the ambient; the work against friction is in turn dissipated as heat $Q_a = -Q'_a = -W_a$ into the ambient. In total, heat and work exchanged by the system are exactly the opposite as in the compression transformation; the heat Q'_a absorbed from the ambient is transformed into work and then finally returned as heat to the ambient. See Fig. 3.2, center.

Let us now consider an entire cycle composed by the compression and the expansion of the gas. The system (gas) returns to its initial state of volume V_i and temperature θ. On the contrary, the ambient doesn't return to its initial state: globally, it does a net work $-W_a$ against friction and

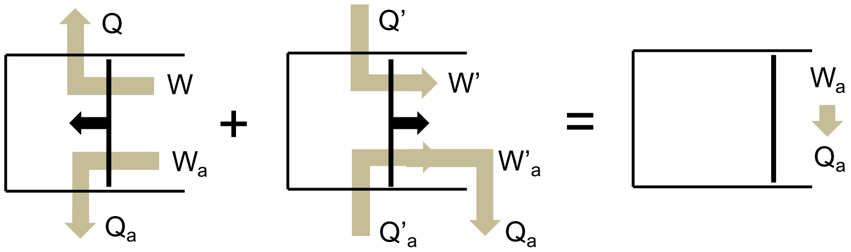


Figure 3.2: Quasi-static isothermal transformations of an ideal gas with friction. Left: compression. Center: expansion. Right: final result after the gas has come back to its initial state.

absorbs a net quantity of heat Q_a. A quantity of work is thus transformed into heat. See Fig. 3.2, right.
Both transformations, compression and expansion, even if quasi-static, are not reversible: when the system returns to its initial state, its ambient doesn't (see again the definition of reversibility in § 1.3).

3.5.3 Irreversible spontaneous compression

Let us now suppose that the initial pressure p_i of the gas is half of the ambient pressure $p_{\text{ext}} = 2p_i$ and that the piston in maintained in a fixed position by a pin. When the pin is removed, the piston is free to move and the gas is compressed until it a reaches a pressure equal to the external pressure, $p_f = p_{\text{ext}}$. The transformation is not quasi-static due to the difference between internal and external pressures. The piston is initially accelerated, then it oscillates around the position of equilibrium corresponding to $p_f = p_{\text{ext}}$; the oscillations are progressively damped and at the end the piston stops.
The compression work is now given by (3.15)

$$W = -\int_i^f p_{\text{ext}}\, dV = -p_{\text{ext}}\, \Delta V\,, \tag{3.25}$$

where the second equality holds if the external pressure stays constant during the transformation. If the transformation is isothermal, the internal energy doesn't vary, $\Delta U = 0$; the energy entering as work outgoes as heat also in this case.

The transformation is irreversible. One cannot recover the initial state of both the gas and its ambient without the external interventions.

3.5.4 Effect of an external field

Let us revert to the isothermal reversible compression of an ideal monatomic gas. Contrary to the previous case (Fig. 3.1, left), the piston now slides in vertical direction (Fig. 3.1, right), so that we should consider the gravity field too.

The *total energy* of the system (say of the gas) is the sum of the kinetic energy of its center of mass $E_{k,0}$, the thermodynamical internal energy U and the potential energy of the external field of gravity $E_{\text{p,ext}} = mgh$, where m labels the mass of the gas and h the height of its center of mass with respect to a reference plane:

$$E_{\text{tot}} \;=\; E_{k,0} \;+\; U \;+\; E_{\text{p,ext}}\,. \tag{3.26}$$

The kinetic energy $E_{k,0}$ has no thermodynamic relevance; we can assume $E_{k,0} = 0$.
For an infinitesimal quasi-static compression, the variation of the total energy is

$$dE_{\text{tot}} \;=\; dU + dE_{\text{p,ext}}\,, \tag{3.27}$$

where $dE_{\rm p,ext} = mg\,dh$.
The infinitesimal compression work is

$$đW = -p\,dV = -p'\,dV - mg\,dh\,, \tag{3.28}$$

where p is the gas pressure, p' is the external pressure (including the effect of the piston weight), $-mg\,dh$ is the contribution due to the gas weight (a volume force); all terms in (3.28) are positive. According to the Firs Law, since for an isothermal transformation of an ideal gas the variation of internal energy is zero, $dU = 0$, the energy balance can be expressed as

$$0 \;=\; dU \;=\; đQ + đW \;=\; đQ - p\,dV \;=\; đQ - p'\,dV - mg\,dh\,. \tag{3.29}$$

Since $mg\,dh = dE_{\rm p,ext}$, the heat exchanged by the gas is

$$đQ \;=\; p\,dV \;=\; p'\,dV + mg\,dh \;=\; p'\,dV + dE_{\rm p,ext} < \;0\,. \tag{3.30}$$

The energy entering as work outgoes as heat. The incoming work can be decomposed in the two contributions of the external pressure and of the force of gravity.

3.6 Magnetisation work

A particularly interesting case of generalised work is the magnetisation work, which is here shortly presented and will be treated in more detail in Part IV, devoted to magnetism and low temperatures.

Let us consider a solenoid of length ℓ and section A, made by N turns through which and electrical current I passes (Fig. 3.3, left). To avoid mathematical complications, let us suppose that the magnetic field is confined within the solenoid, uniform and parallel to the axis of the solenoid. Let us also consider negligible the electrical resistance, in order to neglect the irreversible dissipation of energy.
Our aim is the study of the properties of the magnetic field created by the current I first in the vacuum and then in a material system inserted into the solenoid , in order to calculate the thermodynamical work of magnetisation.

3.6.1 Magnetic field in vacuum

Let us first consider the case of vacuum inside the solenoid.
The intensity of the magnetic field is measured by the magnetic induction vector $\vec{\mathcal{B}}$. Let us introduce since now the vector $\vec{\mathcal{H}}$ (magnetising field), that plays a relevant role in the case of the magnetism of matter.
For the unidimensional case here considered, we can confine ourselves to a purely scalar treatment

$$\mathcal{B} = \mu_0\,\mathcal{H} = \mu_0\,n\,I\,, \tag{3.31}$$

where

- the magnetic induction$\mathcal{B}$ is measured in tesla (T) or in gauss (G), $1\,\mathrm{T} = 10^4\,\mathrm{G}$;
- $\mu_0 = 4\pi \times 10^{-7}$ T m/A is the magnetic permeability in vacuum;
- $n = N/\ell$ is the number of turns for unit length of the solenoid;
- the magnetising field $\mathcal{H} = nI$ is measured in A/m.

Electromagnetic induction

A variation of the current I in a solenoid induced a counter-electromotive force

$$\mathcal{F} \;=\; -\frac{d\Phi_{\mathcal{B}}}{dt} \;=\; -NA\,\frac{d\mathcal{B}}{dt} \;=\; -\,L\,\frac{dI}{dt}\,, \tag{3.32}$$

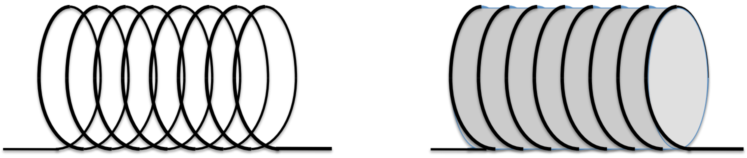


Figure 3.3: Left: a solenoid in vacuum. Right: a material bar is inside the solenoid.

where $\Phi_{\mathcal{B}}$ is the total flux of magnetic induction inside the solenoid and $L = \Phi_{\mathcal{B}}/I$ is the solenoid inductance. In vacuum, $L = n^2\mu_0\ell A = n^2\mu_0 V$, where V is the volume inside the solenoid.
Let us suppose that initially a current I passes in the turns of the solenoid, generating an induction field $\mathcal{B}$; an increment dI of the current induces and increment dB of the induction field; correspondingly, the electrical generator has to do an infinitesimal work $\text{đ}W$ against the counter-electromotive force in the time dt:

$$\text{đ}W \;=\; -\mathcal{F}\, I\, dt \;=\; NAI\, d\mathcal{B} \;=\; L\, I\, dI\,. \tag{3.33}$$

According to (3.31), in vacuum $I = \ell\mathcal{B}/\mu_0 N$, so that (3.33) becomes:

$$\text{đ}W \;=\; \frac{V}{\mu_0}\,\mathcal{B}\, d\mathcal{B} \tag{3.34}$$

Magnetic energy in vacuum

In vacuum, according to (3.33) and (3.34) and taking into account (3.31), the work necessary to increment the current and the induction field can be expressed in the different equivalent forms

$$\text{đ}W_{\text{vac}} \;=\; L\, I\, dI \;=\; \mu_0 V \mathcal{H}\, d\mathcal{H} \;=\; \frac{1}{\mu_0} V\mathcal{B}\, d\mathcal{B}\,. \tag{3.35}$$

By integrating (3.35) one can calculate the work necessary to increase the electric current from zero to a value I. Such a work corresponds to the magneto-static energy stored in vacuum within the solenoid:

$$E_{\text{vac}} \;=\; \frac{1}{2}\, L\, I^2 \;=\; \frac{1}{2}\,\mu_0 V\, \mathcal{H}^2 \;=\; \frac{1}{2\mu_0}\, V\, \mathcal{B}^2\,, \tag{3.36}$$

where $V = \ell A$ is the volume of the solenoid. Dividing he last member of (3.36) by V one obtains the well known expression of the energy density of a magneto-static field.
Let us stress that in vacuum the two fields $\mathcal{H}$ and $\mathcal{B}$ are equivalent, to within the constant μ_0.

Example: A magnetic induction field $\mathcal{B} = 0.1\,\mathrm{T} = 1000\,\mathrm{G}$ in vacuum corresponds, according to (3.31), to a magnetising field $\mathcal{H} \simeq 8{\times}10^4$ A/m.
Let us suppose that the cylindric volume inside the solenoid of Fig. 3.3 ris $V = 1$ dm^3. According to (3.36), the magneto-static energy stored by the field in vacuum lis $E_{\text{vac}} \simeq 4\,\mathrm{J}$.
Let us further suppose that the height of the cylinder is $\ell = 1\,\mathrm{dm}$ and that the solenoid has $N = 100$ turns. According to (3.31), the current is $I \simeq 80\,\mathrm{A}$.

3.6.2 Magnetic field in matter

Let us introduce, inside the solenoid, a cylindrical and homogeneous matter bar occupying exactly the volume $V = \ell A$ (Fig. 3.3, right). By effect of the induction field generated by the electrical current, the bar is magnetised. The magnetisation intensity is measured by the magnetisation density $\mathcal{M}$, say the magnetic moment per volume unit, measured in A/m (the same unit as for the magnetising field $\mathcal{H}$).
The magnetisation of the matter bar modifies the induction field $\mathcal{B}$. The magnetising field $\mathcal{H} = nI$, that only depends on the free current in the turns of the solenoid, remains unaffected.

The magnetisation density $\mathcal{M}$ is linked to the magnetising field $\mathcal{H}$ by the relation

$$\mathcal{M} = \chi_m \mathcal{H} \tag{3.37}$$

where χ_m is the magnetic susceptibility (a-dimensional) of the material by which the bar is made. Let us consider here the two simplest cases:

a) *Diamagnetism:* the magnetisation of the material is due to the distortion of the electronic orbitals induced by the magnetic field. Diamagnetism is present in all materials and gives rise to a negative susceptibility, $\chi_m < 0$, independent of temperature. The ratio between $\mathcal{M}$ and $\mathcal{H}$ is thus independent of temperature too.

b) *Paramagnetism:* the magnetisation is due to the orientation of atomic or molecular magnetic dipoles already present in the material. Only a number of substances are paramagnetic. Paramagnetism gives rise to a positive susceptibility (§ 18.1), whose value is generally much higher than the absolute value of the diamagnetic susceptibility; in paramagnetic materials then$\chi_m > 0$.
The paramagnetic susceptibility decreases when the temperature increases: the magnetic field favours the orientation of the magnetic dipoles, the temperature contrasts it. The relation between $\mathcal{M}$ and $\mathcal{H}$ is thus dependent on temperature.

Only paramagnetism is thermodynamically relevant, since magnetisation depends on temperature. It is worth noting that the paramagnetic susceptibility is some orders of magnitude smaller than unity: $\chi_m \simeq 10^{-5} \div 10^{-3}$ at room temperature.

As a consequence of the magnetisation of matter, the trivial relation (3.31) between induction $\mathcal{B}$ and magnetising $\mathcal{H}$ fields, valid in vacuum, has to be modified to take into account the contribution of the matter magnetisation to the induction field $\mathcal{B}$:

$$\mathcal{B} = \mu_0(\mathcal{H} + \mathcal{M}) = \mu_0(1 + \chi_m)\mathcal{H}\,. \tag{3.38}$$

In (3.38) the magnetising field $\mathcal{H} = nI$ represents again the effect of the current of free charges in the solenoid turns, while $\mathcal{M}$ represents the effect of the magnetisation currents, localised at the atomic level inside matter.

Example: Let us consider again the previous example, where the induction field in vacuum was $\mathcal{B} = 0.1$ T, and insert in the solenoid a cylinder of a paramagnetic material with susceptibility $\chi_m = 10^{-4}$. If the current I is unaltered, so that also the magnetising field $\mathcal{H}$ is unaltered, one can calculate from (3.38) that the relative variation of the induction field $\mathcal{B}$ amounts to 0.01 %. For a paramagnetic system, induction field and magnetising field can be with a good approximation exchanged (obviously to within the constant μ_0).

Note: The magnetic properties of matter can give rise to phenomena by far more complicated than paramagnetism. In Part V, devoted to phase equilibrium and phase transitions, we will hint at the phenomenon of ferromagnetism (§ 22.5). We only stress here that the difference between $\mathcal{B}$ and $\mathcal{H}$, negligible for diamagnetic and paramagnetic materials, is instead relevant for ferromagnetic materials.

3.6.3 Magnetisation work

Let us now consider the material bar as a thermodynamic system and calculate the work necessary for its magnetisation.

To this aim, let us first note that equations (3.32) to (3.33) concerning the electromagnetic induction are of general validity and can be applied also to the case of the material bar inside the solenoid. To calculate the work necessary to increment the current in the solenoid one can start from (3.33): the current I is directly connected to the magnetising field, so that $NAI = V\mathcal{H}$; let us stress that (3.31) and (3.34), valid in vacuum, are not in matter.

By further substituting $d\mathcal{B}$ in (3.33) according to (3.38) one obtains

$$đW = \mu_0 V\mathcal{H}d\mathcal{H} + \mu_0 V\mathcal{H}d\mathcal{M} \;=\; \underbrace{\mu_0 V\mathcal{H}d\mathcal{H}}_{\text{vacuum}} \;+\; \underbrace{\mathcal{H}\,dM}_{\text{matter}}, \tag{3.39}$$

where in the last equality the total magnetisation $M = \mu_0 \, V \, \mathcal{M}$, that is an extensive variable, has been introduced (the factor μ_0 has been included M for convenience).
In the last member of (3.39):

a) The first term $\mu_0 V \mathcal{H} d\mathcal{H} = đW_{\mathrm{vac}}$ is the infinitesima work necessary to increase the magnetic field in vacuum, already considered in (3.35); this term has no thermodynamic relevance since it is not referred to the thermodynamic system here considered, say the material bar. Its integral is given by (3.36).

b) The second term $\mathcal{H}\, dM = đW_{\mathrm{mag}}$ ris the infinitesimal work necessary to modify the magnetisation of the bar, that is the thermodynamic system here considered. The *magnetisation work* is thus

$$\boxed{W_{\mathrm{mag}} \;=\; \int_i^f \mathcal{H}\, dM \;=\; \mu_0 V \int_i^f \chi_m \, \mathcal{H}\, d\mathcal{H}} \tag{3.40}$$

For paramagnetic materials the susceptibility χ_m depends on temperature, so that the integral depends on the intermediate states of the transformation.

The total work $W_{\mathrm{vac}} + W_{\mathrm{mag}}$ is done by the electric generator that supplies the current to the solenoid, as can be inferred from (3.32) and (3.33).

Example: Let us consider again the previous example, with $V = 1\,\mathrm{dm}^3$. We have seen that in vacuum the work necessary to obtain an induction field $\mathcal{B} = 0.1\,\mathrm{T}$ is $W_{\mathrm{vac}} \simeq 4\,\mathrm{J}$, corresponding to the energy E_{vac} stored in the magneto-static field in vacuum.
Let us now calculate the work W_{mag} by means of (3.40) and assuming a magnetisation at constant temperature, with constant susceptibility $\chi_m = 10^{-4}$. It is easy to verify that $W_{\mathrm{mag}} \simeq \chi_m W_{\mathrm{vac}}$. The work W_{mag} is four orders of magnitude smaller than W_{vac}.

Magnetic systems and the First Law of Thermodynamics

According to the First Law, considering the expression (3.19) of the generalised work, the differential variation of the interna energy of a magnetic system is

$$dU = đQ + đW = đQ - p dV + \mathcal{H} dM \,. \tag{3.41}$$

In the energetic balance (3.41), the term $dW_{\mathrm{vac}} = \mu_0 V \mathcal{H} d\mathcal{H}$ is absent, since it has no influence on the thermodynamic properties of the system (the material bar).
The magnetic energy stored in vacuum is anyway part of the total energy. In the general expression (3.14), it contributes to the term $E_{\mathrm{p,ext}}$, say to the potential energy of the external fields.

3.7 Polarisation work

Let us consider a capacitor with flat parallel surfaces of area A at distance ℓ, having a surface density of electric charge σ_{free} (Fig. 3.4, left). Inside the capacitor the electric field is uniform and directed perpendicular to the surfaces (we neglect for simplicity the border effects).
We want to study the properties of the electric field generated by the density of charge σ_{free} first in vacuum and then in a dielectric material inserted in the capacitor, in order to calculate at the end the polarisation work of the dielectric.

3.7.1 Electric field in vacuum

In vacuum one can indifferently use the electric field vector $\mathcal{E}$ or the electric displacement vector $\mathcal{D}$:

$$\mathcal{E} = \frac{\mathcal{D}}{\epsilon_0} = \frac{\sigma_{\mathrm{free}}}{\epsilon_0} \,, \tag{3.42}$$

where

ϵ_0 is the electrical susceptibility of vacuum, lthe electric displacement $\mathcal{D} = \sigma_{\text{free}}$ is measured in C/m^2.

Since the problem is unidimensional, we use the scalar notation.

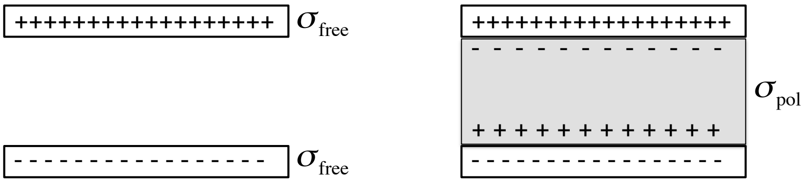


Figure 3.4: Left: charged capacitor in vacuum. Right: the same charged capacitor with a dielectric inserted between the surfaces.

3.7.2 Electric field in matter

Let us now insert a dielectric material between the surfaces of the capacitor (Fig. 3.4, right) and let the dielectric be the thermodynamic system.
The effect of the electric field is the polarisation of the dielectric, measured by the polarisation vector $\mathcal{P}$, corresponding to the moment of electric dipole per volume unit, and measured in cC/m^2 (the same unit as the electric displacement).
The polarisation per unit volume $\mathcal{P}$ is connected to the electric field $\mathcal{E}$ by

$$\mathcal{P} = \chi_e \, \epsilon_0 \, \mathcal{E} \tag{3.43}$$

where χ_e is the electric susceptibility (a a-dimensional quantity).

Let us consider two cases:

a) The polarisation is due to the deformation of the electrons distribution is atoms: this effect is present in all dielectrics. The electric susceptibility $\chi_e > 0$ is independent of temperature.
b) The polarisation is due to the orientation of permanent electric dipoles, and concerns only substances where such permanent dipoles are present. The corresponding contribution to the electrical susceptibility $\chi_e > 0$ is inversely proportional to the temperature: the electric field favours the orientation of the electric dipoles, the temperature opposes to it.

Only the second case is thermodynamically relevant, since it gives rise to a polarisation that is dependent on temperature.

As an effect of the polarisation, the electric field becomes

$$\mathcal{E} = \frac{1}{\epsilon_0}(\sigma_{\text{free}} - \mathcal{P}) = \frac{1}{\epsilon_0}(\mathcal{D} - \mathcal{P}) \tag{3.44}$$

In (3.44) the electric displacement $\mathcal{D}$ again represents the density of free charges on the capacitor surfaces, while $\mathcal{P}$ represents the density of polarisation charge on the dielectric faces.
There is a similarity between the treatments of magnetisation and polarisation, the field $\mathcal{D}$ corresponding to the field $\mathcal{H}$, the field $\mathcal{E}$ corresponds to the field $\mathcal{B}$.
For historical reasons the similarity is however not complete. Actually, to (3.38) it corresponds, for the case of polarisation,

$$\mathcal{D} = \epsilon_0 \mathcal{E} + \mathcal{P} = \epsilon_0 \, (1 + \chi_e) \, \mathcal{E} = \epsilon \, \mathcal{E} \, , \tag{3.45}$$

where $\epsilon = \epsilon_0(1 + \chi_e)$ is the electrical permittivity of the dielectric substance (the ratio $\epsilon_r = \epsilon/\epsilon_0 = 1 + \chi_e$ is the dielectric constant).

3.7.3 Polarisation work

Let us consider the dielectric as a thermodynamic system and calculate the work necessary for its polarisation.
The infinitesimal work required to increase the charge on the capacitor is

$$đW = \mathcal{E}\,\ell\,dq = \mathcal{E}\,\ell\,A\,d\sigma_{\text{free}} = \mathcal{E}\,V\,d\mathcal{D}\,, \tag{3.46}$$

where V is the volume fo the dielectric.
By substituting $d\mathcal{D}$ according to (3.45) one gets

$$đW = \epsilon_0\,V\,\mathcal{E}\,d\mathcal{E} + \mathcal{E}\,V\,d\mathcal{P} \;=\; \underbrace{\epsilon_0\,V\,\mathcal{E}d\mathcal{E}}_{\text{vacuum}} + \underbrace{\mathcal{E}\,dP}_{\text{polar.}} \tag{3.47}$$

where in the last equality the total polarisation $P = V\mathcal{P}$ (an extensive variable) has been introduced.

in the last member of (3.47):

a) $\epsilon_0 V\mathcal{E}d\mathcal{E}$ is the infinitesimal work required to increase the electric field in vacuum; this term has no thermodynamic relevance, since it doesn't refer to the thermodynamic system here considered. Its integral for the entire charge of the condenser is

$$W_{\text{vac}} = V\,\epsilon_0 \int_0^{\mathcal{E}} \mathcal{E}'\,d\mathcal{E}' = \frac{1}{2}\,V\,\epsilon_0\,\mathcal{E}^2\,. \tag{3.48}$$

b) $\mathcal{E}\,dP$ is the infinitesimal work required to increase the polarisation of the dielectric, say of the thermodynamic system. The *polarisation work* is thus

$$W_{\text{pol}} = \int_i^f \mathcal{E}\,dP\,. \tag{3.49}$$

For materials If the polarisation is due to the orientation of permanent dipoles, the susceptibility χ_e depends on temperature, cso that the polarisation work depends on the intermediate states of the transformation.

According to the First Law, the differential of the internal energy of a dielectric is

$$dU = đQ + đW = đQ - pdV + \mathcal{E}dP\,. \tag{3.50}$$

(?) Find the relation between the results of the above discussion and the well known result of electro-static theory according to which the energy density of the electric field in the dielectric is $\epsilon\,\mathcal{E}^2/2$.

Chapter 4

The Second Law of Thermodynamics

The historical development that led to the statement of the Second Law began with the attempts at improving the performances of heat engines. The discovery of the conservation of energy (First Law) allowed in 1850-1851 the expression of the Second Law in a definitive form (for more historical details see Appendix **??**).

In this chapter the Second Law and its consequences (Carnot theorem, absolute temperature, Clausius theorem and inequality, entropy) are introduced according to the traditional method based on cyclic transformations. In Part II a more general axiomatic approach based on the properties of system will be introduced.

4.1 The heat–work conversion

As a starting point, it is convenient to introduce some general properties of the cyclic heat engines and of the refrigerating cycles, useful to understand the statements of the Second Law and to discuss ints consequences.

4.1.1 Cyclic heat engines

A heat engine is a device that can transform a quantity of heat Q into work W through a cyclic transformation of a suitable substance, typically a fluid. A heat engine is a thermodynamical system; during each cycle, a heat engine

- absorbs and gives heat by contact with its surroundings;
- does and receives work by mechanical interactions with its surroundings.

In a cyclic engine, the system returns periodically in the same thermodynamical state; the variation of the internal energy at the end of each cycle is null, $\Delta U = 0$; as a consequence, according to the First Law the energy balance for each cycle is

$$\Delta U = \sum Q_i + \sum W_i = 0 \qquad \text{(for one cycle)} \tag{4.1}$$

where $\sum Q_i$ and $\sum W_i$ are the total quantities of heat and work exchanged by the system with its surroundings during one cycle.

In (4.1) the prescription is maintained of considering as positive both heat and work entering into the system. In what follows, to avoid possible misunderstandings, we will use also the indices "in" and "out" to label the quantities of heat and work incoming and outgoing, respectively.

In order that a cyclic device could be considered an engine, the neat quantity of work produced has to exceed the neat quantity of work absorbed in each cycle:

$$|W_{\mathrm{out}}| - |W_{\mathrm{in}}| > 0\,, \tag{4.2}$$

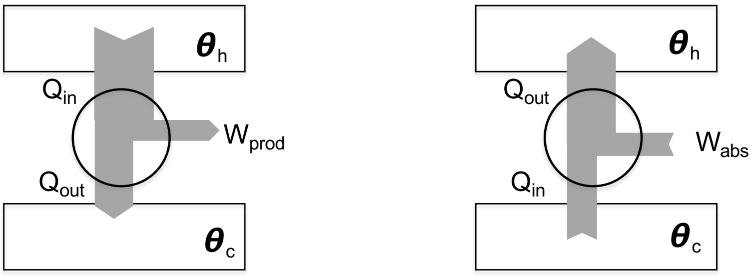


Figure 4.1: Schematic representation of the energy fluxes in a cyclic heat engine (left) and of a refrigerator (right) that operate between two reservoirs at the temperatures $\theta_h > \theta_c$. The rectangles represent the reservoirs, the circle represents the cyclic device.

an so, to satisfy (4.1), the neat quantity of heat absorbed has to exceed the neat quantity of heat given in each cycle:

$$|Q_{\rm in}| - |Q_{\rm out}| > 0\,. \tag{4.3}$$

The neat quantity of useful work produced by an engine in each cycle is thus

$$|W_{\rm useful}| = |W_{\rm out}| - |W_{\rm in}| = |Q_{\rm in}| - |Q_{\rm out}|\,. \tag{4.4}$$

The *efficiency* of a heat engine is defined as:

$$\eta \;=\; \frac{|W_{\rm useful}|}{|\,Q_{\rm in}|} \;=\; \frac{|\,Q_{\rm in}| - |\,Q_{\rm out}|}{|\,Q_{\rm in}|} \;=\; 1 \;-\; \frac{|\,Q_{\rm out}|}{|\,Q_{\rm in}|}\,. \tag{4.5}$$

One easily verifies that the efficiency η of heat engines is necessarily included between 0 and 1.

To focus the attention on the main thermodynamic properties, the heat engine is conveniently schematised as a device that absorbs heat $|Q_{\rm in}| = |Q_{\rm h}|$ from a single reservoir at high temperature θ_h and gives heat $|Q_{\rm out}| = |Q_{\rm c}|$ to a single reservoir at a lower temperature θ_c, per cui $\theta_h > \theta_c$ (Fig. 4.1, left).

A reservoir is by convention a system whose thermal capacity is so large that one can neglect the variations of its thermodynamical state when it exchanges heat with other systems. The temperature of a reservoir is thus constant.

Considering only two reservoirs is not a limitation for the statement of the Second Law and the study of its consequences. From the technical and historical points of view this choice is motivated because in the classical heat engine the exchanges of heat take place in the two processes of evaporation and condensation of water, corresponding to transformations which are contemporarily isothermal and isobaric.

4.1.2 Cyclic refrigerators and heat pumps

A **refrigerator** is a device that extracts heat from a system by means of a cyclic thermodynamic transformation of a suitable substance, typically a fluid. Also a refrigerator, like a heat engine, absorbs and gives energy as both heat and work. The energy balance of each cycle is again expressed by (4.1).

For a refrigerator, the schematisation in terms of two reservoirs is particularly realistic. The refrigerator absorbs heat $|Q_{\rm in}| = |Q_{\rm c}|$ from a volume at low temperature θ_c (a cold room) and emits heat $|Q_{\rm out}| = |Q_{\rm h}|$ to an ambient at higher temperature θ_h (Fig. 4.1, right).

During every cycle the refrigerator absorbs a neat quantity of work

$$|W_{\rm abs}| = |W_{\rm in}| - |W_{\rm out}|\,. \tag{4.6}$$

Since in a cycle $\Delta U = 0$, according to the First Law

$$|Q_{\rm out}| \;=\; |Q_{\rm in}| \;+\; |W_{\rm abs}|\,. \tag{4.7}$$

The *efficiency of a refrigerator* is the ratio between the heat extracted from the system to be cooled and the neat absorbed work:

$$\omega_{\text{fri}} = \frac{|Q_{\text{in}}|}{|W_{\text{abs}}|} = \frac{|Q_{\text{in}}|}{|Q_{\text{out}}| - |Q_{\text{in}}|} . \tag{4.8}$$

The efficiency of a refrigerator can in principle assume any value equal or larger than zero.

A **heat pump** is a refrigerating device that absorbs heat $|Q_{\text{in}}|$ at low temperature θ_c from the exterior of a building and gives heat $|Q_{\text{out}}|$ at a higher temperature θ_h to the interior of the building: it is thus a device useful for heating houses. Il *coefficient of performance of a heat pump* is the ratio between the heat given to the ambient to be heated and the neat work absorbed:

$$\omega_{\text{pump}} = \frac{|Q_{\text{out}}|}{|W_{\text{abs}}|} = \frac{|Q_{\text{out}}|}{|Q_{\text{out}}| - |Q_{\text{in}}|} . \tag{4.9}$$

The coefficient of performance of a heat pump can in principle assume any value equal or larger than zero.

Note: A single device can be used to heat houses in winter and to cool them in summer, running as a heat pump in winter and as a refrigerator in summer.

4.2 Statements of the Second Law

Two different statements of the Second Law were proposed independently by R. Clausius in 1850 and by W. Thomson, lord Kelvin, in1851.

Second Law: Kelvin statement

> *It is impossible to make a cyclic transformation whose unique result is the conversion to work of heat absorbed from a unique reservoir.*

The Kelvin statement (Fig. 4.2, left) asserts the unfeasibility of a heat engine having efficiency $\eta = 1$ (say with $|Q_{\text{out}}| = 0$). According to the Kelvin statement the efficiency of all real heat engines is $\eta < 1$.

Second Law: Clausius statement

> *It is impossible to make a cyclic transformation whose unique result is the transfer of heat from a system at a given temperature to a system at an higher temperature.*

The Clausius statement (Fig. 4.2, right) asserts the impossibility of a refrigerator that doesn't require the input of work from external sources (say with $|W_{\text{abs}}| = 0$). The efficiency ω cannot be infinite.

Equivalence of the two statements

One can easily demonstrate that the two statements of Kelvin and Clausius of the Second Law are equivalent.

Were the Kelvin statement false, one could build an heat engine with efficiency $\eta = 1$. The work so produced could be used to power a refrigerator. The sum of the two devices would be a device violating the Clausius statement.

Were the Clausius statement false, one could transfer heat from a cold to a hot reservoir without the need of external work. The transferred heat could be used as input of a heat engine. The sum of the two devices would be a device violating the Kelvin statement.

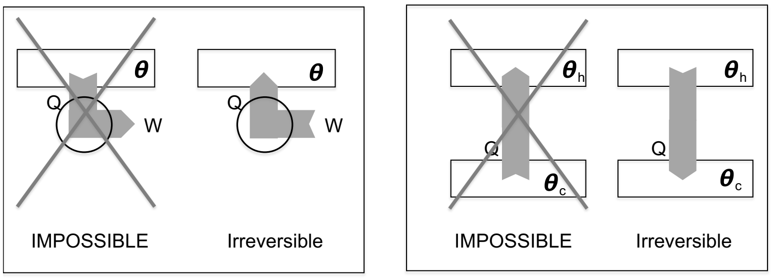


Figure 4.2: Second Law of Thermodynamics: schematic representation of the statements of Kelvin (left) and Clausius (right).

Irreversibility of natural processes

The two statements of Kelvin and Clausius can be interpreted in terms of the irreversibility of natural spontaneous processes.

It is common experience that it is always possible to convert a given amount of work into heat given to a single reservoir (for example by dissipating work through friction or for Joule effect in electrical circuits). The *Kelvin statement* affirms that the dissipation of work into heat is an irreversible process (Fig. 4.2, left).

It is common experience that heat spontaneously flows from a body at a given temperature to a body at a lower temperature. The *Clausius statement* affirms that the flow of heat from a hot body to a cold body is an irreversible process (Fig. 4.2, right).

More generally, it is possible to demonstrate that, as a consequence of the Second Law, all spontaneous natural phenomena are irreversible. Some examples:

- transformations of mechanical or electrical work into heat or into internal energy of a reservoir;
- expansion of gases against lower pressures;
- spontaneous transfers of heat between different systems or within a system;
- chemical reactions;
- diffusion processes.

A detailed analysis can be found, for example, in Zemansky, Chapter 8.

4.3 Carnot theorem, thermodynamic temperature

Sadi Carnot (1753-1823), in his theroetical reserach on the efficiency of heat engines, focused his attention on the engines that exchange heat with only two reservoirs, one at high temperature θ_h, the other at low temperature θ_c (actually, this was not an abstract hypothesis, since vapour engines really work between two temperatures). Besides, Carnot distinguished reversible and irreversible transformations, and fixed his attention on the general properties of the reversible transformations.

4.3.1 Carnot cicle

Generalising the results obtained by Carnot, by *Carnot cycle* we mean whichever cyclic transformation

a) that is reversible (say quasi-static and without friction)
b) that requires only two reservoirs

independent of the system involved (a simple substance, a magnetic system, a dielectric system, a chemical mixture, and so on). The Carnot cycle thus doesn't exclusively refer to heat engines.

Since only two reservoirs are involved, a Carnot cycle is necessarily made by four transformations:

a) two reversible isotherms at the temperatures θ_h and θ_c, during which the system exchanges heat with one of the two reservoirs,
b) two reversible adiabatics, during which the system is transferred from one reservoir to the other without exchanging heat with the ambient.

For a simple substance, whose thermodynamic state is described by only two thermodynamic coordinates (e.g. p and V), the representation of a Carnot cycle on the pV plane depends on the type of substance. In the case of an *ideal gas* the reversible isotherms and the reversible adiabatics are represented by the particularly simple equations $pV =$ costant and $pV^\gamma =$ constant, respectively ($\gamma = c_p/c_v$ is the ratio between the specific heats at constant pressure and volume, and its value is $5/3$ and $7/5$ for monatomic and bi-atomic gases, respectively).
Being reversible, the same Carnot cycle can be performed both clockwise (engine) or anticlockwise (refrigerator) in the pV plane.

Below we will introduce the thermodynamic temperature T and the state function entropy S (§ 4.4); the Carnot cycle assumes a particularly simple form in the TS plane, equal for all systems.

The Carnot cycle, made by reversible transformations, is actually an ideal cycle that cannot be realised in practice. However, it represents a fundamental theoretical instrument of Thermodynamics and can anyway be quite well approximated in many cases.

4.3.2 Carnot theorem

A first consequence of the Second Law of Thermodynamics is the *Carnot theorem*:

> *All reversible cycles operating between two reservoirs (at temperatures θ_h and θ_c, respectively) share the same efficiency, independent of the substance that represents the thermodynamic system.*

The theorem had been initially demonstrated by Carnot within the framework of the caloric theory, as a consequence of the impossibility of the "perpetuum mobile", say of the impossibility, in modern terms, of creating energy from nothing.
In 1850 Clausius succeeded in deriving the theorem from the Second Law. The demonstration is as follows. Let us consider two Carnot cycles A and B operating as heat engines between the same two reservoirs. Let us suppose that the Carnot theorem is false, for example that cycle A has higher efficiency than cycle B ($\eta_A > \eta_B$). Since the cycles are reversible by hypothesis, one run the cycle B, having smaller efficiency, backwards. The global result would violate the Second Law.

4.3.3 Absolute thermodynamic temperature

According to the Carnot theorem, for whichever thermodynamic system the efficiency of a reversible cycle that exchanges heat with two reservoirs only depends on the temperatures θ_h and θ_c of the reservoirs and is independent of the peculiarities of the system. The efficiency (4.5) is thus a function of the two temperatures:

$$\eta_{\text{rev}} \;=\; 1 - \frac{|Q_c|}{|Q_h|} \;=\; f(\theta_h, \theta_c)\,, \tag{4.10}$$

so that event the ratio $|\,Q_c|/|\,Q_h|$ is a function of the temperatures of the two reservoirs:

$$\frac{|Q_c|}{|Q_h|} \;=\; \phi(\theta_h, \theta_c)\ . \tag{4.11}$$

W. Thomson, lord Kelvin, understood that, on the grounds of (4.11), a new temperature scale could be introduced, the absolute thermodynamic scale, whose thermometric property is the heat exchanged by whichever system in a Carnot cycle.

For a demonstration, let us consider three reservoirs at the temperatures $\theta_1, \theta_2, \theta_3$, respectively. Between each one of the three pairs of reservoirs let a Carnot cycle to operate. For the three cycles (4.11)) gives

$$\frac{|Q_1|}{|Q_2|} = \phi(\theta_1, \theta_2)\,, \qquad \frac{|Q_2|}{|Q_3|} = \phi(\theta_2, \theta_3)\,, \qquad \frac{|Q_1|}{|Q_3|} = \phi(\theta_1, \theta_3)\,. \tag{4.12}$$

Multiplying the first two equations and eliminating $|Q_2|$ one obtains

$$\phi(\theta_1, \theta_2)\, \phi(\theta_2, \theta_3) = \phi(\theta_1, \theta_3)\,, \tag{4.13}$$

say

$$\phi(\theta_1, \theta_2) = \frac{\phi(\theta_1, \theta_3)}{\phi(\theta_2, \theta_3)}\,. \tag{4.14}$$

Since (4.14)) has to be valid for whichever value of θ_3, the functions at the numerator and denominator can be factorised as products of a new function $T(\theta)$:

$$\phi(\theta_1, \theta_3) = T(\theta_1)\, T(\theta_3)\,, \qquad \phi(\theta_2, \theta_3) = T(\theta_2)\, T(\theta_3)\,, \tag{4.15}$$

so that from (4.12), (4.14) and (4.15), one obtains

$$\frac{|Q_1|}{|Q_2|} = \phi(\theta_1, \theta_2) = \frac{T(\theta_1)\, T(\theta_3)}{T(\theta_2)\, T(\theta_3)} = \frac{T(\theta_1)}{T(\theta_2)}\,. \tag{4.16}$$

The function $T(\theta)$ introduced in (4.15) allows the introduction of a new temperature scale, the *thermodynamic temperature*, operatively defined by the two properties:

a) $T_f c/T_c h = |\,Q_f c|\,/\,|\,Q_h|$ for whichever Carnot cycle as a consequence of (4.16);
the scale of the thermodynamic temperature is defined in terms of a ratio, then to within an arbitrary multiplicative constant.

b) T =273.16 K at the triple point of water (by convention);
this convention avoids eliminates the arbitrariness of the multiplicative constant and attributes to the triple point of water the same value of the ideal gas scale (§ 2.3).

The thermodynamic temperature T is “absolute” because

- it cannot assume have values, being the ratio of two positive values of heat quantities;
- is independent of the thermometric substance.

Being independent of the thermometric substance, the thermodynamic scale has an universal validity.

The scale of absolute temperatures T (also called Kelvin scale) coincides with the ideal gas scale θ in the temperature interval where a gas thermometer can be used. Actually, if one considers the Carnot cycle of an ideal gas composed by two reversible isotherms at the temperatures θ_1 and θ_2 and two reversible adiabatics, one can easily verify that $|Q_1|/|Q_2| = \theta_1/\theta_2$, whence $T_1/T_2 = \theta_1/\theta_2$.

(?) Demonstrate the relation $|Q_1|/|Q_2| = \theta_1/\theta_2$ pfor the Carnot cycle of an ideal gas.

By exploiting the relation $T_c/T_h = |\,Q_c|\,/\,|\,Q_h|$, the efficiency of a Carnot cycle can be expressed as a function of the thermodynamic temperatures of the two reservoirs. For the heat engine, the refrigerator and the heat pump one has, respectively,

$$\eta \;=\; 1 \;-\; \frac{T_c}{T_h}\,, \qquad \omega_{\rm fri} \;=\; \frac{T_c}{T_h - T_c}\,, \qquad \omega_{\rm pump} \;=\; \frac{T_h}{T_h - T_c}\,. \tag{4.17}$$

Be anyway careful: equations (4.17) refer to the ideal case of the Carnot cycle (by definition reversible) and represent thus limiting values: one speaks of ideal efficiencies.In the real cases the efficiency values are necessarily smaller, in some cases even dramatically smaller.

Note: The absolute thermodynamic temperature is one of the seven base quantities of the International System of Units (SI). Its unit is the kelvin (symbol: K). Up to 2019 the kelvin was defined as the fraction 1/273.16 of the thermodynamic temperature fo the triple point of water. In 2019 new definitions of all the base quantities have been defined. The kelvin is now defined as a function of the Boltzmann constant, to which an exact value has been attributed. We will return to this topic in Part III, dedicated to Statistical Thermodynamics, where the Boltzmann constant will be introduced.

4.3.4 Carnot theorem and irreversible cycles

The Carnot theorem can be extended to the comparison between reversible and irreversible cycles operating between two temperatures T_h and T_c.

> *Of all the possible cycles operating between two reservoirs at different temperatures, irreversible cycles have smaller efficiencies that reversible cycles.*

For a demonstration, let us consider two cycles A (irreversible) and B (reversible) operating between the same two reservoirs and let to suppose, by contradiction, that the irreversible cycle A has an efficiency higher than the reversible cycle B ($\eta_A > \eta_B$). Since B is reversible, it can be operated backwards. One can easily see that the sum of the two devices would violate the Second Law.

Eq. (4.17) can thus be generalised by substituting the equality $=$ (valid only for reversible cycles) with a disequality $\leq$.

Heat engine

For a heat engine the thermodynamic efficiency η is superiorly limited by the relation

$$\eta \;=\; \frac{|W_{\text{useful}}|}{|Q_{\text{in}}|} \;\leq\; 1 \;-\; \frac{T_c}{T_h}\,. \tag{4.18}$$

Since typically T_c is the ambient temperature, the efficiency η can only be increased by increasing the temperature of the hot source T_h.

(?) Let be $T_c = 293\,\text{K}$; plot η_{max} as a function of T_h.

Example: In an internal combustion engine temperatures of the order of $T_h \simeq 3000$ K can be reached. The ideal efficiency of a Carnot cycle is thus $\eta \simeq$0.92. However, a real engine exchanges heat with more than two reservoirs; for example, a petrol-driven engine is generally approximated by an Otto cycle, formed by two adiabatic and two isocore (constant volume) transformations; the real cycle is anyway different even from the ideal Otto cycle Taking into account mechanical friction and other constraints of chemical origin, the efficiency of a typical real petrol-driven engine doesn't exceed generally the value 0.3.

Refrigerator

For a refrigerator the thermodynamic efficiency η is superiorly limited by the relation

$$\omega_{\text{fri}} \;=\; \frac{|Q_{\text{in}}|}{|W_{\text{ass}}|} \;\leq\; \frac{T_c}{T_h - T_c}\,. \tag{4.19}$$

Example 1: For domestic refrigerators generally $T_h \simeq 293$ K (room temperature). Let us suppose that the freezer should be maintained at a temperature $T_c = 253$ ($\simeq -20°$ Celsius): the maximum ideal efficiency $\omega_{\text{fri}} \simeq 6.3$; the real efficiency is smaller, due to mechanical friction in engine and compressor as well as to insulation losses.
The efficiency of a refrigerator is progressively reduced when the low temperature T_c is reduced. This makes difficult to obtain very low temperatures (see Chapter **??**).

Example 2: For air-conditioners generally $T_c \simeq 293$ K (room temperature). Let the outside temperature be $T_h = 303$ K: the maximum ideal efficiency is $\omega_{\text{fri}} \simeq 29$; the real efficiency is smaller due to mechanical friction as well as to insulation losses.

(?) Let be $T_h = 293\,\mathrm{K}$ (room temperature); plot the maximum efficiency $\omega_{\rm fri}$ of a refrigerator as a function of T_c. Compare the maximum efficiency for $T_c = 1\,\mathrm{K}$? and for $T_c = 0.1\,\mathrm{K}$.

(?) Let $T_c = 293\,\mathrm{K}$ (room temperature); plot the maximum efficiency $\omega_{\rm fri}$ of an air-conditioner as a function of the external temperature T_h.

Heat pump

For a *heat pump* the coefficient of performance is superiorly limited by the relation

$$\omega_{\rm pump} \;=\; \frac{|Q_{\rm out}|}{|W_{\rm ass}|} \;\leq\; \frac{T_h}{T_h - T_c}\,. \tag{4.20}$$

Example: For heat pumps used for heating houses, generally $T_h \simeq 293$ K ($\simeq 20°$ Celsius). Let the external temperature be $T_c = 273$ K: the maximum ideal coefficient of performance is $\omega_{\rm pump} \simeq 14.6$. The real coefficient is smaller, due to mechanical friction and to insulation losses; typical values are included between 2 and 4, depending on the value of T_c.

(?) Si ponga la temperatura dell'ambiente da riscaldare al valore $T_c = 293\,\mathrm{K}$ e si grafichi il coefficiente di prestazione massimo $\omega_{\rm cal}$ in funzione della temperatura esterna T_f.

4.3.5 Relevant comments

A

For historical and tutorial reasons, the Carnot theorem is generally explained with reference to heat engines, where the work W us purely mechanical, and by refrigerators, where the work W is typically electric.

Actually, the Carnot theorem has a general validity, independent of the type of system; the work W can thus have different origin, it can for example be magnetisation work or dielectric polarisation work or deformation work of an elastic body, and so on.

B

The Carnot theorem plays a fundamental role for deriving the consequences of the Second Law (see this § 4.3 and next § 4.4), for example the definition of thermodynamic temperature T and entropy S as well as the determination of the limits of efficiency of thermodynamical processes.

However, a Carnot cycle, composed by four reversible transformations, cannot be practically implemented. Even if mechanical friction could be eliminated at all, a basic problem remains for the implementation of a Carnot cycle. The two isothermal transformations require the exchange of heat between the system and the two reservoirs; reversibility requires in turn that the difference of temperature between system and reservoir be negligible. But the speed of heat transfer depends on the difference of temperature; as a consequence, the better are the reversibility conditions fulfilled, the slower is the heat transfer and the work production, say the smaller is the delivered power.

4.4 Clausius theorem.

The consequences of the Carnot theorem were further developed and generalised by Clausius, who introduced a new thermodynamic quantity, the *entropy*, that on the one hand is a new state function suitable to characterise the equilibrium state of a system, on the other allows one to measure the degree of irreversibility of thermodynamic transformations.

To better grasp the meaning of the Clausius theory, let us begin from the case of simple cycles operating between two temperatures (§ 4.4.1), and only afterwards consider the general cas (§ 4.4.2).

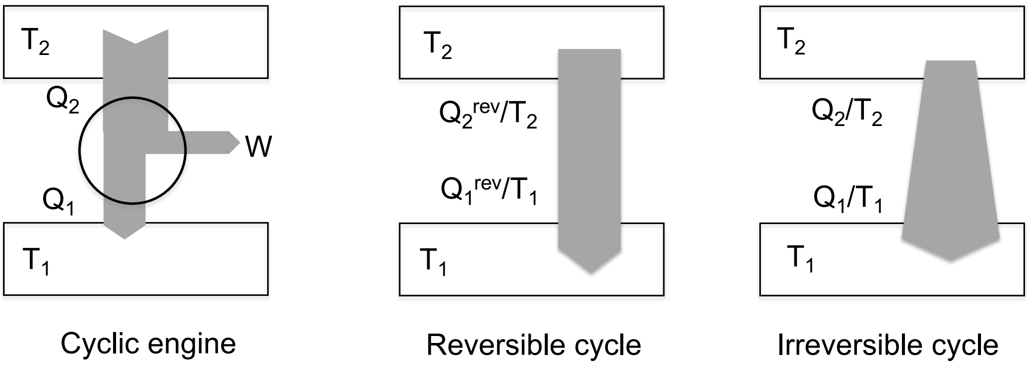


Figure 4.3: Schematic representations referring to the case of a cycle operating between two reservoirs. Left: heat and work fluxes in a cyclic engine. Center: flux of Q/T for a reversible cycle. Right: flux of Q/T for an irreversible cycle.

4.4.1 Clausius theorem, a particular case

Let us consider cyclic devices operating between two reservoirs, at temperatures T_1 and T_2, respectively, where $T_1 < T_2$.

Reversible cycles

Let us fist consider a Carnot cycle, by definition reversible (Fig. 4.3, left, where a cyclic engine is represented).

As a consequence of the Carnot theorem, the absolute thermodynamic temperature T (eq. 4.16) has been defined in such a way that

$$\frac{T_1}{T_2} = \frac{|Q_1^{\text{rev}}|}{|Q_2^{\text{rev}}|} \,. \tag{4.21}$$

From (4.21) one obtains

$$\frac{|Q_1^{\text{rev}}|}{T_1} = \frac{|Q_2^{\text{rev}}|}{T_2} \,. \tag{4.22}$$

While the heat quantities $|Q_1^{\text{rev}}|$ and $|Q_2^{\text{rev}}|$ are different (Fig. 4.3, left), equation (4.22) shows that the quantity $|Q^{\text{rev}}|/T$ is unchanged (Fig. 4.3, center).

Since the cycle is reversible, when the system exchanges heat with each one of the two reservoirs it has its same temperature, T_2 or T_1.

If we now focus aour attention on the cyclic device and take into account the sign of the heat quantities (positive when entering the system, negative when outgoing), since Q_1^{rev} and Q_2^{rev} have opposite signs, from (4.22) one gets

$$\frac{Q_1^{\text{rev}}}{T_1} + \frac{Q_2^{\text{rev}}}{T_2} = 0 \qquad \text{(reversible cycle)} \,. \tag{4.23}$$

At the end of every cycle, the algebraic sum of the heat quantities exchanged divided by the corresponding temperatures is zero.

Since we are considering reversible cycles, the same conclusion holds for refrigerating cycles.

If we focus our attention on the two reservoirs, we could say that the quantity $|Q|/T$ is transferred from the hot reservoir to the cold reservoir (Fig. 4.3, center).

Irreversible cycles

Let us now consider irreversible cycles and compare their behaviour with the behaviour of reversible cycles. It is now necessary to distinguish heat engines from refrigerators.

Let us first consider a *non reversible cyclic engine* and suppose that the heat quantity Q_2 absorbed from the hot reservoir is equal to the quantity of heat $Q_2^{\rm rev}$absorbed by the reversible engine. According to the Carnot theorem, the efficiency η of an irreversible engine operating between between two given temperatures is smaller than the efficiency of a reversible cycle operating between the same temperatures, $\eta_{\rm irr} < \eta_{\rm rev}$. It is thus easy to see that (Fig. 4.3, right)

$$\frac{|Q_1|}{|Q_2|} > \frac{|Q_1^{\rm rev}|}{|Q_2^{\rm rev}|} = \frac{T_1}{T_2} \quad \Rightarrow \quad \frac{|Q_1|}{T_1} > \frac{|Q_2|}{T_2}\,. \tag{4.24}$$

Let us now consider a *non reversible refrigerating cycle* and suppose that the heat quantity Q_1 absorbed from the cold reservoir is equal to the quantity of heat $Q_1^{\rm rev}$ absorbed by the reversible refrigerator. According to the Carnot theorem, the efficiency η of an irreversible refrigerator operating between between two given temperatures is smaller than the efficiency of a reversible cycle operating between the same temperatures, $\omega_{\rm irr} < \omega_{\rm rev}$. It is thus easy to see that

$$\frac{|Q_1|}{|Q_2|} < \frac{|Q_1^{\rm rev}|}{|Q_2^{\rm rev}|} = \frac{T_1}{T_2} \quad \Rightarrow \quad \frac{|Q_1|}{T_1} < \frac{|Q_2|}{T_2}\,. \tag{4.25}$$

Since we are considering irreversible transformations, it is important to remember that the temperatures T in (4.24) and (4.25) are the temperatures of the two reservoirs sono le temperature dei due serbatoi (only for reversible transformations the temperatures of the cyclic device during its different transformations are equal to the temperatures of the reservoirs).

To conclude, let us first focus our attention on the cyclic device (engine or refrigerator) and take into account the sign of the heat quantities exchanged; from (4.24) and (4.25) one obtains

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0 \qquad \text{(irreversible cycle)}\,. \tag{4.26}$$

At the end of each cycle, the algebraic sum of the quantities of heat exchanged by the system, divided by the temperatures of the reservoirs, is always negative.

Let us finally focus the attention on the two reservoirs, that together with the cyclic device are an isolated system. During an irreversible cycle of the device, the heat quantities exchanged by the reservoirs have opposite sign with respect to the heat quantities exchanged by the cyclic device. At the end of each cycle, the cyclic device (engine or refrigerator) returns to its initial state. The quantity $|Q|/T$ increases when heat is transferred from the hot to the cold reservoir through the cyclic device (Fig. 4.3, right).

We will consider again this particular case of the cyclic device operating between two reservoirs, once the function of state entropy will be introduced and its behaviour in irreversible transformations clarified (§ 4.5.2).

4.4.2 Clausius theorem, general case

The equality (4.23) and the inequality (4.26) for reversible and irreversible cycles, respectively, operating between two reservoirs can be generalised to thermodynamic systems undergoing whichever cyclic transformation and exchanging heat with the environment at more than two different temperatures.

Let us first consider a system M interacting with a number of other systems, to be considered as reservoirs of infinite heat capacity. Let Q_i be the heat quantity exchanged by the system M with the i-th reservoir at the temperature T_i. As usual, $Q-i$ is positive or negative according to whether it enters into the system M or goes out.

As a consequence of the Second Law one can demonstrate (see below) that (4.23) and (4.26) can be generalised as

$$\bigcirc \sum_i \left(\frac{Q_i}{T_i}\right) \;\leq\; 0\;, \tag{4.27}$$

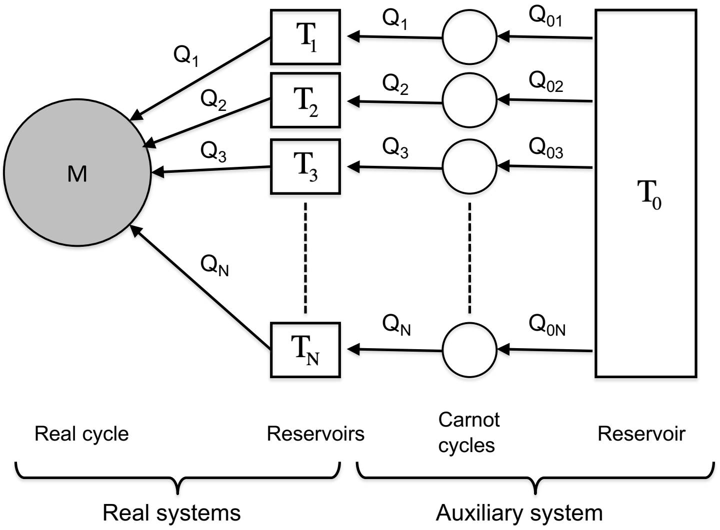


Figure 4.4: Schematic picture supporting the proof of the Clausius theoremwhen the system M exchanges heat with a finite number N of reservoirs at different temperatures T_i.

where the symbol $\bigcirc$ indicates a sum over a cyclic transformation of the system. The $=$ sign holds only for reversible cycles. It is worth remembering that in (4.27) T_i is the temperature of the i-th reservoir. Only for reversible transformations T_i is also the temperature of the system.

Equation (4.27) can be further generalised to the continuum case, where the system M exchanges infinitesimal quantities of heat $\text{đ}Q$ at different temperatures with its environment:

$$\oint \left(\frac{\text{đ}Q}{T}\right) \leq 0 . \tag{4.28}$$

As usual, the symbol $\oint$ indicates the integral over a closed path. Also in (4.28) the $=$ sign holds only if the cycle is reversible and T is the temperature of that part of the environment with which the system exchanges heat; only for reversible cycles T is the temperature of the system too.

Proof of the Clausius theorem

Let us consider a system M undergoing a cyclic transformation, reversible or irreversible. During the cycle, the system exchanges heat with a number of reservoirs at temperatures $T_1, T_2, \ldots, T_N$ (Fig. 4.4). Let Q_i be the heat quantity exchanged with the reservoir at the temperature; ss usual, $Q - i$ is positive or negative according to whether it enters into the system M or goes out.

Our goal is now to verify the sign of the sum

$$\bigcirc \sum_i \left(\frac{Q_i}{T_i}\right) . \tag{4.29}$$

To this aim, let us introduce an auxiliary system made by a reservoir at temperature T_0 connected to each one of the T_i reservoirs by a Carnot cycle (by definition reversible). The auxiliary Carnot cycles are such that each one exchanges with the corresponding reservoir T_i the same quantity of heat Q_i exchanged by the reservoir T_i with the system M.

Exploiting the property (4.23) for each one of the Carnot cycles and correctly taking into account the signs of the heat quantities, one can connect the total quantity of heat Q_0 absorbed by the Carnot cycles from the reservoir T_0 to the heat quantities Q_i absorbed by the system M:

$$Q_0 = \sum_i Q_{0i} = T_0 \sum_i \left(\frac{Q_i}{T_i}\right) , \tag{4.30}$$

(where the symbol $\bigcirc$ has been omitted for concision).
Let us now consider the global system (real system plus auxiliary system): the global results for a cycle is

- the neat absorption of a quantity of heat Q_0 from a single reservoir at a temperature T_0 (all T_i reservoirs are returned to their initial states),
- the absorption of a total work W, algebraic sum of the quantities of work absorbed by the system M and by each one of the Carnot cycles.

As a consequence of the First Law (the total interna energy is not varied in a cyclic transformation) and of (4.30) one gets

$$\Delta U = Q_0 + W = 0 \quad \Rightarrow \quad T_0 \sum_i \left(\frac{Q_i}{T_i}\right) + W = 0\,. \tag{4.31}$$

According to the Second Law it must be $W \geq 0$ (the neat work is made *on* the system). Actually, were $W < 0$, globally the system would produce work at the expenses of heat extracted from a single reservoir. Imposing then $W \geq 0$ in (4.31), one obtains equation (4.27):

$$\bigcirc \sum_i \left(\frac{Q_i}{T_i}\right) \;\leq\; 0\,. \tag{4.32}$$

The artefact of the reservoirs T_i having infinite heat capacity (say whose temperature is insensible to the exchanges of heat) can be overcome by decomposing the finite heat quantities Q_i into sums of infinitesimal quantities $đQ$, so that the sum of (4.32) is transformed into the integral of (4.28):

$$\oint \left(\frac{đQ}{T}\right) \;\leq\; 0\,. \tag{4.33}$$

If the cycle undergone by system M is *reversible*, equation (4.33) holds even if all heat quantities invert their sign, so that

$$\oint \left(\frac{đQ}{T}\right) \;=\; 0 \qquad \text{(reversible cycle.)} \tag{4.34}$$

For reversible cycles, the temperatures in (4.34) refer not only to the reservoirs but also to the system.

4.5 Entropy

A first consequence of the Clausius theorem applied to *reversible cycles* is the possibility of introducing a new state function.
Let us rewrite equation (4.34)

$$\oint \left(\frac{đQ}{T}\right)_{\rm rev} \;=\; 0 \tag{4.35}$$

remembering that T is here the system temperature, since in every infinitesimal transformation of a reversible cycle the temperature of the system is equal to the temperature of the reservoir.
As a consequence of (4.35), for two s whichever equilibrium states A and B of a thermodynamical system, the integral

$$\int_A^B \left(\frac{đQ}{T}\right)_{\rm rev}$$

only depends on the initial and final state A and B, respectively, and is independent of the intermediate states. One can thus define a new state function, called *entropy* S, whose variation in going from state A to state B is given by

$$\Delta S \;=\; S_B \;-\; S_A \;=\; \int_A^B \left(\frac{đQ}{T}\right)_{\rm rev}\,. \tag{4.36}$$

Since the entropy is a state function, its differential exists

$$dS = \frac{đQ}{T} \,. \tag{4.37}$$

While $đQ$ is *not* an exact differential, the ratio $dS = đQ/T$ is.

The entropy is the ratio between a quantity of heat (say energy) and a temperature; the unit of entropy is thus *joule over kelvin* ($\mathrm{J\,K^{-1}}$). Entro, such as energy, is defined by (4.36) to within ad additive constant. If a value of entropy is conventionally attributed to a given state A, the entropy of all other possible states of the system are univocally defined by (4.36).

Note 1: Notice the formal formal analogy between the procedure by which the state function has been here introduced and the procedure by which the potential energy in conservative systems is defined in Mechanics.
A force $\vec{F}$ is said to be conservative when, for whichever closed path, $\oint \vec{F} \cdot d\vec{r} = 0$. As a consequence the mechanical work of a conservative force for a displacement from a point A to a point B is independent of the path and can be expressed as the variation of the potential energy function, $W = \int_A^B \vec{F} \cdot d\vec{r} = -\Delta E_p$.

Note 2: The term "entropy" derives from the ancient greek words *en*=into and *tropè*=modification.

The entropy plays a fundamental role in Thermodynamics. In what follows we will explore its main applications for bot reversible and irreversible transformations.

Example: The differential of entropy, taking into account the First Law, can be expressed as

$$dS = \frac{đQ_{\mathrm{rev}}}{T} = \frac{dU}{T} + \frac{P}{T}\, dV \tag{4.38}$$

Let us consider a *monatomic ideal gas*, for which the thermal and caloric equations of state (2.3) and (3.5), respectively, hold. By substituting in (4.38) the expressions of dU and dV given by the equations of state, one easily finds

$$dS = \frac{3}{2} nR \frac{dT}{T} + nR \frac{dV}{V}$$

whence, by integration, the finite variation

$$\Delta S = \frac{3}{2} nR \ln \frac{T}{T_{\mathrm{ref}}} + nR \ln \frac{V}{V_{\mathrm{ref}}}$$

where T_{ref} and V_{ref} are arbitrary reference values of temperature and pressure for the ideal gas. If one attributes an arbitrary value S_{ref} in correspondence to the values of T_{ref} and V_{ref}, the entropy S can be expressed as a function of the coordinates T and V as

$$S(T,V) = S_{\mathrm{ref}} + \frac{3}{2} nR \ln T + nR \ln V \,. \tag{4.39}$$

One can easily verify that as a function of the coordinates T and p the expression of entropy for a monatomic ideal gas becomes

$$S(T,p) = S_{\mathrm{ref}} + \frac{5}{2} nR \ln T - nR \ln p \,, \tag{4.40}$$

where now S_{ref} refers to the reference values T_{ref} and p_{ref} for the ideal gas.

4.5.1 Entropy as a thermodynamic coordinate

Being a state function, entropy can be used as a thermodynamic coordinate to characterise the thermodynamical state of a system.

For example, let us consider a simple system, consisting in a homogeneous substance without magnetic or dielectric properties. Its the thermodynamic state can be described by two thermodynamic coordinates, for example pressure and volume pV, or temperature and volume TV, or pressure and temperature pT. We will see in Part II how the most suitable choice of coordinates depends on the phenomena one is interested in and that for complex systems more that two coordinates are necessary..

As a consequence of the First and Second Laws two new state functions have been introduced, the internal energy U and the entropy S, both defined to within an additive constant. Being state functions, also the internal energy U and the entropy S can be used as thermodynamic coordinates, whose absolute value is assumed with respect to an arbitrary reference state. The thermodynamic equilibrium state of a simple system can thus be described also by pairs of coordinates such as UV or ST.

The use of internal energy U and entropy S as thermodynamic coordinates is largely exploited in the axiomatic approach to Thermodynamics, to be introduced in Part II.
As we will there see, a great deal of thermodynamical properties depend on the derivatives of the internal energy and of the entropy, so that the arbitrary additive constant is in many cases uninfluent.

It is convenient, at this point, to shortly discuss the problem of the different intuitive meanings of internal energy and of entropy.
The concept of thermodynamical internal energy U is quite intuitive, since one is accustomed to the use of energy in various scientific and technological fields and due also to the relative simplicity of the microscopic interpretation sketched in § 3.3.
By far less immediate is an intuitive understanding of the meaning of entropy. Its introduction as a consequence of the Clausius theorem appears to have a quite abstract purely mathematical character. The actual physical meaning of entropy will become progressively clearer when its use in practical cases will be studied. However, a satisfactory intuitive understanding of entropy is possible only on the grounds of statistical considerations, to the introduced in Part III.

Coming back to the entropy S as a thermodynamic coordinate, let us now consider two important applications.

Reversible adiabatic transformations

In any *reversible adiabatic transformation* the integral $\int(đQ/T)$ is null, because $đQ = 0$, and thus the entropy is unchanged, $\Delta S = 0$. A reversible adiabatic is thus an *iso-entropic* transformation.
It is now interesting to consider the *Carnot cycle*, that is represented by two reversible isothermal and two reversible adiabatic transformations. If S and T (entropy and temperature) are used as thermodynamic coordinates, the plot of the Carnot cycle in the ST plane has the same simple rectangular shape for any system (Fig. 4.5).

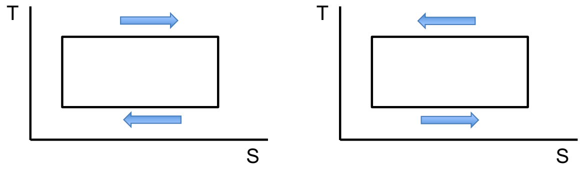


Figure 4.5: Representation of the Carnot cycle in the ST plane. Left: Carnot engine. Right: Carnot refrigerator.

Reversible exchange of heat

As previously stated (§3.4.1, eq. 3.16), the reversible compression work can be expressed as $(đW)_{\text{rev}} = -p\, dV$.

The introduction of the state function entropy allows one to express also the quantity of heat absorbed reversibly in an analogous form, by inverting eq. (4.37): $(đQ)_{\text{rev}} = T\ dS$.

In Chapter 3 we have observed that the First Law is always symmetrical with respect to both heat and work, in both its infinitesimal and finite :

$$dU = đQ + đW\,, \qquad \Delta U = Q + W \qquad \text{(for all transformations)} \tag{4.41}$$

By the introduction of the entropy function, one can express the First Law for *reversible transformations* in a differential form that is again symmetrical with respect to heat and work:

$$dU = T\,dS\ -\ p\,dV\,, \qquad \Delta U = \int_i^f T\,dS - \int_i^f p\,dV \qquad \text{(only for reversible transf.)} \tag{4.42}$$

4.5.2 Entropy and irreversible processes

A further consequence of the Clausius theorem is the possibility of using the entropy S for measuring the *degree of irreversibility* of a thermodynamic transformation.

The Clausius inequality (4.28) concerns the irreversible cyclic transformations. The introduction of the state function entropy S allows one to obtain from the Clausius inequality a relation that concerns any irreversible transformation, even if not cyclic.

Let us consider a generic transformation connecting two equilibrium states of a system, the initial one i and the final one f $(i \to f)$ and a second *reversible* transformation that brings back the system to its initial state $(f \to i)$.
The cyclic integral of (4.28) can be decomposen into the sum of the integrals:

$$\oint \frac{đQ}{T} \;=\; \int_i^f \frac{đQ}{T} \;+\; \int_f^i \left(\frac{đQ}{T}\right)_{\text{rev}} \;\le\; 0\,. \tag{4.43}$$

In the first transformation $i \to f$ the temperature T refers to the ambient of the system; only in the second (reversible) transformation $f \to i$ is the temperature of the system equal to the temperature of its ambient.
The second integral of (4.43) $(f \to i)$ can be substituted by the corresponding variation of entropy, according to (4.36), so that for the generic transformation $i \to f$ one obtains

$$\int_i^f \frac{đQ}{T} \;\le\; S(f) - S(i) \;=\; \Delta S\,. \tag{4.44}$$

It is worth noting that, since the entropy is a state function, its variation ΔS in the transformation of a system from an initial state i to a final state f is independent of the type of transformation (reversible or irreversible) and of the intermediate states.
However, to *calculate* the entropy variation $\Delta S = S(f) - S(i)$ it is necessary to refer to any *reversible* transformation connecting the initial state i to the final state f of the system, and on this reversible transformation to calculate the integral $\int (đQ/T)_{\text{rev}}$ (where T is the system temperature).

Irreversible processes in isolated systems

A very important consequence of equation (4.44) concerns the *isolated systems*. An isolated system cannot exchange nor heat nor work with its ambient. In that case, since $đQ = 0$, the integral on the left of (4.44) is zero, sa that

$$\Delta S \;=\; S_f \;-\; S_i \;\ge\; 0 \qquad \text{(for an isolated system)}\,. \tag{4.45}$$

Otherwise stated, an *isolate system* that initially is in an equilibrium state i can transform into a final equilibrium state f only if (4.45) is fulfilled, say only if the entropy of the final state is not larger than the entropy of the initial state.

If the transformation $i \to f$ is *reversible*, the entropy cannot diminish for the opposite transform $f \to i$ too, so that:

$$\Delta S \;=\; S_f \;-\; S_i \;=\; 0 \qquad \text{(reversible transf. of isolated system)}\,. \tag{4.46}$$

Since all natural processes are irreversible, eq. (4.45) implies that the entropy of an isolated system cannot diminish in any spontaneous process. It can only increase or, at most, remain constant. This statement is often refered to as the *law of entropy increase in isolated systems.*

For a *non isolated system*, the variation of entropy can be positive, null or negative, depending on the transformation. The ensemble of a given system and of all the other systems with which it interacts (its ambient) is anyway an isolated system, and for a spontaneous transformation the global relation holds:

$$\Delta S_{\rm sist} \;+\; \Delta S_{\rm amb} > 0\,. \tag{4.47}$$

The sum of a system and its ambient is often conventionally called an “universe”.

Example 1: Let us come back to the case of cyclic devices operating between only two reservoirs, that was considered in § 4.4.1, and analyse the behaviour of entropy for irreversible transformations.

For concreteness, let us refer to the cyclic engine. The ensemble of the cyclic engine and the two reservoirs can be considered as an isolated system (an “universe”). The entropy of the isolated ensemble is the sum of the entropies of the system and of the two reservoirs.

Let us consider an entire cycle of the engine. At the end of the irreversible cycle, the engine returns to its initial state, so that also its entropy, that is a state function, returns to its initial value. For a cycle, $\Delta S_{\rm engine} = 0$. Pay attention that one cannot use (4.26) for measuring the entropy variation, since according to (4.36) one should consider heat exchanged reversibly.

The reservoirs maintain unchanged their temperatures, thanks to their ideally infinite heat capacities. The entropy variations can thus be calculated by the ratios Q/T. One can easily verify that for an irreversible engine the total variation of entropy of the two reservoirs is positive, $\Delta S_{\rm serb} > 0$ (Fig. 4.3, right).

Example 2: Let us again consider a cyclic engine operating between two reservoirs, and reduce its efficiency down to the value $\eta = 0$. No work is now produced and the entire quantity of heat emitted by the hot reservoir is transferred to the cold reservoir. The situation corresponds to the irreversible transfer of heat Q from a body at temperature T_2 to a body at a lower temperature $T_1 < T_2$. It is immediate to verify that $\Delta S = -Q/T_2 + Q/T_1 > 0$.

Example 3: An instructive example of irreversible process is represented by the free adiabatic expansion of an ideal gas.

Le us consider a thermally insulated vessel, of total volume V, divided in two equal parts by a fixed wall. One of the two parts, of volume $V/2$, is filled by one mole of ideal gas at pressure p, the other part is empty. At a given time the separation wall is removed and the gas expands and fills up the entire volume V. One can easily verify that the process is irreversible.

During the expansion, the gas doesn't exchange nor heat nor work with the ambient; according to the First Law, the internal energy of the final state is equal to the internal energy of the initial state. Since the gas is ideal, the final temperature is equal to the initial temperature too.

To calculate the entropy variation ΔS_{fi} from the initial equilibrium state i to the final equilibrium state f, one must calculate the integral of $đQ/T$ along any *reversible* transformation connecting the two states. Since the initial an final state share the same temperature, it is convenient to choose the isothermal reversible transformation between the initial state $(V/2, p)$ and the final state $(V, p/2)$. One can easily verify that $\Delta S_{fi} = R \ln 2 > 0$, where R is the gas universal constant.

Note: A careful reader could be worried about the possibility that an *isolated* system initially in an *equilibrium* state spontaneously could transform to a different final equilibrium state. Otherwise stated: how is it possible that an isolated system modifies its equilibrium state ? This far from trivial problem is clarified in Chapter 5, at the beginning of Part II.

4.5.3 Increase of entropy and degradation of energy

The First Law of Thermodynamics imposes a constraint on thermodynamical transformations: in an isolated systems, only the transformation for which the internal energy is conserved, $\Delta U = 0$, are possible.
The Second Law imposes a further constraint: in an isolated thermodynamical system only the transformations for which the entropy doesn't decrease are possible. For (ideal) reversible transformations the entropy of an isolated system is conserved; for real irreversible transformations of an isolated system the entropy increases. The law of increase of entropy in isolated systems is a general criterion of evolution fro physical pocesses.

To the increase of entropy of an isolated system it corresponds a degradation of energy, say an irreversible reduction of the possibility of obtaining useful work.
Let us consider the transformation of an isolated thermodynamical system from an initial state i to a final state f. The *lost work*, say the difference between

a) the work obtainable by a perfectly reversible $i \to f$ transformation, an
b) the work obtained by the real irreversible transformation,

is

$$W_{\text{lost}} \;=\; W_{\text{rev}} \;-\; W_{\text{irr}} \;=\; T_0 \, \Delta S \,, \tag{4.48}$$

where T_0 is the lowest available temperature and ΔS is the variation of the entropy of the isolated system.

Example: Let us verify the validity of (4.48) for the simple case considered in § 4.4.1, Fig 4.3. There are two reservoirs, at the temperatures T_2 and T_1, respectively, with $T_2 > T_1$. The direct transfer of a quantity of heat Q from the hot to the cold reservoir is an irreversible process, with no production of work. The increase of entropy is $\Delta S = -Q/T_2 + Q/T_1 = Q(T_2 - T_1)/T_1T_2$. We could alternatively input the heat Q emitted by the hot reservoir into a Carnot engine (reversible) and obtain the work $W = Q(1 - T1/T_2)$. It is immediate to see that $W = T_1 \, \Delta S$. The quantity of heat Q absorbed by the cold reservoir in the irreversible process cannot be used to obtain work, unless one can dispose of another reservoit at a temperature lower than T_1.

A general demonstration of (4.48) is far from trivial.
Let us consider the ensemble made by a thermodynamic system and its ambient. The ensemble (system+ambient) is an isolated system (a "universe").
During an irreversible transformation from an initial state i to a final state f the system exchanges heat and work with its ambient and the entropy of the "universe" increases, $\Delta S_{\text{syst}} + \Delta S_{\text{amb}} = S_f - S_i > 0$.
To perform the same transformation $i \to f$ reversibly, one can add a new auxiliary ambient, connected to a reservoir at the lowest available temperature T_0, which exchanges work and heat with the system through suitable Carnot cycles.
The variation of entropy of the original ensemble is always $\Delta S_{\text{syst}} + \Delta S_{\text{amb}} = S_f - S_i > 0$, since initial and final states are unchanged. The auxiliary ambient undergoes an opposite entropy variation $\Delta S_{\text{aux}} = -\Delta S_{\text{syst}} - \Delta S_{\text{amb}} < 0$, in such a way that the total variation of entropy is null, $\Delta S_{\text{syst}} + \Delta S_{\text{amb}} + \Delta S_{\text{aux}} = 0$. The negative value $\Delta S_{\text{aux}} < 0$ corresponds to a neat transfer of heat Q_{aux} from the auxiliary ambient to the original ensemble. Since the original ensemble undergoes the same transformation $i \to f$ and the same variation of internal energy than in the irreversible transformation, the heat $Q_{\text{aux}} = T_0 \Delta S_{\text{aux}}$ outgoing from the auxiliary ambient has to transform into work, say into work that is lost in the irreversible transformation, so that $W_{\text{lost}} = T_0 \, (S_f - S_i)$.

Example: A body of heat capacity C = 500 J K^{-1}, initially at the temperature $T_i = 400$ K, is immersed in an ambient of infinite heat capacity at the temperature $T_0 = 300$ K. After a sufficiently long time, the body is in equilibrium at the final temperature $T_0 = 300$ K.
The process is irreversible. The heat transferred from the body to the ambient is $Q = C\Delta T = C(T_i - T_0) = 50000$ J. To evaluate the variation of entropy it is necessary to calculate the integrals of $đQ/T = C \, dT/T$ along reversible transformations connecting the initial and final

states; for the body it is convenient to consider a reversible isobar transformtion, for the ambient the ratio Q/T_0 is sufficient:

$$\Delta S_{\mathrm{s,irr}} \;=\; \Delta S_{\mathrm{sist}} + \Delta S_{\mathrm{amb}} \;=\; C\int_{T_i}^{T_0} \frac{dT}{T} + \frac{Q}{T_0} \;=\; 22.82\ \mathrm{JK}^{-1} > 0\,. \tag{4.49}$$

Alternatively, the body could reach the final equilibrium state through a reversible transformation by means of a Carnot engine inserted between the body and the ambient. During the process the temperature of the body progressively decreases. The Carnot engine has to work by a number of infinitesimal cycles, producing infinitesimal variations of the body temperature in each cycle. Since the process is reversible, the global variation of entropy is null, $\Delta S_{\mathrm{rev}} = 0$. For each infinitesimal cycle the efficiency is $\eta = 1 - T_0/T$, where T is the instantaneous temperature of the body, and the work is $đW = -\eta đQ$, where $đQ$ is the quantity of heat given by the body. By integrating $đW$ from T_i to T_0 one gets $W = 6847$ J. One can easily verify that $W = T_0\,\Delta S_{\mathrm{irr}}$.

4.6 Final remarks

In this Chapter 4 the Second Law and its consequences (Carnot and Clausius theorems) have been introduced by considering cyclic transformations of thermodynamic systems, without worrying about the very nature of the systems. By focusing the attention on isolated systems it has been possible to define the state function entropy and to demonstrate the law of increase of entropy in isolated systems. It has also been observed that the increase of entropy represents an evolution criterion for isolated systems.
We conclude now this Chapter with some comments which should help to better understand the relevance of the Second Law and introduce to the developments of next Chapters.

4.6.1 Non-isolated systems

The large majority of the applications of Thermodynamics concern systems which are not isolated. For example: a number of phenomena, such as chemical reactions and phase transitions, take place at constant temperature and pressure, so that the system can exchange work and heat with its surroundings; statistical calculations are instead generally performed by controlling temperature and volume.
It is thus necessary to suitably tailor to non isolated systems the procedures up to now developed for isolated systems, avoiding the need to extend the treatment of a given system to include also its surroundings, in order to obtain an isolated ”thermodynamical universe”. For example, how can the law of entropy increase in isolated systems be adapted to a system maintained at constant temperature and pressure or to a system maintained at constant volume and temperature ?
The problem has been solved by introducing new thermodynamic functions, such as the enthalpy or the free energies of Helmholtz and Gibbs, each one suitable for a different situation.

These topics are treated systematically in Part II, that is based on an axiomatic approach to Thermodynamics, alternative to the cycle approach of this Part I.

4.6.2 Intuitive meaning of entropy

The meaning of temperature and internal energy is in general quite easily understood, since one can refer to quantities of everyday experience (temperature, work, heat).
The meaning of entropy, such as it is introduced in macroscopic terms from the Clausius theorem, is easily understood with reference to the simple examples of heat transfer introduced in § 4.4.1. It is instead little intuitive in many other cases, such as the free adiabatic expansion of a gas considered in a previous example, where the system doesn't exchange heat with its ambient, and the integral of $đQ/T$ has to be performed along a reversible transformation that has no relation with the real transformation.

The meaning of entropy is more easily understood if one refers to its statistical interpretation, that refers to the microscopic structure of thermodynamic systems and will be treated in Part III. In particular, in Chapter,13, we will see that for an isolated system the entropy depends on the number of microscopic states corresponding to the macroscopic equilibrium state. The increase of entropy in an irreversible transformation corresponds to an increase of the number of microscopic states available to the system.

4.6.3 The arrow of time

As already observed, the law of entropy increase in isolated systems represents an evolution criterion for natural processes, which are always irreversible. The law has a general validity, since one can always add to a given system its surroundings in order to obtain an isolated system (a "thermodynamic universe", that in some cases can correspond to the entire Universe).

The irreversibility of natural processes and the entropy increase imply a preferred direction with respect to the time axis. Macroscopic phenomena can only take place in a given time direction, not in the opposite.

A gas can spontaneously expand into a vacuum vessel, the opposite phenomenon cannot take place spontaneously. Heat is spontaneously transferred from a hot to a cold body, the opposite cannot take place spontaneously. And so on.

A deeper understanding of the macroscopic irreversibility will be gained by the statistical approach to Thermodynamics of Part III.

One often says that macroscopic irreversibility establishes the "arrow of time".

This behaviour of macroscopic systems contrasts with the behaviour at the microscopic level. The laws of fundamental interactions are invariant with respect to time inversion (with the exception of some phenomena of weak nuclear interaction).

The connection between the microscopic reversibility and the macroscopic irreversibility is a still unsolved problem.

4.6.4 Irreversibility, disorder and degradation of energy

As already noticed above, irreversibility is connected to the degradation of energy, say to the the loss of the possibility of obtaining useful work.

A sequence of natural irreversible processes gives rise to a progressive increase of entropy that corresponds to a progressive accumulation of energy stored at low temperatures.

According to Statistical Thermodynamics, this behaviour corresponds to a tendency towards macroscopic states that correspond to an increasing number of microscopic states; the result is a reduction of differentiation and an increasing uniformity at the microscopic level.

Such a trend is often interpreted as an increase of the degree of disorder of systems. Whence the use of the term entropy as synonymous of disorder in the everyday language.

Ordered structures can actually spontaneously develop, for example in the growth of living beings, but at the expenses of the increase of entropy, say of disorder, in the environment.

Part II

Equilibrium macroscopic Thermodynamics

In Part I the Laws of Thermodynamics have been introduced according to the traditional approach based on cyclic transformations.

In this Part II a more general approach is followed, based on the coordinate formalism first developed by J. W. Gibbs at the end of the XIX Century.

The treatment is based on the relatively recent axiomatic foundation developed by L. Tisza and H. B. Callen, that allows a formulation which is both elegant form the mathematical point of view and easily adapted to the different fields of application of Thermodynamics.

We will introduce the state functions enthalpy and Helmholtz and Gibbs free energies, and the equilibrium conditions of thermodynamic systems will be discussed. The response function will be introduced and the relations connecting them will be deduced.

Part II is concluded by the study of some relevant thermodynamical processes and an introduction to chemical Thermodynamics.

Chapter 5

Axioms of equilibrium Thermodynamics

In this Part II the attention is focused on the thermodynamic coordinates, according to the Gibbs approach, say on the accurate description of the states of the different possible thermodynamic systems (pure and composite substances, magnetic and dielectric systems, systems affected by chemical reactions or transport phenomena, etc.) The Gibbs approach allows one to adapt in a simple and flexible way the thermodynamic formalism to different systems and to different experimental conditions.

The Gibbs coordinate Thermodynamics can be built on the results of the cycle Thermodynamics introduced in Part I. Alternatively, we follow here the axiomatic approach proposed by L. Tisza and H. B. Callen, that is independent of cyclic transformations and is characterised by flexibility and formal elegance.

In this first Chapter 5 the postulates are introduced on which the axiomatic formulation of equilibrium Thermodynamics is based. The main differences with respect to the classical Cycle Thermodynamics of Part I will be immediately apparent, in particular concerning the definition and role of internal energy and temperature.

5.1 Equilibrium axiom

5.1.1 Thermodynamical coordinates

In the axiomatic approach the *extensive* coordinates play a major role in definingthe equilibrium states of thermodynamical systems. Extensive coordinates are:

- the volume V;
- the internal energy U, that assumes a primitive character in the axiomatic approach;
- the quantity of matter in the system, measured by the number n_i of moles of each omponent;
- the generalised coordinates X^* that are necessary to describe possible physical properties of thermodynamical interest, such as the magnetisation M or the electrical polarisation P (see § 3.4).

A least three extensive coordinates are necessary to describe the thermodynamical state of system, however simple: V, U, n.

Before introducing the postulates of axiomatic Thermodynamics, it is convenient to make a point about internal energy and the components of the system.

Internal energy

In the cycle Thermodynamics the existence of the internal energy U and its conservation in isolated systems are assumed as the First Law of Thermodynamics (§ 3).

In the present axiomatic approach the existence of the internal energy U and its conservation in isolated systems are instead assumed as primitive concepts, which can be traced back to considerations on the microscopic behaviour, in particular to the conservation of energy in fundamental interactions.

As is well known, the potential energy is defined to within ad additive constant, so that also internal energy U is defined to within an additive constant. From the operative point of view, one can thus know only the variations ΔU. However, to simplify the notation, one generally indicates the internal energy U as an absolute value, intended to be referred to an arbitrary reference value. (This procedure is commonly followed, for example, when the potential energy of a spring is said to be $E_e = kx^2/2$).

Operatively, the variations of internal energy ΔU between two states of equilibrium of a system can be evaluated by measuring the adiabatic work connecting the two states. The heat exchanged in a generic transformation can be the evaluated as $Q = \Delta U - W$.
The considerations of § 3.2 on exact differentials and infinitesimal quantities obviously are still valid: $dU = đQ + đW$.

Components of a system

A system can contain one or more components, whose nature depends on the type of system and on the type of phenomenon one wants to describe. Let us give some examples.

- An inert gas, in which no chemical reactions can take place. Its components are molecules (atoms for monatomic gases). One has to specify one number n of moles if only one type of gas is present, two values n_1 and n_2 if the system is a mixture of two gases, and so on.
- A system containing two phases, for example liquid water and its vapour: the components are the water molecules and one has to distinguish the number of moles n_1 of the liquid phase and the number of moles n_2 of the vapour phase.
- A chemical reaction: one has to specify the number of moles $(n_1, n_2, n_3 \ldots, n_i)$ of the chemical species participating to the reaction. For example, for the reaction $2H_2 + O_2 \rightleftharpoons 2H_2O$ one has to specify the numbers n_1, n_2, n_3 of molecules of hydrogen, of oxygen and of water, respectively.
- Electromagnetic radiation confined within a cavity (for example a black body): one can consider the photons (quanta of electromagnetic energy) as components, so that n is the number of photons.
- The behaviour of electrons in a metal is often described by the model of a gas of free electons: the components of the thermodynamical system are the electrons and n is the number of moles of electrons.
- A radioactive material: different isotopes of the same atomic species generally have a different behaviour; the components of the system are the different isotopes; one has thus to specify the number of moles n_i for every isotope.

Let us recall that the mole (symbol "mol") is the quantity of matter of a system that contains exactly the number of Avogadro, $N_0 \simeq 6.022 \times 10^{23}$, of elementary constituents, whose nature has to be explicitly specified: n mol of atoms, of molecules, of electrons, etc..

The number n_i of moles of the different components is necessary tocharacterise the dimensions of a thermodynamical system
In systems containing only one component, the variations of n depend on the possible exchange of matter with the environment or the creation or destruction of components (for example in the case of a photon gas).
In systems containing more than one component, the variation s of the numbers of moles $n_1, n_2, n_3 \ldots, n_i$ can describe not only the possible exchanges with the environment, but also the evolution of chemical reactions, transport phenomena, phase transitions.

5.1.2 Thermodynamical equilibrium

One can now state the first axiom of the coordinate Thermodynamics.

> **Axiom I**: *Thermodynamic systems can be in equilibrium states, completely characterised by the values of the extensive coordinates* $U, V, \{n_i\}, \{X_j^*\}$.

The extensive thermodynamical coordinates completely characterise the thermodynamical state of the system. They define the *Gibbs space*. A point in the Gibbs space represents a thermodynamical equilibrium state of the system.
In what follow, to simplify the notation, we will omit to specify the generalised coordinates X_j^*, if not strictly necessary.

The study of the equilibrium conditions in Chapter 6 will lead to the definition of the intensive coordinates conjugatedto the extensive coordinates (in particular tmperature and pressure). The conditions for the stability of equilibrium will be studied in § 9.6.
Let us stress that the experimental verification of the equilibrium state of a system and of its stability can be far from trivial. See the discussion in § 2.1: if the relaxation time is short with respect to the observation time, one can speak with good approximation of thermal equilibrium. There are however some systems for which the relaxation time is much longer than the tYpical observation times; such systems, even if their thermodynamical coordinates don't change in time, are in metastable equilibrium (for example diamond at ambient temperature and pressure) or even out of equilibrium(for example glasses of radioactive materials).
As we will see, Thermodynamics gives the possibility of evaluating whether a system is in stable or metastable equilibrium or if it is out of equilibrium.

5.2 The basic problem

The the Axiom I, concerning the thermodynamical equilibrium, the First Law of the cycle Thermodynamics is implicitly contained.
In the axiomatic approach a central role is played by the Second Law, that is however no more expressed in terms of the properties of cyclic transformations, but with reference to the properties of the state function entropy, whose very essence is the object of an axioms.
Before stating the entropy axioms, it is convenient to clarify the terms of the fundamental problem that macroscopic Thermodynamics has to solve. To this aim, let us introduce some basic concepts: composite systems, constraints, thermodynamical operations and thermodynamical processes.

Composite systems, walls, constraints

A *composite system* is a system composed of two or more sub-systems separated by suitable walls. The equilibrium state of each one of the sub-systems is characterised by the value of its extensive coordinates, $U^{(j)}, V^{(j)}, \{n_i^{(j)}\}$, where the apex j labels the sub-systems.

The *walls* can be restrictive or non restrictive with respect to the transfer of one or more of the extensive quantities $(U, V, \{n_i\})$ from one sub-system to another.
The transfer of extensive quantities between sub-systems is a *thermodynamical process*, also called a thermodynamical transformation.

The presence of restrictive walls imposes *constraints* to the transfer of extensive quantities within the composite system. The extensive quantities are said to be free (with respect to non restrictive walls) or constrained (with respect to restrictive walls).

Constraints removal and thermodynamical processes

Let us consider an isolated composite system (Fig. 5.1) that initially is in equilibrium. The subsystems, separated by restrictive walls, are in internal equilibrium.

At a given time one or more constraints are removed, the corresponding walls being transformed from restrictive to non restrictive with respect to some extensive quantities. The constraints

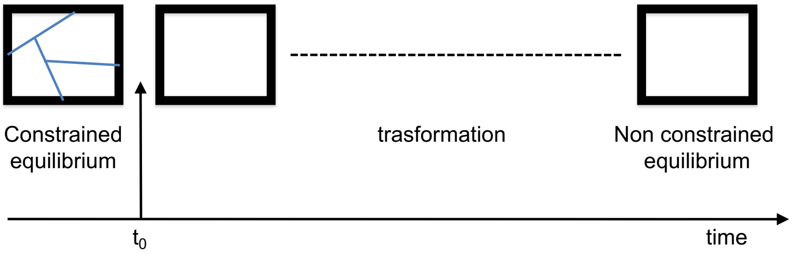


Figure 5.1: Schematic representation of the fundamental problem. An isolated thermodynamical system is initially ($t < t_0$) in a condition on constrained equilibrium. At time t_0 the constraints are removed (thermodynamical operation); as a consequence, a thermodynamical process (transformation) is triggered leading to a new situation of non constrained equilibrium.

removal is termed a *thermodynamic operation*, ideally taking place without exchanges of energy and/or matter between the composite system and its environment.
As a consequence of the constraints removal, some extensive coordinates become free to change their value and a thermodynamic process is triggered. After a suitable time interval, the composite systems reaches a new equilibrium condition.

The fundamental problem is to establish the relation between the properties of the final unconstrained equilibrium state and the properties of the initial constrained equilibrium state.

Examples

Example 1: Free expansion of a gas. A vessel is initially divided in two separated parts of equal volume: $V^{(1)} = V^{(2)}$. Part 1 is filled with gas, part 2 is empty: $n^{(1)} \neq 0, n^{(2)} = 0$; $U^{(1)} \neq 0, U^{(2)} = 0$. The wall separating the two parts is restrictive with respect to the transport of both matter and energy. At a given time the separating wall is removed: the coordinates $n^{(1)}, n^{(2)}, U^{(1)}, U^{(2)}$ become free variables. The system evolves towards a new equilibrium state.

Example 2: A cylinder is divided in two parts by a sliding piston. The two parts contain $n^{(1)}$ and $n^{(2)}$ mol of gas, respectively. Initially the piston is maintained fixed by a pin. At a given time the pin is removed and the piston becomes free to move. The constraint on volume and energy is removed: the coordinates $V^{(1)}, V^{(2)}, U^{(1)}, U^{(2)}$ become free variables. The system evolves towards a new equilibrium state.

Example 3: A system is composed by two bodies at different temperatures, separated by an adiabatic wall.At a given time the wall is removed and the two bodies become free to exchange heat: the coordinates $U^{(1)}, U^{(2)}$ become free variables. The system evolves towards a new equilibrium state.

Example 4: A vessel contains $\{n_1, n_2, n_3, \dots\}$ mol of different chemical reagents in a state of metastable equilibrium. The insertion of a catalysts breaks the metastable equilibrium and triggers a chemical reaction: the coordinates $\{n_i\}$ become free variables. The system evolves towards a new equilibrium state.

5.3 Axioms on entropy

5.3.1 Fundamental axiom on entropy

The fundamental problem of establishing the relation between the properties of the final unconstrained equilibrium state and the properties of the initial constrained equilibrium state (§ 5.2) is solved by an axiom that introduces the state function entropy and its main property.

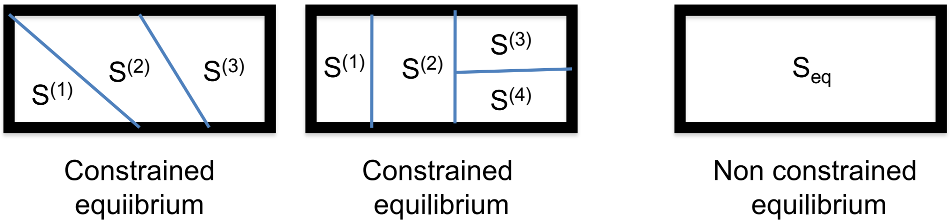


Figure 5.2: Schematic illustration of axiom II. Left and centre: two possible situations of constrained equilibrium. Right: system in the state of non-constrained equilibrium.

> **Axiom II**: *For each thermodynamical system there is a function of the extensive coordinates, entropy $S(U, V, n_1, \ldots, n_i)$, defined in the states of thermodynamical equilibrium. The knowledge of the function $S(U, V, n_1, \ldots, n_i)$ is equivalent to the knowledge of all the thermodynamical properties of the system.*
> *In an* isolated *composite system, if no constraints are present, the extensive quantities $U, V, \{n_i\}$ are distributed among the different possible sub-systems in such a way that the value of the entropy S_{eq} is the highest with respect to the values that entropy could assume in any state of constrained equilibrium:*
>
> $$S_{\text{eq}} > \sum_j S^{(j)} \qquad \text{(isolated system)} \tag{5.1}$$

In (5.1), S_{eq} is the entropy value for the entire system in the state of non constrained equilibrium, $\sum_j S^{(j)}$ is the entropy value for the entire system in any state of constrained equilibrium, expressed as the sum of the entropies of the single sub-systems (Fig. 5.2).

The fundamental equation

The existence of the state function entropy, derived as a consequence of the Second Law in the cycle Thermodynamics (§ 4.4), has been here assumed as an axiom.
In addition, one assumes that the function $S(U, V, n_1, \ldots, n_i)$ contains all the information of the thermodynamical properties of the given system. The function, connecting the value of entropy to the values of the extensive coordinates, is thus called "fundamental equation".
The knowledge of the function $S(U, V, n_1, \ldots, n_i)$ for a given system is thus equivalent to the knowledge of its two equations of state, the thermal one and the and caloric one (§ 3.1) The case of an ideal gas will be studied in § 6.4.
The fundamental equation, such as the equations of state, cannot be obtained on pure thermodynamical grounds; it is generally established from experiment or from theoretical statistical considerations.

Evolution criterion and equilibrium states

Equation (5.1), corresponding to the law of entropy increase in isolated systems, represents the evolution criterion for isolated systems.
One should notice that the sum $\sum_j S^{(j)}$ in (5.1) doesn't necessarily refer only to the real states of constrained equilibrium of a composite system; actually, the sum can be also referred to the possible states of constrained equilibrium that the system could virtually attain if the unavoidable fluctuations with respect to the equilibrium state were frozen by the insertion of suitable constraints (see § 6.2).
As a consequence, equation (5.1) not only represents an evolution criterion for isolated systems. It also characterises the properties of equilibrium states.

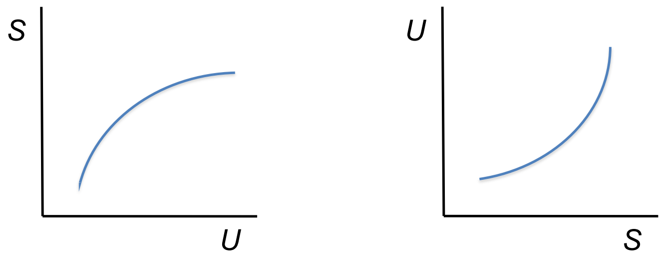


Figure 5.3: Projections on the (U,S) plane of the fundamental equation in the entropy representation $S(U,V,\{n_i\})$ (left) and of the fundamental equation in the energy representation $U(S,V,\{n_i\})$ (right).

5.3.2 Properties of entropy

The properties of entropy are further specified by the third axiom.

> **Axiom III**: *The entropy S is an additive variable ad is a functioncontinuous, differentiable and monotonously increasing of the internal energy U .*

As a consequence of the additivity, the entropy S is a first-order homogeneous function of the extensive coordinates; for any value of the scale parameter λ the following equation holds

$$S(\lambda U, \lambda V, \{\lambda n_i\}) \;=\; \lambda\, S(U,V,\{n_i\})\,. \tag{5.2}$$

Since S is a monotonous function of U,

$$\left(\frac{\partial S}{\partial U}\right)_{V,\{n_i\}} \;>\; 0\,, \tag{5.3}$$

the function $S(U,V,\{n_i\})$ can be inverted to the function $U(S,V,\{n_i\})$ (Fig. 5.3).

Entropy representation and energy representation

As already observed, the knowledge of the function $S(U,V,\{n_i\})$ corresponds to the knowledge of all the thermodynamical equilibrium properties of a system.
The possibility of inverting the function $S(U,V,\{n_i\})$, guaranteed by (5.3), allows one to obtain a new function $U(S,V,\{n_i\})$ which still contains the entire information on the properties of the system.
There are thus two equivalent fundamental equations, corresponding to two different choices of the independent thermodynamical coordinates. The two choices are termed entropy representation and energy representation, respectively:

$$S = S(U,V,\{n_i\}) \qquad \text{entropy representation} \tag{5.4}$$

$$U = U(S,V,\{n_i\}) \qquad \text{energy representation} \tag{5.5}$$

The properties of the two representations will be studied more carefully in Chapter 6. Other representations will be introduced in Chapter 7, which allows one to tailor the thermodynamic formalism to different experimental situations.

Note 1: The entropy S is here defined to within an additive constant, as in the cycle Thermodynamics. As for the internal energy U, the absolute value of S is assumed to be referred to an arbitrary reference value. The large majority of thermodynamical properties depend on derivatives of the entropy or of the energy with respect to other coordinates, so that the value of additive constant is generally irrelevant. An absolute value can be attributed to entropy only on the grounds of quantum statistical considerations.

Note 2: The axiom III asserts that the entropy S is a function monotonously increasing of the internal energy U; as a consequence U monotonously increases with S too. As it will be made clear in Chapter 6, this property is connected to the non-negative value of the thermodynamical temperature. Further considerations on the stability of the thermodynamical equilibrium (to be studied in § 9.6) allow one to conclude that the two curves $S(U)$ and $U(S)$ are downward concave and upper concave, respectively. (Fig. 5.3).

Chapter 6

Entropy and energy representations

In this chapter the equilibrium properties of thermodynamical systems are studied in the two representations of entropy and of energy. At first, the intensive coordinates conjugated to the extensive coordinates will be defined (§ 6.1). The two representations will then be separately studied (§ 6.2 and 6.3). At last, some consequences of the homogeneity of the fundamental equations will be considered (§ 6.4).

6.1 Intensive coordinates

From the two fundamental equations (5.4) and (5.5),

$$S = S(U, V, \{n_i\}) \qquad \text{(entropy representation)} \tag{6.1}$$

$$U = U(S, V, \{n_i\}) \qquad \text{(energy representation)} \tag{6.2}$$

the two corresponding differential equations can be obtained.
In the entropy representation

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,\{n_i\}} dU + \left(\frac{\partial S}{\partial V}\right)_{U,\{n_i\}} dV + \sum\nolimits_i \left(\frac{\partial S}{\partial n_i}\right)_{V,U} dn_i\,. \tag{6.3}$$

In the energy representation

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}} dV + \sum\nolimits_i \left(\frac{\partial U}{\partial n_i}\right)_{V,S} dn_i\,. \tag{6.4}$$

The partial derivatives in (6.3) and (6.4) correspond to intensive coordinates.
By introducing, for the entropy representation the symbols

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,\{n_i\}}, \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,\{n_i\}}, \quad \frac{\mu_i}{T} = -\left(\frac{\partial S}{\partial n_i}\right)_{V,U}, \tag{6.5}$$

and, for the energy representation the symbols

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}}, \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}}, \quad \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V,S}, \tag{6.6}$$

equation (6.3) becomes

$$\boxed{dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \sum\nolimits_i \frac{\mu_i}{T}\,dn_i} \qquad \text{(entropy representation)} \tag{6.7}$$

and equation (6.4) becomes

$$\boxed{dU = T\,dS - p\,dV + \sum\nolimits_i \mu_i\,dn_i} \quad \text{(energy representation)} \tag{6.8}$$

We will show below, by means of suitable examples, that the intensive variables T, p, μ_i are connected to thermal, mechanical and chemical equilibria, respectively. As one can easily expect, the variables T and p correspond to temperature and pressure, respectively. The μ_i intensive variables are termed chemical potentials; their role will be clarified later on.

Since, according to Axiom II (§ 5.3), the entropy S is a monotonously increasing function of the internal energy U, the intensive varible T cannot be negative.

Note: To simplify the notation, the generalised extensive coordinates X_j^*, necessary for some systems such as the magnetic or dielectric ones, have been here omitted in the expression of the fundamental equations. We only observe here that intensive coordinates, termed generalised forces, are associated also to the generalised extensive variables:

$$\frac{\xi_j}{T} = -\left(\frac{\partial S}{\partial X_j^*}\right)_{V,U,\{n_i\},\{X^*_{k\neq j}\}} \qquad \xi_j = \left(\frac{\partial U}{\partial X_j^*}\right)_{V,S,\{n_i\},\{X^*_{k\neq j}\}} \tag{6.9}$$

If one or more extensive generalised coordinates have to be taken into account, the corresponding terms $\pm\xi_j\,dX_j^*$ should be included in (6.7) and (6.8).

6.2 Entropy representation

Let us first better clarify the meaning and the origin of the entropy variations expressed by (6.7). We will then study the concept of thermodynamical equilibrium and the meaning of the intensive coordinates in the entropy representation.

6.2.1 Origin of entropy variations

Let us rewrite (6.7) in the more familiar form

$$T\,dS = dU + p\,dV - \sum \mu_i\,dn_i\,. \tag{6.10}$$

With respect to the expression established in § 4.4, the entropy variation (6.10) contains the additional terms $\mu_i\,dn_i$, that can describe the effect of different phenomena:

- matter exchanges between the system and its environment,
- variations of the quantity of the components of a system, as a consequence for example of chemical reactions of phase transitions,
- transport of matter between sub-system of a composite system.

To better grasp the meaning of the different terms appearing in (6.10), let us consider some suitable examples, without forgetting that (6.10) refers to equilibrium conditions, say to reversible variations of the coordinates.

Example 1: System with $\{n_i\}$ constant

If the quantities of the various components of the systems don't vary, say $\{n_i\}$=constant, equation (6.10) simplifies to:

$$T\,dS \;=\; dU + p\,dV \;=\; dU - đW_p \;=\; đQ_{\rm rev}\,, \tag{6.11}$$

where $đW_p$ is the reversible compression work. The entropy variation, depending on the reversible variations of internal energy and of volume, corresponds to the quantity of heat reversibly exchanged (as in § 4.4): $dS = đQ_{\rm rev}/T$.

Example 2: Open system with one component

Let us now consider an open system, that can exchange matter with its environment; for simplicity, let us assume that the system has only one component. Equation (6.10) becomes:

$$T\,dS = dU + p\,dV - \mu\,dn\,. \tag{6.12}$$

The variation dn of the matter content contributes to the variation of entropy. To quantitatively evaluate the amount of this contribution one should know the chemical potential μ, that depends on the type of substance as well as on temperature and pressure. We will better understand the properties of the chemical potential after the introduction of other thermodynamical functions, in particular the Gibbs free energy (§ 8.4). For the moment we anticipate that the entropy variation can be expressed as

$$T\,dS \;=\; đQ_{\rm rev} \;+\; T\,s\,dn\,, \tag{6.13}$$

where $s = S/n$ is the molar entropy transported by matter.
The entropy variation of an open system depends thus not only on the exchanged heat, $đQ_{\rm rev}/T$, but also on the transport of entropy by matter.
Open systems will be considered in more detail in § 11.3.

Example 3: Chemical reaction in an isolated system

Let us lastly consider an isolated system, where $dU = 0$, $dV = 0$ and there is no exchange of matter with the environment. Let us suppose that in the isolated system one or more components are transformed into other components, for example due to a chemical reaction or a phase transition. Equation (6.7) becomes now

$$T\,dS = -\sum \mu_i\,dn_i \tag{6.14}$$

According to (6.14), the entropy of an isolated system can be modified also as a consequence of the variation of the quantities of the various components. In § 11.4 we will study in some detail the chemical reaction and will further elaborate equation (6.14).

Note: A chemical reaction is generally an irreversible process. In spite of that, the state of the system can be thermodynamically described also during the chemical reaction, provided the thermal and mechanical equilibria remain unaffected. It is then possible to evaluate in any case the entropy variation by means of (6.14).

6.2.2 Virtual thermodynamical processes

We want now better grasp the meaning of thermodynamical equilibrium and its relation with the intensive variables, on the grounds of Axiom II of § 5.3 (law of entropy increase). To this aim, let us introduce the concept of *virtual thermodynamical process.*

We have seen in § 5.2 that the removal of some constraints in a composite system triggers a thermodynamic process by which the system reaches a new state of non constrained equilibrium. Viceversa, a simple thermodynamic system cal always be transformed in a composite system by the insertion of an arbitrary number of constraints.

Let us consider an *isolated system in thermodynamical equilibrium*, say a system whose thermodynamical state is univocally characterised by the values $U, V, \{n_i\}$, which are constant in time. This means that the energy density and the matter density are uniformly distributed in the system (we neglect for the moment the equilibrium with respect to chemical reations and phase transitions).

Let us now imagine a process by which the system temporarily leaves its equilibrium state, for example due to a exchange of energy or matter between the different parts of the system. From a macroscopic point of view, this is a virtual process, that corresponds, from a microscopic point of view, to a fluctuation (Fig. 6.1).
By ideally inserting a suitable number of walls, or more generally of constraints, the virtual non-equilibrium state of the simple system can be transformed into a state of constrained equilibrium of

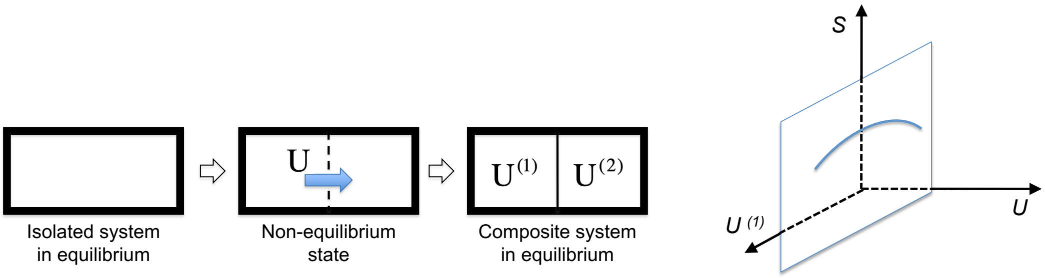


Figure 6.1: Left: A fluctuation of energy in an isolated system leads to a non-equilibrium state, that can be virtually frozen by the insertion of ad adiabatic constraint. Right: plot of entropy S as a function of the variable U_1.

a composite system (Fig. 6.1). One can thus calculate the variation of entropy ΔS corresponding to the virtual process:

$$\Delta S \;=\; S\begin{pmatrix}\text{composite syst.}\\ \text{constrained equil.}\end{pmatrix} \;-\; S\begin{pmatrix}\text{simple syst.}\\ \text{free equil.}\end{pmatrix} \tag{6.15}$$

6.2.3 Equilibrium condition

According to Axiom II (§ 5.3), for any virtual process in an isolated system in equilibrium

$$\boxed{\Delta S < 0} \tag{6.16}$$

The entropy S is maximum with respect to all possible virtual processes that induce deviations from the equilibrium state.

To describe virtual processes in terms of thermodynamical variables one should introduce some walls and create some sub-systems. New thermodynamical variables would thus added, for example $U^{(1)}$ and $U^{(2)} = U - U^{(1)}$; it is with respect to these new variables that S is maximum at equilibrium (Fig. 6.1, right).

The entropy function S is thus stationary with respect to any infinitesimal virtual process inducing a deviation from the equilibrium state. The equilibrium condition is formally represented by

$$\boxed{\delta S = 0} \tag{6.17}$$

Don't confuse the symbol δS in (6.17) with the differential dS in (6.7). The symbol δ refers to virtual processes, and the evaluation of δS requires the thermodynamic operation of inserting some restraint within the system.

6.2.4 Equilibrium and intensive coordinates

Thermodynamic equilibrium is connected to the intensive coordinates introduced in § 6.1. Let us give some significant examples.

Example 1: Thermal equilibrium

Let us consider an isolated system, divided in two sub-systems by a rigid diathermic wall. Initially the entire system is in equilibrium (Fig. 6.2).

Let us first focus our attention on a virtual process consisting in the exchange of an *infinitesimal* quantity of energy $dU^{(1)}$ between the syb-system (1) and the sub-system (2). The new situation could be frozen by making ideally adiabatic constraint the wall separating the sub-system (1) from the sub-system (2).

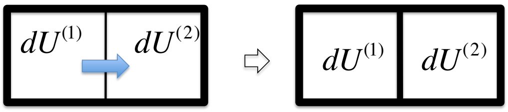


Figure 6.2: An energy fluctuation in an isolated system in thermal equilibrium.

The condition that S is stationary at equilibrium ($\delta S = 0$) can be expressed in terms of the properties of the two sub-systems:

$$\delta S = dS^{(1)} + dS^{(2)} = 0\,. \tag{6.18}$$

By adapting the differential expression (6.7) to the two sub-systems, with $dV^{(1)} = dV^{(2)} = 0$, $dn_i^{(1)} = dn_i^{(2)} = 0$ and $dU^{(1)} = -dU^{(2)}$, one finds

$$\delta S = \frac{1}{T^{(1)}}\, dU^{(1)} + \frac{1}{T^{(2)}}\, dU^{(2)} = \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] dU^{(1)} = 0\,. \tag{6.19}$$

The condition of thermal equilibrium is thus:

$$T^{(1)} = T^{(2)}\,. \tag{6.20}$$

By generalising the result to any number of sub-systems, for a system in thermal equilibrium the intensive variable T has to be uniform within the entire system. The variable T is thus identified with the temperature.

The Zeroth Law of the cycle Thermodynamics (§ 2.1) is so restated.

Let us now consider a virtual process consisting in the trasfer of a *finite* quantity of energy between the two sub-systems. According to (6.16), lthe finite variation of entropy is negative:

$$\Delta S = \Delta S^{(1)} + \Delta S^{(2)} < 0\,. \tag{6.21}$$

As a consequence of the virtual process, the temperatures $T^{(1)}$ and $T^{(2)}$ of the two sub-systems become different. One can anyway observe that, since

$$\Delta S = \int \frac{1}{T^{(1)}}\, dU^{(1)} + \int \frac{1}{T^{(2)}}\, dU^{(2)} < 0 \tag{6.22}$$

and $dU^{(1)} = -dU^{(2)}$, the virtual process induces a transfer of energy U from the sub-system that reduces its temperature to the sub-system that increases its temperature.

Example 2: Thermal and mechanical equilibrium

Let us consider again an isolated system, divided now in two sub-systems by a mobile and diathermic piston(Fig. 6.3). IInitially the system is in thermodynamical equilibrium.

Let us consider a virtual process consisting in an infinitesimal exchange of energy $dU^{(1)}$ and of volume $dV^{(1)}$ between the sub-system (1) and the sub-system (2). The resulting state is frozen by fixing and insulating the piston separating (1) from (2).

The condition that S is stationary at equilibrium ($\delta S = 0$) can be expressed in terms of the properties of the two sub-systems by means of the differential equation (6.7), with $dn_i^{(1)} = dn_i^{(2)} = 0$, $dU^{(1)} = -dU^{(2)}$ and $dV^{(1)} = -dV^{(2)}$:

$$\delta S = dS^{(1)} + dS^{(2)} = \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] dU^{(1)} + \left[\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}}\right] dV^{(1)} = 0\,. \tag{6.23}$$

Since $U^{(1)}$ and $V^{(1)}$ are independent variables, the condition of thermal and mechanical equilibrium implies that

$$T^{(1)} = T^{(2)} \qquad \text{e} \quad p^{(1)} = p^{(2)}\,. \tag{6.24}$$

The intensive variable T has already been identified with the temperature; one can now identify the variable p with the pressure.

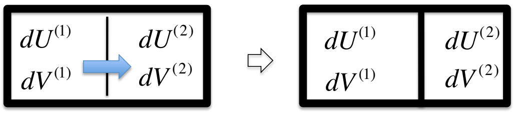


Figure 6.3: A fluctuation of energy and volume in an isolated system in thermal and mechanical equilibrium.

Example 3: Thermal and chemical equilibrium

At last, let us consider an isolated system, divided in two sub-systems by a fixed diathermic wall, permeable to the flux of matter. Initially the system is in thermodynamical equilibrium.
Let us now consider a virtual process consisting in the exchange of infinitesimal quantities of energy $dU^{(1)}$ and of matter $\{dn_i^{(1)}\}$ between the sub-system (1) and the subsystem (2). The resulting state is frozen by insulating making impermeable the wall separating (1) from (2).
The condition that S is stationary at equilibrium ($\delta S = 0$) can again be expressed in terms of the properties of the two sub-systems by means of the differential equation (6.7), with $dV^{(1)} = dV^{(2)} = 0$, $dU^{(1)} = -dU^{(2)}$ and $dn_i^{(1)} = -dn_i^{(2)}$, so that

$$\delta S = dS^{(1)} + dS^{(2)} = \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] dU^{(1)} - \sum_i \left[\frac{\mu_i^{(1)}}{T^{(1)}} - \frac{\mu_i^{(2)}}{T^{(2)}}\right] dn_i^{(1)} = 0\,. \tag{6.25}$$

Since $U^{(1)}$ and $n_i^{(1)}$ are independent variables, the condition of thermal and chemical equilibrium implies that

$$T^{(1)} = T^{(2)} \quad \text{e} \quad \mu_i^{(1)} = \mu_i^{(2)} \ (\forall\, i)\,, \tag{6.26}$$

where μ_i is the chemical potential of the i-th component.

One can qualitatively observe that the chemical potential plays, with respect to matter transfer, a similar role as the temperature with respect to energy transport. However, the chemical potential is not directly connected to the sensorial experience as temperature is. We will better grasp the meaning of the chemical potential later on. For the moment we can anticipate, as an example, that the chemical potential of an ideal gas can be expressed in the form $\mu_i = RT[\phi(T) + \ln p_i]$, where $\phi(T)$ is a function of the temperature.

Example 3 refers to the chemical equilibrium relative to matter transport. The case of the equilibrium in chemical reaction, which is more complicated, will be treated later on, in § 11.4.

6.2.5 Intensive variables and irreversible processes

The above simple examples refer to the equilibrium between two sub-systems. Equilibrium corresponds to the equality of intensive coordinates. The lack of equilibrium between two sub-systems, represented by finite differences of intensive variables $\Delta T, \Delta p, \{\Delta\mu_i\}$ triggers an irreversible process towards an equilibrium state where $\Delta T = 0, \Delta p = 0, \{\Delta\mu_i\} = 0$.

The generalisation to the case of any continuous system is trivial. The condition of thermodynamical equilibrium requires the uniformity of the intensive coordinates $T, p, \{\mu_i\}$ in the entire system.
The presence of gradients of intensive variables in the entropy representation, $\nabla(1/T)$, $\nabla(p/T)$, $\{\nabla(\mu_i/T)\}$, and as a consequence also of ∇T, ∇p, $\{\nabla\mu_i\}$, means that the thermodynamical equilibrium is absent and triggers irreversible processes towards equilibrium.

The finite differences $\Delta T, \Delta p, \{\Delta\mu_i\}$ for discrete systems and the gradients $\nabla T, \nabla p, \{\nabla\mu_i\}$ for continuous systems are often called *generalised forces*, since they are responsible of the irreversible processes that lead the system to an equilibrium state.

6.3 Energy representation

Let us now consider the equilibrium conditions in the energy representation. The energy representation plays a more relevant role than the entropy representation in the further development of the thermodynamical formalism.

6.3.1 Fundamental equation

Axiom III of § 5.3 states that the entropy $S$is a monotonously increasing function of the energy U. As a consequence, the temperature T cannot be negative (§ 6.2).
More information on the dependence of S on U can be obtained from the stability conditions of the thermodynamical equilibrium, to be considered later on. We only anticipate here that, in order to guarantee the stability of thermodynamical equilibrium, it is necessary that

$$\left(\frac{\partial^2 S}{\partial U^2}\right) = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right) < 0\,, \tag{6.27}$$

sat that the heat capacity $\partial U/\partial T$ be positive. Equation (6.27) implies that $S(U)$ is downward concave (Fig. 5.3, left).

As already seen in § 5.3.2, the monotonous dependence of S on U allows one to invert of the fundamental equation $S = S(U, V, \{n_i\})$ and to obtain the fundamental equation in the energy representation:

$$U = U(S, V, \{n_i\})\,. \tag{6.28}$$

The energy U is a monotonously increasing function of the entropy S, upwards concave (Fig. 5.3,right). The fundamental equation (6.28) contains the entire information on the thermodynamical properties of a system, like equation $S = S(U, V, \{n_i\})$.

6.3.2 Energy balance

The differential form (6.8)

$$dU = T\,dS - p\,dV + \sum \mu_i\,dn_i \tag{6.29}$$

represents the energy balance for infinitesimal reversible transformations. Comments:

a) The term $-p\,dV = đW_{\rm rev}$ is the reversible compression work made on the system.
b) For a system in which the quantities of the components are constant ($dn_i = 0$), one has $T\,dS = đQ_{\rm rev}$, and (6.8) reduces to the equation (4.42) of Chapter 4: $dU = đQ + đW$.
c) The terms $\mu_i\,dn_i$ are the variations of energy due to the variations of the quantity of the components; they are sometimes called "cheical work".

For completeness, one can add to (6.8) the terms of possible contributions of generalised work $dW_i^* = \xi_i^*\,dX_i^*$.
We will deepen the topic of the energy balance in § 8.1 of Capter 8, after other thermodynamic functions have been introduced in the energy representation dopo aver introdotto in Chapter 10. For the moment, let us focus our attention on the equilibrium conditions in the energy representation.

6.3.3 Fundamental axiom and equilibrium condition

As it was pointed in § 5.3, the fundamental Axiom II states that in an isolated system (say where U, V are constant and there is no exchange of matter with the environment) the extensive quantities $U, V, \{n_i\}$ are distributed among the various possible sub-systems is such a way that, in equilibrium conditions, the value of the entropy $S_{\rm eq}$ is maximum with respect to the values that entropy could take in any possible virtual state of constrained equilibrium. Otherwise stated, the entropy S of an isolated system in equilibrium is maximum with respect to all possible virtual processes that would induce deviations from the equilibrium state. The equilibrium conditions in the entropy representation are summarised in (6.16) and (6.17):

$$\Delta S < 0\,, \qquad \delta S = \ 0\,.$$

The fundamental axiom can be stated within the energy representation too. In this case, however, instead of an isolated system we have to consider a system where S is constant, and again V is constant and there is no exchange of matter with the environment.
The fundamental axiom states that for such a system, that is initially in a state of constrained equilibrium, the removal of the constraints triggers a thermodynamic process that brings the system to a non constrained equilibrium state characterised by a value of energy U smaller that in the initial state.
Otherwise stated, the internal energy U is minimal, at equilibrium, in the systems for which S and V are constant and there is no exchange of energy with the environment. The equation equivalent to (6.16) is, in the energy representation,

$$\boxed{\Delta U > 0} \tag{6.30}$$

The internal energy function $U(S, V, \{n_i\})$ is minimum with respect to any infinitesimal process that brings the system out of equilibrium maintaining constant S and V and without exchange of matter with the environment. The equilibrium conditions are formally represented by

$$\boxed{\delta U = 0} \tag{6.31}$$

Note: We have again neglected here the chemical reaction, that will be treated in § 11.4.

Dimostrazione dell'equivalenza dei due enunciati

The equivalence of (6.30) and (6.31) to (6.16) and (6.17), respectively, say the equivalence of the two statements of the fundamental axiom in the energy and entropy representations, can be proved by a reductio ad absurdum. The procedure is similar to that previously used to demonstrate the equivalence of the Clausius and Kelvin statements of the Second Law of Thermodynamics in § 4.2.

a) Let us suppose that S be not maximum in a system in equilibrium with U constant (violation of the statement in the entropy representation). A virtual process could then occur leading the system out of equilibrium with $\Delta U = 0, \Delta S > 0$. One could recover the initial entropy value S by expelling an energy quantity $\Delta U = T\,\Delta S$ as heat. Globally, one would obtain a process leading the system out of equilibrium with $\Delta S = 0, \Delta U < 0$. The initial equilibrium condition would thus correspond to having S constant and the value of U non minimum (violation of the statement in the energy representation). In short:

$$\begin{cases} \Delta S > 0 \\ \Delta U = 0 \end{cases} \quad \Rightarrow \quad \begin{cases} \Delta S = 0 \\ \Delta U < 0 \end{cases} \tag{6.32}$$

b) Let us suppose that U be not minimum in a system in equilibrium with Sconstant (violation of the statement in the energy representation). A process could then occur leading the system out of equilibrium, with $\Delta S = 0, \Delta U < 0$. One could recover the initial energy value U by doing work W on the system and dissipating it s heat $Q = T\,\Delta S$. Globally, one would obtain a process leading the system out of equilibrium with $\Delta U = 0, \Delta S > 0$. The initial equilibrium condition would thus correspond to having U constant and the value of S not maximum La situazione di equilibrio iniziale corrisponderebbe cioè a U costante e S non massima (violation of the statement in the entropy representation). In short:

$$\begin{cases} \Delta U < 0 \\ \Delta S = 0 \end{cases} \quad \Rightarrow \quad \begin{cases} \Delta U = 0 \\ \Delta S > 0 \end{cases} \tag{6.33}$$

In the demonstration it was supposed that the volume V is maintained constant and that there is no exchange of matter with the environment.

6.3.4 Example: Thermal equilibrium

Let us study in more detail the conditions of thermal equilibrium for a system maintained with entropy S and volume V constant and without exchanges of matter. In particular, the attention if focused on the condition that entropy be constant, $\Delta S = 0$.

A. At first, let us consider a process connecting an initial state of constrained equilibrium to a final state of non-constrained equilibrium and verify that the process with $\Delta S = 0$ is accompanied by a reduction of the internal energy U.
Let as consider a system composed of two bodies at temperatures T_1 and T_2, respectively, separated by an adiabatic wall that forbids the transfer of energy. If the adiabaticity constraint is removed, the two bodies exchange heat until their temperatures become equal. Let us examine two different possibilities for thermalisation:

1) The two bodies are in direct contact; the irreversible flow of heat from the hot to the cold body generates an increase of the system entropy; to recover the initial value of entropy, so that at the end $\Delta S = 0$, it is necessary to expel a given amount of heat from the system, say to reduce its internal energy ($\Delta U < 0$).
2) The two bodies exchange heat through a reversible (Carnot) engine; the entropy of the system is unchanged ($\Delta S = 0$), and the engine performs work $\tilde{W}$ on the external ambient, so that the energy of the system decreases ($\Delta U = \tilde{W} < 0$).

B. Let us consider now a system that is already in a state of non-constrained equilibrium.
One can devise a transfer of energy dU from a sub-system (1) to a subsystem (2) through a reversible (Carnot) refrigerating cycle operating between the two sub-systems and absorbing work $\tilde{W} > 0$ from the ambient. The entropy is unchanged ($\Delta S = 0$).
The condition that $\delta U = 0$ in the equilibrium state can be expressed as

$$\delta U = dU^{(1)} + dU^{(2)} = T^{(1)}\, dS^{(1)} + T^{(2)}\, dS^{(2)} = (T^{(1)} - T^{(2)})\, dS^{(1)} = 0\,, \tag{6.34}$$

whence the condition of thermal equilibrium:

$$T^{(1)} = T^{(2)}\,. \tag{6.35}$$

One thus recovers in the energy representation the same condition of thermal equilibrium already found in the entropy representation.

By similar procedures one can recover the conditions of mechanical and chemical equilibrium.

6.3.5 Comments

1. A non-negligible difference can be observed between the entropy and energy representations.

- For isolated systems (in the entropy representation) the transition from constrained to non-constrained equilibrium can take place only irreversibly. This fact requires that one resorts to the artefact of virtual processes to describe the fluctuations with respect to equilibrium. It is worth noting that entropy is not a conservative quantity, and can increase even in isolated systems.
- For systems maintained at constant entropy S (in the energy representation) the transition from constrained to non-constrained equilibrium can take place both reversibly or irreversibly. It is not necessary to resort to virtual processes. Real deviations from equilibrium can take place by exchange of energy (a conservative quantity) between the system and its environment.

2. The statements of the fundamental axiom in the representations of entropy and energy can be connected with the Clausius and Kelvin statements of the Second Law, respectively.

a) In an isolated system, the spontaneous flow of heat takes place from a hot to a cold body (Clausius) and the entropy increases (axiom II in the entropy representation).
b) If the entropy of a system is maintained constant, the flow of heat from a hot to a cold boy takes place with release ow work out of the system (Kelvin), say with reduction of the system energy (axiom II in the energy representation).

3. Here and below, $\tilde{W}$ represents the work exchanged by a system with its environment as a consequence of readjustements taking place within the system, without modifications of its extensive coordinates $V, n, \ldots$. The internal energy U represents a sort of potential energy for the work $\tilde{W}$. We will consider again this topic in connection with the introduction of the so-called thermodynamical potentials (Chapter 7).

6.4 Properties of the fundamental equations

As already observed, the fundamental equation for a thermodynamical system in one of the two representations (entropy or energy) can be evaluated with varying degrees of approximation from suitable experiments or statistical calculations.
In this § 6.4 some relevant mathematical properties of the fundamental equations will be introduced, that define their analytic form and facilitate their experimental or theoretical evaluation.
At the end, by way of example, we will take advantage of these properties to find the fundamental equation of an ideal gas in the entropy representation.

6.4.1 State equations

For the two representations, energy and entropy, respectively,

$$U = U(S, V, \{n_i\}) \qquad\qquad S = S(U, V, \{n_i\}) \tag{6.36}$$

one can obtain the variables coordinates as a function of the extensive variables. Such expressions are called state equations:

$$\begin{cases} T = \left(\dfrac{\partial U}{\partial S}\right)_{V,\{n_i\}} = T(S, V, \{n_i\}) \\[2ex] p = -\left(\dfrac{\partial U}{\partial V}\right)_{S,\{n_i\}} = p(S, V, \{n_i\}) \\[2ex] \mu_i = \left(\dfrac{\partial U}{\partial n_i}\right)_{S,V} = \mu_i(S, V, \{n_i\}) \end{cases} \qquad \begin{cases} \dfrac{1}{T} = \left(\dfrac{\partial S}{\partial U}\right)_{V,\{n_i\}} = \dfrac{1}{T}(U, V, \{n_i\}) \\[2ex] \dfrac{p}{T} = \left(\dfrac{\partial S}{\partial V}\right)_{U,\{n_i\}} = \dfrac{p}{T}(U, V, \{n_i\}) \\[2ex] \dfrac{\mu_i}{T} = -\left(\dfrac{\partial S}{\partial n_i}\right)_{U,V} = \dfrac{\mu_i}{T}(U, V, \{n_i\}) \end{cases} \tag{6.37}$$

For a simple system with one component there are three extensive variables and thus three state equations.
The state equations can be obtained from experiment or from statistical theory. Our problem is now to understand how the fundamental equation can be evaluated from the state equations.
Two main difficulties can affect this procedure.

1. In general, if onlythe n first derivatives of a function with respect to its n independent variables are known, the univocal evaluation of the function is impossible. Asa consequence, the knowledge of the state equations (6.37) doesn't correspond, in principle, to a complete knowledge of the fundamental equations (6.36).

2. Not all the state equations can be independently obtained from experiment or from theory. On the other hand, one can ask whether the three state equations (6.37) are really independent. For example, in § 3.1 we have seen that for a simple system with one component two only state equations (the thermal and the caloric one) should be sufficient to define all the thermodynamical properties.

The first difficulty can be solved by considering that also energy and entropy are defined to within an arbitrary additive constant. The second difficulty is solved by considering a further property of the fundamental equations, say their homogeneity, to be introduced immediately below.

6.4.2 Homogeneity of the fundamental equations

As a consequence of the axiom of additivity of S (axiom III), the fundamental equations are homogeneous to first order with respect to the extensive coordinates (§ 5.3). Otherwise stated, if all extensive coordinates are multiplied by a factor λ, the function is multiplied by λ too:

$$U(\lambda S, \lambda V, \{\lambda n_i\}) = \lambda\, U(S, V, \{n_i\})\,, \qquad\qquad S(\lambda U, \lambda V, \{\lambda n_i\}) = \lambda\, S(U, V, \{n_i\})\,. \tag{6.38}$$

It is worth noting that the state equations (6.37) are instead homogeneous of order zero with respect to the extensive coordinates: the values of the intensive coordinates are not modified if the extensive coordinates are multiplied by a scale factor.

Euler relations

The homogeneity (6.38) of the fundamental equations allows one to determine their analytic form. To this aim, let us differentiate the functions (6.38) with respect to the arbitrary scale factor λ:

$$\frac{dU}{d\lambda} = \frac{\partial U}{\partial(\lambda S)}\, S + \frac{\partial U}{\partial(\lambda V)}\, V + \sum_i \frac{\partial U}{\partial(\lambda n_i)}\, n_i = U \tag{6.39}$$

$$\frac{dS}{d\lambda} = \frac{\partial S}{\partial(\lambda U)}\, U + \frac{\partial S}{\partial(\lambda V)}\, V + \sum_i \frac{\partial S}{\partial(\lambda n_i)}\, n_i = S \tag{6.40}$$

Since the value of λ is arbitrary, one can assume $\lambda = 1$ in (6.39) and (6.40). Taking into account the definitions of the intensive coordinates (6.6) and (6.5), from (6.39) and (6.40) one obtains the *Euler relations* in both representations of energy and entropy, respectively:

$$U = T\,S - p\,V + \sum_i \mu_i\, n_i\,, \qquad\qquad S = \frac{1}{T}\, U + \frac{p}{T}\, V - \sum_i \frac{\mu_i}{T}\, n_i\,. \tag{6.41}$$

Two relevant comments can be made on the Euler relations:

1) The Euler relations are linear with respect to the estensive coordinates.
2) If all the state equations (6.37) are known in a given representation (energy or entropy), they can be substituted in the corresponding Euler relation (6.41). The knowledge of all the state equations is thus equivalent to the knowledge of all the thermodynamical properties implicit in the fundamental equations (6.36).

Gibbs-Duhem relations

Further important general relations can be obtained by comparing, for each representation, the fundamental equation (6.36) with the Euler relation (6.41). Let us consider, for example, the energy representation. The differentials of energy calculated from the fundamental equation and from the Euler relation are, respectively

$$\text{fundam. eq.:} \qquad dU = TdS - pdV + \sum \mu_i dn_i \tag{6.42}$$

$$\text{Euler:} \qquad dU = TdS + SdT - pdV - Vdp + \sum \mu_i dn_i + \sum n_i d\mu_i \tag{6.43}$$

Similar equations can be written for the entropy representation.
By equating the second members of the two equations one obtains the Gibbs-Duhem relations (on the left for the energy representation, on the right for the entropy representation):

$$S\,dT - V\,dP + \sum_i n_i\,d\mu_i = 0\,, \qquad U\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{p}{T}\right) - \sum_i n_i\,d\left(\frac{\mu_i}{T}\right) = 0\,. \tag{6.44}$$

Equations (6.44) represent a differential relation between intensive variables.
If in a given representation (energy or entropy) all state equations minus one are known, the missing equation can be obtained, to within an additive constant, by integrating the Gibbs-Duhem relation. Once all state equations are known, one can calculate the fundamental equations, obviously to within ad additive constant.

6.4.3 One-component systems: Molar quantities

For system with only one component, the expression of the fundamental equations is particularly simple.
The thermodynamical state of a one-component system is defined by three extensive coordinates: S, V, n in the energy representation, U, V, n in the entropy representation.

Molar quantities. For a closed system with only one component, it is convenient to resort to molar quantities (molar energy, molar volume, molar entropy), conventionally denoted by lower-case letters:

$$u = U/n\,, \qquad v = V/n\,, \qquad s = S/n\,. \tag{6.45}$$

Fundamental equations. The fundamental equations in the energy and entropy representation

$$U \;=\; U(S,V,n)\,, \qquad S \;=\; S(U,V,n) \tag{6.46}$$

can be expressed in molar terms for a closed system (say with n constant) as

$$u = u(s,v)\,, \qquad s = s(u,v) \tag{6.47}$$

and their differential forms are

$$du = T\,ds - p\,dv\,, \qquad ds = \frac{1}{T}\,du + \frac{p}{T}\,dv\,. \tag{6.48}$$

The fundamental equations (6.47) don't contain extensive coordinate, so that the previous considerations about homogeneity don't apply to them.
In (6.48) two intensive coordinates are present for each representation. If the two corresponding state equations are known – e.g. $T(s,v)$ and $p(s,v)$ in the energy representation – by substituting them in (6.48) and calculating the integral, one can obtain the fundamental equations (6.47), obviously to within an integration constant.

Euler relations. Dividing the Euler relations (6.41)

$$U = T\,S - p\,V + \mu\,n\,, \qquad S = \frac{1}{T}\,U + \frac{p}{T}\,V - \frac{\mu}{T}\,n\,, \tag{6.49}$$

by the number n of moles one obtains the molare Euler equations:

$$u = T\,s - p\,v + \mu\,, \qquad s = \frac{1}{T}\,u + \frac{p}{T}\,v - \frac{\mu}{T}\,. \tag{6.50}$$

If two state equations are known – e.g. $T(s,v)$ and $p(s,v)$ in the energy representation – by substituting them in (6.50) one cannot univocally recover the fundamental equations, since the chemical potential μ is unknown.

Gibbs-Duhem relations. Thei Gibbs-Duhem (6.44) relations for a system with only one component become

$$s\,dT - v\,dp + d\mu = 0\,, \qquad u\,d\Big(\frac{1}{T}\Big) + v\,d\Big(\frac{p}{T}\Big) - d\Big(\frac{\mu}{T}\Big) = 0\,. \tag{6.51}$$

The chemical potential. The chemical potential μ can be calculated, to within ad additive constant, from the state equations – e.g. $T(s,v)$ and $p(s,v)$ in the energy representation –by means of two alternative procedures:

a) from the Euler relations (6.50) once the fundamental equation (6.47) is known,
b) by integrating the Gibbs-Duhem (6.51) relations.

6.4.4 Example: The monatomic ideal gas

The monatomic ideal gas is a simple system, particularly suitable for a tutorial on the concepts introduced above.

State equations

The two state equations for the monatomic ideal gas (§ 3.1)

$$\text{thermal state equation:} \qquad pV = nRT\,, \tag{6.52}$$

$$\text{caloric state equation:} \qquad U = (3/2)nRT\,. \tag{6.53}$$

are obtained experimentally – (6.52) from the Boyle and Gay-Lussac laws, (6.53) from the measurement of specific heats – at the limit for low density.
To be rigorous, the caloric state equation based on the specific heat measurement should contain an arbitrary constant. However, (6.53) is based on the kinetic model of the ideal gas, where the internal energy U is purely kinetic and there are thus no additive constants.

The fundamental equation

We want now to obtain the fundamental equation starting from the knowledge of the empirical state equations (6.52) and (6.53).

We can note that (6.52) and (6.53) correspond to the first two state equations (6.37) in the entropy representation:

$$\frac{p}{T} = \frac{nR}{V}\,, \qquad \frac{1}{T} = \frac{3nR}{2U}\,. \tag{6.54}$$

It is thus convenient to remain within the entropy representation and search for the fundamental equation $S = S(U,V,n)$.
By inserting equations (6.54) in the Euler relation (6.49) for the entropy representation, one obtains

$$S = \frac{5}{2}\,nR - \frac{\mu}{T}\,n\,. \tag{6.55}$$

Equation (6.55) is not sufficient. To obtain a fundamental equation it is necessary to express the intensive coordinate μ/T as a function of the extensive coordinates.

The problem can be dealt by two different procedures, the first one more general, the second one limited to closed system($dn = 0$).

First procedure

The Gibbs-Duhem relations (6.44) connect the differentials of the intensive coordinates. For a system with one component the Gibbs-Duhem relation in the entropy representation

$$U\,d\Big(\frac{1}{T}\Big) + V\,d\Big(\frac{p}{T}\Big) - n\,d\Big(\frac{\mu}{T}\Big) = 0 \tag{6.56}$$

allows the expression on the differential of μ/T as a function of the differentials of the two other intensive variables, that can in turn be calculated by differentiating equations (6.54) with respect to the extensive variables:

$$\begin{aligned} d\Big(\frac{\mu}{T}\Big) &= \frac{U}{n}\,d\Big(\frac{1}{T}\Big) + \frac{V}{n}\,d\Big(\frac{p}{T}\Big) \\ &= \frac{U}{n}\left[-\frac{3nR}{2U^2}\,dU + \frac{3R}{2U}\,dn\right] + \frac{V}{n}\left[-\frac{nR}{V^2}\,dV + \frac{R}{V}\,dn\right] \\ &= -\frac{3}{2}\,R\,\frac{dU}{U} - R\,\frac{dV}{V} + \frac{5}{2}\,R\,\frac{dn}{n}\,. \end{aligned} \tag{6.57}$$

The indefinite integral of (6.57)

$$\frac{\mu}{T} = -\frac{3}{2}\,R\,\ln U - R\,\ln V + \frac{5}{2}\,R\,\ln n + \text{constant}\,, \tag{6.58}$$

once inserted in (6.55), allows the derivation of the fundamental equation for the monatomic ideal gas to within an arbitrary additive constant:

$$S = \frac{5}{2}\,nR + \frac{3}{2}\,nR\,\ln U + nR\,\ln V - \frac{5}{2}\,nR\,\ln n + \text{constant.} \tag{6.59}$$

The presence of the unknown additive constant in (6.59) forbids the verification of the homogeneity of the equation.

It is more convenient to perform the definite integral of (6.57) with reference to a reference state (U_0, V_0, n_0), so obtaining the expression

$$\frac{\mu}{T} = \Big(\frac{\mu}{T}\Big)_0 - \frac{3}{2}\,R\,\ln\frac{U}{U_0} - R\,\ln\frac{V}{V_0} + \frac{5}{2}\,R\,\ln\frac{n}{n_0}\,, \tag{6.60}$$

which, inserted in (6.55), gives the fundamental equation in the form

$$\begin{aligned} S(U,V,n) &= \frac{5}{2}\,nR - n\,\Big(\frac{\mu}{T}\Big)_0 + \frac{3}{2}\,nR\,\ln\frac{U}{U_0} + nR\,\ln\frac{V}{V_0} - \frac{5}{2}\,nR\,\ln\frac{n}{n_0} \\ &= \frac{5}{2}\,nR - n\,\Big(\frac{\mu}{T}\Big)_0 + nR\ln\left[\Big(\frac{U}{U_0}\Big)^{3/2}\Big(\frac{V}{V_0}\Big)\Big(\frac{n}{n_0}\Big)^{-5/2}\right] \end{aligned} \tag{6.61}$$

Some simple comments on the fundamental equation (6.61):

- The equation is homogeneous with respect to the extensive variables U, V, n, as required by Axiom III.
- The entropy S is a monotonously increasing function of the energy U, again as required by Axiom III. The curve $S(U)$ is downward concave.
- The validity of the equation is limited to the temperature interval of validity of the state equations (6.52) and (6.53).
- The equation contains an unknown constant term $(\mu/T)_0$. The reason is that the starting point was represented by only two state equations instead of three. The result is anyway consistent with the entropy being defined in the cycle Thermodynamics to within ad additive constant.

Second procedure

Fo a closed system, where the number n of moles is constant, one can consider molar quantities (6.45) and integrate the differential (6.48)

$$ds = \frac{1}{T}\,du + \frac{p}{T}\,dv\,, \tag{6.62}$$

without resorting to the Gibbs-Duhem relation.
By substituting the state equations in molar form (6.54)

$$\frac{1}{T} = \frac{3R}{2u}\,, \qquad \frac{p}{T} = \frac{R}{v} \tag{6.63}$$

in (6.62) and integrating one obtains:

$$s = s_0 + \frac{3}{2}\,R\,\ln\frac{u}{u_0} + R\,\ln\frac{v}{v_0}\,, \tag{6.64}$$

where s_0 is the molar entropy of a reference state. Comparing with (6.61), and imposing $n = n_0 = 1$, one finds

$$s_0 \;=\; \frac{5}{2}R - \left(\frac{\mu}{T}\right)_0\,. \tag{6.65}$$

The expression of entropy (6.64) is consistent, to within the factor n, with the expression (4.39) calculated in Part I.

Concluding remarks

The previous example concerning the monatomic ideal gas allowed us to determine the analytic form of its fundamental equation and to inquire on the relations between fundamental equation and state functions for a simple system.

In spite of the simplicity of the system, the fundamental equations (6.61) and (6.64) are not so familiar. Actually, their practical usefulness is quite limited, since it is unusual the deal with systems for which one of the independent variables is the internal energy U. More frequently one has to deal with systems whose state is characterised by the value of some intensive coordinate; the independent coordinates could be, for example, volume and temperature V, T or volume and pressure V, p,

It is thus important to inquire whether fundamental equations can be found based on sets of coordinates different from those used in the energy and in the entropy representations. For example, is it possible to establish fundamental equations based on the pair of coordinates $T, V, \{n_i\}$ or $T, p, \{n_i\}$? A solution to this problem will be found in the next Chapter 7, where new representations are introduced, alternative but equivalent to the energy and entropy representations.

At last, let us notice that, according to (6.60), the chemical potential depends on the internal energy U in addition to the coordinates (T, V, n). Thanks to the introduction of new representations in Chapter 7, an expression of the chemical potential as a function of only temperature and pressure will be obtained in § 11.1.

Chapter 7

Alternative fundamental equations

In previous chapters 5 and 6, the thermodynamical state of systems has been specified by extensive coordinates. Two choices of extensive coordinates have been considered, the entropy and the energy representations. For each one of the two representations, the thermodynamical properties of systems are contained in a fundamental equation,

$$S(U, V, \{n_i\}) \qquad \text{or} \qquad U(S, V, \{n_i\})\,. \tag{7.1}$$

The two representations are connected by a simple rotation of the axes in the Gibbs space of extensive coordinates.
In the two representations an intensive coordinate is conjugated to each one of the extensive coordinates (§ 6.1). The intensive can be more easily controlled in the laboratory (a number of experiments are performed in conditions of fixed pressure and temperature). It is thus sound to describe the thermodynamical properties by fundamental equations in which one or more of the extensive coordinates are substituted by intensive coordinates.

7.1 Legendre transforms

The formalism allowing a flexible adaptation of the thermodynamical description to different systems, by substituting some extensive coordinates with intensive coordinates, is founded on the Legendre transforms.

7.1.1 Statement of the problem

Let us focus our attention on the energy representation and denote by X_i and Y_i the extensive and intensive coordinates, respectively. The function $U(X_1, X_2, X_3, \ldots)$, that contains all the thermodynamical information on the system, is assumed to be continuous and differentiable. The first derivatives of $U(X_1, X_2, X_3, \ldots)$ with respect to the extensive coordinates X_i are the intensive coordinates Y_i (such as T, p, μ cor a simple system with one component). As we will see later on, derivatives of higher order with respect to both extensive and intensive coordinates correspond to further quantities characterising the thermodynamical behaviour of a system, such as specific heats, compressibilities, coefficients of thermal expansion. ,
Our goal is now to succeed in expressing all the thermodynamical properties of a system by new functions where one or more extensive coordinates are substituted by the corresponding intensive coordinates. The problem is far from trivial, so that we will first try to solve it in a simple unidimensional case.

7.1.2 Unidimensional case, an inadequate solution

Let the function $U = U_x(X)$ be continuous and differentiable (Fig. 7.1, left). To each value of X one can associate the value of the first derivative $Y(X) = dU_x/dX$. One can then obtain a new function $U = U_y(Y)$ (Fig. 7.1, center).

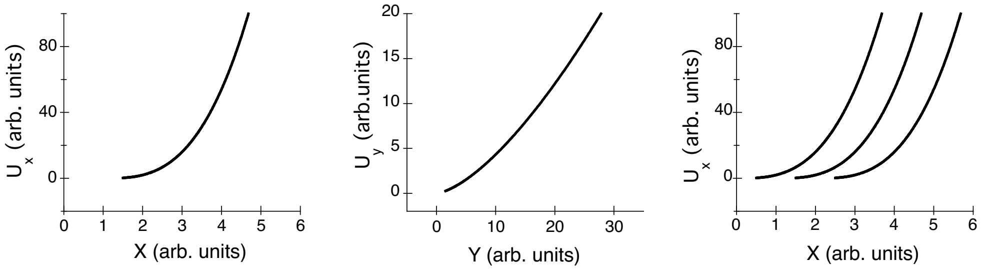


Figure 7.1: With reference to the unidimensional case of § 7.1.2. Left: the initial function $U_x(X)$. Center: the corresponding ffunction $U_y(Y)$, where $Y = dU_x/dX$. Right: examples of different functions U_x corresponding to the same function $U_y(Y)$.

To each function $U_x(X)$ it corresponds only one function $U_y(Y)$.
It is easily verified that to the function $U_y(Y)$ infinite functions $U_x(X)$ correspond (Fig. 7.1, right).
In the transform $U_x(X) \to U_y(Y)$ an amount of information has been lost. .The function $U_y(Y)$ doesn't contain all the information contained in $U_x(X)$ and wouldn't t be a good fundamental function.

Example: Let us consider the function $U = U_x = AX^3$, where A is a constant. Its first derivative is $Y = dU_x/dX = 3AX^2$.
By substituting $X = (Y/3A)^{1/2}$ in U_x, one obtains an expression of U as a function of Y: $U_y(Y) = Y^{3/2}/(3^{3/2}A^{1/2})$.
The new function $U_y(Y)$ doesn't contain all the information contained in $U_x(X)$. Actually, any function $U_x = A(X - X_0)^3$, where X_0 is a constant, gives rise to the same function $U_y(Y) = Y^{3/2}/(3^{3/2}A^{1/2})$. Otherwise stated, if $U_y(Y)$ is known, to each value of Y it corresponds a single value of U, but infinite values of X.

(?) Repeat the procedure of the above example for the two functions $U_x = AX^2$ and $U_x = A \ln X$.

7.1.3 Legendre transforms for the unidimensional case

A sound solution to the problem of substituting an independent variable with is first derivative without losing information is based on the Legendre transforms.
From the geometrical point of view, the curve representing a function $U(X)$ in the X, U plane can be alternatively considered as

a) a locus of points, corresponding to pairs of coordinates (X, U) (Fig. 7.2, left); this picture allows the simple transition from the entropy representation to the energy representation, and viceversa;
b) an envelope of straight lines characterised by a slope Y and an intercept Φ (Fig. 7.2, center); to each point of the curve a pair of values (Y, Φ) univocally corresponds; on this picture the Legendre transform is founded.

Slope Y and intercept Φ of the straight line tangent to a given point are connected by the relation (Fig. 7.2, center)

$$Y = \frac{U - \Phi}{X}\,, \tag{7.2}$$

so that the intercept Φ (that has the same dimensions as the function U) can be expressed as

$$\boxed{\Phi = U - YX} \tag{7.3}$$

The function $\Phi(Y)$ (Fig. 7.2, right) is called the Legendre transform of the function $U(X)$, to which it univocally corresponds.

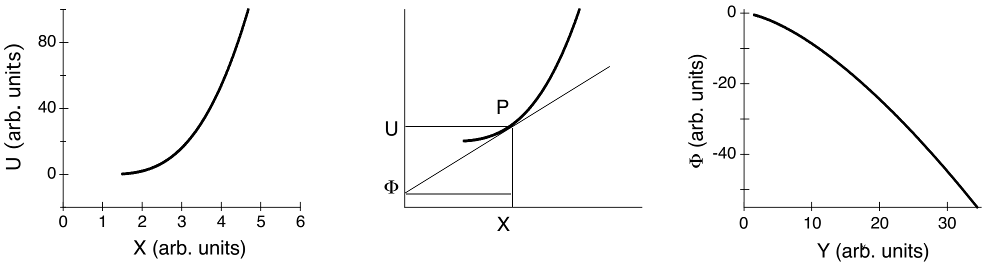


Figure 7.2: With reference to the Legendre transform. Left: the initial function $U(X)$, equal to the function $U_x(X)$ of Fig. 7.1. Center: relation between the variable X, the function U, lhe intercept Φ and the slope Y in a given point P. Right: the Legendre transform $\Phi(Y) = U - XY$.

The differential of $\Phi(Y)$ is

$$d\Phi = dU - Y\,dX - X\,dY = -X\,dY \qquad (\text{because } \ dU = Y\,dX)\,. \tag{7.4}$$

The function $\Phi(Y)$ has the same information content as the function $U(X)$. From $\Phi(Y)$ one can univocally recover $U(X)$ through the inverse transform.
Synthetically, the two equivalent functions are:

$$\begin{aligned} U &= U(X) & \qquad \Phi &= \Phi(Y) \\ dU &= Y\,dX & d\,\Phi &= -X\,dY \\ \frac{dU}{dX} &= Y & \frac{d\Phi}{dY} &= -X \end{aligned} \tag{7.5}$$

connected through the Legendre transforms:

$$\Phi = U - YX \quad \longleftrightarrow \quad U = \Phi + XY\,. \tag{7.6}$$

Example: Let us consider again the function $U(X) = AX^3$ of the previous example. The first derivative is $Y = dU/dX = 3AX^2$, so that $X = (Y/3A)^{1/2}$. The Legendre transform of $U(X)$ is the new function $\Phi(Y) = U - XY = -2\,Y^{3/2}/(3^{3/2}A^{1/2})$.
The inverse transform is $U(X) = \Phi(Y) + XY$. If $\Phi(Y)$ is known, $U(X)$ can be univocally recovered.

(?) Calculate the Legendre transforms of the two functions: $U_x = AX^2$ e $U_x = A\,\ln X$.

(?) What happens if $U = AX + B$, say for a linear dependence of U on X ?

7.1.4 Legendre transforms in several dimensions

Let us now consider the case, relevant for Thermodynamics, of a function of several variables:

$$U = U(X_1, X_2, X_3, \ldots) \tag{7.7}$$

$$dU = \sum\nolimits_i Y_i\,dX_i\,, \qquad\qquad Y_i = \left(\frac{\partial U}{\partial X_i}\right)_{(X_j \neq X_i)} \tag{7.8}$$

By generalising (7.3), one can calculate the Legendre transforms of $U(X_1, X_2, X_3, \ldots)$ with respect to one or more intensive variables Y_i.
For example, the Legendre transform with respect to the two intensive coordinates Y_r and Y_s is

$$\begin{aligned} U[Y_r, Y_s] &= \Phi(X_1, \ldots, X_{r-1}, Y_r, Y_s, X_{s+1}, \ldots) \\ &= U - X_r Y_r - X_s Y_s \end{aligned} \tag{7.9}$$

and its differential is

$$d\,\Phi = -X_r\,dY_r - X_s\,dY_s + \sum_{i\neq r,s} Y_i\,dX_i\,. \tag{7.10}$$

The inverse transform of (7.9),

$$\Phi[X_r, X_s] = \Phi + X_rY_r + X_sY_s \tag{7.11}$$

returns the initial function $U(X_1, X_2, X_3, \ldots)$.

Example: An example of Legendre transform can be found in Analytical Mechanics. The mechanical behaviour of a system can be deduced by the knowledge of the Lagrange function $\mathcal{L}(q_i, \dot{q}_i)$, that is a function of the generalised coordinates q_i and of their derivatives with respect to time $\dot{q}_i$. Alternatively, one can refer to the Hamilton function $\mathcal{H}(q_i, p_i)$, that is a function of the generalised coordinates q_i and of their conjugate momenta $p_i = \partial\mathcal{L}/\partial\dot{q}_i$. The connection between the Lagrange and Hamilton pictures is given by the Legendre transform

$$-\mathcal{H} = \mathcal{L} - \sum\nolimits_i p_i\dot{q}_i$$

.

7.2 Legendre transforms in Thermodynamics

Let us now apply the Legendre transforms to the fundamental equations of Thermodynamics. We focus the attention mainly on the energy representation, whose Legendre transforms are particularly important in practice, and make only a rapid mention to the entropy representation.

7.2.1 Enegry representation

Let us start from the fundamental equation and its differential form

$$U = U(S, V, \{n_i\})\,, \tag{7.12}$$

$$dU = T\,dS - p\,dV + \sum\nolimits_i \mu_i\,dn_i \tag{7.13}$$

and consider its possible Legendre transforms.

Enthalpy

The entalphy H is the Legendre transform of the energy U with respect to the pressure p:

$$U[p] = U + pV = H(S, p, \{n_i\})\,. \tag{7.14}$$

The enthalpy is a function of the independent coordinates $S, p, \{n_i\}$. Its differential is

$$\begin{aligned} dH &= dU + p\,dV + V\,dp \\ &= T\,dS + V\,dp + \sum\nolimits_i \mu_i\,dn_i\,. \end{aligned} \tag{7.15}$$

Helmholtz free energy

The Helmholtz free energy F is the Legendre transform of the energy U with respect to the temperature T:

$$U[T] = U - TS = F(T, V, \{n_i\})\,. \tag{7.16}$$

The Helmholtz free energy is a function of the independent coordinates $T, V, \{n_i\}$. Its differential is

$$\begin{aligned} dF &= dU - T\,dS - S\,dT \\ &= -S\,dT - p\,dV + \sum\nolimits_i \mu_i\,dn_i\,. \end{aligned} \tag{7.17}$$

Note: In the german literature the Helmholtz function is denoted by the letter A (from "Arbeit" = work). The letter A is suggested also by IUPAC (International Union of Pure and Applied Chemistry).

Gibbs free eneergy

The Gibbs free energy G (also called free enhtalpy) is the Legendre transform of the energy U with respect to both the temperature T and the pressure p:

$$U[T,p] = U - TS + pV = G(T,p,\{n_i\})\,. \tag{7.18}$$

The Gibbs free energy can also be considered the Legendre transform of the enthalpy H with respect to the temperature T or of the Helmholts function F with respect to the pressure p.
The Gibbs free energy is a function ofthe independent coordinates $T, p, \{n_i\}$. Its differential is

$$\begin{aligned} dG &= dU - T\,dS - S\,dT + p\,dV + V\,dp \\ &= -S\,dT + V\,dp + \textstyle\sum_i \mu_i\,dn_i\,. \end{aligned} \tag{7.19}$$

Grand-canonical potential

The grand-canonical potential Ω is the Legendre transform of the energy U U with respect to the temperature T and the chemical potentials μ_i:

$$U[T,\{\mu_i\}] = U - TS - \textstyle\sum_i \mu_i\,n_i = \Omega(T,V,\{\mu_i\})\,. \tag{7.20}$$

The grand-canonical potential is a function of the independent coordinates $T, V, \{\mu_i\}$. Its differential is

$$\begin{aligned} d\Omega &= dU - T\,dS - S\,dT - \textstyle\sum_i \mu_i\,dn_i - \sum_i n_i\,d\mu_i \\ &= -S\,dT - p\,dV - \textstyle\sum_i n_i\,d\mu_i\,. \end{aligned} \tag{7.21}$$

For a system with only one component, the grand-canonical potential is

$$U[T,\mu] = U - TS - \mu\,n = \Omega(T,V,\mu)\,, \tag{7.22}$$

say a function of the independent coordinates and its differential is

$$\begin{aligned} d\Omega &= dU - T\,dS - S\,dT - \mu\,dn - n\,d\mu \\ &= -S\,dT - p\,dV - n\,d\mu\,. \end{aligned} \tag{7.23}$$

7.2.2 Consequency of the homogeneity of the fundamental equation

In § 6.4 we have derived the Euler relations (6.41) from the homogeneity of the fundamental equations. In particular, the Euler relation for the energy representation is I

$$U = TS - pV + \textstyle\sum_i \mu_i n_i\,. \tag{7.24}$$

One can easily find the Euler relations for the new functions H, F, G, Ω starting from (7.24):

$$H \;=\; U + pV \;=\; TS + \textstyle\sum_i \mu_i n_i \tag{7.25}$$

$$F \;=\; U - TS \;=\; -\,pV + \textstyle\sum_i \mu_i n_i \tag{7.26}$$

$$G \;=\; U + pV - TS \;=\; \textstyle\sum_i \mu_i n_i \tag{7.27}$$

$$\Omega \;= U - TS - \textstyle\sum_i \mu_i\,n_i \;=\; -\,pV \tag{7.28}$$

Note: The progressive reduction of the number of terms in the second member of the Euler relations when passing from (7.24) to (7.25) and (7.26) and to (7.27) is due to the progressive substitution of extensive variables, with respet to which the function is homogeneous of order 1, by intensive variables, with respect to which the function is homogeneous of degree 0.

Gibbs free energy and chemical potential

For a system with only one component the Euler relation for the Gibbs free energy (7.27) becomes

$$G \;=\; \mu\, n\,; \tag{7.29}$$

for a system with only one component, the chemical potential μ corresponds to the molare Gibbs free energy:

$$\mu \;=\; \frac{G}{n} \;=\; g\,. \tag{7.30}$$

An extreme case

By performing the Legendre transform with respect to *all* the extensive coordinates and comparing the result with the Euler relation (7.24) one finds

$$U[T,p,\{n_i\}] = U - TS + pV - \sum\nolimits_i \mu_i n_i = 0\,. \tag{7.31}$$

The Legendre transform with respect to all the extensive coordinates has no meaning, since the basic information on the system size is lost.

Note: The comparison with the case of the transform between the Lagrange and Hamilton formalisms in Mechanics can be instructive. Let us consider the simple case of a particle free to move. The Lagrange function is $\mathcal{L} = mv^2/2$, the conjugate momentum is $p = d\mathcal{L}/dv$ and the Hamilton function is $\mathcal{H} = pv - \mathcal{L} = mv^2/2$.
The transform with respect to all the variables (in this case only one) is now significant. Why ?

7.2.3 Entropy representation

One can generate new fundamental equations by means of Legendre transforms of the function $S(U,V,\{n_i\})$ in the entropy representation too. The new functions are generally called Massieu functions. For example:

$$S\,[1/T] = \; S - \frac{1}{T}U \qquad = \; -\,\frac{F}{T} \tag{7.32}$$

$$S\,[p/T] = \; S - \frac{p}{T}\,V \tag{7.33}$$

$$S\,[1/T, p/T] = \; S + \frac{1}{T}U - \frac{p}{T}V \;=\; -\,\frac{G}{T}\,. \tag{7.34}$$

7.3 Useful mathematical relations

To conclude this Chapter, let us introduce some mathematical relations that are frequently used in Thermodynamics, for example to connect some quantities that are easily measurable to other non measurable quantities as well as for reducing the number of variables of a given problem.

7.3.1 Maxwell relations

As is well known, if a continuous function $Z = Z(x_1, x_2, ..., x_n)$ of n variables has all the first and second derivatives, one can demonstrate the invariance of the second partial derivatives with respect to the exchange of the order of the independent variables

$$\frac{\partial^2 Z}{\partial x_i \partial x_k} \;=\; \frac{\partial^2 Z}{\partial x_k \partial x_i}\,. \tag{7.35}$$

Let us now consider the differentials of the first four thermodynamical functions considered in § 7.2:

$$dU = T\,dS - p\,dV + \sum\nolimits_i \mu_i dn_i \tag{7.36}$$

$$dH = T\,dS + V\,dp + \sum\nolimits_i \mu_i dn_i \tag{7.37}$$

$$dF = -S\,dT - p\,dV + \sum\nolimits_i \mu_i dn_i \tag{7.38}$$

$$dG = -S\,dT + V\,dp + \sum\nolimits_i \mu_i dn_i \tag{7.39}$$

All the differentials (7.36) - (7.39) have the form

$$\begin{aligned} dZ &= M\,dx + N\,dy + \sum\nolimits_i \mu_i dn_i \\ &= \left(\frac{\partial Z}{\partial x}\right) dx + \left(\frac{\partial Z}{\partial y}\right) dy + \sum\nolimits_i \mu_i dn_i\,. \end{aligned} \tag{7.40}$$

By means of (7.35), one can obtain from (7.40) the relation

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y\,. \tag{7.41}$$

By applying (7.41) to each one of the (7.36)-(7.39) one obtains the following *Maxwell relations*:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{7.42}$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{7.43}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{7.44}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{7.45}$$

Other Maxwell relations can be obtained if also the terms $\mu_i\, dn_i$ or the possible terms of generalised work $\text{đ}W_j^* = \xi_j^*\, dX_j^*$ are taken into account.
We considered here only the Maxwell relations that will be encountered in the next chapters.

Example: In § 10.1 we will study in detail the energy balance of a closed system undergoing an isothermal compression. We will start from the energy differential $dU = T\,dS - p\,dV$ and rewrite it as a function of the variables T and p. Since by hypothesis $dT = 0$, one finds

$$dU = T\left(\frac{\partial S}{\partial p}\right)_T dp - p\left(\frac{\partial V}{\partial p}\right)_T dp\,.$$

The Maxwell relation (7.45) consente di trasformare la derivata dell'entropia S rispetto alla pressione $p$will allow us to transform the derivative of the volume V with respect to the temperature T:

$$dU = -T\left(\frac{\partial V}{\partial T}\right)_p dp - p\left(\frac{\partial V}{\partial p}\right)_T dp\,.$$

The two partial derivatives correspond to easily measurable quantities, say the coefficient of thermal expansion and the isothermal compressimility

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p dp\,, \qquad \chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T dp\,.$$

7.3.2 Other useful mathematical identities

Let three variables x, y, z be connected by the implicit relation

$$F(x,y,z) \;=\; 0\,. \tag{7.46}$$

The two explicit functions $x(y,z)$ and $y(x,z)$ can be differentiated as:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz\,, \qquad dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\,. \tag{7.47}$$

If in the differential dx of the left equation the differential dy of the right equation is substituted, one obtains

$$\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1\right] dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \;=\; 0\,. \tag{7.48}$$

If now x and z are considered as independent variables, equation (7.48) is true for whichever values of dx and dz. The two expressions in square parentheses have then to be identically zero.
By equating to zero the expression in the first square parenthesis of (7.48) one gets the identity

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \;=\; \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}\,.} \tag{7.49}$$

By equating to zero the expression in the second square parenthesis of (7.48) one gets the identity

$$\left(\frac{\partial x}{\partial z}\right)_y \;=\; -\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \,, \tag{7.50}$$

cioè

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \;=\; -1\,.} \tag{7.51}$$

One can demonstrate that the identities (7.49) and (7.51) are valid also in the case of more that three independent variables, for example for an implicit relation $F(x,y,z,w) \;=\; 0$.

The identities (7.49) and (7.51), as the Maxwell relations, are frequently used to modify some equations between thermodynamical quantities and express them as a function of easily measurable quantities.

Example 1: In § 9.4, to demonstrate the relation between specific heats at constant volume and constant pressure, we will resort to (7.49) to transform

$$\frac{1}{\left(\frac{\partial T}{\partial V}\right)_p} \;=\; \left(\frac{\partial V}{\partial T}\right)_p \,.$$

Example 2: In § 10.4, when studying the free adiabatic expansion of gases, we will resort to (7.50) to substitute the derivative of the pressure with respect to the temperature at constant volume:

$$\left(\frac{\partial p}{\partial T}\right)_V \;=\; -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \,.$$

Example 3: In § 9.4, when studying the relations between the response functions, fwe will resort to (7.50) to find an alternative expression of the coefficient of thermal expansion:

$$\left(\frac{\partial V}{\partial T}\right)_p \;=\; -\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T \,.$$

Chapter 8

Thermodynamic potentials

In this Chapter 8 we will study in detail the physical meaning and the practical use of the internal energy U and of its Legendre transforms H, F, G, that have been formally introduced in Chapter 7. The four functions, that are often defined *thermodynamic potentials* for reasons that will be made clear below, describe the thermodynamical properties of systems as a function of different sets of coordinates:

$$\begin{array}{ll} U\,(S,V,\{n_i\},\{X_j\}) & H\,(S,p,\{n_i\},\{X_j\}) \\ F\,(T,V,\{n_i\},\{X_j\}) & G\,(T,p,\{n_i\},\{X_j\}) \end{array} \tag{8.1}$$

The differences between the four functions (8.1) concern the first two coordinates. The internal energy U is used for systems where one can control entropy S and volume V, the enthalpy H is used for systems where one can control entropy S and pressure P, and so on.

Below we will separately examine the four functions U, H, F and G. For each one of the functions we will consider three different applications:

1. Use of the function to describe equilibrium properties and reversible transformations of simple systems.
   In particular, we will be interested in
   - amount of heat reversibly exchanged when the volume V or the pressure p remain constant (comparison between U and H),
   - reversible compression work, performed when the entropy S or the temperature T remain constant (comparison between U and F).
2. Study of processes taking place in composite systems, to determine the sign of the variation of the function in the transformation from an initial state of constrained equilibrium to a final state of non-constrained equilibrium.
   Such variations are are always negative for the four functions, U, H, F and G:
   - for irreversible processes they correspond to an increase of entropy of the isolated system formed by the studied system and its environment (the so called "thermodynamical universe");
   - for reversible processes they measure the maximum work obtainable as a consequence of the constraints removal (whence the name *thermodynamic potentials*).
3. Statement of the conditions for thermodynamical equilibrium.

In § 8.5 we will shortly consider processes of closed systems affected by variations of the coordinates n_i (chemical reactions, matter transport, phase transitions) in order to better understand the meaning of the grand-canonical potential Ω, defined in (7.20).

8.1 Internal energy U

The thermodynamical properties of a system can be summarised in the fundamental equation

$$U = U(S, V, \{n_i\}, \{X_j\}) , \tag{8.2}$$

where S and V are the entropy and the volume of the system, respectively, and n_i are the molar quantities of the different components. The symbol $\{X_j\}$, that denotes all the other possible thermodynamical coordinates, will be omitted in the following of this chapter when not strictly necessary.

8.1.1 Simple systems in equilibrium

For a simple system in thermodynamical equilibrium, the differential o (8.2),

$$dU = TdS - pdV + \sum\nolimits_i \mu_i dn_i + \sum\nolimits_j \xi_j \, dX_j , \tag{8.3}$$

represents the energy balance for an infinitesimal reversible transformation. Let us examine in detail the different terms of the second member of (8.3), by considering some particular cases, following the approach of § 6.3.

Closed and isolated systems

A closed and isolated system doesn't modify its volume and doesn't exchange matter nor energy with its ambient, so that (8.3) becomes

$$dU = TdS + \sum\nolimits_i \mu_i dn_i \;\; = \;\; 0 , \tag{8.4}$$

where the differentials dn_i refer to possible variations within the system, typically due to chemical reactions or phase transitions. The entropy variation dS cannot depend on heat exchanges, since the system is isolated; it can only be due to variations of the n_i values within the system; if $dn_i = 0$ for every i, then also $dS = 0$.

Compression work

The second term in the right member of (8.3), $-p\,dV = đW$, is the compression work reversibly performed on the system. The compression work can be taken as a measure of the interaction of the system with the external pressure field.

For a system where all extensive coordinates remain constant with exclusion of volume V, the variation of internal energy is equal to the compression work:

$$\boxed{dU = -p\,dV \, , \qquad \Delta U = W} \qquad [dS = 0, dn_i = 0, dX_j = 0] \tag{8.5}$$

Note: Ina reversible compression process, the internal pressure is equal to the external pressure.

Generalised work

The terms of the sum $\sum_j đW^*_j = \sum \xi_j \, dX_j$ in (8.3) correspond to the variations of internal energy due to reversible contributions of generalised work. The generalised work terms measure the interactions of the system with external fields too.

Some examples are given in Table 8.1.

Table 8.1: Examples of generalised work.

Magnetisation work	$đW_m = \mathcal{H}\, dM$	§ 3.6
Electrical polarisation work	$đW_p = \mathcal{E}\, dP$	§ 3.7

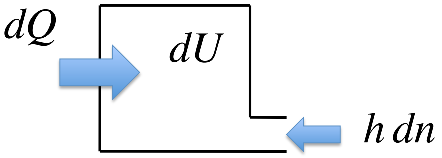


Figure 8.1: Open system with one component. The variation of internal energy is due to both exchange of heat $đQ$ and exchange of matter $h\,dn$.

Closed non-isolated systems - Exchanged heat

If $dn_i = 0$ (closed system with no internal reactions), the first term of (8.3) is the heat reversibly absorbed in an infinitesimal reaction:

$$T\,dS \;=\; đQ_{\text{rev}}\,. \tag{8.6}$$

If in addition $dV = 0$ and $dX_j = 0$, the heat reversibly exchanged is equal to the variation of internal energy:

$$\boxed{dU = đQ_{\text{rev}}\,, \qquad \Delta U = Q_{\text{rev}}} \qquad [dV = 0, dn_i = 0, dX_j = 0] \tag{8.7}$$

In this case, the heat capacity at constant volume C_v is connected to the internal energy by

$$C_v \;=\; \left(\frac{đQ_{\text{rev}}}{dT}\right)_V \;=\; T\left(\frac{\partial S}{\partial T}\right)_V \;=\; \left(\frac{\partial U}{\partial T}\right)_V\,. \tag{8.8}$$

Open systems, the terms $\mu_i\, dn_i$

Let us consider now an open system, that can exchange matter with its environment. For simplicity, let us suppose that the system has a single component and cannot exchange work with the environment, so that $dV = 0$, $dX_j = 0$ (Fig. 8.1).
Equation (8.3) becomes now $dU = T\,dS + \mu\, dn$.
By introducing the molar quantities, so that $T\,dS = T\,d(ns)$, and recalling that according to (7.30) the chemical potential corresponds to the molar Gibbs free energy $\mu = g = u + pv - Ts = h - Ts$, one gets

$$\begin{aligned} dU &= T\,d(ns) + (u + pv - Ts)\,dn \\ &= Tn\,ds + h\,dn\,. \end{aligned} \tag{8.9}$$

According to (8.9), the variation of internal energy dU of an open system can be decomposed as the sum of two contributions:

- reversible exchange of heat $đQ_{\text{rev}} = Tn\,ds$, that leads to a variation ds of the molar entropy of the system;
- exchange of matter dn, that transports molar enthalpy $h = u + pv$: the enthalpy measures the contribution of the molar energy u transported by matter and the contribution due to the introduction of the volume $v\,dn$ at a pressure p.

The total variation of entropy $dS = n\,ds + s\,dn$ doesn't thus depend only on the exchange of heat $đQ$ (see equation 6.13 in § 6.2).

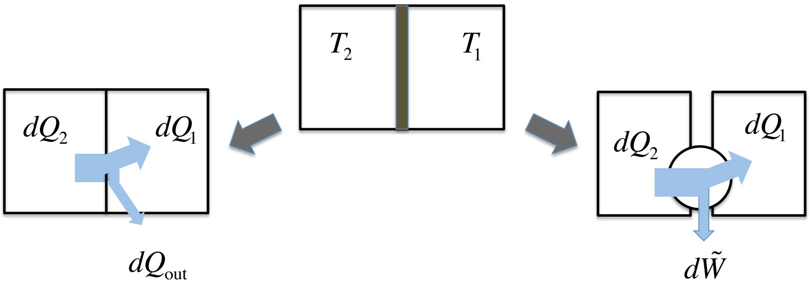


Figure 8.2: Center: a constant-volume composite system maintained in equilibrium by an adiabatic wall. The removal of the wall insulation triggers the energy exchange between the two sub-systems. The entropy of the entire system has to remain unchanged. Two different processes are considered, one completely irreversible (left) with heat emission, the other reversible (right) . Sono illustrati due possibili processi: uno completamente irreversibile (a sinistra), con emissione di calore; l'altro reversibile (a destra) with production of work thanks to a Carnot engine.

Closed systems, the terms $\mu_i\, dn_i$

We will analyse later on, in § 8.5, the meaning of the terms $\mu_i\, dn_i$ of (8.3) for closed systems. The variations dn_i in closed systems can be due to chemical reactions or to phase transitions.

8.1.2 Thermodynamical processes and internal energy

In § 6.3 we have seen that, in a composite system with constant entropy and volume, the removal of constraints triggers a thermodynamical process towards a new state of non-constrained equilibrium, whose internal energy U is smaller than in the initial state.

Let us now study in more detail this type of processes

$$\left[\begin{array}{c}\text{Composite system}\\ \text{(constrained equilibrium)}\end{array}\right] \rightarrow \left[\begin{array}{c}\text{SSimple system}\\ \text{(non-constrained equilibrium)}\end{array}\right]$$

We consider here the behaviour of the internal energy; the cases of the other thermodynamical functions will be analysed later on.

Note: Equation (8.3) only holds for simple systems in equilibrium, and cannot describe the thermodynamical state of a composite system. Actually, the state of a composite system is known if, in addition to $S, V, \{n_i\}$, also the corresponding coordinates of all the sub-systems minus one are known. For a system divided in two sub-systems, it is necessary to know also $S^{(1)}, V^{(1)}, \{n_i^{(1)}\}$.

We will start from simple examples (the first one already considered in § 6.3) to proceed then to suitable generalisations. The two following examples concern processes of internal re-adjustement between sub-systems initially maintained at different temperatures or pressures, respectively.

Example 1

A system maintained with constant volume and composition is divided in two sub-systems of equal heat capacity ($C_{1v} = C_{2v} = C_v$) and of different temperatures T_1 and T_2, respectively, with $T_2 > T_1$. The two sub-systems are initially separated by an adiabatic wall (Fig. 8.2, center). Ata given time the wall insulation is removed and the two sub-systems exchange heat until they achieve thermal equilibrium at the temperature T_f. The process takes place with no variation of the system entropy S, so that for the global system $dS = dV = dn_i = 0$.

Let us consider two extreme cases: a) completely irreversible process and b) reversible process.

a) The thermalisation of the two sub-systems takes place through an *irreversible* transfer of heat. In order that the total entropy remain unchanged, not all the heat amount Q_2 lost by the hot sub-system has to be transferred to the cold sub-system; the cold sub-system has to receive a smaller amount of heat Q_1 and the system has to transfer to its environment the remaining amount of heat Q_{out} (Fig. 8.2, left).

The infinitesimal heat quantities are connected by the relation

$$|đQ_2| = |đQ_1| + |đQ_{\text{out}}|\,. \tag{8.10}$$

To evaluate the finite heat quantities exchanged in the entire process it is convenient to first calculate the temperature T_f of the final equilibrium state.

By hypothesis, the final state of non-constrained equilibrium has the same volume V and the same entropy S of the initial state of constrained equilibrium. To calculate T_f one can consider, for both sub-systems, a reversible transformation leading to the final temperature T_f, by imposing a null variation of entropy:

$$\Delta S \;=\; \int_{T_1}^{T_f} \frac{đQ_1}{T} + \int_{T_2}^{T_f} \frac{đQ_2}{T} \;=\; C_v \int_{T_1}^{T_f} \frac{dT}{T} + C_v \int_{T_2}^{T_f} \frac{dT}{T} \;=\; 0\,. \tag{8.11}$$

From (8.11) one can easily obtain the final equilibrium temperature:

$$\ln\frac{T_f}{T_1} + \ln\frac{T_f}{T_2} = 0 \quad \Rightarrow \quad T_f = \sqrt{T_1 T_2}\,. \tag{8.12}$$

Once T_f known, one can calculate the heat quantities:

$$Q_1 = C_v(T_f - T_1) > 0\,; \quad Q_2 = C_v(T_f - T_2) < 0\,; \tag{8.13}$$

$$|Q_{\text{out}}| = |Q_2| - |Q_1| = C_v\left(\sqrt{T_2} - \sqrt{T_1}\right)^2\,. \tag{8.14}$$

To maintain the entropy S unaltered, the system has to lose a heat amount Q_{out}, thus reducing its internal energy, $\Delta U = Q_{\text{out}} < 0$.

The transformation is irreversible. In order that the entropy of the system remain unaltered, the ambient entropy has to increase. The reduction of the system energy corresponds thus to an increase of the entropy of the thermodynamic universe, that is the sum of the system and its ambient and is by definition isolated.

b) The thermalisation of the two sub-systems is performed *reversibly* by means of a Carnot engine (Fig. 8.2, right). The requirement that the entropies of the initial and final states are equal lead again to (8.11) and to the final equilibrium temperature (8.12), $T_f = \sqrt{T_1 T_2}$. The heat quantities Q_1 and Q_2 are again given by (8.13).

However, in this case no heat is expelled from the system. The difference between the heat quantities Q_2 and Q_1 is instead converted to work $|\tilde{W}| = |Q_2| - |Q_1|$, again with a reduction of the internal energy $\Delta U = \tilde{W} < 0$.

(?) Calculate the final equilibrium temperature for an irreversible thermalisation like that of the previous example, however taking place in an isolated system.

Example 2

The second example is proposed as a problem.

Consider a system represented by a gas enclosed in a cylinder and separated in two sub-systems at different pressures by a fixed piston. When the piston becomes free to move, the system evolves towards a new state of non-constrained equilibrium. Impose that S and V remain constant and show that the internal energy U decreases.

As in the previous example, compare the two cases of a completely irreversible process and a reversible process.

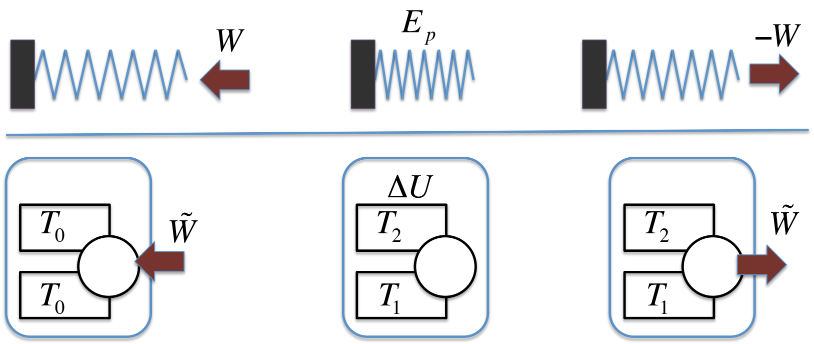


Figure 8.3: Above: the work W performed to compress an elastic spring is stored as potential energy and can be recovered when the spring expands. Below: the work performed on a thermodynamic system with constant entropy and volume can be stored as internal energy by means of a Carnot refrigerating cycle and can be recovered by inverting the cycle.

General conclusions

By generalising the previous examples, one can draw the following conclusions about the processes taking place in closed composite systems with entropy S and volume V constant, after the removal of internal constraints:

1. For a generic process, $\Delta U = Q + \tilde{W} < 0$ where $\tilde{W}$ is the work that the system can exchange with its environment due to the modifications of its internal structure.
2. In completely *irreversible* processes, the system transfers heat to its environment without producing work: $\Delta U = Q < 0$.
3. In *reversible* processes the reduction of internal energy entirely corresponds to work performed on the environment: $\Delta U = \tilde{W} < 0$.

The variation of internal energy ΔU thus measures the maximum work obtainable by the transformation from the initial state of constrained equilibrium to the final state of non-constrained equilibrium.

On more general grounds, a composite system maintained at constant entropy and volume can absorb or lose energy by exchanging work with its ambient (Fig. 8.3): the work reversibly performed on a system can be employed to separate two or more sub-systems in constrained equilibrium; the removal of the constraints allows the recovery of the work.
The internal energy U thus represents a sort of potential energy for the work L$\tilde{W}$. Whence the name “thermodynamic potential” attributed to the internal energy and, as we will see below, also to the thermodynamical functions H, F, G.

Note: Here and in the following $\tilde{W}$ represents the work exchanged by a system with its ambient as a consequence of the removal or insertion of constraints.

8.1.3 Irreversibility and reduction of the internal energy

In § 6.3 it has been formally demonstrated that the axiom of maximum entropy in isolated systems can be re-formulated as an axiom of minimum energy in systems with constant S and V.
Example 1 considered above more intuitively shows how the reduction of the internal energy U in irreversible transformations of a closed system with constant $S$and V is a consequence of Axiom II of § 5.3 (increase of entropy in isolated systems).
In this case, the isolated system is the sum of the given system and its ambient, often called “thermodynamical universe” (not necessarily corresponding to the Universe of astronomy and cosmology).

Since by hypothesis the entropy of the system is constant ($\Delta S_s = 0$), the variation of the entropy of the thermodynamic universe corresponds to the variation of entropy of the ambient (ΔS_a) and has to be positive according to Axion II of § 5.3:

$$\Delta S_s + \Delta S_a = \Delta S_a \geq 0 \tag{8.15}$$

1. For a completely irreversible process (Fig. 8.2, left) the system reduces its internal energy emitting heat $\Delta U_s = -|Q_{\text{out}}| = Q_s < 0$. Heat is absorbed by the ambient producing an increase of its internal energy , $\Delta U_a = +|Q_{\text{out}}| = Q_a = -Q_s = -\Delta U_s > 0$.
   As a consequence, since the volume of the system is constant, $\Delta V_s = 0$,

   $$T_a \Delta S_a \;=\; \Delta U_a \;=\; -\Delta U_s > 0\ : \tag{8.16}$$

   the increase of the entropy of the universe corresponds to a reduction of the internal energy of the system, $\Delta U_s < 0$.
2. In the extreme case of a reversible process (Fig. 8.2, right) the system reduces its internal energy by performing reversible work on the ambient, $\Delta U_s = -|\tilde{W}_{\text{out}}|$. The reversible work $|\tilde{W}_{\text{out}}|$ doesn't increase the internal energy of the ambient, so that so that $T\Delta S_a = \Delta U_a = 0$. Reversible processes take place in isolated systems without entropy variations (in the Thermodynamics of cycles it's a consequnce of the Clausius theorem, § 4.4).

8.1.4 Equilibrium condition

The above considerations confirm the conclusions of § 6.3: for a closed system with constant $S$and V, the thermodynamical equilibrium is characterised by a minimum of the internal energy U. Any deviation from the equilibrium state, reversible or irreversible, gives rise to an increase of the internal energy U. The conditions of equilibrium and of its stability are, respectively

$$\delta U = 0, \qquad \Delta U > 0\,. \tag{8.17}$$

Let us stress again that in non isolated systems the deviations from equilibrium are not necessarily virtual (as is the case instead for isolated systems).

8.2 Enthalpy H

Enthalpy H is obtained by the Legendre transform of the internal energy U with respect to pressure (§ 7.2), so that

$$H = U + pV = H(S, p, \{n_i\})\,, \tag{8.18}$$

where S and p arethe entropy and the pressure of the system, respectively and n_i are the molar quantities of the components. The possible generalised coordinates X_j are no more considered in thi chapter.

8.2.1 Simple systems in equilibrium

The differential of (8.18) is

$$dH = TdS + Vdp + \sum\nolimits_i \mu_i dn_i\,. \tag{8.19}$$

It is convenient to enlighten the similarities and the differences between the differentials (8.19) and (8.3) of the enthalpy H and of the internal energy U.

The difference concerns the second term, $p\,dV$ for the internal energy, $V\,dp$ for the enthalpy. The term $V\,dp$ doesn't correspond to work; as a consequence, la (8.19) doesn't represent an energy balance corresponding to the Fisrt Law.

Closed system - Exchanged heat

When $dn_i = 0$ (closed system without chemical reactions and phase transitions), the first term of (8.19) is the heat amount reversibly absorbed:

$$T\,dS \;=\; đQ_{\text{rev}}\,. \tag{8.20}$$

If the pressure of the system remains constant, $dp = 0$, the heat reversibly exchanged corresponds to the enthalpy variation:

$$\boxed{dH = đQ_{\text{rev}}\,, \qquad \Delta H = Q_{\text{rev}}} \qquad [p = \text{constant}] \tag{8.21}$$

The heat capacity at constant pressure is connected to the enthalpy by the relation

$$C_p \;=\; \left(\frac{đQ_{\text{rev}}}{dT}\right)_p \;=\; T\left(\frac{\partial S}{\partial T}\right)_p \;=\; \left(\frac{\partial H}{\partial T}\right)_p\,. \tag{8.22}$$

Note: The word “enthalpy” is derived from ancient greek *enthalpein*=to heat.

Let us compare equations (8.21) and (8.22) concerning the enthalpy with the corresponding equations (8.7) and (8.8) rconcerning the internal energy.
The heat absorbed at constant volume is equal to the increment of internal energy, the heat absorbed at constant pressure is equal to the increment of enthalpy.

Schematically:

$$\begin{array}{lclcl} V = \text{constant} & \Rightarrow & đW = 0 & \Rightarrow & đQ = dU \\ p = \text{constant} & \Rightarrow & đW \neq 0 & \Rightarrow & đQ \begin{cases} \neq dU \\ = dH = dU + p\,dV \end{cases} \end{array}$$

Example: In the monatomic ideal gas, the iternl energy and the heat capacity at constant volume are

$$U = \frac{3}{2}nRT\,; \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{3}{2}nR\,. \tag{8.23}$$

The enthalpy and the heat capacity at constant pressure are instead

$$H = U + pV = \frac{3}{2}nRT + nRT = \frac{5}{2}nRT\,; \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{5}{2}nR\,. \tag{8.24}$$

A number of real transformation take place at constant pressure (often the athmospheric pressure) rather than at constant volume. Whence the usefulness of enthalpy.

Open systems

Let us consider an open system with one component, maintained at constant pressure ($dp = 0$).
Equation (8.19) becomes $dH \;=\; T\,dS + \mu\,dn$.
By introducing the molar quantities a recalling that $\mu = g = u + pv - Ts$, one obtains

$$\begin{aligned} dH &= T\,d(ns) + (u + pv - Ts)\,dn \\ &= T\,d(ns) + (h - Ts)\,dn \\ &= Tn\,ds + h\,dn\,. \end{aligned} \tag{8.25}$$

The last member of (8.25) is equal to the last member of (8.9). The enthalpy H plays the same role in the systems with constant p as the internal energy U in the systems at constant V. The enthalpy variation in an open system with constant p is the sum of the same two contributions:

- exchange of heat $đQ = Tn\,ds = T\,dS - Ts\,dn$;
- exchange of matter transporting molar enthalpy $h = u + pv$.

8.2.2 Thermodynamical processes and enthalpy

We study now the role of enthalpy in thermodynamical processes taking place as a consequence of the removal of one or more constraints in a composite system maintained at constant entropy and pressure. Let us start from the simple example of § 8.1, adapted here to the case of constant pressure, and proceed then to suitable generalisations.

Example

A system maintained at constant pressure and composition is divided in two sub-systems of equal heat capacity ($C_{1p} = C_{2p} = C_p$) and temperatures T_1 and T_2, respectively, with $T_2 > T_1$. The two sub-systems, two cylinders with movable pistons, are initially separated by an adiabatic wall (Fig. 8.4, center). At a given time, the thermal insulation is removed from the wall and the two sub-systems exchange heat untile they reach the thermal equilibrium at a temperature T_f. The entropy S of the system remains constant by hypothesis.
Let us consider two extreme cases: a) perfectly irreversible process, b) reversible process.

a) The thermalisation of the sub-systems takes place through an *irreversible* heat transfer. In order that the entropy remain constant, the system has to transfer a heat amount Q_{out} to the ambient (Fig. 8.4, left). The infinitesima heat quantities are connected by the relation (8.10): $|đQ_2| = |đQ_1| + |đQ_{\text{out}}|$. The final temperature can be calculated through (8.11) (where C_v has to be substituted by C_p), obtaining $T_f = \sqrt{T_1 T_2}$.
Once the final temperature T_f is known, the heat quantities can be calculated (again substituting C_v with C_p):

$$Q_1 = C_p(T_f - T_1) > 0\,; \quad Q_2 = C_p(T_f - T_2) < 0\,; \tag{8.26}$$

$$|Q_{\text{out}}| = |Q_2| - |Q_1| = C_p \left(\sqrt{T_2} - \sqrt{T_1}\right)^2 . \tag{8.27}$$

To maintain the entropy S constant, the system has to transfer a heat amount Q_{out} to its environment. Differently from the case of § 8.1, however, the volume of the system is not constant. The outgoing heat amount corresponds now to the variation of enthalpy H instead of the variation of internal energy U:

$$Q_{\text{out}} = \Delta U + p\,\Delta V = \Delta U + \Delta(pV) = \Delta H\,. \tag{8.28}$$

The enthalpy thus decreases, $\Delta H = Q_{\text{out}} < 0$.
The transformation is irreversible. To maintain constant the entropy of the system it is necessary that the entropy of the ambient increases. The reduction of the system enthalpy corresponds to an increase of the entropy of the universe (system plus ambient).

b) The thermalisation of the sub-systems takes place *irreversibly* thanks to a Carnot engine connecting the two sub-systems (Fig. 8.4, right). Since the entropy has to remain constant, the final equilibrium temperature is again $T_f = \sqrt{T_1 T_2}$. Also the heat quantities Q_1 and Q_2 are again given by (8.26).
Contrary to the case of the irreversible transformation, however, no heat is expelled by the system; on the contary, the Carnot engine produces work $\tilde{W}$. Since the volume is not constant, there is also expansion work, so that the work $\tilde{W}$ doesn't correspond to the variation of internal energy U, but:

$$\tilde{W} = \Delta U + p\,\Delta V = \Delta U + \Delta(pV) = \Delta H\,. \tag{8.29}$$

Again, the enthalpy decreases: $\Delta H = \tilde{W} < 0$.

General conclusions

By generalising the previous example, one can draw the following conclusions about the processes taking place in closed composite systems with entropy S and pressure p constant, after the removal of internal constraints:

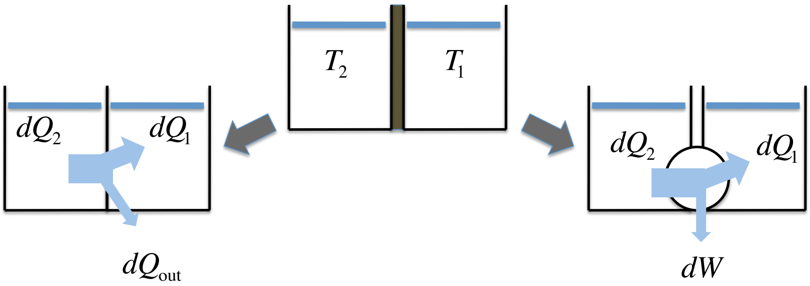


Figure 8.4: A composite system maintained, at constant pressure, in a state of constrained equilibrium by an adiabatic wall (center). The removal of the thermal insulation from the wall triggers a process of heat exchange between the sub-systems. The system has to maintain the entropy unaltered. Two possible processes are illustrated: one completely irreversible (left), with emission of heat, the other reversible (right) with production of work by means of a Carnot engine.

1. For a generic process, $\Delta H = Q + \tilde{W} < 0$ where $\tilde{W}$ is the work that the system can exchange with its environment due to the modifications of its internal structure.
2. In completely *irreversible* processes, the system transfers heat to its environment without producing work: $\Delta H = Q < 0$.
3. In *reversible* processes the reduction of enthalpy entirely corresponds to work performed on the environment: $\Delta U = \tilde{W} < 0$.

The variation of enthalpy ΔH thus measures the maximum work obtainable by the transformation from the initial state of constrained equilibrium to the final state of non-constrained equilibrium. The enthalpy H rrepresents thus a sort of potential energy for the work $\tilde{W}$ in systems maintained at constant entropy and pressure.

8.2.3 Irreversibility and reduction off the enthalpy

One can demosntate that the reduction of the enthalpy H in irreversible transformations of a closed system maintained at constant s and p corresponds to the increase of entropy in the thermodynamical universe (system plus ambient). The procedure is similar to that followed for the internal energy in system with constant s and V, with some relevant differences.

By hypothesis, the entropy of the system is constant ($\Delta S_s = 0$), so that

$$\Delta S_s + \Delta S_a = \Delta S_a \geq 0 \tag{8.30}$$

1. In a completely irreversible process (Fig. 8.4, left), the internal energy of the system is modified through emission of heat and exchange of ompression work, $\Delta U_s = -|Q_{\text{out}}| - p_s\, \Delta V_s = Q_s - p_s\, \Delta V_s$. The ambient in turn absorbs heat and exchanges compression work, so that its internal energy is varied according to $\Delta U_a = Q_a - p_a\, \Delta V_a = +|Q_{\text{out}}| - p_a\, \Delta V_a$.
   Let us analyse in detail ΔS_a, taking into account that the pressure of the system is constant by hypothesis $p_s = p_a$, that the system is closed and that $\Delta V_s = -\Delta V_a$, so that $\Delta U_s = -\Delta U_a$:
   $$T_a \Delta S_a = \Delta U_a + p_a \Delta V_a = -\Delta U_s - p_s \Delta V_s = -\Delta H_s > 0\,; \tag{8.31}$$
   the increase of the entropy of the universe corresponds to a decreaseof the enthalpy of the system, $\Delta H_s < 0$.
2. In the reversible process (Fig. 8.4, right) the internal energy of the system is reduced by the performance of reversible work $|\tilde{W}_{\text{out}}|$ and the exchange of compression work , $\Delta U_s = -|\tilde{W}_{\text{out}}| - p_s\, \Delta V_s$. The reversible work $|\tilde{W}_{\text{out}}|$ doesn't increase the internal energy of the ambient, so that $\Delta U_a = -p_a\, \Delta V_a$, where $\Delta V_a = -\Delta V_s$ and $p_a = p_s$. The entropy balance of the ambient is thus $T \Delta S_a = \Delta U_a + p_a\, \Delta V_a = 0$; again: the reversible processes in isolated systems don't produce entropy variations.

8.2.4 Equilibrium condition

For a closed system with constant entropy S and pressure p the thermodynamical equilibrium is characterised by a minimum of the enthalpy H. Any deviation, reversible or irreversible, from the equilibrium state gives rise to an increase of the enthalpy H. In an equilibrium state

$$\delta H = 0, \qquad \Delta H > 0 \,. \tag{8.32}$$

In a closed system with constant S and p, the enthalpy H is minimum with respect to any process, real or virtual, leading the system out of equilibrium.

8.3 Helmholtz free energy F

The Helmholtz free energy F is the Legendre transform of the internal energy U with respect to the volume (§ 7.2), say

$$F = U - TS = F(T, V, \{n_i\}) \,, \tag{8.33}$$

where T and V are the temperature and the volume of the system and n_i are the molar quantities of the components.

The Helmholtz function is particularly useful for closed systems where temperature T and volume V are easily controllable; it is typically the case of theoretical calculations, including the statistical approach to Thermodynamics.

Note: Part III is dedicated to an introduction to Statistical Thermodynamics . We will see in Chapter 15 that the thermodynamical properties of a simple system with one component are summarised, in Statistica Thermodynamics, in the partition function Z and that the Helmholtz function F is connected to the partition function Z by a particularly simple relation:

$$F = -k_B T \ln Z \,. \tag{8.34}$$

8.3.1 Simple systems in equilibrium

The differential of (8.33) is

$$dF = -S\, dT - p\, dV + \sum\nolimits_i \mu_i dn_i \,. \tag{8.35}$$

It is convenient to enlighten the similarities and the differences between the differentials (8.35) and (8.3) of the Helmholtz function F and of the internal energy U.

Compression work

The differential of the Helmholtz function shares with that of the internal energy the second term $đW = -p\, dV$, that represents the reversible compression work. Different is instead the first term, $-S\, dT$ instead of $T\, dS$.

Let us consider a closed system with no internal reactions ($dn_i = 0$) and compare the effects of a compression work performed at constant entropy or at constant temperature.

- If the system is compressed at constant entropy ($dS = 0$), no exchange of heat takes place between system and ambient, so that, according to (8.3), the reversible compression work $đW$ is equal to the variation dU of the internal energy.
- If the system is compressed at constant temperature ($dT = 0$), according to (8.35) the reversible compression work $đW$ is equal to the variation of the Helmholtz free energy:

$$\boxed{-p\, dV = dF} \qquad [T = \text{constant}] \tag{8.36}$$

Schematically:

$$\begin{array}{lllll} S = \text{constant} & \Rightarrow & đQ = 0 & \Rightarrow & đW = dU \\ T = \text{constant} & \Rightarrow & đQ \neq 0 & \Rightarrow & đW \begin{cases} \neq dU \\ = dF = dU - T\, dS \end{cases} \end{array}$$

Example 1: Let us consider a *real gas* contained in a cylinder closed by a movable piston. A reversible compression work $đW = -p\,dV$ is performed on the gas.

a) If the cylinder is thermally insulated, $đQ = T\,dS = 0$, so that $đW = dU$. When the gas is compressed, the internal energy U increases; by reducing the external pressure one can recover the work at the expenses of the internal energy U. The internale nergy is a sort of potential energy for reversible adiabatic compressions.

b) If the cylinder is maintained at constant temperature, heat can be exchanged with the ambient, $đW = dU - T\,dS = dF$. When the gas is compressed, both the internal energy U and the entropy S of the gas increase; by reducing the external pressure one can recover the work at the expenses of the Helmholtz free energy F. The Helmholtz free energy is a sort of potential energy for reversible isothermal compressions.

Example 2: Particularly interesting is the case of *ideal gases*, for which $dU = 0$ if $dT = 0$. For a reversible isothermal compression of an ideal gas, $đW = -T\,dS = dF$; the compression work reduces the entropy S and increases F.

8.3.2 Thermodynamical processes and Helmholtz function

We study now the role of the Helmholtz free energy in thermodynamical processes taking place as a consequence of the removal of one or more constraints in a composite system maintained at constant temperature and volume.
This time we will start from some general considerations on irreversible processes. We will then re-consider the second example of § 8.1, adapting it to the case of constant temperature instead of constant entropy.

Irreversibility and reduction of the Helmholtz function

To be maintained at constant temperature T, a system has to be in contact with a reservoir, that represents its ambient. Let us demonstrate that the increase of the entropy of the thermodynamical universe (system plus ambient) is accompanied by a reduction of the Helmholtz free energy in a closed system with constant T and V..
Starting point is again the axiom of entropy increase in the isolated systems, so that

$$T\Delta S_s + T\Delta S_a \geq 0\,. \tag{8.37}$$

By hypothesis $\Delta V_s = 0$, so that $\Delta V_a = 0$; besides $\Delta U_s = -\Delta U_a$.
Nothing can be a priori said about the entropy variation ΔS_s due to re-adjustements internal to the system. One can however state that the variation of the entropy of the ambient is connected to the exchange of energy with the system, so that

$$T\Delta S_a = \Delta U_a = -\Delta U_s\,. \tag{8.38}$$

By substituting (8.38) in (8.37) one obtains the equation concerning only the system (for constant T):

$$T\Delta S_s - \Delta U_s = -\Delta F_s \geq 0\,, \quad \Rightarrow \quad dF_s \leq 0\,. \tag{8.39}$$

Example

The system is a gas enclosed in a cylinder maintained at constant temperature by contact with a reservoir; the system is divided by a piston in two sub-systems containing each one the same number of moles n; initially the piston is fixed and pressures and volumes of the two sub-systems are p_1, V_1 and p_2, V_2, respectively, with con $p_1 > p_2$ (Fig. 8.5, center). At a given time, the piston is left free to move, and the system attains a new state of non-constrained equilibrium where the two sub-systems share the same pressure p and the same volume V.
As we did for internal energy and enthalpy, let us consider again two extreme cases.

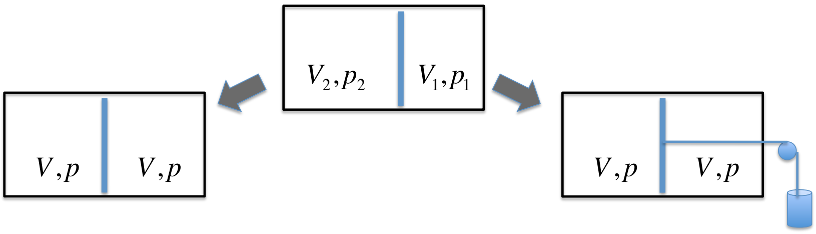


Figure 8.5: A cylinder filled with gas is divided in two sub-systems by a piston. Initially the piston is fixed (center). When the piston is left free to move, a process is triggered leading to a new equilibrium condition of the two sub-systems. The global system has to maintain its temperature unaltered Two possible processes are illustrated: one completely irreversible (left) thhe other reversible (right).

a) The process is completely irreversible: the piston is moved by the difference of pressure $p_1 - p_2$ and oscillates around the equilibrium position until it stops by effect of friction (Fig. 8.5, left). Globally, the system undergoes a variation of internal energy ΔU_s and a variation of entropy ΔS_s, whose sign is a priori unknown. The general considerations which led to equation (8.39) allow us to state that the process takes place with a reduction of the Helmholtz function: $\Delta F = \Delta U_s - T\Delta S_s < 0$.

   - If the gas can be considered as ideal, more detailed quantitative results can be obtained. Actually, for ideal gases whet T is constant the internal energy remains constant too, $\Delta U_s = 0$. By considering a reversible isothermal transformation connecting the initial and final states of both sub-systems, one can easily calculate the entropy variation, $\Delta S_s = nR\ln(V^2/V_2V_1) > 0$. In the case of the ideal gas, since $\Delta U = -\Delta U_a = 0$, the entropy of the ambient is unchanged $\Delta S_a = 0$; the reduction of the Helmholtz function F of the system is only due to the increase of the system entropy S_s.

b) The process takes place reversibly, thanks to the connection of the piston to an external device which progressively adapts the external pressure to the instantaneous difference of pressure between the two subsystems (Fig. 8.5, right). The system performs a work $\tilde{W}$ on the external device. The differential energy balance of the two sub-systems is:

$$\begin{aligned} dU_1 &= TdS_1 - p_1 dV_1 \\ dU_2 &= TdS_2 - p_2 dV_2 \\ dU_s = dU_1 + dU_2 &= TdS_s + (p_1 - p_2)dV_2 = TdS_s + đ\tilde{W} \end{aligned} \tag{8.40}$$

There is again a reduction of the Helmholtz free energy,

$$dU_s - T\,dS_s = dF_s = đ\tilde{W} < 0\,, \tag{8.41}$$

that, for the reversible case, corresponds to the work performed by the system on its ambient. Otherwise stated, ΔF measures the maximum work obtainable by means of a transformation from an initial state of constrained equilibrium to a final state of non-constrained equilibrium in a system at constant T and V.

   - For the ideal gas at constant temperature, $dU_s = 0$; also in the reversible case the reduction of the Helmholtz function F of an ideal gas corresponds only to an increase of its entropy S_s.

8.3.3 Equilibrium condition

For a closed system with constant temperature T and volume V the thermodynamical equilibrium is characterised by a minimum of the Helmholtz free energy F. Any deviation, reversible or irreversible, from the equilibrium state gives rise to an increase of the Helmholtz function F. In an equilibrium state

$$\delta F = 0, \qquad \Delta F > 0\,. \tag{8.42}$$

In a closed system with constant T and V, the Helmholtz function F is minimum with respect to any process, real or virtual, leading the system out of equilibrium.

8.4 Gibbs free energy G

The Gibbs free energy G is the Legendre transform of the internal energy U with respect to both temperature T and pressure p (§ 7.2), say

$$G \;=\; U - TS + pV \;=\; H - TS \;=\; G(T, p, \{n_i\})\,, \tag{8.43}$$

where T and p are the temperature and the pressure of the system, respectively, and n_i are the molar quantities of the components.
The Gibbs function can also be considered as the Legendre transform of the enthalpy H with respet to the temperature$T$; for that reason is called *ree enthalpy'* too.
The Gibbs function is particularly useful for systems where temperature T and pressure p are easily controllable; it is the case of typical experimental conditions.
We have also seen, in § 7.2, that for a system with only one component the molar Gibbs free energy corresponds to the chemical potential μ:

$$g \;=\; G/n \;=\; \mu\,. \tag{8.44}$$

8.4.1 Simple systems in equilibrium

The differential of (8.43) is

$$dG = -S\,dT + V\,dp + \sum\nolimits_i \mu_i dn_i\,. \tag{8.45}$$

In (8.45), the heat exchanged and the compression work don't appear.
For a system with constant T and p constant, (8.45) reduces to $dG = \Sigma_i \mu_i dn_i$. The Gibbs function is particularly suited to processes taking place in closed systems at constant temperature and pressure, where the composition is varied: chemical reactions and phase transitions. Such processes are generally irreversible.

8.4.2 Thermodynamical processes and Gibbs function

We want now to study the role of the Gibbs function in processes taking place in closed systems with T and p constant after the removal of one or more constraints.
As was done for the Helmholtz function, we start from general considerations.

Irreversibility and reduction of the Gibbs function

Let us consider a closed system un equilibrium with its ambient at T and p. We want to demonstrate that the increase of entropy of the universe (system plus ambient) entails a reduction of the Gibbs free energy of the system.
Starting point are the relations

$$T\Delta S_s + T\Delta S_a \geq 0\,, \qquad \Delta U_a = -\Delta U_s\,, \qquad \Delta V_a = -\Delta V_s\,. \tag{8.46}$$

A priori, the variation of the entropy of the system is unknown. The variation of the entropy of the ambient is connected to the exchanges of energy and volume with the system, tat is to say

$$T\Delta S_a = \Delta U_a + p\,\Delta V_a = -\Delta U_s - p\,\Delta V_s\,. \tag{8.47}$$

By inserting now (8.47) in the first one of equations (8.46), one obtains the equation for the system (with T and p constant)

$$T\Delta S_s - \Delta U_s - p\,\Delta V_s = -\Delta G_s \geq 0\,, \quad \Rightarrow \quad \Delta G_s \leq 0\,. \tag{8.48}$$

The processes taking place after the removal of some constraint in closed systems with constant T and p entail a reduction of the Gibbs function G.

For the three functions U, H, F, it was possible to make examples of processes taking place in composite systems initially characterised by imbalances of temperature or pressure.
Such kind of examples are not possible for the Gibbs function. In a system maintained at constant T and p, the possible processes are caused by initial imbalances of the chemical potentials and consist in variations of the mole numbers n_i of the components.
Such processes have to do with chemical equilibrium (see below, § (8.5)).

Note: Processes triggered by imbalances of chemical potential could anyway take place also in systems described by the functions U, H, F.

8.4.3 Equilibrium condition

In a closed system with constant temperature T and pressure p, the thermodynamical equilibrium is characterised by the minimum of the Gibbs function G. Any deviation, reversible or irreversible, from the equilibrium state gives rise to an increase of the Gibbs function G. In an equilibrium state:

$$\delta G = 0, \qquad \Delta G > 0\,. \tag{8.49}$$

In a closed system with constant T and p, the Gibbs function G is minimum with respect to any process, real or virtual, leading the system out of equilibrium.

8.5 The chemical equilibrium

All the differentials of the thermodynamical functions, (8.3), (8.19), (8.35) and (8.45), contain the sum $\sum_i \mu_i\, dn_i$, where the n_i are the numbers of moles of the components of the system.
The sum can refer to different processes concerning the chemical equilibrium:

- In *open systems*, the terms dn_i can measure the exchanges of matter with the surrounding ambient. The effects of matter exchanges on the internal energy and on the enthalpy have already been shortly considered above. The topic will be treated in more detail in § 11.3.

- In *closed systems*, the terms dn_i measure the internal variations of composition. The topic is treated immediately below; it is anyway convenient to made since now a distinction:
  - in *homogeneous systems* the terms dn_i generally refer to chemical reactions,
  - in *heterogeneous systems* the terms dn_i can refer to phase transitions and/or to matter transport.

Note: The different types of thermodynamical transformations listed above can obviously take place at the same time in the same system.

8.5.1 Closed system in thermal and mechanical equilibrium

Let us consider a closed system in thermal and mechanical equilibrium and study the processes that can modify the amounts n_i of the components.
Such processes (chemical reactions and phase transitions) are generally irreversible. One can demonstrate that the state of the system can anyway be described by thermodynamical coordinates even in the absence of chemical equilibrium, provided the system be in the thermal and mechanical equilibrium. It is thus possible to calculate the variations of the thermodynamical functions by the differential expressions introduced in the previous sections.

If the system is isolated ($dU = 0$ and $dV = 0$), the process can be described in the entropy representation and entails an increase of the system entropy:

$$T\,dS \;=\; -\sum\nolimits_i \mu_i\,dn_i \;>\; 0\,. \tag{8.50}$$

If the system is not isolated, the process can be described by one of the thermodynamic functions U, H, F or G:

$$\begin{array}{llll} dU & = \sum_i \mu_i\,dn_i & < \; 0 & S, V = \text{constant} \\ dH & = \sum_i \mu_i\,dn_i & < \; 0 & S, p = \text{constant} \\ dF & = \sum_i \mu_i\,dn_i & < \; 0 & T, V = \text{constant} \\ dG & = \sum_i \mu_i\,dn_i & < \; 0 & T, p = \text{constant} \end{array} \tag{8.51}$$

Even if it is not explicitly apparent in(8.51),the chemical potentials depend on temperature and pressure, $\mu_i(T,P)$. The four inequalities (8.51) thus correspond to different cases and give rise to different equilibrium conditions.

The most interesting case concerns processes taking place at constant temperature T and pressure p, for which the thermodynamic potential is the Gibbs function.

8.5.2 Chemical reactions and Gibbs function

For a chemical reaction at constant T and p, the direction of the reaction is determined by the condition that the Gibbs function has to decrease, $\Delta G < 0$. In equilibrium, the Gibbs function is stationary, $\delta G = 0$.

A chemical reaction can be considered, in principle and sometimes also in practice, as a transition from a state of constrained equilibrium to a state of non-constrained equilibrium.

Example: A mixture of hydrogen and oxygen can remain in a state of equilibrium (that could be said to be constrained) until a suitable catalyst is introduced, that triggers the reaction of water formation (in non-constrained equilibrium).

An effective thermodynamical description of chemical reactions will be introduced in § 11.4. There, the equilibrium condition will be expressed as a function of the chemical potentials of reactants and products.

Here only some simple examples will be proposed to illustrate the energetic and entropic meaning of the reduction of the Gibbs function.

Example 1

Let us consider the chemical reaction

$$A + B \to C + D$$

taking place at constant temperature and pressure.

Initially only the reactants A and B are present, in a state of constrained equilibrium. At a given time a thermodynamical operation (e.g the insertion of a catalyst) triggers the reaction, that leads to a final equilibrium state where only the products C and D are present.

Let the reaction be *endothermic*, that is to say that the enthalpy of the system increases:

$$\Delta H_s \;=\; H(C) + H(D) \;-\; H(A) - H(B\;) > \;0\,.$$

(The enthalpy variation ΔH can be measured by calorimetric techniques or can be calculated from the tables of the standard enthalpies of reactants and products).

The progress of the reaction towards the final equilibrium state is characterised by the decrease of the Gibbs function G:

$$\Delta G_s \;=\; \Delta H_s - T\Delta S_s \;<\; 0\,,$$

where $\Delta S_s = S(\mathrm{C}) + S(\mathrm{D}) - S(\mathrm{A}) - S(\mathrm{B})$ is the variation of the system entropy between the final and initial states.

The disequality $\Delta G_s < 0$ requires that $T\Delta S_s > \Delta H_s$. In order that the reaction take place, the increase of the system enthalpy has to be compensated and overcome by the increase of the entropic term $T\Delta S_s$.

Example 2

Let us consider the process of oxidation of glucose at constant temperature and ambient pressure:

$$\mathrm{C_6H_{12}O_6} + 6\,\mathrm{O_2} \;\rightarrow\; 6\,\mathrm{CO_2} + 6\,\mathrm{H_2O}\,. \tag{8.52}$$

The reaction is esothermic, that is to say that heat is emitted at constant pressure with reduction of enthalpy,

$$\Delta H_s = -2798\,\mathrm{kJ\,mol^{-1}} < 0\,.$$

The variation of the entropy of the system from the initial state of constrained equilibrium to the final state of non-constrained equilibrium is positive and is mainly due to the fragmentation of the complex glucose molecule into simpler molecules:

$$\Delta S_s = 241\,\mathrm{J\,K^{-1}mol^{-1}}\,.$$

If the process takes place at the temperature $T = 310\,\mathrm{K}$ (that is the human body temperature, 37°C), the reduction of the Gibbs free energy is

$$\Delta G_s = \Delta H_s - T\,\Delta S_s = -2873\,\mathrm{kJ\,mol^{-1}} < 0\,.$$

Let us consider two extreme cases.

a) The reaction is completely *irreversible* (fast combustion suitably triggered); the reduction of the system enthalpy corresponds to transfer of heat to the ambient, that correspondingly increases its entropy, $\Delta H_s = -T\Delta S_a > 0$; globally, the increase of the entropy of the unicerse (system plus ambient) is $\Delta S_s + \Delta S_a > 0$.

b) The oxidation takes place *reversibly*, thanks to suitable catalysts, and the *chemical work* $\tilde{W} = \Delta G_s = -2873$ kJ mol^{-1} is obtained (negative because made *by* the system). The cariations ΔS_s and ΔH_s only depend of the initial and final equilibrium states, are are thus the same as in the irreversible case. For a reversible process, the entropy of the universe (system plus ambient) remains unchanged; the positive variation of the system, $\Delta S_s > 0$, has to be compensate by a negative variation of the ambient, $\Delta S_a = -\Delta S_s < 0$. Instead of emitting heat, as in the irreversible case, the system now absorbs heat $T\Delta S_a$ from the ambient; the work $\tilde{W}$ corresponds to the reduction of the enthalpy H_s plus the heat absorbed from the ambient.

Note: The choice of the components of a system is somewhat arbitrary. For example, in (8.52) one can consider as components the four compounds: glucose $\mathrm{C_6H_{12}O_6}$, ogygen $\mathrm{O_2}$, carbon dioxide $\mathrm{CO_2}$ and water $\mathrm{H_2O}$, whose amounts n_i change during the reaction. Alternatively one could consider as components three atomic species, hydrogen H, carbon C and oxygen O, whose amounts n_j remain instead unchanged, but undergo re-adjustements of their chemical aggregations.

Further details on chemical equilibrium will be found in Chapter 11.

8.5.3 Phase equilibria and Gibbs function

Let us consider an heterogeneous system containing two phases α and β of the same component (for example liquid water and water vapour), at constant temperature T and pressure p.
Let $\mu^\alpha(p,T)$ and $\mu^\beta(p,T)$ be the chemical potentials of the two phases; their values depend on temperature and pressure.
Initially the two phases are separated by an impermeable wall. When the wall is removed, an irreversible process is triggered, by which the amounts of the two phases are modified according to (8.48)

$$\Delta G \;=\; \mu^\alpha\,\Delta n^\alpha + \mu^\beta\,\Delta n^\beta < 0\,. \tag{8.53}$$

Since $\Delta n^\alpha = -\Delta n^\beta$, equation (8.53) becomes

$$\Delta G \;=\; (\mu^\alpha - \mu^\beta)\,\Delta n^\alpha \;<\; 0\,. \tag{8.54}$$

According to (8.54) if at the pressure p and temperature T the relation between the chemical potential is $\mu^\alpha(p,T) > \mu^\beta(p,T)$ then the α phase transforms into the β phase, that is $\Delta n^\alpha < 0$ e $\Delta n^\beta > 0$, and viceversa.

Matter moves from the phase with higher chemical potential to the phase with lower chemical potential.

The quilibrium condition (8.49) of the two phases α and β requires that

$$\begin{aligned} \delta G &= \mu^\alpha\, dn^\alpha + \mu^\beta\, dn^\beta \\ &= (\mu^\alpha - \mu^\beta)\, dn^\alpha \;=\; 0\,; \end{aligned} \tag{8.55}$$

the equilibrium is obtained for the values of pressure p and temperature T such that the two phases share the same chemical potential, $\mu^\alpha(p,T) = \mu^\beta(p,T)$.

Recall that the chemical potential corresponds to the molar Gibbs free energy, $\mu = g$.

Phase transitions will be considered in more detail in Part V. In particular, the role of the Gibbs function will be considered in Chapter 23.

8.5.4 Grand-canonical potential Ω

In conclusion of this § 8.5, let us shortly consider the Legendre transform Ω of the internal energy U with respect to the temperture and the chemical potentials, already introduced in Chapter 7, equation (7.20)

For simplicity, let us consider a system with only one component, so that

$$\Omega = U - TS + \mu n\,, \tag{8.56}$$

whose differential is

$$d\Omega = -SdT - pdV + nd\mu\,. \tag{8.57}$$

Let the system be open, so that it can modify the number n of moles of its component, and be maintained at constant temperature T, volume V and chemical potential μ. In equilibrium, the maximum condition for the entropy of the universe (system plus ambient) with respect to the virtual processes leading to states of constrained equilibrium is

$$\begin{aligned} T\Delta S_s + T\Delta S_a &= T\Delta S_s + \Delta U_a - \mu\Delta n_a \leq 0 \\ &= T\Delta S_s - \Delta U_s + \mu\Delta n_s \leq 0 \end{aligned} \tag{8.58}$$

As a consequence, from (8.56) with T, V, μ fixed, one gets

$$\Delta\Omega = \Delta U_s - T\Delta S_s + \mu\Delta n_s \geq 0\,. \tag{8.59}$$

The grand-canonical potential is minimum with respect to virtual processes that lead the system out of equilibrium. Viceversa, processes that lead a system with constant (T, V, μ) from a state of constrained equilibrium to a state of non-constrained equilibrium entail a reduction of the grand-canonical potential Ω.

Chapter 9

Response functions

The response functions measure the dependence of the variations of a given thermodynamical variable on the variations of another variable. In general, the response functions are experimentally measurable.
In this chapter the most important response functions will be considered:

- heat capacities at constant volume or pressure (§ 9.1),
- isothermal and adiabatic compressibilities (§ 9.2),
- coefficient of thermal expansion (§ 9.3).

Useful connections will be established between the response functions and the thermodynamical functions of Chapter 8 as well as between the different response functions (§ 9.4).
The study of the conditions of stability for the thermodynamical equilibrium will show that some response functions (heat capacities and compressibilities) cannot be begative (§9.6).
The response functions are not state functions, their values depend on the type of thermodynamical process considered.

9.1 Heat capacities and specific heats

The heat capacity of a system is the ratio between the infinitesimal amount of heat absorbed and the corresponding infinitesimal variation of temperature:

$$C = \frac{đQ}{dT}\,. \tag{9.1}$$

The values of the heat capacity of a given system depend on the peculiar conditions of the heat transfer. Particularly important are the heat capacities for the processes taking place at constant volume or at constant pressure. For *reversible transformations*, the heat exchanged $đQ$ is connected to the variations of internal energy U or of enthalpy H according to the simple relations (§ 8.2:

for constant volume V, $(đQ)_v = dU = T\,(dS)_v$
for constant pressure p, $(đQ)_p = dH = T\,(dS)_p$

Accordingly, the heat capacities at constant volume or pressure are expressed by, respectively

$$\boxed{C_v = \left(\frac{\partial U}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v} \qquad \boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p} \tag{9.2}$$

From the differential expressions of the Helmholtz function (7.17) and of the Gibbs function (7.19), one can easily find that the entropy can be expressed as

$$S = -\left(\frac{\partial F}{\partial T}\right)_v = -\left(\frac{\partial G}{\partial T}\right)_p\,. \tag{9.3}$$

By substituting the first and the second expressions of S of (9.3) in the first one and the second one of the equations (9.2), respectively, one obtains the heat capacities as second derivatives of the Helmholtz and Gibbs functions, respectively, with respect to the temperature:

$$\boxed{C_v \;=\; -T\left(\frac{\partial^2 F}{\partial T^2}\right)_v} \qquad\qquad \boxed{C_p \;=\; -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p} \tag{9.4}$$

As a consequence of the stability of the thermodynamical equilibrium, one can demonstrate that the heat capacities cannot be negative (§ 9.6): a system that absorbs heat cannot decrease its temperature.

9.1.1 Specific heats

The heat capacities depend on the amount of matter contained in the given system. The specific heats are instead independent of the system size. By convention, the heat capacities are denoted by the uppercase C, the specific heats by the lower-case c.
Two types of specific heats are commonly in use:

- Specific heats per unit mass, measured in kJ K^{-1} kg^{-1}:

$$\tilde{c}_v \;=\; \frac{C_v}{m}\,, \qquad\qquad \tilde{c}_p \;=\; \frac{C_p}{m}\,. \tag{9.5}$$

- Molar specific heats, measured in J K^{-1} mol^{-1}:

$$c_v \;=\; \frac{C_v}{n}\,, \qquad\qquad c_p \;=\; \frac{C_p}{n}\,. \tag{9.6}$$

In general one measures and list in tables the specific heats per unit mass. The molar specific heats, more useful for comparisons with microscopic theories, can be obtained multiplying the specific heats per unit mass by the molar masses (expressed in atomic mass units).

Note 1: To distinguish the specific heats for unit mass and the molar specific heats, we use here the symbol $\tilde{c}$ for the first ones, c for the second ones.

Note 2: When the mole us used to measure the matter amount, it is necessary to specify the type of elementary constituents. For example, the expression "one mole of NaCl" has a different meaning according to whether one refers to a mole of atoms or to a mole of molecules. In the first case one refers to N_A atoms, in the second case to $2N_A$ atoms ($N_A \simeq 6.023 \times 10^{23}$ is the Avogadro number).

9.1.2 Examples

The heat capacities depend on temperature. The experimental measurement of the dependence on temperature of the heat capacities is one of the most important methods to get information on how energy is stored in matter.
Equation (9.2) shows that the heat capacity at constant volume C_v is directly linked to the internal energy U. However, in general it is easier to measure the heat capacity at constant pressure C_p. The two heat capacities, at constant volume or pressure, are connected by a general relation that will be obtained in § 9.4.

Example 1: Monatomic idel gas

For the monatomic ideal gas, the heat capacities at constant volume or pressure are independent of the temperature and of the atomic species:

$$C_v = \frac{3}{2}nR\,, \qquad C_p = \frac{5}{2}nR\,, \tag{9.7}$$

where $R = 8.31$ J K^{-1} mol^{-1} is the gas constant. By inverting the derivatives of (9.2) one finds that the internal energy U and the enthalpy H linearly increase with temperature:

$$U(T) = U_0 + \frac{3}{2}nR\,(T - T_0)\,, \qquad H(T) = H_0\,\frac{5}{2}nR\,(T - T_0)\,, \tag{9.8}$$

where T_0 is an arbitrary reference temperature, U_0 and H_0 are the internal energy and the enthalpy, respectively, at the temperature T_0.

In the kinetic model of the ideal gas the energy is purely kinetic and the equations (9.8) become

$$U(T) = \frac{3}{2} nRT\,, \qquad H(T) = \frac{5}{2} nRT\,. \tag{9.9}$$

The temperature dependence of U and H expressed in (9.9) is the same for constant volume as for constant pressure.

By integrating $dS = dU/T$ (at constant volume) or $dS = dH/T$ (at constant pressure) one finds that the entropy S increases proportionally to the logarithm of T; the dependences are different at constant volume and at constant pressure:

$$S_v(T) = S_0 + \frac{3}{2} nR \ln\left(\frac{T}{T_0}\right)\,, \qquad S_p(T) = S_0 + \frac{5}{2} nR \ln\left(\frac{T}{T_0}\right)\,. \tag{9.10}$$

The expression for S_v (at constant volume) in (9.10) is consistent with the fundamental equation for the ideal gas in the entropy representation (6.64) derived in Chapter 6.

The value of C_v in (9.7) is consistent with the classical theorem of the equipartition of energy, according to which at each degree of freedom it corresponds a contribution $nRT/2$ to the average energy of the system. In the monatomic gas there are three degrees of freedom per atom (three-dimensional translational motion) and thus three quadratic contributions to the average energy: $\langle mv_x^2/2\rangle, \langle mv_y^2/2\rangle, \langle mv_z^2/2\rangle$.

Example 2: Bi-atomic ideal gas

In most cases, the values of the heat capacities of bi-atomic ideal gases, measured at room temperature ($T \simeq 300\,\mathrm{K}$), are

$$C_v = \frac{5}{2} nR\,, \qquad C_p = \frac{7}{2} nR\,. \tag{9.11}$$

The experimental value of the constant-volume heat capacity C_v is consistent with the classical theorem of equipartition of energy if, in addition to the three translational degrees of freedom, one considers also the two rotational degrees of freedom around the two independent axes perpendicular to the inter-atomic link, to which two quadratic contributions to the energy of each molecule correspond, $\langle I\omega_1^2/2\rangle, \langle I\omega_2^2/2\rangle$.

Actually, a bi-atomic molecule could store also vibrational energy in one further degree of freedom, to which two further quadratic contributions to the energy of each molecule would correspond, $\langle \mu v^2/2\rangle, \langle \mu\omega^2 x^2/2\rangle$, where μ is the reduced mass and k the elastic constant. The constant-volume heat capacity should then be $C_v = (7/2)nR$ instead of $(5/2)nR$.

The discrepancy between the experimental and theoretical values is explained by Quantum Mechanics as follows (see also Chapter 31).

The levels of rotational energy are quantised according to the relation

$$E_{\mathrm{rot}} \;=\; \frac{L^2}{2I} \;=\; \frac{\hbar\ell(\ell+1)}{2I}\,, \qquad (\ell = 1, 2, 3..., n, ...) \tag{9.12}$$

The levels of vibrational energy are quantised according to the relation

$$E_{\mathrm{vib}} \;=\; (n + 1/2)\,\hbar\omega\,, \qquad (\nu = 0, 1, 2, 3..., n, ...) \tag{9.13}$$

At a given temperature T, the rotational or vibrational levels are excited if $\Delta E_{\mathrm{min}} < k_B T$ (where $k_B \simeq 8.6 \times 10^{-5}\,\mathrm{eV/K}$). For the CO molecule, for example, $\Delta E_{\mathrm{rot,min}} = 3.5 \times 10^{-4}$ eV and $\Delta E_{\mathrm{vib}} \simeq 0.27\,\mathrm{eV}$. At the room temperature $T = 300\,\mathrm{K}$, $k_B T \simeq 0.025$ eV, so that the rotational levels are excited and contribute to the heat capacity while the vibrational levels are not excited and don't contribute to the heat capacity. If the temperature is enough reduced, the rotational contribution is eliminated, if the temperature is enough increased, the vibrational contribution is added.

Example 3: Non-metallic crystalline solids

In crystalline solids, the constant-volume heat capacity C_v significantly depends on temperature. Let us here first consider non-metallic crystals. The temperature dependence of the heat capacity (and of the specific heat) is different for different substances, but for all substances it shares two characteristics (Fig 9.1, left):

- At sufficiently high temperatures, typically around room temperature, the value of the constant-volume heat capacity is independent of temperature, $C_v = 3nR$, where n is the number of moles of single atoms. This behaviour is known as the Dulong and Petit rule and is consistent with the classical law of equipartition of energy between the vibrational modes of the crystalline structure.
- Et low temperatures, the heat capacity decreases, and, for $T \to 0, C_v \to 0$,with $C_v \propto T^3$. This behaviour is inconsistent with classical statistics, but is explained in terms of quantisation of the vibrational energy levels.

The behaviour at intermediates temperatures as well as the temperature that is conventionally assumed as the boundary between the classical to the quantum behaviour (known as Debye temperature) depend on the type of substance.

The difference between the constant-pressure and the constant-volume specific heats, C_p and C_v, respectively, is much smaller in the crystal than in the gases.

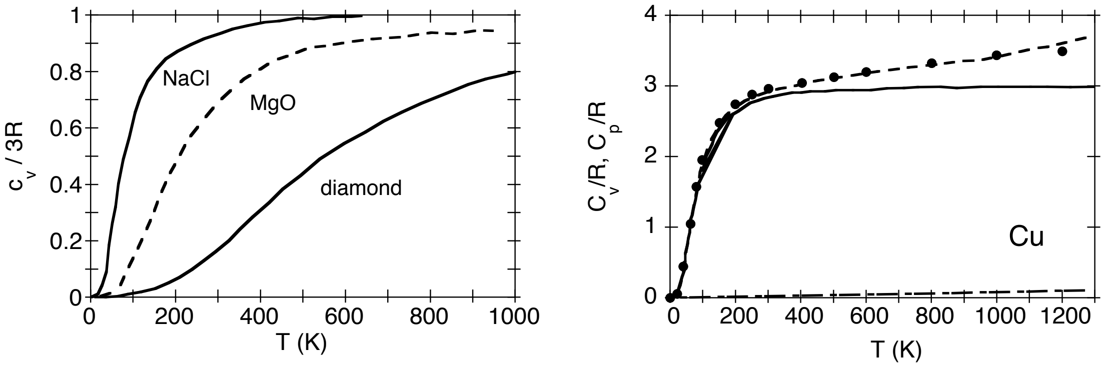


Figure 9.1: Right: examples of constant-volume molar specific heats $c_v/3R$ (the moles refer to single atoms) for three different crystalline solids. Right: comparison of different contributions to the molar specific heats of copper Cu, divided by R; the points are experimental values of c_p: the lines are calculated values: total c_p (dashed line), vibrational contribution to c_v (continuous line), electronic contribution (dash-dotted line) [from Q. Bian et al., J. Phys. Chem. Solids 69, 168 (2008)].

Example 4: Metallic crystalline solids

In metallic crystalline solids the thermal energy can be stored not only in the vibrations of the ions of the crystalline lattice but also by the conduction electrons. As a consequence, the heat capacity (and the specific heat) of metals is larger than in non-metals.

As a first approximation, the conduction electrons can be considered as free particles. To calculate their contribution to the heat capacity it is however necessary to take into account the quantum symmetry properties of the electronic wave-functions and to resort to a specific statistical theory, the Fermi-Dirac statistics (see Chapter 16). The resulting electronic contribution to C_v linearly depends on temperature, and is generally much smaller that the vibrational contribution.

As an example, let us consider copper (Fig 9.1, right); at the temperature $T = 315\,\mathrm{K}$, the vibrational contribution to the molar specific heat is $c_v^{(\mathrm{vib})} \simeq 3R \simeq 25\,\mathrm{J\,mol^{-1}\,K^{-1}}$, while the electronic contribution is much smaller, $c_v^{(\mathrm{el})} \simeq 0.21\,\mathrm{J\,mol^{-1}\,K^{-1}}$. At very low temperatures, however, the linear temperature dependence of $c_v^{(\mathrm{el})}$ prevails on the parabolic dependence of $c_v^{(\mathrm{vib})}$. At $T < 15\,\mathrm{K}$ one finds $c_v^{(\mathrm{el})} > c_v^{(\mathrm{vib})}$.

Example 5: The water specific heat

The molar specific heat of water at constant pressure is shown in Fig. 9.2 for different temperature intervals. Here one mole corresponds to the Avogadro number N_A of molecules H_2O. The differences between the solid, liquid and gaseous phases are evidenced, as well as the dependence on temperature.

Let us first consider the *gaseous phase*. The H_2O molecule has nine degrees of freedom: three translational, three rotational and three vibrational. To the nine degrees of freedom, 12 quadratic contributions to the energy correspond. According to the classical equipartition of energy , one would expect $c_v/R = 6$ e $c_p/R = 7$. Such values are observed only at high temperature (Fig. 9.2, left). At low temperature, only translational and rotational degrees of freedom contribute, and $c_p/R = 4$. The three vibrational modes correspond to values $\hbar\omega$ of 0.19 eV ("bending"), 0.45 eV ("symmetric stretching") e 0.46 eV ("asymmetric stretching"), respectively, and are progressively excited when the temperature increases. The values higher than $c_p/R = 7$ at very high temperature can be attributed to anharmonicity effects.

Let us consider now the *crystalline phase*. In the molecular crystal of water (ice), for each mole one can single out $3N_A$ low-frequency vibrational modes connected to the weak inter-molecular forces ($3R$ contribution), $3N_A$ intermediate-frequency librational modes due to molecular oscillations and $3N_A$ high-frequency modes due to the strong intra-molecular forces (that are also responsible for the vibrations of the gas molecules). The dependence on temperature (Fig. 9.2, center) suggests that below 273,K the librational modes are progressively excited, while the high-frequency vibrational modes are not yet excited.

At last, let us consider the *liquid phase* (Fig. 9.2, right). The specific heat is about two times larger in the liquid phase than in the solid and gaseous phases. This fact suggests that a larger number of degrees of freedom exist in the liquid than in the other phases. The dependence on temperature is remarkable too, characterised by a minimum at about 310 K.

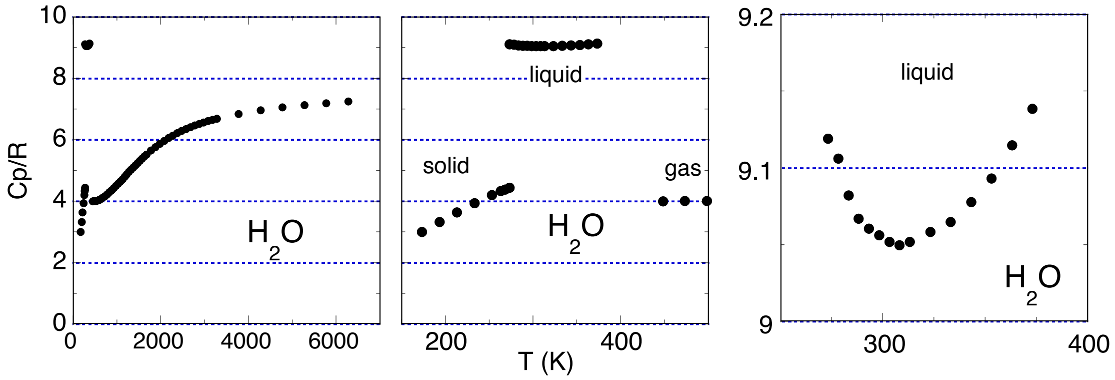


Figure 9.2: Molar specific heat at constant pressure of water. Left: in an extended temperature interval. Center: in a restricted temperature interval, where the differences between the three phases are best evidenced. Right: an enlarged view of the specific heat of the liquid phase.

Example 6: Non-crystalline solids

In non-crystalline solids, and in particular in glasses, the specific heat can be much different that the specific heat of the corresponding crystals in the low temperature region. For example, in Fig. 9.3

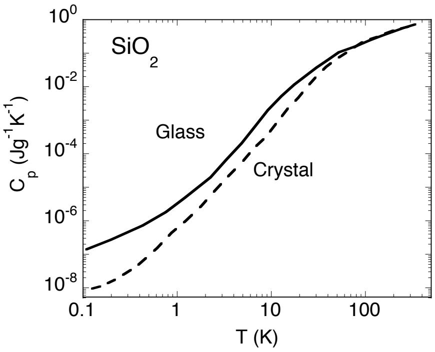


Figure 9.3: Specific heat crystalline (dashed line) and vitreous (continuous line) SiO$_2$ [from R.C. Zeller e R.O. Pohl, Phys. Rev. B 4, 2029 (1971)]. Pay attention to the logarithmic scales.

the specific heats per unit mass of crystalline and vitreous silica are compared sono confrontati i calori specifici per unità di massa della silice cristallina e vetrosa. The specific heat of crystalline silica exhibits the low-temperature standard behavior $\propto T^3$. The low-temperature specific heat of the glass is much higher. The origin of this behaviour is not yet completely understood.

9.2 Compressibilities

The compressibility of a system measures the volume variation with respect to the pressure variation, normalised to the volume.
One distinguishes the isothermal compressibility χ_T, measured at constant temperature, and the adiabatic compressibility χ_S, measured at constant entropy, defined as, respectively,

$$\boxed{\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T} \qquad \boxed{\chi_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S} \tag{9.14}$$

Le compressibilities have the dimension of inverse pressure, and are measured in Pa^{-1} or in bar^{-1}.
Starting from the differentials of the Gibbs function, (8.45), and of the enthalpy, (8.19), one can express the volume as

$$V = \left(\frac{\partial G}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_S . \tag{9.15}$$

By substituting the volume V of (9.15) in (9.14) one obtains the compressibilities as second derivatives with respect to the pressure of the Gibbs function and of the enthalpy:

$$\boxed{\chi_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_T} \qquad \boxed{\chi_S = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial p^2}\right)_S} \tag{9.16}$$

One can demonstrate, as a consequence of the stability of the thermodynamical equilibrium (see § 9.6), that the compressibilities cannot be negative: when the pressure increases, the volume cannot increase.

The relation between volume and pressure is sometimes measured by the inverse of the compressibilities, called *volume moduli*:

$$B_T = \frac{1}{\chi_T}, \qquad B_S = \frac{1}{\chi_S}. \tag{9.17}$$

9.2.1 Examples

The compressibilities depend on the thermodynamical state, and in particular on the temperature. Let us consider some examples.

Example 1: Ideal gases

, From the equations of the reversible isotherm, $pV =$ constant, and of the reversible adiabatic,

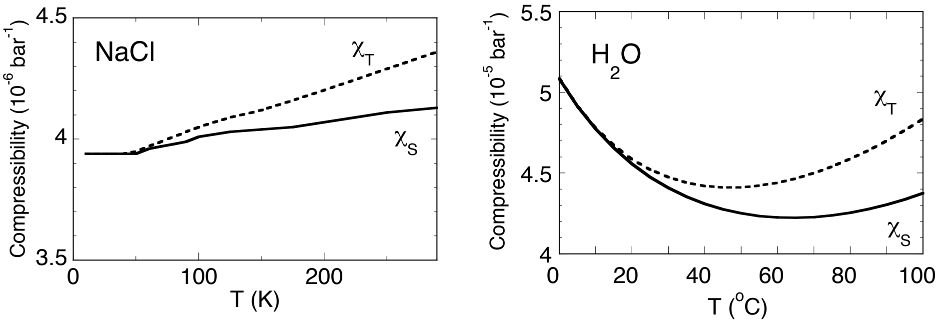


Figure 9.4: Isothermal and adiabatic compressibilities of NaCl (left) and of liquid water (right). Pay attention to the different horizontal and vertical scales.

pV^γ = costante (where $\gamma = c_p/c_v$ is the ratio of the constant-pressure to the constant-volume specific heat) one easily obtains

$$\chi_T \;=\; \frac{1}{p}\,, \qquad\qquad \chi_S \;=\; \frac{1}{\gamma p}\,. \tag{9.18}$$

The compressibilities of the ideal gases are independent of the temperature but strongly depend on the pressure. The behaviour of the compressibilities of the ideal gases can be easily inferred by considering the plots of the reversible isotherms and adiabatics in the pV plane.
To compare with other systems, it is useful to consider that at the atmospheric pressure (1 bar) the value of the isothermal compressibility of ideal gases is 1 bar^{-1}.

Example 2: Crystalline solid: NaCl

The isothermal and adiabatic compressibilities of NaCl are shown in Fig. 9.4 (left). Both compressibilities, measured at atmospheric pressure, weakly increase with the temperature. Notice that the values remain finite for $T \to 0$. At low temperatures $\chi_S \simeq \chi_T$, at high temperatures $\chi_T > \chi_S$.
The values at atmospheric pressure, $\chi_T \simeq 4 \times 10^{-6}$ bar^{-1}, are small with respect to the ideal gas values.

Example 3: Liquids

The compressibilities of liquids are generally included between 10^{-4} and 10^{-5} bar^{-1}, larger than those of solids but much smaller than those of gases. In general, the compressibility of liquids increases with temperature, as a consequence of the weakening of the repulsive forces between molecules. An exception is water, whose isothermal and adiabatic compressibilities Fa eccezione l'acqua, le cui compressibilità isoterma e adiabatica decrease with increasing temperature in a large low-temperature interval (Fig. 9.4, right).

9.3 Coefficient of therml expansion

The coefficient of thermal expansion β of a system measures the variation of volume V with respect to the variation of temperature T at constant pressure, normalised to the volume:

$$\boxed{\beta \;=\; \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p} \tag{9.19}$$

According to (9.15), the volume is the partial derivative of the Gibbs function with respect to pressure, so that the coefficient of thermal expansion can be expressed s the mixed second derivative of the Gibbs function:

$$\boxed{\beta \;=\; \frac{1}{V}\left(\frac{\partial^2 G}{\partial p\,\partial T}\right)} \tag{9.20}$$

The coefficient f thermal expansion is measured in K^{-1}.

9.3.1 Linear thermal expansion

The coefficient of *linear* thermal expansion measures the variation of a length ℓ with respect to the variation of temperature:

$$\alpha \;=\; \frac{1}{\ell}\left(\frac{\partial \ell}{\partial T}\right)_p . \tag{9.21}$$

The coefficient of linear thermal expansion may depend on the direction. Experimentally, in solids one measures the coefficients of linear expansion α. To recover the volume coefficients (9.19) it is necessary to know the relation between β and α, that depends on the symmetry properties of the system.

If the axes of the crystal cells are orthogonal, the volume coefficient β is connected to the three linear coefficients along the directions x, y, z by the simple relation

$$\beta = \alpha_x + \alpha_y + \alpha_z \,. \tag{9.22}$$

Actually, since $V = \ell_x \ell_y \ell_z$, one has

$$\begin{aligned} \beta \;&=\; \frac{1}{V}\left(\frac{\partial \ell_x}{\partial T}\right)_p \ell_y \ell_z + \frac{1}{V}\ell_x \left(\frac{\partial \ell_y}{\partial T}\right)_p \ell_z + \frac{1}{V}\ell_x \ell_y \left(\frac{\partial \ell_z}{\partial T}\right)_p \\ &=\; \frac{1}{\ell_x}\left(\frac{\partial \ell_x}{\partial T}\right)_p + \frac{1}{\ell_y}\left(\frac{\partial \ell_y}{\partial T}\right)_p + \frac{1}{\ell_z}\left(\frac{\partial \ell_z}{\partial T}\right)_p \;=\; \alpha_x + \alpha_y + \alpha_z \,. \end{aligned}$$

In crystals with non orthogonal axes (monoclinic and triclinic systems) the relation between the linear and volume coefficients is more complicated.

In *isotropic systems* (gases, liquids, glasses, crystals with cubic symmetry) the linear expansion is independent of direction, so that $\beta = 3\alpha$.

9.3.2 Examples

The coefficient of thermal expansion depends on the thermodynamical state, and in particular on temperature. Let us consider some examples.

Example 1: Ideal gas

From the thermal equation of state $pV = nRT$ one deduces that at constant pressure the volume linearly increases with temperature and that

$$\beta \;=\; \frac{1}{T} \,. \tag{9.23}$$

When the temperature increases, the coefficient of thermal expansion of the ideal gas rapidly decreases; the molar volume increases proportional to the temperature: $v = RT/p$.

Example 2: Crystalline solid: NaCl

In crystalline solids the temperature dependence of the coefficient of thermal expansion is similar to that of the specific heat: $\beta \to 0$ when $T \to 0$, while at high temperatures β approaches a constant value. The case of NaCl is shown in Fig. 9.5 (left).

While the specific heat can be calculated with very good approximation by treating the atomic vibrations within the harmonic approximation, the thermal expansion depends on the anharmonicity of the vibrational potential energy; a perfectly harmonic crystal would not be affected by thermal expansion.

The relation between specific heat and coefficient of thermal expansion will be considered in more detail in § 9.4.

Example 3: Liquid water

The coefficient of thermal expansion of water is negative for temperatures lower than 4 ° K (Fig. 9.5, right).

Example 4: Negative thermal expansion in crystals

Not always is the thermal expansion positive. For example, some crystals with anisotropic

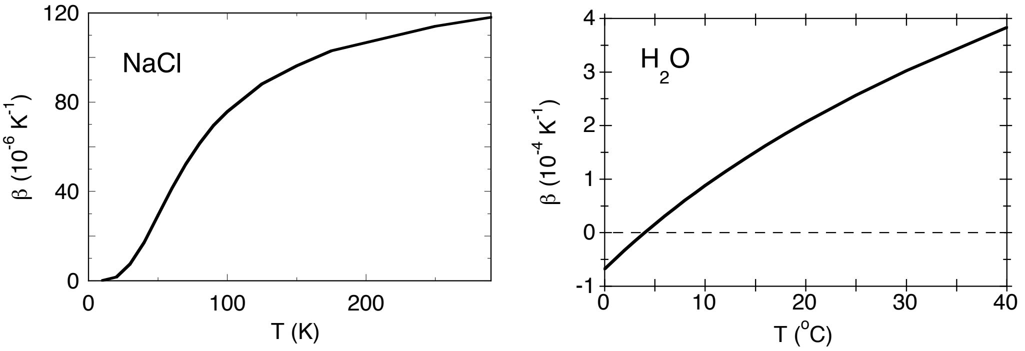


Figure 9.5: Coefficient of volume thermal expansion of NaCl (left) and of water (right).

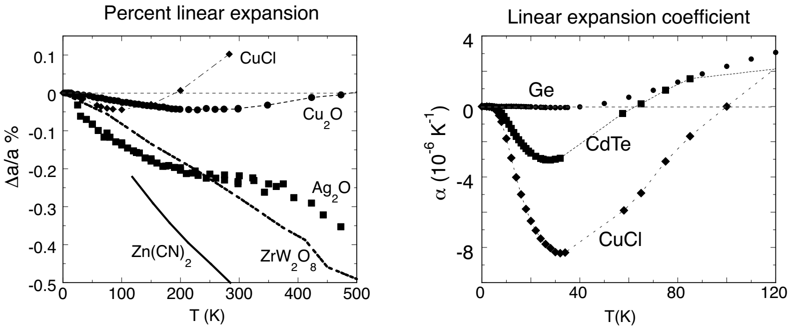


Figure 9.6: Examples of isotropic negative thermal expansion in crystals. Left: percent linear expaansion of some crystals with different crystal structures with cubic symmetry. Right: linear expansion coefficient α of three crystals with the same crystalline structure of zincblende; The volume coefficient is $\beta = 3\alpha$.

structure exhibit negative expansion in one direction, at least in a given temperature interval, and positive expansion in the remaining two directions.

A little number of cubic crystal exhibit isotropic negative expansion. In some crystals the negative expansion is relatively weak and confined in a limited temperature interval: it is the case of silicon, germanium and some crystals with the zincblende structure; some examples are shown in Fig 9.6 (right).

In some crystals the negative expansion can be strong and present in large temperature intervals; some examples are shown in Fig. 9.6 (left). Particularly interesting is zirconium tungstate, whose thermal expansion was found in 1996 to be negative from 2 to 1050 K.

9.3.3 Thermal expansion and entropy

An altenative expression of the thermal expansion coefficient can be found taking into account the Maxwell relations introduced in § 7.3. From (7.45) one gets

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T \tag{9.24}$$

The thermal expansion, say the dependence of volume on temperature at constant pressure is connected to the dependence of entropy on pressure at constant temperature. The last member of (9.24) can be further expanded as

$$\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T$$

so that, introducing the isothermal compressibility (9.14), the thermal expansion coefficient becomes:

$$\beta \;=\; \chi_T \left(\frac{\partial S}{\partial V}\right)_T . \tag{9.25}$$

Since the compressibility χ_T cannot be negative (as we will see in § 9.6), according to (9.25)

- the expansion is positive if the entropy S increases when the volume increases,
- the expansion is negative if the entropy S decreases when the volume V increases.

Example 1: Let us consider the *ideal gas* case.

A positive *variation of temperature* $\Delta T > 0$ at constant pressure p gives rise to a positive volume variation $\Delta V > 0$. According to (9.24), the coefficient of thermal expansion is thus positive. The process entails input of heat $Q > 0$, variation of internal energy $\Delta U > 0$ and production of work $W < 0$. The entropy variation is $\Delta S = nc_p \ln(V_f/V_i)$.

Let us now consider equation (9.25). A positive *isothermal* variation of volume, $\Delta V > 0$ (T constant), gives rise to a positive variation of entropy, $\Delta S > 0$. The process entails input of heat $Q > 0$ and production of work $W < 0$ but no variations of internal energy, $\Delta U = 0$. The entropy variation is $\Delta S = nR \ln(V_f/V_i)$.

Example 2: The coefficient of thermalexpansion of *liquid water* is negative in the temperature interval betwe en0° and 4° C. The negative expansion can be connected, through equation (9.25), to the breaking of tetrahedral hydrogen bonds as a consequence of compression and to the consequent increase of entropy.

9.4 Relations among the response functions

The different response functions are not independent. The theory depicted in previous chapters allows one to establish some relations among the response functions. Here we consider three particularly important relations:

- the difference between the heat capacities at constant pressure and volume,
- the ratio between heat capacities at constant pressure and volume,
- the relation among thermal expansion, heat capacities and compressibilities.

9.4.1 Difference of heat capacities

Heat capacities at constant volume and at constant pressure are different. One can demonstrate (see below) that the difference can be expressed as a function of the coefficient of thermal expansion and the isothermal compressibility as follows:

$$\boxed{C_p - C_v \;=\; \frac{TV\beta^2}{\chi_T}}\,, \qquad\qquad \boxed{c_p - c_v \;=\; \frac{Tv\beta^2}{\chi_T}}\,, \tag{9.26}$$

where V is the volume, $v = V/n$ is the molar volume.
From (9.26) one can draw the following general conclusions:

- The constant-pressure heat capacity is never smaller than the constant-volume heat capacity, $C_p \geq C_v$ (because $\chi_T > 0$ always).
- When $T \to 0$, the difference $C_p - C_v \to 0$ (because $\beta \to 0$ and $\chi_T > 0$).
- If $\beta = 0$, then $C_p = C_v$.

Example 1: For the ideal gas, where $\beta = 1/T, \chi_T = 1/p$,

$$C_p - C_v = \frac{TV\beta^2}{\chi_T} = \frac{pV}{T} = nR\,, \qquad c_p - c_v = nR\,. \tag{9.27}$$

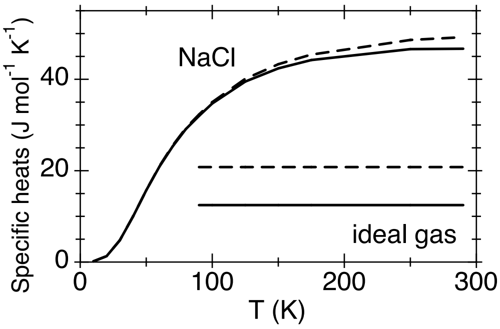


Figure 9.7: Specific heats at constant volume (continuous lines) and at constant pressure (dashed lines) for an ideal gas and for NaCl.

The difference between the two heat capacities is independent of temperature (Fig. 9.7).

Example 2: In crystalline solids the difference $C_p - C_v$ increases with temperature and is generally negligible at low temperatures ed è generalmente trascurabile a basse temperature. The specific heats of NaCl are compared with the specific heats of an ideal gas in Fig. 9.7.

Demonstration of (9.26)

Let us consider the amount of heat reversibly exchanged by a pure substance, $đQ_{\text{rev}} = T\,dS$, and express the entropy as a function of two different state variables,

$$S(T,p,n)\,, \qquad S(T,V,n)\,, \tag{9.28}$$

where n is mainatined constant ($dn = 0$). It is worth noting that (9.28) are not fundamental equations, because they don't contain the complete information on the thermodynamic systems which would be instead contained in the function $S(U,V,n)$. Equations (9.28) are anyway suitable for the sought demonstration.

By differentiating (9.28) one gets the two expressions

$$T\,dS \;=\; T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp \qquad = \; C_p\,dT + T\left(\frac{\partial S}{\partial p}\right)_T dp\,, \tag{9.29}$$

$$T\,dS \;=\; T\left(\frac{\partial S}{\partial T}\right)_v dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \qquad = \; C_v\,dT + T\left(\frac{\partial S}{\partial V}\right)_T dV\,. \tag{9.30}$$

Let us now subtract (9.30) from (9.29)

$$0 \;=\; (C_p - C_v)\,dT \;+\; T\left(\frac{\partial S}{\partial p}\right)_T dp \;-\; T\left(\frac{\partial S}{\partial V}\right)_T dV\,. \tag{9.31}$$

The two partial derivatives appearing in (9.31) vannot be easily measured. It is thus convenient to substitute them by means of the Maxwell relations (7.45) and (7.44) of § 7.3:

$$(C_p - C_v)\,dT \;=\; T\left(\frac{\partial V}{\partial T}\right)_p dp \;+\; T\left(\frac{\partial p}{\partial T}\right)_v dV\,. \tag{9.32}$$

Equating the differential dT from (9.32) to the differential of the function $T(p,V)$ one gets:

$$dT = \frac{T}{C_p - C_v}\left(\frac{\partial V}{\partial T}\right)_p dp + \frac{T}{C_p - C_v}\left(\frac{\partial p}{\partial T}\right)_v dV = \left(\frac{\partial T}{\partial p}\right)_v dp + \left(\frac{\partial T}{\partial V}\right)_p dV\,. \tag{9.33}$$

Since p and V are independent variables, the coefficients of dp as well as the coefficients of dV in the second and in the third members of (9.33) must be equal.

Let us focus the attention on the coefficients of dV; by equating them and exploiting the identities (7.49) and (7.51) one gets

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_p = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T \tag{9.34}$$

whence (9.26).

9.4.2 Ratio between heat capacities

One can demonstrate (see below) that the ratio between the heat capacities is equal to the ratio between the compressibilities:

$$\boxed{\frac{C_p}{C_v} \;=\; \frac{\chi_T}{\chi_S}}\,. \tag{9.35}$$

From (9.35) one can draw the followint general conclusions:

- Since $C_p \geq C_v$, also $\chi_T \geq \chi_S$.
- When $C_p = C_v$, then $\chi_T = \chi_S$.

Example: For the ideal gas, where, $\chi_T = 1/p, \chi_S = 1/\gamma p$,

$$\frac{C_p}{C_v} = \frac{\chi_T}{\chi_S} = \gamma\,. \tag{9.36}$$

Demonstration of (9.35)

Let us start again from the expressions $T\,dS$ of (9.29) and (9.30) and take again advantage of the Maxwell relations (7.45) and (7.44) of § 7.3:

$$T\,dS \;=\; C_p\,dT + T\left(\frac{\partial S}{\partial p}\right)_T dp \;=\; C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_p dp\,, \tag{9.37}$$

$$T\,dS \;=\; C_v\,dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \;=\; C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dV\,. \tag{9.38}$$

Let us now consider a process at constant entropy. By imposing $dS = 0$ in (9.37) and (9.38) one obtains

$$C_p\,(dT)_s = T\left(\frac{\partial V}{\partial T}\right)_p (dp)_s\,, \qquad\qquad C_v\,(dT)_s = -T\left(\frac{\partial p}{\partial T}\right)_v (dV)_s \tag{9.39}$$

whence the ratio

$$\frac{C_p}{C_v} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_S\,, \tag{9.40}$$

and (9.35). In the last equation the identity (7.51) has been used.

9.4.3 Thermal expansion and Grüneisen function

The dependence on temperature of the thermal expansion coefficient of solids is similar to that of the heat capacities. To focus the attention on the peculiar behaviour of different substances it is convenient to decompose the thermal expansion coefficient β as the product of a number of factors, according to the following procedure.

By exploiting the identity (7.51) one can evidence the contribution of the isothermal compressibility:

$$\beta \;=\; \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \;=\; -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \;=\; \chi_T\left(\frac{\partial p}{\partial T}\right)_V \tag{9.41}$$

The derivative of pressure with respect to temperature can be further expanded

$$\left(\frac{\partial p}{\partial T}\right)_V \;=\; \left(\frac{\partial p}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V \tag{9.42}$$

to evidence the contribution of the constant-volume heat capacity too:

$$\beta \;=\; \chi_T\,\frac{C_v}{V}\left[\frac{\partial p}{\partial (U/V)}\right]_V\,. \tag{9.43}$$

In (9.43) the derivative of pressure with respect to the internal enrgy U has been substituted by the derivative with respect to the density of internal energy U/V.
The third factor on the right in (9.43)

$$\gamma = \left[\frac{\partial p}{\partial(U/V)} \right]_V \tag{9.44}$$

is called Grüneisen function. The thermal expansion coefficient can be finally expressed as

$$\boxed{\beta = \gamma \chi_T \frac{C_v}{V} = \gamma \chi_T \frac{c_v}{v}} \tag{9.45}$$

where the ratio between the molar specific heat c_v and the molar volume v has been introduced in the last equality.
According to (9.45), the thermal expansion can be decomposed in three logical (not temporal !) steps:

1. An increase of temperature corresponds to an increase of internal energy, measured by the constant-volume specific heat c_v (never negative).
2. The increase of internal energy gives rise to a variation of pressure, that can be positive or negative, and is measured by the Grüneisen function (9.44). If $\gamma > 0$, an increase of internal energy gives rise to an increase of the internal pressure with respect to the equilibrium pressure (say tothe constant external pressure); if $\gamma < 0$, an increase of internal energy gives rise to a decrease of internal pressure.
3. Since the system has to remain in equilibrium with its ambient at constant (external) pressure, the possible upward trend of the internal pressure due to heating ($\gamma > 0$) has to be compensated by a reduction of the pressure obtained through an increase of the volume (χ_T is never negative); viceversa, a possible downward trend of the internal pressure due to heating ($\gamma < 0$) has to be compensated by an increase of the pressure obtained through a reduction of the volume.

The dependence of the Grüneisen function on temperature is peculiar for each substance. Inparticular, since both χ_T and C_v are non negative, the possible negative sign of the thermal expansion coefficient β corresponds to the negative sign of the Grüneisen function.

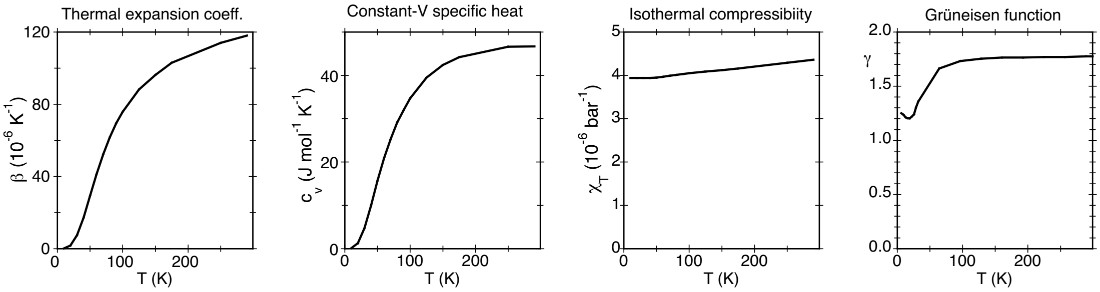


Figure 9.8: Thermal expansion of NaCl. From left to right: coefficient of volume thermal expansion β, constant-volume molar specific heat c_v, isothermal compressibility χ_T and Grüneisen function γ. The four functions are connected by (9.45); the variations of the molar volume v are very small, from 0.0264 L/mol at 10 K to 0.027 L/mol at 290 K.

Note: Don't mistake the symbol γ of the Grüneisen function for the ratio $\gamma = C_p/C_v$ dbetween the heat capacities of ideal gases.

Example 1: For the monatomic ideal gas, starting from the state equations $pV = nRT$ and $U = 3nRT/2$, one finds that the Grüneisen function is constant, $\gamma = 2/3$. One can easily

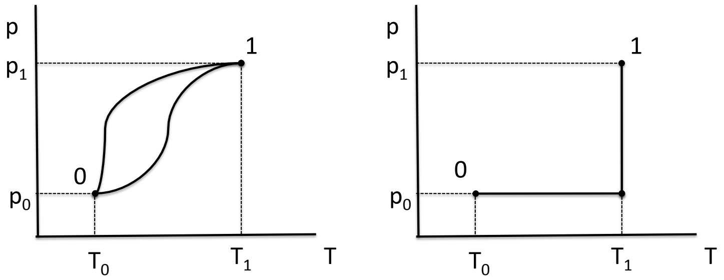


Figure 9.9: Evaluation of the variation of the Gibbs function between a reference state 0 and a generic state 1. Left: lthe variation of the state function G is independent of the transformation path (provided it is reversible). Right: a possible convenient integration path.

verify (9.45) by inserting the known values of β, χ_T and C_v.

Example 2: An example of the different functions appearing in (9.45) is given for the NaCl crystal in Fig. 9.8. The Grüneisen function of NaCl is always positive, its values are of the order of unity with evident variations in the low temperature region.

9.5 Response functions and Gibbs function

It has been previously stated that the knowledge of one of the thermodynamical potentials U, H, F, G as a function of its independent coordinates corresponds to the knowledge of all the thermodynamical properties of a system. Once the response functions have been introduced, one can show how the expression of a thermodynamical potential can be obtained from experiment.

To this aim, let us focus our attention on a closed system with one component, so that $dn = 0$. The independent variables more easily controlled in an experiment are the pressure p and the temperature T: we will then consider the Gibbs function $G(T, p, n)$. The state of the system can be represented as a point in the (T, p) plane (Fig. 9.9). To each point of the (T, p) plane it corresponds a value of the Gibbs function G (to within an arbitrary additive constant, equal for all points). Since G is a state function, its variation ΔG between any two points of the (T, p) plane doesn't depend on the specific transformation connecting the two points.

Our problem is the following: once an arbitrary reference value G_0 in a point (T_0, p_0) has been chosen, how can the values of G in any other point (T, p) be evaluated ?
The problem can be solved by the experimental measurement of some response functions.
The response functions which depend on the independent variables p and T, that is C_p, β and χ_T, are quite easily measurable. The three above response functions are connected to the second derivatives of the Gibbs function:

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p, \qquad \beta = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T\,\partial p}\right), \qquad \chi_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_T. \tag{9.46}$$

Since we are considering a system with only one component, it is convenient to refer to the molar quantities $c_p = C_p/n, g = G/n, v = V/n$, and re-write (9.46) as:

$$c_p = -T\left(\frac{\partial^2 g}{\partial T^2}\right)_p, \qquad \beta = \frac{1}{v}\left(\frac{\partial^2 g}{\partial T\,\partial p}\right), \qquad \chi_T = -\frac{1}{v}\left(\frac{\partial^2 g}{\partial p^2}\right)_T. \tag{9.47}$$

Once a value has been arbitrarily attributed to the Gibbs function for a given reference state "0", $g_0 = g(T_0, p_0)$, the molar Gibbs function can be calculted for any other state "1" by means of an integral along any reversible path (Fig. 9.9, left):

$$g(T_1, p_1) \;=\; g\,(T_0, p_0) + \int_0^1 dg\,. \tag{9.48}$$

It is convenient to choose an easy integration path; for example (Fig. 9.9, right) one can consider the sequence of

- an isobaric transformation at the pressure p_0 from (T_0, p_0) to (T_1, p_0);
- an isothermal transformation at the temperature T_1 from (T_1, p_0) to (T_1, p_1).

By inserting the differential of the molar Gibbs function, $dg = -s\,dT + v\,dp$ into (9.48), one gets

$$g(T_1,p_1) \;=\; g\,(T_0,p_0) - \int_{T_0}^{T_1} s(T,p_0)\,dT + \int_{p_0}^{p_1} v(T_1,p)\,dp\,. \tag{9.49}$$

The first integral of (9.49), at constant pressure p_0, requires the knowledge of the molar entropy s, that in turn can be calculated from the knowledge of the constant-pressure molar specific heat:

$$s(T,p_0) \;=\; s\,(T_0,p_0) + \int_{T_0}^{T} \frac{c_p(T')}{T'}\,dT'\,. \tag{9.50}$$

The value $s_0 = s(T_0,p_0)$ in (9.50) can be arbitrarily chosen; in some cases it could be evaluated on the grounds of the Third Principle ($S \to 0$ for $T \to 0$, see Chapter 20).
The second integral of (9.49), at constant temperature T_1 costante, requires the knowledge of the molar volume v, that in turn can be calculated from the knowledge of the isothermal compressibility:

$$v(T_1,p) \;=\; v\,(T_1,p_0) - \int_{p_0}^{p} v\,\chi_T(T_1,p')\,dp'\,. \tag{9.51}$$

The value $v_0 = v(T_1,p_0)$ in (9.51) can be measured.

In conclusion, the molar Gibbs function g can be evaluated from the knowledge of the specific heat c_p and of the dependence of volume on pressure, to within the additive constants $g_0 = g(T_0,p_0)$ and $s_0 = s(T_0,p_0)$.

The molar Gibbs function corresponds to the chemical potential, $g = \mu$. Later on, in § 11.2, we will see how the chemical potential of the ideal gases can be calculated.

9.6 Stability of thermodynamicl equilibrium

In § 6.2 it was shown that the condition of thermodynamical equilibrium for an isolated system is that the entropy S be maximum with respect to all the possible virtual processes initiating from the initial equilibrium state: $\Delta S < 0$.
The thermodynamical description has then been extended to non-isolated systems, by introducing the energy representation (§ 6.3) and the thermodynamical potentials in the energy representation (Cap. 8). For each different choice of the independent thermodynamical coordinates the condition of equilibrium corresponds to a minimum condition of the corresponding thermodynamical potential.
Now it is time to analyse the stability of the thermodynamical equilibrium; we will see that the stability condition for isolated systems entails the presence ofsome constraints on the response functions.

9.6.1 General considerations

In Mechanics, the equilibrium can be stable, metastable, unstable or indifferent. The condition of stability depends on the shape of the potential energy surface as a function of the generalised coordinates. A mechanical system can be in a state of unstable equilibrium, if external forces are completely absent.

In Thermodynamics equilibrium is necessarily *stable*. A thermodynamical system is made by an extremely large number of elementary constituents, and it is thus impossible to avoid microscopic fluctuations with respect to the state of equilibrium.

For example, in an isolated system, the fluctuations give rise to transfers of extensive quantities U, V, n_i among the different parts of the system, and are described, at the macroscopic level, as virtual processes. Were an equilibrium state unstable, fluctuations could be possible leading to an increase of entropy, $\Delta S > 0$; the system could then spontaneously settle into the new state with larger entropy.
The ability of a thermodynamical system in equilibrium to recover from the unavoidable fluctuation is a consequence of the Axiom II of § 5.3; it is sometimes referred to as "Le Chatelier' principle".

It is anyway important to stress that states of *metastable equilibrium* can be obtained and maintained for relatively long times in particular conditions. Metastable states of an isolated system are characterised by a relative maximum of the entropy S that don't correspond to the absolute maximum; a typical example is the diamond phase of carbon. *Non-equilibrium* states can also sometimes be obtained and maintained; an important example are the solids in the vitreous state. Such metastable and non-equilibrium states are present when the energy barrier to be overcome in order to reach the stable equilibrium state is higher with respect to the extent of the possible fluctuations (see Capter 22). The extent of the fluctuations depends in turn on kinetic factors at the microscopic level.

9.6.2 Stability conditions

Let us consider a closed system with one component. The independent thermodynamical coordinates are U, V, n. The thermodynamic function is the entropy $S(U, V, n)$.
The condition of stability of the thermodynamical equilibrium entails the following constraints (9.52), (9.53), (9.54) on the response functions, whose demonstration will be given in § 9.6.3.

Thermal stability

The stability of thermodynamical equilibrium requires that the constant-volume specific heat be positive:

$$\boxed{c_v \; > \; 0} \tag{9.52}$$

According to equation (9.26) of § 9.4, the constant-pressure specific heat cannot be smaller than the constant-volume specific heat, so that $c_p > 0$ too.

Let us try to better grasp the physical relation of (9.52) with the stability of equilibrium. In a state of equilibrium, the temperature is homogeneous in the entire system. Let us consider a virtual process by which an amount of heat is transferred from sub-system 1 to sub-system 2. According to (9.52), the sub-system 2 increases its temperature and sub-system 1 reduces its temperature. The fluctuation creates an unbalance of temperature, that in turn gives rise to a heat flux from sub-system 2 to sub-system 1 and brings back the system to equilibrium. The energy fluctuations are thus spontaneously re-absorbed by the system.

Note: In crystals, when $T \to 0$ also the specific heat $c_v \to 0$. Actually, the temperature $T = 0$ is unattainable (Third Law of Thermodynamics, Chapter 20), so that the inequality $c_v > 0$ is always valid. Notice that, when c_v decreases, the temperature gradients created by a given energy fluctuation increase.

Mechanical stability

The stability of the thermodynamical equilibrium requires that the isothermal compressibility be positive:

$$\boxed{\chi_T \; > \; 0} \tag{9.53}$$

According to (9.35) of § 9.4, the ratio between adiabatic and isothermal compressibilities is always positive, so that $\chi_S > 0$ too.

Let us try to better grasp the physical relation of (9.53) with the stability of equilibrium. Fro concreteness, let us consider a gas enclosed in a cylinder divided in two equal sub-systems by a sliding piston. In the state of equilibrium, the pressure is homogeneous in the entire system. Let us consider a virtual process by which the piston moves, reducing the volume of sub-system 1 and correspondingly increasing the volume of sub-system 2. According to (9.53) and to the definition (9.14) of compressibility, the sub-system 2 decreases its pressure and the sub-system 1 increases its pressure. The fluctuation creates an unbalance of pressure, that in turn gives rise to a transfer of volumes from sub-system 2 to sub-system 1 and brings back the system to equilibrium. The volume fluctuations are thus spontaneously re-absorbed by the system.

Chemical stability

At last, the stability of thermodynamical equilibrium requires that

$$\boxed{\left(\frac{\partial \mu}{\partial n}\right)_{pT} > 0} \tag{9.54}$$

Let us try to better grasp the physical relation of (9.54) with the stability of equilibrium. For concreteness, let us consider a gas enclosed in a rigid cylinder. In the equilibrium state, the chemical potential μ is homogeneous in the entire system. Let us consider a virtual process by which matter is transferred from one half of the system (syb-system 1) to the other half (sub-system 2). The sub-system 2 increases its density and, according to (9.54), increases its chemical potential too; viceversa, sub-system 1 decreases its density and its chemical potential. The fluctuation crates an unbalance of chemical potential, that in turn gives rise to a flux of matter from sub-system 2 to sub-system 1. The dentity fluctuations are thus spontaneously re-absorbed by the system.

9.6.3 Demonstration of (9.52), (9.53) and (9.54)

Let here short hint at the demonstration of the three inequalities (9.52)-(9.54), without entering into mathematical details.

Let us again consider a closed and isolated system with one component, described by the extensive variables U, V, n, that will be generically denoted by the symbol X_i. In order to study the effects of a fluctuation with respect to the equilibrium state, let us divide the system in two equal sub-systems, labeled by the index $\alpha = 1, 2$.

Let us consider a virtual process consisting in the exchange of energy U, volume V and matter n between the two subsystems.

The differential entropy variation of each sub-system is given by the well-known relation

$$\begin{aligned} dS^{(\alpha)} &= \left(\frac{\partial S^{(\alpha)}}{\partial U^{(\alpha)}}\right)_{V,n} dU^{(\alpha)} + \left(\frac{\partial S^{(\alpha)}}{\partial V^{(\alpha)}}\right)_{U,n} dV^{(\alpha)} + \left(\frac{\partial S^{(\alpha)}}{\partial n^{(\alpha)}}\right)_{V,U} dn^{(\alpha)} \\ &= \sum_i \left(\frac{\partial S^{(\alpha)}}{\partial X_i^{(\alpha)}}\right) dX_i^{(\alpha)} \ . \end{aligned} \tag{9.55}$$

Let us now consider the entropy variation of each sub-system for a finite fluctuation. Such a variation can be expanded in power series with respect to the variations of the extensive variables ΔX_i. Let us consider only the first two terms of the expansion. For each one of the two sub-systems $(\alpha = 1, 2)$ it is

$$\begin{aligned} \Delta S^{(\alpha)} &= S^{(\alpha)} - S_0^{(\alpha)} \\ &= \sum_i \left(\frac{\partial S^{(\alpha)}}{\partial X_i^{(\alpha)}}\right)_0 \Delta X_i^{(\alpha)} + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 S^{(\alpha)}}{\partial X_i^{(\alpha)} \partial X_j^{(\alpha)}}\right)_0 \Delta X_i^{(\alpha)} \Delta X_j^{(\alpha)} , \end{aligned} \tag{9.56}$$

where the index 0 labels the equilibrium condition.

The total variation of the entropy of the system, according to the stability condition, has to obey the equation

$$\Delta S_{\text{tot}} = \Delta S^{(1)} + \Delta S^{(2)} < 0 . \tag{9.57}$$

The contribution to ΔS of the simple sums in (9.56) is null,

$$\sum_i \left(\frac{\partial S^{(1)}}{\partial X_i^{(1)}}\right)_0 \Delta X_i^{(1)} \;+\; \sum_i \left(\frac{\partial S^{(2)}}{\partial X_i^{(2)}}\right)_0 \Delta X_i^{(2)} \;=0\,, \tag{9.58}$$

because $\Delta X_i^{(2)} = -\Delta X_i^{(1)}$ and the partial derivatives in (9.58), corresponding to the intensive variables, are equal in equilibrium conditions.

The entropy variation of the entire system due to the finite fluctuation is then determined by the double sums in (9.56):

$$\Delta S_{\text{tot}} \;=\; \frac{1}{2}\sum_{\alpha=1,2}\sum_{ij}\left(\frac{\partial^2 S^{(\alpha)}}{\partial X_i^{(\alpha)}\partial X_j^{(\alpha)}}\right)_0 \Delta X_i^{(\alpha)}\Delta X_j^{(\alpha)} \;\le\; 0\,. \tag{9.59}$$

Equation (9.59) is a null or negative quadratic form. To obtain the stability conditions some algebraic steps have to be made. The un-interested reader can skip the demonstration and directly go the the final expression (9.69).

Let us rewrite (9.59) in an extended form, where the different variables are now distinguished:

$$\begin{aligned}\Delta S_{\text{tot}} = \frac{1}{2}\sum_{\alpha=1,2} \Delta U_\alpha &\left[\frac{\partial}{\partial U_\alpha}\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)\Delta U_\alpha + \frac{\partial}{\partial V_\alpha}\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)\Delta V_\alpha + \frac{\partial}{\partial n_\alpha}\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)\Delta n_\alpha\right] \\ +\Delta V_\alpha &\left[\frac{\partial}{\partial U_\alpha}\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)\Delta U_\alpha + \frac{\partial}{\partial V_\alpha}\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)\Delta V_\alpha + \frac{\partial}{\partial n_\alpha}\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)\Delta n_\alpha\right] \\ +\Delta n_\alpha &\left[\frac{\partial}{\partial U_\alpha}\left(\frac{\partial S_\alpha}{\partial n_\alpha}\right)\Delta U_\alpha + \frac{\partial}{\partial V_\alpha}\left(\frac{\partial S_\alpha}{\partial n_\alpha}\right)\Delta V_\alpha + \frac{\partial}{\partial n_\alpha}\left(\frac{\partial S_\alpha}{\partial n_\alpha}\right)\Delta n_\alpha\right]\end{aligned} \tag{9.60}$$

By substituting

$$\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right) = \frac{1}{T_\alpha}\,, \qquad \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right) = \frac{p_\alpha}{T_\alpha}\,, \qquad \left(\frac{\partial S_\alpha}{\partial n_\alpha}\right) = -\frac{\mu_\alpha}{T_\alpha}\,, \tag{9.61}$$

equation(9.60) can be re-written as

$$\Delta S_{\text{tot}} = \frac{1}{2}\sum_{\alpha=1,2}\left\{\Delta U_\alpha \Delta\left(\frac{1}{T_\alpha}\right) \;+\; \Delta V_\alpha \Delta\left(\frac{p_\alpha}{T_\alpha}\right) \;-\; \Delta n_\alpha \Delta\left(\frac{\mu_\alpha}{T_\alpha}\right)\right\}\,. \tag{9.62}$$

By expanding

$$\Delta\left(\frac{1}{T_\alpha}\right) = -\frac{1}{T_\alpha^2}\,\Delta T_\alpha \tag{9.63}$$

$$\Delta\left(\frac{p_\alpha}{T_\alpha}\right) = \frac{1}{T_\alpha}\,\Delta p_\alpha - \frac{p_\alpha}{T_\alpha^2}\,\Delta T_\alpha \tag{9.64}$$

$$\Delta\left(\frac{\mu_\alpha}{T_\alpha}\right) = \frac{1}{T_\alpha}\,\Delta \mu_\alpha - \frac{\mu_\alpha}{T_\alpha^2}\,\Delta T_\alpha \tag{9.65}$$

substituting

$$\Delta U_\alpha \;=\; T_\alpha\,\Delta S_\alpha - p_\alpha\,\Delta V_\alpha + \mu_\alpha\,\Delta n_\alpha \tag{9.66}$$

and reducing the similar terms one obtains a simpler form of (9.62):

$$\Delta S_{\text{tot}} = \frac{1}{2T}\sum_{\alpha=1,2}\left[-\,\Delta T_\alpha\,\Delta S_\alpha + \Delta p_\alpha\,\Delta V_\alpha - \Delta \mu_\alpha\,\Delta n_\alpha\right]\,. \tag{9.67}$$

Let us now assume $T_\alpha, V_\alpha, n_\alpha$ as independent variables and express the variation of each one of the three dependent variables $\Delta S_\alpha, \Delta p_\alpha, \Delta\mu_\alpha$ as a first-order expansion of the three independent variables.

Taking into account the definitions of the response functions and taking advantage of the Maxwell relations, one gets the new quadratic form

$$\begin{aligned}\Delta S_{\text{tot}} = \frac{1}{2}\sum_{\alpha=1,2} & \Delta T_\alpha \left[-\frac{C_v}{T}\,\Delta T_\alpha - \frac{\beta}{\chi_T}\,\Delta V_\alpha + \frac{\mu_\alpha}{T_\alpha}\,\Delta n_\alpha\right] \\ & +\Delta V_\alpha \left[+\frac{\beta}{\chi_T}\,\Delta T_\alpha - \frac{1}{V_\alpha \chi_T}\,\Delta V_\alpha + \left(\frac{\partial p_\alpha}{\partial n_\alpha}\right)\Delta n_\alpha\right] \\ & +\Delta n_\alpha \left[-\frac{\mu_\alpha}{T_\alpha}\,\Delta T_\alpha - \left(\frac{\partial \mu_\alpha}{\partial V_\alpha}\right)\Delta V_\alpha - \frac{\partial \mu}{\partial n_\alpha}\Delta n_\alpha\right]\end{aligned} \tag{9.68}$$

The non-diagonal terms can be reduced.
It remains a diagonal form with respect to the three variables T, V, n:

$$\boxed{\Delta S_{\text{tot}} \;=\; -\,\frac{1}{2T}\sum_{\alpha=1,2}\left\{\frac{C_v}{T}\left[\Delta T^{(\alpha)}\right]^2 + \frac{1}{V\chi_T}\left[\Delta V^{(\alpha)}\right]^2 + \frac{\partial \mu}{\partial n}\left[\Delta n^{(\alpha)}\right]^2\right\} \;<\; 0} \tag{9.69}$$

Since the fluctuations $\Delta T^{(\alpha)}, \Delta V^{(\alpha)}, \Delta n^{(\alpha)}$ are independent, the inequality (9.69) entails the three conditions (9.52), (9.53) and (9.54).

Chapter 10

Thermodynamical proceses

The formalism introduced in the previous chapters allows us to analyse in this chapter some thermodynamical processes relatively simple but of great practical importance. We will limit our attention to simple closed systems with only one component.
The first two cases concern the reversible isothermal and adiabatic compressions of any system (§ 10.1 and § 10.2, respectively), that is the two types of transform which compose the Carnot cycle t (§ 10.3).
We will then focus our attention on gases and consider the effects of a free expansion (§ 10.4) and of a Joule-Thomson expansion (§ 10.5).

10.1 Reversible isothermal compression

Let us consider a closed system with one component, maintained at constant temperature and submit the system to a reversible compression by increasing the external pressure p (which corresponds to the system pressure for a reversible transformation). We want to analyse the energy balance and in particular to understand whether the system absorbs or gives heat during the compression. The energy balance is given by

$$dU \ = \ đQ + đW \ = \ T\,dS - p\,dV\,. \tag{10.1}$$

Since we are studying the effect of pressure on a system maintained at constant temperature, it is convenient to choose the pressure p and the temperature T as independent coordinates, so that entropy S and volume V are functions of p and T.
By differentiating the functions $S(T,p)$ and $V(T,p)$, taking into account that $dT=0$ and using th Maxwell relation (7.45), equation (10.1) can re-written as:

$$dU \ = \ T\left(\frac{\partial S}{\partial p}\right)_T dp - p\left(\frac{\partial V}{\partial p}\right)_T dp = \ -T\left(\frac{\partial V}{\partial T}\right)_p dp - p\left(\frac{\partial V}{\partial p}\right)_T dp\,. \tag{10.2}$$

Note: Let us stress the physical meaning of the Maxwell relation (7.45):

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T\,. \tag{10.3}$$

> The sign of the thermal expansion is connected to the ratio between the entropy variation and the pressure variation at constant temperature. The thermal expansion of a system is positive if its entropy decreases when the system is compressed and viceversa.

Let us now introduce in (10.2) the response functions χ_T (isothermal compressibility) and β (coefficient of thermal expansion), defined in § 9.2 and 9.3, respectively:

$$dU \ = \ -TV\beta\,dp \ + \ pV\chi_T\,dp\,. \tag{10.4}$$

From (10.4) one can easily evidence the effects of an increase of pressure ($dp > 0$) on the energy balance of any system.

1. The *work* done on the system is always positive, because $\chi_T > 0$:
$$\text{đ}W = pV\chi_T\, dp > 0\,. \tag{10.5}$$
2. The sign of the *absorbed heat*
$$\text{đ}Q = -TV\beta\, dp \tag{10.6}$$
, depends on the sign of the coefficient of thermal expansion β:
   - if $\beta > 0$, the system emits heat when compressed; actually, according to (10.3) the entropy decreases when the pressure increases;
   - if $\beta < 0$, the system absorbs heat when compressed; actually, according to (10.3) lthe entropy increases when the pressure increases.

   .
3. The variation of *internal energy*
$$dU = (-T\beta + p\chi_T)\, V\, dp \tag{10.7}$$
can be positive or negative:
   - if $\beta < 0$, $dU > 0$ always;
   - if $\beta > 0$, the sign of dU is not a priori determined.

Example 1: Ideal gas

By substituting in (10.4) the values $\beta = 1/T$ and $\chi_T = 1/p$ given by (9.23) and (9.18), respectively, one obtains $dU = 0$. The work done on the system is thus equal the emitted amount of heat, and viceversa.
According to (10.5), in a reversible isothermal transformation of the ideal gas $\text{đ}W = V\,dp$. One can easily verify, on the grounds of the relation $pV =$ costante, that $\text{đ}W = -p\,dV = V\,dp$.

Esemple 2: liquid water

At atmospheric pressure, the thermal expansion of water is negative ($\beta < 0$) in the temperature interval from 0°C to 4°C, is positive ($\beta > 0$) above 4°C. For T=4°C the expansion is null ($\beta = 0$). Let us consider the behaviour at the three temperatures 0, 4 and 10°C. In a positive compression, $dp > 0$, the second term of (10.4), giving the work done on the system, is positive for all the three temperatures.

- For $T = 0$°C, since $\beta < 0$, the compression is accompanied by absorption of heat, so that $dU > 0$.
- For $T = 4$°C, since $\beta = 0$, there is no heat exchange, so that $dU = \text{đ}W > 0$.

Table 10.1: Coefficients of thermal expansion and isothermal compressibilities of liquid water and of the NaCl crystal for some selected temperatures. In the last column, the values of $-\beta T + \chi_T p$ at atmospheric pressure ($p = 1$ bar), to be inserted in (10.7), are listed.

	T	β ($10^{-6}\,\text{K}^{-1}$)	χ_T ($10^{-6}\,\text{bar}^{-1}$)	$-\beta T + \chi_T p$
H_2O liquid	0°C	−67.	51.5	$+1.8 \times 10^{-2}$
	10°C	+89.	48.8	-2.5×10^{-2}
NaCl	10 K	0.17	3.94	$+2.2 \times 10^{-6}$
	100 K	75.8	4.05	-7.5×10^{-3}

- For $T = 10°\mathrm{C}$, since $\beta > 0$, the compression is accompanied by heat emission; to evaluate the sign of dU it is necessary to calculate the factor $(-T\,\beta + p\,\chi_T)$ in (10.7); from the values of β and χ_T for water at $T = 10°\mathrm{C}$ (Table 10.1) one can easily see that the internal energy decreases, $dU < 0$.

Example 3: NaCl crystal

The coefficient of thermal expansion β of NaCl is always positive; its variations with temperature are much stronger than the variations of the isothermal compressibility χ_T (Table 10.1).
Let us consider the effect of a reversible isothermal compression, $dp > 0$. For low temperatures (e.g. at 10 K) the mechanical term, always positive, dominates, and the energy U increases when the pressure increases. At high temperatures (e.g. at100 K) the entropic term dominates and $dU < 0$ when $dp > 0$.

10.2 Reversible adiabatic compression

In a reversible adiabatic compression no heat is exchanged between the system and its ambient, $đQ = 0$. The energy balance is simple, the variation of the internal energy is entirely due to work, $dU = đW$. It is anyway interesting to see how the temperature varies when the pressure is varied. Let us start from the function $S(T,p)$: for a reversible adiabatic transformation

$$đQ \;=\; T\,dS \;=\; T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp \;=\; 0\,. \tag{10.8}$$

From (10.8) one can easily obtain the relation connecting temperature and pressure for the reversible adiabatic transformation:

$$\left(\frac{\partial T}{\partial p}\right)_S \;=\; -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} \;=\; -\frac{T}{C_p}\left(\frac{\partial S}{\partial p}\right)_T \;=\; +\frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p \;=\; \frac{Tv\beta}{c_p}\,. \tag{10.9}$$

The second last equality is supported by the Maxwell relation (7.45); in the last equality the molar volume and the molar specific heat have been introduced.
According to (10.9), the sign of the temperature variation caused by a reversible adiabatic variation of pressure depends on the sign of the coefficient of thermal expansion β.

- If $\beta > 0$, the compression causes heating, the expansion causes cooling.
- If $\beta < 0$, the compression causes cooling, the expansion causes heating.

Example 1: Ideal gases

By inserting the coefficient of thermal expansion of the ideal gas $\beta = 1/T$ in (10.9), one can see that an adaibatic compression always gives rise to an increase of temperature. The extent of the temperature variation depends however on the number of atoms per molecule; for example:
for monatomic gases

$$c_p = \frac{5}{2}R \qquad \text{so that} \qquad \left(\frac{\partial T}{\partial p}\right)_S \;=\; \frac{2v}{5R}\,; \tag{10.10}$$

for bi-atomic gases

$$c_p = \frac{7}{2}R \qquad \text{so that} \qquad \left(\frac{\partial T}{\partial p}\right)_S \;=\; \frac{2v}{7R}\,. \tag{10.11}$$

for a given pressure variation dp, the variation of temperature is larger for the monatomic gases than for the bi-atomic ones.

Let us now consider the variation of internal energy. For a reversible adiabatic transformation of an ideal gas, $pV^\gamma =$ constant, where $\gamma = c_p/c_v$, so that

$$dU \;=\; đW \;=\; -p\,dV \;=\; \frac{1}{\gamma}\,V\,dp\,. \tag{10.12}$$

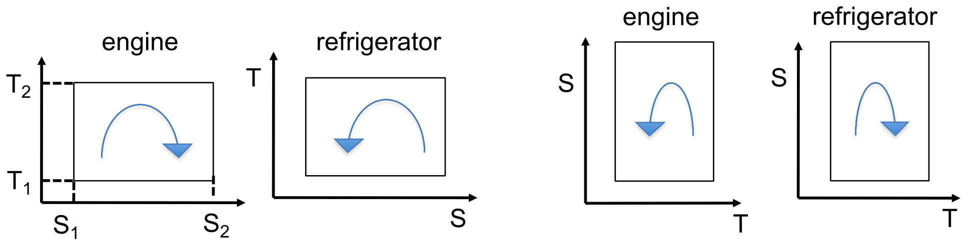


Figure 10.1: Carnot cycles for an engine and a refrigerator in the (S,T) plane (left) and in the (T,S) plane (right).

Since $\gamma = 1.66$ for monatomic gases and $\gamma = 1.4$ for bi-atomic gases, equation (10.12) shows that, for a given pressure variation dp, the variation of internal energy is smaller for the monatomic gases than for bi-atomic ones.
The same result can be obtained from (10.9):

$$dU \;=\; C_v\, dT \;=\; C_v \left(\frac{\partial T}{\partial p}\right)_S dp \;=\; C_v \frac{TV\beta}{C_p}\,. \tag{10.13}$$

Example 2: Liquid water

Fro water, $\beta < 0$ below 4°C and $\beta > 0$ above 4°C. Therefore:

- for $T < 4°$C, compression causes cooling, expansion causes heating,
- for $T > 4°$C, compression causes heating, expansion causes cooling.

Example 3: NaCl crystal

The coefficient of thermal expansion β is always positive for NaCl, an adiabatic compression thus always causes an increase of temperature.

10.3 Carnot cycle

A Carnot cycle is made by two reversible adiabatic transformations and two reversible isothermal transformations (§ 4.3). After any cyclic transformation the internal energy reverts to its initial value, $\Delta U = 0$; therefore, for an entire cycle $Q = -W$.
In the (S,T) plane a Carnot cycle is always represented by a rectangle, independent of the composition of the system. The area of the rectangle corresponds to the net amount of heat exchanged by the system with the two reservoirs.

10.3.1 Carnot cycle in the (S,T) plane

In general, the extensive coordinate S is chosen as abscissa and the intensive coordinate T as ordinate (Fig 10.1, left). For this hoice:

- the engine cycle is is run clockwise:

$$Q = T_2(S_2 - S_1) + T_1(S_1 - S_2) = (T_2 - T_1)(S_2 - S_1) > 0\,; \tag{10.14}$$

- the refrigerating cycle is run anti-clockwise

$$Q = T_2(S_1 - S_2) + T_1(S_2 - S_1) = (T_2 - T_1)(S_1 - S_2) < 0\,. \tag{10.15}$$

If the temperature T is chosen as abscissa and the entropy S as ordinate, the rotation directions are inverted, the engine cycle is run anti-clockwise and the refrigerating cycle clockwise (Fig 10.1, right).

10.3.2 Carnot cycle in the (V, p) plane

The shape of the Carnot cycle in the (V, p) plane depends on the substance composing the system. The area within the cycle always measures the net work exchanged by the system with its ambient. According to § 10.1 and 10.2:

- for reversible isothermal transformations

$$đW = pV\chi_T\, dp\,, \qquad đQ = -TV\beta\, dp\,, \tag{10.16}$$

- for reversible adiabatic transformations

$$dT = \frac{TV\beta}{C_p}\, dp\,. \tag{10.17}$$

The signs of both $đQ$ and dT depend on the sign of the coefficient of thermal expansion β. Let us consider below the examples of two systems with β positive and negative, respectively. For both systems the engine cycle in the two planes (S, T) and (V, p) is studied. Let us begin both cyclic transformations from the point (S_1, T_2) of the plot in Fig. 10.1, left.

Example 1: Ideal gas, $\beta > 0$

Since $\beta > 0$, the sign of $đQ$ is opposite to the sign of dp.

1–2 Reversible isothermal transformation T: $S_1, T_2) \rightarrow (S_2, T_2)$
$đQ = T\,dS > 0 \Rightarrow dp < 0$,$đW < 0$; the engine absorbs heat and does work.
2–3 Reversible adiabatic transformation at high S
$đQ = 0\,, dT < 0 \Rightarrow dp < 0$,$đW < 0$; the engine does work.
3–4 Reversible isothermal transformation at high T
$đQ = T\,dS < 0 \Rightarrow dp > 0$,$đW > 0$; the engine releases heat and absorbs work.
4-1 Reversible adiabatic transformation at low S
$đQ = 0\,, dT > 0 \Rightarrow dp > 0$,$đW > 0$; the engine absorbs work.

The engine cycle is run clockwise in bot the (V, p) and (S, T) planes. In the (V, p) plane the points of the high-temperature isotherm are above the points of the low-temperature isotherm.

Example 2: Liquid water between 0 and 4 °C, $\beta < 0$

Since $\beta < 0$, the sign of $đQ$ is equal to the sign of dp.

1–2 Reversible isothermal transformation at high T
$đQ = T\,dS > 0 \Rightarrow dp > 0$,$đW > 0$; the engine absorbs both heat and work.
2–3 Reversible adiabatic transformation at high S
$đQ = 0\,, dT < 0 \Rightarrow dp > 0$,$đW > 0$; the engine absorbs work.
3–4 Reversible isothermal transformation at low T
$đQ = T\,dS < 0 \Rightarrow dp > 0$,$đW < 0$; the engine releases heat and performs work.
4-1 Reversible adiabatic transformation at low S
$đQ = 0\,, dT > 0 \Rightarrow dp < 0$,$đW < 0$; the engine performs work.

The engine cycle is again run clockwise in both the (S, T) and (V, p) planes. In the (V, p) plane, however, the points of the high-temperature isotherm are below the points of the low-temperature isotherm.

10.4 Joule effect: free adiabatic expansion of a gas

The adiabatic free expansion of a gas, bot real or ideal, is an irreversible process. Defined values of the thermodynamical coordinates exist for both the initial and final equilibrium state, not for the intermediate non-equilibrium states of the process.
It is convenient to describe the initial and final equilibrium states by the values of temperature and volume, (T_i, V_i) and (T_f, V_f), respectively. Also the internal energy U is defined only for the initial and final equilibrium states. Since the expansion is free and adiabatic, $W = 0$ e $Q = 0$, so that $\Delta U = U_f - U_i = Q + W = 0$: the internal energy remains unchanged.

Our goal now is to check whether the free adiabatic expansion of a gas is accompanied by a variation of the temperature, as well as if the possible variation of temperature depends on the extent of the expansion.

The problem was experimentally studied by Joule in the first half of the XIX Century. Once established an initial state was (T_i, V_i) he measured the final temperature T_f as a function of the volume of the final state V_f. The pairs of values(T_f, V_f) are conveniently plotted in the (T, V) plane. The trend of the discrete points (T_f, V_f) (Fig. 10.2, left) can be approximated by a continuous line, that represents a reversible path. From the function $T(V)$ one obtains the *Joule coefficient*

$$\eta \;=\; \left(\frac{\partial T}{\partial v}\right)_U \,, \tag{10.18}$$

where v is the molar volume.

The dependence of the Joule coefficient η on the response functions can be found by means of the following procedure. Let us first consider the reversible variation of internal energy as a function of the variations of temperature and volume:

$$dU \;=\; T\,dS - p\,dV \;=\; C_v\,dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV\,. \tag{10.19}$$

Taking advantage of the Maxwell relation (7.44) and of the identity (7.51), one can substitute

$$\left(\frac{\partial S}{\partial V}\right)_T \;=\; \left(\frac{\partial p}{\partial T}\right)_V \;=\; -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \,, \tag{10.20}$$

whence, introducing the response functions,

$$dU \;=\; C_v\,dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV \;=\; C_v\,dT + \left[T\frac{\beta}{\chi_T} - p\right] dV\,. \tag{10.21}$$

Let us now consider again the continuous line joining the experimental points (T_f, V_f) of the free expansion (Fig. 10.2, left). By setting $dU = 0$ in (10.21) and considering molar quantities, one obtains two equivalent expressions of the Joule coefficient:

$$\eta \;=\; \left(\frac{\partial T}{\partial v}\right)_U \;=\; -\frac{1}{c_v}\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] \tag{10.22}$$

$$\;=\; -\frac{1}{c_v}\left[T\frac{\beta}{\chi_T} - p\right]. \tag{10.23}$$

Example 1: Ideal gas. One can easily verify, on the grounds of (10.22) or (10.23) and of the thermal equation of state $pV = nRT$, that the Joule coefficient is null for the ideal gas, $\eta = 0$. The free adiabatic expansion of the ideal gas doesn't give rise to temperature variations.

Example 2: Real Van der Waals gas. Real gases can be described with good approximation by the Van der Waals equation of state (§ 24.5); for one mole

$$\left(p + \frac{a}{v^2}\right)(v - b) \;=\; RT\,, \tag{10.24}$$

where a, b are two constants whose value depends on the type of gas:

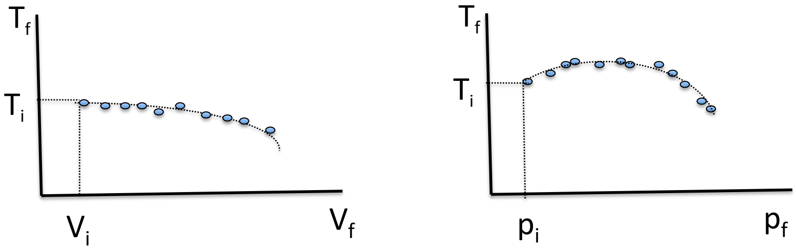


Figure 10.2: Left: free adiabatic expansion of real gas, plot of experimental points T_f vs V_f; the dashed line best fitting the points has a negative slope. Right: Joule-Thomson expansion of a real gas, plot of experimental points T_f vs P_f; the dashed line best fitting the points is downward concave and can exhibit a maximum, corresponding to the inversion temperature T_{inv}.

- the parameter $b > 0$ (the "covolume") takes into account the fact that that the molecules have a finite volume (in the ideal gas molecules are instead punctiform), so that the volume really available to the real gas is smaller than the volume of the container;
- the parameter $a > 0$ depends on the attractive forces of interaction between molecules, which reduce the pressure p measured on the walls of the container with respect to the pressure in the interior.

From (10.24) one can obtain the pressure p and its first derivative

$$p = \frac{RT}{v-b} - \frac{a}{v^2}\,, \qquad \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{v-b} \tag{10.25}$$

which, inserted in (10.22), give

$$\eta = \left(\frac{\partial T}{\partial v}\right)_U = -\frac{1}{c_v}\frac{a}{v^2} < 0\,. \tag{10.26}$$

The free adiabatic expansion of a Van der Waals gas always gives rise to a temperature reduction: $\Delta U = 0, \Delta T < 0$.

By integrating (10.26) one obtains the temperature variation as a function of the variation of the molar volume:

$$T_f - T_i = -\frac{a}{c_v}\left(\frac{1}{v_i} - \frac{1}{v_f}\right)\,. \tag{10.27}$$

Example 3: Let us consider the case of one mole of nitrogen N_2, initially at the temperature $T_i = 300\,\mathrm{K}$ and at atmospheric pressure $p_i = 10^5\,\mathrm{Pa} = 1\,\mathrm{bar}$. From available tables one can get the values of the Van der Waals parameters : $a = 0.14\,\mathrm{Pa\,m^6\,mol^{-2}}$, $b = 3.4\times10^{-5}\,\mathrm{m^3\,mol^{-1}}$. The value of b is negligible with respect to the molar volume of the ideal gas. For $T_i = 300\,\mathrm{K}$, the initial molar volume is $v_i = 25\times10^{-3}\,\mathrm{m^3\,mol^{-1}}$.

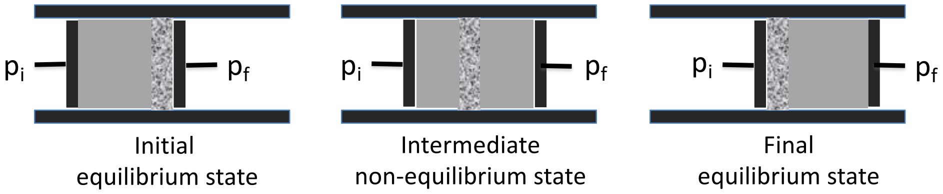
If the volume is doubled by the free expansion, $v_f = 2v_i$, from (10.27) one gets that the variation of temperature is $\Delta T = -0.13\,\mathrm{K}$.

Example 4: For a comparison, let us consider again the expansion of the previous example: 1 mol of nitrogen N_2 doubles its volume, $v_f = 2v_i$, but suppose that the adiabatic expansion be *reversible*, with performance of work. In the ideal gas approximation, the reduction of temperature now amounts to $\Delta T = -72\,\mathrm{K}$.

By comparing the last two examples, one can see that the free expansion is not an effective method for reducing the temperature of a gas.

10.5 Joule-Thomson effect

Cooling by free adiabatic expansion of a real gas is too weak for most practical applications. Significant reductions of temperature can instead be obtained by throttling the gas through a thin



Initial equilibrium state

Intermediate non-equilibrium state

Final equilibrium state

Figure 10.3: Schematic representation of the Joule-Thomson effect. Left: initial equilibrium state, all the gas is on the left of the porous plug. Right: final equilibrium state, all the gas is on the right of the porous plug. The intermediate states are non-equilibrium states; the transformation is not reversible.

hole or a porous material (Joule-Thomson effect).

Description of the process

A gas, contained in an adiabatic vessel, is force to go through a porous plug (or a thin hole), maintaining two constant pressure p_i and p_f in front and past of the porous plug, with $p_i > p_f$ (Fig. 10.3).
The initial state (T_i, p_i) and the final one (T_f, p_f) are equilibrium states: all the gas is in front or past the separating porous plug; in the two states the initial and final volumes, V_i and V_f, respectively, are different. The process is irreversible: one cannot recover the initial state without modifying the two values of pressure. As a consequence, the intermediate states cannot be described in terms of thermodynamic coordinates.
The process is adiabatic, there is no exchange of heat with the environment, $Q = 0$. An amount of work has to be done on the gas, and $\Delta U = W$. Since the internal energy is a state function, one can calculate the variation ΔU by considering any reversible process connecting the initial state to the final state:

$$\Delta U = U_f - U_i \;=\; W \;=-\int_{V_i}^{0} p_i\, dV \;-\; \int_{0}^{V_f} p_f\, dV \;=\; p_i V_i - p_f V_f\,. \tag{10.28}$$

From (10.28) one obtains

$$U_i + p_i V_i \;=\; U_f + p_f V_f\,, \qquad \text{that is} \qquad \boxed{H_i \;=\; H_f}\,. \tag{10.29}$$

In the Joule-Thomson expansion, the enthalpy $_f$ of the final equilibrium state is equal to the enthalpy H_i of the initial equilibrium state. One cannot attribute a value of entropy to the non-equilibrium intermediate states (one cannot thus say that “entropy is conserved” during the process)

The Joule-Thomson coefficient

Our goal now is to check whether the Joule-Thomson expansion is accompanied by a variation of the temperature, as well as if the possible variation of temperature depends on the extent of the expansion. The problem was experimentally studied by J. Joule in cooperation with W. Thomson (lord Kelvin) in the middle of the XIX Century.
The experiment consists in choosing an initial state (p_i, T_i) and in measuring the temperature T_f for different values of the final pressure p_f. The result of the experiment can be plotted with the pressure p as abscissa and the temperature T as ordinate. The plot consists in a set of points, corresponding to the initial pair (p_i, T_i) and to all the measured final pairs (p_f, T_f) (Fig. 10.2, right). All points are characterised by the same value of the enthalpy $H = U_i + p_i V_i$. By fitting a continuous line to the experimental points, one obtains an iso-enthalpic curve $T(p)$ (each one of the thin lines in Fig. 10.4).

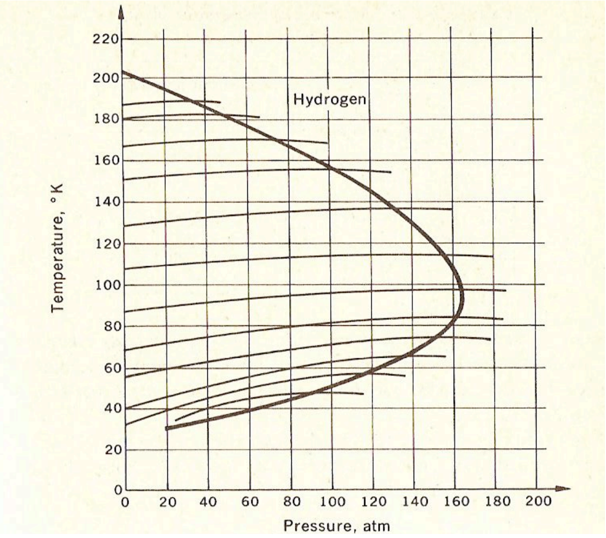


Figure 10.4: Iso-enthalpic curves for hydrogen (thin lines). The thick line joins the maximum points of all the iso-enthalpic curves. The intersection of the thick line with the ordinate axis ($p = 0$) gives the maximum inversione temperature ($T = 202\,\mathrm{K}$) .

From the curve $T(p)$ at constant enthalpy one can calculate the *Joule-Thomson coefficient*

$$\mu_j = \left(\frac{\partial T}{\partial p}\right)_H . \tag{10.30}$$

In general an iso-enthalpic curveis downward concave. The maximum value of the curve corresponds to its *inversion temperature* T_{inv}:

- in the low-pressure region where $\mu_j > 0$ the expansion gives rise to cooling,
- in the high-pressure region wherei $\mu_j < 0$ the expansion gives rise to heating.

If the initial condition (T_i, p_i) is varied, one can obtain different sets of (T, p) points fitted by different iso-enthalpic curves. At each iso-enthalpic curve it corresponds an inversion temperature T_{inv}. The case of hydrogen is shown in Fig. 10.4.

For any value of enthalpy H, a Joule-Thomson expansion taking place in a region with $\mu_j > 0$ gives rise to a decrease of temperature and can be used to cool the gas.

The inversion temperature corresponding to the pressure $p = 0$ is the maximum inversion temperature $T_{\mathrm{max,inv}}$. For temperatures higher than the maximum inversion temperature, the Joule-Thomson coefficient is always negative, $\mu_j < 0$, and the expansion always gives rise to an increase of temperature.

The Joule-Thomson effect can thus be used to cool a gas only below its maximum inversion temperature. The maximum inver sion temperature is different for different gases; for example:

- for nitrogen, $T_{\mathrm{max,inv}} = 621\,\mathrm{K}$; the cooling of nitrogen by Joule-Thomson effect can take place from ambient temperature down to the condensation temperature (78 K);
- for hydrogen $T_{\mathrm{max,inv}} = 202\,\mathrm{K}$; to cool hydrogen by the Joule-Thomson effect down to the condensation (20.28 K) it is necessary to cool it previously below 202 K by other techniques, for example by contact with liquid nitrogen or by means of a reversible adiabatic expansion;
- for helium $T_{\mathrm{max,inv}} \simeq 40\,\mathrm{K}$; also to cool helium by the Joule-Thomson effect it is necessary to previously cool it below 202 K by other techniques, typically by means of a reversible adiabatic expansion.

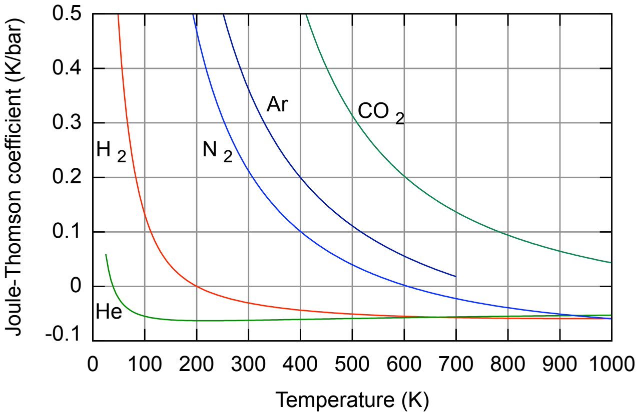


Figure 10.5: Joule-Thomson coefficients of different gases measured at atmospheric pressure, in $\mathrm{K\,bar}^{-1}$, as a function of temperature.

Joule-Thomson coefficient and response functions

Let us now express the Joule-Thomson coefficient μ_j as a function of the response functions. To this aim, let us consider a reversible process at constant enthalpy in the (p,T) plane. The differential of molar enthalpy is

$$dh \;=\; T\,ds + v\,dp\,, \tag{10.31}$$

where s is the molar entropy and v is the molar volume. By expressing the molar entropy as a function of (T,p) one obtains

$$\begin{aligned} dh \;&=\; T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp + v\,dp \\ &= c_p\,dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp \\ &= c_p\,dT - (Tv\beta - v)\,dp\,. \end{aligned} \tag{10.32}$$

By imposing $dh = 0$ one finds

$$\mu_j \;=\; \left(\frac{\partial T}{\partial p}\right)_H \;=\; \frac{v}{c_p}\,(\beta T - 1)\,. \tag{10.33}$$

As a consequence:

if $\beta > 1/T$, then $\mu_j > 0$ and the process gives rise to cooling;
if $\beta < 1/T$, then $\mu_j < 0$ and the process gives rise to heating.

Example: For ideal gases $\beta = 1/T$, so that $\mu_j = 0$. For a Joule-Thomson expansion of an ideal gas, $T_f = T_i$; from the thermal equation of state one gets that $p_f V_f = p_i V_i$. Then, since $H_f = H_i$, it is also $U_f = U_i$ and $W = 0$.

The Joule-Thomson coefficients of different gases at atmospheric pressure are compared in Fig. 10.5.

Chapter 11

Chemical equilibrium

This chapter contains an introduction to chemical equilibrium, that is equilibrium with respect to transport of matter and to chemical reactions.

In particular, we will advance our understanding of the meaning of the chemical potentials, introduced in (6.5) and (6.6) and up to now little onsidered (for example at the end of § 6.2).

In § 11.1 the analytic expression of the chemical potential is calculated for a particularly simple system, the ideal gas.

In § 11.2 the mixtures of ideal gases are considered: the total entropy of a mixture is expressed as a function of the entropies of the components (Gibbs theorem); the irreversible mixing of ideal gases is then considered and the role of the chemical potentials is evidenced.

In § 11.3 the problem of matter exchange in open systems is shortly considered.

At last, § 11.4 is dedicated to some basic concepts on the equilibrium of chemical reactions, such as the degree of advancement and the affinity. We will take particular advantage of such concepts in Part VI, dedicated to the Thermodynamics of irreversible processes.

11.1 Chemical potential of ideal gases

11.1.1 Chemical potential and molar Gibbs function

As is was shown in § 7.2, equation (7.30), the chemical potential μ of a substance corresponds to its molar Gibbs function g:

$$\mu \;=\; g \;=\; u + pv - Ts \;=\; h - Ts\,. \tag{11.1}$$

Equation (11.1) has a general validity. The explicit dependence of g on the variables T and p depends on the type of substance. From the differential dG of (8.45) one can obtain the molar dg for a pure substance in a closed system (where $dn = 0$):

$$d\mu = dg \;= -s\,dT + v\,dp\,. \tag{11.2}$$

From (11.2) we can draw a first general conclusion. The molar volume v is obviously positive; according to the statistical interpretation which will be given in Part III, the molar entropy s is non negative. Therefore the chemical potential $\mu = g$ increases when the temperature decreases or when the pressure increases.

In the rest of this § 11.1 some general expressions will be derived, valid for any substance, to focus then the attention on the simplest case, that is on the ideal gas.

11.1.2 Thermodynamical quantities of ideal gases

The independent coordinates for the Gibbs function are the temperature T and the pressure p. We will then start from the expression of u, h and s as a function of T and p to calculate $g = h - Ts$.

Internal energy

By generalising the procedure of § 10.1, let us express the differential of the internal energy as a function of temperature and pressure for *any substance*:

$$\begin{aligned} du &= T\,ds - p\,dv \\ &= T\left(\frac{\partial s}{\partial T}\right)_p dT \;+\; T\left(\frac{\partial s}{\partial p}\right)_T dp \;-\; p\left(\frac{\partial v}{\partial T}\right)_p dT \;-\; p\left(\frac{\partial v}{\partial p}\right)_T dp \\ &= c_p\,dT \;-\; Tv\beta\,dp \;-\; pv\beta\,dT \;+\; pv\chi_T\,dp \\ &= [c_p - pv\beta]\,dT \;+\; [p\chi_T - T\beta]v\,dp\,, \end{aligned} \tag{11.3}$$

where β and χ_T are the coefficient of thermal expansion and the isothermal compressibility, respectively.

For the *ideal gas*, from the thermal equation of state $pv = RT$ one gets $\beta = 1/T$ e $\chi_T = 1/p$ (see Chapter 9.By inserting these values in (11.3) one finds that for the ideal gas

$$du \;=\; c_p\,dT - R\,dT \;=\; c_v\,dT\,. \tag{11.4}$$

According to (11.4), the variation of the internal energy of the ideal gas only depends on the temperature. To calculate the finite variation of the molar internal energy from a reference state (T_r, p_r) and any other state (T, p) the integration with respect to the temperature is sufficient:

$$u \;= u_r \;+\; \int_{T_r}^{T} c_v\,dT\,. \tag{11.5}$$

Example: For a monatomic ideal gas $c_v = 3R/2$, independent of T. Therefore $u = u_r + (3/2)R(T - T_r)$.

Enthalpy

By the same procedure used for (11.3), one finds that the differential of enthalpy for *any substance* is

$$\begin{aligned} dh &= T\,ds + v\,dp \\ &= c_p\,dT \;-\; Tv\beta\,dp \;+\; v\,dp \\ &= c_p\,dT \;+\; [1 - T\beta]v\,dp\,. \end{aligned} \tag{11.6}$$

For the *ideal gas*, for which $\beta = 1/T$,

$$dh \;=\; c_p\,dT\,. \tag{11.7}$$

The molar enthlpy h of an ideal gas in a generic state (T, p) can be calculated from the molar enthalpy h_r of the reference state (T_r, p_r) by an integration with respect to the sole temperature:

$$h = \; h_r \;+ \int_{T_r}^{T} c_p\,dT\,. \tag{11.8}$$

Example: For a monatomic ideal gas $c_p = 5R/2$, independent of T. Therefore $h = h_r + (5/2)R(T - T_r)$.

Entropy

Let us first find the general expression of $T\,ds$ as a function of temperature and pressure. By using the Mawell relation (7.45), one finds, for *any substance*, f

$$T\,ds \;=\; c_p\,dT + T\left(\frac{\partial s}{\partial p}\right)_T dp \;=\; c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \;=\; c_p\,dT - Tv\beta\,dp\,. \tag{11.9}$$

For the *ideal gas*, for which $\beta = 1/T$, equation (11.9) becomes

$$T\,ds \;=\; c_p\,dT - v\,dp\,. \tag{11.10}$$

The molar entropy s of an ideal gas in a generic state can be calculated from the molar entropy s_r of an arbitrary reference state r by integrating (11.10):

$$s \;=\; s_r \;+\; \int_{T_r}^{T} c_p\,\frac{dT}{T} \;-\; \int_{p_r}^{p} \frac{v}{T}\,dp \;=\; s_r \;+\; \int_{T_r}^{T} c_p\,\frac{dT}{T} - R\,\ln\frac{p}{p_r}\,, \tag{11.11}$$

where T_r and p_r are temperature and pressure of the reference state.
By introducing the new reference constant $s_0 = s_r + R\,\ln p_r$, equation (11.11) becomes

$$s = \;s_0 \;+ \int_{T_r}^{T} c_p\,\frac{dT}{T} - R\,\ln p \;=\; R\,[\sigma(T) - \ln p]\;. \tag{11.12}$$

where $\sigma(T)$ is an increasing function of the sole temperature T.

Example: For a monatomic ideal gas, $c_p = 5R/2$, independent of T. Therefore $R\sigma(T) = s_r + R\ln p_r + (5/2)R\ln(T/T_r)$.

Note: Pay attention to the measurement units in passing from $\ln(p/p_r)$ to $\ln p - \ln p_r$. The argument of a logarithm is a dimensionless quantity. In the expression $\ln p$, p has to be considered not as the physical quantity "pressure', but its numerical value with respect to a well defined unit. Both p and p_r have then to be measured in the same unit, e.g the bar.

Gibbs function, chemicl potential

Once the molar enthalpy h ant the molare entropy s have been calculated, the molar Gibbs function of an ideal gas can be obtained by

$$g = \;h - Ts \;=\; h_r \;+ \int_{T_r}^{T} c_p\,dT - RT\;[\sigma(T) - \ln p] \;=\; RT\,[\phi(T) + \ln p]\;, \tag{11.13}$$

where in the last equality the function $\phi(T)$ depending on the sole temperature has been introduced.

Therefore the chemical potential $\mu = g$ of an ideal gas can be written as

$$\boxed{\mu = \;\mu_0(T) + RT\,\ln p} \qquad \text{con} \quad \mu_0(T) \;=\; RT\,\phi(T)\,. \tag{11.14}$$

The dependence of the chemical potential on pressure is evident in (11.14): at constant temperture, the chemical potential increases as the logarithm of the pressure.

Real gases

The behaviour of *real gases* is different from that of ideal gas, due to the presence of interaction forces between the molecules, attractive at relatively large distances, repulsive at very short distances. For the real gases, the expression of the chemical is anyway similar to that of the ideal gas (11.14): the difference is that the pressure p is substituted by the fugacity f, a quantity which is anyway closely conneted to the pressure: $\mu = \;\mu_0(T) + RT\,\ln f$.

11.2 Mixtures of ideal gases

To better grasp the meaning and the role of the chemical potential, it iuseful to consider the relatively simple case of the mixing of ideal gases. Let us study first the general properties of the mixtures of ideal gases and then the process of irreversible mixing of two or more ideal gases.

11.2.1 Mixtures of ideal gases, Gibbs theorem

Let us consider a mixture of N ideal gases enclosed in a volume V at the total pressure P, and let n_k be the number of moles of the k-th component.

Molar fraction

The molar fraction of the k-th component is the ratio

$$x_k \;=\; \frac{n_k}{\sum_k n_k}\,. \tag{11.15}$$

From the thermal equation of state of ideal gases one obtains the relation between the total pressure P of the mixture and the partial pressures p_k of the components:

$$P \;=\; \frac{\sum n_k}{V}\,RT \;=\; \sum\nolimits_k \left[\frac{n_k}{V}\,RT\right] \;=\; \sum\nolimits_k p_k\,. \tag{11.16}$$

The partial pressure p_k of gas k is the pressure that n_k moles of the gas k would exert if they were alone in the volume V.
According to (11.17), the total pressure P is the sum of the partial pressures p_k.
Each partial pressure is thus connected to the total pressure by the relation

$$p_k \;=\; \frac{n_k}{V}\,RT \;=\; \frac{n_k}{\sum n_k}\,P \;=\; x_k P\,. \tag{11.17}$$

Entropy of the mixture

We seek now the relation between the entropy S of the mixture and the entropies $S_k$of the single component ideal gases. For the sake of simplicity, let us consider a mixture of only two gases, A_1 and A_2, initially contained in the left half of a vessel of total volume V and maintained at the temperature T (Fig. 11.1, left).
Our goal is to perform an *isothermal reversible* transformation to a final state in which the two gases separately fill up each one one half of the vessel (Fig. 11.1, right).
To this aim, we take advantage of two semi-permeable membranes, that allow the selective passage of some gases and forbid the passage of other. The practical construction of semi-permeable membranes is far from trivial, their theoretical use is however always possible.
Let us use a sliding frame including half of the total volume V, closed on its left by a membrane permeable only to gas A_1, on its right by a membrane impermeable to both gases. A membrane permeable only to the gas A_2 is fixed in the middle of the vessel.
In the initial state the mixture is maintained in the left part of the vessel by the impermeable membrane on the right of the frame (Fig. 11.1, left). Let us now slide the frame to the right without friction (Fig. 11.1, center); the frame drives to the right the gas A_2 and leaves the gas A_1 on the left half of the vessel. At the end of the process, the two gases are completely separated (Fig. 11.1, right).

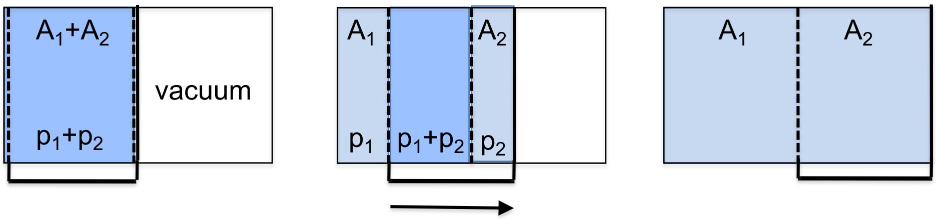


Figure 11.1: Reversible isothermal separation of two ideal gases A_1 and A_2. The vessel is divided in two equal parts by a membrane permeable only to the gas A_2. The mobile frame is made by a right wall impermeable and by a left wall permeable only to the gas A_1.

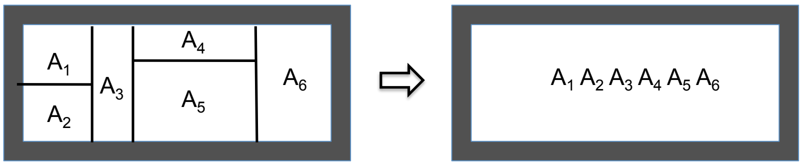


Figure 11.2: Spontaneous adiabatic mixing of ideal gases.

The transformation is by hypothesis reversible and isothermal; there are no finite differences of pressure on the two sides of the frame, since on the two walls (left and right, respectively) the same pressure p_2 is exerted in opposite directions.
The energy balance is the following:

$$\begin{aligned} \Delta U &= 0 && \text{(for an ideal gas at constant temperature)} \\ W &= 0 && \text{(the frame is in mechanical equilibrium)} \\ Q &= \Delta U - W = 0 \end{aligned}$$

Since tre transformation is reversible, $Q = T\,\Delta S = 0$. Therefore there is no variation of entropy: the entropy of the mixture of two ideal gases is equal to the sum of the entropies of the two single gases.
The conclusion is generalised to the case of any number of gases by the *Gibbs theorem*: the entropy of a mixture of ideal gases is equal to the sum of the entropies of the components,

$$\boxed{\text{Gas ideale:} \qquad S_{\text{miscela}} = \sum\nolimits_k S_k} \tag{11.18}$$

By reversing the motion of the frame in Fig. 11.1 one can reversibly mix the two gases, again with no entropy variation.

Note: If the gases of the mixture are not ideal, $\Delta U \neq 0$ for an isothermal transformation; the interaction potential energy can be different for the different pairs A_1A_2, A_2A_2 and A_1A_2. Therefore not necessarily $\Delta S = 0$.

(?) Discuss the case of a reversible adiabatic separation and mixing of two gases (instead of isothermal).

11.2.2 Spontaneous mixing of ideal gases

We have just seen that the *reversible* separation and the reversible mixing of two or more ideal gases takes place Without entropy variations.
We focus our attention now on the *irreversible* spontaneous mixing of ideal gases. Let us consider a vessel with *rigid insulating walls*, divided in N vessels containing N *different ideal gases* at the same temperature T and pressure P (Fig. 11.2, left). When the internal walls separating the internal vessels are removed, the gases are irreversibly mixed (Fig. 11.2, right).
The energy balance is:

$$\begin{aligned} W &= 0 && \text{(the vessel walls are rigid)} \\ Q &= 0 && \text{(the vessel walls are adiabatic)} \\ \Delta U &= Q + W = 0 \end{aligned}$$

Because the gases are ideal and $\Delta U = 0$, then $\Delta T = 0$.
Moreover the initial pressure had the same value P for all the gases. Since nor temperature nor volume are varied, the final pressure of the mixture is again P.

Entropy variation

The process of mixing of ideal gases described above takes place at constant internal energy U and volume V. The evolution criterion of the irreversible process consists in the increase of the entropy function $S(U,V)$. We want now to calculate the entropy increase.

The initial entropy is the sum of the entropies of the single gases, each one of which is at the pressure P; the molar entropy of a single gas is given by (11.12), so that the initial total entropy is

$$S_i \;=\; R \sum\nolimits_k n_k \left[\sigma_k(T) - \ln P\right] . \tag{11.19}$$

According to the Gibbs theorem (11.18), the final entropy of the mixture of ideal gases, each one of which is at the partial pressure p_k, is the sum of the partial entropies, so that

$$S_f \;=\; R \sum\nolimits_k n_k \left[\sigma_k(T) - \ln p_k\right] . \tag{11.20}$$

The entropy variation is

$$\Delta S \;=\; S_f - S_i \;=\; -R \sum\nolimits_k n_k \ln \frac{p_k}{P} \;=\; -R \sum\nolimits_k n_k \ln x_k \;>\; 0 . \tag{11.21}$$

The value ΔS of (11.21) is called *entropy of mixing*.

Example: Let us consider the mixing of two ideal gases, 1 mol of gas A, 1 mol of gas B. By means of (11.21) one finds

$$\Delta S \;=\; -2R \ln(0.5) \;=\; 2R \ln 2 . \tag{11.22}$$

For what concerns entropy, the mixing of the two gases is equivalent to the sum of the separated free expansions of the two gases.

Note 1: Let us compare the *irreversible* mixing of two ideal gases of the previous example with the *reversible* mixing (the opposite of the separation process of Fig. 11.1). In the second case (reversible) the two gases share the same density before and after mixing, in the first case (irreversible) the densities are reduced by mixing.

Note 2: For the irreversible mixing of *real gases* the conclusions drawn for the ideal cases are not valid. For real gases $p_k \neq x_k P$ and $S_{\text{mixture}} \neq \sum_k S_k$. Anyway, also for real gases the mixing gives rise to an increase of entropy, $\Delta S > 0$.

Extreme case: indistinguishablel gases, Gibbs paradox.

A interesting case is encountered when the difference between the gases are progressively reduced until they become undistinguishable. For the sake of simplicity let us consider only two identical gases, $A_1 = A_2$. In this case the above treatment of the entropy of the mixture and of the mixing process have to be revisited.

1. *Entropy of the mixture.* Two indistinguishable gases cannot be separated by any semipermeable membrane. During the of Fig. 11.1, if the two gases are indistinguishable, the pressure is uniform in the entire region on the left of the impermeable wall of the sliding frame. If the process takes place with $W = 0$, it corresponds to an irreversible free expansion, and $DeltaS > 0$. In order that the process be reversible, it is necessary to exert a force on the frame, so that $W \neq 0$ and hence $T\,\Delta S \neq 0$. The Gibbs theorem (11.18) thus doesn't apply.

2. *Irreversible mixing.* If the gases are indistinguishable, it makes no sense to speak of mixing. By removing the separating wall there is no entropy increase, $S_f = S_i$. Equation (11.21) doesn't apply.

The statistical interpretation of the entropy within the framework of Classical Physics (see Part III), cannot explain the different behaviour of distinguishable and indistinguishable gases. To this difference, apparently anomalous, the name was given of *Gibbs paradox*. As we will se in Chapter 16, the Gibbs paradox is solved within the framework of Quantum Mechanics, where a different statistical treatment is reserved to distinguishable and indistinguishable particles.

Variation of the Gibbs function

The process of spontaneous mixing of ideal gases considered above takes place not only at constant internal energy U and volume V, but also at constant temperature T and pressure P. The evolution criterion of the irreversible process corresponds not only to an increase of entropy but also to a decrease of the Gibbs function $G(T,P)$.

Let us calculate the reduction of the Gibbs free energy for the mixing of ideal gases. Beginning from the expression of the molar Gibbs function (11.13) and taking into account that $G = \sum n_k g_k$, one obtains:

(i) Initial state: $G_i = RT \sum_k n_k \, [\phi_k(T) + \ln P]$

(f) Final state: $G_f = RT \sum_k n_k \, [\phi_k(T) + \ln p_k]$

Therefore

$$\Delta G = RT \sum_k n_k \ln x_k < 0 \,. \tag{11.23}$$

Note 1: The variation of G in the mixing process depends on the temperature T but not on the total pressure P.

Note 2: Only for an ideal gas can the two conditions U,V constant and T,P constant take place together; for a real gas the two conditions are incompatible.

For the irreversible mixing of two or more *real gases* the two cases have to be separately considered:

a) at constant U and V, the process takes place with increase of entropy, $\Delta S > 0$;

b) at constant T and P, the process takes place with decrease of the Gibbs function, $\Delta G < 0$.

Variation of enthalpy

As it was shown above, for *ideal gases* the process of mixing doesn't give rise to increase of internal energy U and of volume V. Threfore the enthalpy H is unchanged too:

$$\Delta H = \Delta U + P\,\Delta V = 0 \qquad \text{(ideal gas)} \,. \tag{11.24}$$

The variation of the Gibbs function G, since T is constant, can be calculated as

$$\Delta G = \Delta H - T\,\Delta S < 0 \qquad \text{(ideal gas)} \,. \tag{11.25}$$

Since $\Delta H = 0$, equation (11.25) shows that for an ideal gas the reduction of the Gibbs function is only due to the increase of the entropy.

For *real gases*, the variation of internal energy is not zero in the mixing processes, owing to the influence of the forces of interaction between molecules; therefore $\Delta H \neq 0$ too.

Equation (11.25) holds for any system maintained at constant T,P also for non gaseous systems. While however the variation of entropy is always positive in the mixing processes, $\Delta S > 0$, the sign of ΔH depends on the relation between the interaction forces in the different pairs $A_1 - A_1$, $A_1 - A_2$ and $A_2 - A_2$. If the forces in the homologous pairs $A_1 - A_1$ and $A_2 - A_2$ are stronger than the forces in the heterologous pairs $A_1 - A_2$, it can be that $\Delta H > T\,\Delta S$; in such a case $\Delta G > 0$ and the mixing process cannot take place. The above considerations are particularly relevant for the study of liquid and solid solutions.

11.2.3 Role of the chemical potential

To better grasp the meaning of the chemical potential μ, that for pure substance corresponds to the molar Gibbs function $\mu = g$, let us consider the two cases of the mixing of ideal gases and of the transport of matter.

1) Chemical potential and mixtures of ideal gases

For an ideal gas at pressure p, equation (11.13) shows that the chemicl potential is

$$\mu \;=\; g \;=\; RT\,[\phi(T) + \ln\, p]\;. \tag{11.26}$$

For a mixture of ideal gases at the total pressure P, where $p_k = Px_k$ and x_k are the partial pressure and the molar fraction of gas k, the Gibbs function is

$$G \;=\; \sum\nolimits_k n_k \mu_k \;=\; RT \sum\nolimits_k n_k\,[\phi_k(T) + \ln\, P + \ln x_k]\;. \tag{11.27}$$

The chemical potential of the k-th component of the mixture is

$$\mu_k \;=\; RT\,[\phi_k(T) + \ln\, P + \ln x_k]\;. \tag{11.28}$$

The dependence of the chemical potential μ_k on the concentration x_k can be better grasped by considering the two extreme cases:

- if $x_k \to 0$, then $\mu_k \to -\infty$,
- if $x_k \to 1$, then $\mu_k \to g$ (single non mixed gas).

Example: mixing of two ideal gases

Let consider a vessel divided i two equal parts, 1 and 2, by an impermeable wall. Initially, part 1 contains 1 mol of gas A, part 2 contains 1 mol of gas B (Fig. 11.3, left). Ad a given time the wall is removed and the gases mix. (Fig. 11.3, center). The final state f is a mixture of gases $A + B$ which takes up the entire vessel (Fig. 11.3, right).
Let us study the variations of the concentrations of the two gases, measured by the molar fraction x_k (11.15), from the initial to the final state.

Initial state	Flows	Final state
$x_A^{(1)} = 1;\quad x_A^{(2)} = 0$	$A:\ (1) \to (2)$	$x_A^{(f)} = 0.5$
$x_B^{(1)} = 0;\quad x_B^{(2)} = 1$	$B:\ (2) \leftarrow (1)$	$x_B^{(f)} = 0.5$

Once the concentrations x_k are known, making use of (11.28), one can now calculate the chemical potentials μ_k of the initial and final states. In the initial state, the chemical potentials are different for the two gases in the two sub-systems. In the final state, the chemical potentials are equal.

Initial state	Variation	Final state
$\mu_A^{(1)} = RT\,[\phi_A(T) + \ln P]$	decreases	$\mu_A^{(f)} = \mu_A^{(1)} - 0.693\,RT$
$\mu_A^{(2)} = -\infty$	increases	
$\mu_B^{(1)} = -\infty$	increases	$\mu_B^{(f)} = \mu_B^{(2)} - 0.693\,RT$
$mu_B^{(2)} = RT\,[\phi_B(T) + \ln P]$	decreases	

Let us now consider the Gibbs function of the entire system. In the initial state

$$G_{\text{in}} = \mu_A^{(1)} n_A + \mu_B^{(2)} n_B\,, \tag{11.29}$$

because all the gas A is in part 1 and all the gas B is in part 2.
In the final state

$$G_{\text{fin}} = \mu_A^{(f)} n_A + \mu_B^{(f)} n_B\,. \tag{11.30}$$

Since $\mu_A^{(1)} > \mu_A^{(f)}$ and $\mu_B^{(2)} > \mu_B^{(f)}$, it is easy to see that $G_{\text{fin}} < G_{\text{in}}$, that is that G decreases in the process of mixing at constant T and P.

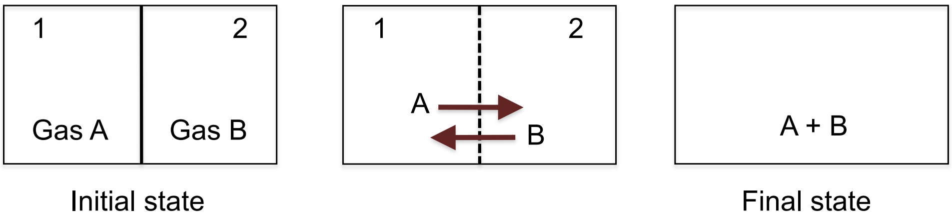


Figure 11.3: Mixing of two gases A and B. Left: initial equilibrium state, the two gases are separated in the parts 1 and 2 of the vessel. Center: the process of mixing. Right: final equilibrium state.

2) Chemical potential and transport of matter

In the process of gas mixing, studied above, an initially heterogeneous system (two separate gases) becomes homogeneous (mixture of gases). In other systems, a process can connect an initial heterogeneous state to a final heterogeneous heterogeneous as well; it is the case, for example, of systems where two or more phases of the same material are present, and an amount of matter is transferred from one phase to the other.
Let us now analyse the role of the chemical potential in thermodynamical processes characterised by transport of matter.

Let us consider a system with a number of components, in equilibrium at constant T and P and divided in two sub-systems (1) and (2). The equilibrium condition (8.54) requires that the chemical potentials of all the components are equal:

$$\mu_k^{(1)} = \mu_k^{(2)} . \tag{11.31}$$

Example: transport of matter between two phases

Let us consider a closed system made by two phases α and β of the same material (for example liquid water and water vapour).
The two phases are characterised by the chemical potentials $\mu_\alpha(T, p)$ and $\mu_\beta(T, p)$, respectively. If $\mu_\alpha < \mu_\beta$, then a transport of matter takes place from the β phase to the α phase.
If the temperature T and the pressure p are maintained constant, the process of transport of matter from β to α continues until the β phase completely disappears (Fig. 11.4, left).
If the system is instead isolated, the progressive transformation of the β phase to the α phase modifies temperature and pressure, so that the chemical potentials $\mu_\alpha(T, p)$ and $\mu_\beta(T, p)$ are modified (Fig. 11.4, right). The process stops when one of the two phases disappears *or* when new values of temperature and pressure are attained for which $\mu_\alpha(T, p) = \mu_\beta(T, p)$.

Example: Let us consider water H_2O and let α be the liquid phase, β the vapour phase. For fixed temperature $T = 400\,\mathrm{K}$ and *prssure* $p = 1\,\mathrm{bar}$, the transformation $\alpha \to \beta$ takes place with the complete vaporisation of the liquid phase. For fixed temperature and *volume*, instead, the

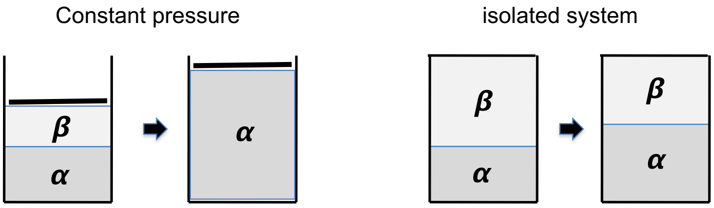


Figure 11.4: Transport of matter between the two phases α and β maintained at T, and p constant (left) or in a rigid and isolated vessel (a right).

transformation $\alpha \to \beta$ gives rise to a progressive increase of the pressure p, and to the consequent variations of the two chemical potentials $\mu_\alpha(T,p)$ and $\mu_\beta(T,p)$, so that at equilibrium, where $\mu_\alpha = \mu_\beta$ both phases are still present.

11.3 Open systems

In § 11.2 we delt with thermodynamical processes in which the total amounts n_i of chemical species remain constant. In what follows we consider the processes in which n_i can be modified:

a) due to the exchange of matter between the system and its ambient (in this § 11.3); in such cases the system is open;
b) due to a chemical reaction in a closed system (in the next § 11.4); in such cases anyway the chemical species are modified, not their basic constituents, that is the atomic species.

Let us consider an open system with only one component, which exchanges matter with its ambient.

Open system, entropy varition

The total entropy of the system is $S = ns$. Its reversible variation

$$dS \;=\; n\,ds + s\,dn \tag{11.32}$$

is due to both the variation of molar entropy ds and to the variation dn of the number of moles. The variation of molare entropy is in turn connected to the reversible flow of heat by the relation $ds = đq/T$ (where $đq$ is the amount of heat absorbed by one mole of matter). Therefore (11.32) can be re-written as

$$dS \;=\; đQ/T + s\,dn\,. \tag{11.33}$$

In conclusion, the variation of entropy is due to two causes:

- the reversible exchange of heat $đQ$ with the ambient (as for closed systems),
- the exchange of matter, carrying the molar entropy s, with the ambient.

For open systems $đQ \neq T\,dS$ also for reversible processes.

Open system, energy balance

Let us now consider the variation of internal energy for an open system with one component:

$$dU \;=\; T\,dS - p\,dV + \mu\,dn\,. \tag{11.34}$$

Substituting $dS = n\,ds + s\,dn$ and $\mu = g = h - Ts$, where h is the molar enthalpy, (11.34) becomes

$$dU \;=\; Tn\,ds - p\,dV + h\,dn\,. \tag{11.35}$$

Since the exchanged heat is $đQ = Tn\,ds$, from (11.35) one obtains the energy balance:

$$\boxed{dU \;=\; đQ - p\,dV + h\,dn\,.} \tag{11.36}$$

The variation of the internal energy of an open system is thus due to:

- heat exchange $đQ$,
- exchange of compression work $-p\,dV$,
- exchange of matter carrying molar enthalpy, $h\,dn$; the enthalpic term can in turn be decomposed as $h\,dn = u\,dn + pv\,dn$; the contribution to the energy variation of the system is due to both the transport of molar energy u and to the work done for the introduction of new matter.

It is easily verifid that the variation of enthalpy is

$$dH \;=\; Tn\,ds + V\,dp + h\,dn\,. \tag{11.37}$$

At constant pressure, $dp = 0$, (11.37) reduces to (8.25) of § 8.2.

11.4 Chemical reactions

Let us come back to the closed systems and introduce some basic concepts of the Thermodynamics of chemical reactions.

11.4.1 Nomenclature

Let us schematise a chemical reaction with the following notation:

$$-\nu_1 A_1 - \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4 \,, \tag{11.38}$$

where

a) A_i are the chemical species which participate to the reaction (they could be nuclear species or elementary particles for other types of reactions);

b) on the left of the symbol $\rightleftharpoons$ are the reactants, on the right are the products of the reaction; to represent a generic case, in (11.38) two reactants and two products have been considered; in real cases the number of reactants and of products can obviously be different;

c) ν_i are the stoichiometric coefficients, whose signs are conventionally chosen as follows:

   $\nu_i < 0$ for the reagents,
   $\nu_i > 0$ for the products.

   The above convention on the sign of the stoichiometric coefficients allows one to formally rewrite (11.38) as

$$0 \rightleftharpoons \sum\nolimits_i \nu_i A_i \,. \tag{11.39}$$

Examples: The following two examples should clarify the use of the sign of stoichiometric coefficients:

$$\begin{array}{rcll} 2\mathrm{O} & \rightleftharpoons & \mathrm{O}_2 & (\nu_1 = -2;\ \nu_3 = 1) \\ 2\mathrm{H}_2 + \mathrm{O}_2 & \rightleftharpoons & 2\mathrm{H}_2\mathrm{O} & (\nu_1 = -2;\ \nu_2 = -1;\ \nu_3 = 2) \end{array} \tag{11.40}$$

Scale factor of a chmical reaction

For the sake of simplicity, we consider here only chemical reaction for which the maximum amounts of reactants and of products are proportional to the respective stoichiometric coefficients.

Example: Let us consider the second of the reactions of (11.40): when the reaction is completely on its left side, we suppose that exactly 2 mol of H_2 and 1 mol of O_2 are present, while when the reaction is completely on its right side we suppose that exactly 2 mol of H_2O are present.

We want now to express the molar quantities n_i of all the components as a function of only one scale factorcn_0. If the equilibrium of the reaction (11.38) is completely on the left , that is only reactants are present, then

$$n_1^{\max} = -\nu_1 \, n_0 \,, \qquad n_2^{\max} = -\nu_2 \, n_0 \,, \tag{11.41}$$

while if the equilibrium of the reaction is completely on the right, that is only products are present, then

$$n_3^{\max} = \nu_3 \, n_0 \,, \qquad n_4^{\max} = \nu_4 \, n_0 \,. \tag{11.42}$$

Degree of advancement of a chemical reaction

The degree of advancement of a chemical reaction is measured by a parameter ξ defined as

$$\xi \;=\; \frac{n_1^{\max} - n_1}{n_1^{\max}} \;=\; \frac{n_2^{\max} - n_2}{n_2^{\max}} \;=\; \frac{n_3}{n_3^{\max}} \;=\; \frac{n_4}{n_4^{\max}} \,. \tag{11.43}$$

It is evident that $0 \le \xi \le 1$:

- when the equilibrium is completely on the left (only reactants), $\xi = 0$,
- when the equilibrium is completely on the right (only products), $\xi = 1$.

By inserting (11.41) and (11.42) in (11.43), the numbers of moles of reactants and of products can be expressed as a function of the parameter ξ and of the scale factor n_0:

$$n_{\rm reag} = -n_0\, \nu_{\rm reag}\, (1-\xi)\,, \qquad n_{\rm prod} = n_0\, \nu_{\rm prod}\, \xi \tag{11.44}$$

(it is worth to remind that by convention $\nu_{\rm reag} < 0$ and $\nu_{\rm prod} > 0$).
The variations of the numbers of moles of the single components can be expressed as a function of the variation of the degree of advancement that is of a sole parameter, by the simple relation

$$\boxed{dn_i \;=\; n_0\, \nu_i\, d\xi} \tag{11.45}$$

11.4.2 Evolution criterion

In general, a chemical reaction is an irreversible process. One can imagine an initial condition of constrained equilibrium, in which the reactant don't actually react, for example because it is necessary to cross an energy barrier in order to trigger the reaction. The reaction can be triggered by a suitable thermodynamical operation (lighting of a spark, insertion of a catalyst, removal of an anti-catalyst). The reaction terminates in a state of non-constrained equilibrium.

Note: A chemical reaction can be thermodynamically described also in the absence of chemical equilibrium, provided the thermal and mechanical equilibria are guaranteed (see Zemansky, § 16.7). That's why one can make use of the differential notation typical of equilibrium Thermodynamics.

Fundamental axiom

Let us recall the differential expression of the energy variation:

$$dS = \frac{1}{T}\, dU + \frac{p}{T}\, dV - \sum \frac{\mu_i}{T}\, dn_i\,. \tag{11.46}$$

For a reaction taking place in an isolated system (where $\Delta U = 0, \Delta V = 0$), according to the fundamental axiom of § 5.3 the evolution criterion is $\Delta S > 0$. The first two terms on the right of (11.46) are null. Therefore during the reaction the term

$$\sum \frac{\mu_i}{T}\, dn_i \tag{11.47}$$

decreases and becomes zero when the final equilibrium is achieved. The values of the chemical potentials μ_i depend on the values of temperature and pressure, that change during a process taking place in an isolated vessel.

If the system is not isolated (if for example it is maintained at constant temperature and/or pressure) the fundamental axiom of entropy increase has to be referred to the thermodynamical universe, sum of the system and its ambient:

$$\Delta S_{\rm tot} \;=\; \Delta S + \Delta S_{\rm amb} \;>\; 0\,. \tag{11.48}$$

Isothermal reactions

From now on, we consider chemical reactions taking place in a closed non-isolated system, maintained at constant temperature T. In such a case, the variation of the ambient entropy is $\Delta S_{\rm amb} = -Q/T$, where Q is the amount of heat absorbed by the system. The evolution criterion (11.48) becomes

$$Q - T\,\Delta S \;<\; 0\,. \tag{11.49}$$

Equation (11.49) shows that the emission of heat ($Q < 0$, exothermic reaction) and the increase of entropy ($\Delta S > 0$) positively contribute to the evolution. Obviously also an endothermic reaction

($Q > 0$) can spontaneously take place, provided the heat absorption be accompanied by a suitable decrease of the entropy, so that (11.49) is fulfilled.

We can now go further in the analysis of isothermal reactions, by considering two different cases: constant volume or constant pressure.

Isothermal reactions at constant volume

If, in addition to temperature, the volume is maintained constant, the absorbed amount of heat is equal to the variation of internal energy, $Q = \Delta U$. By introducing the Helmholtz function $F = U - TS$ and recalling that, at constant temperature T, $\Delta F = \Delta U - T\,\Delta S$, the evolution criterion (11.49) becomes

$$\Delta F = \Delta U - T\,\Delta S \ < \ 0\,. \tag{11.50}$$

Isothermal reactions at constant pressure

If, in addition to temperature, the pressure is maintained constant, the absorbed amount of heat is equal to the variation of enthalpy, $Q = \Delta H$. By introducing the Gibbs function $G = H - TS$ and recalling that, at constant temperature T, $\Delta G = \Delta H - T\,\Delta S$, the evolution criterion (11.49) becomes

$$\Delta G = \Delta H - T\,\Delta S \ < \ 0\,. \tag{11.51}$$

Equation (11.51) corresponds to (11.48) because $-T\,\Delta H$ measures the entropy variation of the ambient, and ΔS measures the variation of entropy of the system. At low temperatures, $T\,\Delta S$ is generally small with respect to ΔH, so that $\Delta G \simeq \Delta H$: at low temperatures the exothermic reactions are favoured.

11.4.3 Equilibrium conditions

From now on, we only deal with chemical reactions taking place ina closed system maintained at constant temperature T and pressure p. The evolution criterion, given by (11.51), is $\Delta G < 0$. The equilibrium condition with respect to the degree of advancement ξ of the reaction is $dG = 0$.
At constant temperature and pressure,

$$(dG)_{Tp} \ = \ \sum\nolimits_i \mu_i dn_i \ = \ n_0 \left(\sum\nolimits_i \mu_i \nu_i\right) d\xi\,. \tag{11.52}$$

Therefore the equilibrium condition $dG = 0$ corresponds to

$$\boxed{\sum\nolimits_i \mu_i \nu_i \ = \ 0\,.} \tag{11.53}$$

In general, the chemical potentials depend on the temperature T, on the pressure p and on the concentration of the single chemical species. Here we consider the case of constant T and p; while the reaction takes place, the degree ξ of the reaction changes so that also the values n_i and the concentrations of the chemical species change; as a consequence also the chemical potentials μ_i are modified.
The reaction is at equilibrium when the degree of advancement has the value ξ_e for which (11.53) is fulfilled.

Example: Let us consider the reaction

$$\mathrm{O_2} \ \rightleftharpoons \ 2\mathrm{O}\,,$$

of the type $-\nu_1 A_1 \rightleftharpoons \nu_2 A_2$ according to te nomenclature of (11.38), with $\nu_1 = -1, \nu_2 = 2$. The equilibrium condition (11.53) becomes in this case

$$-\mu(\mathrm{O_2}) \ + \ 2\mu(\mathrm{O}) \ = \ 0\,.$$

Therefore, in equilibrium $\mu(\mathrm{O_2}) = 2\mu(\mathrm{O})$, that is, the chemical potentials weighted by the stoichiometric coefficients are equal.

Heat of reaction

By substituting in (11.53) the expression $\mu_i = g_i = h_i - T s_i$ of the chemical potentials, one obtains for the equilibrium conditions

$$\sum\nolimits_i \nu_i h_i \; = \; T \sum\nolimits_i \nu_i s_i \,. \tag{11.54}$$

The sum on the left side is the heat of reaction $\Delta H = \sum_i \nu_i h_i$. Since the stoichiometric coefficients of the reactants are negative and those of the products are positive, one can easily see that the heat of reaction ΔH is the difference between the sum of the molar enthalpies of the products (p) and the sum of the molar enthalpies of the reactants (r), each one weighted by the corresponding stoichiometric coefficient:

$$\Delta H \; = \; \sum\nolimits_i \nu_i h_i \; = \; \sum\nolimits_p \nu_p h_p - \sum\nolimits_r |\nu_r| h_r \,. \tag{11.55}$$

Ideal gases, equilibrium constant

By substituting, in the equilibrium condition (11.53), the chemical potential of ideal gases (11.28)

$$\mu_i \; = \; RT\,[\phi_i(T) + \ln P + \ln x_i] \tag{11.56}$$

and separating the terms depending on temperature from the terms depending on pressure, one obtains the *law of mass action*

$$\sum\nolimits_i [\nu_i \ln P + \nu_i \ln x_i] \; = \; \sum\nolimits_i \nu_i \phi_i(T) \,. \tag{11.57}$$

The first member of (11.57) can be re-written as

$$\sum\nolimits_i [\nu_i \ln P + \nu_i \ln x_i] \; = \; \ln \left[P^{\sum \nu_i} \prod x_i^{\nu_i} \right] \tag{11.58}$$

so that the law of mass action is generally expressed as

$$\boxed{P^{\sum \nu_i} \prod x_i^{\nu_i} \; = \; K(T)\,,} \tag{11.59}$$

where $K(T)$ is the *equilibrium constant*

$$\ln K(T) = -\sum\nolimits_i \nu_i \phi_i(T) \,. \tag{11.60}$$

The law of mass action connects the equilibrium molar fractions of the chemical species to the temperature.

Example: Let us consider the gaseous reaction

$$O_2 \; \rightleftharpoons \; 2O \,.$$

From (11.59) one gets

$$K(T) \; = \; P\,\frac{x_{O_2}}{x_O^2} \,.$$

Heat of reaction and equilibrium constant

Let us recall that the functions $\phi_i(T)$ appearing in (11.60) are defined in (11.13)

$$\phi_i(T) = \frac{h_{0i}}{RT} + \frac{1}{RT}\int_{T_0}^{T} c_{pi}\, dT - \frac{s_{0i}}{R} - \frac{1}{R}\int_{T_0}^{T} c_{pi}\, \frac{dT}{T} \,. \tag{11.61}$$

By differentiating ϕ_i with respect to T one obtains the molar enthalpies at the temperature T:

$$\frac{\partial \phi_i}{\partial T} \; = \; -\frac{h_i}{RT^2} \,. \tag{11.62}$$

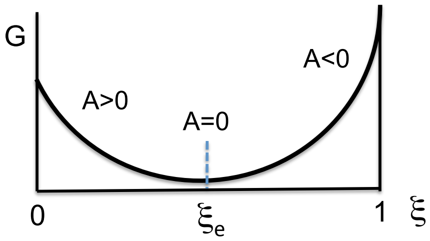


Figure 11.5: Schematic plot of the Gibbs function G as a function of the degree of advancement ξ of a chemical reaction. For the equilibrium value ξ_e, the affinity is null, $A = 0$.

Let us now differentiate the equilibrium constant K from (11.60) with respect to T

$$\frac{\partial \ln K}{\partial T} = -\sum\nolimits_i \nu_i \frac{\partial \phi_i}{\partial T} = \frac{\Delta H}{RT^2} . \tag{11.63}$$

Equation (11.63), called *Van't Hoff isobar*, connects the heat of reaction ΔH to the derivative of the equilibrium constant. It is used experimentally to evaluate ΔH from the values of molar fractions x_i.

Note: The expression of $\phi_i(T)$ contains the two constants h_0 and s_0. The values h_0 of each chemical species are calculated with respect to the standard molar enthalpies of chemical elements, whose value is assumed as zero. The non-arbitrariness of $K(T)$is an experimental proof of the Third Law ($S \to 0$ when $T \to 0$).

11.4.4 Affinity of a chemical reaction

Let us always consider chemical reactions taking place at constant T and p. As it has been already stated, the thermodynamical description of a chemical reaction is possibie even out of equilibrium, provided thermal and mechanical equilibria are guaranteed.
In the differential (11.52) of the Gibbs function at constant T and p

$$(dG)_{Tp} = n_0 \left(\sum\nolimits_i \mu_i \nu_i\right) d\xi , \tag{11.64}$$

the sum $\sum_i \mu_i \nu_i$, that is null in conditions of chemical equilibrium, can be used also to measure the distance of a reaction from equilibrium.
The affinity of a reaction is defined as

$$A = -\sum\nolimits_i \mu_i \nu_i = -\left(\frac{\partial G}{\partial \xi}\right)_{Tp} \frac{1}{n_0} \tag{11.65}$$

thus corresponding, to within the sign, to the derivative of G with respect to ξ (Fig. 11.5). In equilibrium conditions $A = 0$. If $A > 0$, the reaction goes forward (ξ increases). If $A < 0$, the reaction goes backwards (ξ decreases).
Equation (11.64) can thus be synthetically written as

$$(dG)_{Tp} = -n_0 \, A \, d\xi . \tag{11.66}$$

Example 1: Let us again consider the reaction

$$O_2 \rightleftharpoons 2O .$$

The affinity is $A = \mu(O_2) - 2\mu(O)$. If $A > 0$, that is $\mu(O_2) > 2\mu(O)$, the reaction transforms O_2 in 2O. If $A < 0$, that is $\mu(O_2) < 2\mu(O)$, the reaction transforms 2O in O_2.

The affinity corresponds to the difference of the chemical potentials, weighted by the stoichiometric coefficients.

Example 2: Let us consider a reaction among ideal gases. The chemical potential of each gas is given by (11.53): $\mu_i = RT\,[\phi_i(T) + \ln P + \ln x_i]$. The affinity is

$$A \;=\; -\sum\nolimits_i \mu_i \nu_i \;=\; RT\left[\ln K(T) - \ln\left(P^{\sum \nu_i} \prod\nolimits_i x_i^{\nu_i}\right)\right]\,,$$

where $K(T)$ is the equilibrium constant.

Affinity and entropy production

The affinity of a chemical reaction measures the tendency of an irreversible process to take place, as is the case of the gradients of temperature and pressure.
The variation of entropy (11.46)

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \sum \frac{\mu_i}{T}\,dn_i\,.$$

for a chemical reaction at constant T and p can be expressed as

$$dS \;=\; \frac{1}{T}đQ + n_0\,\frac{A}{T}\,d\xi\,, \tag{11.67}$$

where $đQ = dU + p\,dV$ is the exchanged heat and A is the affinity.

Anticipating the language of the Thermodynamics of irreversible processes (Part VI), one can distinguish, for the total entropy variation dS, the contribution due to the exchange with the ambient dS_e and contributions due to entropy creation within the sytem dS_i. In (11.67)

1. $d_eS = đQ/T$ is the variation of the system entropy caused by the exchange of heat with the ambient; $d_eS > 0$ or $d_eS < 0$ according to whether the reaction is endothermic or exothermic.
2. $d_iS = n_0\,(A/T)\,d\xi$ is the variation of the system entropy due by the entropy creation caused by the irreversible chemical reaction; $d_iS > 0$ always.

Affinity and Gibbs function

The differential of the Gibbs function is

$$dG \;=\; dH - T\,dS\,. \tag{11.68}$$

Tking into account that at constant pressure $dH = đQ$, and substituting in (11.68) the expression dS of (11.67), one gest

$$dG \;=\; -n_0\,A\,d\xi\,. \tag{11.69}$$

The reduction of the Gibbs function, $dG < 0$, during the reaction corresponds to the creation of entropy, $d_iS > 0$.

Heat and entropy

The energy balance of a closed system maintained in thermal and mechanical equilibrium is

$$dU \;=\; đQ - p\,dV\,. \tag{11.70}$$

The differential of the internal energy (6.8) can be also expressed as a function of the affinity A

$$dU \;=\; T\,dS - p\,dV + \sum\nolimits_i \mu_i\,dn_i \;=\; T\,dS - p\,dV - n_0 A\,d\xi\,. \tag{11.71}$$

Comparing (11.71) with (11.70) one gets

$$đQ \;=\; T\,dS - n_0 A\,d\xi\,. \tag{11.72}$$

The axchanged heat corresponds to the contribution d_eS of the total entropy variation dS of the system.

11.4.5 Stability of chemical equilibrium

The equilibrium condition of a chemical reaction is $\sum \mu_i \nu_i = 0$, that is $A = 0$.
It has been demonstrated in § 9.6 that the stability of chemical equilibrium for a system with one component requires that

$$\left(\frac{\partial \mu}{\partial n}\right)_{Tp} \geq 0\,. \tag{11.73}$$

The equilibrium condition (11.73) can be generalised to the case of chemical reactions. For more than one component, the chemical potential μ of (11.73) has to be substituted by $\sum \mu_i \nu_i$, and the deviation from equilibrium is measured by $d\xi$ instead of by dn. The stability condition of chemical equilibrium is thus

$$\frac{\partial}{\partial \xi}\left[\sum \mu_i \nu_i\right] \geq 0\,, \qquad \text{ovvero} \quad \left(\frac{\partial A}{\partial \xi}\right)_{Tp} \leq 0\,. \tag{11.74}$$

If a chemical reaction is in equilibrium, $\xi = \xi_e$, a positive variation of ξ at constant T and p gives rise to a reduction of A, and viceversa. Otherwise stated, the affinity A varies in such a way as to drive the system towards equilibrium.
Considering the Gibbs function (Fig. 11.5), in equilibrium conditions

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{Tp} = -n_0 \left(\frac{\partial A}{\partial \xi}\right)_{Tp} \geq 0\,. \tag{11.75}$$

11.4.6 Thermodynamics and Chemical Kinetics

Thermodynamics deals with equilibrium conditions; out of equilibrium, Thermodynamics allows one to calculate the affinity, that is the force driving a chemical reaction. Thermodynamics doesn't deal with the velocity of chemical reactions. The velocity of chemical reactions is studied by Chemical Kinetics.
The direction of a chemical reaction is *reagenti→prodotti* if the Gibbs free energy of the products is lower than the one of the reactants.
The velocity of the reaction depends on the height of the potential barrier to be overcome, called the *acivation energy* E_a.
The velocity of a chemical reaction can be increased

a) by increasing the temperature, thus reducing the ratio E_a/k_BT ;
b) by using catalysts, that reduce E_a.

Part III

Statistical Thermodynamics

Part III contains a tutorial introduction to Statistical Thermodynamics.

Statistics allows the interpretation of the laws and of the quantities of macroscopic Thermodynamics, introduced in Part I and Part II, in terms of the microscopic structure of matter. The largest is the number of elementary constituents of a system (atoms, molecules, normal vibrational modes, photons, ...), the more stable become some of its average properties, that correspond to macroscopic thermodynamic quantities.
In particular, by statistical methods one can attribute an intuitive meaning to the entropy and to the Second Law of Thermodynamics.

In Chapter 12, the classical and quantum descriptions of systems containing an exceedingly large number of elementary constituents are reviewed, and the basic concept of *statistical ensembles* is introduced.
Chapter 13 is devoted to the *micro-canonical ensemble*, suited for the treatment of isolated systems. The simplest intuitive statistical interpretation of entropy is given within the framework of the micro-canonical ensemble.
Chapter 14 is devoted to the *canonical ensemble*, suited for the treatment of systems maintained at constant temperature and volume. The canonical approach is very powerful and allows a relatively simple connection between the macroscopic thermodynamic quantities and the structure of the energy levels of a system containing a large number of elementary constituents. To this micro-macro connection is devoted Chapter 15.

For the sake of completeness, Part III is concluded by Chapter 16, devoted to the Particle Statistics.

Chapter 12

Introduction to Statistical Thermodynamics

This chapter begins (§ 12.1) with an introductory discussion of the main differences between the macroscopic approach of the previous Parts I and II and the statistical approach of this Part III. The classical and quantum description of the microscopic states of a single particle and of a system of many particles are rewiewed in § 12.2 ad § 12.3, respectively. The basic methods of statistics are introduced in § 12.4, and in particular § 12.5 is devoted to the basic concept of statistical ensembles.

12.1 Macroscopic Thermodynamics and statistical approach

Let us begin our discussion by reviewing some relevant concepts of the macroscopic Thermodynamics, introduced in Part I and Part II.

- The equilibrium state of a thermodynamic system is described by a limited number of macroscopic variables, such as the internal energy U, the volume V, the temperature T, and so on. For example, to characterise the state of a simple system with one component, only two coordinates are sufficient, such as pressure and temperature (p, T) or internal energy and volume (U, V).
- The criterion of spontaneous evolution between two equilibrium states of an isolated system, triggered by the removal of some constraints, is the increase of entropy S.
- A number of laws of general character, suited for whichever system, independent of its constitution, are deduced fro a very small number of simple axioms.
- The thermodynamical properties of a given system (a real gas, a solid, a magnetic system, and so on) can be obtained by measuring a small number of macroscopic quantities and determining the correlations among them; the experimental results are summarised in a small number of empirical equations of state, from which one can obtain the fundamental equation $S = S(U, V, N_i)$ or other equivalent fundamental equations.

The axioms and the laws of macroscopic Thermodynamics prescind from the very nature of the considered system. This property explains the broad range of applicability of macroscopic Thermodynamics to systems of very different nature.

It is however in some respects unsatisfactory the fact that two fundamental quantities, that is the entropy S and, to a lesser extent, the temperature T are not amenable to a simple intuitive interpretation, as is instead the case for the mechanical quantities such as the volume V or the pressure p.

The development of the atomistic theory allowed one to consider the thermodynamic systems as composed by an exceedingly large number of microscopic constituents, typically atoms or molecules. In the second half of the XIX century a big effort was made, mainly by J.K. Maxwell, L. Boltzmann and J.W. Gibbs, to find an interpretation of the temperature and of the Second Law funded on the microscopic structure of the thermodynamical systems. The basic idea is that the thermodynamical quantities can be connected to some average properties of the microscopic state of the system.

The main difficulty of this approach is that the microscopic state cannot be exactly known. In Classical Physics one cannot actually measure the instantaneous values of position and velocity of a very large number ($\simeq 10^{23}$) of atoms or molecules; and in any case the measures would be affected by experimental uncertainties. In Quantum Physics one should take into account also the uncertainty principle, that limits the accuracy of simultaneous measures of position and velocity.

Moreover, a given macroscopic state can correspond to a very large number of possible microscopic states. For example, let us consider a gas contained in a rigid isolated vessel, with constant internal energy U and volume V; the well defined macroscopic thermodynamical state can in principle correspond, from the point of view of classical Physics, to an infinite number of microscopic states, that is to an infinite number of possible distributions of positions and velocities of the molecules. Otherwise stated, one can have only a partial knowledge of the microscopic state of a given system.

The evaluation of some average properties of an ensemble starting from a limited number of pieces of information is a frequently encountered problem, not only in strictly scientific fields, but also in sociology, demography, and so on; the problem can be solved by statistical methods, that can be different for different applications.

A reader expert in Physics is familiar with the statistical methods employed in the laboratories to evaluate the average value and the uncertainty of a physical quantity on the base of a limited number of measurements. In that case, one estimates the properties of an infinite population (the ensemble of all the possible results of measurement of a physical quantity) on the base of a limited sample (the values actually measured in the laboratory).

In the present case of Thermodynamics, the statistical methods allow the evaluation of some relevant average properties of the microscopic state of a system, made by an exceedingly large number of elementary constituents, on the base of a limited number of information elements.
To this aim, the basic instrument is represented by the *statistical ensembles*, first introduced by J.W. Gibbs. A statistical ensemble is a collection of a very large number of copies of the considered macroscopic system; each copy is characterised by a different microscopic state, compatible with the known macroscopic properties (e.g. the internal energy U and the volume V). The different microscopic states corresponding to different copies of the system are considered as equiprobable. The average microscopic properties of the system are calculated as averages on the copies of the the system making up the statistical ensemble.

We will deeply analyse the concept of statistical ensemble and its use later on, in §12.4 and §12.5. Let us here summarise the basic properties of Statistical Thermodynamics.

- The microscopic structure of thermodynamical systems is considered; the systems are made by an exceedingly large number of elementary constituents and of microscopic quantities describing their state.
- In order to cope with the exceedingly large number of microscopic variabes it is necessary to resort to statistical methods. It is just the exceedingly large number of elementary constituents which allows some average properties to be stable in time and to be connected to the relevant quantities of the macroscopic Thermodynamics.
- One can attribute a microscopic meaning to the quantities entropy S and temperature T and give a microscopic interpretation to the principle of entropy increase in isolated systems (Second Law of Thermodynamics).
- In a limited number of simple cases one can deduce the equations of state from the microscopic structure and the forces of interaction between elementary constituents.

In Statistical Thermodynamics, the energy is assumed as a primitive concept. As in the axiomatic approach of macroscopic Thermodynamics of Part II, also in Statistical Thermodynamics the conservation of energy is assumed as already established, explained by the symmetry of the fundamental interaction forces with respect to time translations.

Starting point of Statistical Thermodynamics is thus the concept of microscopic state and of its analytic description.
In what follows, the elementary constituents of a thermodynamic system are conventionally called "particles", whether they actually be particles (typically atoms or molecules) or collective excitations (e.g. the normal modes of vibration of a solid or of an electromagnetic field).

The description of the microscopic state of a thermodynamic system is actually far from trivial, and is different for the classical and quantum approaches. In what follows, we will consider first the description of the state of a single particle (§ 12.2) and then of a thermodynamic system containing an exceefingly large number of particles (§ 12.3). The fundamental concept of statistical ensemble will be considered in§ 12.5.

12.2 Microscopic state of a single particle

For concreteness, let us consider a system made by a single helium atom (He), free to move in a cubic vessel of side L=0.1 m. Let us suppose that the collisions of the atoms with the wall of the vessel are elastic, so that the kinetic energy of the atom remains constant. At last, let us assume that the kinetic energy of the atom be $\epsilon = 0.04\,\text{eV} = 6.4 \times 10^{-21}$ J (corresponding to the average kinetic energy of helium atoms in a vessel maintained at the temperature of 300 K); such an energy value is small with respect to the excitation and ionisation energies of electrons in an He atom, so that for our purposes the atom can be considered as structureless.
This simple example should allow us to stress the main differences between the classical and quantum approaches.

12.2.1 The classical approach

According to classical Physics, the dynamical state of the atom is characterised by the instantaneous values of the three spatial coordinates and of the three components of the linear momentum. The six values x, y, z, p_x, p_y, p_z identify a point in the abstract six-dimensional *phase space.*
As time goes on, the atom moves along a trajectory in the three-dimensional real space; the spatial coordinates and the momentum components are progressively modified; correspondingly, the representative point in the six-dimensional phase space moves along a trajectory too.
Within the vessel, the trajectory of the atom is rectilinear, with constant p_x, p_y, p_z values. When the atom impinges on a wall of the vessel, it is elastically scattered and one of the momentum components changes its sign.

(?) Plot a possible trajectory in different two-dimensional projections of the phase space: $x - y$, ... $x - p_x$, ... $p_x - p_y$, ...

The evolution of the dynamical state of the atom is perfectly deterministic.
By varying the initial conditions, one can obtain infinite different trajectories in both the real and phase spaces. All the possible trajectories have anyway to be consistent with the conservation of kinetic energy

$$\epsilon \;=\; \frac{1}{2m}\,(p_x^2 + p_y^2 + p_z^2) \;=\; \text{constant}\,. \tag{12.1}$$

Because of (12.1), the three momentum components are not independent: the possible trajectories in the six-dimensional phase space are constrained to belong to a five-dimensional hyper-surface.

Actually, one should take into account the fact that the collisions of the atom with the vessel walls are generally not perfectly elastic, so that the conservation of energy (12.1) is not perfectly fulfilled. Moreover, the possible experimental measurement of the dynamical state at a given time is affected by uncertainty, that corresponds to an uncertainty of the energy value ϵ. As a consequence, the trajectory in the phase space is constrained within a layer of points characterised by energy values $\epsilon \pm \delta\epsilon$ instead of within the five-dimensional hyper-surface ϵ=constant, of zero thickness. This topic will be considered again later on.

12.2.2 The quantum approach

In the quantum approach, because of the Heisenberg uncertainty principle, one cannot know at the same time the exact values of the coordinates and of their conjugate momenta; as a consequence, the concept of trajectory in both the real and phase spaces is meaningless.
A stationary state of an atom with energy ϵ within in a cubic vessel of side L is expressed, in the Dirac formalism, as

$$|\psi_n(t)\rangle \;= |\phi_n\rangle\, e^{-i\epsilon t/\hbar}\,, \tag{12.2}$$

where the exponential $\exp(-i\epsilon t/\hbar)$ gives the trivial dependence on time and $|\phi_n\rangle$ is a solution of the time-independent Schrödinger equation

$$\mathcal{H}\,|\phi_n\rangle = \epsilon\,|\phi_n\rangle\,. \tag{12.3}$$

$\mathcal{H}$ is the Hamiltonian operator, corresponding to the total energy (in the present case the energy is purely kinetic). The states $|\phi_n\rangle$ are energy eigenstates. Different states $|\phi_n\rangle$ can be solutions of (12.3) for a given value of energy ϵ: the eigenvalue ϵ of energy is thus degenerate.

The meaning of (12.2) and (12.3) can be more easily grasped if the equations are projected in the coordinate reprentation. In the coordinate representation, the states $|\psi_n(t)\rangle$ correspond to three-dimensional stationary waves

$$\psi_{n_x n_y n_z}(x,y,z,t) = \psi_{n_x}(x,t)\,\psi_{n_y}(y,t)\,\psi_{n_z}(z,t)\,; \tag{12.4}$$

The finite size of the vessel imposes discrete values to the components of the wave-vectors: $\vec{k} = \vec{p}/\hbar$: $k_x = n_x\pi/L, k_y = n_y\pi/L, k_z = n_z\pi/L$.
The relation between the energy ϵ and the components of the wave-vectors is

$$\epsilon \;=\; \frac{\hbar^2}{2m}\,(k_x^2+k_y^2+k_z^2) \;=\; \frac{\pi^2\hbar^2}{2L^2m}\,(n_x^2+n_y^2+n_z^2)\,, \tag{12.5}$$

where the n_i are positive integer numbers. To a given energy value ϵ different terns of values (n_x, n_y, n_z), say different eigenstates, can correspond: as already observed, the energy eigenvalue ϵ is degenerate.
Each energy eigenstate is thus characterised by three integer numbers, that is by a point in a three-dimensional abstract lattice spanned by the values (n_x, n_y, n_z). The three-dimensional abstract lattice spanned by the discrete values (n_x, n_y, n_z) can be considered as the quantum analogue of the classical phase space.

The energy eigenstates $|\phi_n\rangle$ are not the only possible quantum states of the system, that is of the helium atom. Any linear combination of the eigenstates $|\psi_n\rangle = |\phi_n\rangle \exp(-i\epsilon t/\hbar)$, that is

$$|\Psi(t)\rangle = \sum_n c_n(t)|\phi_n\rangle\,, \tag{12.6}$$

is again a solution of the Schrödinger equation and thus represents a possible a possible quantum state of the atom. The meaning of the coefficients $c_n(t)$ of (12.6), that contain the trivial dependence on time, is the following. A suitable measurement performed on the system in the state $|\Psi(t)\rangle$ will give as a result a well defined eigenstate $|\phi_n\rangle$, with probability $|c_n|^2$. The coefficients have to satisfy the normalisation condition of the probability theory $\sum |c_n(t)|^2 = 1$.

Note: By means of superpositions (12.6) of states of different linear momenta one can obtain wave-packets. In a wave-packet the linear momentum is not univocally defined; the uncertainty of the linear momentum allows the reduction of the uncertainty of the position and a partial spatial localisation.

A state such as $|\Psi(t)\rangle$ of (12.6) is said to be a "pure state", whose knowledge corresponds to the full knowledge of the dynamical quantum state of the atom. Once a system has been prepared in a state $|\Psi\rangle$ at the time $t = 0$, its time evolution is determined by the time-dependent Schrödinger equation.

Let us stress the difference between classical state and quantum state. In the classical case, the state of a particle is characterised by a point in the phase space. In the quantum case, not only is the simultaneous knowledge of position and momentum impossible; the quantum state can also be a linear superposition (12.6) of many eigenstates of the linear momentum, so that the state of the particle is characterised by all the discrete points of the (n_x, n_y, n_z) space which correspond to the eigenstates $|\phi_n\rangle$ of (12.6), each one weighted by the corresponding probability $|c_n|^2$.

The expectation value of an observable quantity A in the pure state $|\Psi(t)\rangle$ is $\langle A\rangle = \langle\Psi|A|\Psi\rangle$. By exploiting the projection (12.6), the expectation value $\langle A\rangle$ can be referred to the base states $|\phi_n\rangle$:

$$\langle A\rangle = \sum_{nm} c_n^* c_m \langle\phi_n|A|\phi_m\rangle = \sum_{nm} c_n^* c_m A_{nm}\,; \tag{12.7}$$

the values A_{nm} are called the matrix element of the variable A in the base $|\phi_n\rangle$.

Note: To simplify the notation, A will here identify both the observable quantity and the corresponding quantum operator.

Also in the quantum approach, as in the classical approach, a perfectly defined energy ϵ is not realistic. In addition to the reasons already considered for the classical case, in the quantum case one should take into account that, because of the principle of uncertainty energy-time, obtaining an exact value of energy would require an infinite observation time.

Also in the quantum case, thus, one has to consider an interval of energy values $\epsilon \pm \delta\epsilon$, to which it generally corresponds a very large number of terns (n_x, n_y, n_z).

The density matrix

It is now convenient to introduce an alternative description of the pure states $|\Psi(t)\rangle$, as a preliminary step to the statistical study of many-particle systems. The new description more clearly enlightens the probability distribution of the pure state in the (n_x, n_y, n_z) space.

Let us first stress that the coefficients $c_n(t)$ are the projections of the pure state $|\Psi(t)\rangle$ on the eigenstates $|\phi_n\rangle$

$$c_n(t) = \langle\phi_n|\Psi(t)\rangle\,. \tag{12.8}$$

As a consequence, the products

$$c_n^* c_m = \langle\phi_n|\Psi\rangle\langle\Psi|\phi_m\rangle = w_{mn} \tag{12.9}$$

can be considered as the matrix elements in the base $\{|\phi_m\rangle\}$ of an operator $w = |\Psi\rangle\langle\Psi|$, called the *density operator*.

The normalisation condition of the c_n coefficients for a pure state can be expressed in terms of the trace of the density matrix, that is of the sum of its diagonal elements:

$$\sum\nolimits_n |c_n|^2 = \sum\nolimits_n w_{nn} = \mathrm{Tr}(w) = 1\,. \tag{12.10}$$

The expectation value (12.7) of an observable A can be expressed in the alternative form in terms of the density matrix:

$$\begin{aligned}\langle A\rangle &= \sum_{nm} c_n^* c_m A_{nm} = \sum_{nm} \langle\phi_m|\Psi\rangle\langle\Psi|\phi_n\rangle\langle\phi_n|A|\phi_m\rangle \\ &= \sum_{nm} \langle\phi_m|w|\phi_n\rangle\langle\phi_n|A|\phi_m\rangle \\ &= \sum_{m} \langle\phi_m|wA|\phi_m\rangle = \mathrm{Tr}(wA)\,; \end{aligned} \tag{12.11}$$

it is the trace of the product wA of the two matrices. In the second last equality, the closure relation $\sum_n |\phi_n\rangle\langle\phi_n| = 1$ has been exploited.

12.3 Microscopic state of a many-particle system

Let us now consider a system composed by a number N of particles; for the systems of thermodynamical interest, N is an exceedingly large nuber, typically of the order of the Avogadro number.
To take advantage of the previous treatment of a single particle, let us again consider a cubic vessel of side L=0.1 m and suppose that the vessel contains helium gas in standard conditions of temperature and pressure, so that $N \simeq 10^{22}$. Let us neglect, for the moment, any interaction between atoms, and consider the collisions of atoms with the vessel walls as perfectly elastic. At last, let us suppose, again for the moment, that all the atoms have the same energy ϵ.

12.3.1 Ideal model

Classical description

In the classical approach, the instantaneous microscopic state of the system is characterised by the values of the $3N$ coordinates and of the $3N$ components of the linear momenta of the N atoms: $q_i, p_i (i = 1, ...3N)$. At a given time, the state of the system is characterised by N points in the real three-dimensional space and by a single point in the $6N$-dimensional abstract phase space. The total energy of the system is the sum of the energies of the single atoms, $E = N\epsilon$. As time goes on, each atom moves along its own trajectory in the three-dimensional real space; the entire system moves along a single trajectory in the $6N$-dimensional phase space. Because the total energy E is constant by hypothesis, the representative point in the phase space is constrained to move on a ($6N$-1)-dimensional hyper-surface.

Quantum description

In the quantum approach, each eigenstate of a single atom i is characterised by three integer numbers, n_{ix}, n_{iy}, n_{iz}. A system of N atoms has $f = 3N$ degrees of freedom (three for each atom). The total energy E of the system is $N\epsilon$.
The eigenstates $|\Phi_s\rangle$ o the energy E of the entire system are obtained by solving the time-independent Schrödinger equation

$$\mathcal{H}_0 \, |\Phi_s\rangle = E \, |\Phi_s\rangle \,, \tag{12.12}$$

where $\mathcal{H}_0$ is the unperturbed Hamiltonian, which does'n take into account the possible interactions between the gas atoms.
All the possible eigenstate of the system are represented by a lattice of $3N$ integer values (n_{ix},n_{iy}, n_{iz}), where $i = 1...N$, in an abtract $3N$-dimensional space. Each single eigenstate $|\Phi_s\rangle$ of the system is thus represented by a single point of the discrete lattice.

The pure quantum state of the system, in its more general form, is represented by a linear combination of the system eigenstates

$$|\Psi(t)\rangle = \sum_k c_s(t)|\Phi_s\rangle \,, \tag{12.13}$$

where, if no interactions are present between the atoms, the $c_k(t)$ coefficients only contain the trivial dependence on time.
The linear superposition (12.13) is conveniently described by means of the density operator $w = |\Psi\rangle\langle\Psi|$ which, projected on the energy eigenstates, gives rise to the density matrix $w_{mn} = \langle\Phi_n|\Psi\rangle\langle\Psi|\Phi_m\rangle$.
A pure state (12.13), linear combination of energy eigenstates, is represented by a cluster of points of the lattice of $3N$ integer values (n_{ix},n_{iy}, n_{iz}), each point being weighted by a diagonal element w_{kk} of the density matrix.

Note: In the classical case, the state of the system is represented by a single point in the phase space; the points moves along a trajectory even is no interactions between atoms are present. In the quantum case, a pure stationary state is represented by a cluster of points in the lattice of quantum numbers (n_{ix},n_{iy}, n_{iz}) which remains unaltered if no interactions between the atoms are present.

12.3.2 Realistic description

The above descriptions, both classical and quantum, of a many-atomic system are not realistic, for at least two reasons, that are analysed below.

1.

The ideal gas model in which the atoms share the same purely kinetic energy is clearly unrealistic. First of all, it is practically impossible to prepare a system in which all the atoms have exactly the same energy ϵ. Secondly, all the atoms interact; even for noble gases the interaction, although very weak (Van der Waals forces), is not negligible. As a consequence, the total energy E of the system, even if it is maintained constant by external constraints, is differently distributed among the different atoms and between the potential and kinetic components.

In the *classical description*, this means that on the ($6N$-1)-dimensional hyper-surface in the phase space, corresponding to the total energy E, a much larger number of states is possible, and also a much larger number of trajectories, with respect to the case in which all atoms share the same constant energy ϵ.

In the *quantum description*, the groups of $3N$ discrete values in the $3N$-dimensional (n_{ix}, n_{iy}, n_{iz}) space are constrained by the condition $\sum_i \epsilon_i = E$, that is less restrictive than $E = N\epsilon$.

The presence of interactions between the atoms and with the vessel walls requires that, in the Schrödinger equation, an interaction term $\mathcal{H}_{\mathrm{int}}$ has to be added to the unperturbed Hamiltonian $\mathcal{H}_0$. For weak interactions, one can resort to perturbative methods (further details can be found in standard texts on quantum mechanics). The instantaneous state of the system can again be described by a linear combination (12.13) of stationary energy eigenstates; the effects of the interactions are transitions of the systems among the different stationary states. As time goes on, the cluster of points representing the system in the (n_{ix}, n_{iy}, n_{iz}) lattice moves.

2.

In practice, no system can be considered as completely isolated. The interaction of the system with its environment, even if weak, affect the microscopic state of the system and continuously modify its total energy E. In general, the fluctuations with respect to the average value E are small, but not completely negligible. In addition, one has to consider the contribution of the measurement uncertainty and, in the quantum case, of the time-energy uncertainty. In conclusion, the total energy of the system should be considered as included in a layer of width δE around the nominal value E.

This situation is easily understood in the classical case, where the energy values can be continuously changed; it requires more attention in the quantum case, where the energy values are quantised. For a system with a very large number of elementary constituents, the possible levels of total energy E are very densely spaced (consider for example the energy difference between two levels characterised by $3N-1$ equal quantum numbers $n_{i\alpha}$ and the residual quantum number differing by the unity), so that also very weak interactions with the environment can modify the total energy of the system.

Note: It is interesting to compare the quantum description of a simple system, such as the atomic structure, and of a macroscopic system. To maintain an atom in the stationary state of its electronic structure is relatively easy, because the interactions of the atom with its environment are generally weak with respect to the energy difference between the ground state and the first excited levels of the atom. For a macroscopic system the situation is completely different, because the distance between the total energy levels is very small.

12.3.3 Other examples

Up to now we have referred to the particularly significant case of a gas contained in a vessel. Let us now shortly consider two other simple examples, that will be analysed in more detail later on and for which only the quantum approach is relevant.

Example 1: A system consists in N independent harmonic oscillators (it is the case of the simplified Einstein model for the atomic vibrations in crystalline solids). The degrees of freedom are

$f = N$. The energy of the i-th oscillator is $\epsilon_i = (1/2 + n_i)\,\hbar\omega$. The energy levels are not degenerate. The microstate of the system is characterised by the N values n_i, that is by the amounts of energy stored in each oscillator.

Example 2: A system consists in N independent spins, with fixed spatial positions. Each spin can assume two values, *up* and *down*. The degrees of freedom are $f = N$. The microstate of the system is characterised by the orientations of all the N spins.

The examples up to now considered refer to systems of "weakly interacting" particles, for which the microscopic state of the entire system can be easily expressed in terms of the microscopic states of the single constituents. In any case, the residual weak interactions (due for example to the collisions between the gas molecules) contribute to the evolution of the microscopic state of the system.

The condition of weak interaction, that can be treated by perturbative methods in the quantum cases, facilitates the understanding of the foundations of the statistical description, but is not strictly necessary. Also the systems whose elements are strongly interacting can be treted by statistical methods, as will be explained later on.

12.4 The methods of StatisticalThermodynamics

Aim of Statistical Thermodynamics is to connect the macroscopic thermodynamical quantities to average properties of the microscopic states of a system.

Let us consider a system maintained in a state of *macroscopic equilibrium*: as time goes on, its *microscopic state* is continuously modified. A first approach to the problem of the micro-macro relation consists in trying to connect the macroscopic quantities to suitable averages of time-dependent microscopic properties, that is to connect the macroscopic quantities to the *time averages* of microscopic properties.

However, because of the very large number of particles and of the complexity of the interactions involved, a description of the microscopic time evolution of a thermodynamical system is far from trivial, if not totally out of question, both for a classical approach, by following the trajectory of the system in the phase space, and for a quantum approach, by following te evolution of a pure state like (12.13). Moreover, an a priori evaluation of the duration of the time interval sufficient to obtain significant averages is far from trivial too.

The alternative and most effective solution of the problem, first suggested by G.W. Gibbs, consists in substituting the time averages with *canonical averages*. The canonical averages are obtained by comparing the instantaneous microscopic states of an exceedingly large number of copies of the same macroscopic system. A suitably built up set of the copies of the system is called a *statistical ensemble*.

General properties of statistical ensembles

The *statistical ensembles* are made by a very large number of copies of a given system, that share the same macroscopic properties (e.g. the internal energy or the temperature) but differ in the properties of the microscopic state (e.g. the distribution of ebergy among the different atoms).

The statistical ensembles are built up differently for different situations, as will be shown later on in § 12.5. We consider here only their general properties, that are different for the classical and the quantum case, respectively.

It is worth noting that the statistical ensembles can describe not only the properties of systems in thermodynamical equilibrium, but also the evolution of systems out of equilibrium.

Classical case: lthe density in the phase space

For concreteness, let us again consider the example of a gas maintained in a vessel with constant volume and total energy. In the classical case, the microscopic state of an N-particle system is represented by a point in the $6N$-dimensional phase space, whose position evolves in time according to the laws of Newton Mechanics.

A statistical ensemble is made by a large number $\mathcal{N}$ of copies of the given system; the statistical ensemble is thus represented by $\mathcal{N}$ independent points in the phase space, each one of which moves in time according to the Newton Mechanics. Clearly the number $\mathcal{N}$, though in principle arbitrary, has to be very large and the statistical ensemble has to guarantee a fair representation of the different possible microscopic states; this point will be considered in more detail later on.

Since the number $\mathcal{N}$ of copies of the system is arbitrarily large, the number of points (that is of systems) per unit volume of the phase space is conveniently represented by a *phase density* $\rho(q,p,t)$, where by (q,p) all the coordinates and momenta of the particles are synthetically indicated and t is time.

As time goes on, the single systems composing the statistical ensemble move along different trajectories of the $6N$-dimensionale phase space; the phase density $\rho(q,p,t)$ is correspondingly modified in time. The properties of the density $\rho(q,p,t)$ are established by the *Liouville theorem*, derived from Newton Mechanics principia. The main conclusion of the Liouville theorem is that $d\rho/dt = 0$, say that the *total* derivative of the phase density ρ with respect to time is always null: the phase density remains constant along the trajectories of the systam in the phase space; as a consequence, also the volume dv occupied by a number dN of points at a given time is not modified as the points move along their trajectories (the single trajectories can anyway progressively diverge and the volume dv can progressively loose compactness, still maintaining unaltered its total value).

Let us now consider the particular case of a system in a state of *macroscopic equilibrium*, that is of thermodynamical equilibrium. In such a case, the macroscopic properties of the system are time invariant; therefore, the properties of the statistical ensemble are time invariant too. Therefore, the phase density has to be stationary, its value has to be time invariant in every point of the phase space, so that its *partial* derivative with respect to time is null:

$$\frac{\partial\rho(q,p)}{\partial t} = 0 \qquad \text{(for macroscopic equilibrium)}\,. \tag{12.14}$$

Two solutions of (12.14) are particularly important from the physical standpoint:

1. $\rho(q,p)$= constant in the portion of phase space which fulfils the given macroscopic conditions; this solution corresponds to the *microcanonical* statistical ensemble, suitable to describe systems at constant total energy (§ 12.5 and Chapter 13);
2. $\rho(q,p) = \rho(\alpha)$: that is ρ can be expressed as a function of a quantity α which is a constant of motion, typically energy; this solution corresponds to the *canonical* statistical ensemble, suitable o describe systems maintained at constant temperature (§ 12.5 and Chapter 14).

As already observed, an exact determination of position and velocity of the single particles is actually impossible event in the classical case; the instantaneous state of the entire system cannot thus be realistically represented by a a single point in the phase space. To take into account the uncertainties of positions and velocities, it is convenient to divide the phase space in volume elements δv, whose extent (equal for all elements) corresponds to the uncertainty of the microscopic state of the system. To the microstates belonging to a given volume element δv of the phase space one attributes a value of probability $\delta P = \int_{\delta v} \rho(q,p,t)\, dv$, corresponding to the integral of the phase density ρ within the volume δv.

The transition from the continuous description in terms of phase density ρ to the discrete description in terms of volume elements δv and corresponding probability values δP plays an important role in the classical statistical definition of the entropy as well as in the connection between the classical and quantum approaches, as we will see later on.

Quantum case: the statistical density matrix

In the quantum case, a single system is described by a pure stationary state (12.13), linear superposition of many energy eigenstates, that can be conveniently described by the density operator $w = |\Psi\rangle\langle\Psi|$ and by its projection on the energy eigenstates, that is by the density matrix $w_{mn} = \langle\Phi_n|\Psi\rangle\langle\Psi|\Phi_m\rangle$.

For an ideal gas of N atoms, a single energy eigenstate $|\Phi_s\rangle$ is represented by a point in the discrete lattice of the possible values (n_{ix}, n_{iy}, n_{iz}) in an abstract $3N$-dimensional space. A pure state (12.13) is represented by a cluster of points, each one weighted by the corresponding diagonal element of the density matrix $w_s = w_{ss}$. Because of the weak interactions among the atoms and with the vessel walls, the cluster of points evolves as time goes on.

A statistical ensemble is made by a large number $\mathcal{N}$ of copies of the given system. The representation of the statistical ensemble in the (n_{ix}, n_{iy}, n_{iz}) lattice is made by $\mathcal{N}$ independent clusters, each one of which corresponds to a pure state (12.13). Because of the interactions among the atoms and with the vessel walls, the set of clusters evolves as time goes on.
The statistical ensemble is thus a mixture of pure states $|\Psi_k\rangle$, each one of which is characterised by a density operator $w_k = |\Psi_k\rangle\langle\Psi_k|$ which gives its distribution of the energy eigenstates.
Each pure state of the statistical ensemble is characterised by a probability P_k (corresponding to the probability of the volume elements δv of the phase space in the classical case).
The statistical ensemble is conveniently described, in the quantum case, by the *statistical density* operator $\tilde{w}$, defined as the sum of the densities w_k of the single pure states, weighted by the corresponding probabilities P_k:

$$\tilde{w} \;=\; \sum_k p_k \, w_k \;=\; \sum_k P_k \, |\Psi_k\rangle\langle\Psi_k| \,. \tag{12.15}$$

The statistical density takes into account two different probabilistic effects, the first one intrinsic to the quantum description, the second one due to the statistical mixture; the two contributions are indistinguishable in practice, even if they correspond to two intrinsically different effects: a pure state is a linear combination of eigenstates, and as such subject to interference effects, the statistical ensemble is a simple weighted sum of pure states.
The expectation value of an observable quantity A can be expressed as a function of the matrix elements of the statistical density operator, that is as a function of the elements of the statistical density matrix:

$$\begin{aligned} \langle A\rangle \;&=\; \sum_k p_k \sum_{mn} (c_k)_m (c_k)^*_n A_{nm} = \sum_k p_k \sum_{mn} \langle\phi_m|w_k|\phi_n\rangle\langle\phi_n|A|\phi_m\rangle \\ &=\; \sum_m \langle\phi_m|\tilde{w}A|\phi_m\rangle = \mathrm{Tr}(\tilde{w}A) \,. \end{aligned} \tag{12.16}$$

The expectation value of an observable A is thus the trace (sum of the diagonal elements) of the product of the two matrices representing $\tilde{w}$ and A in the base $|\phi_n\rangle$.
One can easily verify that $\mathrm{Tr}(\tilde{w}) = 1$.

12.5 Statistical ensembles

Statistical Thermodynamics makes use of statistical ensembles, that is of sets of copies of a given system sharing the same macroscopic properties but differing in the microscopic properties.
The statistical ensembles can be built up in different modes depending on the conditions imposed to the given thermodynamical system.

12.5.1 Statistical ensembles for systems in equilibrium

Let us consider here the three statistical ensembles most frequently used to study the properties of systems in thermodynamical equilibrium.

Microcanonical statistical ensemble

The microcanonical statistical ensemble is made by copies of *isolated systems*, that is of systems with constant energy $E \pm \delta E$; the uncertainty δE takes into account the unavoidable interactions of the system with its environment.

The microcanonical ensemble is based on a fundamental postulate, that is on the hypothesis of *equal a priori probability* of all the microstates, that is of the equi-probability of the singe systems that compose the ensemble. The validity of such a fundamental postulate is basically guaranteed by the practical verification of its consequences.

- In the *classical case*, the microcanonical ensemble is represented by a set of points in the phase space, grouped in a layer corresponding to the energy values between E and $E + \delta E$. The equal a priori probability implies that the phase density $\rho(q, p)$ is uniform in the allowed energy layer.
- In the *quantum case*, the microcanonical ensemble is represented by a set of points in the lattice spanned by the values of quantum numbers corresponding to the possible energy eigenstates. To each one of these points it corresponds the same probability P_k

The microcanonical ensemble, that will be considered in detail in Chapter 13, is the statistical equivalent of the entropy representation in the macroscopic Thermodynamic (Chapter 5). The microcanonical ensemble is very important from the fundamental point of view, since it allowed Boltzmann to obtain the famous simple relation (13.9) between the entropy and the number of microstates. It has however less practical interest, due to the difficulty of the enumeration of the microstates in not so simple systems, as well as because Thermodynamics seldom has to deal with really isolated systems.

Canonical statistica ensemble

The canonical statistical ensemble is made by copies of a given system maintained at constant volume and temperature; to that purpose, the system is in contact with a reservoir with which it can exchange energy E. The canonical ensemble is thus connected to thermal equilibrium and to the statistical definition of temperature.
The canonical ensemble, that will be considered in detail in Chapter 14, is the statistical equivalent of the Helmholtz representation of macroscopic Thermodynamics (Chapter 7). The phase density (in the classical case) and the microstates probability (in the quantum case) are not uniform, as is the case of the microcanonical ensemble, but obey a well defined distribution as a function of energy, the so-called canonical distribution.
One will see in Chapter 15 that all the laws of Thermodynamics valid for closed systems with a constant number of elementary constituents can be derived from the study of the properties of the canonical ensemble. One will also see that, for systems with a very large number of constituents, the energy distribution is sharply peaked around the average value, so that the canonical distribution is suitable to describe also systems which are practically isolated.

Grancanonical statistical ensemble

The grancanonical statistical ensemble is made by copies of a given system maintained at constant volume and in contact with a reservoir which allows the exchange of bot energy and matter; the grandcanonical ensemble is connected to the definition of the chemical potential (in addition of temperature).
In the following, the grandcanonical ensemble will be no more considered.

12.5.2 The ergodic problem

The method of statistical ensembles, developed by J.W. Gibbs at the end of the XIX century, has been particularly effective in the development of Statistical Mechanics and Statistical Thermodynamics. The macroscopic quantities are obtained as averages over all the systems composing a statistical ensemble (the *canonical averages*), calculated at a given time.
At the beginning of the development of Statistical Mechanics, L. Boltzmann focussed is attention on the time evolution of a single system. Within this approach, the macroscopic quantities should be obtained as *time averages* on the microscopic states of a single system, calculated over a conveniently long time interval.

The equivalence of the two approaches, that is the equivalence of canonical averages and time averages, is far from obvious. The study of this equivalence represents the so called *ergodic problem*, whose details can be found in the specialised literature.

Chapter 13

Microcanonical ensemble. Entropy

In this chapter, we deal with the statistics of isolated thermodynamical systems. To that purpose, we resort to the microcanonical ensemble, made by an exceedingly large number of copies of an isolated system.
At first, we will state the fundamental postulate of equiprobability of the microstates for a system in macroscopic equilibrium (§ 13.1). By a procedure similar to tat of Chapter 5, we will then analyse the processes triggered by the removal of constraints within the system in equilibrium (§13.2). By considering the ratio between the number of microstates corresponding to the initial macrostate of constrained equilibrium and to the final macrostate of non-constrained equilibrium, we will state the fundamental relation connecting the entropy to the number of microstates (§13.3). Some examples of calculation of the number of microstates in some particularly simple systems will be presented in §13.4.
In conclusion of the chapter, some hints will be given on the possibility of statistically describing the processes connecting two equilibrium states, the initial one and the final one (§13.5).

13.1 Equiprobability of microstates

Variability of microstates

In principle, an isolated system should be characterised by a constant value of total energy E.
Actually, because of the unavoidable weak interactions of the system with its environment, we have already stressed in §12.3 that the energy value fluctuates within a layer δE around the nominal value E, with $\delta E \ll E$. In §12.3 we have also seen that the particles constituting a macroscopic systems interact among themselves and that such an interaction cannot be completely eliminated. These two factor (the interactions internal and external to the system) cause a continuous variation of the microstates as time goes on.

As it was already stated in § 12.4 and 12.5, the statistical approach to Thermodynamics is based on canonical averages over statistical ensembles rather than on time averages over a single system. The ensemble of a very large number $\mathcal{N}$ of copies of an *isolated system* is called *microcanonical ensemble.*

Quantum description of microstates

To single out and possibly count the microstates corresponding to a given macrostate it is convenient to resort to a quantum perturbative approach. The Hamiltonian of the system is expressed as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 , \tag{13.1}$$

where:

$\mathcal{H}_0$ is the unperturbed term, that takes into account the leading properties of the system, typically the behaviour of the particles considered as independent in a system with constant energy E,

$\mathcal{H}_1$ is the perturbation term, that takes into account the weak interactions among the particles and with the environment.

Example 1: For a diluted gas, $\mathcal{H}_0$ is a purely kinetic term, sum of the kinetic energies of single atoms, and corresponds to the ideal gas approximation. The term $\mathcal{H}_1$ is due to the weak interaction among the molecules and with the vessel walls.

Example 2: Let us consider a crystal and focus our attention on the vibrations of atom around their equilibrium positions. In this case, the potential energy contributions due to the interaction among the atoms are *not negligible* with respect to the kinetic energies. Within the harmonic approximation (in which only the quadratic contributions to the Hamiltonian are considered) one can anyway express the dynamic behaviour of the system in term of collective vibrations of atoms, the so called "normal modes". The normal modes can be considered as independent particles described by and unperturbed Hamiltonian $\mathcal{H}_0$; ithe term $\mathcal{H}_1$ of (13.1) takes into account the weak interactions among normal modes.

Let us consider as possible *microscopic states* of the system the eigenstates of the unperturbed Hamiltonian $\mathcal{H}_0$, corresponding to the total energy E; such eigenstate will be labelled by the indices $r, s, \ldots$.

Example 1: In the ideal-gas case, the microstates differ by the different ways in which the total energy E is distributed among the atoms, and, for each atom, by the different values of the linear momentum components.

Example 2: For an harmonic crystal, the microstates differ by the different ways in which the total energy E is distributed among the different normal modes.

The weak interactions among the particles and with the environment, taken into account by the perturbation term $\mathcal{H}_1 \neq 0$ of the Hamiltonian, give rise to continuos transitions of the system among the different eigenstates of $\mathcal{H}_0$, that is $r \to s$.

As time goes on, the system is characterised by different microstates. In the statistical ensemble picture, this situation is taken into account by a microcanonical ensemble whose constituent systems are in different microstates $r, s, \ldots$.

Probability of the microstates

Let P_r be the probability of the eigenstate r of the unperturbed Hamiltonian $\mathcal{H}_0$, tcorresponding to one of the possible microstates of the system.

In the microcanonical ensemble Nell'insieme statistico micro-canonico, made by $\mathcal{N}(\to \infty)$ independent copies of the given isolated system, the probability P_r is the ratio between the number $\mathcal{N}_r$ of systems characterised by the microstate r and the total number $\mathcal{N}$ of systems of the entire microcanonical ensemble:

$$P_r \;=\; \frac{\mathcal{N}_r}{\mathcal{N}} \;=\; \frac{\text{number of system in the } r \text{ state } r}{\text{total number of systems}} \tag{13.2}$$

Obviously, the normalisation condition of probability theory holds:

$$\sum\nolimits_r P_r \;=\; 1\,. \tag{13.3}$$

Note: The microcanonical picture allows one to consider all the possible microstates of an isolated system. One could then, in principle, follow the evolution of a system which modifies the different probabilities P_r of the microstates as time goes on, for example in the transition from a non-equilibrium state to an equilibrium state (see §13.5 later on). This possibility would not be guaranteed by an approach based of the time averages over a single system.

Equiprobability postulate

In any state of a system (in equilibrium or out of equilibrium) the probabilities P_r can . assume any value, provided the normalisation condition §13.3 is fulfilled. It is anyway reasonable to expect that the probabilities P_r could depend on time only out of equilibrium (this statement will be justified in § 13.5); as a consequence, the normalisation condition (13.3) could be differently stated:

$$\sum_r P_r = 1 \quad \text{at equilibrium}\,; \qquad \sum_r P_r(t) = 1 \quad \text{out from equilibrium} \tag{13.4}$$

Let us now focus our attention on the *equilibrium states.*
For a system in equilibrium, it is reasonable to assume that all the different possible microstates are equivalent; otherwise stated, there is no reason to believe that some microstates can have a larger weight than other.
This intuitive assumption led to the statement of the fundamental postulate of Statistical Thermodynamics:

> *In a statistical microcanonical ensemble, made by $\mathcal{N}$ isolated systems in thermdynamical equilibrium, when $\mathcal{N} \to \infty$ the frequency of any microstate is equal to the frequency of any other microstate.*

Therefore, in equilibrium all the microstates are equiprobable:

$$P_r = P_s = \text{constant} \quad (\forall\; r, s) \quad [\text{isolated system in equilibrium}] \tag{13.5}$$

If Ω is the total number of possible microstates of the system, due to the equiprobability, the normalisation condition (13.4) can be re-written, for a system in equilibrium, as

$$1 \;=\; \sum_r P_r \;=\; \Omega\, P_r\,, \qquad \text{so that} \quad P_r \;=\; \frac{1}{\Omega}\,. \tag{13.6}$$

The validity of the fundamental equiprobability postulate for microstates of systems in macorscopic equilibrium is founded on the verification of its consequences, and in particular on the possibility of reproducing the laws of macroscopic Thermodynamics.

Relaxation time

When studying the macroscopic Thermodynamics in Parts I and II, we observed that thermodynamic systems spontaneously evolve from non-equilibrium to equilibrium states.
This behaviour is taken into account by Statistical Thermodynamics too. In this Part III we mainly deal with systems in macroscopic equiibrium. ci occuperemo prevalentemente della descrizione degli stati di equilibrio. The statistical evolution of systems out of equilibrium will be shortly considered in § 13.5.
We only recall here that the time duration of a transition from a non-equilibrium to an equilibrium state is measured by the *relaxation time* τ. Relaxation times can differ by various orders of magnitude for different systems: they are very short for the free expansion of a gas, they can be very long for the plastic deformation of a solid body.
The peculiar description of a phenomenon depends on the relation between the relaxation time τ and the time of experimental observation t_{exp}:

a) when $\tau \ll t_{\text{exp}}$, the system attains very quickly equilibrium, and one can safely resort to the methods of equilibrium statistica;
b) when $\tau \gg t_{\text{exp}}$, the process is very slow, so that, during the relatively short observation time, one can again resort to the methods of equilibrium statistics;
c) when $\simeq t_{\text{exp}}$, is is necessary to resort to the methods of Physical Kinetics.

13.2 Thermodynamical processes in isolated systems

We want now to find a direct connection between the microscopic and macroscopic descriptions. We will be able to give a statistical interpretation of the Second Law and of entropy in terms of the count of microstates.

To this aim, let us deal again with the "fundamental problem" introduced in § 5.2 within the macroscopic approach. Let us consider an isolated system in an initial state of constrained equilibrium, remove the constraints and wait until a new condition of non-constrained equilibrium is established. The fundamental problem consists in determining the properties of the final state as a function of the properties of the initial constrained state.

In § 5.2, the macroscopic analysis of the fundamental problem led to state the postulate of entropy increase in isolated systems. The analysis of the fundamental problem will be now performed in statistical terms by considering the behaviour of microstates.

Thermodynamical processes and microstates of the system

For simplicity, let us consider an isolated system divided in only two sub-systems by an internal constraint. For concreteness, think of a vessel divided in two parts by a rigid and impermeable wall and suppose that the two parts, 1 and 2, are filled with a diluted gas at the same pressure.

The statistical description is made through a microcanonical ensemble composed by $\mathcal{N}$ copies of the given isolated system.

In the *initial state* of constrained equilibrium, the macroscopic states of sub-systems 1 and 2 correspond to Ω_1 and Ω_2 possible microstates, consistent with the constraint. Globally, the macroscopic state of the entire system corresponds to

$$\Omega_i \;=\; \Omega_1\,\Omega_2 \tag{13.7}$$

microstates (eigenstates of $\mathcal{H}_0$) consistent with the constraints. Because the state is an equilibrium state, according to the fundamental postulate all the microstates are equiprobable. This means that, in the microcanonical ensemble, each microstate corresponds to the same number of system copies.

After the *constraint removal*, a larger number of microstates is at disposal of the system: $\Omega_f \gg \Omega_i$. Immediately after the constraint removal, however, only about Ω_i microstates are present. Otherwise stated, not all the possible microstates are present with the same probability: the macrostate is a non-equilibrium state: in the microcanonical ensemble, different microstates correspond to a different number of system copies.

The interactions among the particles and the environment (term $\mathcal{H}_1$ of the Hamiltonian) give rise to continuous transition among the different possible microstates. Through this mechanism, the probabilities of all the Ω_f final microstates progressively equilibrate until (after a relaxation time τ) the final equilibrium state is obtained.

$$\begin{bmatrix}\text{Initial state}\\ \text{(constrained}\\ \text{equilibrium)}\\ \\ \Omega_i\\ \textit{equiprobable}\\ \textit{states}\end{bmatrix} \begin{matrix}\text{constraint}\\ \text{removal}\\ \Longrightarrow\end{matrix} \begin{bmatrix}\text{Non}-\text{equilibrium}\\ \text{state}\\ \\ \Omega_f \gg \Omega_i\\ \textit{non}\\ \textit{equiprobable states}\end{bmatrix} \overset{\tau}{\Longrightarrow} \begin{bmatrix}\text{Final state}\\ \text{(non-constrained}\\ \text{equilibrium)}\\ \\ \Omega_f\\ \textit{equiprobable}\\ \textit{states}\end{bmatrix}$$

We considered here the simple case of constraint removal in a vessel completely filled with gas. In any case of more complicated isolated systems the same conclusion is found. The transition from a state of constrained equilibrium to a state of non-constrained equilibrium entails an increase of the microstates at disposal of the system:

$$\Omega_f \gg \Omega_i\,. \tag{13.8}$$

Example 1: Free expansion of a gas. Let us consider a vessel divided in two equal parts, A and B. Initially part A is filled with $N = 10^{23}$ gas molecules, part B is empty. The macrostate corresponds to Ω_i microstates. At a given time, the partition is removed and the gas diffuses in part B. Each molecule can now be in part A or part B with equal probability: at each initial microstate it correspond now 2^N final microstates (2 per molecole). The total number of final states is $\Omega_f = 2^N\,\Omega_i$. The probability that, in the final state, a microstate corresponding to the initial state (that is with all the molecules in part A) is $P = 0.5^N = \Omega_i/\Omega_f$.

Example 2: Removal of an adiabatic constraint. Let us consider a vessel divided in two parts A and B by an adiabatic wall. Initially the two parts are filled with a gas at different temperatures, T_A and T_B. The macrostate icorresponds to $\Omega_i = \Omega_A\Omega_B$ different microstates, that in turn correspond to the different modes by which the energies E_A and E_B of the two sub-systems are distributed among the atoms. When the adiabaticity constraint is removed, the two sub-systems reach a new equilibrium condition at the same temperature. The total energy E_A+E_B is now distributed among the atoms in a number $\Omega_f \gg \Omega_i$ of modes. Contrary to the previous example, however, the calculation of the ratio Ω_f/Ω_i is far from trivial.

13.3 Entropy

The conclusion of the previous § 13.2 allows one to establish a simple connection between the number of microstates and the entropy for isolated systems in equilibrium.
Let us again consider the thermodynamical process triggered by the removal of a constraint in a system composed by two sub-systems and compare the macroscopic description, based in *entropy* S (§ 5.2), with the microscopic descripiton, based on the *number* Ω *of microstates.*

Schematically:

	Initial state		Final state
MACRO	$S_i = S_1 + S_2$	irrev. process $\Longrightarrow$	$S_f > S_i$
MICRO	$\Omega_i = \Omega_1\Omega_2$		$\Omega_f > \Omega_i$

Both S and Ω can be expressed as a function of the macroscopic parameters which describe the state of the system, e.g. (U, V, n_i).
Two main conclusions can be drawn from the above schema:

a) in a composite system, the entropies of the components are added, the number of microstates are multiplied;
b) any irreversible process in an isolated systems gives rise to an increase of both the entropy and the number of microstates.

These conclusions suggest the possibility of a connection between the entropy S and the number of microstates Ω.

Boltzmann definition of the entropy

The connection between entropy and the number of microstates was suggested by L. Boltzmann in the second half of the XIX century. For an *isolated system in equilibrium* the relation between entropy S and number of microstates Ω is

$$S = k_B \ln\Omega\,. \tag{13.9}$$

Equation (13.9) transforms the products $\Omega_1\Omega_2$ into sums $S_1 + S_2$. The quantity S so defined is positive and additive and increases in the irreversible processes in isolated systems.

The *Boltzmann constant* k_B connects the logarithm of a pure number (Ω) with a quantity (the entropy S) previously defined as the ratio between energy and temperature. The approximate value of the Boltzmann constant is $k_B \simeq 1.38 \times 10^{-23}$ J/K $\simeq 8.6 \times 10^{-5}$ eV/K.

Let us analyse in detail equation (13.9).

a) The Boltzman definition allows the attribution of an intuitive meaning to the entropy, at least for isolated systems in equilibrium. This is a remarkable progress with respect to the Clausius definition (Chapter 4) and to the axiomatic assumptions of Chapter 5

b) Also the postulate of entropy increase for the irreversible processes in isolated systems can be intuitively better understood.

c) Since the number Ω of microstates can in principle be univocally defined, the Boltzmann definition (13.9) allows the attribution to entropy of an absolute value; there is no need for the arbitrary additive constant of macroscopic Thermodynamic. We will consider this topic in more detail in § 13.4, by comparing the classical and quantum descriptions of a diluted gas.

d) Obviously $\Omega \geq 1$, so that $S \geq 0$. The entropy cannot assume negative values.

From the operative point of view, however, the computation of the number Ω of microstates is generally far from trivial (the topic will be considered in more detail in § 13.4). For that reason, the canonical ensemble, that refers to systems maintained in contact with a heat reservoir, is by far more useful than the microcanonical ensemble, as we will see in Chapters 14 and 15.

Reversibility and irreversibility

In an isolated system, the spontaneous processes connecting two equilibrium states (typically triggered by the removal of constraints) are intrinsically irreversible.
From the macroscopic point of view, an irreversible process in an isolated system gives rise to an increase of entropy S. From the statistical point of view, is gives rise to an increase of the number of microstates Ω.
The Boltzmann equation (13.9) connects the mcorscopic and microscopic descriptions.

Example: Let us consider again the free expansion of 1 mol of an ideal gas from the volume V to the volume $2V$. We have already found that macroscopically $\Delta S = R \ln 2$. Let us now use the statistical definition of entropy:

$$\Delta S = S_f - S_i = k_B(\ln\Omega_f - \ln\Omega_i) = k_B \ln(\Omega_f/\Omega_i)\,. \tag{13.10}$$

It is easy to see that $\Omega_f/\Omega_i = 2^{N_A}$, where N_A is the Avogadro number (each molecule doubles the number of states at her disposal) . Therefore

$$\Delta S = k_B \ln 2^{N_A} = k_B\, N_A \ln 2 \qquad \Rightarrow \qquad k_B\, N_A = R\,, \tag{13.11}$$

where R is the universal gas constant.

A perfectly *reversible* process in an isolated system should take place maintaining the value of the entropy S constant. From the statistical point of view, a reversible process would require that the number Ω of microstates accessible to the system be constant and that the microstates remain equiprobable.
To picture a reversible process in a perfectly isolated system is far from trivial ...

Metrological remarks

The International System of units (SI) is based on seven base quantities: time interval, length, mass, temperature, amount of substance, intensity of electrical current, luminous intensity.
In 2018 the 26th General Conference of Weights and Measures (C.G.P.M.) re-defined all the seven base units connecting their values to seven fundamental constants, which are assumed as exact constants. The new definitions are operative since May 2019.

The seven fundamental constants include the Boltzmann constant, whose exact value is

$$k_B \;=\; 1.380\,649 \times 10^{-23}\ \mathrm{J/K} \tag{13.12}$$

and the Avogadro number, whose value is

$$N_A \;=\; 6.022\,140\,76 \times 10^{23} \tag{13.13}$$

The universal gas constant, $R = k_B\,N_A$ has thus an exact value too. Moreover, the definition of the kelvin, temperature unit, now refers to the value of the Bolzmann constant.

Consequences of the uncertainty of energy

In § 13.2 and 13.3 we considered a constant total energy E, neglecting the unavoidable uncertainty δE due to the interaction of the system with its environment.
In what follows, we show that the influence of the uncertainty δE on the number Ω of microstates and on the entropy S is actually negligible.

One can demonstrate that $\Omega \propto E^f$, where f is the number of degrees of freedom of the system. An intuitive explanation is the following. The total energy E is the sum of f terms, each one corresponding to the energy stored in a single degree of freedom; when the total energy E increases, the number of modes in which it is distributed among the different degrees of freedom increases proportionally to E^f.
The uncertainty δE is generally much smaller than E, although it is larger than the spacing between the energy levels of the system. Let $\omega(E) = d\Omega/dE$ be the *density of states* of the system corresponding to the energy E: the number of microstates of the system in the energy interval δE around the value E can be expressed as

$$\Omega(E) \;=\; \omega(E)\,\delta E\,. \tag{13.14}$$

Let us now consider two different uncertainty values, δE and $\delta' E$. One has:

$$\Omega(E) = \omega(E)\,\delta E; \qquad \Omega'(E) = \omega(E)\,\delta' E; \qquad \Rightarrow \quad \Omega' = \Omega \frac{\delta' E}{\delta E}\,. \tag{13.15}$$

The entropy S depends on the logarithm of Ω, and

$$\ln \Omega' \;=\; \ln \Omega + \ln \frac{\delta' E}{\delta E} \;\simeq\; f\,\ln E + \ln \frac{\delta' E}{\delta E}\,. \tag{13.16}$$

The number f of degrees of freedom is generally very large (of the order of 10^{23}); the second termln$(\delta' E/\delta E)$ in (13.16) is negligible with respect to the first one, so that the value of entropy S can be considered as largely independent of the value of δE.

Entropy as a function of energy

The number of microstates increases as $\Omega(E) \propto E^f$, where f is the number of degrees of freedom, if the total energy of the system is not too low. When the system energy is large, $S = k_B \ln\Omega \simeq k_B\,f \ln E$.
In the quantum approach, the energy of a system has a finite lower limit E_0, corresponding to the energy of the *ground state*.
When $E \to E_0$, the number Ω of microstates decreases considerably, and the value of the entropy S becomes negligible, $S \to 0$. This topic will be considered in more detail in Chapter 20, devoted to the Third Law of Thermodynamics.
The typical dependence of entropy on energy is shown in Fig. 13.1, that can be compared with Fig. 5.3 of Chapter 5.

Example: Let us consider again the example 1 of the end of § 12.3. The system is made by N independent harmonic oscillators. The energy of the i-th harmonic oscillator is $\epsilon_i = (1/2 + n_i)\,\hbar\omega$. The energy levels are not degennerate. In the ground state, all oscillators are characterised by the lowest energy, $\epsilon_0 = (1/2)\,\hbar\omega$. The total energy is $E_0 = N\epsilon_0$. The macroscopic state correspond to only one possible microstate, so that $\Omega = 1$ and $S = 0$.

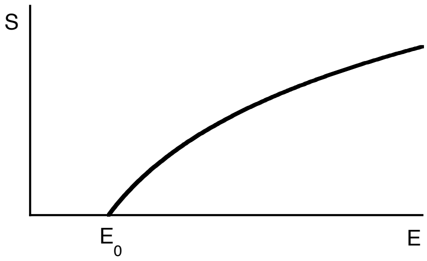


Figure 13.1: Dependence of the entropy on the energy

13.4 Computation of the number of microstates

The computation of the number of microstates can be easily performed only for particularly simple systems. Let us consider here some examples.

13.4.1 Example 1: Diluted gas

For a diluted gas, the unperturbed Hamiltonian $\mathcal{H}_0$ describes the behaviour of the ideal gas, the perturbation $\mathcal{H}_1$ take into account the weak interactions that allow the gas to attain an equilibrium state.
This example is suitable for comparing the classical and the quantum approaches and evidences the difficulties encountered in the computation of the number Ω of microstates in the classical case.

Classical phase space

In classical Physics, the state of a particle is characterised by a point in the abstract phase space, spanned by the coordinates q and by the components of linear momentum p (§ 12.2).
For N non-interacting particles contained in a volume V (§ 12.3), the total energy, purely kinetic, is

$$E = \frac{1}{2m} \sum_{i=1}^{3N} p_i^2 \tag{13.17}$$

where the index i counts the $3N$ components of the generalised momenta. Let us consider also the uncertainty $\pm\delta E$ due to the weak interaction of the system with its environment.
The phase space of the system has $6N$ dimensions. The number Ω of microstates is proportional to the volume in the phase space V_{phase} corresponding to the energy values included in the layer $E \pm \delta E$:

$$\Omega(E) \propto V_{\text{phase}} = \int_{E-\delta E}^{E+\delta E} \underbrace{(dq_1, dq_2, ..., dq_{3N})}_{V^N} (dp_1, dp_2, ..., dp_{3N}) \tag{13.18}$$

In the integral of (13.18), the two sub-spaces of coordinates and momenta have been separated. Since any particle can be found in any portion of the real space, the volume in the sub-space of coordinates is V^N.
In the sub-space of momenta, the system has $f = 3N$ degrees of freedom, with the contraint of constant energy. The states whose energy is included in the layer $E \pm \delta E$ rcorrespond to a hyper-spherical shell of radius $r = \sqrt{2mE}$ and width $2\delta E$ in the sub-space of momenta. The extent of the surface is proportional to $r^{f-1} = (2mE)^{(f-1)/2}$. The volume in the phase space is thus

$$V_{\text{fasi}} \propto V^N (2mE)^{(f-1)/2} \delta E \propto E^{f/2} \delta E\,. \tag{13.19}$$

Classical ideal gas

Let us consider a monatomic ideal gas of N atoms in the real-space volume V and let $(\Delta q \Delta p)_{\delta E}$ be the volume V_{phase} of the phase space corresponding to the states of energy $E \pm \delta E$.

The number of microstates Ω contained in V_{phase} can be enumerated only after a measurement unit has been defined for the volume in the phase space. In the classical approach, such a measurement unit is altogehter arbitrary. For concreteness, let us denote the arbitrary unit by C^{3N}, where C^{3N} has the dimensions of $\Delta q \Delta p$. The number of microstates and the entropy are, respectively, (13.9),

$$\Omega \;=\; \frac{(\Delta q \Delta p)_{\delta E}}{C^{3N}}\,, \qquad\qquad S \;=\; k_B \ln \frac{(\Delta q \Delta p)_{\delta E}}{C^{3N}}\,,. \tag{13.20}$$

In the classical approach, the number of microstates Ω is thus defined to within an arbitrary factor, the measurement unit C^{3N}. As a consequence, the entropy S is defined to within an arbitrary additive constant, as in the macroscopic approach.

Quantum ideal gas

For a gas enclosed in a finite volume one can define the states of the unperturbed Hamiltonian $\mathcal{H}_0 \mathcal{H}_0$ (Chapter 12) and is is thus possible to attribute a well defined value to the number of microstates Ω. In the quantum approach, the entropy is thus univocally defined without any arbitrary additive constant.

It is interesting to see how the quantum and classical approaches can be connected, starting from the classical phase space. In quantum Mechanics, the uncertainty principle $\delta q \delta p \geq h$, where h is the Planck constant, imposes a lower limit to the minimum volume which can be actually singled-out in the phase space. The arbitrariness of the measurement unit of the volume in the classical phase space can thus be removed by imposing:

$$C^{3N} \;=\; \begin{cases} h^{3N} & \text{for distinguishable particles} \\[2ex] N!\, h^{3N} & \text{for indistinguishable particles} \end{cases} \tag{13.21}$$

The difference between distinguishable and indistinguishable particles has a purely quantum nature. In classical Mechanics, all particles are distinguishable, since it is always possible, at least in principle, to precisely determine their trajectories. This possibility is instead not guaranteed in quantum Mechanics, because of the uncertainty principle which forbids the simultaneous knowledge of the exact values of position and momentum. A He atom and an Ar atom are obviously still distinguishable, two He atoms are instead indistinguishable.
The factor $N!$ in the expression of C^{3N} for indistinguishable particles is of purely quantum origin; we will consider it in more detail in Chapter 16. For the moment, let us stress that its presence is necessary to explain the Gibbs paradox, that will be considered in § 11.2.

13.4.2 Example 2: Einstein crystal

In the model proposed by Einstein in 1905, the thermal motion of the N atoms of a crystal is interpreted as the motion of $3N$ independent one-dimensional harmonic oscillators of equal angular frequency ω. The oscillator energy is quantised, $\epsilon = (n + 1/2)\hbar\omega$. Let U be the total thermal energy, that is the vibrational energy minus the zero point terms $(1/2)\hbar\omega$.

The Einstein model is quite crude, since it neglects the strong interactions among the atoms of the crystal. It has however an important historical relevance, since it allowed for the first time a qualitative explanation of the low-temperature behaviour of the specific heat of crystals (§ 9.1, Fig. 9.1) as due to the quantisation of the energy levels of the harmonic oscillator. In the present case, the interest of the Einstein model is due to the relative easiness of the computation of the number of microstates.

The number Ω of microstates corresponds to the number of modes by which the total thermal energy U can be distributed among the $3N$ harmonic oscillators, that is to the number of modes by which the $U/\hbar\omega$ energy quanta of the entire system can be distributed among the $3N$ oscillators.

The problem can be solved by ideally placing on a straight line the $U/\hbar\omega$ energy quanta and $3N-1$ "separating walls" between different oscillators, and calculating the different possible permutations of quanta and separating walls. The number of microstates is Il numero di microstati è

$$\Omega \;=\; \frac{(3N-1+U/\hbar\omega)\,!}{(3N-1)\,!\,(U/\hbar\omega)\,!} \;\simeq\; \frac{(3N+U/\hbar\omega)\,!}{3N\,!\,(U/\hbar\omega)\,!}\,. \tag{13.22}$$

By means of the Stirling formula, $\ln(m!) \simeq m\,(\ln m) - m$ (valid for $m \to \infty$), one can find the expression of entropy:

$$S = k_B \ln\Omega = 3Nk_B\, \ln\left[1+\frac{U}{3N\hbar\omega}\right] + \frac{U}{\hbar\omega}k_B\, \ln\left[\frac{3N\hbar\omega}{U}+1\right]. \tag{13.23}$$

Equation (13.23) represents the fundamental relation $S(U,V,N)$ for the model of independent oscillators of equal frequency. The thermal equation of state is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{k_B}{\hbar\omega}\, \ln\left[\frac{3N\hbar\omega}{U}+1\right], \tag{13.24}$$

from which one can get the total energy as a function of temperature and the heat capacity:

$$U(T) = \frac{3N\hbar\omega}{e^{\hbar\omega/k_BT}-1} \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_V = 3N\left(\frac{\hbar\omega}{k_BT}\right)^2 k_B\,\frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT}-1)^2}\,. \tag{13.25}$$

At *high temperatures* the classical behaviour is reproduced: U linearly increases with T, C_v is constant, and the entropy $S \to \infty$ (Fig. 13.2, left).
At *low temperatures* the deviation from the classical behaviour is qualitatively reproduced: U is not proportional to T, and C_v tends to zero.
The Einstein model makes possible a computation of the number of microstates and a *semi-quantitative* reproduction of the experimental dependence of the heat capacity on temperature. However, the model is too crude to *accurately* account for the experimental behaviour of the heat capacity.
The crudeness of the Einstein model is evidenced by the fact that it cannot reproduce the mechanical behaviour of the crystal: actually, by differentiating the entropy with respect to the volume one obtains an inconsistent result:

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} = 0\,.$$

Note: More refined models have been developed to describe the lattice dynamics of crystals by taking into account the strong interactions among the atoms. Such models are based on the normal modes of vibration, each one characterised by a different frequency. The computation of the microstates in the microcanonical formalism is prohibitively difficult for these more realistic models. In these cases, the thermodynamical quantities can be more effectively obtained by the canonical formalism, to be considered in Chapters 14 and 15.

13.4.3 Example 3: Two-level system

Let us consider a system made by N atoms, with only two energy levels available to each atom, whose energy is 0 (ground state) and ϵ (excited state), respectively.
The total energy U of the system is thus distributed on the number U/ϵ of the atoms which are in the excited state. The number Ω of possible modes of this distribution corresponds to the number of modes by which U/ϵ objects can be extracted from a set of N objects, that is to the number of combinations of N taken U/ϵ at a time:

$$\Omega = \binom{N}{U/\epsilon} = \frac{N!}{(U/\epsilon)!\,(N-U/\epsilon)!} \tag{13.26}$$

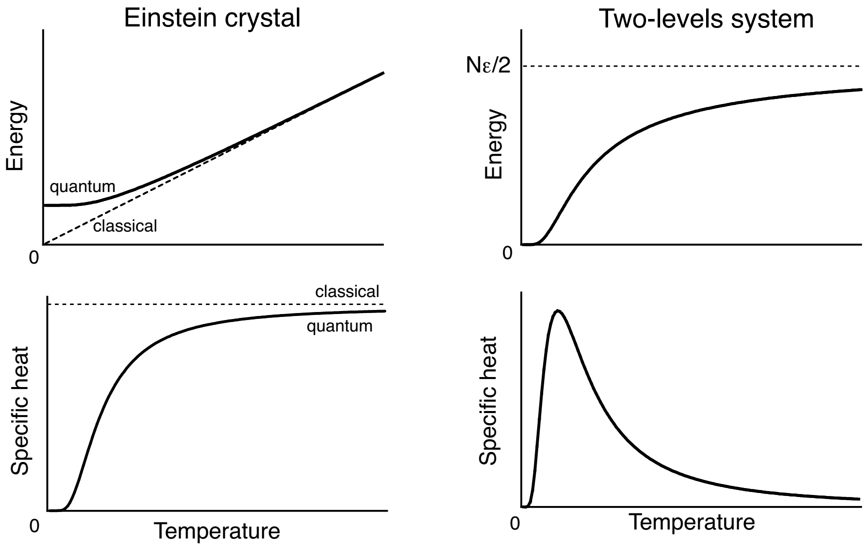


Figure 13.2: Einstein crystal (left) and two-levels system (right). Dependence on temperature of the energy (top row) and of the specific heats (bottom row).

(notice that $U \leq N\epsilon$, so that $U/\epsilon \leq N$). By using the Stirling formula, $\ln(m!) \simeq m\,(\ln m) - m$ ($m \to \infty$), one can find the expression of the entropy:

$$S = \left(\frac{U}{\epsilon} - N\right) k_B \ln\left[1 - \frac{U}{N\epsilon}\right] - \frac{U}{\epsilon} k_B \ln\frac{U}{N\epsilon}\,. \tag{13.27}$$

The thermal equation of state is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{k_B}{\epsilon}\ \ln\left[\frac{N\epsilon}{U} - 1\right]\,, \tag{13.28}$$

whence one can obtain the total energy as a function of temperature and the heat capacity:

$$U(T) = \frac{N\epsilon}{e^{\epsilon/k_BT} + 1}\,; \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{N\epsilon}{\left(e^{\epsilon/k_BT} + 1\right)^2}\, e^{\epsilon/k_BT}\, \frac{k_B\epsilon}{(k_BT)^2}\,. \tag{13.29}$$

When the temperature increases, the total energy asymptotically tends to the finite value $N\epsilon/2$. The heat capacity increases up to a maximum value, then it asymptotically returns to zero (Schottky anomaly) (Fig. 13.2, right). For short:

$$T \to 0 \begin{cases} U \to 0 \\ C_v \to 0 \\ S \to 0 \end{cases} \qquad T \to \infty \begin{cases} U \to N\epsilon/2 \\ C_v \to 0 \\ S \to Nk_B \ln 2 = k_B \ln 2^N \end{cases} \tag{13.30}$$

The presence of a limited number of levels implies that the total energy is superiorly limited. For $T = 0$, the total energy is zero: only the lowest level is populated, there is only one possible microstate and the entropy is zero. For $T \to \infty$, the energy tends to the asymptotic value $U = N\epsilon/2$: both levels are equally populated and the entropy assumes its maximum value.

(?) Is it realistic to imagine a situation in which the upper level has a larger population than the lower level, so that $N\epsilon/2 < U < N\epsilon$? Which would be the values of entropy and temperature in that case ? We will consider again this topic later on.

Note: In practice, two-level sub-systems of a given system (or more generally sub-systems with a finite number of energy levels) are thermodynamically relevant in quasi-equilibrium situations, where the exchange of energy among the degrees of freedom of the two-level sub-system and the other degrees of freedom of the system (e.g. the vibrational degrees of freedom of a crystal) are relatively slow. The presence of two-level subsystem is experimentally evidenced by the presence of Schottky anomalies in the low-temperature specific heats.

13.5 Evolution of the microstates

We conclude this Chapter 13 by an introductory account on the time evolution of microstates, in bot equilibrium and non-equilibrium conditions.

The probability of the microstates obey the following rules.
In equilibrium

$$P_r = P_s = \text{constant} \quad (\forall\ r,s) \qquad \sum\nolimits_r P_r \;=\; 1 \qquad P_r = \frac{1}{\Omega}\,. \tag{13.31}$$

Out of equilibrium

$$P_r(t) \neq \text{constant} \qquad\qquad \sum\nolimits_r P_r(t) = 1 \tag{13.32}$$

Let us now study how the probability P_r of a single microstate evolves as time goes on.

Transition probability

Let the microstates $|r\rangle, |s\rangle, ...$ be the eigenstates of an unperturbed Hamiltonian $\mathcal{H}_0$. The weak interactions among the particles of the system and between the system and its environment, taken into account by the perturbation Hamiltonian $\mathcal{H}_1$, give rise to transitions among the different microstates of the system: $r \to s$. Let W_{rs} be the probability per unit time of the transition $r \to s$. By means of the time-dependent perturbation theory limited to the first order of approximation, one can see that the probability per unit time of the transition $r \to s$ is proportional to the squared modulus of the matrix element of the perturbation Hamiltonian between the two eigenstates $|r\rangle$ and $|s\rangle$:

$$W_{rs} \;\propto\; |\langle s|\mathcal{H}_1|r\rangle|^2 \;=\; \langle s|\mathcal{H}_1|r\rangle^* \, \langle s|\mathcal{H}_1|r\rangle\,. \tag{13.33}$$

The hermitian property of the Hamiltonian operator ($\tilde{\mathcal{H}}_1^* = \mathcal{H}_1$), connected to the reality of its eigenvalues, requires that

$$\langle s|\mathcal{H}_1|r\rangle^* \;=\; \langle r|\mathcal{H}_1|s\rangle\,, \qquad \langle s|\mathcal{H}_1|r\rangle \;=\; \langle r|\mathcal{H}_1|s\rangle^*\,, \tag{13.34}$$

so that the probabilities per unit time of the transitions $r \to s$ and $s \to r$ are equal

$$W_{rs} \;=\; W_{sr}\,, \tag{13.35}$$

for any pair o microstates r and s.

Master equation

The probabiity P_r of the system being in the state r can vary due to two possible mechanisms:

1. transitions *to* the state r *from* other states$s \neq r$, with probability W_{sr} (P_r increases);
2. transizions *from* the state r *to* othes states $s \neq r$, with probability W_{rs} (P_r decreases).

This behaviour is summarised in the *master equation*:

$$\frac{dP_r}{dt} \;=\; \sum_s P_s\, W_{sr} \;-\; \sum_s P_r\, W_{rs}\,. \tag{13.36}$$

The Ω equations (13.36) referring to the Ω microstates of the system, globally describe the time evolution of the system. Introducing the equality (13.35) $W_{rs} = W_{sr}$, the master equation becomes

$$\frac{dP_r}{dt} = \sum_s W_{rs}\,(P_s - P_r)\,. \tag{13.37}$$

Let us now analyse in detail the master equation (13.37).

a) For a system in equilibrium, the equiprobability of the microstates $P_r = P_s (\forall r, s)$ entails that, due to (13.37), $dP_r/dt = 0$: the probability of any microstate is independent of time.

b) Viceversa, if $dP_r/dt = 0$, the system not necessarily is in equilibrium: the differences $(P_s - P_r)$ on the right of (13.37) can have different signs for different states s. It is the case, for example, of systems in stationary states of non-equilibrium (see Chapter **??**), that are however inconsistent with the condition of isolation of the system considered in this chapter.

c) Is the isolated system is out of equilibrium, the master equation (13.37) describes the evolution of its microstates towards equilibrium.
The macroscopic irreversibility of spontaneous natural phenomena is connected to the fact that the master equation is a first order differential equation with respect to time, and is thus not invariant with respect to time inversion. Actually, if te sign of time is inverted $t \to -t$, equation (13.37) becomes

$$\frac{dP_r}{dt} = -\sum_s W_{rs}\,(P_s - P_r)\,.$$

Note: The equation of motion of a single particle are invariant with respect to the time inversion (if the potential energy doesn't depend on velocity, as is the case when magnetic fields are present). One Le equazioni del moto di particella singola sono invarianti rispetto all'inversione temporale (se l'energia potenziale non dipende dalla velocità, ad esempio se sono assenti campi magnetici). One speaks of *microscopic reversibility.*
The time inversion $t \to -t$implies that $\vec{r}(-t) = \vec{r}(t)$, $\vec{p}(-t) = -\vec{p}(t)$.
In *classical Mechanics*, the invariance with respect to the time inversion $t \to -t$ is connected to the fact that the equation of motion contains a second derivative with respect to time:

$$\frac{d^2\vec{p}}{dt^2} = \vec{F}(\vec{r}) = \frac{d^2\vec{p}}{d(-t)^2}\,. \tag{13.38}$$

By inverting the sign of time, the direction of motion is inverted, $\vec{p}(-t) = -\vec{p}(t)$, but the equation of motion remains unchanged.
In *quantum Mechanics*, the Schrödinger equation contains the first derivative with respect to time,

$$i\hbar\frac{\partial}{\partial t}\,\Psi(\vec{r},t) = \mathcal{H}\,\Psi(\vec{r},t)\,. \tag{13.39}$$

Let us consider aa time-independent Hamiltonian;the kinetic term depends on p^2, that is it is invariant with respect to the inversion $\vec{p} \to -\vec{p}$; the potential term depends on $\vec{r}$ and is invariant with respect to time inversion too. The time inversion is accompanied by the complex conjugation of the eigenfunctions of the Schrödinger equation. By inversting $t \to -t$ one thus obtains

$$i\hbar\frac{\partial}{\partial t}\,\Psi^*(\vec{r},-t) = \mathcal{H}\,\Psi^*(\vec{r},-t)\,. \tag{13.40}$$

Therefore, the microscopic reversibility is connected, in quantum Mechanics, to the complex character of the wavefunction.

The Boltzmann H theorem

To study the mcroscopic time evolution of an isolated system, L. Boltzmann introduced a quantity $\mathbf{H}$, defined as

$$\mathbf{H} = \langle \ln P_r \rangle = \sum\nolimits_r P_r \ln P_r\,. \tag{13.41}$$

The quantity **H** is negative and can depend on time.

If the isolated system is in thermodynamical equilibrium, the probabilities of all microstates are independent of time and equal: $P_r = 1/\Omega$, so that $\ln P_r = -\ln\Omega$. Therefore, for an isolated system in equilibrium $-\mathbf{H}$ corresponds to the value of the entropy S of (13.9), to within the a-dimensional constant k_B.

If the isolated system is out of equilibrium, the entropy S is not defined. It is anyway possible to follow the evolution of the quantity **H**. By differentiation of (13.41) with respect to time, one obtains

$$\frac{d\mathbf{H}}{dt} = \sum_r \left(\frac{dP_r}{dt}\ln P_r + \frac{dP_r}{dt}\right) = \sum_r \left(\frac{dP_r}{dt}\right)(\ln P_r + 1)\,. \tag{13.42}$$

Let us substitute in (13.42) the expression of dP_r/dt of the master equation (13.37); by exchanging r with s one obtains two equivalent expressions:

$$\frac{d\mathbf{H}}{dt} = \begin{cases} \sum_r\sum_s W_{rs}(P_s - P_r)(\ln P_r + 1) & = & -\sum_r\sum_s W_{rs}(P_r - P_s)(\ln P_r + 1) \\ \\ \sum_s\sum_r W_{sr}(P_r - P_s)(\ln P_s + 1) & = & -\sum_r\sum_s W_{rs}(P_r - P_s)(-\ln P_s - 1) \end{cases} \tag{13.43}$$

where use has been made of the relation $W_{rs} = W_{sr}$. Let us now sum up the two right members of (13.43) and divide the result by two

$$\frac{d\mathbf{H}}{dt} = \frac{1}{2}\sum_r\sum_s W_{rs}\,(P_r - P_s)\,(\ln P_r - \ln P_s)\,. \tag{13.44}$$

Since the logarithm is a monotonously increasing function of its argument, all the terms of the sums are products of factor of equal sign, that is positive (or zero if $P_r = P_s$). Therefore

$$\frac{d\mathbf{H}}{dt} \leq 0\,. \tag{13.45}$$

The quantity **H** is always negative and cannot increase as time goes on. If all the probabilities P_r are equal, as in the equilibrium states, where **H** minimo is minimum, then **H** remains constant as time goes on. If instead $P_r \neq P_s$ for some pairs r, s, then **H** decreases until $P_r = P_s$.

Example: Let us consider an irreversible process leading an isolated system from an initial state of constrained equilibrium to a final state of non-constrained equilibrium. The removal of the constraint makes accessible to the system a number of new microstates, whose probability, initially very small, increases as time goes on, at the expenses of the probabilities of the microstates of the initial constrained state. The trend towards equilibrium reduces the average value of the probabilities P_r.

Chapter 14

Canonical ensemble. Canonical distribution

In the previous chapter 13 the connection $S = k_N \ln \Omega$ has been established between the entropy S and the number of microstates Ω for an isolates system. In § 13.4 we succeeded in computing the number of microstates for some particularly simple systems, as well as to determine the fundamental equation $S(U, V, N)$ for the Einstein model (13.23) and for a two-levels system (13.27).
However, for the great majority of real systems, the computation of the number of microstates Ω is nearly impossible, so that the determination of the fundamental equation in the entropy representation based on the microcanonical formalism is not the best way to connect the laws of macroscopic Thermodynamics to the microscopic structure.

The by far most effective approach is based on the so called *canonical* formalism, in which the considered system is still closed with constant volume, but is *not isolated*: the system can exchange energy with its environment, which is considered as a second system with infinite heat capacity (that is a reservoir at constant temperature).
The statistical treatment of the non-isolated system is through a *canonical statistical ensemble*, made by $\mathcal{N}(\to\infty)$ copies of the system, each one in contact with its reservoir (Fig. 14.1).

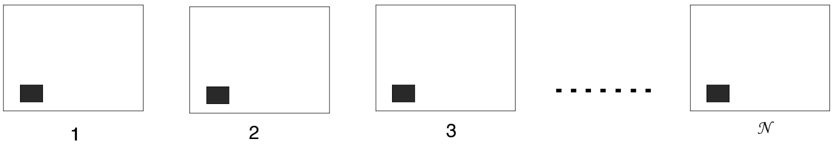


Figure 14.1: Canonical statistical ensemble: $\mathcal{N}$ copies of a system immersed in its own reservoir at constant temperature.

The canonical formalism developed in this chapter is the instrument which allows the simplest connection between the macroscopic thermodynamical quantities and the microscopic structure, as we will see in next Chapter 15.
The cnonical statistical ensemble is thus made by $\mathcal{N}$ copies of a thermodynamical system, that is of a system composed by a very large number N of particles. Thermodynamical systems are *macroscopic* systems, and so obviously *distinguishable*.

The canonical formalism which will be developed in this chapter can be applied, with the due cautions, also to canonical ensembles made by $\mathcal{N}$ *microscopic systems*. In those cases, each system is represented by a single particle (e.g an atom, a molecule, a normal vibrational mode): they are thus *not* thermodynamical systems. This type of systems will be treated in Chapter 16, where the distinction between distinguishable and indistinguishable particles will be considered and the suitable different statistics will be introduced.

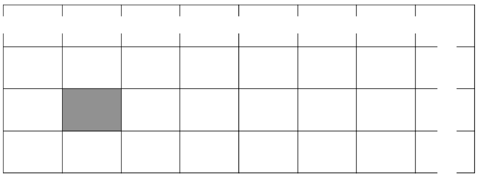


Figure 14.2: Alternative picture of the canonical statistical ensemble: the reservoir of a system is represented by its very $\mathcal{N}$ copies.

14.1 Boltzmann-Plank method

An elegant approach to the canonical formalism is represented by the Boltzmann-Plank method.
Instead of considering $\mathcal{N}$ copies of the given thermodynamical system, each copy being immersed in its own reservoir as in Fig. 14.1, in the Boltzmann-Plank method one considers an ensemble made by $\mathcal{N}$ thermodynamical systems immersed in the same reservoir, weakly interacting and thus able to exchange energy. Otherwise stated, for each system the other $\mathcal{N}-1$ systems represent the reservoir (Fig. 14.2).

The entire statistical ensemble has to be considered as an isolated system, with constant total energy $\mathcal{E} \pm \delta\mathcal{E}$. The energy of the single systems is instead not constant.

One can define an average energy of the systems composing the statistical ensemble:

$$\langle E \rangle \; = \; \frac{\mathcal{E}}{\mathcal{N}} \,. \tag{14.1}$$

Actually, each system instantaneously its own energy E, generally different from the average value $\langle E \rangle$, and corresponding to one of allowed levels E_i (eigenvalues of the unperturbed Hamiltonian). The levels E_i are equal for all systems.

In thermodynamical systems, composed by a very large number N of particles, the levels are very close together, and can generally be treated as a continuous distribution with density of states $\omega(E)$.

Distributions of energy

The total energy $\mathcal{E}$ of the canonical ensemble can be distributed in many different ways among its $\mathcal{N}$ systems.

A particular distribution of the energy among the different systems can be characterised by specifying, for each energy level E_i, the number N_i of systems which share that vauel fo energy (Fig. 14.3, left). Let g_i be the degeneracy of the i-th level. The normalisation conditions on the total number $\mathcal{N}$ of systems and on the total energy $\mathcal{E}$ must hold:

$$\sum\nolimits_i N_i \; = \; \mathcal{N} \tag{14.2}$$

$$\sum\nolimits_i E_i N_i \; = \; \mathcal{E} \tag{14.3}$$

where the sums are extended to all the energy levels of the systems.

Each distribution of the total energy of the ensemble among the different systems can be characterised by the values N_1, N_2, N_3, ... N_i... Each one of these energy distributions can correspond to a number of different microstates, characterised by the different possible choices of the systems which share a given energy level(Fig. 14.3, right). We will synthetically indicate one of these distributions by $\{\mathcal{N}_j\}$:

$$\{\mathcal{N}_j\} \; \equiv = \; (N_1, N_2, N_3, ...N_i...) \,. \tag{14.4}$$

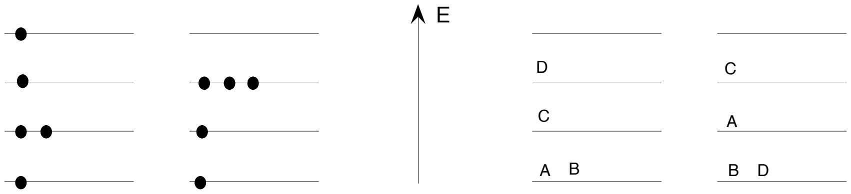


Figure 14.3: Left: two different distributions of the energy of the canonical ensemble on the energy levels E_i of the systems; each point represents a system. Right: the same distribution can correspond to different microstates: the letters A, B, C .. correspond to different systems.

Computation of the microstates

Let us now solve the following problem: to how many different microstates corresponds a given distribution $(N_1, N_2, N_3, ...N_i...) \equiv \{\mathcal{N}_j\}$?

The solution is given by the combinatorial calculus. Let us first calculate in how many different ways one can accomodate N_1 systems on the level 1: the answer is the number of combination of $\mathcal{N}$ objects taken N_1 at a time, taking into account the degeneracy g_1 of the level:

$$\frac{\mathcal{N}\,(\mathcal{N}-1)\,(\mathcal{N}-2)...(\mathcal{N}-N_1+1)}{N_1!}\;g_1^{N_1} \tag{14.5}$$

Let us now calculate in how many different ways one can accomodateN_2 systems on the level 2, extracting them from the $\mathcal{N}-N_1$ remaining systems:

$$\frac{(\mathcal{N}-N_1)\,(\mathcal{N}-N_1-1)\,(\mathcal{N}-N_1-2)...(\mathcal{N}-N_1-N_2+1)}{N_2!}\;g_2^{N_2}\,. \tag{14.6}$$

Considering all the levels and multiplying the results for each single level, one obtains the final expression for the number of modes $\Omega(\{\mathcal{N}_j\})$ in which a given distribution $\{\mathcal{N}_j\}$ can be built up:

$$\Omega(\{\mathcal{N}_j\}) \;=\; \frac{g_1^{N_1}\,g_2^{N_2}\,...\,g_i^{N_i}\,...}{N_1!\,N_2!\,...\,N_i!\,...}\,\mathcal{N}! \;=\; \prod_i \frac{g_i^{N_i}}{N_i!}\,\mathcal{N}!\,. \tag{14.7}$$

Note: The factor $\mathcal{N}!$ is connected to the distinguishability of the thermodynamical systems. As we will see in Chapter 16, when the systems are single particles, the factor $\mathcal{N}!$ has to be substituted by 1.

14.2 Search of the most probable distribution

The canonical statistical ensemble is an isolated system. Each one of the $\Omega(\{\mathcal{N}_j\})$ ways in which a given distribution $\{\mathcal{N}_j\}$ of the energy can be built up represents a microstate of the canonical ensemble. The total number of microstates is thus $\Omega_{\text{tot}} = \sum_j \Omega(\{\mathcal{N}_j\})$.

Because the canonical ensemble is an isolated system, the fundamental postulate that *all microstates of an isolated system in equilibrium are equi-probable* (§ 13.1) holds. All the possible $\Omega(\{\mathcal{N}_j\})$ microstates corresponding to any distribution are thus equi-probable.

Different distributions $\{\mathcal{N}_j\}$ are generally characterised by a different number $\Omega(\{\mathcal{N}_j\})$ of microstates. The different distributions $\{\mathcal{N}_j\}$ can thus be characterised by different values of probability: a distribution is more probable than another distribution if it corresponds to a larger number of microstates.

Let us now search for the most probable distribution $\{\mathcal{N}_j\}$ of the energy among the different systems of the canonical ensemble.

Statement of the problem

The most probable distribution is the distribution which corresponds to the largest number $\Omega(\{\mathcal{N}_j\})$ of microstates, that is the distribution $(N_1, N_2, N_3, ...N_i...)$ which contemporarily fulfils the following conditions:

$$\begin{array}{lcll} \Omega(\{\mathcal{N}_j\}) & = & \text{maximum} & \Rightarrow \quad \ln\Omega = \text{maximum} \\ \sum_i N_i & = \mathcal{N} = & \text{constant} & \\ \sum_i E_i N_i & = \mathcal{E} = & \text{constant} & \end{array} \tag{14.8}$$

One has to search for the conditions which maximise $\Omega(\{\mathcal{N}_j\})$, with the constraints that the total number of systems and the total energy remain constant; it is thus the search for a *constrained maximum.*

Maximising $\ln \Omega$ instead of $\Omega(\{\mathcal{N}_j\})$ leads to the same results with the advantage of simpler calculations.

Solution of the problem

Let us calculate the logarithm of $\Omega(\{\mathcal{N}_j\})$ from (14.7) and simplifyit through the Stirling formula $\ln m! = m\ln(m) - m$:

$$\begin{aligned} \ln\Omega &= \ln\mathcal{N}! - \sum_i \ln N_i! + \sum_i N_i \ln g_i \\ &= \mathcal{N}\ln\mathcal{N} - \mathcal{N} - \sum_i (N_i \ln N_i - N_i) + \sum_i N_i \ln g_i \\ &= \mathcal{N}\ln\mathcal{N} - \sum_i N_i \ln N_i + \sum_i N_i \ln g_i \,, \end{aligned} \tag{14.9}$$

where the sum is extended to all the energy levels of the systems. The differential is

$$d(\ln\Omega) \;=\; -\sum_i \ln(N_i/g_i)\, dN_i - \sum_i dN_i \;=\; -\sum_i \ln(N_i/g_i)\, dN_i \,. \tag{14.10}$$

The differential condition of constrained maximum is

$$\begin{array}{ll} \sum_i \ln(N_i/g_i)\, dN_i & = 0 \\ \sum_i dN_i & = 0 \\ \sum_i E_i dN_i & = 0 \end{array} \tag{14.11}$$

The terms dN_i can be made independent through the method of the Lagrange multipliers, that is adding to the first equation the remaining two, multiplied by the two coefficients (Lagrange multipliers) α and β, respectively:

$$\sum_i \left[\ln(N_i/g_i) + \beta E_i + \alpha\right] dN_i \;=\; 0\,. \tag{14.12}$$

Now all the terms in square parentheses has to be identically null for each i, so that

$$N_i \;=\; g_i\, e^{-\alpha-\beta E_i} \qquad (\forall i)\,. \tag{14.13}$$

By further considering the normalisation condition $\sum N_i = \mathcal{N}$, one obtains

$$e^{-\alpha} \;=\; \frac{\mathcal{N}}{\sum_i g_i e^{-\beta E_i}}\,. \tag{14.14}$$

14.3 Canonical distribution

The most probable distribution of the total energy $\mathcal{E}$ of the canonical ensemble among its different systems is thus, in *equilibrium* conditions, the distribution to which it corresponds, for the i-th level of energy E_i, the fraction of systems (that is the probability)

$$P_i = \frac{N_i}{\mathcal{N}} = \frac{g_i\, e^{-\beta E_i}}{\sum_i g_i\, e^{-\beta E_i}} \qquad \text{(sum over the energy levels)} \tag{14.15}$$

At each level of energy E_i it generally correspond g_i states. If $g_i \neq 1$ the level is said to be degenerate. One can express the canonical distribution in terms of the sum over the states instead as the sum over the levels. To the j-th level it corresponds the probability

$$P_j = \frac{N_j}{\mathcal{N}} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \qquad \text{(sum over the states)} \tag{14.16}$$

The canonical partition function Z

The quantity at the denominator of the canonical distribution (14.15) or (14.16)

$$Z = \sum\nolimits_i g_i \, e^{-\beta E_i} = \sum\nolimits_j e^{-\beta E_j} \tag{14.17}$$

is called *partition function* or *sum over the states* (in German *Zustandssumme*, whence the symbol Z).

The canonical distribution can thus synthetically be written as

$$P_i = \frac{1}{Z} \, g_i \, e^{-\beta E_i} \tag{14.18}$$

The partition function Z on both the energy levels of the system and on the Lagrange parameter β. The meaning of the partition function will be considered in more detail later on. We anticipate here that the partition function plays a fundamental role in statistical Thermodynamics; actually, as we will see in Chapter 15, the knowledge of Z corresponds to the exhaustive knowledge of the thermodynamical properties of a system and allows one to calculate the values of all its thermodynamical quantities.

The β parameter and the thermal equilibrium

The β parameter is connected to the normalisation condition on total energy and thus depends on the total energy of the canonical ensemble. Let us now demonstrate that β is connected to the thermal equilibrium and thus plays the same role that the temperature T plays in macroscopic Thermodynamics.

Let us consider two canonical ensemble in thermal contact. The first ensemble is made by $\mathcal{N}$ systems, the second one by $\hat{\mathcal{N}}$ systems. In an equilibrium condition, let be

Ω	the number of states corresponding to the distribution $\{N_1, N_2, ...N_i, ...\}$ of the first ensemble
$\hat{\Omega}$	the number of states corresponding to the distribution $\{\hat{N}_1, \hat{N}_2, ...\hat{N}_i, ...\}$ of the second ensemble
$\bar{\Omega} = \Omega\hat{\Omega}$	the number of states corresponding to the distribution of the sum of the two ensembles

Let us search for the most probable distribution for the sum of the two statistical ensembles, by maximising $\bar{\Omega}$ by the same procedure previously used. To simplify the notation, we consider the sums over the states rather than over the levels. The condition of constrained maximum is

$$\begin{array}{ll} \sum_i \ln N_i \, dN_i + \sum_j \ln \hat{N}_j \, d\hat{N}_j & = 0 \\ \sum_i dN_i & = 0 \\ \sum_j d\hat{N}_j & = 0 \\ \sum_i E_i dN_i + \sum_j \hat{E}_j d\hat{N}_j & = 0 \end{array} \tag{14.19}$$

Let us again resort to the method of Lagrange multipliers, by adding to the first equation the other three, multiplied by α, $\hat{\alpha}$ and β, respectively. There are two constraints on the number of particles, one for each ensemble, but there is only a constraint on energy, since the two ensembles are in thermal equilibrium and can exchange energy. The distributions for the two ensembles are:

$$N_i = e^{-\alpha - \beta E_i} \, ; \qquad \hat{N}_j = e^{-\hat{\alpha} - \beta \hat{E}_j} \, . \tag{14.20}$$

Substitutin α nd $\hat{\alpha}$, one obtains at last

$$P_i = \frac{N_i}{\mathcal{N}} = \frac{1}{Z} e^{-\beta E_i}\,; \qquad \hat{P}_i = \frac{\hat{N}_i}{\hat{\mathcal{N}}} = \frac{1}{\hat{Z}} e^{-\beta \hat{E}_j}\,. \tag{14.21}$$

The two canonical ensembles are characterised by different distributions: the energies E_i and $\hat{E}_j$ of their levels as well as their degeneracies are generally different, so that the partition functions Z and $\hat{Z}$ are generally different. The two distribution share nevertheless the same parameter β. This equality reflects the fact that the two systems are in thermal equilibrium, so that only the total energy $\mathcal{E} + \hat{\mathcal{E}}$ of the sum of the two ensembles is constant as time goes on.

β parameter and temperature

The previous discussion shows that the β parameter plays the same in statistical Thermodynamics role as the parameter T in the macroscopic Thermodynamics.

Later on, in Chapter 15, we will show that β and T are connected by the relation $\beta = 1/k_BT$, where k_B is the Boltzmann constant. β and T have an inverse behaviour: when $T \to 0$, β diverges to infinity; viceversa, $\beta = 0$ corresponds to an infinite temperature.

By substituting $\beta = 1/k_BT$ and considering gain the sum over the levels instead of the sum over the states, the canonical distribution can be expressed in a more familiar way:

$$P_i = \frac{1}{Z}\, g_i\, e^{-E_i/k_BT}\,, \qquad Z = \sum\nolimits_i g_i\, e^{-E_i/k_BT} \tag{14.22}$$

Probability of the canonical distribution

We have demonstrated above that the canonical distribution is the most probable among the various possible distributions of the energy among the systems of the canonical ensemble. Other less probable distributions of the energy anyway exist among the systems of the canonical ensemble. In order to better grasp the relevance of the canonical distribution, we should answer the following question: how much is the canonical distribution more probable with respect to the other possible distributions ?

When the number $\mathcal{N}$ of systems composing the canonical ensemble increases, the number $\Omega_{\rm can}$ of states corresponding to the canonical distribution progressively dramatically predominates with respect to the number of states corresponding to the alternative distributions; this trend can be easily verified already with a number $\mathcal{N}$ of systems of the order of a few tens.

For $\mathcal{N} \to \infty$ (perfect reservoir) $\Omega_{\rm can} \simeq \Omega_{\rm tot}$, where $\Omega_{\rm tot}$ is the total number of possible modes by which the energy can be distributed among the systems of the canonical ensemble. The canonical distribution can thus be considered as practically unique in equilibrium conditions.

For a system in thermal equilibrium the plot of $\ln P_j$ (probability of the j-th state) against E_j is a straight line:

$$\ln P_j = \ln(N_J/\mathcal{N}) = \ln(1/Z) - \beta E_j\,. \tag{14.23}$$

A system for which the points $(\ln P_j, E_j)$ are inconsistent with a straight line is out of equilibrium. In such a case it is impossible to attribute a value to the β parameter.

Dependence of the canonical distribution on energy

To better grasp the physical meaning of the canonical distribution for a thermodynamical system, let us refer to its expression (14.22), where instead of the β parameter the more familiar temperature T appears.

For a given value of the system temperature T (equal to the temperature of the reservoir) the partition function Z of (14.17) is univocally determined by the energy structure of the system.

Fora given value of T, the factor $\exp(-E_i/k_BT)$ monotonously decreases when the value of the energy E_i increases. If all the energy levels are non degenerate, so that $g_i = 1$ for any i, then also the probability P_i monotonously decreases when the value of the energy E_i increases. If the energy levels are degenerate, it can be that the values g_i increase when E increases; in such cases, it can be that the distribution P_i increases for small values of E and decreases for large values of E; it can then exist a value of energy E_m for which the distribution exhibits a maximum.

Density of states

Equation (14.18) expresses the probability as a function of the values of the discrete energy levels E_i. If the levels are densely packed, as it generally happens for thermodynamical systems, one can resort to a continuous representation. The discrete probabilities P_i are substituted by a probability density $P(E)$. The canonical distribution now expresses the probability that the system be in an energy interval dE around the value E:

$$P(E)\,dE = \frac{1}{Z}\,\omega(E)\,e^{-\beta E}\,dE\,, \tag{14.24}$$

where

a) $\omega(E)$ is the *density of states*, determined both by the degeneracy of the single levels included in the interval dE and by the density of the levels. In general, the density of states $\omega(E)$ increases when E increases.

b) the partition function is now expressed by an integral

$$Z = \int \omega(E)\,e^{-\beta E}\,dE\,, \tag{14.25}$$

wil consider again this topic in the next Chapter 15.

Chapter 15

Statistical interpretation of thermodynamical quantities

In this chapter 15 we will see how the canonical approach, introduced in the previous Chapter 14, allows one to establish an effective statistical connection between the microscopic properties of a system and its thermodynamical quantities (internal energy, entropy, and so on).
We will consider relatively simple systems: pure substances in the absence of external fields (such as electric or magnetic fields), for which the energy of the canonical ensemble is the sum of the kinetic energies of the particles and of the potential energies of the interactions within the ensemble.

15.1 Thermodynamical internal energy

Let us consider a system of N ($\simeq 10^{23}$) particles, in thermal contact with a reservoir. The system is not isolated and its energy is thus not a constant. In the Boltzmann-Plank approach (§ 14.1), the reservoir is composed by $\mathcal{N}-1$ copies of the system. The canonical statistical ensemble made by the system and its reservoir is an isolated global system.

Average energy of the system

Being an isolated system, the canonical statistical ensemble has a constant total energy $\mathcal{E}$. Let us suppose that each single system can assume only discrete energy values E_i (the hypothesis is reasonable for a finite quantum system). energy of the statistical ensemble is the sum of the energies of the single systems,$\mathcal{E} = \sum_i N_i E_i$, where N_i is the number of systems sharing the energy value E_i.
The energy E_i of a single system is not constant, since the systems interacts with the reservoir (say with the other systems); we can nevertheless define an average value as the ratio between the total energy of the statistical ensemble and the number of its systems:

$$\langle E\rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{1}{\mathcal{N}}\sum_i N_i E_i = \sum_i \frac{N_i}{\mathcal{N}} E_i = \sum_i P_i E_i\,. \tag{15.1}$$

In the last equality, the probabiity $P_i = N_i/\mathcal{N}$ that the system energy be E_i has been introduced. In equilibrium conditions, the probabilities P_i are given by the canonical distribution (14.18), so that the average energy can be expressed as

$$\langle E\rangle = \sum_i P_i E_i = \frac{1}{Z}\sum_i g_i E_i e^{-\beta E_i}\,. \tag{15.2}$$

Note 1: Once the energy levels E_i of the system and their degeneracies g_i (microscopic information) as well as the value of the parameter β (that is of the temperature) are known, one can calculate the partition function Z, the average energy $\langle E\rangle$ and, as we will see, the other thermodynamical quantities. The energy plays thus a primitive role in the statistical approach.

Note 2: The values E_i refer to the energy levels of the entire system. In practice, their accurate knowledge is in most cases nearly impossible (typically when the particles of the system are strongly interacting).

To better grasp the characteristics of the average energy of a system made by a large number N of particles, let us begin with a simple, even if not realistic, example.

Example: Let us consider a thermodynamical system composed by N harmonic oscillators of equal angular frequency ω, corresponding to the Einstein crystal already introduced in § 13.4. Each harmonic oscillator can be on a non degenerate energy level $\epsilon_n = \hbar\omega\,(1/2+n)$. The total energy E of the thermodynamical system is the sum of the energies of the single oscillators. Each level E_i of the total energy of the system corresponds to a very large number of possible distributions of the total energy on the single oscillators; the levels E_i are thus degenerate, and one easily understand that the degeneracy g_i rapidly increases when the number N of oscillators increases.

The conclusions of the previous example can be generalised to more complex systems. The energy levels E_i of a system composed by a number $N \simeq 10^{23}$ of particles are di particelle are very close to each other (the distances between the levels are negligible with respect to the absolute values E_i) and strongly degenerate.

In many cases, it is convenient to consider a continuous distribution of energy, as in (14.22) and (14.24):

$$P(E)\,dE = \frac{1}{Z}\,\omega(E)\,e^{-\beta E}\,dE\,, \qquad Z = \int \omega(E)\,e^{-\beta E}\,dE\,, \tag{15.3}$$

where $\omega(E)$ is the density of states, a function steeply increasing of energy.

Energy fluctuations

Let us now improve our understanding of the meaning of average energy and verify the possible connection with the thermodynamical internal energy U.

Since the system is not isolated, one expects that its energy E fluctuates with respect to the average value $\langle E\rangle$. However, if the system is very large, the number of particles interacting with the reservoir is negligible with respect to the total number of particles, and one thus expects that the fluctuations are not particularly large.

To draw quantitative conclusions, let us measure the fluctuations of the energy E with respect to the average value $\langle E\rangle$ by means of the standard deviation $\sigma = \sqrt{\sigma^2}$, where σ^2 is the variance, defined as:

$$\sigma^2 = \left\langle (E - \langle E\rangle)^2 \right\rangle = \langle E^2\rangle - \langle E\rangle^2\,. \tag{15.4}$$

In equilibrium, the average $\langle E\rangle$ is calculated through the canonical distribution (15.2)

$$\langle E\rangle = \sum_i E_i P_i = \frac{\sum_i g_i E_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}\,. \tag{15.5}$$

One can easily verify, making use of (15.5), that

$$\frac{\partial\langle E\rangle}{\partial\beta} = \langle E\rangle^2 - \langle E^2\rangle\,, \qquad \text{so that} \qquad \sigma^2 = -\frac{\partial\langle E\rangle}{\partial\beta}\,. \tag{15.6}$$

Since by definition $\sigma^2 > 0$, one gets $\partial\langle E\rangle/\partial\beta < 0$: the average energy decreases when β increases (that is when the temperature $T = 1/k_B\beta$ increases).

Viceversa, when the temperature T increases, the average energy $\langle E\rangle$ increases and the canonical distribution tends to spreadout, that is σ increases.

These first conclusions are independent of the system size. Let us now consider the behaviour of systems with very large N (thermodynamical systems). The average energy depends on the size of the system, $\langle E\rangle \propto N$. The β parameter is instead independent of the system size, so that

$$-\frac{\partial\langle E\rangle}{\partial\beta} \propto N\,. \qquad \text{that is} \qquad \sigma^2 \propto N\,. \tag{15.7}$$

The amount of *absolute fluctuations*, measured by the standard deviation σ, is thus proportional to $\sqrt{N}$.

More important is, for our purposes, the amount of the *relative fluctuations*

$$\frac{\sqrt{\langle E^2\rangle - \langle E\rangle^2}}{\langle E\rangle} = \frac{\sigma}{\langle E\rangle} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}\,, \tag{15.8}$$

that decrease proportionally to the inverse of the square root of the system size. For $N \simeq 10^{23}$, the energy distribution of the system is strongly peaked around its average value: the average value is nearly coincident with the maximum of the distribution an the relative fluctuations are proportionally small.

Average energy and internal energy

A macrosopic system in thermal equilibrium with a reservoir has a well defined internal energy U. From the microscopic point of view, the relative fluctuations of the energy E with respect to the average value $\langle E\rangle$ are very small, $\propto 1/\sqrt{N}$. For $N \to \infty$ (thermodynamic limit) the relative fluctuations tend to zero. If the energy E is the sum of only contributions internal to the system, that is there are no contributions of external fields, it is reasonable to establish the equivalence

$$U \;=\; \langle E\rangle \tag{15.9}$$

for a thermodynamical system in thermal equilibrium with a reservoir.

Note: If the energy E contains contributions due to external fields, e.g potential energy of magnetic fields, the simple equation $U = \langle E\rangle$ doesn't hold. We will consider this topic in more detail in Chapter 18, devoted to the statistical Thermodynamics of magnetic systems.

Energy fluctuations and heat capacity

By substituting $\beta = 1/k_BT$ in the canonical distribution, one can easily verify that

$$\sigma^2 \;=\; \langle E^2\rangle - \langle E\rangle^2 \;=\; k_BT^2\,\frac{\partial\langle E\rangle}{\partial T}\,. \tag{15.10}$$

Therefore, if one identifies $\langle E\rangle = U$, one gets

$$\sigma^2 \;=\; k_BT^2\,\frac{\partial U}{\partial T} \;=\; k_BT^2\,C_v \tag{15.11}$$

where C_v is the constant-volume heat capacity of the system. The energy fluctuations are proportional to the heat capacity. Actually, the largest is the heat capacity of a system, the largest is its possibility of exchanging energy for a given temperature variation.

The extent of the relative energy fluctuations is

$$\frac{\sqrt{\sigma^2}}{\langle E\rangle} \;=\; \frac{T\sqrt{k_BC_v}}{U}\,. \tag{15.12}$$

Example: For a monatomic ideal gas of N atoms, $U = (3/2)Nk_BT$ and $C_v = (3/2)Nk_B$. The extent of the relative energy fluctuations is thus $\sqrt{2/3N}$.

Note: Large values of the heat capacity C_v correspond to large local fluctuations of the energy of a system which take place in correspondence of some phase transitions, e.g. near the critical point in continuous phase transitions (see Chapter 23).

15.2 Entropy

For an *isolated system* in thermodynamical equilibrium, the entropy S is connected to the total number of equiprobable microstates by the relation (13.9):

$$S \;=\; k_B \, \ln\Omega \tag{15.13}$$

In the macroscopic Thermodynamic (Parts I and II), the entropy S is defined also for *non-isolated systems*, provided they are in thermal and mechanical equilibrium. However, the number of microstates Ω is not univocally determined for a non-isolated system; in what follows, we show how a statistical definition of entropy is possible even for non-isolated systems.

Entropy of the canonical ensemble

Let us first consider the entire canonical ensemble, composed by $\mathcal{N}$ copies of the given system. The canonical ensemble is an isolated global system, with energy $\mathcal{E} \pm \delta\mathcal{E}$, so that one can define the total entropy of the canonical ensemble as

$$\mathcal{S}_{\rm ens} \;=\; k_B \, \ln\Omega_{\rm tot}\,, \tag{15.14}$$

where $\Omega_{\rm tot}$ is the total number of microstates of the canonical ensemble (it was shown in § 13.3 that the uncertainty δE doesn't significantly influence the value of $\Omega_{\rm tot}$).
When the number $\mathcal{N}$ of systems composing the canonical ensemble is sufficiently large, the canonical distribution (14.15) becomes dominant (see §14.3), so that $\Omega_{\rm tot} \simeq \Omega_{\rm can}$: the total number of microstates of the canonical ensemble is well approximated by the number of microstates of the canonical distribution. Because $\mathcal{N}$ is arbitrarily large, one can substitute $\Omega_{\rm tot}$ with $\Omega_{\rm can}$ in (15.14):

$$\mathcal{S}_{\rm ens} \;=\; k_B \, \ln\Omega_{\rm can}\,. \tag{15.15}$$

Average entropy of the system

Let us now consider the single system (composed by N particles), which is in thermal equilibrium with the other $\mathcal{N}-1$ systems of the canonical ensemble. The average entropy of the system is defined as

$$\langle S\rangle \;=\; \frac{\mathcal{S}}{\mathcal{N}} \;=\; \frac{k_B}{\mathcal{N}}\ln\Omega_{\rm can}\,. \tag{15.16}$$

The value of $\Omega_{\rm can}$ can be obtained from (14.7)

$$\Omega_{\rm can} = \mathcal{N}!\prod_i \frac{g_i^{N_i}}{N_i!}\,; \qquad \ln\Omega_{\rm can} = \ln\mathcal{N}! - \sum_i \ln N_i! + \sum_i N_i\ln g_i \tag{15.17}$$

where N_i are the numbers of systems on the different energy levels according to the canonical distribution (14.15). Making use of the Stirling fluc, one obtains

$$\begin{aligned}
\langle S\rangle \;&=\; \frac{k_B}{\mathcal{N}}\left[\mathcal{N}\ln\mathcal{N} - \mathcal{N} - \sum_i N_i\ln N_i + \sum_i N_i + \sum_i N_i\ln g_i\right] \\
&=\; \frac{k_B}{\mathcal{N}}\left[\left(\sum_i N_i\right)\ln\mathcal{N} - \sum_i N_i\ln\frac{N_i}{g_i}\right] = k_B\sum_i\left[\frac{N_i}{\mathcal{N}}\ln\mathcal{N} - \frac{N_i}{\mathcal{N}}\ln\frac{N_i}{g_i}\right] \\
&=\; k_B\sum_i\left[-\frac{N_i}{\mathcal{N}}\ln\frac{N_i}{g_i\mathcal{N}}\right]
\end{aligned} \tag{15.18}$$

so that the average entropy of the system becomes

$$\langle S\rangle \;=\; -k_B\sum_i P_i\ln\frac{P_i}{g_i} \;=\; -k_B\left\langle\frac{P}{g}\right\rangle\,, \tag{15.19}$$

where P_i are the probabilities of occupation of the different energy levels according to the canonical distribution (14.15).

Note: When the degeneracy of the levels increases, $\ln(P/g)$ decreases and $\langle S\rangle$ increases.

Example: Let us consider a system in its ground state, with energy E_0. The probabilities are $P_1 = 1$ and $P_i = 0$ for $i \neq 1$. If the level is not degenerate, then $\langle S\rangle = 0$. When g increases, $\langle S\rangle$ increases too.

It is convenient to substitute the sum over the levels (i) with the sum over the states (j) in the expression of the average entropy. The level i-th, with probability P_i, is made by g_i states with probabilities P_j, so that $P_i = g_i P_j$. Therefore

$$\begin{aligned}\langle S\rangle &= -k_B \sum_i P_i \ln \frac{P_i}{g_i} \\ &= -k_B \sum_j P_j \ln P_j = -k_B \langle \ln P_j\rangle \,. \end{aligned} \tag{15.20}$$

Note: The expression (15.20) of the entropy corresponds, to within the sign and the and the k_B dimensional constant, with the expression (13.41) of the quantity **H** of the Boltzmann **H** theorem (§ 13.5). The same expression for entropy is used in the Information Theory.

Thermodynamical limit

We are considering systems composed by a very large number N of particles. For $N \to \infty$ (in the real cases for $N \simeq 10^{23}$) the relative fluctuations of the energy E with respect to the average value $\langle E\rangle$ are negligible, so that the system, although not isolated, can be considered with good approximation as an energy with constant energy $E \pm \delta E$. The thermodynamical internal energy U has thus been identified with the average energy, $U = \langle E\rangle$.
The levels E_i for whicch the canonical probability $P_i \neq 0$ are confined within a relatively narrow range of values, within which the differences between the values P_i (as well s g_i) can be neglected and the microstates can be considered as equiprobables, as for isolated systems.
If the Ω_{sys} microstates corresponding to the canonical distribution for a system with very lrge number N of particles can be considered as equiprobable, $P_j \simeq 1/\Omega_{\text{sys}}$ and $\langle \ln P_j\rangle = \ln P_j$. Therefore

$$\langle S\rangle = k_B \ln \Omega_{\text{sys}} \tag{15.21}$$

and the average value $\langle S\rangle$ of (15.20) can be identified with the macroscopic entropy S.

15.3 Heat, work and temperature

In this chapter we are considering *non isolated systems*, that can exchange energy with their environment. From the macroscopic point of view, the exchange of energy corresponds to work or to heat. We can now give a statistical interpretation of the difference between work and heat.
The internal energy U coincides, for a system in equilibrium with its environment when no external fields are present, with the average energy $\langle E\rangle$. The average energy can be expressed as a sum over the energy levels weighted by their canonical probabilities:

$$U = \langle E\rangle = \textstyle\sum_i E_i P_i \,, \qquad (P_i = N_i/\mathcal{N}) \,. \tag{15.22}$$

Heat and work

When a system reversibly interacts with its environment, the differential variation of the average energy can be expressed as the sum of two different sets of terms:

$$d\langle E\rangle = \sum_i P_i \, dE_i + \sum_i E_i \, dP_i \,. \tag{15.23}$$

The *first term* of (15.23) depends on the variation of the energy values E_i of the levels, without modifications of the probabilities P_i (probabilities of the canonical distribution). The energy of the levels is modified (Fig. 15.1, levels) if the external macroscopic parameters, such as the volume, are modified. The first term of (15.23) thus corresponds to the *thermodynamical work*,

$$đW \;=\; \sum_i P_i\, dE_i\,. \tag{15.24}$$

The *second term* of (15.23) corresponds to a variation of the average energy $\langle E\rangle$ with no variation of the energy levels, that is in the absence of thermodynamical work (Fig. 15.1, right) . The second term of (15.23) thus corresponds to *heat*,

$$đQ \;=\; \sum_i E_i\, dP_i\,. \tag{15.25}$$

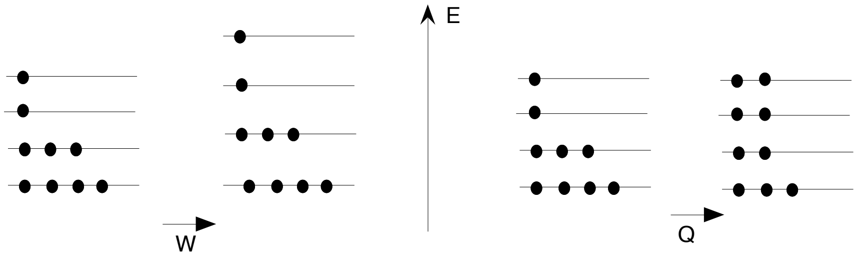


Figure 15.1: Schematic representation of the different effect of work (left) and heat (right) on the energy levels and on their population. Each dot schematically represents a system of the canonical ensemble.

Heat, entropy and temperature

The reversible transfer of heat is connected to the entropy variation by the macroscopic relation $đQ = T\,dS$ (§ 4.4 and 6.3). Let us now analyse the statistical interpretation of this relation.
According to (15.20), the entropy S can be expressed as a function of the degeneracies g_i and of the canonical probabilities P_i of the energy levels of the system:

$$S \;=\; -k_B \sum_i P_i \,\ln\left(\frac{P_i}{g_i}\right) \;=\; -k_B \sum_i P_i\,[\ln\,P_i - \ln\,g_i]\;. \tag{15.26}$$

Taking into account that $\sum_i dP_i = 0$, the differential dS is easily calculated:

$$dS \;=\; -k_B \sum_i \ln\left(\frac{P_i}{g_i}\right)\,dP_i\,. \tag{15.27}$$

The canonical distribution (14.18) connects the probability values P_i with the energy values E_i of the levels:

$$\frac{P_i}{g_i} = \frac{1}{Z}\,e^{-\beta E_i}\,, \qquad \ln\left(\frac{P_i}{g_i}\right) = -\beta E_i - \ln Z\,, \tag{15.28}$$

where $Z = \sum_i e^{-\beta E_i}$ is the canonical partition function.
Therefore, by substituting the values P_i/g_i, the differential dS can be rewritten as a function of the energy values E_i:

$$dS = -k_B \sum\nolimits_i [-\beta E_i - \ln Z]\;dP_i = k_B\beta\;\sum\nolimits_i E_i\,dP_i + k_B\;\ln Z\,\sum\nolimits_i dP_i \tag{15.29}$$

Taking into account that $\sum_i dP_i = 0$ and considering the statistical expression (15.25) of heat $đQ$, one finds the statistical relation between dS and $đQ$:

$$dS = k_B\beta \sum_i E_i\, dP_i = k_B\beta\, đQ\,. \tag{15.30}$$

The comparison between the macroscopic and the statistical expressions of the relation between dS and $đQ$

$$dS \;=\; \frac{đQ}{dT} \;=\; k_B\beta\, đQ \tag{15.31}$$

leads to the connection between the statistical parameter β and the thermodynamical temperature T already anticipated in § 14.3: $\beta = 1/k_BT$.

Note 1: The parameter β has dimensions inverse to those of energy, while the product k_BT has the dimensions of energy. The ratio E_i/k_BT appearing in the canonical distribution plays a fundamental role in the evaluation of the population of energy levels. Since $k_B \simeq 8.6\times10^{-5}$ eV/K, one can easily see that, for $T = 300$ K, $k_BT \simeq 25$ meV.

Note 2: As already observed in § 13.3, since 2019 the units of the seven base quantities of the International System are referred to the values of seven fundamental constants, assumed as exact. The Boltzmann constant is one of these. The kelvin, unit of temperature, is now connected to the value of the Boltzmann constant as follows: The increase of temperature of 1 K gives rise to an increase of microscopic energy of $k_BT = 1.380649\times10^{-23}$ J.

Temperature and canonical distribution

By substituting $\beta = 1/k_BT$, the canonical distribution (14.18) becomes

$$P_i = \frac{1}{Z}\, g_i\, e^{-E_i/k_BT}\,, \qquad Z = \sum_i g_i\, e^{-E_i/k_BT}\,. \tag{15.32}$$

Let us now advance our understanding of the statistical meaning of the temperature and of the partition function Z. Once a temperature value T has been fixed,

$$\begin{aligned} &\text{if} \quad E_i \gg k_BT, \qquad \text{then} \quad e^{-E_i/k_BT} \simeq 0 \\ &\text{if} \quad E_i \ll k_BT, \qquad \text{then} \quad e^{-E_i/k_BT} \simeq 1 \end{aligned} \tag{15.33}$$

The partition function $Z = \sum g_i \exp(-E_i/k_BT)$ counts the states accessible to the system at the temperature T (the states whose $E_i \ll k_BT$ are weighted by g_i, the states whose $E_i \gg k_BT$ are weighted zero).

Note: The transitions between energy levels differing by $\Delta E \leq k_BT$ can take place spontaneously and are said to be “thermally activated”

When the temperature T increases, the number of levels such that $E_i < k_BT$ increases; therefore Z increases. In more detail, when T increases:

$$\begin{aligned} &\text{if} \quad E_i \gg k_BT, \quad P_i \simeq 0 \\ &\text{if} \quad E_i \simeq k_BT, \quad P_i \text{ increases} \\ &\text{if} \quad E_i \ll k_BT, \quad P_i \simeq g_i/Z \qquad \text{decreases because } Z \text{ increases} \end{aligned} \tag{15.34}$$

When the temperature increases, the barycentre of the canonical distribution moves towards higher energies, its absolute width σ increases but its relative width $\sigma/\langle E\rangle$ increases.

This chapter is dedicated to macroscopic system containing a very large number N of particles. This allowed us to find the connection between the statistical parameter β and the thermodynamic temperature T. A deeper understanding of the meaning of the factor k_BT in the canonical distribution will be possible after the comparison of the macroscopic systems with the systems composed by one particle which will be made in Chapter 16, il suo ruolo per sistemi piccoli, tipicamente con $N = 1$ con il suo ruolo per i sistemi macroscopici.

15.4 Partition function and thermodynamical quantities

The knowledge of the canonical partition function corresponds to the knowledge of the thermodynamical properties of system. In the following, we will see how the thermodynamical quantities (internal energy, entropy, enthalpy, and so on) can be obtained from the partition function.

If the external constraints are known (e.g. the volume V for a hydrostatic system or the magnetic field $\mathcal{H}$ for a magnetic system), the energy levels E_i and their degeneracies g_i can, at least in principle, be calculated. It is the possible to obtain the partition function

$$Z \;=\; \sum\nolimits_i g_i e^{-\beta E_i} \;=\; \sum\nolimits_i g_i e^{-E_i/k_B T} \tag{15.35}$$

as a function of the temperature.

Note: The computation of the levels E_i is far from trivial: it can be relatively easy for a system of non-interacting particles, such as an ideal gas, it can however be prohibitively difficult for a system of strongly interacting particles.

Once the partition function Z iis known as a function of the temperature T and of the external parameters (e.g. $V, \mathcal{H}$), one can calculate all the thermodynamical functions of a system. For concreteness, let us consider an hydrostatic system, for which $Z = Z(V,T)$.

Internal energy

By differentiating (15.35) with respect to T, the average energy of the system $\langle E\rangle$ can be expressed as

$$\langle E\rangle \;=\; k_B\,T^2 \left(\frac{\partial}{\partial T}\ln Z\right)_V . \tag{15.36}$$

As already stressed in § 15.1, if the energy E contains only contributions internal to the system, that is if there are no contributions due to external fields (e.g. magnetic or electric), one can establish theequivalence of the thermodynamical internal energy with the average energy, $U = \langle E\rangle$. Therefore, through (15.36), one can connect the internal energy to the partition function:

$$U \;=\; k_B\,T^2 \left(\frac{\partial}{\partial T}\ln Z\right)_V . \tag{15.37}$$

The energy levels E_i are defined to within an arbitrary ϵ. If the energy levels are modified,

$$E_i \;\to\; E_i^* \;=\; E_i + \epsilon\,, \tag{15.38}$$

the partition function is modified too:

$$Z \;\to\; Z^* \;=\; Z\,e^{-\epsilon/k_B T} \tag{15.39}$$

As a consequence, Z is defined to within a multiplicative factor. Using (15.37), one can see that also the internal energy U is defined to within the arbitrary constant ϵ:

$$U \;\to\; U^* \;=\; U + \epsilon\,. \tag{15.40}$$

The canonical distribution is instead insensitive to the additive constant of the energy; È rilevante notare che la distribuzione canonica è invece insensibile alla costante additiva dell'energia; as a matter of fact

$$P_i^* \;=\; \frac{1}{Z^*} e^{-E_i^*/k_B T} \;=\; \frac{1}{Z e^{-\epsilon/k_B T}} e^{-E_i/k_B T} e^{-\epsilon/k_B T} \;=\; \frac{1}{Z} e^{-E_i/k_B T} \;=\; P_i \tag{15.41}$$

Entropy

Starting from (15.20),

$$S \;=\; -k_B \sum_i P_i \,\ln\left(\frac{P_i}{g_i}\right)\,, \tag{15.42}$$

and substituting the values P_i given by the canonical distribution, $P_i/g_i = \exp(-E_i/k_BT)/Z$, one can easily verify that

$$S \;=\; \frac{\langle E\rangle}{T} + k_B\,\ln Z \;=\; \frac{U}{T} + k_B\,\ln Z\,, \tag{15.43}$$

where the internal energy U is connected to the partition function Z through (15.36). Therefore, also the entropy S can be obtained from the knowledge of the partition function Z.

Let us verify the effect on entropy of the arbitrary additive constant of the energy ϵ dell'energia. Since

$$U \to U^* = U + \epsilon\,, \qquad Z \to Z^* = Z\,e^{-\epsilon/k_BT}\,, \tag{15.44}$$

by means of (15.43) one finds

$$S \to S^* = S\,, \tag{15.45}$$

that is the entropy S is independent of the constant of energy. As a matter of fact, the entropy depends on the number of microstates, that is independent of their energy values.

Let us now compare the expression (15.43) of the entropy with the expression (15.21) obtained at the end of § 15.2. For a system with a very large number of particles, the levels E_i for which the canonical probability is substantially relevant, that is $P_i \neq 0$, made a relatively narrow band $\langle E\rangle \pm \delta E$, with $\langle E\rangle = U$. Within that band, the $\Omega_{\rm sis}$ microstates are substantially equiprobable. The relevant contribution to the partition function is given by the states included in that energy band, so that

$$Z \;=\; \sum_i g_i\; e^{-E_i/k_BT} \;=\; \Omega_{\rm sis}\,e^{-\langle E\rangle/k_BT} \tag{15.46}$$

and

$$k_B\,\ln\,Z \;=\; k_B\,\ln\Omega_{\rm sis} - \langle E\rangle/T \;=\; S - U/T\,, \tag{15.47}$$

in agreeement with (15.43).

Helmholtz free energy

Starting rom the definition (7.16) of the Helmholtz function, $F = U - TS$, and making use of (15.43), one finds

$$F \;=\; -k_B\,T\,\ln Z\,. \tag{15.48}$$

The particularly simple connection between F and Z can be explained by considering that, for a system whose independent variables are T and V, the knowledge of $F(T,V)$ corresponds to the knowledge of all thermodynamical properties of the system, as is the case for the knowledge of $Z(T,V)$. Otherwise stated, for a system whose independent variables are T and V, the canonical statistical approach corresponds to the macroscopic Helmholtz representation (se Chapters 7 and 8).

Note 1: Let us consider a spontaneous process connecting two equilibrium states at constant T and V. As already seen in § 8.3, the process gives rise to a reduction of F, corresponding to an increase of the entropy of the Universe. Equation (15.48) shows that the process gives rise to an increase of Z. The partition function Z plays the same role for a system at constant (T,V) that the entropy S plays for an isolated system.

Note 2: By inverting (15.48), one finds $Z = \exp(-F/k_BT)$. The canonical distribution can thus be expressed in the alternative form

$$P_i \;=\; g_i\,e^{-(E_i-F)/k_BT}\,. \tag{15.49}$$

For $T = 0$ the Helmholtz function corresponds to the internal energy, $F = U - TS = U$; from (15.49) one can see that for $T = 0$ the probability is $P_i = 0$ for any i unless $E_i = F$; otherwise stated, for $T = 0$ only one level can be populated, the ground state with energy $E_0 = F$; lthe internal energy is then $U = E_0$.

Pressure

Since $p = -(\partial F/\partial V)_T$, from (15.48) one finds

$$p \;=\; k_B T \left(\frac{\partial}{\partial V}\ln Z\right)_T . \tag{15.50}$$

Enthalpy

Starting from $H = U + pV$, making use of (15.36) and (15.50), one finds

$$H \;=\; k_B T^2 \left(\frac{\partial}{\partial T}\ln Z\right)_V + k_B TV \left(\frac{\partial}{\partial V}\ln Z\right)_T . \tag{15.51}$$

Gibbs free energy

Starting from $G = H - TS$ one finds

$$G \;=\; k_B TV \left(\frac{\partial}{\partial V}\ln Z\right)_T - k_B T \ln Z . \tag{15.52}$$

15.5 Entropy and temperature of the ideal gas

Equations (15.24) and (15.25) of § 15.3 show that work and heat can be statistically interpreted in terms of the energy levels of a system and of their occupation.

Let us now try to better understand those concepts, as well as the statistical meaning of entropy and temperature.

To that aim, let us refer to a particularly simple case, say to the monatomic ideal gas and let ϵ_i be the energies of the levels of single atoms and n_i the corresponding occupation numbers.

If external fields are absent, the internal energy of the system corresponds to the average total energy and can be expressed as a function of the energies ϵ_i of single atoms as

$$U \;=\; \langle E\rangle \;=\; \sum\nolimits_i \epsilon_i \,\langle n_i\rangle \tag{15.53}$$

The differential dU can be decomposed as

$$\begin{aligned} dU &= đQ + đW \;=\; T\,dS - p\,dV \\ &= d\langle E\rangle \;=\; \sum\nolimits_i \epsilon_i\, d\langle n_i\rangle + \sum\nolimits_i \langle n_i\rangle\, d\epsilon_i \end{aligned} \tag{15.54}$$

A variation dV of the system volume gives rise to a variation of the energy levels ϵ_i induced by the quantisation of the linear momentum: if the volume decreases, the levels increase their distance, and viceversa. Equation (15.54) shows that heat and work correspond to the variations of the populations n_i and of the values ϵ_i, respectively.

Let us now verify how (15.54) accounts for different possible transformations of the monatomic ideal gas. For each transformation, the corresponding plot in the $T - S$ plane is considered.

Reversible adiabatic compression

In an adiabatic compression no heat is exchanged, so that

$$dU = \text{đ}W = \sum\nolimits_i \langle n_i \rangle \, d\epsilon_i \,. \tag{15.55}$$

Both internal energy U and temperature T increase, while the entropy S remains constant.
The work done on the system gives rise to an increase of the separation of energy levels. The distribution of the atoms on the levels is instead not modified, because there is no heat exchange. However, the distribution with respect to the energy axis is modified (Fig. 15.2, left).

Reversible isothermal compression

In an isothermal compression of te ideal gas both temperature and internal energy remain constant: $dU = 0$ and $dT = 0$. Heat and work have equal values and opposed sign. The gas gives up heat to its environment and reduces its entropy.

$$\text{đ}W = -\text{đ}Q \,, \qquad \Rightarrow \qquad \sum\nolimits_i \epsilon_i \, d\langle n_i \rangle = -\sum\nolimits_i \langle n_i \rangle \, d\epsilon_i \tag{15.56}$$

The work made on the systems gives rise to an increase of the separation of the levels. The distribution of the atoms on the levels is modified too, since there is heat exchange. However, the distribution with respect to the energy axis is not modified (Fig. 15.2, center).

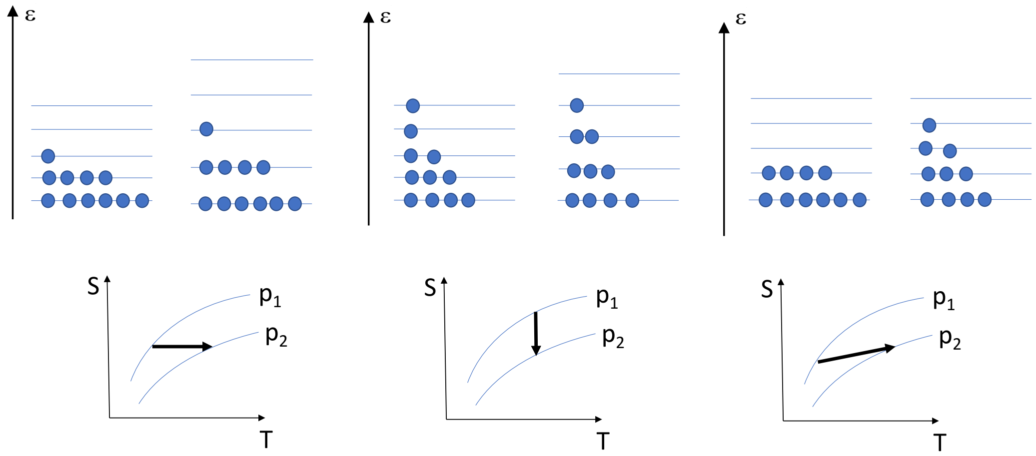


Figure 15.2: Schematic representation of the effects of three different transformations of the ideal gas on the energy levels and on their populations. From left to right: adiabatic compression, isothermal compression, heating at constant volume. The two isobaric curves in the $T - S$ plane refer to two pressure values $p_2 > p_1$.

Heating at constant volume

The system only exchanges heat, the work is zero.

$$dU = (\text{đ}Q)_V = \sum\nolimits_i \epsilon_i \, d\langle n_i \rangle \tag{15.57}$$

The interna energy U, the temperature T and the entropy S increase.
The energy levels are not modified, since the work is zero. The distribution of the atoms is modified with respect to both the single levels and the energy axis (Fig. 15.2, right).

Temperature and entropy

In the simple transformations of the ideal gas considered above, a simple interpretation of the variations of temperature and entropy and of their difference is possible in relation to the occupation of the atomic energy levels:

a) a variation of temperature T corresponds to a variation of the distribution of the atoms with respect to the energy axis;
b) a variation of entropy S corresponds to a variation of the distribution of the atoms with respect to their energy levels.

We will find a similar analysis later on, when treating the statistica of paramagnetic systems in Chapter 18.

Heating at constant pressure

If the heating is performed a constant pressure, the gas does work on its environment. All terms of the energy balance

$$dU \;=\; đQ + đW \;=\; \sum\nolimits_i \epsilon_i \, d\langle n_i\rangle + \sum\nolimits_i \langle n_i\rangle \, d\epsilon_i \tag{15.58}$$

are different from zero.
The internal energy U, the temperature T and the entropy S increase, and the energy levels are modified.
The heat exchanged at constant pressure corresponds to the variation of enthalpy:

$$dH \;=\; (đQ)_p \;=\; dU - đW \;=\; dU + p\,dV \;=\; \sum\nolimits_i \epsilon_i \, d\langle n_i\rangle \,. \tag{15.59}$$

$=$

Chapter 16

Statistics of particles

In Chapter 14 we introduced the canonical ensemble, made by $\mathcal{N}$ copies of a *macroscopic system*, composed in turn by a very large number N of particles, and representing thus a thermodynamic system. We then derived the canonical distribution, that was connected to the thermodynamical quantities in Chapter 15.

As anticipated at the beginning of Chapter 14, the canonical formalism can be applied, with the due cautions, also to canonical ensembles made by $\mathcal{N}$ *microscopic systems* composed by a single particle (e.g. an atom, a molecule, a normal mode of vibration) and as such being *not* thermodynamical systems.

In this chapter, we introduce the application of statistical ensembles to systems composed by one particle.
To this aim, it is preliminarily necessary to clarify the fundamental aspect of the distinguishability of identical particles (§ 16.1). The problem, of genuine quantum nature, has remarkable theoretical implications as well as important practical applications. The problem was not considered when treating macroscopic (thermodynamical) systems in the previous chapters 14 and 15, because macroscopic systems are clearly distinguishable.
The fundamental characteristics of the statistics of identical particles are studied in § 16.2. The distributions of Maxwell-Boltzmann for distinguishable identical particles, of Bose-Einstein indistinguishable particles of integer spin and of Fermi-Dirac for the indistinguishable particle of half-integer spin are introduced in 16.3.
The Maxwell-Boltzmann distribution for distinguishable identical particles formally corresponds to the canonical distribution of Chapter 14 applied to systems composed by only one particle ($N = 1$) and is considered in detail in § 16.4. The different treatment for distinguishable and indistinguishable identical particles will allow, at the end of § 16.4, a satisfactory explanation of the Gibbs paradox concerning the mixing of gases(§ 11.2).
Some properties of the Bose-Einstein and Fermi-Dirac statistics are further analysed in § 16.5 and 16.6, respectively.

16.1 Distinguishability and indistinguishability

Let us consider a system composed by N identical particles (N electrons, N hydrogen atoms, N normal modes of a crystal, etc).
For a system composed by a very large number of particles ($N \simeq 10^{23}$), one cannot consider the system in a stationary state described by a single wavefunction (as is instead possible for a many-electrons atom). Because of the interactions, though weak, with the environment, the total energy of the system is not perfectly constant, $E \pm \delta E$, and the system continuously moves through different microscopic states. It is thus necessary to resort to a statistical approach, in which one refers to the stationary states of the single particles, that can vary slowly as time goes on, due to the weak interactions among the particles and with the environment.

In classical Mechanics, identical particles are always distinguishable, because position and velocity can be evaluated, at least in principle, with sufficiently small uncertainty to allow an univocal determination of their trajectory.
In quantum Mechanics, the uncertainty principle forbids the simultaneous precise evaluation of position and velocity of a particle. Therefore, the trajectory of particles cannot be precisely defined. Let us consider, for example, two particles, 1 and 2, approaching each other, interacting and finally moving away; after the interaction, one cannot distinguish particle 1 from particle 2, because it was impossible to distinguish their trajectories.

The analysis of the quantum behaviour of matter led to separately considering not only distinguishable and indistinguishable identical particles, but also, among the indistinguishable particles, the particles with integer spin and the particles with half-integer spin.
There exist thus three different types of particles, characterised by different properties of symmetry of their wavefunctions and by different statistical distributions.

a) Identical distinguishable particles

In quantum Mechanics, like in classical Mechanic, the atoms of a crystal, that oscillate around fixed lattice positions, as well as the normal vibrational mode, are distinguishable.
Identical distinguishable particles obey the so called Maxwell-Boltzmann statistics, as we will see later on.

The wavefunction of a stationary state of two distinguishable identical particles 1 and 2 is the product of single-particle wavefunctions:

$$\Psi = C\,\psi_a(1)\,\psi_b(2)\,, \tag{16.1}$$

where a and b label two possible states (which can also coincide) and C is a normalisation constant.
Two distinguishable identical particles 1 and 2 can be distributed in two states a nd b in 4=2×2 different modes, corresponding to the 4 different wavefunctions

$$\psi_a(1)\,\psi_b(2)\,,\quad \psi_a(2)\,\psi_b(1)\,,\quad \psi_a(1)\,\psi_a(2)\,,\quad \psi_b(1)\,\psi_b(2)\,. \tag{16.2}$$

By generalising to N particles, the wavefunctions of each possible stationary state of the N particles are products of the N single-particle wavefunctions, each one corresponding to a well determined state:

$$\Psi = C\,\psi_{a_1}(1)\,\psi_{a_2}(2)\ \cdots\ \psi_{a_N}(N)\,, \tag{16.3}$$

where the a_i indices label the possible single-states (which can also coincide).
N distinguishable identical particles can be distributed among N states in $N \times N$ different modes (each particle can be in each one of the N states).

Example: The atoms of an Einstein crystal, already considered in § 13.4, are a good example of distinguishable particles, sono un esempio di particelle distinguibili, because they are constrained to the positions of the crystal lattice.

b) Indistinguishable particles with integer spin

Atoms of ^{4}He, photons (quanta of the electromagnetic field) and phonons (quanta of the normal vibrational modes) are examples of particles with integer spin, that obey the Bose-Einstein statistic and are thus called *Bosons*.

The properties of systems composed by bosons are interpreted by assuming that their wavefunction is symmetrical with respect to the exchange of any two particles. To guarantee the symmetry, the wavefunction of two bosons 1 and 2 has to be expressed as

$$\Psi = A\,\left[\psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2)\right]\,, \tag{16.4}$$

where a and b are two possible states (which can also coincide) and A is a normalisation constant.
The exchange of the two bosons 1 and 2 doesn't modify the wavefunction.

The two bosons 1 and 2 can be distributed between the states a and b in 3 different ways, corresponding to the 3 wavefunctions, respectively

$$[\psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2)]\ , \quad \psi_a(1)\,\psi_a(2)\,, \quad \psi_b(1)\,\psi_b(2)\,. \tag{16.5}$$

In comparison with tdistinguishable particles, the bosons have a higher probability of gouping in the same state.
The wavefunction of each stationary state of N bosons is obtained by summing over all the possible permutations of the N particles:

$$\begin{aligned}\Psi = A \quad & [\quad \psi_{a_1}(1)\,\psi_{a_2}(2)\ \cdots\ \psi_{a_N}(N) \\ & +\quad \psi_{a_1}(2)\,\psi_{a_2}(1)\ \cdots\ \psi_{a_N}(N)] \\ & +\quad \ldots \\ & +\quad \text{the other permutations}\ ]\,, \end{aligned} \tag{16.6}$$

where the indices a_i label the possible single-particle states (which can also coincide).

Example 1: The elementary particles with integer spin, such as mesons (e.g. pions) , are bosons.

Example 2: The atoms or which the sum of protons, neutrons and electros is an even number, so that the total spin is integer (e.g. the isotope ^{4}He of helium) are bosons.

Example 3: The photons, that is the quanta of energy of the electromagnetic field, to which the spin 1 is attributed, are bosons. Photons can be easily created and annihilated: the photon statistics is thus not constrained to a constant number N.

Example 4: The phonons, that is the quanta of energy of the vibrational modes of crystals, obey the Bose-Einstein statistics and are therefore bosons. Also phonons, like photons, can be easily created and annihilated: their statistics is thus not constrained to a constant number N.

c) Indistinguishable particles with half-integer spin

Electrons, protons, neutrons, atoms of ^{3}He are examples of particles with half-integer spin, that obey the Fermi-Dirac statistic and are thus called *Fermions.*

The properties of systems composed by fermions are interpreted by assuming that their wavefunction is anti-symmetrical (that is it changes its sign) with respect to the exchange of any two particles. To guarantee the anti-symmetry, the wavefunction of twofermions 1 and 2 has to be expressed as

$$\Psi = A\ [\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)] = A \begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix}\,, \tag{16.7}$$

where a and b label two possible states and A is a normalisation constant.
Two fermions 1 and 2 can be distributed in two states a and b in only one way, one fermion per state; as a matter of fact, if two fermions are in the same state, the wavefunction is zero (Pauli exclusion principle).
The expression of the wavefunction as a determinant allows its easy extension to the case of N fermions ($N \times N$ determinant).

Example 1: The elementary particles with half-integer spin such as leptons (e.g. electrons, muons, neutrinos) and baryons (e,g, oritons and neutrons) are fermions.

Example 2: The atoms or which the sum of protons, neutrons and electros is an odd number, so that the total spin is half-integer (e.g. the isotope ^{3}He of helium) are fermions.

Two possible statistical approaches

The statistical treatment of a system of N particles can be performed by two different approaches, both based on the canonical formalism (see the beginning of Chapter 14).

First approach

The first approach consists in considering

- a macroscopic system composed by all the N particles,
- a canonical ensemble composed by $\mathcal{N}$ copies of the macroscopic system; . these copies are obviously distinguishable and weakly interacting.

The validity of this approach (depicted in Chapter 14) doesn't depend on the type of particles (distinguishable or not) nor on the extent of their interactions. In any case, the canonical distribution holds. Once the energy levels E_i of the entire system are known, one can calculate the partition function (14.17)

$$Z \;=\; \sum\nolimits_j e^{-E_j/k_BT}\,; \tag{16.8}$$

(the sum is here on the states j, not on the levels i, of the entire system). Once the the partition function is known, one can calculate the thermodynamical functions (§ 15.4). Particularly direct is the relation (15.48) between the partition function and the Helmoltz function:

$$F \;=\; -k_B T\,\ln Z\,. \tag{16.9}$$

The probability that the entire system is in the j-th state is

$$P_j \;==\; \frac{\mathcal{N}_j}{\mathcal{N}} \;=\; \frac{1}{Z}\,e^{-E_j/k_BT} \;=\; e^{-(E_j-F)/k_BT}\,. \tag{16.10}$$

If (and only if) the particles are weakly interacting, the energies E_j of the states of the entire system can be expressed as sums of the energies of the states of single particle ϵ_s, so that

$$Z \;=\; \sum\nolimits_j e^{-(n_1\epsilon_1+n_2\epsilon_2\dots)/k_BT} \tag{16.11}$$

The average number of particles in the single-particle state s with energy ϵ_s is then

$$\langle n_s\rangle \;=\; \sum\nolimits_j n_s\,P_j \;=\; \frac{1}{Z}\sum\nolimits_j n_s\,e^{-(n_1\epsilon_1+n_2\epsilon_2\dots)/k_BT} \tag{16.12}$$

(We are here considering the states, not the levels, of single particle; different states can correspond to the same degenerate energy level).
For distinguishable particles and for bosons, the numbers n_s can assume any value, for fermions the numbers n_s can only be 0 or 1 (Pauli exclusion principle).
The distribution of the energy on the single levels ϵ_i (given by the n_i values) depends on the distinguishability properties of the particles. Therefore, also the computation of Z depends on the particles distinguishability. To take into account these properties, one has to resort to the second approach.

Second approach

The second approach consists in considering the single-particle statistics, to which this chapter is specifically dedicated. In this second approach, the distinguishability properties of the particles has to be taken into due account.

a) For *distinguishable* and *weakly interacting* particles
   - each system is composed by a sigle particle,
   - the canonical ensemble is composed by N copies, distinguishable and weakly interacting, of the single particle; the canonical ensemble has constant energy $E \pm \delta E$.

   This approach leads to the canonical distribution for single particles, called Maxwell-Boltzmann (M.B.) distribution.

b) For *indistinguishable* particles, two procedures, different from the canonical one, have to be used wit, leading to two types of distributions:
   - the distribution of Bose-Einstein (B.E.) for particles with integer spin;
   - the distribution of Fermi-Dirac (F.D.) for particles with half-integer spin.

16.2 Computation of microstates

The different properties of identical particles lead to different distribution laws. To determine the different distribution laws, is is convenient to follow the same procedure which in Chapter 14 led to the canonical distribution. One computes the number of microstates which correspond to a generic distribution $\{n_i\}$ and one determines then the distribution which maximises the number of microstates.

Let N be te number of particles, ϵ_i the energy of the single particle levels and g_i the levels degeneracy, and let n_i be the number of particles sharing the energy ϵ_i. The umber of microstates for the different types of particles is computed below. In the following § 16.3 the most probable distribution will be determined for each type of particles.

a) Distinguishable identical particles

To compute the number Ω_{MB} of microstates corresponding to a distribution $\{n_1, n_2, n_3 ... n_i ...\}$ for distinguishable identical particles per particelle identiche distinguibili one follows the same procedure as that of § 14.1 leading to the canonical distribution (that actually refers to distinguishable identical systems). Let us thus re-consider equation (14.7), taking into account the differences of the two cases and substituting $\mathcal{N}!$ by $N!$ and the values N_i with the values n_i:

$$\Omega_{\mathrm{MB}} = N! \prod_i \frac{g_i^{n_i}}{n_i!} \tag{16.13}$$

b) Indistinguishable particles with integer spin (bosons)

The computation of the microstates of bosons differs from that for distinguishable particles and requires a different procedure. In the i-th level g_i microstates are possible. The n_i particles can distribute over the g_i states of the i-the level in any way.

To facilitate the computation, let us schematically consider the n_i particles on the i-th level mixed with $g_i - 1$ walls (Fig. 16.1): particles and walls can be globally permuted in $(n_i + g_i - 1)!$ ways. However, the separate permutations of the n_i particles and of the $g_i - 1$ walls correspond to the same microstate, so that a division by $n_i!$ and by $(g_i - 1)!$ is necessary.

Figure 16.1: Scheme useful for the computation of the boson microstates corresponding to n_i particles on an energy level with degeneracy g_i. Black dots represent the n_i particles, vertical lines represent the $g_i - 1$ walls.

The total number of microstates is obtained by multiplying the number of microstates corresponding to each separate level:

$$\Omega_{\mathrm{BE}} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \tag{16.14}$$

c) Indistinguishable particles with half-integer spin (fermions)

In the case of fermions, at most one particle can be occupy each one of the available states. The number of particles on a given level cannot exceed the degeneracy of the level: $n_i \leq g_i$.

Let us first consider a single given energy level: the first particle to be inserted in the i-th level has g_i different possibilities, the second one has $g_i - 1$ possibilities, and so on up to the last particle, which has $g_i - n_i + 1$ possibilities. It is however necessary to take into account that the permutations of the n_i particles correspond to the same microstate.

The total number of microstates is obtained by multiplying the number of microstates corresponding to each separate level:

$$\Omega_{\rm FD} = \prod_i \frac{g_i(g_i-1)(g_i-2)...(g_i-n_i+1)}{n_i!} = \prod_i \frac{g_i!}{n_i!(g_i-n_i)!} \tag{16.15}$$

d) Indistinguishable particles, classical limit

We have seen above that the number of microstates is different for the three cases: distinguishable particles, bosons, fermions.

It is however relevant that the numbers of microstates of bosons and fermions approach the same value when the populations of the single levels become more and more diluted, so that the average number of particles per level is much smaller than the level degeneracy. This situation becomes typically more probable when the temperature increases,

When $n_i \ll g_i$, that is when the levels are little populated, the following appeoximations can be made in the computation of microstates for bosons and fermions, respectively:

$$\text{forr } \Omega_{\rm BE}: \quad \tfrac{(n_i+g_i-1)!}{(g_i-1)!} = (g_i+n_i-1)(g_i+n_i-2)....g_i \simeq g_i^{n_i}$$

$$\text{for } \Omega_{\rm FD}: \quad g_i(g_i-1)(g_i-2)...(g_i-n_i+1) \simeq g_i^{n_i}$$

Therefore the number of microstates tends to the same limit for both bosons and fermions:

$$\begin{bmatrix} \Omega_{\rm BE} \\ \Omega_{\rm FD} \end{bmatrix} \longrightarrow \prod_i \frac{g_i^{n_i}}{n_i!} = \Omega_{\rm cl} \tag{16.16}$$

The value $\Omega_{\rm cl}$ is the *classical limit* for indistinguishable particles.

The value $\Omega_{\rm cl}$ of (16.16) differs by a factor $N!$ from the value $\Omega_{\rm MB}$ of (16.13) for identical distinguishable particles. The indistinguishability reduces by a factor $N!$ the number of microstates corresponding to a given distribution. This difference between distinguishable and indistinguishable particles is the base for explaining, at the end of 16.4, the Gibbs paradox concerning the mixture of ideal gases (see § 11.2).

16.3 Most probable distributions

Once the number Ω of microstates, corresponding to a given distribution $\{n_1, n_2, n_3...n_i...\}$ of the particles on their energy levels, has been calculated for each type of particle, one can determine the corresponding most probable distributions.

To this aim, we resort to the same procedure used in § 14.1 to obtain the canonical distribution for thermodynamical systems.

Let us assume that all microstates are equiprobable in equilibrium conditions and maximise $\ln\Omega$ for the different types of particles, with the constraints $\sum n_i = N$ and $\sum \epsilon_i n_i = E$, makin use of the Lagrange multipliers method.

Without going into the mathematical details, let us list below the results, expressed both in terms of the n_i values and of the *occupation indices* n_i/g_i.

a) Distinguishable identicl particles: Maxwell-Boltzmann

For identical distinguishable particles, the most probable distribution is the Maxwell-Boltzmann distribution (MB)

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i}}, \qquad \frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta\epsilon_i}} = e^{-\alpha-\beta\epsilon_i} \tag{16.17}$$

The MB distribution corresponds to the canonical distribution of § 14.1, the only difference being that here it refers to weakly-interacting single particles instead of thermodynamical systems. We will study the MD distribution in more detail in § 16.4.

b) Indistinguishable particles with integer spin: Bose-Einstein

For identical indistinguishable particles with integer spin, the most probable distribution is the Bose-Einstein distribution (BE):

$$n_i \;=\; \frac{g_i}{e^{\alpha+\beta\epsilon_i}-1}\,, \qquad \frac{n_i}{g_i} \;=\; \frac{1}{e^{\alpha+\beta\epsilon_i}-1} \tag{16.18}$$

We will study the BE distribution in more detail in § 16.5.

c) Indistinguishable particles with half-integer spin: Fermi-Dirac

For identical indistinguishable particles with half-integer spin, the most probable distribution is the Fermi-Dirac distribution (FD):

$$n_i \;=\; \frac{g_i}{e^{\alpha+\beta\epsilon_i}+1}\,, \qquad \frac{n_i}{g_i} \;=\; \frac{1}{e^{\alpha+\beta\epsilon_i}+1} \tag{16.19}$$

The denominator in (16.19) cannot be less than one, so that $n_i/g_i \leq 1$, or $n_i \leq g_i$. The occupation index cannot be larger than one, as expected from the anti-symmetry of the fermions wavefunction, and according to the Pauli exclusion principle.

In this respect, the FD is very different from the MB and BE distributions, for which the occupation index n_i/g_i can be only limited by the total number of particles N.

We will study the FD distribution in more detail in § 16.6.

d) Indistinguishable particles, classical limit

A synthetic way for representing and comparing the three distributions MB, BE and FD consists in expressing them by means of the inverse of the occupation index n_i/g_i. The three distributions can be summarised in a single formula, in which the differences are expressed by a parameter δ:

$$\frac{g_i}{n_i} + \delta \;=\; e^{\alpha+\beta\epsilon_i}\,, \qquad \text{where} \quad \delta = \begin{cases} \;\;0 \text{ (MB)} \\ +1 \text{ (BE)} \\ -1 \text{ (FD)} \end{cases} \tag{16.20}$$

The differences among the three distributions are negligible when $g_i/n_i \gg 1$, that is when $n_i \ll g_i$ say when the levels are loosely populated.

As we have seen above, in these situations the number of mcrostates $\Omega_{\rm BE}$ (16.14) and $\Omega_{\rm FD}$ (16.15) tend to the classical limit $\Omega_{\rm cl}$ (16.16).

The resulting distribution for $n_i \ll g_i$ is thus

$$n_i \;\simeq\; \frac{g_i}{e^{\alpha+\beta\epsilon_i}}\,, \qquad \frac{n_i}{g_i} \;\simeq\; \frac{1}{e^{\alpha+\beta\epsilon_i}}\,, \tag{16.21}$$

Equation (16.21) is identical to (16.17): the distribution doesn't depend on the particles distinguishability. The computation of microstates is however different, according to (16.13) and (16.16); the difference is due to the factor $N!$, that doesn't influence the maximisation procedure, since $d\ln N! = 0$, but influences the calculation of the entropy S.

Important remark

According to what already said in relation to the canonical distribution in Chapter 14, the four single-particle distributions considered above are the *most probable*, not the uniques. However, for very large values of N (typically $N \simeq 10^{23}$) the most probable distribution becomes largely dominant.

The β parameter

The β parameter is present in all the distributions, as the Lagrange multiplier connected to the energy conservation, $\sum \epsilon_i n_i = E$.
For all the distributions, the β parameter characterises the thermal equilibrium. The demonstration can be performed by the same procedure of § 14.3, that is by considering two ensembles of particles in thermal contact and verifying that the two ensembles share the same value of β.
The identification $\beta = 1/k_B T$ is made by supposing that at least one of the ensembles obeys the MB distribution.

The α parameter

Also the α parameter is present in all the distributions, as the Lagrange multiplier connected o the conservation of the number of particles, $\sum n_i = N$.
The computation of the α parameter is different for the three distribution. It is relatively simple for the Maxwell-Boltzmann distribution (§16.4), where, similarly to the case of the canonical distribution, it gives rise to the molecular partition function z; it is more more complex for the Bose-Einstein (§16.5) and Fermi -Dirac (§16.6) distributions.
A particular case of the Bose-Einstein distribution is represented by systems for which the number N is not a constant, for example systems composed by photons or phonons, which can be created or annihilated. In such cases, the Lagrange multiplier for the conservation of particles doesn't exist and $\alpha = 0$

16.4 Maxwell-Boltzmann statistics

Let us now consider in more detail the Maxwell-Boltzmann distribution for distinguishable particles and the classical approximate distribution for indistinguishable particles.
In particular, we will establish a connection between the Maxwell-Boltzmann distribution for single particles composing a thermodynamical system and the canonical distribution for the entire thermodynamical system.

16.4.1 Molecular and canonical partition functions

The normalisation condition $\sum n_i = N$ of the Maxwell-Boltzmann distribution (16.17) and of the classical limit of the quantum distributions (16.21) imposes that

$$N \;=\; \sum\nolimits_i n_i \;=\; \frac{1}{e^{\alpha}} \sum\nolimits_i \frac{g_i}{e^{\beta\epsilon_i}} \tag{16.22}$$

so that

$$e^{-\alpha} = \frac{N}{\sum_i g_i e^{-\beta\epsilon_i}} = \frac{N}{z}\,, \qquad \text{with} \quad z = \sum\nolimits_i g_i e^{-\beta\epsilon_i}\,. \tag{16.23}$$

The quantity z is the *molecular partition function*, which formally corresponds to the canonical partition function Z of thermodynamical systems introduced in § 14.3.
The occupation index of the energy level i can be re-written as

$$\frac{n_i}{g_i} \;=\; \frac{N}{z}\, e^{-\epsilon_i/k_B T} \tag{16.24}$$

The distributions (16.17) and (16.21) can be rewritten, in terms of probabilities of levels, as

$$p_i = \frac{n_i}{N} = \frac{1}{z}\, g_i\, e^{-\beta\epsilon_i}\,. \tag{16.25}$$

Connection between the partition functions Z and z

The two partition functions, canonical Z and molecular z, although formally similar, refer to very different situations:

- Z is the sum over the states of the entire system of N particles and is connected to the canonical distribution of macroscopic systems; the knowledge of Z is equivalent to the knowledge of te thermodynamical properties of the system (see § 15.4), so that, once Z is known, all thermodynamical functions of a system can be calculated;
- z is the sum over the states of single particle.

A useful connection can nevertheless be established between the two partition functions z and Z. For *weakly interacting identical particles*, the energy E_j of the j-th state of the thermodynamical system composed by N particles is connected to the single-particle energy values ϵ_i by the relation

$$E_j = \sum\nolimits_i n_i \epsilon_i \,, \tag{16.26}$$

where n_i is the number of particles on the i-th energy level, of energy ϵ_i. Therefore

$$Z \;=\; \sum\nolimits_j e^{-\beta E_j} \;=\; \sum\nolimits_j e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 \ldots)} \,, \tag{16.27}$$

where j labels the states of the system (not the levels), so that the degeneracy factors g are absent. Let us now substitute the sum over the states j of the system with the sum over all the possible distributions $\{n_1, n_2, ...\}$ of the system energy on the single-particle energy levels ϵ_i, taking into account their degeneracies g_i.

For *distinguishable particles*, each distribution corresponds to the number $\Omega_{\rm MB}$ microstates given by (16.13), so that:

$$\begin{aligned} Z &= \sum_{\{n_1,n_2,\ldots\}} \left(N! \prod_i \frac{g_i^{n_i}}{n_i!} \right) e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 \ldots)} \\ &= \sum_{\{n_1,n_2,\ldots\}} \frac{N!}{\prod n_i!} \left(g_1 e^{-\beta\epsilon_1}\right)^{n_1} \left(g_2 e^{-\beta\epsilon_2}\right)^{n_2} \ldots \\ &= \left(g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + \ldots\right)^N = \left(\sum\nolimits_i g_i\, e^{-\beta\epsilon_i}\right)^N = z^N \,, \end{aligned} \tag{16.28}$$

where in the last line the expression of the N-th power of a binomial has been exploited. According to (16.23), $z = e^\alpha/N$, so that the logarithm of Z is

$$\ln Z \;=\; N \ln z \;=\; N\alpha - N \ln N \,. \tag{16.29}$$

For *indistinguishable particles in the classical limit* (Bose-Einstein or Fermi-Dirac with $g_i \gg n_i$), the number of microstates corresponding to a distribution $\{n_1, n_2, ...\}$ is given by (16.16), say

$$\Omega_{\rm cl} \;=\; \frac{1}{N!}\,\Omega_{\rm MB} \tag{16.30}$$

so that $Z = z^N/N!$.

To schematically summarise the two cases (distinguishable identical particles and indistinguishable particles in the classical limit), the relations between canonical and molecular partition functions are:

$$\left[\begin{array}{c} \text{Distinguishable particles} \\ \\ Z_{\rm MB} \;=\; z^N \end{array}\right] \qquad \left[\begin{array}{c} \text{Indistinguishable particles} \\ \text{(classical approx.)} \\ Z_{\rm cl} \;=\; z_N/N! \end{array}\right] \tag{16.31}$$

16.4.2 Examples

Example 1: System of harmonic oscillators

Let us consider a system composed by N harmonic oscillators of equal angular frequency angolare $\omega = 2\pi\nu$. The energy levels are $\epsilon_n = \hbar\omega\,(1/2+n)$, where $\hbar$ is the reduced Planck constant and $n \geq 0$ is an integer number.

This example is similar to the example of the Einstein model already introduced in § 13.4, within the microcanonical approach. However, while in § 13.4 we considered an isolated system composed by N harmonic oscillators and computed the microstates of the entire system, here we focus our attention on each single oscillator in thermal contact with a reservoir made by other $N-1$ similar oscillators. The N oscillators can be the normal modes of a crystal, instead of the single atoms, and can in any case be considered as identical distinguishable particles obeying the Maxwell-Boltzmann distribution.

The energy levels of harmonic oscillator are not degenerate, $g_i = 1$: to each level only one state corresponds. The molecular partition function (14.17) is

$$z \;=\; \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(1/2+n)} \;=\; e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty}\left(e^{-\beta\hbar\omega}\right)^n \;=\; \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} \tag{16.32}$$

where the last equality is based on on the equation $\sum_{n=0}^{\infty} x^n = 1/(1-x)$ if $|x|<1$. Examples of partition functions for the harmonic oscillator are shown in Fig. 16.2, left.

The Maxwell-Boltzmann distribution

$$p_n = \frac{1}{z}\,e^{-\beta\epsilon_n} = \frac{1}{z}\,e^{-\epsilon_n/k_BT} \tag{16.33}$$

shows that, for a given temperature T, the probability p_n that an oscillator have the energy ϵ_n exponentially decreases when the energy increases (Fig. 16.2, right).

The canonical partition function of the entire system is

$$Z \;=\; z^N \;=\; \left[\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right]^N \tag{16.34}$$

In more realistic cases, oscillators (normal modes) of different frequencies ω_s have to be considered. In such cases, the particles (the oscillators) are not identical. The canonical partition function of the entire system can anyway be expressed as the product of the molecular partition functions of the different oscillators:

$$Z \;=\; \prod_s \frac{e^{-\beta\hbar\omega_s/2}}{1-e^{-\beta\hbar\omega_s}} \tag{16.35}$$

Example 2: Diluted gas

Let us consider a system composed by N atoms of a diluted monatomic gas contained in a cubic vessel of side L. Also this example was already considered in § 13.4, in connection with the microcanonical approach.

The particles are indistinguishable, we can nevertheless resort to the classical limit because of the gas dilution.

The energy levels ϵ_i, are degenerate. Each level corresponds to g_i different states characterised by different components of the linear momentum. One can consider again equation (12.5),

$$\epsilon_i \;=\; \frac{2\pi^2\hbar^2}{Lm}\,(n_{ix}^2+n_{iy}^2+n_{iz}^2)\,, \tag{16.36}$$

wherei n_{ij} are positive integer numbers. When the energy ϵ_i increases, also the groups of three values n_{ij} fulfilling (16.36) increases. The degeneracy g_i increases with energy.

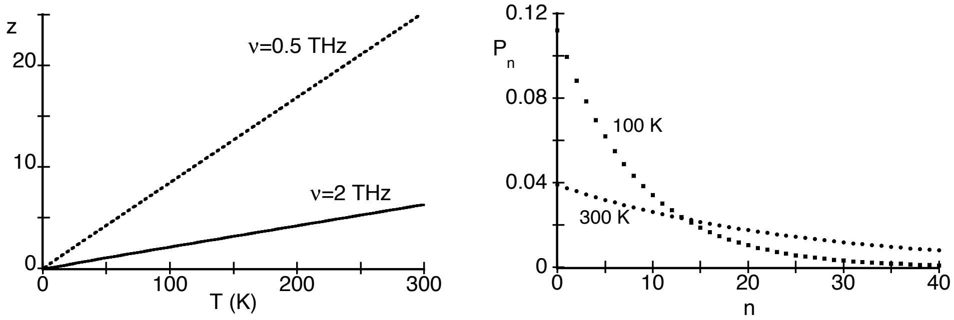


Figure 16.2: Left: molecular partition functions for harmonic oscillators of frequency $\nu = 0.5$ and 2 THz, plotted as a function of temperature. Right: Maxwell-Boltzmann distributions for harmonic oscillators of frequency $\nu = 0.5$ THz for two different temperatures, 100 and 300 K.

Since the energy levels are very closely spaced, one can substitute the degeneration index g_i with the density of states $g(\epsilon)$, that can be demonstrated to be

$$g(\epsilon)\, d\epsilon = \frac{2\pi}{h^3}\,(2m)^{3/2}\, V\,\sqrt{\epsilon}\, d\epsilon. \tag{16.37}$$

The molecular partition function is

$$z \;=\; \int_0^\infty g(\epsilon)\, e^{-\epsilon/kT}\, d\epsilon \;=\; \frac{V\,(2\pi m k T)^{3/2}}{h^3}\,. \tag{16.38}$$

According to (16.37), the density is proportional to the square root of ϵ; this behaviour is contrasted by the decreasing exponential factor $\exp(-\beta\epsilon)$ of the distribution (Fig. 16.3, left).
The Maxwell-Boltzmann distribution is expressed as a probability density

$$f_\epsilon(\epsilon) = \frac{2\pi}{(\pi k T)^{3/2}}\,\sqrt{\epsilon}\, e^{-\epsilon/kT}. \tag{16.39}$$

and doesn't depend on the type of gas (Fig. 16.3, centre).
The Maxwell-Boltzmann distribution for single particles is not sharply peaked around the average value of energy, as was the case for the canonical distribution for macroscopic systems, in spite of the formal similarity of the two distributions. For the canonical distribution the standard deviation is $\sigma \propto 1/\sqrt{N}$, where N is typically a number of the order of 10^{23}.
In addition to the energy distribution $f_\epsilon(\epsilon)$, it is useful to consider also the velocity distribution (31.20):

$$f_v(v) = 4\pi\left(\frac{m}{2\pi k T}\right)^{3/2} v^2\, e^{-mv^2/2kT}\,. \tag{16.40}$$

The velocity distribution depends on the atomic mass, and is different for different types of gases (Fig. 16.3, right).

16.4.3 Thermodynamical quantities

For weakly interacting particles, the relations of (16.31) allow the computation of the canonical partition function Z and of the thermodynamical functions once the single-particles energy levels ϵ_i and their degeneracies g_i are known.

Internal energy of the system

The internal energy of the system can be obtained, through (15.36) and (16.31), as

$$U \;=\; k_B T^2\left(\frac{\partial}{\partial T}\ln Z\right) \;=\; N\,k_B T^2\left(\frac{\partial}{\partial T}\ln z\right)_v\,. \tag{16.41}$$

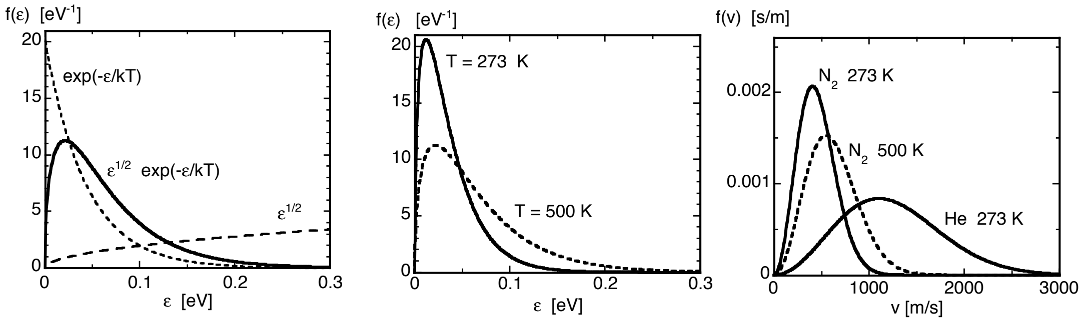


Figure 16.3: Diluted ideal gas. Left: comparison between the contributions of the density of states $\propto \sqrt{\epsilon}$ and of the exponential factor $\exp(-\beta\epsilon)$ and their product. Al centro: MB energy distributions for an ideal gas at two different temperatures. Right: MB velocity distributions for different gases at different temperatures.

The expression of U as a function of the molecular partition function z *doesn't* depend on the particles distinguishability ($N!$ doesn't depend on T).
Alternatively,

$$U \;=\; \langle E\rangle \;=\; \sum\nolimits_i n_i\epsilon_i\,, \tag{16.42}$$

where the values n_i are determined by the distribution $n_i = g_i \exp(-\beta\epsilon_i)/z$.

Example: Let us consider again the system of $N \simeq 10^{23}$ harmonic oscillators of equal frequency. Through (16.41) and (16.32), one can calculate the total energy of the system

$$U \;=\; k_BT^2\left(\frac{\partial}{\partial T}\ln Z\right)_V \;=\; \sum_s \frac{1}{2}\hbar\omega_s + \sum_s \frac{1}{e^{\hbar\omega_s/k_BT}-1}\,. \tag{16.43}$$

The first sum contains the zero point energies of the oscillators, the second one contains the contributions to the energy dependent on temperature.
The values of the energy levels E_i of the system are about 10^{23} times larger than the energy values of single oscillators, say much larger than the thermal factor $k_BT \simeq 25$ meV, and are characterised by very large degeneracies g_i.

Entropy of the system

The connection of the entropy S to the partition function Z is different for distinguishable particles and for indistinguishable particles in the classical limit:

$$S = \frac{U}{T} + k_B\ln Z = \begin{cases} U/T + Nk_B\ln z & = S_{\text{dist}} \\ \\ U/T + Nk_B\ln z - k_B\ln N! & = S_{\text{indist}} \end{cases} \tag{16.44}$$

Even if the single-particle energy levels and the internal energy are the same, the entropy of the system is different for the two cases:

$$S_{\text{dist}} \;=\; S_{\text{indist}} + k_B\,\ln N!\,, \qquad\qquad S_{\text{dist}} > S_{\text{indist}}\,. \tag{16.45}$$

To the same result one can come by considering the entropy definition for an isolated system, $S = k_B\ln\Omega$, and taking for Ω the values (16.13) and (16.16), respectively:

$$S_{\text{dist}} = k_B\,\ln\Omega_{MB}\,, \qquad\qquad S_{\text{indist}} = k_B\,\ln\Omega_{cl}\,. \tag{16.46}$$

Average energy of particles

Through (16.41), one finds

$$U = \langle E \rangle = N \langle \epsilon \rangle = N\, k_B T^2 \left(\frac{\partial}{\partial T} \ln z \right)_V . \tag{16.47}$$

The average energy of a single particle $\langle \epsilon \rangle$ is expressed as a function of z in the same way as the average energy of the macroscopic system $\langle E \rangle$ is expressed as a function of Z.

Note: The single-particle energy values ϵ can strongly fluctuate with respect to the average value $\langle \epsilon \rangle$. As already observed (Fig. 16.3), the Maxwell-Boltzmann distribution is not sharply peaked as the canonical distribution of macroscopic systems.

Heat and work

Heat and work exchanged by the thermodynamical system can be expressed in terms of the single-particle energy levels:

$$U = \sum\nolimits_i n_i \epsilon_i \quad \Rightarrow \quad \underbrace{\sum \epsilon_i dn_i}_{đQ} + \underbrace{\sum n_i d\epsilon_i}_{đW} \tag{16.48}$$

Distinguishable and indistinguishable particles, a summary

As we have seen above,

for distinguishable particles $\ln Z = N \ln z$
for indistinguishable particles (classical limit) $\ln Z = N \ln z - \ln N!$

The quantities that only depend on the derivatives of $\ln Z$ are equal for distinguishable particles and indistinguishable particles at the classical limit:

$$\begin{aligned} U &= N\, k_B T^2 \left(\frac{\partial}{\partial T} \ln z \right)_V \\ p &= N\, k_B T \left(\frac{\partial}{\partial V} \ln z \right)_T \\ H &= N\, k_B T^2 \left(\frac{\partial}{\partial T} \ln z \right)_V + N\, k_B T V \left(\frac{\partial}{\partial V} \ln z \right)_T \end{aligned}$$

The expression of the other quantities is different for distinguishable particles and indistinguishable particles at the classical limit:

Distinguishable part.	Indistinguishable part. (classical limit)
$S = U/T + Nk_B \ln z$	$S = U/T + Nk_B \ln z - k_B \ln N!$
$F = -Nk_B \ln z$	$F = -Nk_B \ln z + k_B T \ln N!$

16.4.4 Mixtures of indistinguishable gases. The Gibbs paradox

In § 11.2 we considered the spontaneous mixing of two ideal gases; we concluded that the process is irreversible and entails an entropy increase equal to the entropy increases of the separate free expansions of the two gases. The calculation of the entropy variation is independent of the nature of the two gases.

The calculation is however meaningless if the two gases are indistinguishable; actually, it makes no sense to speak of mixing of indistinguishable gases, since there is no variation of the thermodynamical state and there is thus no entropy variation. The apparently anomalous behavior of indistinguishable gases was named *Gibbs paradox*.

The solution of the Gibbs paradox depends on the fact that the atoms or moleules of the ideal gas are *indistinguishable* particles; therefore, the number of microstates of a system of N atoms or molecules is smaller than the number of microstates for distinguishable objects.
As it was noticed above, the entropy for indistinguishable particles in the classical limit is

$$S \;=\; \frac{U}{T} \,+\, Nk_B\,\ln z \,-\, k_B\,\ln N! \tag{16.49}$$

One can demonstrate that the molecular partition function for a monatomic ideal gas is

$$z \;=\; \frac{V\,(2\pi mkT)^{3/2}}{h^3}. \tag{16.50}$$

By substituting, in the expression of entropy, the values of z and $U = 3Nk_BT/2$, one obtains

$$S \;=\; Nk_B\,\ln\left(\frac{V}{N}\right) \,+\, \text{terms indepennent of } V\,. \tag{16.51}$$

For the problem of gas mixing only the term dependent on the specific volume V/N is relevant.
Let us consider the simple case of two ideal gases, e.g.1 mol of gas A and 1 mol of gas B contained in equal volumes V. Therefore, also $N_A = N_B$.
If the two gases are different (and thus distinguishable), the initial entropy is

$$S_i \;=\; N_Ak_B\,\ln\left(\frac{V}{N_A}\right) + N_Bk_B\,\ln\left(\frac{V}{N_B}\right) \tag{16.52}$$

and the final entropy is

$$\begin{aligned} S_f \;&=\; N_Ak_B\,\ln\left(\frac{2V}{N_A}\right) + N_Bk_B\,\ln\left(\frac{2V}{N_B}\right) \\ &=\; S_i \,+\, (N_A+N_B)k_B\,\ln 2 \;=\; S_i + 2N_Ak_B\,\ln 2\,. \end{aligned} \tag{16.53}$$

If the two gases are equal (and thus indistinguishable), $N_A = N_B = N$, the initial entropy is again

$$S_i \;=\; Nk_B\,\ln\left(\frac{V}{N}\right) + Nk_B\,\ln\left(\frac{V}{N}\right) \;=\; 2Nk_B\,\ln\left(\frac{V}{N}\right) \tag{16.54}$$

but the final entropy is

$$S_f \;=\; (2N)k_B\,\ln\left(\frac{2V}{2N}\right) \;=\; S_i\,. \tag{16.55}$$

16.5 Bose-Einstein statistics.

For the Bose-Einsten distribution (16.18)

$$n_i \;=\; \frac{g_i}{e^{\alpha+\beta\epsilon_i}-1}\,, \qquad\qquad \frac{n_i}{g_i} \;=\; \frac{1}{e^{\alpha+\beta\epsilon_i}-1} \tag{16.56}$$

the evaluation of the α parameter is by far more complicated than for the Maxwell-Boltzmann distribution.
However, in the case of photons and phonons, energy quanta of the electromagnetic field and of the crystal vibrations, respectively, the parameter $\alpha = 0$, because the number N of particles is not constant.

Sistems of bosons with N variable: photons and phonons

Let us again consider the normal modes of the electromagnetic field and of the atomic vibrations in crystals. They are distinguishable entities, characterised by different frequencies and wavevectors, that have been treated in § 16.4 as examples of application of the Maxwell-Boltzmann statistics, obtaining the expression (16.43) for the total energy of the system.
The energy can be stored in the normal modes only discontinuously, as a sum of discrete quanta $\hbar\omega_s$ (indistinguishable entities). One can consider an electromagnetic cavity or a crystal as containing a gas of quanta, and seek for a thermodynamic description in terms of the statistics of indistinguishable particles, instead of statistics of distinguishable normal modes. To this aim, let n_s be the number of energy stored in the n-th normal mode. The energy quanta of the electromagnetic field (photons) and of the atomic vibrations in crystals (phonons) can be created or annihilated: their number N is thus not a constant.
The total energy (16.43) can be expressed as

$$U = \sum_s \left[\frac{1}{2} + n_s\right] \hbar\omega_s \tag{16.57}$$

where

$$n_s = \frac{1}{e^{\hbar\omega_s/k_BT} - 1} \tag{16.58}$$

obeys the Bose-Einstein distribution with $\alpha = 0$ and $g_s = 1$. Photons and phonons are thus considered as bosons; to the photon an integer spin = 1 is attributed. The normalisation condition $\sum n_i = N$ has no meaning here, because photons and phonons can be created and annihilated through absorption or emission of electromagnetic radiation or of amounts of heat, respectively.

In conclusion, the thermodynamical properties of a system of electromagnetic waves or of a crystal can be interpreted, at the level of particle statistics, in terms of both a set of normal modes (a fixed number of distinguishable particles obeying the MB statistics)) or of a set of energy quanta (a variable number of indistinguishable particles obeying the BE statistics).
This possibility of different interpretations is a peculiar example of the wave-particle duality of Quantum Physics.

16.6 Fermi-Dirac statistics. Electron gas.

An most important application of the Fermi-Dirac statistics is the electron gas model that explains, to a first $g(\epsilon)$, the electronic properties of metals. In this model, the conduction electrons of a metal are considered as an ideal gas of free and independent particles, immersed in a homogeneous distribution of positive charge (due to the ions). In spite of being rather crude, the model is able to explain some properties of metals, in particluar the electron contribution to the specific heat.
The density of states $g(\epsilon)$ is calculated as for an ideal atomic gas enclosed in a volume V, taking into account that for each value of the momentum $\vec{p}$ there are two possible spin orientations:

$$g(\epsilon) = 2\,\frac{2\pi}{h^3}\,(2m)^{3/2}\,V\,\sqrt{\epsilon} \tag{16.59}$$

For an electron gas one can demonstrate that the α parameter can be substituted by $\alpha = -\mu/k_BT$, where μ is the chemical potential. The chemical potential μ weakly depends on temperature; its value for $T \to 0$ is called *Fermi energy* and is indicated by the symbol ϵ_F. The occupation index for fermions is thus generally written as

$$\frac{n_i}{g_i} = \frac{1}{e^{(\epsilon_i - \epsilon_F)/k_BT} + 1} \tag{16.60}$$

Part IV

Magnetic systems and low temperatures

Studying magnetic systems is interesting for a number of reasons.

The study of magnetic systems require the extension of the concepts of macroscopic Thermodynamics introduced in Part II; peculiar thermodynamical functions and response functions have to be introduced (Chapter 17).

The statistics of paramagnetic systems (Chapter 18) is a relatively simple application of the concepts introduced in Part III. However, differently from the cases considered in Part III, the statistical treatment of paramagnetic systems refers to the levels of the potential energy of a field external to the thermodynamical system; the potential energy doesn't contribute to the internal energy of the system. Therefore, the connection between the statistical approach and the macroscopic approach is more complicated than in the cases considered in Part III.

The adiabatic demagnetisation represents a fundamental tool for achieving very low temperatures. Chapter 19 is dedicated to cryogenic techniques..

The issue of low temperatures naturally leads to the introduction of the Thidr Law of Thermodynamics and to its interpretations (Chapter 20).

Part IV ends with a short account on the meaning of negative kelvin temperatures (Chapter **??**).

Chapter 17

Thermodynamics of magnetic systems

In this chapter, a number of basic concepts are introduced concerning the thermodynamical treatment of magnetic systems: magnetic thermodynamical variables, fundamental equations, Maxwell relations (§ 17.1) as well as the response functions, among which the magnetic susceptibility is particularly relevant (§ 17.2). Some important processes are then considered, in particular the Carnot magnetising cycle (§ 17.3). The chapter ends with a short introduction to magneto-mechanical effects (§ 17.4).

17.1 Basic concepts

In order to introduce the magnetic thermodynamical variables, it is convenient to refer to the magnetisation work introduced in Chapter 3.

17.1.1 Magnetisation work

In § 3.6 we considered a cylindrical and homogeneous matter bar inserted in a solenoid of length ℓ and section A, made by N coils through which an electric current I flows (Fig. 3.3, left). To avoid mathematical complexities, the magnetising field was considered uniform, confined within the solenoid and parallel to the axis of the solenoid. The electrical resistance of the circuit was neglected as well.

The total magnetisation work made by the power supply for establishing the electric current is

$$đW_{\text{mag}}^{\text{tot}} = \mu_0 V \mathcal{H}\, d\mathcal{H} + \mu_0 V \mathcal{H}\, d\mathcal{M} = V \mathcal{H}\, d\mathcal{B} \tag{17.1}$$

where $\mathcal{H}$ is the magnetising field, that is the external magnetic field produced by the electrical current, $\mathcal{M}$ is the magnetisation per unit volume of the material sample and $\mathcal{B}$ is the magnetic induction field, $\mathcal{B} = \mu_0(\mathcal{H} + \mathcal{M})$.

In (17.1) two contributions to the total work are singled out:

$\mu_0 V \mathcal{H}\, d\mathcal{H}$ refers to the empty space
$\mu_0 V \mathcal{H}\, d\mathcal{M}$ refers to the material sample

Let us recall the S.I. units of the quantities in (17.1):

- the magnetising field $\mathcal{H}$ and the magnetisation density $\mathcal{M}$ are both measured in ampere/meter (A/m)
- the magnetic induction $\mathcal{B}$ is measured in tesla (T) or in gauss (G), $1\,\text{T} = 10^4\,\text{G}$;
- $\mu_0 = 4\pi \times 10^{-7}$ T m/A is the vacuum magnetic permeability.

Note 1: Magnetising field, magnetic induction and magnetisation are in principle vectorial quantities. We consider here a unidimensional case, so that only scalar quantities are necessary. In diamagnetic materials the magnetisation $\mathcal{M}$ has opposite direction with respect to the magnetising field $\mathcal{H}$, in paramagnetic materials the magnetisation $\mathcal{M}$ has the same direction as the magnetising field $\mathcal{H}$.

Note 2: To enlighten the basic thermodynamical properties, we consider the simple ideal system of Fig. 3.3. Actually, to obtain a uniform magnetisation $\mathcal{M}$ in a uniform magnetising field the sample should be elliptical instead of cylindrical.

The thermodynamical system is represented by the material sample, the energy contribution of the empty space is not taken into account.
The variation of internal energy can be thus expressed as

$$dU \;= đQ \;+\; đW_{\mathrm{mec}} \;+\; đW_{\mathrm{chim}} \;+\; \mu_0 V \mathcal{H}\, d\mathcal{M}\,. \tag{17.2}$$

17.1.2 Magnetic thermodynamical coordinates

Two new thermodynamical variables have been introduced to describe the magnetic systems:

a) the magnetising field $\mathcal{H}$ (intensive variable);
b) the total magnetisation of the material sample $M = \mu_0 V \mathcal{M}$ (extensive variable).

The magnetic work (only referred to the material sample)

$$\boxed{đW_{\mathrm{mag}} \;=\; \mu_0 V \mathcal{H}\, d\mathcal{M} \;=\; \mathcal{H}\, dM} \tag{17.3}$$

is thus expressed in the standard form $Y\,dX$, where Y and X are intensive and extensive quantities, respectively.

Note: The axiomatic treatment of isolated systems of Chapter 5 is based on the existence of walls impermeable to extensive quantities (U, V, n_i) and on the search for the equilibrium condition attained by the system when one of such constraints is removed. For magnetic systems no “walls” exist impermeable to the magnetisation and it makes no sense to speak of the transfer of magnetisation between two sub-systems. In this respect, the total magnetisation is an anomalous extensive variable. It is anyway possible to develop a suitable thermodynamical formalism for magnetic systems in equilibrium, as we will see below.

17.1.3 Fundamental equations

The thermodynamical state of a magnetic systems is characterised by the values of its extensive coordinates , and its thermodynamical properties can be derived from a fundamental equations:
a) in the entropy representation, the fundamental equation is

$$S \;=\; S(U, V, M, \{n_i\})\,; \tag{17.4}$$

b) in the energy representation, the fundamental equation is

$$U \;=\; U(S, V, M, \{n_i\})\,. \tag{17.5}$$

In what follows, we focus our attention of the *energy representation.*
The differential of the internal energy is

$$dU \;=\; T\,dS \;-\; p\,dV \;+\; \mathcal{H}\,dM \;+\; \sum\nolimits_i \mu_i\, dn_i\,, \tag{17.6}$$

so that

$$\mathcal{H} \;=\; \left(\frac{\partial U}{\partial M}\right)_{S,V,n_i}\,. \tag{17.7}$$

The Euler equation (6.41), introduced in § 6.4, becomes for a magnetic system

$$U = T\,S - p\,V + \mathcal{H}M + \sum_i \mu_i\, n_i\,. \tag{17.8}$$

The Gibbs-Duhem relation (6.44) becomes in turn

$$S\,dT - V\,dp + M\,d\mathcal{H} + \sum_i n_i\,d\mu_i = 0\,. \tag{17.9}$$

17.1.4 Thermodynamical functions

The formalism of Legendre transform allows one to obtain thermodynamical functions specifically tailored to the different possible choices of independent thermodynamical coordinates (Chapters 7 and 8). Let us now dal with the case of magnetic systems. For simplicity, a closed system with a single component is considered, so that (17.6) reduces to

$$dU \;=\; T\,dS \;-\; p\,dV \;+\; \mathcal{H}\,dM\,. \tag{17.10}$$

The Legendre transforms of the internal energy U with respect to the mechanical and thermal variables give the known thermodynamical functions:

- $H(S, p, M, n)$, enthalpy
- $F(T, V, M, n)$, Helmholtz free energy
- $G(T, p, M, n)$, Gibbs free energy

The Legendre transforms with respect to the magnetic coordinates allow the introduction of new thermodynamical functions. We consider here only the two most important, the magnetic enthalpy and the magnetic Gibbs function.

Magnetic enthalpy

The magnetic enthalpy $H^*(S, p, \mathcal{H}, n)$ is the Legendre transform of the internal energy with respect to both the pressure p and the magnetising field $\mathcal{H}$:

$$H^* = U + pV - \mathcal{H}M\,, \qquad dH^* = T\,dS + V\,dp - M\,d\mathcal{H}\,. \tag{17.11}$$

For a system maintained at constant pressure p and magnetising field $\mathcal{H}$, the variation of magnetic enthalpy corresponds to the absorbed heat: $dH^* = T\,dS = đQ$.

In the next Chapter 18, dedicated to the statistics of magnetic systems, further details on the meaning of the magnetic enthalpy will be given (§ 18.4).

Magnetic Gibbs function

The magnetic Gibbs function $G^*(T, p, \mathcal{H}, n)$ is the Legendre transform of the magnetic enthalpy with respect to the temperature:

$$G^* = U + pV - \mathcal{H}M - TS\,, \qquad dG^* = -S\,dT + V\,dp - M\,d\mathcal{H}\,. \tag{17.12}$$

The magnetic Gibbs function is minimal for systems maintained in equilibrium at constant $T, p, \mathcal{H}$.

17.1.5 Maxwell relations

From the differentials dU, dH^*, dF, dG^*

$$dU = T\,dS - p\,dV + \mathcal{H}\,dM \tag{17.13}$$

$$dH^* = T\,dS + V\,dp - M\,d\mathcal{H} \tag{17.14}$$

$$dF = -S\,dT - p\,dV + \mathcal{H}\,dM \tag{17.15}$$

$$dG^* = -S\,dT + V\,dp - M\,d\mathcal{H} \tag{17.16}$$

one obtains new Maxwell relations in addition to those introduced in § 7.3; the new relations involve the magnetic coordinates:

$$\left(\frac{\partial T}{\partial M}\right)_{SV} = \left(\frac{\partial \mathcal{H}}{\partial S}\right)_{VM} \tag{17.17}$$

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{Sp} = -\left(\frac{\partial M}{\partial S}\right)_{p\mathcal{H}} \tag{17.18}$$

$$\left(\frac{\partial S}{\partial M}\right)_{TV} = -\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{VM} \tag{17.19}$$

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp} = \left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}} \tag{17.20}$$

17.2 Response functions

For a magnetic system, new response functions have to be considered, in addition to those introduced in Chapter 9: the isothermal and adiabatic susceptibilities, that play an important role in characterising the magnetic properties of materials.
Also the heat capacities are different for heat exchanges performed at constant magnetisation M or at constant magnetising field $\mathcal{H}$.

17.2.1 Magnetic suscebtibilities

In Chapter 9 we introduced the isothermal and adiabatic compressibilities, χ_T and χ_S (9.14), both defined as in terms of the ratio between volume and pressure variations.

If in (9.14) the pressure p is substituted by the magnetising field $\mathcal{H}$ and the volume V by the magnetisation M, one obtains the magnetic susceptibilities, bot isothermal

$$\chi_T^* = \frac{1}{\mu_0 V}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_{Tp} = \left(\frac{\partial \mathcal{M}}{\partial \mathcal{H}}\right)_{Tp} \tag{17.21}$$

ad adiabatic

$$\chi_S^* = \frac{1}{\mu_0 V}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_{Sp} = \left(\frac{\partial \mathcal{M}}{\partial \mathcal{H}}\right)_{Sp} \tag{17.22}$$

In both cases, the derivatives of $\mathcal{M}$ with respect to $\mathcal{H}$ are considered at constant pressure p.
The magnetic susceptibilities are a-dimensional quantities, since $\mathcal{M}$ and $\mathcal{H}$ have the same dimensions.
In (17.21) and (17.22) the magnetic susceptibilities χ^* are labeled by an asterisk to be distinguished from the mechanical compressibilities. In the following, the asterisk will be omitted when only magnetic properties are considered and no confusion is possible.

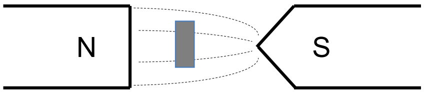


Figure 17.1: Schematic device suitable to measure the magnetic susceptibility. The N and S poles of a magnet are shaped so that the the $\mathcal{H}$ field be more intense near the S pole than near the N pole (the dashed lines are field lines). The black rectangle represents the sample.

The magnetic susceptibility can be measured by inserting the sample in a non uniform magnetising field and measuring the force acting on it (Fig. 17.1).
Three main types of behaviour can be singled out:

a) A purely *diamagnetic* material is weakly attracted towards the region of weaker field; the magnetisation is created by the external field and disappears when the field is removed.
b) A purely *paramagnetic* material is weakly attracted towards the region of stronger field; the magnetisation is created by the external field and disappears when the field is removed.
c) A *ferromagnetic* material is strongly attracted towards the region of stronger field; the magnetisation is present even if the external field is absent.

In this Part IV we deal only with diamagnetic and paramagnetic materials. Ferromagnetic materials are shortly treated in the § 22.5, of Part V dedicated to phase transitions.

Diamagnetic materials

In diamagnetic materials the magnetisation $\mathcal{M}$ has opposite direction with respect to the magnetising field $\mathcal{H}$. The diamagnetic susceptibility has the following properties (Fig. 17.2):

- is negative, $\chi_T^{\rm dia} < 0$, so that diamagnetic materials weaken the external applied field,
- is independent, in general, of temperature and of magnetising field,
- its absolute values are relatively small, $|\chi_T^{\rm dia}| \simeq 10^{-9} \div 10^{-5}$.

From the microscopic point of view, the diamagnetism can be attributed, in semiclassical terms, to the variation of the total angular momentum $\vec{J}$ of the atoms induced by the effect of the induction field $\vec{\mathcal{B}}$ on the electronic orbitals: $\Delta\vec{J} \propto \vec{\mathcal{B}}$. To the angular momentum $\vec{J}$ it corresponds a magnetic moment $\vec{\mu} = -g(e/2m)\vec{J}$; therefore $\Delta\vec{\mu} \propto -\vec{\mathcal{B}}$. For a spherical electronic distribution one can show that $\Delta\vec{\mu} \propto -\langle r^2\rangle\vec{\mathcal{B}}$ (Langevin diamagnetic susceptibility).
All substances are affected by diamagnetism; in some substances, however, diamagnetism can be hidden by other more strong effects, such as paramagnetism.

Examples of purely diamagnetic substances are: C, Hg, Sg, Cu, Zn, ammonia NH_3, molecular hydrogen H_2, noble gases, water.

Note: A relevant case of diamagnetism is present in superconductor metals. When a superconductor is immersed in a not too strong magnetising field $\mathcal{H}$, the magnetic induction $\mathcal{B}$ within the sample is null (Meissner-Ochsenfeld effect): the effect of the external field is counterbalanced by electrical currents induced on the surface of the sample. The superconductor is said to be a perfect diamagnet. A sufficiently strong field can instead destroy the superconductivity.

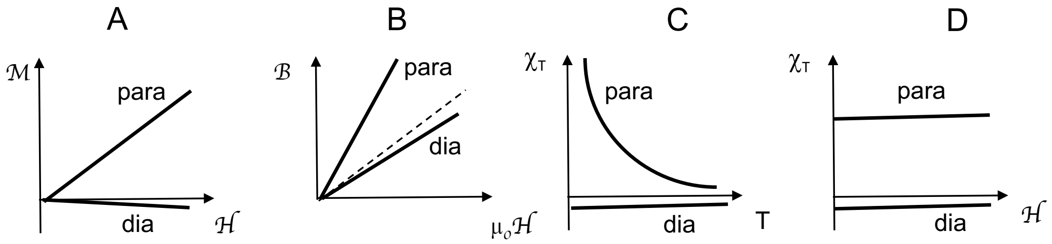


Figure 17.2: Schematic comparison (not to scale) between the properties of diamagnetic and paramagnetic substances. A) Magnetisation as a function of the external field. B) Magnetic induction as a function of the external field; the dashed line corresponds to a hypothetical non magnetic substance. C) Dependence of the isothermal susceptibility on temperature. D) Dependence of the isothermal susceptibility on the external field.

Paramagnetic materials

In paramagnetic materials, the magnetisation $\mathcal{M}$ has the same direction as the magnetising field $\mathcal{H}$. The paramagnetic susceptibility has the following properties (Fig. 17.2):

- is positive, $\chi_T^{\text{para}} > 0$, so that paramagnetic materials strengthen the external applied field,
- is independent of the magnetising field,
- strongly depends on temperature:
  - at not too low temperatures, for some paramagnetic materials, called *ideal paramagnets*, the *Curie law* holds:
    $$\chi_T^{\text{para}} = \frac{A}{T}\,, \qquad (A = \text{constant})\,; \tag{17.23}$$
  - for the other paramagnetic materials, the more general *Curie-Weiss law* holds:
    $$\chi_T^{\text{para}} = \frac{C}{T+\tau}\,, \qquad (C, \tau \text{ constants})\,; \tag{17.24}$$
- its absolute values are generally much larger than the values of diamagnetic susceptibility, $\chi_T^{\text{para}} \simeq 10^{-5} \div 10^{-3}$

Examples of paramagnetic substances are: molecular oxygen O_2, Pt, rare earths, alcali metals.

For very strong magnetising fields $\mathcal{H}$ (and low temperatures) the phenomenon of saturation can take place, so that the magnetisation ceases to increase when the magnetising field increases.

From the microscopic point of view, paramagnetism depends on the presence of permanent magnetic moments at the atomic or molecular level, that can be partially oriented by the external field $\mathcal{H}$.

Note 1: If the paramagnetism is due to the conduction electrons of metals (Pauli paramagnetism), the susceptibility χ_T^{para} only weakly depends on temperature.

Note 2: The parallelism between the response functions compressibility and magnetic susceptibility is incomplete. The isothermal and adiabatic compressibilities χ are always positive, as a consequence of the stability of thermodynamical equilibrium (Chapter 9). The magnetic susceptibilities χ^* can instead be positive or negative and is not connected to the stability of thermodynamical equilibrium; actually, as already observed, one cannot conceive of spontaneous magnetisation processes triggered by the removal of some constraint in isolated systems.

17.2.2 Dependence of magnetisation on temperature

In § 9.3 the coefficient of thermal expansion β as the ratio between the volume and temperature variations (eq. 9.19).

By substituting the volume V with the magnetisation M in (9.19), one obtains a new response function β^* which accounts for the dependence of magnetisation on temperature:

$$\beta^* = \left(\frac{\partial \mathcal{M}}{\partial T}\right)_{p\mathcal{H}} = \frac{1}{\mu_0 V}\left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}}\,. \tag{17.25}$$

According to what has been previously said,

- $\beta^* = 0$ in diamagnetic substances,
- $\beta^* < 0$ in paramagnetic substances.

17.2.3 Heat capacites

In § 9.1 the thermal het capacities at constant volume and constant pressure, C_v and C_p, have been introduced. When considering magnetic systems, only the processes at constant pressure are generally relevant. It is however necessary to distinguish the cases of heat exchanged at constant magnetising field $\mathcal{H}$ and at constant magnetisation M.

Heat capacity at constant $\mathcal{H}$ field

The heat capacity at constant $\mathcal{H}$ field is defined as

$$C_{p\mathcal{H}} = \frac{(đQ)_{p\mathcal{H}}}{dT} = T\left(\frac{\partial S}{\partial T}\right)_{p\mathcal{H}}. \tag{17.26}$$

To understand the influence of the magnetising field on the heat capacity, it is convenient to find the difference between the heat capacity $C_{p\mathcal{H}}$ (17.26) for non-zero field and the heat capacity C_p for zero field. To this aim, let us calculate the derivative of $C_{p\mathcal{H}}$ with respect to the field $\mathcal{H}$ at constant temperature T and pressure p and exploit the properties of the mixed second derivative:

$$\left(\frac{\partial C_{p\mathcal{H}}}{\partial \mathcal{H}}\right)_{Tp} = T\left[\frac{\partial}{\partial \mathcal{H}}\left(\frac{\partial S}{\partial T}\right)_{p\mathcal{H}}\right]_{Tp} = T\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp}\right]_{p\mathcal{H}} \tag{17.27}$$

The last member of (17.27) can be transformed through the Maxwell relation (17.20), so that

$$\left(\frac{\partial C_{p\mathcal{H}}}{\partial \mathcal{H}}\right)_{Tp} = T\left[\frac{\partial}{\partial T}\left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}}\right]_{p\mathcal{H}} = T\left(\frac{\partial^2 M}{\partial T^2}\right)_{p\mathcal{H}}. \tag{17.28}$$

It has been observed above that the magnetic susceptibility χ_T^* is independent of the $\mathcal{H}$ field; one can substitute $M = \mu_0 V \chi_T^* \mathcal{H}$, where only χ_T^* can depend on temperature, so that

$$\left(\frac{\partial C_{p\mathcal{H}}}{\partial \mathcal{H}}\right)_{Tp} = \mu_0 V T \mathcal{H}\left(\frac{\partial^2 \chi_T^*}{\partial T^2}\right)_{p\mathcal{H}}. \tag{17.29}$$

Equation (17.29) allows the expression of the relation between $C_{p\mathcal{H}}$ for non-zero $\mathcal{H}$ field and C_p for zero $\mathcal{H}$ field:

$$C_{p\mathcal{H}} = C_p(\mathcal{H}=0) + \mu_0 V T \int_0^{\mathcal{H}} \left(\frac{\partial^2 \chi_T^*}{\partial T^2}\right)_{p\mathcal{H}} \mathcal{H}'\, d\mathcal{H}'. \tag{17.30}$$

Example 1: In *diamagnetic substances* the susceptibility is independent of temperature. From (17.30) one thus finds that $C_{p\mathcal{H}} = C_p$, the heat capacity is independent of the magnetising field.

Example 2: In *ideal paramagnetic substances* the susceptibility is inversely proportional to temperature, $\chi_T^* = A/T$ (Curie law), so that

$$\left(\frac{\partial^2 \chi_T^*}{\partial T^2}\right) = \frac{2A}{T^3} \tag{17.31}$$

and (17.30) becomes

$$C_{p\mathcal{H}} = C_p + \mu_0 V \chi_T \frac{\mathcal{H}^2}{T} = C_p + \frac{M\mathcal{H}}{T}. \tag{17.32}$$

The heat amount absorbed by a paramagnetic substance for a given temperature increase is larger within a magnetising field $\mathcal{H}$ than at zero field. As we will see in Chapter 18, when the temperature of a paramagnetic substance increases at constant external field, the magnetisation M decreases. The extra heat amount which, according to (17.32), has to be supplied to the system when the field $\mathcal{H}$ is present is necessary to counterbalance the forces which tend to orient the elementary magnets.

Heat capacity at constant magnetisation M

The heat capacity at constant magnetisation M is defined as

$$C_{pM} = \frac{(đQ)_{pM}}{dT} = T\left(\frac{\partial S}{\partial T}\right)_{pM}. \tag{17.33}$$

It is worth noting that, in order to maintain constant the magnetisation M of a paramagnetic substance when the temperature is changed, also the magnetising field $\mathcal{H}$ has to be changed.

17.2.4 Relation between the heat capacities

The difference between the heat capacities at constant pressure and at constant volume can be expressed as a function of the coefficient of thermal expansion and of the isothermal compressibility (see § 9.4):

$$C_p - C_v \;=\; \frac{TV\beta^2}{\chi_T}\,. \tag{17.34}$$

A similar relation exists for the difference between the heat capacities at constant magnetising field (17.26) and at constant magnetisation (17.33):

$$C_{p\mathcal{H}} - C_{pM} \;=\; \mu_0 \frac{TV(\beta^*)^2}{\chi_T^*}\,, \tag{17.35}$$

where β^* is defined in (17.25) and χ_T^* is defined in (17.21).

Demonstration

The demonstration of (17.35) is similar to the one of (9.26). Here one starts from the functions

$$S(T,p,\mathcal{H})\,, \qquad S(T,p,M)\,. \tag{17.36}$$

By differentiating the (17.36) one obtains

$$T\,dS \;=\; C_{p\mathcal{H}}\,dT + T\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp} d\mathcal{H}\,, \tag{17.37}$$

$$T\,dS \;=\; C_{pM}\,dT + T\left(\frac{\partial S}{\partial M}\right)_{Tp} dM\,. \tag{17.38}$$

By subtracting (17.38) from (17.37) and using the Maxwell relations (17.19) and (17.20) one obtains

$$(C_{p\mathcal{H}} - C_{pM})\;dT \;=\; -\,T\left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}} d\mathcal{H} \;-\; T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{pM} dM\,. \tag{17.39}$$

Let us now compare the differential dT calculated from (17.39) with the differential of the function $T(\mathcal{H},M)$. Since $\mathcal{H}$ and M are independent variables, the coefficients of both $d\mathcal{H}$ and dM must be equal in the two expressions.
Let us focus our attention on the coefficient of dM; from their equality, exploiting the identities (7.49) and (7.51) one obtains

$$C_{p\mathcal{H}} - C_{pM} = -T\left(\frac{\partial \mathcal{H}p}{\partial T}\right)_{pM}\left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}} = T\left(\frac{\partial M}{\partial T}\right)^2_{p\mathcal{H}}\left(\frac{\partial \mathcal{H}}{\partial M}\right)_{T} \tag{17.40}$$

whence (17.34).

Esemples

Example 1: In diamagnetic substances $\beta^* = 0$ because the susceptibility is independent of temperature. Therefore $C_{p\mathcal{H}} = C_{pM}$. We have also shown above that $C_{p\mathcal{H}} = C_p$, independent of the magnetising field.

Example 2: For a paramagnetic substance $\chi_T^* > 0$ and $(\beta^*)^2 > 0$. Therefore $C_{p\mathcal{H}} > C_{pM}$.

Example 3: For an *ideal paramagnetic substance* the Curie law $\chi_T^* = A/T$ holds, and χ_T^* is independent of the $\mathcal{H}$ field, so that $M = \mu_0 VA\mathcal{H}/T$. Therefore

$$\beta^* \;=\; \frac{1}{\mu_0 V}\left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}} \;=\; \left[\frac{\partial}{\partial T}(\chi_T^*\mathcal{H})\right]_{p\mathcal{H}} \;=\; \mathcal{H}\left(\frac{\partial \chi_T^*}{\partial T}\right)_{p\mathcal{H}} \;=\; -\mathcal{H}\,\frac{A}{T^2}\,. \tag{17.41}$$

As a consequence

$$C_{p\mathcal{H}} - C_{pM} \;=\; \mu_0 V \chi_T^* \frac{\mathcal{H}}{T} \;=\; \frac{M\mathcal{H}}{T}\,. \tag{17.42}$$

By comparing (17.42) with (17.32) on can see that, fo an ideal paramagnetic substance, $C_{pM} = C_p$, independent of $\mathcal{H}$ e da M.
At last, one can notice the formal similarity of (17.42) with the relation for ideal gases

$$C_p - C_v \;=\; \frac{pV}{T}\,. \tag{17.43}$$

17.3 Thermodynamical processes in magnetic systems

Let us consider here three of the possible thermodynamical processes in magnetic systems:

1. reversible isothermal magnetisation at constant volume,
2. reversible isothermal magnetisation (or demagnetisation) at constant pressure,
3. reversible adiabatic magnetisation (or demagnetisation) at constant pressure.

The first process, at constant volume, has mainly theoretical interest. The other two processes are more important from the practical point of view and are the elements of the magnetic Carnot cycle.
In this § 17.3 the magnetic susceptibility is denoted by χ, without asterisk.

17.3.1 Reversible isothermal magnetisation at constant volume

Our aim is to evaluate the change of internal energy U. Starting from the differential (17.10)

$$dU \;=\; T\,dS - p\,dV + \mathcal{H}\,dM\,, \tag{17.44}$$

imposing $dV = 0$ and using the Maxwell relation (17.19) one obtains

$$\left(\frac{\partial U}{\partial M}\right)_{TV} \;=\; T\left(\frac{\partial S}{\partial M}\right)_{TV} \;+\; \mathcal{H} \;=\; -T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{VM} \;+\; \mathcal{H}\,. \tag{17.45}$$

Since $M = \mu_0 V \chi \mathcal{H}$, one can substitute $\mathcal{H} = M/\mu_0 V\chi$ and obtain:

$$\begin{aligned}\left(\frac{\partial U}{\partial M}\right)_{TV} \;&=\; -\frac{T}{\mu_0 V}\left[\frac{\partial}{\partial T}\left(\frac{M}{\chi}\right)\right]_{VM} + \frac{1}{\mu_0 V}\left(\frac{M}{\chi}\right)\\ &=\; \frac{1}{\mu_0 V}\,\frac{M}{\chi}\left[\frac{T}{\chi}\left(\frac{\partial \chi}{\partial T}\right)_{VM} + 1\right]\,.\end{aligned} \tag{17.46}$$

In the last equality one considered that $(\partial M/\partial T)_{MV} = 0$.

Diamagnetic substances

For diamagnetic substances, the susceptibility χ is independent of temperature. The first term of (17.46) (entropic term) is null: there is no heat exchange in an isothermal magnetisation. Diamagnetic substances have little thermodynamical interest.
Starting from

$$\left(\frac{\partial U}{\partial M}\right)_{TV} \;=\; \frac{1}{\mu_0 V}\,\frac{M}{\chi} \;=\; \mathcal{H} \tag{17.47}$$

one can anyway evaluate the variation of internal energy for a finite magnetisation:

$$U(M,T,V) - U(M=0,T,V) \;=\; \int_0^M \mathcal{H}\,dM \;=\; \frac{M^2}{2\chi} = \frac{M\mathcal{H}}{2} = \frac{\chi\mathcal{H}^2}{2} \;=\; W \;<\; 0\,. \tag{17.48}$$

The variation of internal energy is negative, the system performs work on its ambient.

Note: Recall that the M and $\mathcal{H}$ have opposite signs for a diamagnetic substance.

Paramagnetic substances

For paramagnetic substances the susceptibility χ is positive and decreases when the temperature increases. The entropic term of (17.46) is always negative; during the isothermal magnetisation, the paramagnetic system absorbs work and emits heat. The sign of dU is a priori undetermined.

Ideal paramagnetic substances

For ideal paramagnetic substances, the susceptibility has the simple dependence on temperature $\chi = A/T$, so that

$$\left(\frac{\partial \chi}{\partial T}\right)_{VM} = -\frac{A}{T^2} = -\frac{\chi}{T}\,; \tag{17.49}$$

by inserting (17.49) in (17.46) one obtains

$$\left(\frac{\partial U}{\partial M}\right)_{TV} = 0\,. \tag{17.50}$$

The entropic and magnetic terms cancel out, so that $dU = 0$. The system absorbs work and emits heat without variation of the internal energy (notice the analogy with the behaviour of ideal gases undergoing isothermal compression).

17.3.2 Reversible isothermal magnetisation at constant pressure

Let us now consider a system maintained at constant temperature and pressure and increase its magnetisation through an increase of the external magnetising field $\mathcal{H}$. The magnetisation requires that work $\mathcal{H}\,dM$ is performed on the system. We want to know whether the magnetisation is accompanied by absorption or emission of heat by the system.
For a reversible transformation, $đQ = T\,dS$; we can thus consider the dependence of the entropy on the magnetising field:

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp} = \left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}} = \mu_0 V \mathcal{H} \left(\frac{\partial \chi}{\partial T}\right)_{p\mathcal{H}}\,. \tag{17.51}$$

In (17.51) we took advantage of the Maxwell relation (17.20) and of the relation between magnetisation and magnetising field $M = \mu_0 V \chi \mathcal{H}$. According to (17.51), the dependence of the entropy on the magnetising field is connected to the dependence of the susceptibility on the temperature.

Diamagnetic substances

In diamagnetic substances, the susceptibility is independent of the temperature. The reversible isothermal magnetisation at constant pressure takes place without entropy variations and thus without heat exchange.

Paramagnetic substances

In paramagnetic substances, the susceptibility is positive and decreases when the temperature increases (Fig. 17.2):

$$\left(\frac{\partial \chi}{\partial T}\right)_{p\mathcal{H}} < 0 \qquad \Rightarrow \qquad \left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp} < 0\,. \tag{17.52}$$

The reversible isothermal magnetisation at constant pressure gives rise to a decrease of the entropy which corresponds to a transfer of heat from the system to the ambient.
Viceversa, the reversible isothermal demagnetisation gives rise to an increase of the entropy which corresponds to a transfer of heat from the ambient to the system.
For an *ideal paramagnetic substance* $\chi = A/T$, so that (17.51) becomes

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp} = -\mu_0 A V \frac{\mathcal{H}}{T^2}\,, \tag{17.53}$$

and the finite entropy variation for a variation of the magnetising field from $\mathcal{H}_1$ to $\mathcal{H}_2$ is

$$\Delta S \;=\; -\mu_0 AV \frac{1}{T^2} \int_{\mathcal{H}_1}^{\mathcal{H}_2} \mathcal{H}' \, \underset{\cdot}{\mathrm{H}}' \;=\; -\mu_0 AV \frac{1}{2T^2} \left(\mathcal{H}_2^2 - \mathcal{H}_1^2\right) . \tag{17.54}$$

The entropy variation is inversely proportional to the square of the temperature, so that the exchanged heat $Q = T \, \Delta S$ is inversely proportional to the temperature.

17.3.3 Reversible adiabatic magnetisation at constant pressure

In a reversible adiabatic transformation there is no exchange of heat and $\Delta S = 0$. We want to know how the temperature changes when the magnetisation is changed at constant pressure. To his aim, let us start from the differential of the entropy as a function of temperature and magnetising field

$$dS \;=\; \left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp} d\mathcal{H} \;+\; \left(\frac{\partial S}{\partial T}\right)_{p\mathcal{H}} dT \, . \tag{17.55}$$

By imposing the condition $dS = 0$, from (17.55) one obtains

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{Sp} \;=\; \frac{(\partial S/\partial \mathcal{H})_{Tp}}{(\partial S/\partial T)_{p\mathcal{H}}} \;=\; -\frac{T}{C_{p\mathcal{H}}} \left(\frac{\partial M}{\partial T}\right)_{p\mathcal{H}} , \tag{17.56}$$

where the Maxwell relation (17.20) and the definition of heat capacity at constant field (17.26) have been used.

By considering the relation between magnetisation and magnetising field $M = \mu_0 V \chi \mathcal{H}$, equation (17.56) becomes

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{Sp} \;=\; -\mu_0 V \mathcal{H} \, \frac{T}{C_{p\mathcal{H}}} \left(\frac{\partial \chi}{\partial T}\right)_{p\mathcal{H}} . \tag{17.57}$$

Diamagnetic substances

For diamagnetic substances, the susceptibility is independent of temperature. The reversible adiabatic magnetisation doesn't give rise to temperature variations.

Paramagnetic substances

For paramagnetic substances, the susceptibility decreases when the temperature increases; its derivative is thus negative.

The reversible adiabatic magnetisation gives rise to an increase of temperature.

Viceversa, the reversible adiabatic demagnetisation gives rise to a reduction of temperature.

The variation of temperature induced by the magnetising field without heat exchange is called *magneto-caloric effect.*

For an *ideal paramagnetic substance* $\chi = A/T$, and (17.57) becomes

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{Sp} \;=\; \mu_0 V \frac{A\mathcal{H}}{T \, C_{p\mathcal{H}}} \, . \tag{17.58}$$

The temperature variation is inversely proportional to the temperature. The magneto-caloric effect is more effective at low temperatures.

17.3.4 Magnetic Carnot cycle

A Carnot cycle (§ 4.3) is made by two reversible isothermal transformations and two reversible adiabatic transformations. For paramagnetic substances, the Carnot cycle is achieved a constant pressure by suitably varying the magnetising field $\mathcal{H}$ and, as a consequence, the system magnetisation M.

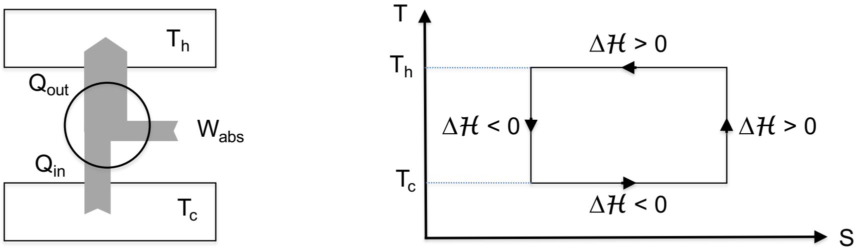


Figure 17.3: Refrigerating Carnot cycle for a paramagnetic substance. Left: schematic representation; during a cycle, the paramagnetic substance (represented by the circle) transfers heat from the reservoir at the lower temperature T_c to the reservoir at the higher temperature T_h. Right: ST plot; the refrigerating cycle is run anti-clockwise.

A Carnot cycle can be run as an engine or a refrigerator. For paramagnetic systems, the refrigerating Carnot cycle is more relevant, due to its cryogenic applications (see Chapter 19).
Let us onsider a refrigerating Carnot cycle operating between two reservoirs at the two temperatures T_h (higher) and T_c (lower) (Fig. 17.3 , left).The refrigerating Carnot cycle is composed by the four transformations (Fig. 17.3, right):

a) The paramagnetic substance is in contact with the hot reservoir at T_h: the substance is isothermally magnetised ($\Delta\mathcal{H} > 0$) and gives up heat to the reservoir.
b) The paramagnetic substance is thermally insulated and adiabatically demagnetised ($\Delta\mathcal{H} < 0$), so that its temperature decreases to the value T_c.
c) The paramagnetic substance is in contact with the cold reservoir at T_c and further isothermally demagnetised ($\Delta\mathcal{H} < 0$), so that it absorbs heat from the reservoir.
d) The paramagnetic substance is thermally insulated and adiabatically re-magnetised ($\Delta\mathcal{H} > 0$), so that its temperature increases to the value T_h.

The refrigerating cycle transfers heat from the cold to the hot reservoir, absorbing work from the power supply of the magnetising field.

In the practical applications of the magnetic Carnot cycle to cryogenic techniques (see Chapter 19) the cold reservoir of Fig. 17.3 is substituted by a finite system, that progressively reduces its temperature during each cycle.

17.4 Magneto-mechanical effects

In addition to the thermal effects of magnetic fields (*magnetotermal* effects, of which some examples have been considered in § 17.3), interesting correlations can take place between magnetic and mechanical properties.

Magnetostrictive effect

In isothermal (or adiabatic) conditions at constant pressure p, an increase of the magnetising field $\mathcal{H}$ can give rise to a variation, positive or negative, of the volume V.
The effect is described by the derivatives

$$\left(\frac{\partial V}{\partial \mathcal{H}}\right)_{T,p}, \qquad \left(\frac{\partial V}{\partial \mathcal{H}}\right)_{S,p}, \tag{17.59}$$

connected by the relation

$$\left(\frac{\partial V}{\partial \mathcal{H}}\right)_{S,p} = \left(\frac{\partial V}{\partial \mathcal{H}}\right)_{T,p} + \left(\frac{\partial V}{\partial T}\right)_{\mathcal{H},p} \left(\frac{\partial T}{\partial \mathcal{H}}\right)_{S,p} \tag{17.60}$$

Magnetoelastic effect

In isothermal (or adiabatic) conditions at constant $\mathcal{H}$ field, n increase of the pressure p can give rise to a variation, positive or negative, of the magnetisation M.

The effect is described by the derivatives

$$\left(\frac{\partial M}{\partial p}\right)_{T,\mathcal{H}}, \qquad \left(\frac{\partial M}{\partial p}\right)_{S,\mathcal{H}}, \tag{17.61}$$

connected by the relation

$$\left(\frac{\partial M}{\partial p}\right)_{S,\mathcal{H}} = \left(\frac{\partial M}{\partial p}\right)_{T,\mathcal{H}} + \left(\frac{\partial M}{\partial T}\right)_{p,\mathcal{H}} \left(\frac{\partial T}{\partial p}\right)_{S,\mathcal{H}} \tag{17.62}$$

Relation between the two effects

The two effects, magnetostrictive and magnetoelastic, are not independent. The relation between the two effects is based on the Maxwell relations that one obtains by coupling mechanical and magnetic terms.

Let us consider the differentials of the magnetic enthalpy H^* and of the magnetic Gibbs function G^*:

$$dH^* = T\,dS + V\,dp - M\,d\mathcal{H}\,, \tag{17.63}$$

$$dG^* = -S\,dT + V\,dp - M\,d\mathcal{H}\,. \tag{17.64}$$

The two Maxwell relations

$$\left(\frac{\partial V}{\partial \mathcal{H}}\right)_{S,p} = -\left(\frac{\partial M}{\partial p}\right)_{S,\mathcal{H}}, \qquad \left(\frac{\partial V}{\partial \mathcal{H}}\right)_{T,p} = -\left(\frac{\partial M}{\partial p}\right)_{T,\mathcal{H}} \tag{17.65}$$

connect the two effects, in adiabatic and isothermal conditions, respectively.

If the volume V increases when the $\mathcal{H}$ field increases, the magnetisation M decreases when the pressure p increses.

Chapter 18

Statistics of paramagnetic systems

As we have seen in the previous chapter, systems characterised by magnetic dipole moments at the atomic level have thermodynamical interest. The simplest of such systems are the paramagnetic substances, in which the magnetisation appears only when an external magnetising field is present and disappears when the magnetising field is removed.

In this chapter, the statistics of paramagnetic systems is studied. We first review the basics of atomic magnetism and its quantisation (§ 18.1). An atom immersed in a magnetising field acquires magnetic potential energy (§ 18.2). The magnetic potential energy is quantised: its levels are the starting point for the statistical treatment.

The statistical treatment is here first applied to a particularly simple system, where only two levels of magnetic potential energy are present (§ 18.3). By reducing the mathematical complexity, one can thus better focus the attention on the fundamental aspects, mainly concerning the connection with the macroscopic Thermodynamics, that is in some respects different from the connection for the simple systems considered in Chapter 15.

In § 18.4 the results obtained for a two-level system are extended to magnetic systems with an higher number (in any case finite) of energy levels. The § 18.4 ends with the description of some processes relevant for applications to cryogeny, that will be further considered in Chapter 19.

18.1 Basics of atomic magnetism

To the angular momentum of elementary particles it corresponds a momentum of magnetic dipole. The ratio between the magnetic dipole momentum and the angular momentum is different for the orbital and the spin angular momenta, and in both cases is different fo the different constituents of the atom (electrons, protons and neutrons).

In the following we first consider the magnetic moment of electrons, then the magnetic moment of nucleons (protons and neutrons).

18.1.1 Magnetic moment of electrons

Orbital magnetic moment of electrons

For a system of electrons whose total spin is null, $\vec{S}=0$, the magnetic dipole moment $\vec{\mu}$ is connected to the orbital angular momentum $\vec{L}$ by the relations

$$\vec{\mu}_\ell \;=\; -\frac{e\hbar}{2m_e}\,\frac{\vec{L}}{\hbar} \;=\; -\mu_B\,\frac{\vec{L}}{\hbar}\,, \qquad\qquad \mu_z \;=\; -\mu_B\, m_\ell\,, \tag{18.1}$$

where e is the value (positive) of the elementary charge, m_e is the electron mass and $\hbar = h/2\pi$ is the reduced Planck constant.

The left part of (18.1) refers to the vectors $\vec{\mu}_\ell$ e $\vec{L}$, the right part refers to their components along a given z direction. The magnetic dipole moment and the angular momentum have opposite directions.

The quantity μ_B in (18.1) is the *Bohr magneton*

$$\mu_B \;=\; \frac{e\hbar}{2m_e} \;=\; 5.788\times 10^{-5}\,\text{eV/T} \;=\; 9.274\times 10^{-24}\,\text{J/T} \tag{18.2}$$

and has the same dimensions as the magnetic dipole moment; the ratio $L/\hbar$ is adimensional.

Note 1: Equation (18.1) can be explained also by a classical approach, if one assumes that the electron moves on a circular orbit of radius r with angular velocity ω: the corresponding angular momentum is $L = m_e\omega r^2$, the electric current is $I = e(\omega/2\pi)$ and the magnetic moment is $e\omega r^2/2$.

Note 2: The unit of the magnetic dipole and the Bohr magneton is generally expressed as the ratio between an energy and a magnetic induction, eV/T. This choice is consistent with the expression (18.10) of the magnetic potential energy, to be introduced in § 18.2.

Spin magnetic moment of electrons

For an electron or a set of electrons whose orbital angular momentum is null, $\vec{L}=0$, the magnetic dipole moment $\vec{\mu}$ depends on the total spin $\vec{S}$ according to

$$\vec{\mu}_s \;=\; -g_s\,\mu_B\,\frac{\vec{S}}{\hbar}\,, \qquad\qquad \mu_z \;=\; -g_s\,\mu_B\,m_s\,. \tag{18.3}$$

Also in (18.3) the left part refers to vectors, the right part refers to their components along a given direction z. The quantity g_s is the *gyromagnetic ratio of the electron* or *spin g factor*. It exact value is $g_s = 2.002319$, generally approximated by $g_s = 2$.

Equation (18.3) (spin) differs from equation (18.1) (orbital angular momentum) by a factor 2. Sometimes one inserts also in (18.1) a factor $g_\ell = 1$, called *orbital g factor*.
For a single electron, $m_s = \pm 1/2$, so that $\mu_B = |\mu_z|$: the Bohr magneton is the value of the spin magnetic moment of a single electron.

Total magnetic moment of electrons

For a generic system of electrons, for which both $\vec{L}\neq 0$ and $\vec{S}\neq 0$, it is necessary to consider the total angular momentum $\vec{J}$. The total magnetic moment $\vec{\mu}$ depends on the total angular momentum $\vec{J}$ according to the relations

$$\vec{\mu}_J \;=\; -g_J\,\mu_B\,\frac{\vec{J}}{\hbar}\,, \qquad\qquad \mu_z \;=\; -g_J\,\mu_B\,m_J\,. \tag{18.4}$$

The quantity g_J is the *Landé factor*, whose value is given by

$$g_J \;=\; \frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}\,. \tag{18.5}$$

One can easily verify that if $L = 0$, then $g_J = 2$, while if $S = 0$, then $g_J = 1$. Equation (18.4) summarises thus all possible cases.

18.1.2 Magnetic moment of nucleons

The nuclear magneton

For a proton, the relation between magnetic moment and orbital angular momentum is similar to the one of the electron (18.1), the differences are due to the different mass and do the different sign of the electric charge:

$$\vec{\mu}_\ell \;=\; \frac{e\hbar}{2m_p}\,\frac{\vec{L}}{\hbar} \;=\; \mu_N\,\frac{\vec{L}}{\hbar}\,, \tag{18.6}$$

where m_p is the proton mass, which is 1836 times larger than the electron mass.

The quantity μ_N is the *nuclear magneton*

$$\mu_N \;=\; \frac{e\hbar}{2m_p} \;=\; 3.152\times10^{-8}\,\text{eV/T} \;=\; 5.050\times10^{-27}\,\text{J/T} \tag{18.7}$$

which is 1836 times smaller than the Bohr magneton, $\mu_N = \mu_B/1836$.

Spin of protons and neutrons

Protons and neutrons, like electrons, are characterised by a spin angular momentum $\vec{s}$; to the spin it corresponds a magnetic moment for the electron too, in spite of the absence of an electric charge. The relation between magnetic moment $\vec{\mu}$ and spin $\vec{s}$ of single nucleon is

$$\vec{\mu}_s \;=\; g\,\mu_N\,\frac{\vec{s}}{\hbar}\,, \tag{18.8}$$

where the quantity g has different values for protons and neutrons:

- for protons $g_p = 5.58$ (positive), so that the magnetic moment is $\mu_{sp} = 2.7927\,\mu_N$
- for neutrons $g_n = -3.826$ (negative), so that the magnetic moment is $\mu_{sn} = -1.9131\,\mu_N$

Nuclear spin

The total angular momentum $\vec{I}$ of a nucleus (called *nuclear spin*) is the sum of the orbital and spin contributions of the nucleons. The corresponding magnetic moment is

$$\vec{\mu}_I \;=\; g_I\,\mu_N\,\frac{\vec{I}}{\hbar}\,, \qquad\qquad \mu_z \;=\; g_I\,\mu_N\,m_I\,, \tag{18.9}$$

where g_I is the gyromagnetic ratio of the nucleus.

18.2 Magnetic potential energy

For a magnetic dipole of moment $\vec{\mu}$ inserted in a field of magnetic induction $\vec{\mathcal{B}}$ directed along the z axis, the potential energy is

$$\epsilon_m \;=\; -\vec{\mu}\cdot\vec{\mathcal{B}} \;=\; -\mu_z\mathcal{B}\,. \tag{18.10}$$

The potential energy (18.10) is minimum when $\vec{\mu}$ and $\vec{\mathcal{B}}$ are parallel, it is maximum when they are anti-parallel.

For an electron or a system of electrons, (18.10) becomes

$$\epsilon_m \;=\; g_J\,m_J\,\mu_B\,\mathcal{B}\,; \tag{18.11}$$

the potential energy is minimum when the quantum number m_J has the minimum (negative) value. The g_J factor and the quantum number m_J have different values for different atoms.

For a nucleus, (18.10) becomes

$$\epsilon_m = -g_I\,m_I\,\mu_N\,\mathcal{B}\,. \tag{18.12}$$

The g_J factor and the quantum number m_I have different values for different systems. For a single proton, $g > 0$ and the potential energy has the minimum value when the quantum number m has the maximum value. For a single neutron, $g < 0$ and the potential energy has the minimum value when the quantum number m is minimum.

Note: The magnetic induction field $\mathcal{B}$ is connected to the magnetising field $\mathcal{H}$ by the relation $\mathcal{B} = \mu_0(1+\chi_m)\mathcal{H}$, where χ_m is the magnetic susceptibility. Since $\chi_m \ll 1$ for paramagnetic systems, sometimes the magnetic properties, such as the potential energy, are expressed and plotted as a function of $\mathcal{H}$ instead of $\mathcal{B}$. Such an approximation is anyway good when the magnetic atoms are dispersed in a non magnetic matrix, as is the case of paramagnetic salts (see below, §18.4).

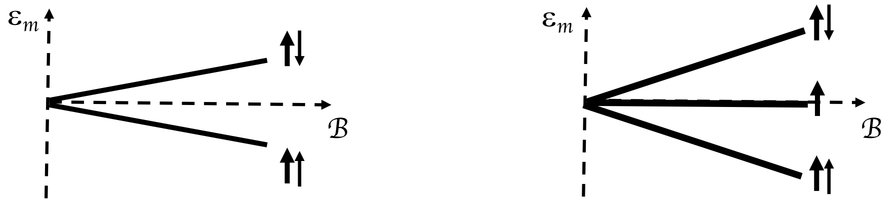


Figure 18.1: Magnetic potential energy as a function of the induction field $\mathcal{B}$ (represented by the up-directed thick arrows) for a system with $L = 0, S = 1/2$ (left) and with $L = 0, S = 1$ (right).

Examples

Example 1: he simplest case is represented by an atom with total orbital angular momentum null, $\vec{L} = 0$, and only one unpaired electron, so that $m_s = \pm 1/2$. Since $g_s = 2$, the potential energy can take only two values

$$\epsilon_m \;=\; -g_s m_s \mu_B \mathcal{B} \;=\; \mp \mu_B \mathcal{B} \;: \tag{18.13}$$

positive value $\epsilon_m = +\mu_B \mathcal{B}$ when $\vec{\mu}$ and $\vec{\mathcal{B}}$ have opposite direction,
negative value $\epsilon_m = -\mu_B \mathcal{B}$ when $\vec{\mu}$ and $\vec{\mathcal{B}}$ have the same direction.

When the $\mathcal{B}$ field increases, the difference between the two energy levels increases linearly (Fig. 18.1, left). For example:

a) if $\mathcal{B}$=0.1 T, then $\epsilon_m \pm 5.788 \times 10^{-6}$ eV,
b) if $\mathcal{B}$=2 T, then $\epsilon_m \pm 1.157 \times 10^{-4}$ eV.

Example 2: The hydrogen molecule H_2 in its ground state is *not* paramagnetic. The two electrons occupy the lowest bonding level $1\sigma_g$, with anti-parallel spins to fulfil the Pauli exclusion principle. Therefore $L = 0$ and $S = 0$, so that the magnetic dipole moment is zero.
The energy of the molecule is insensitive to the magnetic field.

Example 3: The oxygen molecule O_2 in its ground state is paramagnetic. The electron configuration of an oxygen atom is $1s^2\,2s^2\,2p^4$. The magnetic properties of the O_2 molecule are determined by the electrons of the atomic 2p orbitals, which contribute to form the bonding molecular orbitals π_u and σ_g and the anti-bonding molecular orbitals π_g^* e σ_u^* (listed in order of increasing energy). Of the eight 2p electrons present in the molecule, four fill up the π_u orbital and two fill up the σ_g orbital. The remaining two electron sit in the π_g^* orbital, without filling it up: the two electrons have parallel spins, according to the first Hund rule (the ground-state spin of an atom has the highest possible value consistent with the Pauli exclusion principle). The O_2 molecule has orbital momentum $L = 0$ and spin momentum $S = 1$, corresponding to three values $m_s = +1, 0, -1$. In presence of an induction field $\mathcal{B}$, the ground state level splits into three levels, with magnetic energy $-2\mu_B\mathcal{B}, 0, +2\mu_B\mathcal{B}$, respectively (Fig. 18.1, right).

Example 4: Paramagnetic salts are substances in which a paramagnetic ion is diluted in a matrix of non-paramagnetic different atomic species. Paramagnetic salts are interesting for the easiness of the statistical treatment as well as for their cryogenic applications (Chapter 19).
Let us consider two examples:

(a) $Cr_2\,(SO_4)_3 \cdot K_2SO_4 \cdot 24\,H_2O$
(b) $Fe_2\,(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24\,H_2O$

In the first case *(a)* the magnetic ion is Cr^{3+}. The electron configurations of the Cr atom and of the Cr^{3+} ion are $[Ar]\,4s^1\,3d^5$ and $[Ar]\,4s^0\,3d^3$, espectively. The three 3d electrons of the Cr^{3+} ion have parallel spins, according to the first Hund rule, while the orbital angular

momentum is null, owing to the interaction with the matrix. As a result, $L = 0$ and $S = 3/2$. There are four values $m_s = +3/2, +1/2, -1/2, -3/2$.
In the second case *(b)* the magnetic ion is Fe^{3+}. The electron configurations of the Fe atom and of the Fe^{3+} ion are [Ar] 4s^2 3d^6 and [Ar] 4s^0 3d^5, respectively. The five 5d electrons of the Fe^{3+} ion have parallel spins, according to the first Hund rule, while the orbital angular momentum is null, owing to the interaction with the matrix. As a re sult,$L = 0$ and $S = 5/2$. There are six values $m_s = +5/2, +3/2, +1/2, -1/2, -3/2, -5/2$.

Example 5: At last, let us consider nuclear magnetism. The simplest case is the hydrogen nucleus, with a single proton and no neutrons. The spin is 1/2, so that there are only two levels of magnetic energy (Fig. 18.1, left). Making use of (18.12), with $g_I = g_p$=5.58 and $m_j = 1/2$, let us evaluate the energy levels corresponding to the same values of induction $\mathcal{B}$ of the Example 1 above, concerning the electron of the hydrogen atom:

a) if $\mathcal{B}$=0.1 T, then $\epsilon_m \pm$ 8.79×10^{-9} eV,
b) if $\mathcal{B}$=2 T, then $\epsilon_m \pm$ 1.758×10^{-8} eV.

For the same induction field $\mathcal{B}$, the separation of the magnetic energy levels is much smaller for the proton spin than for the electron spin.

18.3 Two-level systems

We want now to study the statistical properties ofa paramagnetic system.
To this aim, let us consider a system of paramagnetic atoms dispersed in a non-magnetic crystalline matrix, so as to be very weakly interacting; it is the case of paramagnetic salts of the Example 5 above.
Let us consider only on the magnetic contribution to the energy, neglecting the other degrees of freedom, typically the vibrational ones. This amounts to consider a purely magnetic sub-system, that exchanges energy with the vibrational sub-system so slowly to be considered isolated. Such an approximation, that is actually acceptable only at very low temperatures, where only the low-energy levels can be excited and exchange energy, allows one to focus the attention only on the statistical properties of the magnetic sub-system.
To maintain the treatment as simpler as possible, we consider in this § 18.3 a system with only two levels of magnetic energy.

18.3.1 Statistics of particles

Le us consider the statistics of a system of distinguishable atoms with spin $S = 1/2$ and orbital angular momentum $L = 0$. The atoms are distinguishable because they are bound to the positions of a crystal lattice.
In presence of a field of magnetic induction $\mathcal{B}$, the magnetic energy of each atom can have one of the two values (18.13), according to whether its magnetic moment is parallel or anti-parallel to the field $\mathcal{B}$:

$$\epsilon_1 = -\mu_B \mathcal{B}\,, \qquad \epsilon_2 = +\mu_B \mathcal{B} \tag{18.14}$$

Atomic partition function

Since the atoms are distinguishable, one can resort to the Maxwell-Boltzmann statistics of § 16.4. The atomic partition function is

$$z \;=\; \sum_{i=1}^{2} e^{-\epsilon_i/kT} \;=\; e^{\mu_B \mathcal{B}/kT} + e^{-\mu_B \mathcal{B}/kT} \;=\; 2\,\cosh \frac{\mu_B \mathcal{B}}{kT}\,, \tag{18.15}$$

where $k = k_B \simeq 8.6 \times 10^{-5}$ eV K^{-1} is the Boltzmann constant.

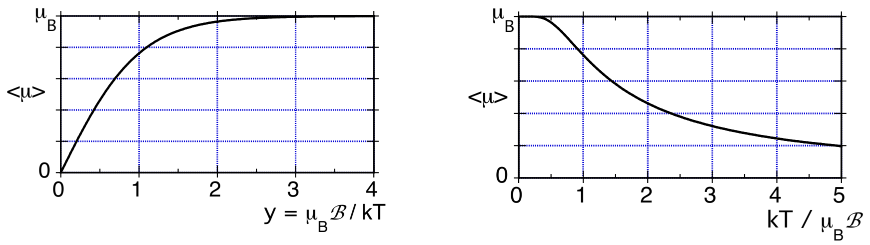


Figure 18.2: Two-levels magnetic system. Average magnetisation $\langle\mu\rangle$ as a function of the ratio $y = \mu_B\mathcal{B}/kT$ (left) and of the inverse ratio $kT/\mu_B\mathcal{B}$ (right).

Average population of the two levels

The probability that an atom be in one of the two energy levels is

$$P_i \;=\; \frac{n_i}{N} \;=\; \frac{1}{z}\,e^{-\epsilon_i/kT} \;=\; \begin{cases} P_2 & = \dfrac{1}{e^{2\mu_B\mathcal{B}/kT}+1} \\[2ex] P_1 & = \dfrac{1}{e^{-2\mu_B\mathcal{B}/kT}+1} \end{cases} \tag{18.16}$$

Let us study the dependence of the probabilities (18.16) on the temperature T and on the induction field $\mathcal{B}$.

For a constant non-zero field, $\mathcal{B}$, one can easily verify the dependence on temperature:

$$\begin{array}{c|c} T\to 0 & T\to\infty \\ \hline P_2\to 0 & P_2\to 1/2 \\ P_1\to 1 & P_1\to 1/2 \end{array} \tag{18.17}$$

At low temperatures, the population gathers on the lowest level; at high temperatures, the population tend to be uniform on the two levels. Such a behaviour is consistent with the conclusions of § 15.5 for the ideal gas.

For a constant temperature T, one can easily verify the dependence on the field $\mathcal{B}$:

$$\begin{array}{c|c} \mathcal{B}=0 & \mathcal{B}\to\infty \\ \hline P_2=1/2 & P_2\to 0 \\ P_1=1/2 & P_1\to 1 \end{array} \tag{18.18}$$

When the field is zero, the populations of the two levels are equal. Actually, for zero field there is only one degenerate level; the effect of the field is to remove the degeneracy, splitting in two the level, and to progressively increase the population of the lower level and decrease the population of the higher level.

Average magnetisation

The average magnetisation of a single atom is

$$\langle\mu\rangle \;=\; \sum_{i=1}^{2} P_i\,\mu_i \;=\; \frac{1}{z}\sum_{i=1}^{2}\mu_i\,e^{-\epsilon_i/kT} \tag{18.19}$$

where μ_i is the magnetisation corresponding to the energy level $\epsilon_i = \mp\mu_B\mathcal{B}$ and the probability P_i is given by (18.16). By substituting the partition function (18.15) in (18.19) one obtains (Fig. 18.2):

$$\langle\mu\rangle \;=\; \mu_B\,\frac{e^{\mu_B\mathcal{B}/kT}-e^{-\mu_B\mathcal{B}/kT}}{e^{\mu_B\mathcal{B}/kT}+e^{-\mu_B\mathcal{B}/kT}} \;=\; \mu_B\,\tanh\frac{\mu_B\mathcal{B}}{kT}\,. \tag{18.20}$$

The argument of the hyperbolic tangent contains the ratio y between the magnetic energy $\mu_B\mathcal{B}$ and the thermal energy kT:

$$y = \frac{\mu_B\mathcal{B}}{kT} \simeq 0.67\,\frac{\mathcal{B}}{T}\,, \tag{18.21}$$

where $\mathcal{B}$ is measured in tesla and T in kelvin.
One can easily verify the two limiting conditions:

a) For small values of the ratio y between magnetic and thermal energy, that is for weak fields and/or high temperatures,

$$y \ll 1 \Rightarrow \tanh y \simeq y \quad \Rightarrow \quad \langle\mu\rangle = \frac{\mu_B^2\mathcal{B}}{kT}\,. \tag{18.22}$$

Equation (18.22) corresponds to the macroscopic Curie law (17.23):

$$\chi_T = \frac{1}{\mu_0 V}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_{Tp} \propto \frac{1}{T} \tag{18.23}$$

Actually, the total magnetisation M (Chapters 3 and 17) is connected to the average atomic magnetisation $\langle\mu\rangle$ by $M = N\mu_0\langle\mu\rangle$, where N is the total number of paramagnetic atoms and μ_0 is the magnetic permeability; besides, $\mathcal{B} = \mu_0(1+\chi_T)\mathcal{H} \simeq \mu_0\mathcal{H}$, because $\chi_T \ll 1$ for paramagnetic substances.

b) For large values of the ratio y between magnetic and thermal energy, that is for strong fields and/or low temperatures

$$y \gg 1 \Rightarrow \tanh y \simeq 1 \quad \Rightarrow \quad \langle\mu\rangle = \mu_B \tag{18.24}$$

and saturation takes place.

18.3.2 Thermodynamical quantities

Let us now calculate the thermodynamical quantities for a magnetic two-levels system in terms of the Maxwell-Boltzmann single-particle statistics introduced above.
It is convenient first to clarify two points.

A.

In this Chapter 18 dedicated to statistics we referred $\mathcal{B}$, that is the local field acting on single atoms as an effect of both the free current of the power supply and of the matter magnetisation.
In § 3.6 and in Chapter 17 the magnetisation work ahas been instead expressed in terms of the magnetising field $\mathcal{H}$, considered as a thermodynamical coordinate.
The relation between the two field is $\mathcal{B} = \mu_0\,\mathcal{H}\,(1+\chi_m)$. In paramagnetic materials, the susceptibility is typically included between 10^{-5} and 10^{-3}, much smaller than one, so that one can approximate $\mathcal{B} \simeq \mu_0\,\mathcal{H}$ and consider the two fields as equivalent, to within the μ_0 constant.

B.

The connection between Statistics and macroscopic Thermodynamics can be made according to the guidelines of Chapter 15, with an important difference.
In Chapter 15 the thermodynamical internal energy was identified with the average energy $\langle E\rangle$ calculated by statistical methods (eq. 15.9). Such an identification is however possible if the energy E only contains kinetic and potential contributions *internal* to the system, as is the case for system composed by gas molecules or vibrational modes of a crystal.
For a magnetic system, the energy levels (18.14) of the statistical treatment refer to the potential energy of an *external* field; as a consequence, equation $U = \langle E\rangle$ doesn't hold. It will be shown below that, in the connection between Statistics and Thermodynamics for magnetic systems, a key role is plaid by the magnetic enthalpy H^*.

System partition function

Let us first express the partition function Z of the system as a function of the single-particle partition function z of (18.15). Since the paramagnetic atoms are bound to the points of a crystal lattice, one can rely on the prescription of § 16.4for distinguishable particles:

$$Z \;=\; z^N\,, \qquad \ln Z \;=\; N\,\ln z \;=\; N\,\ln\left[2\,\cosh\frac{\mu_B\mathcal{B}}{kT}\right]\,. \tag{18.25}$$

Once known the partition function Z, one can obtain the thermodynamical functions through the canonical distribution formalism.

Magnetic potential energy

The average potential energy due to the magnetic field is, according to (15.36),

$$\langle E_m\rangle \;=\; kT^2\,\frac{\partial \ln Z}{\partial T} \;=\; NkT^2\,\frac{\partial \ln z}{\partial T}\,. \tag{18.26}$$

Substituting Z from (18.25) and differentiating one obtains

$$\begin{aligned}\langle E_m\rangle \;=\; -N\mu_B\,\mathcal{B}\,\tanh\frac{\mu_B\mathcal{B}}{kT} \quad &= \quad -N\,\langle\mu\rangle\,\mathcal{B} && (18.27)\\ &= \quad -N\,\langle\mu\rangle\,\mu_0\,\mathcal{H} \;=\; -M\,\mathcal{H}\,. && (18.28)\end{aligned}$$

To be consistent with the treatment of Chapters 3 and 17, in (18.28) the magnetic energy $\langle E_m\rangle$ is expressed in terms of the total magnetisation M (that includes the constant μ_0) and of the magnetising field $\mathcal{H}$

The dependence ofi $\langle E_m\rangle$ on the field $\mathcal{B}$ (or on the field $\mathcal{H}$) and on the temperature T is shown in Fig. 18.3: the graphs of energy correspond to the graphs of the magnetisation of single atoms (Fig. (18.2)), to within the change of sign on the vertical axis. The value of the magnetic potential energy $\langle E_m\rangle$ is always negative.

If the temperature T is maintained constant (Fig. 18.3, left),

- if $\mathcal{B} = 0$, then $\langle E_m\rangle = 0$: for zero field there is only one degenerate level, the degeneracy is removed by the field $\mathcal{B}$,
- if $\mathcal{B} \to \infty$, then $\langle E_m\rangle \to -N\mu_B\mathcal{B}$, minimum value, corresponding to the complete alignment of the magnetic dipoles (saturation condition).

If the field is maintained constant to a value $\mathcal{B} \neq 0$ (Fig. 18.3, right),

- if $T \to 0$, then $\langle E_m\rangle \to -N\mu_B\mathcal{B}$, minimum value, corresponding to the complete alignment of the magnetic dipoles (saturation condition),
- if $T \to \infty$, then $\langle E_m\rangle \to 0$, the two single-particle levels are equally populated.

The magnetic energy $\langle E_m\rangle$ is the potential energy of an external field and doesn't contribute to the internal energy U. The internal energy cannot thus be connected to the partition function through the simple equation (15.37). To find the correct expression for the internal energy, it is conventient to first consider the entropy.

Magnetic entropy

The general relation between entropy, magnetic potential energy and partition function is given by the first equality of (15.43), so that:

$$S_m \;=\; \frac{\langle E_m\rangle}{T} + k\,\ln Z \;=\; -Nk\left(\frac{\mu_B\mathcal{B}}{kT}\right)\,\tanh\left(\frac{\mu_B\mathcal{B}}{kT}\right) \;+\; Nk\,\ln\left[2\,\cosh\left(\frac{\mu_B\mathcal{B}}{kT}\right)\right]\,. \tag{18.29}$$

The magnetic entropy S_m is a function of the ratio $\mathcal{B}/T$.

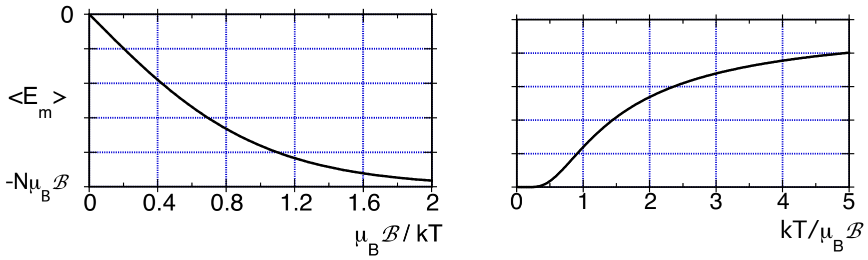


Figure 18.3: Two-levels magnetic system. Magnetic potential energy $\langle E_m \rangle$ as a function of the ratio $\mu_B \mathcal{B}/kT$ (left) and of the inverse ratio $kT/\mu_B \mathcal{B}$ (right).

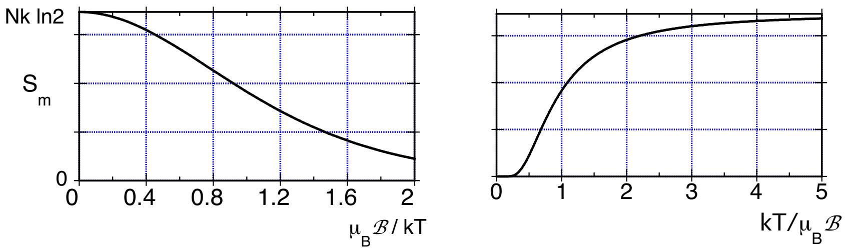


Figure 18.4: Two-levels magnetic system. Magnetic entropy as a function of the ratio $\mu_B \mathcal{B}/kT$ (left) and of the inverse ratio $kT/\mu_B \mathcal{B}$ (right).

In Fig. 18.4 the magnetic entropy S_m is shown as a function of the ratio $\mu_B \mathcal{B}/kT$ (left) and of the inverse ratio $kT/\mu_B \mathcal{B}$ (right).

When $T/\mathcal{B} \to 0$ (low temperatures an/or strong magnetic field), the magnetic entropy tends to the value $S_m = 0$: the magnetic dipoles of single atoms tend to be perfectly aligned, giving rise to a single microstate.

When $T/\mathcal{B} \to \infty$ (high temperatures and/or weak, but not zero, magnetic field) the entropy tends to the limiting value $S_m = Nk\,\ln 2 = k\,\ln 2^N$: the populations of the two levels tend to be equal, each one of the N atoms has the same probability of being in one or the other of the two levels.

Magnetic energy and internal energy

The magnetic energy $\langle E_m \rangle = -N \langle \mu \rangle \mathcal{B} = -M\,\mathcal{H}$ doesn't contribute to the internal energy. The total energy of the system is the sum of the internal energy and the magnetic potential energy:

$$E_{\text{tot}} \;=\; U - \mathcal{H}M\,. \tag{18.30}$$

By differentiating (18.30) and taking into account that $dU = T\,dS - p\,dV + \mathcal{H}\,dM$, one obtains

$$\begin{aligned} dE_{\text{tot}} &= T\,dS - p\,dV + \mathcal{H}\,dM - \mathcal{H}\,dM - M\,d\mathcal{H} \\ &= T\,dS - p\,dV - M\,d\mathcal{H}\,. \end{aligned} \tag{18.31}$$

The magnetisation work $\mathcal{H}\,dM$ made on the system corresponds to a reduction $-\mathcal{H}\,dM$ of the magnetico potential energy; the two contributions cancel out in (18.31).

Magnetic enthalpy

The magnetic enthalpy

$$H^* \;=\; U + pV - \mathcal{H}M \;=\; E_{\text{tot}} + pV\,. \tag{18.32}$$

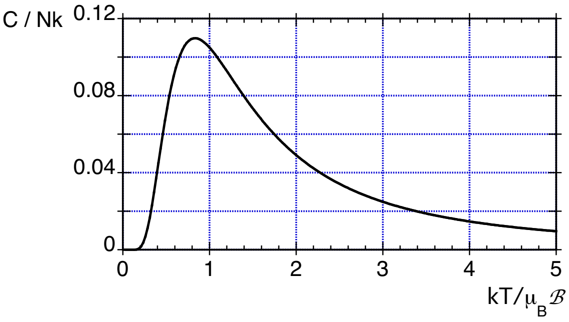


Figure 18.5: Two-levels magnetic system. Magnetic contribution to the specific heat (here divided by Nk).

corresponds to the total energy, to within the term pV. Its differential can be expressed in terms of the thermodynamical variables

$$dH^* = T\,dS + V\,dp - M\,d\mathcal{H}\,, \tag{18.33}$$

as well as in terms of the total energy

$$dH^* = dE_{\text{tot}} + d(pV) \simeq dE_{\text{tot}} \tag{18.34}$$

(the term $d(pV)$ is generally negligible).

Magnetic contribution to the heat capacity

The heat capacity at constant pressure p and magnetising field $\mathcal{H}$ is defined in (17.26). Taking into account the differential (18.33) of the magnetic enthalpy, one finds

$$C_{p\mathcal{H}} = \frac{(\text{đ}Q)_{p\mathcal{H}}}{dT} = T\left(\frac{\partial S}{\partial T}\right)_{p\mathcal{H}} = \left(\frac{\partial H^*}{\partial T}\right)_{p\mathcal{H}}\,, \tag{18.35}$$

that is

$$C_{p\mathcal{H}} = \left(\frac{\partial H^*}{\partial T}\right)_{p\mathcal{H}} = \left(\frac{\partial U}{\partial T}\right)_{p\mathcal{H}} + \left(\frac{\partial (pV)}{\partial T}\right)_{p\mathcal{H}} + \left(\frac{\partial (-\mathcal{H}M)}{\partial T}\right)_{p\mathcal{H}}\,. \tag{18.36}$$

Let us focus our attention on the last term, that is on the magnetic contribution to the heat capacity, that becomes particularly important at low temperatures, when the vibrational contribution becomes negligible. The magnetic contribution to the heat capacity can be calculated by differentiating (18.27):

$$C_m = \left(\frac{\partial E_m}{\partial T}\right)_{\mathcal{H}} = Nk\left(\frac{\mu_B\mu_0\mathcal{H}}{kT}\right)^2 \operatorname{sech}^2\left(\frac{\mu_B\mu_0\mathcal{H}}{kT}\right)\,. \tag{18.37}$$

The dependence of the magnetic heat capacity on temperature, shown in Fig. 18.5, is typical of systems with a finite number of levels: at low temperatures C_m increases when T increases; it reaches a maximum value and then decreases towards zero.

18.4 Thermodynamics and statistics of magnetic substances

In § 18.3, by dealing with the two-levels system, we succeeded in enlightening without complex mathematics the most relevant properties of the statistics of magnetic systems.
In most cases, however, the levels of magnetic potential energy are more than two, as in the examples considered at the end of § 18.2. In any case, the number of levels is finite, giving rise

to a lower limit to the magnetic potential energy (saturation condition) and to a behaviour of the magnetic specific heat similar to that of Fig. 18.5, characterised by a maximum value followed by a decrease towards zero when the temperature increases.

Actually, a purely magnetic system, with a finite number of energy levels doesn't exist. Any real system can store energy in other ways. For example, a crystal with magnetic properties is affected also by vibrational degrees of freedom, that can absorb energy over an unlimited number of levels and give rise to a contribution to the specific heat like the one shown in Fig. 9.1 of § 9.1.

However, at low temperatures the contribution to the specific heat of the magnetic sub-system (Fig. Fig. 18.5) can prevail over the vibrational contribution. The magnetic contribution appears then as an anomalous hump on the graph of the total specific heat (Schottky anomaly).

18.4.1 Paramagnetic salt

A particularly interesting example of realistic magnetic system is a paramagnetic salt, like the ones considered in the last example of § 18.1,

(a) $Cr_2\,(SO_4)_3 \cdot\ K_2SO_4 \cdot\ 24\,H_2O$
(b) $Fe_2\,(SO_4)_3 \cdot\ (NH_4)_2SO_4 \cdot\ 24\,H_2O$

where paramagnetic ions are dispersed in a matrix composed by different non-paramagnetic atomic species. In case *(a)* the magnetic ion is Cr^{3+}, in case *(b)* the magnetic ion is Fe^{3+}.

The magnetic ions of a paramagnetic salt can be considered as a subsystem of a larger system. The total energy of the salt, when in presence of a magnetising field $\mathcal{H}$, is the sum of three contributions:

a) magnetic potential energy due to the presence of the external field $\mathcal{H}$, with a finite number of levels,
b) potential energy due to the internal crystal fields (Stark effect), that reduce the degeneracy of the ground level even if the external field is absent,
c) vibrational energy, with an unlimited number of levels.

The second and third contributions represent the internal energy U of the subsystem.

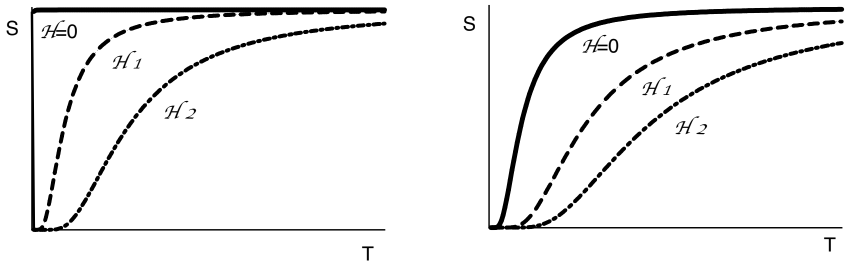


Figure 18.6: Typical behaviour of the magnetic entropy as a function of temperature for different values of the magnetising field, $\mathcal{H} = 0$, $\mathcal{H}_1$ e $\mathcal{H}_2 > \mathcal{H}_1$. The graph on the left refers to the ideal situation, when internal fields are absent. The graph on the right takes into account also the contribution of internal electrical and magnetic field.

18.4.2 Entropy

In § 18.3, thanks to the relative simplicity of the two-levels system, we succeeded in calculating the expression (18.29) of the entropy as a function of the temperature T and of the fields $\mathcal{B}$ or $\mathcal{H}$ (Fig. 18.4).

The calculation is more complicated for a many-levels system. The behaviour of the entropy is anyway similar to that of Fig. 18.4.

In the left graph of Fig. 18.6 the typical behaviour of the magnetic entropy as a function of temperature is shown for different values of the field $\mathcal{H}$. When $\mathcal{H} = 0$, the entropy is maximum and doesn't depend on temperature: the atomic magnetic dipoles are randomly oriented at any temperature. The effect of the field $\mathcal{H}$ is the partial orientation of the atomic dipoles, counteracting the disordering effect of temperature. For a given temperature, the entropy decreases when the $\mathcal{H}$ field increases.
To addition to the effects of the external field $\mathcal{H}$, one has to consider the effects of internal fields, both electrical and magnetic, that contribute o the orientation of the atomic dipoles even when $\mathcal{H} = 0$. The behaviour of the entropy in presence of internal fields is shown on the right graph of Fig. 18.6.

In 18.6 the thermal contribution to the entropy, typically due to the vibrational motion of atoms and always present, has been omitted. As already observed above, the thermal contribution is generally negligible at sufficiently low temperatures.
The situation can be qualitatively clarified by Fig. 18.7, where the contributions to the entropy and to the specific heat of the internal fields, of the external field $\mathcal{H}$ and of thermal vibrations are evidenced. At sufficiently low temperatures the vibrational contributions can actually be neglected.

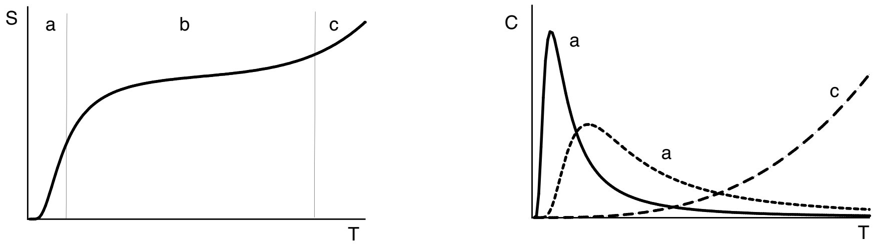


Figure 18.7: Left: typical behaviour of the entropy as a function of the temperature when an external field $\mathcal{H}$ is present; the letters a, b, c label the zones where the different contributions prevail: internal fields, external field $\mathcal{H}$ and thermal vibrations, respectively. Right: typical behaviour of the different contributions to the specific heat at low temperatures: of internal fields (a), of the external field $\mathcal{H}$ (b) and of thermal vibrations (c).

18.4.3 Energy

The expression (18.30) for the total energy is valid for any magnetic system, including paramagnetic salts. It becomes more interesting if the information on the levels occupation is added:

$$\langle E_{\rm tot}\rangle \;=\; \sum \langle n_i\rangle \epsilon_i \;=\; U - \mathcal{H}M \;=\; H^* - pV\,. \tag{18.38}$$

As already observed, the energy levels ϵ_i depend on three contributions:

a) interaction of the atomic dipoles with the external field $\mathcal{H}$, giving rise to the term c$-\mathcal{H}\,M$,
b) interaction of the atomic dipoles with the internal crystalline fields, independent of the external field $\mathcal{H}$, ontributing to the internal energy U,
c) vibrational energy, contributing to the internal energy U.

At sufficiently low temperatures, the vibrational contribution can be neglected.

The magnetic enthalpy H^* corresponds, to within the term pV, to the total energy $\langle E_{\rm tot}\rangle$. Starting from (18.38), let us calculate the differential dH^*, taking into account that for a solid system maintained at constant ambient pressure the differential $d(pV) = pdV$ can be neglected:

$$\begin{aligned} dH^* \;\simeq\; d\langle E_{\rm tot}\rangle \;&=\; dU - \mathcal{H}\,dM - M\,d\mathcal{H} \\ &=\; T\,dS \quad - M\,d\mathcal{H}\,. \end{aligned} \tag{18.39}$$

In obtaining the second line of (18.39) one has considered that the magnetisation work is $đW = \mathcal{H}\,dM$, so that $dU - \mathcal{H}\,dM = đQ = T\,dS$.

Let us now express the differential $d\langle E_{\rm tot}\rangle$ with reference to the energy levels $\epsilon_i$and their occupations numbers n_i, similarly to the case of the ideal gas in § 15.5:

$$dH^* \;\simeq\; d\langle E_{\rm tot}\rangle \;=\; \sum \epsilon_i\, d\langle n_i\rangle \;+ \sum \langle n_i\rangle\, d\epsilon_i\,. \tag{18.40}$$

By comparing (18.40) with (18.39) one can identify, as for the ideal gas,

$$T\,dS \;=\; đQ \;=\; \sum \epsilon_i\, d\langle n_i\rangle\,. \tag{18.41}$$

The exchange of heat corresponds to the variation of the populations n_i.
The equation

$$-\,M\,d\mathcal{H} \;=\; \sum \langle n_i\rangle\, d\epsilon_i\,, \tag{18.42}$$

involving the variation of the levels ϵ_i, induced by the variation of the external field $\mathcal{H}$, can be considered as a “statistical work”.

Let us stress the difference between paramagnetic systems and ideal gas. For the ideal gas, when no external fields are present, the internal energy U corresponds to the total average energy and the work is due to the mechanical compression, $đW = -p\,dV$. In a solid paramagnetic system, the work $-p\,dV$ is negligible; the external field $\mathcal{H}$, necessary to create the magnetic behaviour, gives rise to the potential energy $-\mathcal{H}\,M$, and the total energy, according to (18.38), doesn't correspond to the total energy U.

Note: In (18.38) the total energy has been expressed as the sum of the internal energy and of the potential energy of the external field. Let us compare the case of the magnetic system with the case of an ideal gas subject to the external field of gravity, already considered in § 3.5.
The total energy is $\langle E\rangle = U + mgh$ for the ideal gas, it is $\langle E\rangle = U - \mathcal{B}\,M$ for the magnetic system.
The differential of the total energy for the ideal gas is

$$\begin{aligned} d\langle E\rangle &= dU + d(mgh) \\ &= dU + mg\,dh \\ &= T\,dS - p'\,dV - mg\,dh + mg\,dh \;=\; T\,dS - p'\,dV \end{aligned}$$

where p' is the pressure of the external ambient (corresponding to the internal pressure p if the gravity field is negligible).
The differential of the total energy for the magnetic system is

$$\begin{aligned} d\langle E\rangle &= dU - d(\mathcal{H}M) \\ &= dU - \mathcal{H}\,dM - M\,d\mathcal{H} \\ &= T\,dS - p'\,dV\mathcal{H}\,dM - \mathcal{H}\,dM - M\,d\mathcal{H} \;=\; T\,dS - M\,d\mathcal{H}\,, \end{aligned}$$

where one has taken into account that for a solid system $dV \simeq 0$.
The differences between the two cases are the different effect of pressure on a gas and on a solid as well as the fact that the gravity field mg is constant, while the magnetising field $\mathcal{H}$ is variable.

18.4.4 Thermodynamical processes

Some examples of simple reversible transformations should clarify the role of the magnetic enthalpy and of the relation between the differential dH^* and the variations of the levels ϵ_i and of their populations n_i.
As in §17.3, we will consider the processes of adiabatic and isothermal magnetisation (and demagnetisation), which form the magnetic Carnot cycle (Fig. 17.3); we will also consider the process of heating at constant magnetic field.

Reversible adiabatic magnetisation

Let us consider a thermally insulated paramagnetic system and let us increase the external magnetic field from a value $\mathcal{H}_1$ to a value $\mathcal{H}_2 > \mathcal{H}_1$, maintaining the pressure p unchanged.
From (18.39), taking into account that $dS = 0$ and $d\mathcal{H} > 0$, one finds a negative enthalpy variation

$$dH^* \;=\; -M\,d\mathcal{H} \;<\; 0 \tag{18.43}$$

In § 17.3, from purely macroscopic considerations, we have found that in a reversible adiabatic magnetisation at constant pressure the temperature increases; from (17.57), since the susceptibility of paramagnetic substances decreases when the temperature increases, one finds (see Fig. 18.8, left):

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{Sp} \;=\; -\mu_0 V \mathcal{H}\,\frac{T}{C_{p\mathcal{B}}}\left(\frac{\partial \chi}{\partial T}\right)_{p\mathcal{H}} \;>\; 0\,. \tag{18.44}$$

Let us now consider the expression (18.40) of dH^* and impose the constraint that the first sum, corresponding to $T dS$, is zero:

$$dH^* \;\simeq\; \sum \langle n_i\rangle\, d\epsilon_i\,. \tag{18.45}$$

In an adiabatic magnetisation, when $\mathcal{H}$ increases the energy levels drift apart, but the populations of single levels remain unchanged, because $dS = 0$ (Fig. 18.8, right); the increase of the distance between the levels gives rise to a widening of the distribution of the populations with respet to the energy axis. This last effect is the statistical meaning of the temperature for a purely magnetic system.

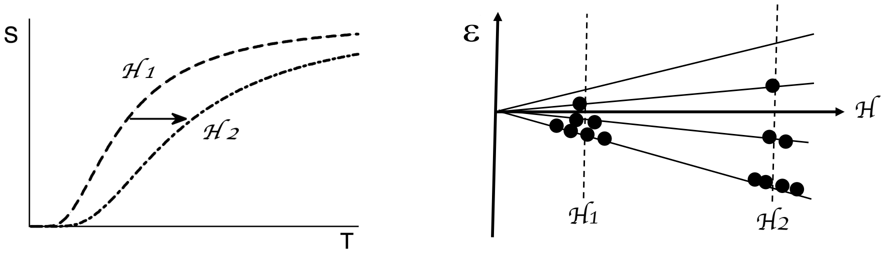


Figure 18.8: Reversible adiabatic magnetisation. Left: entropy-temperature graph (the arrow shows the direction of the process). Right: schematic representation of the population of the energy levels.

Reversible isothermal magnetisation

Let us now consider a paramagnetic system maintained at constant temperature T and pressure p and suppose again that the external magnetic field increases from a value $\mathcal{H}_1$ to a value $\mathcal{H}_2 > \mathcal{H}_1$. in § 17.3, again from purely macroscopic considerations, we have found that in a reversible isothermal magnetisation at constant pressure the entropy decreases, and the system gives up an amount of heat $đQ$ to its ambient; from (17.51), since the susceptibility of paramagnetic substances decreases when the temperature increases, one finds (Fig. 18.9, left):

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{Tp} \;=\; \mu_0 V \mathcal{H}\left(\frac{\partial \chi}{\partial T}\right)_{p\mathcal{H}} \;<\; 0\,. \tag{18.46}$$

From (18.39), since $dS < 0$ and $d\mathcal{H} > 0$, one finds that the variation of magnetic enthalpy is negative:

$$dH^* \;=\; T\,dS - M\,d\mathcal{H} \;<\; 0. \tag{18.47}$$

Since $dS \neq 0$, both terms in the right member of (18.40) are different from zero,

$$dH^* \;\simeq\; \sum \epsilon_i\, d\langle n_i\rangle \;+ \sum \langle n_i\rangle\, d\epsilon_i\,. \tag{18.48}$$

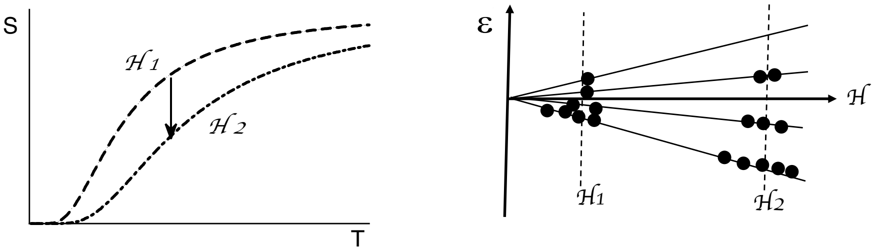


Figure 18.9: Reversible isothermal magnetisation. Left: entropy-temperature graph (the arrow shows the direction of the process). Right: schematic representation of the population of the energy levels.

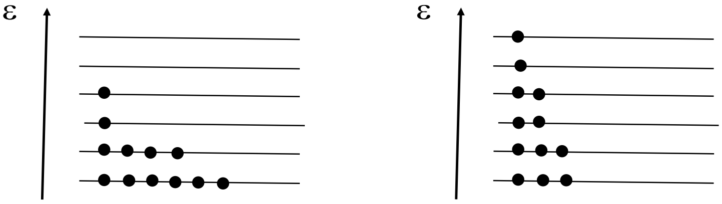


Figure 18.10: Schematic representation of the populations of the energy levels for a process of heating a paramagnetic system maintaining the external field $\mathcal{H}$ constant.

The increase of the magnetic field $\mathcal{H}$ splits apart the energy levels ϵ_i, the entropy variation modifies the populations n_i of the levels. The invariability of the temperature T corresponds to the invariability of the distribution of the populations n_i iwith respect to the energy axis.

Heating at constant magnetic field

Let us at last consider a paramagnetic system maintained at constant pressure p and constant external field $\mathcal{H}$ which absorbs an amount of heat.
Since $d\mathcal{H} = 0$, equation (18.39) becomes

$$dH^* \;\simeq\; T\,dS \;=\; dU - \mathcal{H}\,dM \;=\; \text{đ}Q \;> 0\,. \tag{18.49}$$

Actually, we have already observed in § 17.1 that the magnetic enthalpy H^* corresponds to the amount of heat absorbed by the system in a process where the pressure and the magnetic field remain constant.
Heating a system with constant $\mathcal{H}$ gives rise to an increase of the entropy S and of the temperature T. The magnetisation M decreases (see Fig. 18.2). The increase of the temperature at constant magnetic field gives rise to a reduction of the alignment of the atomic magnetic dipoles with respect to the magnetic field direction.

Since $d\mathcal{H} = 0$, the energy levels ϵ_i are not modified, and (18.40) reduces to

$$dH^* \;\simeq\; \sum \epsilon_i\, d\langle n_i\rangle\,. \tag{18.50}$$

Only the populations of the levels are modified (Fig. 18.10), giving rise to an increased dispersion with respect to both the levels (increase of entropy S) and to the energy axis (increase of temperature T).

Chapter 19

Thermodynamics of low temperatures

Obtaining temperatures lower than the ambient temperature is important for both the science and technology.

For what concerns scientific interests, the first attempts at liquefying some gases date back to te end of the XVIII century; the main aim was to better understand the relation between the different states of aggregation of matter. New properties of matter at low temperatures have been progressively discovered, among which particularly important are superconductivity and superfluidity, that appear only at extremely low temperatures.

For what concerns technology, the first applications concern probably food preservation: in the second half of the XIX century the first refrigerating devices allowed the construction of refrigerated ships and railway cars. Today, liquid nitrogen and even liquid helium are used in food industry, in medical devices and in a number of industrial applications.

In this chapter, some basic concepts of cryogeny, that is of the set of techniques suitable for achieving very low temperatures, are summarised (§ 19.1). Particular attention is given to the techniques based on paramagnetic salts, that allowed one to attain temperatures of the order of 10^{-6} K (§ 19.2).

19.1 Cryogenic fluids and related techniques

To maintain low the temperature of a system, one places it in contact with a refrigerating substance.

For temperatures as low as about 1 K, the refrigerating substances are consist generally in liquefied gases. When a gas is maintained at its boiling point, the heat transferred from the system to be refrigerated to the liquefied gas fives rise to the evaporation of the gas without increasing its temperature.

In order to liquefy cryogenic gases two techniques are possible, the reversible adiabatic expansion (§ 10.2) and the Joule-Thomson effect (§ 10.5), some times implemented in series.

One can obtain temperatures lower than the boiling point of the liquefied gas by rapidly pumping its vapours, until to the solidification temperature is attained.

In Tabella 19.1 some properties of the most important cryogenic liquids are summarised. Liquid nitrogen, whose temperature is 77.3 K, is widespread in scientific, medical and industrial applications. Liquid helium, whose temperature is 4.2 K, is by far more expensive and is mainly used in scientific applications.

The main cryogenic techniques are listed in the right column of Table 19.1, and are analysed in some detail below.

Table 19.1: Relevant temperature values (in kelvin) of some cryogenic liquids.

Property	*Gas*				*Technique*
	N_2	H_2	He^4	He^3	
					adiabatic expansion
Maximum inversion temperature	621	202	40		⟵
					Joule-Thomson effect
Boiling point (at 1 bar)	77.3	20.4	4.2		⟵
					rapid vapour pumping
Freezing point	63.1	14	—	—	
Minimum temperature			$\simeq 1$	$\simeq 0.3$	⟵
					Magnetic methods ⇓

19.1.1 Cooling by reversible adiabatic expansion

A gas undergoing a reversible (or quasi-reversible) adiabatic expansion cools down.
Let us refer to § 10.2, and modify the $T\,dS$ equation (10.8) through the fourth Maxwell relation (7.45):

$$\begin{aligned} T\,dS &= T\left(\frac{\partial S}{\partial T}\right)_p dT \;+\; T\left(\frac{\partial S}{\partial p}\right)_T dp \\ &= T\left(\frac{\partial S}{\partial T}\right)_p dT \;-\; T\left(\frac{\partial V}{\partial T}\right)_p dp \\ &= C_p dT \;-\; TV\beta\,dp\,. \end{aligned} \tag{19.1}$$

In the last equality, the heat capacity at constant pressure C_p and the coefficient of thermal expansion β have been introduced.

For an adiabatic expansion, $dS = 0$ and $dp < 0$, so that

$$dT \;=\; \frac{TV\beta}{C_p}\,dp \;<\; 0 \tag{19.2}$$

because $C_p > 0$ alwys, and for a gas $\beta > 0$.

A gas cools down if it undergoes a reversible adiabatic expansion from a higher pressure p_2 to a lower pressure p_1 ($a \to b$ in Fig. 19.1, left). The pressure of the gas can be brought back to the value p_2 by an isothermal compression, by which the entropy is reduced ($b \to c$ in Fig. 19.1, left)

$$dS \;=\; -V\,\beta\,dp \;<\; 0 \tag{19.3}$$

The sequence of adiabatic expansion and isothermal compression can be repeated many times so as to progressively reduce the temperature of the gas.

The process becomes less and less effective as the temperature decreases. As a matter of fact, from (19.2) one obtains

$$\frac{dT}{dp} \;=\; \frac{TV\beta}{C_p} \;\simeq\; \frac{V}{C_p}\,, \tag{19.4}$$

where the last equality refers to the ideal gas, for which $\beta = 1/V$. The volume V decreases when the temperature T decreases at constant pressure (in the present case, at the two work pressures p_1 and p_2). Therefore, according to (19.4), the temperature variation ΔT for a given adiabatic expansion becomes progressively smaller as the temperature T and the volume V decrease.

In addition, when the temperature decreases, the technical difficulties connected to the lubrication of the mechanical system increase, and the irreversibility of the process increases.

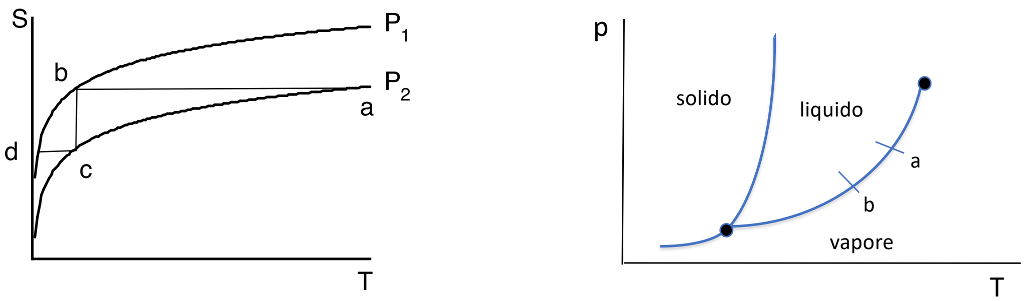


Figure 19.1: Left: entropy-temperature graph for a sequence of adiabatic expansions and isothermal compressions of a gas, with $p_2 > p_1$. Right: the slope of the liquid-vapour coexistence curve in the $T - p$ phase diagram is positive; for the solid phase, the graph can be very different with respect to the figure; for helium, in particular, the solid phase can be obtained only for pressures larger than 25 bar (Fig. 22.5).

Once the inversion temperature T_{inv} has been attained, the procedures based on the Joule-Thomson effect become generally more convenient.

19.1.2 Cooling by Joule-Thomson effect

The Joule-Thomson effect (§ 10.5) takes place when a gas enclosed in an adiabatic vessel is forced through a thin hole (or a porous plug) maintaining two constant pressures p_i and p_f on the two sides of the ole, with $p_i > p_f$ (Fig. 10.3).
Below the maximum inversion temperature $T_{\text{max,inv}}$, that is different for different gases (Table 19.1), the Joule-Thomson coefficient is positive (§ 10.5)

$$\mu_j = \left(\frac{\partial T}{\partial p}\right)_H > 0\,, \tag{19.5}$$

so that below $T_{\text{max,inv}}$ the Joule-Thomson expansion always gives rise to a temperature decrease, independent of the values of pressure.
By a sequence of Joule-Thomson expansions one obtains the gas liquefaction.

19.1.3 Cooling by rapid pumping of vapours

The cryogenic liquid can be further cooled below its boiling point by the rapid pumping of its vapour.
By this procedure, the vapour pressure p_{vap} is reduced, and, if the liquid-vapour equilibrium is maintained, the temperature is reduced too (transition from a to b in Fig. 19.1, right).
The lowest temperature limit is the freezing point, except for helium, that can be frozen only when submitted to a pressure of at least 25 bar (see the phase diagram of He^4 in Fig. 22.5). The rapid pumping of helium vapours allows one to attain temperatures of the order of some tenth of kelvin.

Note: In Table 19.1 the properties of two stable isotopes of helium are listed, He^4 (nucleus with twoprotons and two neutrons) and He^3 (nucleus with two protons and one neutron). The He^4 isotope is predominant in nature. The fraction of the He^3 isotope in nature is 1.37 ppm (parts per million).

19.2 Cooling by adiabatic demagnetisation

Temperatures much lower than one kelvin can be attained by exploiting the thermodynamical properties of paramagnetic salts (§ 18.4).

19.2.1 Atomic magnetic demagnetisation

Let us consder a system composed by a paramagnetic salt, for example $Fe_2\,(SO_4)_3\cdot\,(NH_4)_2SO_4\cdot\,24\,H_2O$. The magnetic ion Fe^{3+} is embedded in a non-magnetic matrix made by the other elements. costituita dagli altri elementi. The Fe^{3+} ions are thus a magnetic sub-system of the total system. Their dilution guarantees that the reciprocal magnetic interaction is very weak.

The freezing process can be described by the following sequence of processes.

1. The paramagnetic salt is put in contact with a reservoir of liquid helium at the temperature T =1 K. The thermal contact is guaranteed by a cavity filled with low-pressure helium gas. After a convenient time, the paramagnetic salt attains the equilibrium temperature 1 K.
2. Once the equilibrium has been attained at the temperature T= 1 K, an external magnetising field $\mathcal{H}$ is applied to the system. The spins of the Fe^{3+} ions align themselves with the magnetic field and the system becomes magnetised. Since the system is still in thermal contact with the reservoir at 1 K, the one deals with an *isothermal magnetisation*, in which the levels of magnetic energy are spread out and the system entropy decreases (see equation 17.52 and Fig. 18.9).
3. The system is thermally insulated from the reservoir by pumping the gas helium from the connecting cavity. The magnetising field is now removed, $\mathcal{H} \to 0$. Since the system is now thermally insulated, one deals with an *adiabatic demagnetisation*, in which the temperature of the magnetic sub-system decreases (see equation 17.58 and Fig. 18.8, taking into account that here one considers the inverse process).
   The so cooled magnetic sub-system absorbs heat from the remaining part of the system, thus producing its global cooling.

By adiabatic demagnetisation of atomic spins, temperatures of the order of the milli-kelvin (10^{-3} K) have been attained in laboratory. The lowest limit of this technique is due to the fact that the weak interaction between magnetic ions cannot be avoided , so that a residual weak magnetisation remains also when the external field is completely removed.

19.2.2 Nuclear adiabatic demagnetisation

Temperatures lower than some milli-kelvin have been attained by the adiabatic demagnetisation of nuclear spins.
The nuclear magneton μ_N is much smaller than the Bohr magneton μ_B (§ 18.1): $\mu_N = \mu_B/1836$. Therefore, for the same magnetising field $\mathcal{H}$, the levels of nuclear magnetic energy are much more close than the atomic magnetic levels.
Once the milli-kelvin temperature has been attained by the adiabatic demagnetisation of atomic spins, the temperature can be further reduced by repeating the sequence of isothermal magnetisation and adiabatic demagnetisation of nuclear spins. By adiabatic demagnetisation of nuclear spins, temperatures of the order of the micro-kelvin (10^{-6} K) have been attained in laboratory.

Chapter 20

The Third Law of Thermodynamics

The classical macroscopic Thermodynamics is built on the three principles introduced in Part I: Zeroth, First and Second Laws. Also the axiomatic approach of Part II refers, although in a peculiarly different way, to the same principles.

There are however some experimental facts which cannot be interpreted in terms of these three classical laws.
An example is the *Gibbs paradox* concerning the mixing of identical ideal gases (§ 11.2), that can be solved only by quantum mechanics and its different statistical treatment of distinguishable and indistinguishable identical particles (see the last part of § 16.4).

In this chapter we deal with another relevant case, concerning the behaviour of thermodynamical systems at very low temperatures, close to the absolute zero. The increasing experimental difficulties encountered when very low temperatures are sought as well as the possible incongruences that would originated if the absolute zero could be attained led, in the classical macroscopic approach, to the proposal of a new principle, the Third Law, that in its first statement postulated the unattainability of the absolute zero.
The statistical interpretation of the entropy and the quantum view of the energy levels allowed a deeper understanding of the behaviour of systems at low temperatures. A new statement of the Third Law has thus been proposed, referred to as Planck statement or as Nernst theorem, that actually cannot be considered as a postulate, but instead as a consequence of statistical laws applied to quantum systems.

In § 20.1 the possible incongruences connected with the attainment of the absolute zero are considered. The classical statements of the Third Law are presented in § 20.2 and 20.3. The quantum approach and its consequences are at last introduced in § 20.4.

20.1 The problem of absolute zero

The empirical temperature scales (§ 2.2) don't provide for an "absolute zero". The values of the empirical scales are purely conventional: the Celsius scale, for example, includes both positive and negative values.
The temperature of the gas thermometer (§ 2.3) is instead positive by definition; the gas thermometer cannot however measure all the possible temperatures, since at a sufficiently low temperature every gas liquefies, so that it makes non sense to speak of zero temperature for a gas thermometer.

The concept of "absolute zero" arises with the introduction of the *absolute thermodynamical temperature* T as a consequence of the Second Law and of the Carnot theorem (§ 4.3). The values of the absolute temperature T are defined by the ratios between heat quantities Q exchanged in the two isothermal transformations of a Carnot cycle:

$$\frac{T_1}{T_2} \;=\; \frac{Q_1}{Q_2}\,. \tag{20.1}$$

The efficiency of a Carnot engine can be expressed, according to (4.17), as

$$\eta \;=\; 1-\frac{T_c}{T_h}\,, \tag{20.2}$$

where T_c and T_h are the temperatures of the cold and the hot reservoirs, respectively. When the temperature T_c of the cold reservoir decreases, the efficiency η of the Carnot engine increases.
In principle, there is no lower limit to the thermodynamic temperature T, provided it is non negative.
One can ask what would happen if the temperature of the cold reservoir became zero, that is if $T_c = 0$, provided this result would be experimentally attainable. Actually, the value $T_c = 0$ would give rise to relevant conceptual difficulties:

a) for $T_c = 0$, as a consequence of (20.1), the heat amount exchanged with the cold reservoir would be null, $Q_c = 0$, so that $|W| = |Q_h|$; otherwise stated, an amount of heat Q_h absorbed by a unique source would be totally transformed into work, contrary to the Kelvin statement of the Second Law (§4.2); the efficiency (20.2) of the Carnot engine would be $\eta = 1$;
b) for $T_f = 0$, since $Q_c = 0$, the transformation of the thermodynamic system in contact with the cold reservoir would be contemporarily isothermal ($T_c = 0$) and adiabatic ($Q_c = 0$); being reversible, it should be isentropic too.

These conceptual difficulties are connected to the possibility of attaining the absolute zero. Actually, is the absolute zero really attainable ? The problem was faced in different ways when time went on.

20.2 Unattainability statement

Let us start from the expression (4.19) of the efficiency of a refrigerator operating between the two temperatures T_c and T_h:

$$\omega_{\rm fri} \;=\; \frac{|Q_{\rm in}|}{|W_{\rm ass}|} \;\leq\; \frac{T_c}{T_h - T_c}\,, \tag{20.3}$$

where the sign = holds for a Carnot cycle (reversible).
The efficiency $\omega_{\rm fri}$ of the ideal Carnot refrigerator progressively decreases when the temperature T_c of the system to be cooled decreases, the efficiency of any real refrigerator is smaller.

Actually, the various cryogenic techniques introduced in Chapter 19 allow the decrease of the temperature T by progressively smaller intervals:

- gas liquefying devices (by adiabatic expansion and Joule-Thomson effect): $T_{\rm min} \simeq 4.2$ K
- rapid pumping of liquid helium vapours: $T_{\rm min} \simeq 0.8$ K
- atomic adiabatic demagnetisation: $T_{\rm min} \simeq 10^{-3}$ K
- nuclear adiabatic demagnetisatione: $T_{\rm min} \simeq 10^{-6}$ K

The progressively increasing experimental difficulties encountered when seeking for extremely low temperatures led the chemist W. Nernst, at the beginning of the XX century, to enunciate the *unattainability statement*, that has been assumed as a Third Law of Thermodynamics:

> *The absolute zero is unattainable by a finite number of thermodynamical transformations.*

Let us now recall that the temperature is not directly measurable, since one cannot define an addition of temperatures. The absolute temperature is defined in terms of ratios Q_1/Q_2 between directly measurable quantities (the heat amounts).

One cannot thus conceive a linear temperature scale in a similar way as the linear scales of length or mass or time: the same difference ΔT has different physical relevance for different values of T. The situation can be better understood by referring to the statistical approach, where the thermal equilibrium is accounted for by the quantity $\beta = 1/k_B T$, that is by the inverse of the absolute temperature (Chapter 14). When $T \to 0$, that is when the absolute zero is approached, $\beta \to \infty$. The β parameter is better suited than T to account for the difficulties in attaining the absolute zero.

20.3 Nernst-Simon statement

A deeper understanding of the behaviour of thermodynamical systems when the absolute zero is approached ($T \to 0, \beta \to \infty$) is obtained by considering the entropy variations ΔS in isothermal transformations induced, for example, by variations of pressure p or of magnetising field $\mathcal{H}$.

The topic can be better introduced by some examples.

Example 1: Let us consider the two allotropic forms of sulfur, that differ in the crystal structure:
a) the α form has orthorhombic structure ($a \neq b \neq c, \alpha = \beta = \gamma = 90°$);
b) the β form has monoclinic structure ($a \neq b \neq c, \alpha = \beta = 90°, \gamma \neq 90°, \gamma \neq 120°$).
One can experimentally measure the entropy difference $\Delta S_{\alpha\beta}$ between the two forms at a relatively high temperature T .
One can then calculate the entropy variations of each form in the transition from the temperature T to zero temperature by extrapolating to zero kelvin the experimental values of specific heats according to the low-temperature theoretical behaviour $c_p \propto T^3$:

$$\Delta S_\alpha(0 \to T) = \int_0^T c_p^\alpha \, \frac{dT}{T}\,; \qquad \Delta S_\beta(0 \to T) = \int_0^T c_p^\beta \, \frac{dT}{T}\,..$$

It is thus possible to extrapolate to zero kelvin the entropy difference of the two allotropic forms of sulfur. One finds that the difference is zero:

$$\Delta S_{\alpha\beta}(T=0) = \Delta S_{\alpha\beta}(T \neq 0) + \int_0^T c_p^\alpha \, \frac{dT}{T} - \int_0^T c_p^\beta \, \frac{dT}{T} = 0\,.$$

Example 2: Let us consider the reversible isothermal compression of a solid body, induced by a pressure variation $p_i \to p_f$. The entropy variation can be calculated, taking into account the Maxwell relation (7.45), as

$$(\Delta S)_T = \int_{p_i}^{p_f} \left(\frac{\partial S}{\partial p}\right)_T dp \;=\; - \int_{p_i}^{p_f} \left(\frac{\partial V}{\partial T}\right)_p dp\,.$$

One observes experimentally that the coefficient of thermal expansion

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

tends to zero when $T \to 0$. As a consequence, also the entropy variation tends to zero, $(\Delta S)_{T=0} \to 0$, when the compression takes place for $T \to 0$.

Example 3: Let us consider an isothermal and isobaric chemical reaction (§ 11.4). The Gibbs free energy decreases (eq. 11.51):

$$\Delta G = \Delta H - T\,\Delta S \;<\; 0\,.$$

The experiments show that at low temperatures esotermic reactions are favoured; otherwise stated, the term $T\,\Delta S$ is generally small with respect to the term ΔH, so that $\Delta G \simeq \Delta H$.
This behaviour suggested to Walter Nernst (1864-1941) that the entropic contribution ΔS becomes negligible at low temperatures.

Considerations such as those suggested by the above examples led to the Nernst-Simon statement of the Third Law:

For any reversible isothermal transformation of a condensed system, $\Delta S \to 0$ when $T \to 0$.

20.3.1 Equivalence of the two statements

One can demonstrate that the Nernst-Simon statement and the unattainability statement are equivalent.

For the demonstration, one can refer to the case of a *paramagnetic salt*.

Let us first consider the isothermal variation of entropy $(\Delta S)_T$ connected to an isothermal variation of the magnetising field $(\Delta \mathcal{H})_T$ and study the behaviour of such variation when $T \to 0$. That is, let us calculate

$$\lim_{T\to 0} \left[S(T,\mathcal{H}_i) - S(T,\mathcal{H}=0)\right] .$$

To perform the calculation, let us consider two states i and f having the same entropy $S_i = S_f$ and different tmperatures T_i and T_f, corresponding to the magnetising fields $\mathcal{H}_i$ and $\mathcal{H}_f = 0$, respectively. The entropy values $S_i(T_i)$ and $S_f(T_f)$ are connected to the entropy values at $T=0$ by

$$S_i(T_i,\mathcal{H}_i) \;=\; S(T=0,\mathcal{H}_i) + \int_0^{T_i} \frac{c_{\mathcal{H}i}}{T}\, dT \qquad (20.4)$$

$$S_f(T_f,\mathcal{H}=0) \;=\; S(T=0,\mathcal{H}=0) + \int_0^{T_f} \frac{c_0}{T}\, dT \qquad (20.5)$$

so that, by equating the first members of the two equations, one finds

$$\lim_{T\to 0} \left[S(T,\mathcal{H}_i) - S(T,\mathcal{H}=0)\right] \;=\; \int_0^{T_f} \frac{c_0}{T}\, dT - \int_0^{T_i} \frac{c_{\mathcal{H}i}}{T}\, dT \,.$$

One can now verify the equivalence of the two statements.

a) Were the unattainability statement false, one could start from any temperature T_i and attain the temperature $T_f = 0$. The first integral on the right would be zero, so that

$$\lim_{T\to 0} \left[S(T,\mathcal{H}_i) - S(T,\mathcal{H}=0)\right] \;<\; 0 \,,$$

and the Nernts-Simon statement would be false too.

b) Were the Nernst-Simon statement false, so that the entropy variation were different from zero when $T \to 0$, a temperature value T_i would exist such that $T_f = 0$, and the unattainability statement would be false.

20.4 Planck statement

The two statements of unattainability and of Nernst-Simon are based on the results of macroscopic experiments.

A stronger statement of the Third Law was based on two theoretical advancements, that have been reviewed in Part III:

1) the statistical interpretation of the entropy in terms of the number Ω of micro-states corresponding to a given equilibrium macro-state of a system, that for an isolated system gives rise to the Boltzmann equation (13.9): $S = k_B \ln\Omega$;
2) the development of quantum mechanics, according to which discrete energy levels exist.

On the ground of these developments, the Third Law has been expressed in a new statement, referred to as the Planck statement or as the strong form of the Third Law:

> *The entropy of a pure condensed substance, that at $T = 0$ is in a non-degenerate ground state, is zero, $S = 0$.*

The Planck statement is a consequence of the statistical definition of entropy. In greater detail:

1) for an isolated system, $S = k_B \ln\Omega$: in the ground state, that is in the state of minimum energy,
   1a) if the ground state is non degenerate, $\Omega_0 = 1$ and $S = 0$;
   1b) is the ground state is degenerate, with degeneration g_0, then $\Omega_0 = g_0$ and $S = k_B \ln g_0$;
2) for a system maintained at constant temperature, $S = -k_B \sum_i P_i \ln(P_i/g_i)$, where g_i is the degeneracy of the i-th level; in the ground state, only the term of the sum containing P_0 is different from zero, so that
   2a) if the ground state is non degenerate, $P_0 = 1$, $g_0 = 1$ and $S = -k_B P_0 \ln P_0 = 0$;
   2b) sis the ground state is degenerate, with degeneration g_0, then $S = -k_B P_0 \ln(P_0/g_0) = k_B \ln g_0$.

The Plank statement of the "Third Law" is actually not a postulate but a theorem depending of the statistical definition of entropy and on the principles of quantum mechanics.

Let us add two specifications:

1. The possible degeneracy of the ground state is generally so small to be neglected in comparison with the entropy variations induced by any small temperature increase.
2. The ground state to which the Planck statement refers depends on the physical phenomena that are considered when the energy levels are determined. The following example should clarify this point.

Example 1: Let us consider a perfect crystal and suppose that its energy can be stored only in the normal modes of atomic vibrations. In the ground state (state of minimum energy) to each normal mode it corresponds only the zero-point energy, $\epsilon_i = \hbar\omega_i/2$. Such a condition can be fulfilled in only one way, so that there is only one micro-state, $\Omega = 1$ and $S = 0$.

Example 2: The case of the previous example is more complicate if atomic and nuclear spins are taken into account. Even when external magnetic fields are absent, the weak interaction of the spins with the internal crystal fields (§ 18.4) gives rise to the presence of different energy levels which contribute to the entropy of the system. The contribution of the spins is relevant for temperatures much lower with respect to the contribution of atomic vibrations (see Fig. 18.7, right) and the corresponding ground state is obtained at much lower temperatures.

In principle, the Planck statement of the Third Law allows one to attribute an absolute value to te entropy S. In practice, singling out all the possible contributions to the system energy, so as to uniquely determine the ground state, is far from trivial.

It is more correct to say that the Planck statement allows one to determine an absolute reference value of the entropy which depends on the contributions to the system energy that can be actually taken into account.

20.4.1 Planck statement and unattainability statement

One can demonstrate that the Planck statement entails the unattainability of the absolute zero by a finite number of thermodynamical transformations.

As a matter of fact, by drawing a qualitative graph of the entropy S as a function of the temperature T, on can easily see that any two curves $S(T)$ (corresponding for example to two different values of the magnetising field $\mathcal{H}$) must join when $T = 0$, as a consequence of the Planck statement. Therefore, an infinite sequence of reversible adiabatic and isothermal transformations is necessary to attain $T = 0$.

20.4.2 Consequences of the Planck statement

Thermodynamic equilibrium

The Planck statement allows an operative definition of the thermodynamical equilibrium at low temperatures.

Let us consider a substance in the gas state, at a relatively high temperature T, so that the entropy S can be calculated according to purely statistical considerations.
Let us now slowly reduce the temperature by extracting heat from the system and calculate the entropy variation as $\Delta S = \int (đQ/T)$.
According to the Planck statement, one expects that $S \to 0$ when $T \to 0$, that is when the ground state is approached. If the entropy doesn't tend to zero, three can be the causes:

1. The ground state is degenerate: the degeneracy is anyway generally small and the entropy value is small.
2. A sufficiently low temperature has not been attained.
3. Some degrees of freedom are frozen even when $T \to 0$ and the system doesn't attain the thermodynamical equilibrium. It is the case, for example, of substances in the vitreous state. One speaks, in this case, of *residual entropy.*

Specific heat of solids

Let us consider the expression of the heat capacity of solids at constant volume,

$$C_v \;=\; T\left(\frac{\partial S}{\partial T}\right)_v \;=\; \left(\frac{\partial S}{\partial(\ln T)}\right)_v ,$$

and calculate the entropy variation from $T = 0$ to T_f:

$$\Delta S \;=\; S_f - S_0 \;=\; S_f \;=\; \int_0^{T_f} \frac{C_v}{T}\, dT ,$$

where one has imposed $S_0 = 0$ according to the Planck statement.
In order that the value of S_f be finite, it is necessary that the integral be finite, which is possible only if $C_v \to 0$ when $T \to 0$.

Note: In classical Physics, where the equipartition of energy holds at all temperatures, the heat capacity would remain finite even when $T \to 0$, so that $S \to -\infty$. The actual behaviour of the heat capacity at low temperatures is a purely quantum effect.

Chapter 21

Negative kelvin temperatures

In thermodynamical equilibrium, the absolute temperature (measured in kelvin) is defined as non negative (or even as positive, if the absolute zero is assumed as unattainable).
Negative kelvin temperatures would then appear as nonsense.
However, as we will see in the present chapter, one can speak of negative kelvin temperatures for systems characterised by a finite number of energy levels, when the levels of higher energy are more populated than the levels of lower energy. One such condition is in principle out of thermodynamical equilibrium; however, if the interaction of the system with its ambient is sufficiently slow, this condition can last for a sufficiently long time to be considered as of quasi-equilibrium.

In chapter 18 we have seen that the magnetic potential energy of an atomic system is characterised by a finite number of levels. For paramagnetic salts (§18.4 and 19.2), the exchange of energy between the magnetic levels of the paramagnetic ions (finite in number) and the vibrational levels of the entire system (unlimited in number) can be so slow that the magnetic sub-system can be considered as quasi-isolate for a non negligible time interval.

The population inversion of the energy levels in a *quasi-equilibrium* state can be obtained for a short time in magnetic sub-systems. The interest of such a phenomenon is more academic than practical; its study can anyway allow a deeper understanding of the statistical meaning of thermodynamical quantities.

The population inversion in the energy levels has a strong practical interest in the case of Lasers (acronym for "Light Amplification by Stimulated Emission of Radiation"). In lasers, the population inversion in the levels of electron energy is necessary to obtain the emission of electromagnetic radiation. To guarantee a continuous operation of lasers, the population inversion has to be maintained in time. The system has thus to be maintained in a *stationary state of non-equilibrium.* Non-equilibrium stationary states will be considered in Part VI, dedicated to the Thermodynamics of irreversible processes.

21.1 Meaning of negative kelvin temperature

21.1.1 Thermodynamical temperature, a review

In the cycle Thermodynamics (Part I), the temperature characterised the thermal equilibrium between two systems or among the different parte of a system (§ 2.1). The absolute temperature is defined, as a consequence of the Carnot theorem, as

$$T = T_{\text{rif}} \frac{Q}{Q_{\text{rif}}}, \tag{21.1}$$

where T_{rif} is a reference value and Q nd Q_{rif} are heat amounts exchanged by the system in two reversible isothermal transformations connected by reversible adiabatic transformations (Carnot cycle).

The reference value has been chosen at the triple point of water, $T_{\rm rif}$= 273.16 K. The temperature T cannot be negative, because it is defined by the ratio between two positive quantities (the heat amounts).

In the axiomatic approach, (Part II), the thermodynamical properties of a system in equilibrium are contained in the function $S(U,V,...)$ in the entropy representation or in then function $U(S,V,...)$ in the energy representation (Chapter 5). The temperature is defined by the derivative.

$$T = \left(\frac{\partial U}{\partial S}\right)_V . \tag{21.2}$$

Since the entropy S is a monotonously increasing function of the energy U, the temperature T is non negative.

21.1.2 Statistics: systems with an *unlimited* number of levels

In statistical Thermodynamics (Part III), a system maintained at constant temperature obeys the canonical distribution (14.15), the thermal equilibrium being characterised by the parameter $\beta = 1/k_BT$.

Also in particle statistics (Chapter 16), the thermal equilibrium is characterised by the parameter $\beta = 1/k_BT$. In particular, for distinguishable particles and for indistinguishable particles i the classical limit, the Maxwell-Boltzmann distribution (16.25) reproduces the same formalism of the canonical distribution.

In equilibrium, the ratio between the populations of any two levels is given by the Boltzmann factor

$$\frac{n_2}{n_1} = e^{-\beta(\epsilon_2-\epsilon_1)} . \tag{21.3}$$

All real systems have an unlimited number of energy levels ϵ_i.

Let us consider for example a solid state system. The energy levels are of vibrational nature. When the average vibrational energy attains the value corresponding to the melting point, the solid melts. New higher energy levels become accessible in the liquid state, then in the gaseous state and at last in the plasma state, without an upper limit.

Let us look over the relation between the sign of the temperature T (and of the parameter β) and the populations of the levels.

- For positive temperatures ($T > 0$, $\beta > 0$), when $\epsilon_2 > \epsilon_1$ then, according to the Boltzmann factor, $n_2 < n_1$: the levels of higher energy are less populated than the levels of lower energy;
- For possible negative temperatures ($T < 0$, $\beta < 0$), when $\epsilon_2 > \epsilon_1$ then, the Boltzmann factor would require $n_2 > n_1$: the levels of higher energy should be progressively more populated, so that the system would require an infinite amount of energy.

Therefore, in equilibrium necessarily $\beta > 0$ and $T > 0$.

21.1.3 Statistics: systems with a *finite* number of levels

Let us now consider a system with a finite number of energy levels.

For the sake of simplicity, let us consider a system of N particles with only two possible energy levels, as in § 18.3, and let the energies of the two levels $\epsilon_1 = -\epsilon$ and $\epsilon_2 = +\epsilon$, respectively.

Initially let it be $n_1 \gg n_2$, that is the upper level be much less populated that the lower level. When $n_2/n_1 \to 0$, according to the Boltzmann factor $\beta \to \infty$, that is $T \to 0$.

Let us now heat the system, increasing its energy without modifying the values , $\pm\epsilon$. The temperature T progresssively increases (β decreases) and the upper level ϵ_2 becomes progressively more populated.

The trend towards an equal population of the two levels ($n_2 \to n_1$) corresponds to $T \to \infty$, that is $\beta \to 0$.

If further energy is supplied to the system, the population of the upper level can become larger that the population of the lower level, $n_2 > n_1$.Such a condition corresponds to $\beta < 0$, that is $T < 0$.
A negative kelvin temperature corresponds to an inversion of the populations of the energy levels. Such a situation would be anyway possible in equilibrium only if the system had only a finite number of energy levels. Actually, any system has an unlimited number of energy levels.

If the possibility of the population inversion is accepted, the behaviour of the kelvin scale is quite odd: when the populations of the levels become equal, the temperature T changes abruptly from the value $+\infty$ to the value $-\infty$.
More intuitive is the behaviour of the β parameter; when the populations become equal, the β parameter changes from positive to negative values, crossing the zero value.

21.2 How negative temperatures can be obtained

No real system has a finite number of energy levels, so that the kelvin temperature of any system is necessarily positive.

However, in some cases it is possible to isolate some sub-systems with a finite number of levels (for example, sub-systems composed by atomic or nuclear magnetic moments) which are anyway in thermal contact with subsystems characterised by an unlimited number of levels (for example corresponding to the vibrational energy of solids).
If the relaxation time of the first sub-system is much shorter than the relaxation time between the two sub-systems (for example the spin-lattice relaxation), a condition can take place of quasi-equilibrium of the first sub-system, that subsists for a time comparable with the relaxation time between the two sub-systems.

Example: The nuclear spins of LiF area subsystem with a finite number of energy levels. The relaxation time of the sub-system is of the order of 10^{-5} s. The spin-lattice relaxation time is about 2 minutes. Therefore, for a time interval of the order of minute, the subsystem of nuclear spins can be maintained in an equilibrium state different from that of the global system.

For concreteness, let us a two-levels magnetic sub-system submitted to an external magnetising field $\mathcal{H}$, so that each one of the N magnetic moments composing the sub-system has two possible energy levels $\pm\epsilon$. In § 18.3 the magnetic energy and the entropy was calculated for such a system, and it was found that

a) when $T \to 0^+$, that is $\beta \to +\infty$
the magnetic energy tends to its minimum value $\langle E_\mathrm{m}\rangle \to -N\epsilon$ (only the lower level is populated)
the entropy $S \to 0$ (only one micro-state is possible);
b) when $T \to +\infty$, tha is $\beta \to 0$
the magnetic energy $\langle E_\mathrm{m}\rangle \to 0$ (the two levels are equally populated)
the entropy attains its maximum value $S \to N\,k_B\,\ln 2$

Let us suppose that initially the system is in equilibrium with a finite temperature T.
A population inversion giving rise to a negative value of temperature can be obtained by inverting the direction of the external field $\mathcal{H}$ very rapidly; the magnetic moments have no time to invert their direction, so that the signs of the two energy levels are exchanged: the more populated lower level becomes the upper level, and viceversa. For a time interval shorter than the spin-lattice relaxation time, that is in quasi-equilibrium conditions, the upper level remains more populated than the lower level and the kelvin temperature is negative.
The limiting condition takes place when only the upper level is populated, so that

c) when $T \to 0^-$, that is $\beta \to -\infty$
the magnetic energy tends to its maximum value $\langle E_\mathrm{m}\rangle \to +N\epsilon$
the entropy $S \to 0$ (only one micro-state is possible)

21.3 Negative temperatures and Thermodynamics

The concept of negative kelvin temperature has been base in § 21.1 on purely statistical grounds. A negative temperature corresponds to an inversion of the level populations. Such a condition can be obtained only for a limited time interval and doesn't correspond to a genuine equilibrium state.

One can inquire whether a system which is in a state characterised by negative temperature can be described in terms of macroscopic Thermodynamics. Let us limit ourselves here to some considerations of general character.

The formalism of Thermodynamics built in Parts I and II only refers to systems in equilibrium states. Would it be possible to implement the macroscopic thermodynamical formalism also to a state of quasi-equilibrium of a system with negative temperature ?

In the axiomatic approach, the III postulate (§ 5.3) asserts that the entropy S is a monotonously increasing function of the internal energy. As a consequence, the temperature, defined by (6.5) and (6.6)

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,\{n_i\}}, \qquad T = \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}}. \tag{21.4}$$

is necessarily non negative.
A condition of negative temperature, where the entropy decreases when the internal energy increases, is inconsistent with the III postulate.

Actually, in the case of magnetic sub-systems, the average potential magnetic $\langle E_{\rm m}\rangle$, whose levels undergo the population inversion, doesn't contribute to the internal energy U. As already stated (§18.3), the thermodynamical function most convenient to connect the macroscopic and statistical approaches, is the magnetic enthalpy H^*, that corresponds, to within the term pV, to the total energy of the system: $H^* = U + pV - \mathcal{H}M = E_{\rm tot} + pV$. The differential of the magnetic enthalpy is

$$dH^* \;=\; T\,dS + V\,dp - M\,d\mathcal{H} \tag{21.5}$$

so that the temperature T and the β parameter are

$$T \;=\; \left(\frac{\partial H^*}{\partial S}\right)_{p\mathcal{H}} \qquad\qquad \beta \;=\; \frac{1}{k_B}\left(\frac{\partial S}{\partial H^*}\right)_{p\mathcal{H}}. \tag{21.6}$$

If the internal energy U and the pV product are unchanged, one can assume, to within an irrelevant additive constant, $H^* = -\mathcal{H}M$. Particularly significant is the graph of S as a function of $H^* = -\mathcal{H}M$, which exhibits the shape of a dome. For the maximum and minimum values of H^*, the entropy $S = 0$ and thus $\beta = \pm\infty$. When the magnetic enthalpy assumes its average value $H^* = -\mathcal{H}M = 0$, the entropy assumes its maximum value, so that $\beta = 0$.

Part V

Phase equilibria and phase transitions

An important application of Thermodynamics concerns the rational treatment of the equilibrium conditions between the different phases of substances as well as of the processes of phase transitions.

Chapter 22 contains a phenomenological introduction to phase equilibria and phase transitions. The attention is mainly focused of the one-component systems: phase diagrams, critical transition of fluids, stable and metastable phases of solids. Other phase are then introduced: superionic, superfluid, order-disorder, ferromagnetic, ferroelectric. The chapter ends with a short introduction to phase equilibria in many-component systems.

Chapter 23 is dedicated to the Thermodynamics of phase equilibria and phase transitions; the relevance of the Gibbs function is stressed. Two kinds of phase transitions are distinguished, the first-order transitions and the continuous transitions, the second ones characterised by the order parameters and the critical exponents. The chapter ends with a section dedicated to the stability of phase equilibria.

A detailed analysis of the liquid-vapour equilibrium is made in chapter 24, including an introduction to the Van der Waals theory.

Chapter 25 contains a short introduction to the many-component systems.

Chapter 26 starts with the distinction between crystalline and non crystalline solids; attention is the focussed on the glasses, an the phenomenology of the glass transition, and on its thermodynamical aspects.

Chapter 22

Phenomenology of phase equilibria and phase transitions

This chapter is dedicated to an introduction of the basic concepts concerning phase equilibria and to an overview of the different phase transitions that will be studied by a thermodynamical approach in the next chapter 23.

22.1 Introduction

The term *phase* means a macroscopic portion of a substance which is homogeneous and neatly separated by other different regions. Different phases of a thermodynamical system can differ in the type of atomic aggregation (solid, liquid or gaseous states), in the way the various components are mixed or in other physical properties (magnetic, electrical, etc.)

Example 1: Let us consider a closed vessel containing a given amount of water H_2O. Above liquid water a mixture of air and water vapour is present. The system is composed by two phases: liquid water and the gaseous mixture. Notice that any gas forms only one phase, because all its components are perfectly miscible.

Example 2: Let us pour an amount of alcohol in the water of the previous example. Since alcohol is perfectly miscible with water, there are again two phases: a liquid one and a gaseous one.

Example 3: Let us pour a few drops of mercury in the water of the first example. Mercury is not miscible with water. There are now three phases, two liquids (water and mercury) and one gaseous (water vapour). The mercury phase can be composed by different drops dispersed on the bottom of the vessel; a single phase doesn't necessarily correspond to a single geometrical region.

Example 4: Let us introduce an ice block in the water of the first example. There are now three phases, one solid, one liquid and one gaseous. However, it can happen that the solid phase progressively disappears (the ice melts). The three initial phases were in a condition of thermodynamical non-equilibrium.

The last example introduces the issue of phase equilibria and of the transformations between different phases. It is relevant to determine under which conditions (of pressure, temperature, possible external fields, etc.) a given phase of a substance can be present or two or more phases can coexist in thermodynamical equilibrium. It is also relevant to understand the mechanisms responsible of the transition between two phases.

22.2 One-component systems: states of aggregation

In one-component systems, once the amount of matter is known, the thermodynamical state is defined by two coordinates. In general, temperature T and pressure p are chosen as independent

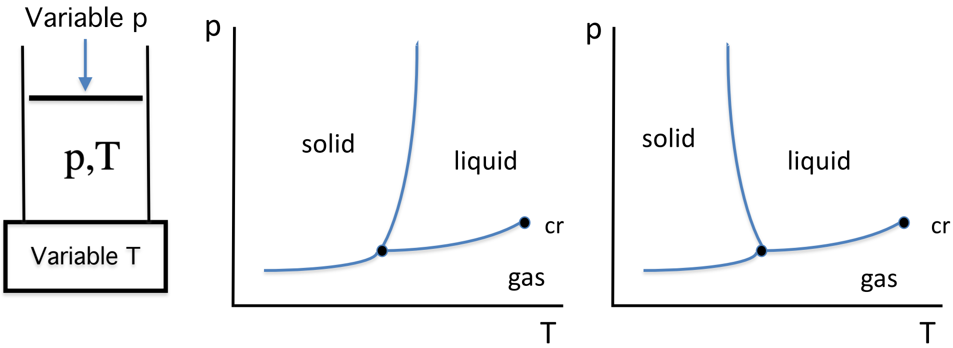


Figure 22.1: Schematic representation of phase diagrams (T, p) for a one-component system. The three regions (solid, liquid and gas phases) are separated by coexistence curves. The curve corresponding to the liquid–solid equilibrium can exhibit positive slope (left graph), or, less frequently, negative slope (right graph). The three coexistence curves meet at the triple point. The liquid–gas coexistence curve abruptly ends at the critical point (cr).

coordinates, because they are easily controlled in the laboratories and in the everyday life.

22.2.1 Temperature-pressure diagrams

An equilibrium state corresponds to each value of temperature and pressure; and to ach equilibrium state it corresponds a well defined phase. The simplest examples are given by the aggregation states of matter, solid, liquid and gaseous, that are represented in the (T, p) diagrams, with T as abscissa p as ordinate.

In the (T, p) diagrams, the plane is divided in *monophasic regions*, each one corresponding to a given aggregation state. The different phases can be macroscopically distinguished by qualitative properties (solids have proper volume and form, liquids have only a proper volume, gases have no proper volume nor proper form) or by quantitative properties (e.g. the molar volume v and the molar entropy s). The different phases can be distinguished at the microscopic level too, according to the atomic arrangement, detectable for example through X-ray diffraction.

The monophasic regions are separated by *coexistence curves*, corresponding to the (T, p) values for which two different phases coexist in equilibrium. Along the coexistence curves the system is physically separated in two spatial regions containing the two different phases, with different values of molar volume v and molar entropy s.

Three coexistence curves can meet in a *triple point*, at whose (T, p) values three different phases coexist in equilibrium. At a triple point, the system is physically separated in three spatial regions corresponding to the three phases.

22.2.2 The solid–liquid–gas equilibrium

For any substance, at least three monophasic regions can be singled out, corresponding to the aggregation states: solid, liquid and gas (Fig. 22.1). In the solid state different phases can be present; we deal with this further division of the (T, p) plane later on, in § 22.3. Let us study here the main characteristics of the solid–liquid–gas equilibria.

There are (at least) three coexistence curves, meeting in the *triple point*, where the three states, solid, liquid and gas, coexist (Fig. 22.1).

The slope of the *solid–gas* and *liquid–gas* coexistence curves is always positive.

The slope of the *solid–liquid* coexistence curve can be positive or negative:

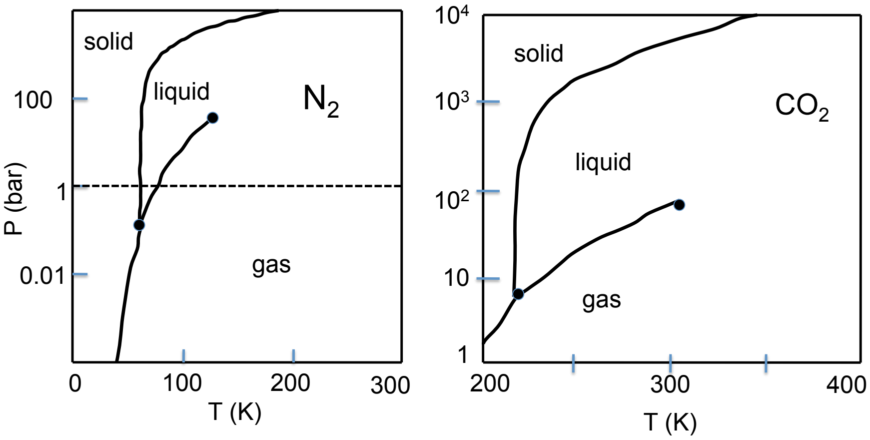


Figure 22.2: Phase diagrams of nitrogen N_2 (left) and of carbon dioxide CO_2 (right).

a) for most substances, the slope is positive (Fig. 22.1, left): these substances increase their volume when melting (Chapter 23);
b) for a few substances, the slope is negative (Fig. 22.1, right); these substances decrease their volume when melting (Chapter 23); examples are water, Bi, Sb, Ge.

The *liquid–gas* coexistence starts at the triple point and ends at the *critical point* (T_{cr}, p_{cr}). It is possible to go from the liquid state to the gas state without crossing the coexistence curve, that is without discontinuities in the molar volume v and in the molar entropy s, by choosing a path in the Tp plane going around the critical point. Liquid and gas can thus be considered as different modifications og a unique phase, the fluid phase.
On the liquid–gas coexistence curve the system is physically separated in two regions (liquid and gas) with different values of molar volume v and entropy s. When one moves along the coexistence curve towards right, the differences of v and s between the liquid and the gas progressively decrease, and become zero at the critical point.

The gaseous modification of the fluid phase is generally called *vapour* when $T < T_{cr}$,. It is called gas when $T > T_{cr}$.
When $T > T_{cr}$ and $p > p_{cr}$, the fluid is said to be in a *supercritical* state.
When the vapour (that is the gas below T_{cr}) is in equilibrium with the liquid, it is said to be saturate.
Temperature and pressure of the triple and critical points of some substances are listed in Table 22.1.

Examples

Example 1: The phase diagram of nitrogen $N_2$is shown in Fig. 22.2, left. The critical temperature is $T_{cr} = 126.3\,$K, lower than the ambient temperature (Table 22.1). One cannot liquefy or solidify nitrogen at ambient temperature by only varying its pressure. One can instead liquefy and solidify nitrogen at ambient pressure by progressively reducing its temperature (§19.1). The pressure of the triple point (0.125 bar) is lower than the ambient pressure (1.013 bar).

Example 2: The phase diagram of carbon dioxide CO_2 is shown in Fig. 22.2, right. The critical temperature is $T_{cr} = 304\,$K, lower than the ambient temperature (Table 22.1). Also carbon dioxide cannot be liquefied at ambient temperature by only varying its pressure. The pressure of the triple point, 5.17 bar, is higher than the ambient pressure; therefore the liquid phase cannot be present at ambient pressure; the gas phase directly transforms to the solid phase,

Table 22.1: Temperature and pressure of the triple point and of the critical point of some substances.

	Triple point		Critical point	
	T (K)	p (bar)	T (K)	p (bar)
N_2 (nitrogen)	63.18	0.125	126.3	33.9
CO_2 (carbon dioxide)	216.55	5.17	304.	74.
H_2O (water)	273.16	0.061	647.4	220.

and viceversa; the solid phase of carbon dioxide is often called “dry ice”. The slope of the solid–liquid coexistence curve is positive, as in the schematic left diagram of Fig. 22.1.

Example 3: At last, let us consider water H_2O (Fig. 22.4, left). The critical temperature is $T_{cr} = 674.4\,\text{K}$, higher than the ambient temperature. The gaseous phase of water is thus a vapour. The slope of the coexistence curve of water is negative, as in the right diagram of Fig. 22.1 . The pressure of the triple point (0.061 bar) is lower than the ambient pressure (1.013 bar); if water is maintained at the ambient pressure, one can progressively go from the liquid phase to the solid phase by reducing the temperature.

Nomenclature of solid–liquid–gas transitions

The transitions between the different states of aggregation of matter are characterised by a well established terminology, that is schematised in Table 22.2, where, for the sake of completeness, a fourth state of aggregation has been included, the ionised gas or “plasma”.

Let us draw an horizontal line in a (T,p) diagram, in correspondence with the atmospheric pressure $p = 1.013\,\text{bar}$. The intersection of the horizontal straight line with the solid–liquid coexistence curve is called *melting point*. The intersection of the horizontal straight line with the liquid–gas coexistence curve is called *boiling point*.

Table 22.2: Nomenclature of the phase transitions between the different aggregation states of matter, including the plasma state. The start states are listed in the first column, the end states in the first row.

	Solid	**Liquid**	**Gas**	**Plasma**
Solid		melting - fusion	sublimation	
Liquid	freezing		vaporisation	
Gas	deposition	condensation		ionisation
Plasma			recombination	

22.2.3 The critical transition of fluids

The liquid–gas (or liquid–vapour) coexistence curve abruptly ends at the critical point (Fig. 22.1). The behaviour of fluids near the critical point is worth being analysed in detail, since it presents some peculiar characteristics which are common to other phenomena to be considered later on (§ 22.5 and 23.4).

Let us consider a generic point on the liquid–gas coexistence curve: the system is physically separated in two regions, liquid and gas (liquid and vapour) with different values of molar volume v and entropy s. The ratio between the amounts of the two phases (two modifications of the fluid phase) can be modified by exchange of heat with the ambient, maintaining unchanged both temperature and pressure. In the limiting cases, the system can contain only the liquid or the gas phase, with different values of molar volume, v_l and v_g, and of molar entropy, s_l e s_g.

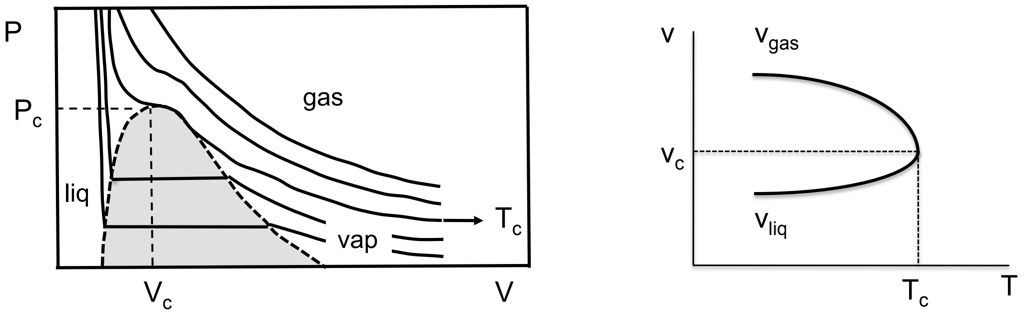


Figure 22.3: Left: isothermal curves in the pV plane; in the grey zone, the liquid and the gas (saturated vapour) coexist. Right: molar volumes of the liquid phase v_{liq} and of the gas phase v_{gas} as a function of temperature for system whose molar volume is equal to the critical volume v_{cr}.

Let us now move along the coexistence curve towards the critical point. The differences between the two phases progressively diminish, and at the critical point become zero. At the critical point, T_{cr} and p_{cr}, the molar volume has a unique value v_{cr}.
The phenomenon can be better understood with the aid of the Andrews graph, wich represents the isothermal curves in the Vp plane (Fig. 22.3, left). The points of the coexistence curve in the (Tp) diagram correspond, in the Andrews graph, to the isothermal horizontal segments within the region delimited by the bell-shaped curve.

Let us now consider a system whose molar volume is constrained to a value equal to the critical molar volume v_{cr} (vertical dashed line in Fig.. 22.3, left). Let the temperature of the system increase along the liquid–gas coexistence curve in the (Tp) diagram, that is in the up direction along the vertical line in the (Vp) graph. The differences between the molar volumes v_l and v_g and between the molar entropies s_l and s_g of the liquid and of the gas progressively decrease and become zero at the critical point (Fig. 22.3, right).
At the critical point, a phase transition takes place, between a set of states where two different modifications of the fluid state coexist, to a set of states where the fluid phase is undifferentiated. The critical transition takes place without discontinuities in the molar volume and molar entropy.
Let us consider the behaviour of the density ρ of the two phases, liquid and gas, as a function of the temperature. The difference $\rho_l - \rho_g$ progressively decreases when the temperature increases, and becomes zero at the critical point, where $T = T_{cr}$.
The critical transition can be considered as the transition from a more ordered state (two different physical regions, liquid and gas) to a less ordered state (a single undifferentiated region). Therefore, the difference of the densities $\rho_l - \rho_g$ is named *order parameter* of the transition.

22.3 Solid phases

Let us now focus our attention on the solid state. A number of substances can exhibit different crystal structures in different regions of the (T, p) plane; otherwise state, different solid phases can exist. The phenomenon is named polymorphism or allotropy. The experimental study of solid phases can be very difficult, typically at high pressures, so that the phase diagrams of some substances are still incomplete.

Example 1: Solid water (ice) exhibits a large number o crystalline phases, that are labeled by roman numbers. Some of thee phases are shown in the diagram of Fig. 22.4, left. The low-pressure structure is named "ice I". Up to now, 14 different phases have been identified, from ice I to ice XIV.

Example 2: Tin (50–Sn) exhibits to allotropic forms at ambient pressure:
1. for $T < 13.2°$C the stable form is α tin, or gray tin: density $\rho = 5.769$ g/cm^3, electrical insulator, fragile, diamond cubic crystal structure;

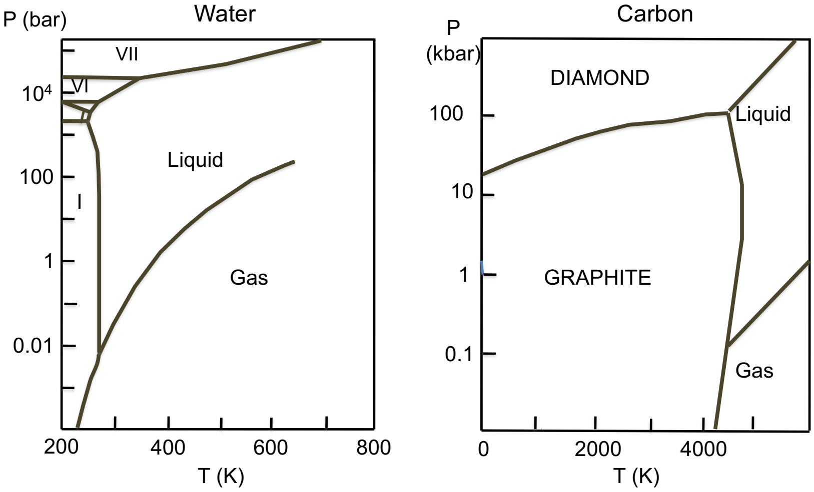


Figure 22.4: Examples of polymorphism of solids. For water (left) the different solid phases are labeled by roman numbers. For carbon (right) the approximate diagram enlightens the difference between the diamond and graphite phases.

2. for $T > 13.2°\mathrm{C}$ the stable form is β tin, or white tin: density $\rho = 7.265$ g/cm^3, metal, malleable, tetragonal crystal structure ($a = b \neq c; \alpha = \beta = \gamma = 90°$).
The two allotropic forms differ in molar volume and crystal structure. At high pressures, of the order of some kilobar, two other allotropic forms have been identified, named δ and γ tin.

Example 3: Carbon (C) can be found in two crystalline phases, graphite and diamond, that are thermodynamically stable in different regions of the (T, p) plane (Fig. 22.4, right) and exhibit very different physical properties.
a) At relatively low pressures, below some tens of kilobar, *graphite* is the thermodynamically stable phase of carbon. In graphite, the carbon atoms, connected by strong covalent bonds, form planar lattices of hexagonal rings. The planes are maintained parallel by weak Van der Waals bonds. The lamellar structure of graphite explains its use in pencils or as a lubricant. Graphite is a good electrical conductor. Unique mechanical and electrical properties are exhibited by the single isolated planes, named “graphene”.
b) At high pressures, the thermodynamically stable phase of carbon is *diamond*, in which the strong covalent bonds give rise to an isotropic three-dimensional structure: each atom is tetrahedrally bonded to four nearest neighbours. Diamond is characterised by a high degree of hardness and is a good electrical insulator.

Poly-amorphism

Polymorphism is generally considered a peculiar property of crystalline solids. However, experimental evidence has been recently obtained that some liquids, or more generally some amorphous substances laking crystalline order, can exhibit different phases when subjected to high pressures. One speaks, in these cases, of “poly-amorphism”.
Because liquids and amorphous solids don’t exhibit long range crystalline order, the difference between the different phases concern the short-range and the medium-range order: for example, they can differ in the coordination number, that is in the average number of nearest-neighbours.

22.4 Metastable phases and systems out of equilibrium

The phase diagrams of Figs. 22.1, 22.2 and 22.4 show the regions of the (T, p) plane in which the different phases are in thermodynamical equilibrium. As we will see in Chapter 23, the stable

equilibrium phase for a given pair of (T, p) values is characterised by the minimum value of the Gibbs free energy G.
However, some systems can assume and maintain indefinitely in time a state that doesn't correspond to the absolute minimum of the Gibbs function. It is the case of metastable phases, corresponding to relative minima (different from the absolute minimum) of the Gibbs function, or event of states far from thermodynamical equilibrium.

Example 1: A classical example is *carbon*, whose thermodynamically stable phase at ambient temperature and pressure is graphite l(Fig. 22.4, right). However, one can find and maintain in ambient conditions also diamond, whose Gibbs function has a larger value than the Gibbs function of graphite. The diamond phase has been originated in geological conditions of very high pressure and remains frozen also at lower pressures, in a condition of metastable equilibrium. The transition to the graphite stable phase would require a modification of the atomic structure, that would in turn require to cross a high potential energy wall, in order to break the diamond strong covalent bonds to form the new bonds of graphite.

Example 2: Another interesting example is *tin.* The β phase (white tin) is thermodynamically stable at ambient temperature and pressure. Below 13.2°C, the stable phase is instead α tin (grey tin). If the β phase is cooled below 13.2°C, it slowly transforms to the α phase, a phenomenon known as tin pest, favoured by the presence of aluminum and zinc impurities; to avoid the $\beta \to \alpha$ transition, small amounts of antimony and bismuth are added to tin and succeed in blocking the transformation kinetics.

The above examples evidence the importance of microscopic kinetics for the attainment of thermodynamical equilibrium in solids. In gases and in liquids, the unstable phases are very short-lived, owing to the high mobility of molecules. In solids, instead, metastable and unstable phases can last for long times.

A very interesting family of materials is composed by non-crystalline materials, whose structure is frozen in a state of non-equilibrium owing to the high viscosity.
In particular, glasses are non-crystalline materials which are obtained when a liquid is cooled so rapidly that a regular crystalline structure has no time to form. The cooling speed depends on the substance. In materials in which the atomic bonds are covalent, and thus directional, rigid units containing a few atoms form already in the liquid phase, and require a relatively long time to be re-oriented and form a long-range crystalline structure. In metals, on the contrary, the bonds are not directional and the crystal structure takes place very rapidly.
For example, boron oxide B_2O_3 can be found can be found almost uniquely in the vitreous state; the structural units are triangles with boron in center and oxygen at the vertices, the triangles are in turn connected to form rings with random spatial orientation. Crystal B_2O_3 can be obtained with difficulty, by heating the glass for a long time: the high temperature favours the kinetic of reorientation of the structural units.
Metals are characterised by a completely different behaviour. Metallic glasses can be obtained only as alloys of two or more components through very fast cooling, in some cases of the order of hundreds or thousands of kelvin per second. The presence of different atomic species in alloys slows down the kinetic and favours the glass formation.

New techniques have been developed in the last decades, that allow the production of solid materials through atom by atom deposition of one or more substances on a suitable substrate. By such techniques, one can obtain stable non-equilibrium states, if the substrate temperature is sufficiently low to block the single atoms in the position of their arrival on the substrate, thus preventing the formation of crystalline order. When the substrate temperature is instead sufficiently high, one can obtain mono-crystalline films; one speaks then of "epitaxial growth".

22.5 One-component systems: other phase transitions

Up to now, we considered the phase equilibria and phase transitions related to the atomic structure, that is to types of atomic aggregation.

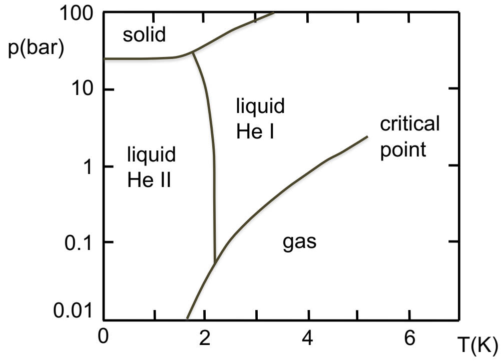


Figure 22.5: Phase diagram of helium (isotope 4).

Other phase equilibria and phase transitions exist which are related to different physical properties, e.g. electrical or magnetic. In some cases, such phase transitions are accompanied by structural variations, in other cases the structure remains unchanged.

Below, some significant cases are presented, for which electrical, magnetic, and other physical properties have to be considered and new thermodynamical coordinates have to be introduced.

It is worth noting that the phase transitions to be considered are generally studied as a function of temperature at constant ambient pressure; only rarely the effects of pressure have been studied.

22.5.1 The superionic transition

The electrical conductivity due to the motion of ions (both positive and negative) is well known for liquids, in particular for molten salts. There are also a number of crystals which, above a given temperature, exhibit electrical conductivity due to the ion motion. A typical example of such crystals is silver iodide AgI.

Below $T = 410\,\mathrm{K}$, silver iodide is in the non-conducting β phase; the crystal structure is hexagonal (wurtzite structure), each iodine atom is surrounded by four silver atoms, and viceversa.

Above $T = 410\,\mathrm{K}$, silver iodide is in the α phase, where the iodine ions I^- form a crystal lattice with body-centred cubic symmetry, and the Ag^+ ions are highly mobile and can give rise to an electrical current comparable to that of molten salts. Silver iodide in the α phase is said to be a “superionic” conductor.

The superionic transition $\beta \to \alpha$ of AgI at $T = 410\,\mathrm{K}$ is characterised by the abrupt change of electrical conductivity as well as by the abrupt change of the crystal structure, with a discontinuous variation of the molar volume v and of the molar entropy s.

22.5.2 The superfluid transition of liquid helium

In the phase diagram of helium (isotope 4) there is no triple point solid–liquid–gas (Fig. 22.5). To obtain solid helium, a pressure of at least 25 bar has to be applied; at such pressures there is no gas phase. Solid and gaseous phases cannot coexist.

Helium 4 cannot be frozen at ambient pressure because the quantum zero point energy of atomic vibrations is larger than the binding energy of the weak Van der Waals forces (of the order of 0.001 eV).

Of the utmost interest is the existence of two liquid phases, labeled He I and He II, respectively. The low-temperature He II phase, called “superfluid”, is characterised by extremely small values of viscosity as well as by other peculiar properties, such as negative thermal expansion and very large thermal conductivity. These and other unusual properties make superflua very interesting scientific subject.

The phase transition between the phase I and the phase II (superfluid) takes place without discontinuities in the molar volume and molar entropy, as the critical transition in normal fluids.

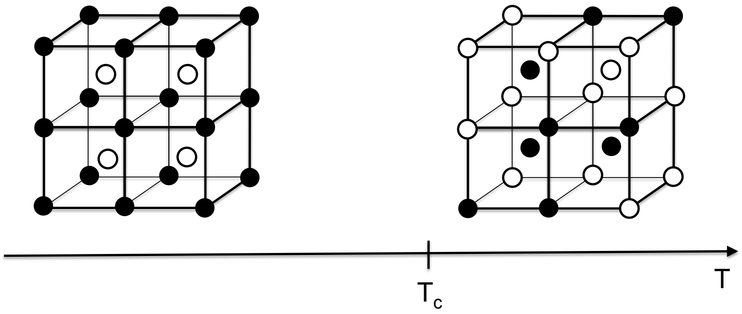


Figure 22.6: Order–disorder transition in the CuZn alloy. White and black circles represent the two atomic species.

The phase diagram of Fig. 22.5 shows the existence of two triple points (liquid-liquid-solid and liquid-iquid-gas).

22.5.3 Order-disorder transition in the CuZn alloy

Brass is a Cu–Zn alloy with different possible compositions (Fig. 22.9). Let us consider here the stoichiometric composition, 50% copper, 50% zinc. This composition has no practical applications, but it exhibits a behaviour particularly relevant for the classification of phase transitions.

The crystal structure of stoichiometric 50%-50% CuZn alloy is body-centred cubic, formed by the interpenetration of two simple-cubic sub-lattices: each point of the sublattice A is at the center of a cube of the sublattice B, and viceversa.

At very low temperatures, Cu atoms are placed at the points of the sublattice A and Zn atoms are placed at the points of sublattice B (Fig. 22.6, left). When the temperature increases, the system becomes progressively more disordered, some Cu atoms can occupy points of the sublattice B and Zn atoms can occupy points of the sublattice A. At the temperature $T_c = 733\,\mathrm{K}$ the crystal becomes completely disordered, so that for $T > T_c$ a given point of any one of the two sublattices can be occupied indifferently by a Cu or by a Zn atom (Fig. 22.6, right).

The phase transition is named *order–disorder phase transition.* The re-distribution of the Cu and Zn atoms from the low-temperature perfectly ordered phase to the perfectly disordered phase for $T \geq T_c$ takes place gradually, without abrupt variations. There is a similarity with the critical transition of fluids.

Also for order–disorder transitions one can define an *order parameter* that progressively decreases when the temperature increases and becomes zero at and above the transition temperature T_c. Let us choose one of the two sublattices, for example the A sublattice, and let w_{Cu} and w_{Zn} be the numbers of copper and zinc atoms, respectively, present in the sublattice. The order parameter is defined as

$$\eta \;=\; \frac{|w_{\mathrm{Cu}} - w_{\mathrm{Zn}}|}{w_{\mathrm{Cu}} + w_{\mathrm{Zn}}}\,. \tag{22.1}$$

Above the transition temperature T_c, the probability of finding a Cu atom in a given point of the sublattice is equal to the probability of finding a Zn atom, and the order parameter is $\eta = 0$. At sufficiently low temperatures, all points of the sublattice are occupied by a single atomic species, and $\eta \to 1$.

22.5.4 Ferromagnetic phase transition

Paramagnetic materials, studied in Chapter 4, when in presence of an external magnetisation field exhibit a magnetisation proportional to the field. The magnetisation is due to the orientation of permanent magnetic dipoles of atomic dimensions already present in the material.

Ferromagnetic materials can exhibit permanent magnetisation, independent of the presence of an external magnetising field. In the absence of the external field, the ferromagnetic material is

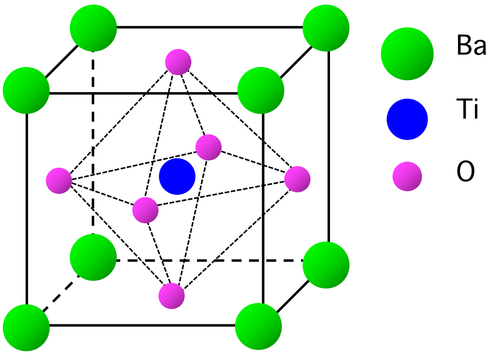


Figure 22.7: Crystal structure of barium titanate $BaTiO_3$.

composed of a large number of small regions, the magnetic domains, each one characterised by the orientation of all its magnetic dipoles in the same direction.

Let us consider here only some aspects relevant for the thermodynamical description, without going in the details of the phenomenon. For the sake of simplicity, let us consider only one-dimensional magnetisation along the two possible directions *up* and *down* and let us suppose that there is no external field.

At low temperatures, each domain is strongly magnetised along one of the two directions, up or down; the inversion of the magnetisation direction is a phase transition whose properties are similar to those of the transition between aggregation states, the magnetisation inversion substituting the variation of the molar volume; for ferromagnetism there is however no entropy variation.

When the temperature increases, the magnetisation of domains progressively decreases, and becomes zero at the Curie temperature T_c For $T > T_c$ the system is paramagnetic, that is the magnetisation requires the presence of an external field. The transition from ferromagnetism to paramagnetism takes place takes place gradually, without abrupt variations, and is similar to the critical transition in fluids: the *order parameter* is the modulus of the magnetisation in zero external field.

Iron (Fe) and cobalt (Co) are ferromagnetic materials; their Curie temperatures are $T_c = 1043\,\mathrm{K}$ and $T_c = 1388\,\mathrm{K}$, respectively.

22.5.5 Ferroelectric phase transition

Some materials exhibit permanent electrical polarisation below a given temperature T_c, while above T_c are not polarised. Due to the analogy with ferromagnetism, they are called ferroelectric materials.

The prototype of ferroelectric materials is barium titanate $BaTiO_3$.

At high temperature, for $T > T_c$, barium titanate has the cubic structure of perovskite, like many other ferroelectric materials (Fig. 22.7: the Ti^+ ion is surrounded by a regular octahedron of six O^- ions; the O^- ions, in turn, occupy the centres of the faces of a cube at which vertices the Ba ions sit. In this configuration, the system has no electric dipole moment.

At low temperature, for $T \ll T_c$, the Ti^+ ion is displaced with respect to the cage of the O^- ions, giving rise to a local electric dipole moment; the displacement of the Ti^+ ions reduces the crystal symmetry from cubic to tetragonal, so that the system acquires a permanent electric dipole moment.

When the temperature increases towards T_cT, the displacement of the Ti^+ ions with respect to the cage of O^- ions progressively decreases and becomes zero at $T_c = 120°\mathrm{C}$. Also the ferroelectric transition is similar to the critical transition of fluids; the *order parameter* is the electric polarisation.

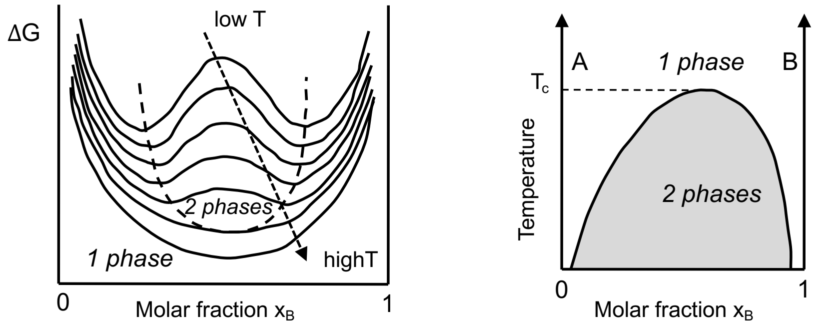


Figure 22.8: Two-components fluid mixture AB with a positive contribution of the mixing enthalpy. Left: variation ΔG of the Gibbs free energy as a function of the composition at different temperatures (the temperature increases from top to bottom); the dashed curve delimits the two-phases region. Left: (xT) phase diagram at constant pressure: the monophasic and two-phasic regions are singled out.

22.6 Systems with two or more components

Phase equilibria of systems containing two or more components represent a wide field of scientific and technological interest. The thermodynamical state of such systems is defined, in addition to temperature and pressure, also by the molar percent amount of the different components. One is interested in understanding if and how the different components are mixed and structurally organised as a function not only of temperature and pressure but even of the ratios between their amounts.

The graphic display is more complex than for one-component systems. For example, for two-components systems one often resorts to diagrams with the percent amount of one of the two components in abscissa and the temperature on the ordinate; the pressure is assumed to be the ambient pressure (Fig. 22.8, right).

Let us first consider the simple case of a two-component fluid mixture, then the more complex case of the metallic alloy Cu–Zn.

22.6.1 Two-components fluid mixtures

Let us consider a fluid mixture (typically liquid) of two components A and B. The composition of the mixture is given by the molar fraction of one of the two components, for example $x_A = n_A/n$; obviously, $x_B = 1 - x_A$.

If the interaction forces between all the pairs $A-B$, $A-A$ and $B-B$ are equal, the mixture is said to be an *ideal mixture*. For an ideal fluid mixture, the variation of the Gibbs function as a consequence of mixing has the same expression (11.23) of ideal gases, introduced in § 11.2:

$$\Delta G \;=\; RT\,(n_A \ln x_A + n_B \ln x_B) \;=\; nRT\,(x_A \ln x_A + x_B \ln x_B) \;<\; 0\,. \tag{22.2}$$

The mixing reduces the Gibbs free energy.

The *real mixtures* are formed by molecules for which the interactions $A-A$, $A-B$ and $B-B$ are different. As a consequence, the enthalpic contribution ΔH to the variation $\Delta G = \Delta H - T\Delta S$ can be non negligible. In particular, if the process of mixing gives rise to large positive variations of the enthalpy (because the attraction force of the pairs $A-B$ is much weaker than the attraction forces of the pairs $A-A$ and $B-B$) the variation of the Gibbs function can be positive, $\Delta G = \Delta H - T\Delta S > 0$, for sufficiently low temperatures. In that case, the mixing process is energetically not convenient. In some cases, the mixing process can be characterised by a negative entropy variation, due to the molecular organisation.

The behaviour of fluid mixtures with a positive contribution of the mixing enthalpy is shown in the graph of the mixing Gibbs free energy ΔG as a function of the concentration x_A (Fig. 22.8, left).

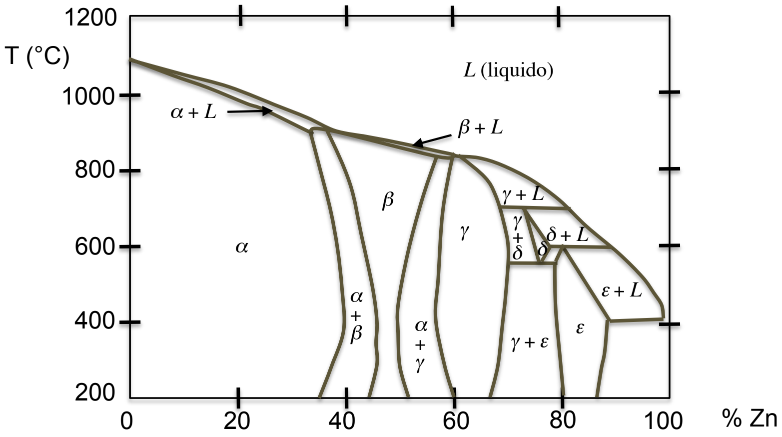


Figure 22.9: Phase diagram of brass (Cu–Zn alloy) at atmospheric pressure as a function of composition (horizontal axis, % Zn) and of temperature (vertical axis).

At high temperature, the graph is always upward concave. At sufficiently low temperatures, the curve $G(x_A)$ is characterised by two minima in correspondence of two values x_A^α and x_A^β. Within the interval $x_A^\alpha < x_A < x_A^\beta$ the Gibbs function G exhibits a maximum. For the mixture it is energetically more convenient, in the interval $x_A^\alpha < x_A < x_A^\beta$, to separate in two different phases, one rich in the A component, the other rich in the b component.

The corresponding phase diagram (Fig. 22.8, right) is characterised by two regions. Outside the dome-shaped curve one homogeneous phase exists. Below the dome-shaped curve, the systems separates into two phases, one rich in the A component, the other rich in the B component.

It is interesting to stress the similarity between the coexistence of the two fluid phases in the AB mixture here considered and the coexistence of liquid and gas (vapour) along the coexistence curve of pure substances.

Also in the case of mixtures, when the temperature increases, the extent of the interval $x_A^\alpha < x_A < x_A^\beta$ progressively decreases, and becomes zero at the critical temperature T_c, in correspondence of a critical composition.

It is another example of critical phenomenon, that characterised by the order parameter

$$\eta \;=\; x_A^\alpha - x_A^\beta \,. \tag{22.3}$$

22.6.2 Two-components solid alloys

A simple example of two-components solid alloy is represented by brass, the alloy formed by copper Cu and zinc Zn. The phase diagram of the Cu–Zn alloy is shown in Fig. 22.9.

Different phases can form as a function of temperature and composition: the liquid phase at high temperatures or single solid phases of different crystal structure $(\alpha, \beta, \gamma, \delta)$. In some regions of the phase diagram two phases can coexist, both crystalline or one cristalline and the other liquid.

Chapter 23

Thermodynamics of phase equilibria

In this chapter is devoted to the thermodynamic description of phase equilibria and phase transitions.

The fundamental role of the Gibbs function for characterising the equilibrium between the different phases of a substance is enlightened in § 23.1. The problem of the possibility of coexistence of two or more phases for sys tems with one or more components is solved in § 23.2 by the Gibbs phases rule.

The effects of temperature and pressure on the phase equilibria are considered in § 23.3, where the Clausius–Clapeyron equation is introduced and its application to the liquid–solid and liquid–gas equilibria is studied.

§ 23.4 is dedicated to the classification of phase transitions into first order and continuous phase transitions; continuous transitions are characterised by order parameters and critical exponents.

The chapter ends, in § 23.5, with some considerations on the relation between the stability of thermodynamical equilibrium and the phase transitions; the difference between first order and continuous transitions is enlightened.

23.1 Phase equilibri and Gibbs function

The independent coordinates useful for describing the solid–liquid–gas phase equilibria are temperature and pressure. The suitable thermodynamic potential is thus the Gibbs function $G(T, P, \{n_i\})$.

23.1.1 Phase equilibria and chemical potentials

The equilibrium condition for a system maintained at constant temperature and pressure (§ 8.4) is

$$dG \;=\; \sum\nolimits_i \mu_i \, dn_i \;=\; 0\,, \tag{23.1}$$

where $\mu_i = g_i$ are the chemical potentials of the components of the systems, corresponding to the molar Gibbs functions g_i.

If the equilibrium of the different phases $\alpha, \beta, \gamma, \ldots$ of a given substance in a closed system is considered, (23.1) becomes

$$dG \;=\; \mu_\alpha \, dn_\alpha + \mu_\beta \, dn_\beta + \mu_\gamma \, dn_\gamma + \cdots \;=\; 0\,. \tag{23.2}$$

The differentials dn_i are not independent, because the total number of moles of he substance doesn't change in a phase transition, so that

$$\sum\nolimits_i dn_i = 0\,. \tag{23.3}$$

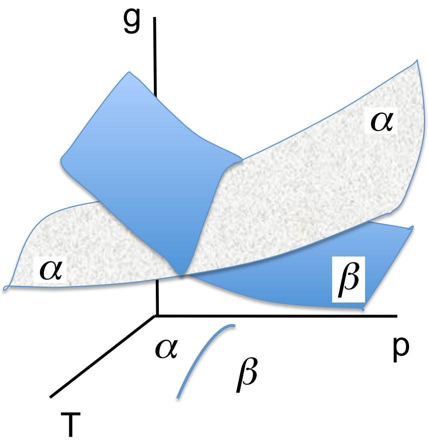


Figure 23.1: Schematic representation of two surfaces g_α and g_β, corresponding to two phases α and β, in the three-dimensional space (T, p, g) and their projection on the (T, p) plane. The two surfaces intersect in a coexistence curve.

The extremum problem (23.2) constrained by (23.3) can be solved by the general method of Lagrange multipliers:

$$\sum_i \mu_i \, dn_i + \xi \sum_i dn_i \;=\; \sum_i (\mu_i - \xi)\, dn_i \;=\; 0\,, \tag{23.4}$$

where ξ is the Lagrange multiplier. Since the differentials dn_i in (23.4) are now independent, that is arbitrary, (23.4) is fulfilled if

$$\mu_i \;=\; \xi \qquad (\forall i)\,. \tag{23.5}$$

In equilibrium conditions, the chemical potential of all the phases present are equal:

$$\boxed{\mu_\alpha = \mu_\beta = \mu_\gamma = \cdots} \qquad \text{or} \qquad \boxed{g_\alpha = g_\beta = g_\gamma = \cdots} \tag{23.6}$$

In what follows, when referring to a single phase, the symbols of the chemical potential μ and of the molar Gibbs function $g = G/n$ will be used indifferently.

Note: For chemical reactions (Chapter 11), (23.1) is always fulfilled, but (23.3) is not .

23.1.2 Phase diagrams and Gibbs function

The thermodynamical properties of a one-component system can de described by a three-dimensional graph, whose three axes correspond to the values of temperature T, pressure p and molar Gibbs function g (Fig. 23.1).

In principle, to each phase $(\alpha, \beta, \gamma, \ldots)$ of the system one can associate a function $g(T, p)$, so that different functions $g_\alpha(T, p), g_\beta(T, p), g_\gamma(T, p)$ ... correspond to the different phases in the (T, p, g) space. A quantitative evaluation of the functions $g(T, p)$ is generally far from trivial; we will limit ourselves here to consider their qualitative properties, from which one can anyway obtain important information.

For each value of temperature and pressure (T, p), the thermodynamically stable phase is characterised by the lowest value of the molar Gibbs function (chemical potential) $g(T, p) = \mu(T, p)$.

It is common practice to project the $g(T, p)$ surfaces on the (T, p) plane and obtain graphs like those of Fig. 22.1. In each zone, the function $g(T, p)$ of a given phase is smaller than the functions$g(T, p)$ of the other phases. The coexistence curves are the projections of the intersection curves of different surfaces $g(T, p)$, where $g_\alpha = g_\beta$. At a triple point, $g_\alpha = g_\beta = g_\gamma$.

Let us now study some general properties of the $g(T, p)$ function. Starting point is the differential for a one-component closed system

$$dg \;=\; -s\, dT \;+\; v\, dp\,. \tag{23.7}$$

23.1.3 Dependence of the Gibbs function on temperature

Let us assign a fixed value to the pressure p and study the dependence of the molar Gibbs function g on the temperature T, starting from the solid phase and ending to the gas phase (Fig. 23.2, top left).

For each phase, one can determine some general properties of the $g(T)$ function (Fig. 23.2,top center). From (23.1) one can obtain the first and second derivatives of g with respect to T:

$$\left(\frac{\partial g}{\partial T}\right)_p = -s < 0\,, \qquad \left(\frac{\partial^2 g}{\partial T^2}\right)_p = -\left(\frac{\partial s}{\partial T}\right)_p = -\frac{c_p}{T} < 0\,. \tag{23.8}$$

The value of s has been assumed to be positive as a consequence of the statistical definition of entropy. The $g(T)$ curve at constant pressure has negative slope and is downward concave for all phases. The absolute value of the slope is the molar entropy s, that increases when the temperature increases within each phase region.

In the coexistence points of two phases α and β, the two curves $g_\alpha(T)$ and $g_\beta(T)$ meet: the molar Gibbs function g is continuous, $g_\alpha = g_\beta$. Its first derivative exhibits instead a discontinuity, because the molar entropies of different phases are different in the equilibrium points: $s_{\rm sol} < s_{\rm liq}$ e $s_{\rm liq} < s_{\rm gas}$. For each phase, the molar entropy s increases when the temperature T increases (Fig. 23.2, top right); the first derivative is c_p/T, where c_p is the specific heat at constant pressure.

Latent heat

In the points of equilibrium between two phases there is a discontinuity Δs in the molar entropy, and thus a divergence of the specific heat (first derivative of s and second derivative of g).

The finite entropy variation multiplied by the temperature is the molar enthalpy of the phase transition, $\Delta h_{\rm tra} = T\Delta s$, often called *latent heat of transition.* The latent heat of a transformation is and amount of heat exchanged between the system and its ambient without modification of the temperature. The exchange of heat at constant temperature corresponds to a divergence of the specific heat.

Example: To melt aa solid and transform it to a liquid without temperature variation, energy has to be supplied to the system in order to transform the atomic bonds.

23.1.4 Dependence of the Gibbs function on pressure

Let us now a fixed value to the temperature T and study the dependence of the molar Gibbs function g on the pressure p. For concreteness, let us consider a system whose solid–liquid coexistence curve ha positive slope; let us start from the low-pressure gas phase and end to the high-pressure solid phase (Fig. 23.2, bottom left).

For each phase, some general properties of the molar Gibbs function $g(p)$ can be evidenced (Fig. 23.2,bottom center). From (23.7) one can calculate the first and second derivatives of g with respect to p:

$$\left(\frac{\partial g}{\partial p}\right)_T = v > 0\,, \qquad \left(\frac{\partial^2 g}{\partial p^2}\right)_T = \left(\frac{\partial v}{\partial p}\right)_T = -v\chi_T < 0\,. \tag{23.9}$$

The $g(p)$ curve at constant temperature has positive slope and is downward concave for all phases. The slope corresponds to the molar volume v, and decreases when the pressure increases within each phase.

In the coexistence points of two phases α and β, the molar Gibbs function g is continuous, $g_\alpha = g_\beta$; the first derivative, that is the molar volume v, is discontinuous, $v_{\rm gas} > v_{\rm liq}$ and $v_{\rm liq} > s_{\rm sol}$.

For each phase, the molar volume v decreases when the pressure p increases (Fig. 23.2, bottom right). The first derivative corresponds to $-v\chi_T$. At the phase transitions there are discontinuous variations of molar volume Δv, so that the isothermal compressibility χ_T diverges.

(?) Study the case of negative slope for the solid–liquid coexistence curve (e.g. the case of water).

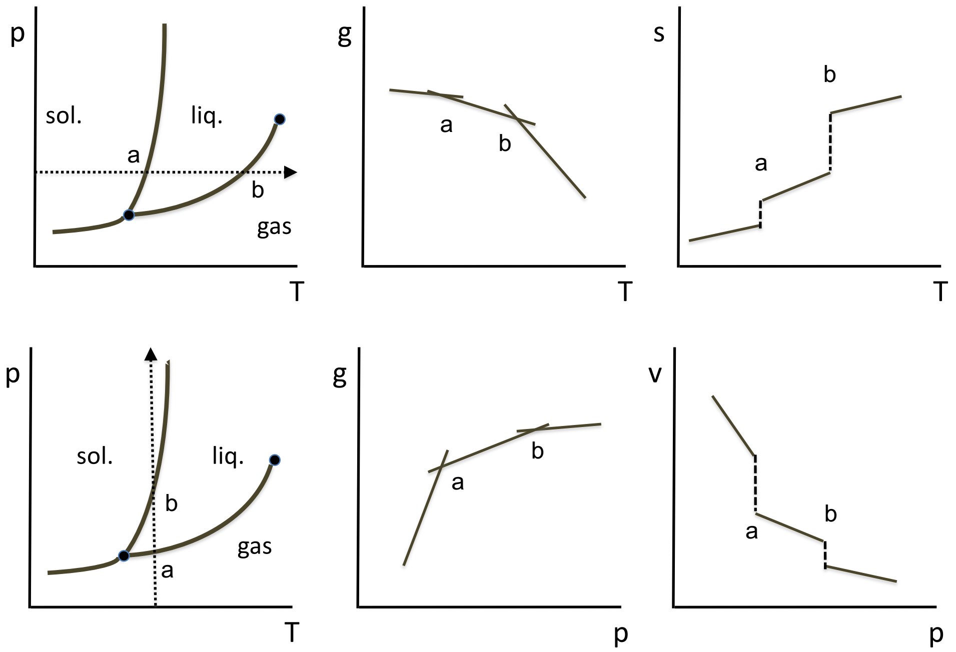


Figure 23.2: Molar Gibbs function g and phase transition. Left: (T, p) graphs. Centre: dependence of g on temperature (top) and on pressure (bottom). Right: dependence of the molar entropy on temperature (top) and dependence of the molar volume on pressure (bottom).

23.2 Gibbs phase rule

The phase diagram of a one-component substance is characterised by the presence of mono-phasic regions, bi-phasic coexistence lines and triple points. One could ask: can extended regions of coexistence of two or more phases exist ? or coexistence curves of three phases ? or quadruple points ?
A general answer to the problem is given by the Gibbs phase rule, that connects the number f of free variables of a thermodynamical system to the total number of variables and the number of constraint equations

$$(\text{free vriables}) \;=\; (\text{total variables}) \;-\; (\text{constraints})\,. \tag{23.10}$$

The Gibbs phase rule holds also for many-component systems, such as those considered in the examples of § 22.6). In what follows, we consider first the phase rule for one-component systems and then for many-component systems.

One-component systems

For a one-component system, the phase rule is:

$$f \;=\; 2-(\phi-1) \qquad \text{that is} \qquad \boxed{f \;=\; 3-\phi} \tag{23.11}$$

where:

- → 2 is the total number of variables, typically T and p,
- → ϕ is the number of coexisting phases,
- → $\phi - 1$ is the number of constraints, corresponding to the equilibrium equations:
  - if only one phase is present, there are no constraints tothe values of T and p, so that $\phi - 1 = 1 - 1 = 0$,

  - for two coexisting phases, the equation $g_\alpha = g_\beta$ is a constraint, $\phi - 1 = 2 - 1 = 1$,
  - for three coexisting phases (triple point), the equations $g_\alpha = g_\beta = g_\gamma$ are two constraints, $\phi - 1 = 3 - 1 = 2$

From (23.11) one deduces that

- if only one phase is present ($\phi = 1$) there are $f = 2$ free variables, T and p;
- if two phases coexist ($\phi = 2$) there is only one free variable: T and p are constrained on a coexistence curve;
- if three phases coexist ($\phi = 3$) there are no free variables, T and p can only get the triple point values;
- it is impossible that four or more phases can coexist in equilibrium.

Many-components systems

Let us now consider a system containing c components (without chemical reactions). For example, the Cu–Zn alloy of Fig. 22.9 has $c = 2$ components.
The number of coexisting phases be again ϕ.

The *total number of variables* is $2 + c\phi$:

→ 2 variables are T e p,
→ $c\phi$ are the concentration values of the c components in the ϕ different phases.

Example: Let us again consider the Cu–Zn alloy of Fig. 22.9: in a mono-phasic region ($\phi = 1$) the $c\phi = 2$ variables are the two concentrations of Cu and Zn; along the coexistence curve of two mon-phasic regions ($\phi = 2$), the $c\phi = 4$ variables are the Cu and Zn concentrations in each one of the two phasee.

The number of *constraints* is $c(\phi - 1) + \phi$:

→ $c(\phi - 1)$ are the equations that make equal the chemical potentials of the each one of the c components in each one of the ϕ coexisting phases,
→ ϕ are the equations that make equal to 100 the sums of the percent amounts of all the components in each one of the coexisting phases.

Example: Let us again consider the Cu–Zn alloy of Fig. 22.9: in a mono-phasic region, $\phi = 1$ e $2(\phi - 1) = 0$, along a coexistence curve of two phases, $\phi = 2$ e $2(\phi - 1) = 2$.

The number of degrees of freedom f is the difference between the total number of variables and the number of constraints; the phase rule for a many-components system is:

$$f \;=\; 2 + c\phi - c(\phi - 1) - \phi\,, \quad \text{that is} \quad \boxed{f = 2 + c - \phi} \tag{23.12}$$

For a one-component system ($c = 1$), equation (23.12) reduces to (23.11).

Example: For the Cu–Zn alloy of Fig. 22.9 the phase rule is $f = 4 - \phi$. In a mono-phasic region, $f = 3$: temperature, pressure and relative concentration can vary independently. Along a coexistence line, $f = 2$: only two variables can vary independently, the third one is univocally determined once the values of the other are given.

23.3 Coexistence curves: Clausius–Clapeyron equation

In § 23.1, we separately considered the dependence of the molar Gibbs function g on temperature T or on pressure p. We want now to consider the joint effects of temperature and pressure on the phase equilibria, starting from the important example of the dependence on pressure of the melting and boiling points of simple substances.

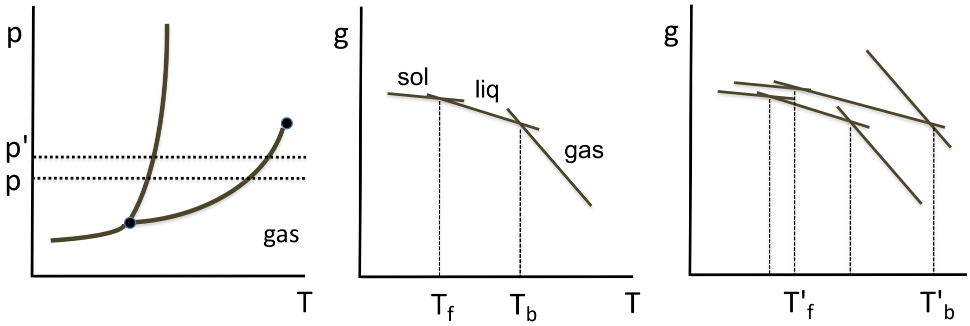


Figure 23.3: Dependence of the melting and boiling points on pressure. Left: (Tp) diagram together with two isobars at p andp'. Centre: the function $g(T)$ at pressure p with melting point T_f and boiling point T_b. Right: variation of $g(T)$ when the pressure changes fron p to p' and new melting point T'_f and boiling point T'_b .

23.3.1 Dependence of melting and boiling points on pressure

Let us consider again the dependence of the molar Gibbs function g on temperature for a given value of pressure p (Fig. 23.3).

The equilibrium temperature between the solid and liquid phases is the *melting point* T_f at pressure p. The equilibrium temperature between the liquid and gas phases is the *boiling point* T_b at pressure p.

Let us increase the pressure from the value p to a value p' (Fig. 23.3, left). The corresponding variation of the molar Gibbs function g for each value of temperature depends, according to (23.9), on the molar volume v. The molar volume is much larger in the gas phase than in the liquid phase (as long as far from the critical point); the boiling point significantly increases when the pressure increases (Fig. 23.3, right). The molar volume is generally larger in the liquid phase than in the solid phase; the melting temperature increases when the pressure increases. (Exceptions are substances like water, for which the molar volume is larger in the solid phase than in the liquid phase).

23.3.2 Clausius–Clapeyron equation

A general quantitative expression can be found for the relation between temperature and pressure of two phases in equilibrium.

In any point of a coexistence curve between two phases α and β, the Gibbs function has the same value for the two phases: $g_\alpha = g_\beta$. If one moves along the coexistence curve by an infinitesimal displacement (dT, dp), the Gibbs functions in the new point of the curve have again the same value for the two phases: $g_\alpha + dg_\alpha = g_\beta + dg_\beta$. Therefore, the variations of g for the two phases are equal:

$$\left[\begin{array}{l} g_\alpha = g_\beta \\ g_\alpha + dg_\alpha = g_\beta + dg_\beta \end{array}\right] \qquad \Rightarrow \qquad dg_\alpha = dg_\beta\,. \tag{23.13}$$

By substituting the differetials dg of (23.13) according to (23.7) one obtains:

$$-\,s_\alpha dT + v_\alpha dp \;=\; -s_\beta dT + v_\beta dp\,, \tag{23.14}$$

whence

$$[v_\alpha - v_\beta]\,dp \;=\; [s_\alpha - s_\beta]\,dT\,, \tag{23.15}$$

and at last

$$\boxed{\frac{dp}{dT} \;=\; \frac{s_\alpha - s_\beta}{v_\alpha - v_\beta}} \tag{23.16}$$

Equation (23.16), known as Clausius-Clapeyron equation, connects the slope of the coexistence curve of two phases α and β in the T, p diagram to the ratio between the difference of molar entropy and the difference of molar volume.

An alternative expression of the Clausius-Clapeyron equation can be found as follows. Since the phase transition takes place at constant pressure, the variation of molar entropy is connected to the amount of heat exchanged at constant pressure, that is to the variation of the molar enthalpy h: $h_\alpha - h_\beta = T(s_\alpha - s_\beta)$. Therefore

$$\boxed{\frac{dp}{dT} = \frac{h_\alpha - h_\beta}{T\,(v_\alpha - v_\beta)}} \tag{23.17}$$

The variation $\Delta h = h_\alpha - h_\beta$ of molar enthalpy is the molar latent heat of the transition.

23.3.3 Solid–liquid equilibrium

For the solid–liquid coexistence curve, (23.17) becomes

$$\frac{dp}{dT} = \frac{\Delta h_{\text{fus}}}{T\,\Delta v_{\text{fus}}}, \tag{23.18}$$

where

- the molar fusion enthalpy $\Delta h_{\text{fus}} = h_{\text{liq}} - h_{\text{sol}}$ is always positive,
- the variation of molar volume $\Delta v_{\text{fus}} = v_{\text{liq}} - v_{\text{sol}}$ is
  - positive for most substances, so that $dp/dT > 0$,
  - negative for a few substances, among which water, so that $dp/dT < 0$.

Example: Let us consider water. For $T \simeq 273$ K and atmospheric pressure,

$$\Delta h_{\text{fus}} = 6.01 \text{ kJ/mol}, \qquad \Delta v_{\text{fus}} = -1.7 \text{ cm}^3\text{/mol},$$

so that

$$\frac{dp}{dT} = \frac{\Delta h_{\text{fus}}}{T \Delta v_{\text{fus}}} \simeq -1.28 \times 10^7 \text{ Pa/K} = -1.28 \times 10^2 \text{ bar/K}.$$

(?) Evaluate the slope of the coexistence curve near $T = 273$ K.
Let us relate the molar fusion enthalpy to the averag energy per molecule. Since 1 eV $= 1.6 \times 10^{19}$ J, lthe fusion enthalpy $\Delta h_{\text{fus}} = 6.01$ kJ/mol corresponds to about 0.16 eV/molecole.

23.3.4 Liquid–gas equilibrium

For the liquid–gas coexistence curve, (23.17) becomes

$$\frac{dp}{dT} = \frac{\Delta h_{\text{vap}}}{T\,\Delta v_{\text{vap}}}, \tag{23.19}$$

where both the molar enthalpy of vaporisation Δh_{vap} and the molar volume of vaporisation Δv_{vap} are positive.

Equation (23.19) can be made simpler if

- one takes into account that the molar volume v_{gas} of the gas phase is generally much larger than the molar volume v_{liq} of the liquid phase (if sufficiently far from the critical point), so that $\Delta v_{\text{vap}} \simeq v_{\text{gas}}$
- one relies on the ideal gas approximation, $v_{\text{gas}} \simeq RT/p$,

so that

$$\frac{dp}{dT} \simeq \frac{\Delta h_{\text{vap}}}{RT^2}\, p\,, \quad \text{that is} \quad \boxed{\frac{d\ln p}{dT} \simeq \frac{\Delta h_{\text{vap}}}{RT^2}} \tag{23.20}$$

Example: Let us consider again water. For $T \simeq 373$ K and $p = 1$ bar,

$$\Delta h_{\text{vap}} = 40.66 \text{ kJ/mol}\,,$$

so that, from (23.20) one finds

$$\frac{dp}{dT} = 3.51 \times 10^{-2} \text{ bar/K}\,.$$

The slope of the liquid–gas coexistence curve at $T = 373$ K is smaller than the absolute value of the slope of the solid–liquid coexistence curve, although the molar enthalpy of vaporisation is larger than the molar enthalpy of fusion. The explanation relies on the fact that the difference between the gas and liquid molar volumes is much larger than the difference between the solid and liquid molar volumes.
Since 1 eV $= 1.6 \times 10^{19}$ J, the enthalpy of vaporisation $\Delta h_{\text{fus}} = 46.66$ kJ/mol corresponds to about 1.24 eV/molecole.

We will consider in more detail the liquid–gas coexistence in Chapter 24.

23.4 Classification of phase transitions

The phase transitions can be divided in two categories, the first order transitions and continuous transitions.

23.4.1 First order phase transitions

The solid–liquid–gas phase transitions, considered in § 23.1, are characterised by the following properties of the molar Gibbs function (Fig. 23.2):

- lthe slope of the g function undergoes an abrupt variation;
- the first derivatives of the molar Gibbs functions, that is s an v, undergo a discontinuity,
- the second derivatives of the molar Gibbs function, that is the response functions c_p, β, χ_T, abruptly diverge without previous notice.

The phase transitions, for which the first derivatives of the Gibbs function are discontinuous, are said to be "first order" phase transitions.
For example, is first order the superionic transition considered in § 22.5; by the way, in this case the variation of the electrical conductivity is accompanied by a modification of the crystal structure.

The expression "first order transitions" is historically motivated by the old unsuccessful attempt to classify all phase transitions in terms of the degree of the derivative of g for which the first discontinuity takes place.

23.4.2 Continuous transitions

A number of phase transitions cannot be included in the first order category. For example (§ 22.5), lthe critical transition of fluids, the order-disorder transition in binary alloys, the ferromagnetic and ferroelectric transitions, the superfluid transition of liquid helium are characterised by the following properties:

- lthe slope of the g function doesn't undergo any abrupt variation;
- lthe first derivatives of the g function are continuous;
- the specific heat exhibits, when the transition temperature is approached, a behaviour whose shape is similar to the greek letter lambda (λ); there is some sort of notice of the transition already within the monophasic regions.

Since the first derivatives of the Gibbs function are continuous, these phase transitions are generally called "continuous transitions"; sometimes also the name "higher order transitions" can be found. In many cases, the thermodynamical treatment requires the introduction of specific coordinates (electrical or magnetic fields, etc) and the derivatives of the Gibbs function have to be considered also with respect to these new coordinates.

Order parameters

A property common to all continuous phase transitions is the possibility of defining a quantity, the *order parameter*, that is different from zero in the low-temperature phase and equal to zero in the high temperature phase. In the low temperature phase, the order parameter progressively and continuously decreases when the transition temperature is approached, and becomes zero at the transition temperature.
Let us give some examples.

1. In the *critical transition of fluids* (§ 22.2), a possible order parameter is the difference between the density of the liquid and the density of the gas, $\rho_{\mathrm{liq}} - \rho_{\mathrm{gas}}$. In general, one prefers to consider the normalised
$$\frac{\rho_{\mathrm{liq}} - \rho_{\mathrm{gas}}}{\rho_{\mathrm{cr}}}\,, \tag{23.21}$$
where ρ_{cr} is the density at the critical point. The order parameter becomes zero at the critical point, where the two modifications of the fluid phase coincide.
The order parameter (23.21) is a scalar quantity.

2. In the *ferromagnetic transition* (§ 22.5), the order parameter is the total magnetisation $\vec{M}$ of one domain when the external magnetising fied is zero ($\vec{\mathcal{H}} = 0$). The magnetisation $\vec{M}$ decreases when the temperature increases and becomes zero at the Curie temperature T_c.
In this case, the order parameter is a vector quantity.

According to the type of transition, the order parameter can be a scalar, a vector or a tensor quantity s well as a complex number.

Critical exponents

A general property of critical transitions is the similar and relatively simple dependence on temperature of some relevant quantities, such as the order parameter and the response functions, when the transition temperature is approached.
The approach to the critical temperature is measured by the a-dimensional parameter

$$\epsilon \;=\; \frac{T - T_{\mathrm{cr}}}{T_{\mathrm{cr}}}\,, \qquad \begin{cases} \epsilon < 0 & \text{for } T < T_{\mathrm{cr}} \\ \epsilon > 0 & \text{for } T > T_{\mathrm{cr}} \end{cases} \tag{23.22}$$

The experimental behaviour of the relevant quantity (order parameter or response function) is generally fitted by simple functions as

$$f(\epsilon) \;=\; A\,\epsilon^{\lambda} \tag{23.23}$$

or by more complicated functions as

$$f(\epsilon) \;=\; A\,\epsilon^{\lambda}\,[1 + B\epsilon^{y}\,\ldots] \tag{23.24}$$

The exponent λ in (23.23) and (23.24) is called *critical exponent.*
Let us consider some examples.

1. In *critical transition of fluids*, the order parameter follows an exponential law (23.23), with the value of the critical exponent being similar for a number of fluidscon esponente critico simile per molti fluidi:
$$\frac{\rho_l - \rho_v}{\rho_c} \propto (-\epsilon)^\beta\,, \qquad \beta \simeq \frac{1}{3} \tag{23.25}$$
The constant-volume specific heat follows an exponential law (23.23) too, the exponent is however different according to whether the critical temperature is approached from bottom or from top:
$$c_v \;=\; (-\epsilon)^{-\alpha'}\,, \qquad c_v \;=\; (\epsilon)^{-\alpha}\,, \qquad (0 \leq \alpha, \alpha' \leq 0.2)\,. \tag{23.26}$$

2. Also in the *ferromagnetic transition* the order parameter, that is the total magnetisation M, follows an exponential law (23.23):
$$M \propto (-\epsilon)^\beta\,, \qquad \beta \simeq \frac{1}{3}\,. \tag{23.27}$$

The parametrisation of the behaviour of different quantities (order parameter and response functions) in terms of exponential functions is relevant for a number of reasons.

- The similarity of critical exponents for different systems stimulates the search for general treatments (for example in terms of laws of corresponding states).
- The ability to calculate accurate values of the critical exponents is a good test for the theoretical approaches to phase transitions.
- General thermodynamical or statistical considerations can lead to relations connecting the values of different critical exponents.

23.4.3 Symmetry considerations

Phase transitions can often be connected to symmetry variations. In general, the high temperature phase is more symmetric than the low temperature phase. One speaks of “symmetry breaking” for the transition from a higher symmetry phase to a lower symmetry phase.
Let us consider some examples.

- The gas → solid and liquid → solid transitions are characterised by a breaking of the translational symmetry: the fluid state (liquid or gas) is more symmetric than the solid state with respect to spatial translations.
- In the liquid–gas transitions there is no symmetry breaking, in agreement with liquid and gas being considered as two modifications of a unique fluid phase.
- In a ferromagnetic transition the rotational symmetry is broken; in the high temperature paramagnetic phase the system is isotropic, while below the Curie T_c temperature the magnetisation direction is singled out.

The first order transitions are characterised by a discontinuous symmetry breaking; there is no connection between the symmetry of the two phases. In the continuous transitions the variation of symmetry is continuous and is measured by the variation of the order parameter.

23.5 Stability of equilibrium and phase transitions

The stability of thermodynamical equilibrium was first analysed in § 9.6. The stability condition for isolated systems implies some constraints on the values of some response functions; in particular, specific heats and compressibilities must be positive, $c_v \geq 0, \chi_T \geq 0$.
Let us now consider the topic form a different point of view, particularly suited to study the thermodynamical stability of phases.

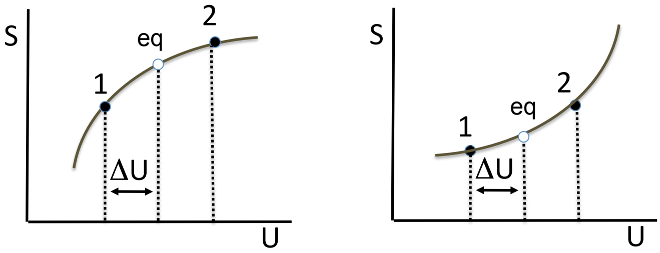


Figure 23.4: Left: to guarantee the stability of equilibrium, the $S(U)$ function has to be downward concave. Right: were the function upward concave, there could not be stable equilibrium.

23.5.1 Stability in the different representations

Entropy representation

According to Axiom III of § 5.3, the entropy S is a monotonously increasing function of the internal energy U. The stability condition requires that the function $S(U)$ is downward concave. As a consequence, the specific heat is necessarily positive (§ 9.6).

Actually, let us consider an isolated system divided in two identical subsystems by a diathermic wall, and study the effects of a fluctuation consisting in the transfer of an energy amount ΔU from subsystem 1 to subsystem 2 (Fig. 23.4).

For the equilibrium to be stable, the transfer of energy from subsystem 1 to subsystem 2 has to give rise to a reduction of entropy S, so that the system tends spontaneously to the equilibrium state corresponding to the maximum value of entropy. The $S(U)$ curve has thus to be downward concave (Fig. 23.4, left).

Were the $S(U)$ curve upward concave (Fig. 23.4, right), the energy fluctuation would lead the system to a state of larger entropy and there would not be the trend to re-establish the initial state.

A similar reasoning can be made for the $S(V)$ function, and, more generally, for the $S(U,V)$ surface. The local stability conditions are

$$\frac{\partial^2 S}{\partial U^2} \leq 0\,, \qquad \frac{\partial^2 S}{\partial V^2} \leq 0\,. \tag{23.28}$$

Energy representation

One can easily verify that, in the energy representation, the stability of equilibrium requires that the $U(S,V)$ surface be upward concave with respect to both S and V. The local stability conditions are

$$\frac{\partial^2 U}{\partial S^2} \geq 0\,, \qquad \frac{\partial^2 U}{\partial V^2} \geq 0\,. \tag{23.29}$$

Let us now consider the Helmholtz function $F = U - TS$. Since $c_v \geq 0, \chi_T \geq 0$, one can easily verify that the stability conditions are

$$\frac{\partial^2 F}{\partial T^2} \leq 0\,, \qquad \frac{\partial^2 F}{\partial V^2} \geq 0\;: \tag{23.30}$$

The $F(T,V)$ function is downward concave with respect to T, upward concave with respect to V.

At last, let us consider the Gibbs function $G = F + pV$. One can easily verify that the stability conditions are

$$\frac{\partial^2 G}{\partial T^2} \leq 0\,, \qquad \frac{\partial^2 G}{\partial p^2} \leq 0\;: \tag{23.31}$$

The $G(T,p)$ function is downward concave with respect to both T and p (see Fig. 23.2, center) .

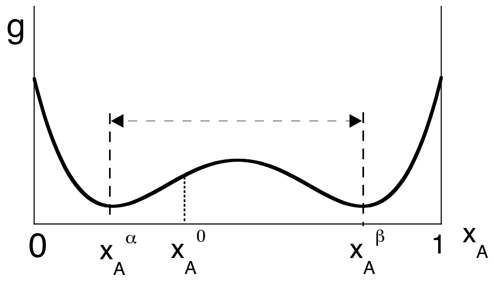


Figure 23.5: Molar Gibbs function g of a real fluid mixture AB at fixed temperature T and pressure p, if the mixing enthalpy is large and positive (as in the low-T cases of Fig. 22.8). In the horizontal axis the concentration x_A.

23.5.2 Gibbs function

In what follows, we focus our attention of the properties of the Gibbs function for systems maintained at constant temperature T and pressure p.

As is was shown in § 8.4, in a closed system with constant temperature T and pressure p, the thermodynamical equilibrium is characterised by the minimum of the Gibbs function G with respect to any process, real or virtual, leading the system out of equilibrium.

In particular, we consider some important cases: binary fluid mixtures, phase diagrams of pure substances, liquid–gas equilibrium. At last we introduce the Ginzburg-Landau theory for continuous transitions.

23.5.3 Fluid mixtures

Let us consider the fluid binary mixtures AB introduced in § 22.6. It was shown (Fig. 22.8) that, if the mixing process gives rise to large positive variations of the enthalpy, at sufficiently low temperatures the $g(x_A)$ curve is characterised by two minima in correspondence of two values x_A^α and x_A^β (Fig. 23.5). For a mixture whose concentration x_A^0 is within the interval $x_A^\alpha < x_A < x_A^\beta$, it is energetically more convenient to split into two different phases, the one rich in A, with concentration x_A^β, the other rich in B, with concentration x_A^α.

The two minima of the molar Gibbs function g for $x_A = x_A^\alpha$ and $x_A = x_A^\beta$ correspond to two conditions of stable thermodynamical equilibrium. Possible local fluctuations of the concentration give rise to an increase of g and are thus reabsorbed.

In equilibrium conditions, the function g is upward concave with respect to the variable $x_A = n_A/n$ (n_A is an extensive coordinate).

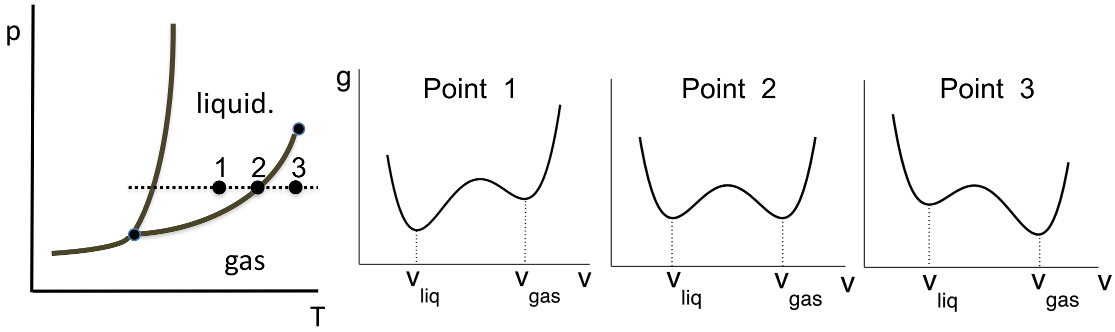


Figure 23.6: Transizione liquido–vapore. I tre grafici a destra mostrano l'energia libera molare di Gibbs g in funzione del volume molare nei tre punti 1, 2 e 3 del grafico a sinistra.

23.5.4 First order phase transitions

Let us now consider the Tp phase diagram of a pure substance (Fig. 23.6), and focus our attention of the three points labeled 1, 2 e 3, corresponding to the same pressure but to different temperature T. In point 1 the system is in the liquid phase, in point 3 the system is in the gas phase, point 2 is on the liquid–gas coexistence curve. In each one of the three points, both temperature T and pressure p are fixed. The system can however undergo local or global fluctuations of molar volume v and/or of molar entropy s.

For each point, let us plot the molar Gibbs function g as a function of the molar volume v (similar plots could be drawn as a function of the molar entropy s). In correspondence of the molar volumes of the liquid phase v_{liq} and of the gas phase v_{gas}, the g function is characterised by local minima. In point 1 the absolute minimum of g corresponds to v_{liq}; the stable equilibrium corresponds to the liquid phase. In point 3 the absolute minimum of g corresponds to v_{gas}; the stable equilibrium corresponds to the gas phase. In point 2, on the liquid–gas coexistence curve, the two minima of g are equivalent; liquid and gas (vapour) can coexist; the exchange of heat between the system and its ambient gives rise to a progressive modification of the relative amounts of the two phases (along the isothermal and isobar horizontal lines in the grey zone of Fig. 22.3).

23.5.5 Continuous transitions, Ginzburg–Landau theory

The Ginzburg-Landau theory allows a phenomenological interpretation of the continuous transitions. The qualitative agreement with experiment is good, less good is often the quantitative agreement.

Phenomenological starting point

The basic idea of the theory can be understood by considering the behaviour schematised in Fig. 23.7 for the critical transition of fluids.

In the left graph, the behaviour ig the molar Gibbs function g is shown as a function of the molar volume v for the first order transition liquid–gas (see again Fig. 23.6).

In the right graph, the behaviour of the molar Gibbs function g as a function of the molar volume v is considered along the liquid–gas coexistence curve up to the critical point and beyond. The two minima of the $g(v)$ function progressively approach and at the critical point give rise to unique large flat minimum, that progressively narrows beyond the critical point. The large flat minimum at the critical point physically corresponds to large fluctuations of the molar volume.

Mathematical approach

Let us consider a fluid system whose molar volume is constrained to be equal to the critical value, $v = v_c$, and let us increase the temperature along the liquid–gas coexistence curve (Fig. 23.7, right). When the temperature increases, the two minima of the $g(v)$ come progressively closer up to coincide at the critical temperature T_c. For $T \geq T_c$, the $g(v)$ function exhibits a single minimum. This behaviour can be suitably described by the difference between the molar volumes of the two phases, normalised to the critical value, giving rise to the critical parameter

$$\eta = \frac{v_{\text{gas}} - v_{\text{liq}}}{v_{\text{cr}}} \quad \begin{cases} = 0 & \text{per } T \geq T_c \\ \neq 0 & \text{per } T < T_c \end{cases} \tag{23.32}$$

For the case here considered of a fluid the order parameter is positive when $T < T_c$ and zero when $T \geq T_c$, so that η is never negative.

Let us now consider the case of a one-dimensional ferromagnetic system, for which the magnetisation M can only gave two values, positive and negative. The order parameter $\eta = M$ is in this case symmetrical with respect to zero.

In what follows, for mathematical convenience, symmetrical values of the order parameter with respect to zero are considered.

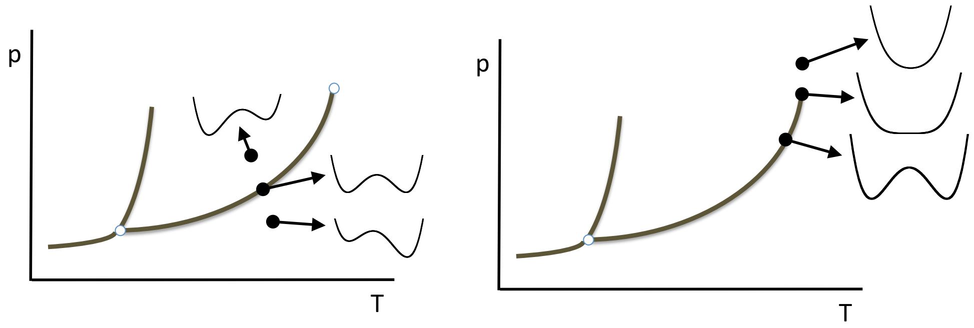


Figure 23.7: Left: liquid–gas first order phase transition. Right: critical transition of fluids. The inserted plots show the molar Gibbs function as a function of the molar volume.

Let us focus our attention on a small temperature interval around the critical temperature T_c, and study the general dependence of the g function on both temperature T and order parameter η that allows to reproduce the qualitative behaviour of the order parameter as a function of temperature (we don't consider the dependence on the pressure p, because p and T are not independent along the coexistence curve).

Since the order parameter η is small, it is convenient to expand the g function g as a power series of η:

$$g(T,\eta) \;=\; g_0 \;+\; \alpha_1(T)\,\eta \;+\; \alpha_2(T)\,\eta^2 + \cdots \tag{23.33}$$

The g function cannot depend on the sign of the order parameter η, so that only the terms of (23.33) containing even powers are non zero:

$$g(T,\eta) \;\simeq\; g_0 \;+\; \alpha_2(T)\,\eta^2 \;+\; \alpha_4(T)\,\eta^4\,. \tag{23.34}$$

The phenomenological behaviour of the $g(T,\eta)$ function requires that

- for $T < T_c$, one has $\alpha_2(T) < 0$ and $\alpha_4(T) > 0$ (two minima and one maximum),
- for $T = T_c$, one has $\alpha_2(T) = 0$ and $\alpha_4(T) > 0$,
- for $T > T_c$, one has $\alpha_2(T) > 0$ and $\alpha_4(T) > 0$.

Let us now introduce the further approximation that α_2 linearly depends on $T - T_c$, that is $\alpha_2(T) = \alpha_2^0\,(T - T_c)$. As a consequence, by imposing $\alpha_2^0 > 0$, one has that α_2 is positive for $T > T_c$ and negative for $T < T_c$. Equation (23.34) becomes

$$g(T,\eta) \;\simeq\; g_0 \;+\; \alpha_2^0\,(T-T_c)\,\eta^2 \;+\; \alpha_4(T)\,\eta^4\,. \tag{23.35}$$

The stability of the thermodynamical equilibrium at a given temperature requires that g be minimum with respect to the possible values of the order parameter η. Let us calculate the first derivative of (23.35) with respect to η and impose that it be zero:

$$\frac{\partial g}{\partial \eta} \;\simeq\; 2\eta\left[\alpha_2^0\,(T-T_c) + 2\,\alpha_4(T)\,\eta^2\right] \;=\; 0 \tag{23.36}$$

Let us consider the consequences of (23.36):

- For $T > T_c$, since $\alpha_2 > 0$ and $\alpha_4 > 0$, equation (23.36) is fulfilled only for $\eta = 0$.
  One can easily verify that the second derivative of g is positive for $\eta = 0$; in the super-critical region there is thus a single minimum of the g function.
- For $T < T_c$, since $\alpha_2 < 0$ and $\alpha_4 > 0$, equation (23.36) is fulfilled
  - for $\eta = 0$;
    the second derivative of g is negative for $\eta = 0$; the solution corresponds to a maximum of g, that is to an unstable state;

- for $\eta^2 = \alpha_2^0\,(T_c - T)/2\alpha_4$;
  there are two minima of g for the two equivalent values $\eta = \pm[\alpha_2^0\,(T_c - T)/2\alpha_4]^{1/2}$, corresponding to a stable solution.

The stable solutions for $T < T_c$ show that

$$\eta \propto \left(\frac{T_c - T}{T_c}\right)^{1/2} = (-\epsilon)^{1/2}. \tag{23.37}$$

According to the theory, the order parameter approaches the critical point by a power law; the theoretical critical exponent 1/2 is however different from the experimental value 1/3.

Chapter 24

Equilibrium and transitions of fluids

It was noticed in Chapter 22 that the liquid and gas phases of a substance can be considered as two modifications of a unique fluid phase. In the present chapter the phase equilibria and transitions of fluids are studied in detail.

As already observed in § 22.2, below the critical temperature the gas is generally called vapour. In § 24.1 the liquid–vapour coexistence curve is studied and the concept of saturated vapour and vaporisation enthalpy is introduced, with a particular reference to water.

The liquid ↔ vapour transitions (condensation, vaporisation and ebullition) are then studied in a region so far from the critical point that liquid and vapour can be considered as two different phases (the liquid being characterised by a proper volume). In § 24.2 we preliminarily consider the surface tension of a liquid in equilibrium with its vapour. In § 24.3 we then study the surface tension effects on the liquid ↔ vapour transitions, with a particular reference to water.

In § 24.4 our attention is extended to neighbourhood of the critical point, in order to better understand the critical transition of fluids, already shortly presented at the end of § 22.2.

The chapter is concluded by the Van der Waals theory (§ 24.5), that allows to obtain a function of state for real gases and to qualitatively describe the liquid–vapour critical transition.

24.1 The liquid–vapour coexistence curve

Let us start from the liquid–vapour coexistence curve in the (T, p) plane, already introduced in § 22.2.

As an example, the graph of the liquid–vapour coexistence curve of water is shown in Fig. 24.1, in the entire region from the triple point to the critical point (left) and in more restricted temperature intervals (center and right).

24.1.1 The pressure of saturated vapour

Let us insert a given amount of liquid in a closed vessel maintained at constant volume and constant temperature. At the beginning, the volume above the free surface of the liquid is empty. When time goes on, some molecules come out from the liquid and give rise to a vapour phase in the initially empty volume (vaporisation process). When the number of molecules in the gas phase increases, also increases the probability that some of them go back in the liquid phase (condensation process). After a sufficiently long time interval, a dynamical macroscopic equilibrium state sets up, the average number of molecules going from the liquid to the vapour phase being equal to the average number of molecules undergoing the opposite process.

In this equilibrium state, the vapour is said to be *saturated* and its pressure is the *saturated vapour pressure* at the T temperature.

For example, for water at the temperature $T = 20°\text{C} = 293.15\,\text{K}$:

- the saturated vapour pressure is $p_{\rm sat} = 0.023\,$bar
- the molar volume of the liquid phase is $v_{\rm liq} = 1.8 \times 10^{-5}\,{\rm m}^3/{\rm mol}$
- the molar volume of the vapour phase is $v_{\rm vap} = 1\,{\rm m}^3/{\rm mol}$

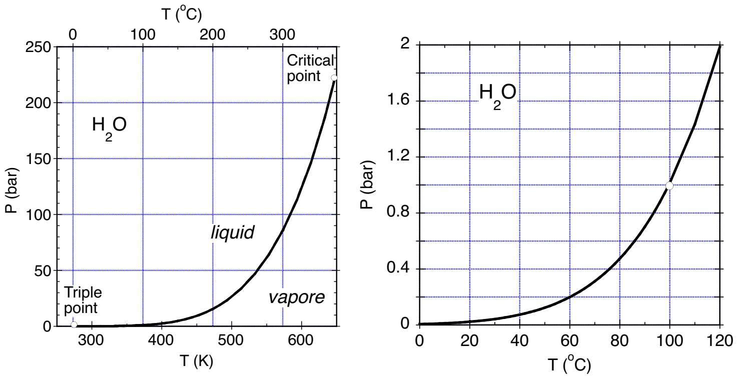


Figure 24.1: Liquid–vapour coexistence curve of water in different temperature intervals. Left: the entire curve from the triple point ($T = 273.16\,$K, $p = 0.061\,$bar) to the critical point ($T = 647.4\,$K, $p = 220\,$bar). Centre: from the triple point to the boiling point at atmospheric pressure. Right: in the temperature interval between 0 and 40°C.

If the fluid temperature T is modified, the saturated vapour pressure changes. The coexistence curve represents the saturated vapour pressure as a function of the temperature.

24.1.2 Latent heat and transformation enthalpy

When the liquid and the vapour are in equilibrium, that is on the coexistence curve, the relative quantities of the two phases can change through exchange of heat. The amount of heat absorbed or given up by the liquid phase is called *latent heat* (or enthalpy) of vaporisation or of condensation. As a consequence, at constant T and p, the total volume can change. The process corresponds to the horizontal part of the Andrews isotherms in the (V,p) graph (see Fig. 22.3).

The molecules going from the liquid phase to the gas phase are on the average the fastest (that is carrying more energy). As a consequence, evaporation gives rise to cooling of the liquid. To maintain the liquid at constant temperature during evaporation, heat must be supplied by the ambient. Evaporation at constant T and p takes thus place with an increase of the system enthalpy. The molar vaporisation enthalpy of water is shown in Fig. 24.2 (left) as a function of temperature. The vaporisation enthalpy goes to zero at the critical point (647 K for water).

24.1.3 Alternative derivation of the Clausius-Clapeyron equation

In § 23.3 we have shown that the relation between pressure and temperature along a coexistence curve of two phases is expressed by the Clausius-Clapeyron equation, in the two equivalent forms (23.16) and (23.17). For the liquid–vapour equilibrium, the Clausius-Clapeyron equation (23.17) can be derived in an alternative way.

To this aim, let us consider the Andrews graph (V,p) of a fluid (§ 22.2) and focus our attention on the region of liquid–vapour coexistence (light grey in Fig. 24.2, right. Let us consider two isothermal–isobaric lines with temperature and pressure T,p and $T-dT, p-dp$, respectively.

Let us start from the initial state in which the fluid is entirely in the liquid state at pressure p and temperature T and takes up the volume V_1. The following Carnot cycle can now be considered:

1. Isothermal expansion at temperature T and pressure p from the volume V_1 to the volume V_2, with total evaporation of the liquid.

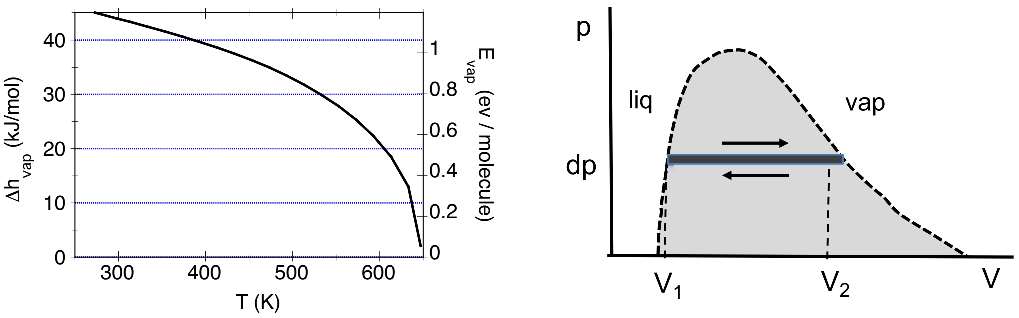


Figure 24.2: Left: molar vaporisation enthalpy of water as a function of temperature; the left and right vertical scales correspond to the values in kJ per mole and in eV per molecule, respectively. Right: infinitesimal Carnot engine cycle (dark grey) allowing the alternative derivation of the Clausius-Clapeyron equation.

2. Adiabatic expansion of the vapour from the pressure p to the pressure $p - dp$ with temperature variation from T to $T - dT$.
3. Isothermal compression at temperature $T - dT$ and pressure $p - dp$ from the volume V_2 to the volume V_1, with total condensation of the vapour.
4. Adiabatic compression of the liquid from the pressure $p - dp$ to the pressure p with temperature variation from $T - dT$ to T.

The total work performed by the system during the entire cycle corresponds to the area enclosed by graph od the cycle (dark grey rectangle in Fig. 24.2, right): $|W_{\text{prod}}| = (V_2 - V_1)\,dp = \Delta V\,dp$. The heat amount absorbed during the isothermal and isobaric expansion corresponds to the vaporisation enthalpy $Q_{\text{in}} = \Delta H_{\text{vap}}$.

By equating the general expression of the efficiency of a thermal engine with the expression of the efficiency of the Carnot cycle as a function of the operating temperatures

$$\eta = \frac{|W_{\text{prod}}|}{Q_{\text{in}}} = \frac{\Delta V\,dp}{\Delta H_{\text{eva}}} = 1 - \frac{T - dT}{T} = \frac{dT}{T} \tag{24.1}$$

one gets the Clausius-Clapeyron equation in the form (23.17):

$$\frac{dp}{dT} = \frac{\Delta H_{\text{eva}}}{T\,\Delta V}\,. \tag{24.2}$$

24.1.4 Liquid–vapour equilibrium for water

Liquid water and water vapour are present in everyday life. In general, water vapour is mixed with atmospheric air. In the following, we inquire on the meaning of the liquid–vapour coexistence curve (Fig. 24.3) in a number of significant cases.

1.

A pot, half filled with pure water, is maintained without cover in an ambient at temperature 25°C and pressure 1 bar.

From the microscopic point of view, the molecules which continuously get out from the liquid and form water are progressively dispersed in air and only in little number come back into the liquid (provided the air is not saturated with water vapour, that is provided the partial pressure of water vapour in air is not equal to the saturated water vapour at the temperature 25°C).

From the macroscopic point of view, for a closed system the stable phase of water at 25°C and 1 would be the liquid phase. In this case, however, the system is open and exchanges matter with its ambient. If air is not saturated with water vapour, the system (the liquid water) progressively looses matter through evaporation; the macroscopic state is out of equilibrium. After a convenient time interval all liquid water evaporates and the pot remains empty.

2.
Let us now close the pot, half filled with liquid water at 25°C, with an airtight cover. By means of a pump, let us evacuate the volume over the free surface of liquid water.
Now the molecules which get out from the liquid occupy the initially empty space, but cannot be dispersed in air. The system is closed. After a convenient time, a dynamic microscopic equilibrium state will take place (an equal number of molecules go from one phase to the other and viceversa).
From the macroscopic point of view, water is in an equilibrium state at a pressure equal to the saturated vapour pressure at $T = 25°\mathrm{C}$, that is, according to the graph of Fig. 24.3, at $p = 32\,\mathrm{mbar}$.

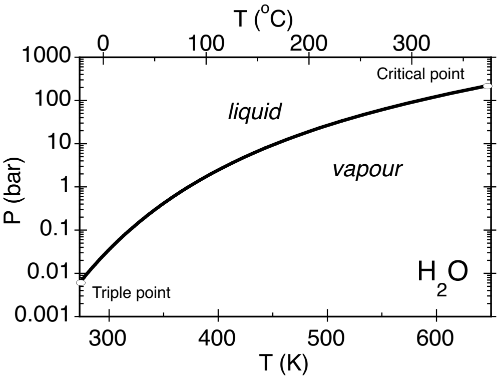


Figure 24.3: Liquid–vapour coexistence curve of water. The temperature is measured in kelvin and in Celsius degrees in the lower and in the upper horizontal scales, respectively. The pressure scale is logarithmic.

3.
Let us again close the pot, half filled with liquid water at 25°C, with an airtight cover, but let the air within the volume above the free liquid surface.
The molecules outgoing from the liquid phase mix with the air molecules below the cover, but cannot be dispersed in the atmosphere. The system is closed. After a convenient time, a dynamic microscopic equilibrium state will again take place (an equal number of molecules go from one phase to the other and viceversa).
From the macroscopic point of view, liquid water is in a state of equilibrium at a pressure equal to the sum of the air atmospheric pressure and the partial pressure of the water vapour. The partial vapour pressure corresponds to the saturated vapour pressure at $T = 25°\mathrm{C}$, that is, according to the graph of Fig. 24.3, at $p = 32\,\mathrm{mbar}$.

4.
Let us maintain the pot, containing water and air at atmospheric pressure, closed with the airtight cover. The cover is now provided with an outlet valve calibrated to the pressure $p = 2\,\mathrm{bar}$ (pressure cooker). Let us increase the temperature. The saturated vapour pressure progressively increases when the temperature increases; when the total pressure (air + vapour) attains the value 2 bar, the outlet valve opens, and the gas progressively gets out. As the gas gets out of the pot, the partial air pressure progressively decreases and the partial vapour pressure increases. When the gas phase is completely made of water vapour, the temperature is $T = 120°\mathrm{C}$, corresponding to the temperature of liquid–vapour coexistence at the pressure 2 bar (Fig. 24.1, center).

5.
Let us come back to the initial condition of the pot without cover at ambient temperature and pressure. Let us progressively increase the temperature. When the temperature T=100°C is attained, corresponding to the liquid–vapour equilibrium temperature at the 1 bar ambient pressure, the water starts to boil and its temperature remains constant. Ebullition gives rise to a fast evaporation of the liquid.

The ebullition of a liquid (not only of water) is a quite complex phenomenon. We consider it in detail in § 24.3, after an introduction to surface tension in § 24.2.

24.1.5 Absolute and relative humidity

According to the above examples, in a number of situations the water vapour is dispersed in atmospheric air. The water vapour thus contributes to the atmospheric pressure with a partial pressure p_{vap}, whose value depends on the molar fraction of water with respect to the molar fraction of anhydrous air. The partial pressure of water vapour is connected to the concept of humidity.

If, at a given temperature, the partial pressure of the water vapour is equal to the pressure of saturated vapour at that temperature, the humidity is said to be 100%. In that situation, the air is saturated with water vapour. A light increase of pressure or a light decrease of temperature gives rise to the condensation of part of the saturated vapour.

Example 1: Let the ambient temperature be 20°C. According to Fig. 24.3 the saturated vapour pressure is 23.3 mbar. The humidity is 100% at 20°C if the partial pressure of the water vapour is 23.3 mbar (with respect to the total pressure 1 bar). The humidity cannot increase above 100%: a further increase of the molar fraction of water vapour at constant temperature would give rise to the condensation of the vapour in excess.

Example 2: Let the ambient temperature initially be 20°C and the air be saturated by vapour at a partial pressure 23.3 mbar (100% humidity). Let now suppose that the temperature decreases to the value 19°C, corresponding to which the saturated vapour pressure is 21.4 mbar. Part of the vapour which was present at 20°C condensates in order to reduce its partial pressure from 23.3 mbar to 21.4 mbar; humidity remains 100%.

The *relative humidity* is the ratio between the water vapour pressure measured at a given temperature and the saturated vapour pressure at the same temperature. Hygrometers (humidity measuring instruments) generally measure the value of relative humidity.

Example 1: Let the ambient temperature be 20°C and the partial vapour pressure be $p_{\mathrm{vap}} =$ 10 mbar. Since the saturated vapour pressure at 20°C is 23.3 mbar, the relative humidity is 10/23.3, that is 43%.

Example 2: Let the ambient temperature be again 20°C and the partial vapour pressure be again $p_{\mathrm{vap}} = 10$ mbar (humidity 43%). Let us now suppose that the temperature increases to the value 25°C, to which it corresponds a saturated vapour pressure 32 mbar. The relative humidity reduces to 10/32, that is to 31%.

The dew point (or dew temperature) is the temperature at which the vapour, for a given value of partial pressure, condensates.

Example: Let the partial pressure of water vapour be 8 mbar. The dew point is the temperature corresponding to the intersection of the isobaric line at 8 mbar with the liquid–vapour coexistence curve (Fig. 24.1, right); in this case its value is 4°C.

24.2 Surface tension

To get a deeper understanding of the mechanism of the liquid ↔ vapour transitions (§ 24.3) it is necessary to preliminarily introduce the concept of surface tension.

24.2.1 Definition

Let us consider a liquid, for example water, contained in an open vessel (Fig. 24.4, left) at a temperature much lesser than the critical. The surface separating the liquid and the above gas (typically a mixture of air and vapour) is flat; it is an equi-potential surface with respect to the gravity force.

One has to distinguish the case of the molecules within the liquid and the molecules near the surface.

a) Within the liquid (in the "bulk") the inter-molecular forces act isotropically on each molecule; the displacement of a molecule within the liquid doesn't require work.

b) Near the free surface of the liquid, in a layer whose thickness is comparable with the range of molecular forces (that is of the order of the nanometer) isotropy is destroyed. The molecules of the surface layer are subjected to a resultant force directed towards the interior of the liquid; the attraction of the molecules of the gas above the surface being is actually negligible, in view of the much smaller density of the gas with respect to the liquid (obviously far from the critical point).

To move a molecule from the interior of the liquid to the free surface requires the performance of work against the inter-molecular forces. By the same token work is necessary to increase the area A_s of the liquid surface, because it is necessary to move molecules from the interior to the surface.

24.2.2 Thermodynamical aspects

The work W_s required to increase the area A_s of the liquid free surface, increasing the number of molecules of the surface layer, corresponds to the increase of a potential energy E_s proportional to the area A_s:

$$E_s \;=\; \sigma\, A_s\,, \tag{24.3}$$

where the proportionality constant σ is called *surface tension*and is measured in $\mathrm{J/m^2}$, or equivalently N/m. Therefore

$$đW_s \;=\; \sigma\, dA_s \;=\; dE_s \tag{24.4}$$

($đW_s$ is a type of generalised work) and the variation of internal energy of the system is

$$dU \;=\; T\, dS \;-\; p\, dV \;+\; \sigma\, dA_s\,. \tag{24.5}$$

The most suitable thermodynamical potential is the Gibbs function,

$$dG \;=\; -S\, dT \;+\; V\, dp \;+\; \sigma\, dA_s\,. \tag{24.6}$$

For a process taking place at constant temperature T and pressure p, $dG = \sigma\, dA_s$, and the surface tension is

$$\sigma \;=\; \left(\frac{\partial G}{\partial A_s}\right)_{Tp}\,. \tag{24.7}$$

24.2.3 Forces of surface tension

At constant temperature T and pressure p, the system tends to minimise the Gibbs function$G$, that is, according to (24.6), to minimise the free surface A_s.

The surface tension corresponds thus to the presence of forces tangent to the surface, that oppose the increasing of its area, The work (24.4) necessary to increase the area of the free surface can be expressed as

$$đW_s \;=\; \sigma\, dA_s \;=\; \sigma L\, dx \;=\; F\, dx\,, \tag{24.8}$$

where dx is a unidimensional displacement and F is the external force which has to be applied to equilibrate the surface tension and increase the area A_s of the free surface. Otherwise stated,

$$F = \sigma L\,, \qquad \sigma = F/L\,; \tag{24.9}$$

the surface tension is actually measured in N/m.

Note: The force (24.9) doesn't originate from the interaction between the molecules of the surface layer. Such interaction would give rise to an approximatively elastic force, proportional to the elongation x.

Example: The effects of surface tension can be easily evidence by using soapy water (the effect of soap is to reduce the surface tension and facilitate the formation of thin films). If a wire frame, for example of square shape, is immersed in soapy water and extracted, a thin film can be observed within the frame. The film is a thin volume, limited by two surfaces. If one of the sides of the frame is mobile, the film tends to contract as an effect of surface tension; to maintain the area of the film unchanged a counter-acting force has to be applied on the mobile side of the frame.

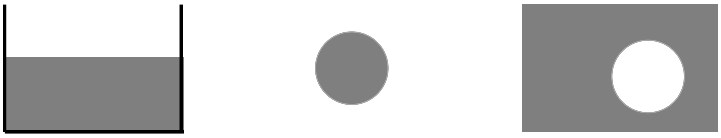


Figure 24.4: Flat free surface (left), convex surface (centre) and concave surface (right).

24.2.4 Shape of the free surface

If external forces are absent, an amount of liquid takes on the spherical shape, that minimises the free surface for a given volume, and thus minimises the surface energy E_s (Fig. 24.4, centre).
If a uniform external force field is present (such as gravity), and no other forces are present (such as friction or support reactions), the liquid again takes on the spherical shape.
A liquid contained in a vessel is subject, in addition to the gravity force, to the support reaction force (Fig. 24.4, left). In the equilibrium state, the free surface is flat.
In the region of contact between the liquid and the walls of the vessel, the free surface can be deformed by surface tension forces due to the liquid–solid contact. These effects can give rise to capillarity effects in thin pipes. In the following, we will not consider the effects of liquid–solid contact.

24.2.5 Surface curvature and vapour pressure

The liquid–vapour coexistence curve in the (T, p) plane (Fig. 24.3) refers to a flat surface of separation between the liquid and vapour phases.
To understand the mechanisms of the liquid ↔ vapour transitions (§ 24.3) it is necessary to study the behaviour of the curved free surfaces.

Convex surface

Let us consider a convex surface, for example the surface of a liquid sphere (Fig. 24.4, centre).
The surface potential energy is, according to (24.3), $E_s = \sigma A_s$. A reduction of the radius r of the sphere gives rise to a reduction of the area A_s of the surface and thus to a reduction of the surface energy E_s.
The evaporation causes the reduction of the radius r of the liquid sphere and of the potential surface energy E_s. The reduction of E_s facilitates the evaporation from a convex spherical surface with respect to evaporation from a flat surface (for which evaporation doesn't cause reduction of E_s).
Therefore the liquid–vapour equilibrium for a liquid sphere takes place at a vapour pressure $p_>$ higher that the saturated vapour pressure p_{sat} for a flat surface at the same temperature.
The difference between the pressures $p_>$ and p_{sat} increases when the radius r of the sphere decreases: $p_> - p_{\mathrm{sat}} \propto 2\sigma/r$.

Example: A liquid sphere paced in the neighbourood of a flat surface of the same liquid evaporates completely, because the vapour spontaneously transfers from the region at higher pressure $p_>$ to the region at lower pressure p_{sat}.

The surface tension gives rise to a pressure p_s within the spherical volume. To evaluate the amount of p_s one can equate the variation dE_s of the surface potential energy due to a variation dA_s of the surface area, that is

$$dE_s \;=\; \sigma\, dA_s \;=\; \sigma\, 8\pi r\, dr\,, \tag{24.10}$$

to the generalised work corresponding to the variation dA_s

$$đW_s \;=\; \sigma\, dA_s \;=\; p_s\, dV \;=\; p_s\, 4\pi r^2\, dr\,; \tag{24.11}$$

by equating (24.11) to (24.10) one obtains (for a spherical surface)

$$p_s = \frac{2\sigma}{r}\,. \tag{24.12}$$

The pressure p_s due to the surface tension increases when the radius r of the sphere decreases.

The purely hydrostatic pressure within the sphere, P_{int}, is smaller than the pressure outside the sphere, P_{ext}, since the equilibrium requires that

$$P_{\text{ext}} = P_{\text{int}} + p_s\,. \tag{24.13}$$

Note: For a flat surface the hydrostatic pressure within the liquid is equal to the external hydrostatic pressure, $P_{\text{ext}} = P_{\text{int}}$; as a matter of fact, for a flat surface $r = \infty$, so that, according to (24.12), $p_s = 0$. Besides, evaporation from a flat surface doesn't cause a variation of the surface area A_s, while for a convex surface evaporation causes a reduction of the surface area.

Superficie concava

Let us now consider a concave surface, for example the surface of a spherical air bubble embedded in a liquid (Fig. 24.4, right).
The evaporation of the liquid within the bubble causes an increase of the radius r and thus an increase of the surface energy. The increase of E_s makes the evaporation from a concave surface more difficult than from a flat surface. Therefore the liquid–vapour equilibrium is obtained with a vapour pressure $p_<$ within the bubble smaller than the pressure of saturated vapour p_{sat} over a flat surface at the same temperature.
The bubble tends spontaneously to lcose.
The difference between the pressures p_{sat} and $p_<$ increases when the radiur r of the bubble decreases: $p_{\text{sat}} - p_< \propto 2\sigma/r$.

24.3 Condensation and ebullition

Let us now consider the effects of surface tension on two phenomena of liquid–vapour transition: the condensation and the ebullition processes.

24.3.1 Condensation of the atmospheric vapour

Let us consider a mass of air saturated with water vapour (that is a mass of air in which the partial pressure of water vapour corresponds to the value of the coexistence curve at the given temperature). In such a situation, the water vapour tends to condense into the liquid phase. The condensation of the water vapour present in the atmosphere gives rise to rain, fog, etc.
At the microscopic level, the condensation process takes place through the mechanisms of nucleation and growth of the liquid phase; these mechanisms are common to all first order phase transitions.
Let us suppose that, due to a casual fluctuation of the local vapour density, a liquid condensation nucleus is formed, made by a small number of water molecules. As it was said above, the vapour pressure $p_>$ around the nucleus (approximated by a sphere) is larger than the pressure p_{sat} of the saturated vapour at than temperature, and the smaller is the radius of the sphere the larger is the pressure difference.
If the size of the nucleus is very small, the vapour pressure $p_>$ is larger than the pressure of the saturated vapour of the atmosphere, and the nucleus rapidly dissolves.
In order that the condensation be stable, the partial pressure of the saturated vapour in the atmosphere has to be larger than the pressure $p_>$ near the condensation nuclei.
The condensation is facilitated by the presence of powders, that favour the formation of relatively large nuclei, with relatively small $p_>$. For example, the formation of fog is favoured by the presence of particulate matter in air.

In particular, electrically charged impurities, such as ionised atoms, are particularly effective in favouring the condensation: the repulsive forces of the electric charges equilibrate the attractive forces due to the surface tension, that are in turn responsible of the reduction of the size of condensation nuclei.

Supersaturated vapour

If there are no impurities that favour the formation of condensation nuclei, the vapour can remain unaltered at higher temperatures and/or smaller pressures with respect to the values of the coexistence curve. In these cases, the vapour is said to be supersaturated.
(Consider the corresponding graphical representations in the (T, p) plane and in the (V, p) plane).

Cloud chamber

The cloud chamber was devised by the Scottish physicist C. T. R. Wilson in 1912 as a detector for ionising particles of cosmic rays.
The cloud chamber is filled with the saturated vapour of a liquid, such as a misture of alcool and water dispersed in argon. A fast adiabatic expansion causes a cooling of the vapour; if no impurities are present, the vapour remains in a supersaturated state.
Ionising particles traversing the cloud chamber cause the ionisation of the argon gas, that in turn favours the vapour condensation along the particles trajectories; the trajectories can thus be easily recorded on photographic plates.

24.3.2 Ebullition

The process of vaporisation of a liquid mass can be described in terms of nucleation and growth of the new phase, as the process of condensation considered above. However, in the case of vaporisation, the creation of nuclei caused by local density fluctuations is very difficult, due to the high density of liquid water.
The nucleation of the vapour phase generally requires that a gas, typically air, is already mixed with water. According to the Henry law, a gas that exerts a pressure on the surface of a liquid enters in solution in the liquid and the pressure it acquires within the liquid is equal to the pressure exerted above the free surface. Therefore, little bubbles of air are dispersed in liquid water.
Water evaporates within the little air bubbles. At low temperature, however, the surface tension of the concave surface tends to crush the little bubbles. The little ir bubbles saturated by water vapour are thus unstable.
When the temperature increases, the saturated vapour pressure within the unstable bubbles increases too.
When the pressure of the saturated vapour within the little bubbles is equal to the sum of the external atmospheric pressure + the hydrostatic pressure of water + the pressure due to the surface tension, then the bubbles can expand and, due to the Archimedes principle, go up to the surface (where the hydrostatic pressure becomes zero). The phenomenon of ebullition takes place.
The temperature of the saturated vapour outgoing from the liquid free surface is called boiling point. The boiling point decreases when the external pressure decreases. The boiling point of water at the atmospheric pressure 1.013 is 100°C=373.15 K. At an altitude of 1000 m above the sea level, the average pressure reduces to 0.897 bar and the water boiling point reduces to 96.7°C.

Superheated liquid

If no gas bubbles are present, a liquid can remain unaltered at higher temperatures and/or lower pressures than the values of the liquid–vapour coexistence curve. The liquid is then said to be superheated.
(Consider the corresponding graphical representations in the (T, p) plane and in the (V, p) plane).

Quasi-critical conditions

In the neighbouroud of the critical point, where $v_{\mathrm{liq}} \simeq v_{\mathrm{vap}}$, that is the densities of the liquid and vapour phases are similar, the ebullition can take place even if no gas is dissolved in the liquid. Fluctuations of the density of the liquid phase can lead some regions to exhibit the vapour phase density, and then expand and give rise to an intense ebullition.

Cloud chamber

The bubble chamber was devised by the American physicist D. A. Glaser in 1952 as a detector of ionising particles produced in collisions within particles accelerators.
A suitable liquid (hydrogen, propane, helium, etc.), previously heated and compressed, is led to a superheated metastable state through a fast reduction of the external pressure when crossed by the elementary particles. The particles are slowed down by the liquid, causing a local heating which favours the formation of vapour bubbles along their trajectory. The trajectories of particles can so be recorded on photographic plates.
The high density of the liquid filling the bubble chamber allows an effective slowing down of the particles, so that their entire trajectories can be evidenced and studied; in the cloud chamber, on the contrary, the gas density is much smaller, and only a little part of the trajectories can be evidenced.

24.4 The liquid–vapour critical transition

Let us focus our attention on the liquid–vapour coexistence, represented by the coexistence curve in the (T, p) graphs of Fig. 22.1 as well as by the region below the bell-shaped curve in the (v, p) graph of Fig. 22.3, in order to study the critical transition.

24.4.1 Liquid–vapour coexistence

The liquid and vapour phases are characterised by different values of both molar entropy s and molar volume v.

In a given point of the coexistence curve of Fig. 22.1, the transition between the two phases takes place at constant temperature T and pressure p. The finite variation of entropy and volume, Δs and Δv, respectively, entails the divergence of the specific heat at constant pressure c_p, of the isothermal compressibility χ_T and of the coefficient of thermal expansion β.
When the critical point is approached along the coexistence curve, the entropy and volume differences between the two phases progressively decrease, and at the critical point $\Delta s = 0$ and $\Delta v = 0$.

Let us now consider a point in the region below the bell-shaped curve in the (v, p) graph of Fig. 22.3 and modify the pressure (and the temperature) maintaining unaltered the molar volume v. The transformation, represented by a vertical line in the graph, corresponds to a variation of the ratio between the amounts of the two phases, liquid and vapour. The constant-volume specific heat c_v maintains a finite value.

24.4.2 Phenomenology of the critical point

With reference to Fig. 24.5, let us start from a temperature higher than the critical temperature $T > T_c$, and study the process of cooling of a fluid for three different values of molar volume: $v_1 < v_{\mathrm{cr}}$, v_{cr} and $v_2 \simeq v_{\mathrm{cr}}$, where v_{cr} is the molar critical volume.

Case 1: $v_1 < v_c$

Cooled at constant molar volume $v_1 < v_c$, the system doesn't undergo any discontinuity in going from the gaseous phase to the liquid phase when crossing the critical isotherm $T = T_c$.

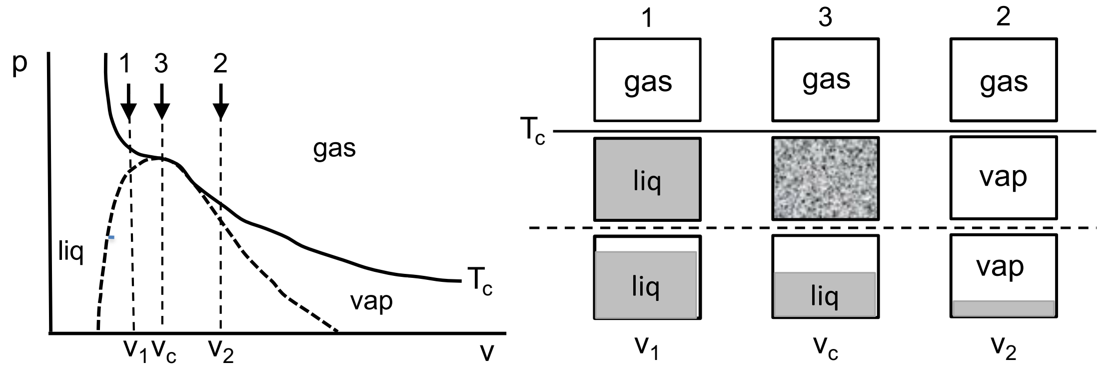


Figure 24.5: Cooling of a fluid from the gaseous phase above the critical temperature down to the region of liquid–vapour coexistence for three different values of molar volume, $v_1 < v_{\mathrm{cr}} < v_2$. Left: p, V Andrews diagram. Right: schematic representation of the three cases.

When the temperature is further reduced below T_c and the bell-shaped curve is crossed, a small amount of vapour appears on top of the liquid phase. The liquid → vapour transition takes place at constant volume. The relative amount of vapour phase progressively increases when the temperature T decreases. For each value of T, the relative amounts of the liquid and vapour phases are given by the lever rule.

Cas2 2: $v_2 > v_c$

Cooled at constant molar volume $v_2 > v_c$, the system remains in the gaseous phase when crossing the critical isotherm $T = T_c$.
When the temperature is further reduced below T_c and the bell-shaped curve is crossed, a small amount of liquid appears at the bottom of the container. The vapour → liquid transition takes place at constant volume. For each value of T, the relative amounts of the liquid and vapour phases are given by the lever rule.

Case 3: $v \simeq v_c$

Let us now consider the cooling at constant molar volume $v \simeq v_c$.
Above the critical isotherm ($T > T_c$) there is a homogeneous gaseous phase. The values of c_p, χ_T, β are finite.

Below the critical isotherm ($T < T_c$) the system is divided in two phases, liquid and vapour, separated by a neat surface.

In the neighboroud of the critical temperature, $T \simeq T_c$, an abrupt transition takes place, accompanied by large fluctuations of energy and density, that cause the phenomenon of critical opalescence. Immediately after the transition, finite amounts of both phases appear (in cases 1 and 2, on the contrary, one of the two phases appears gradually below the bell-shaped curve).

Note: In case 3, the molar volume of the system has not to exactly correspond to the critical value, $v = v_c$, in order that the critical transition could take place. Actually, at the critical point the critical isotherm in the (V, p) plane exhibits an inflection, so that the isothermal compressibility diverges:

$$\chi_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \infty . \tag{24.14}$$

The tiny variation of hydrostatic pressure along the vertical direction due to the gravity field causes large variations of the density ρ. The meniscus of separation between the two phases appears where $\rho \simeq \rho_c$.

Response functions

In the entire region below the bell-shaped curve in the Andrews V, p diagram, the values of c_p, χ_T, β diverge.

24.4.3 Density: order parameter and critical exponent

Let us study the behaviour of the liquid and vapour densities, ρ_{liq} and ρ_{vap}, respectively, as a function of temperature.
Above the critical temperature, for $T > T_c$,

$$\rho_{\text{liq}} = \rho_{\text{vap}} \,, \qquad \Delta\rho = \rho_{\text{liq}} - \rho_{\text{vap}} = 0 \,. \tag{24.15}$$

Below the critical temperature, for $T < T_c$, in the coexistence region below the bell-shaped vurve in the Andrews diagram,

$$\Delta\rho = \rho_{\text{liq}} - \rho_{\text{vap}} > 0 \,; \tag{24.16}$$

the difference $\Delta\rho$ increases when the temperature decreases.

The graph of ρ_{liq} and ρ_{vap} as a function of the temperature is different for different substances. However, if the reduced coordinates T/T_c and ρ/ρ_c are used, where T_c and ρ_c are the temperature and the density at the critical point, respectively, the graph of ρ/ρ_c as a function of T/T_c is similar for a number of substances (for example for the noble gases, and for N_2, O_2, CO, CH_4). This is an example of the so-called law of corresponding states.

One defines as *order parameter* for the critical transition of fluids the ratio

$$\eta \;=\; \frac{\rho_{\text{liq}} - \rho_{\text{vap}}}{\rho_c} \;=\; \frac{\rho_{\text{liq}}}{\rho_c} - \frac{\rho_{\text{vap}}}{\rho_c} \,; \tag{24.17}$$

the distance from the critical temperature is measured by the parameter

$$\epsilon \;=\; \frac{T - T_c}{T_c} \;=\; \frac{T}{T_c} - 1 \,. \tag{24.18}$$

The behaviour of the order parameter η for $T < T_c$ ($\epsilon < 0$) is consistent with the expression

$$\eta \;=\; (-\epsilon)^{\beta} \,. \tag{24.19}$$

For a number of substances the critical exponent β has the same value $\beta = 1/3$.

24.4.4 Specific heat at constant volume: critical exponents

Let us consider the critical transition at constant molar volume $v = v_c$.
The temperature dependence of the specific heat at constant volume has a behaviour similar to the greek letter lambda (λ), and can be described in terms of two critical exponents α and α':

$$\text{if } T > T_c \quad (\epsilon > 0) \qquad \Rightarrow \qquad c_v \simeq \epsilon^{-\alpha} \tag{24.20}$$

$$\text{if } T < T_c \quad (\epsilon < 0) \qquad \Rightarrow \qquad c_v \simeq (-\epsilon)^{-\alpha'} \tag{24.21}$$

24.4.5 Critical transition and fluctuations

It was shown in § 15.1 that the heat capacity at constant volume C_v is proportional to the variance of the energy distribution of a system:

$$k_B T^2 C_v \;=\; k_B T^2 \left(\frac{\partial U}{\partial T}\right)_v \;=\; \langle E^2 \rangle - \langle E \rangle^2 \,. \tag{24.22}$$

The divergence of the specific heat c_v when $T \to T_c$ means that the energy fluctuations of the system become very large.

Also the isothermal compressibility diverges at the critical point, corresponding to large density fluctuations.

24.5 Van der Waals theory

From the kinetic model of ideal gases one can obtain the thermal equation of state

$$pV = nRT\,, \qquad pv = RT\,, \tag{24.23}$$

(here for n moli or for one mole, respectively). The kinetic model is based on the assumptions of dimensionless molecules and absence of inter-molecular interactions.
The Van der Waals theory, dated 1873, is free from these assumptions; it is useful

- to describe the behaviour of real gases,
- to give a qualitative interpretation of the liquid–vapour phase transition.

A short introduction to the interaction forces between the gas molecules is necessary to understand the Van der Waals theory.

24.5.1 Inter-molecular interaction forces

Attractive forces

The weak attractive forces between electrically neutral molecules with filled electron shells are called Van der Waals forces. The attraction between non-polar molecules is due to fluctuating dipole forces. For concreteness, let us consider a monatomic gas (such as a noble gas), whose molecules contain only one atom, and follow a simplified phenomenological approach.
Even if an atom is electrically neutral, its negatively charged electron cloud can oscillate with respect to the positively charged nucleus; the atom behaves as a quantum harmonic oscillator.
The instantaneous electric dipole $\vec{p}_1$ due to the oscillation of the electron cloud of atom 1 generates an instantaneous electric field of intensity E proportional to p_1/r^3 at a distance r. In turn, the electric field induces an instantaneous electric dipole in a neighbouring atom 2, of modulus $p_2 = \alpha E \propto \alpha P_1/r^3$ (where α is the tomic polarisability).
The two dipoles attract each other. The interaction between the two dipoles causes a reduction of energy proportional to $p_1 p_2/r^3$, that is to $\alpha p_1^2/r^6$.
The attractive force due to the fluctuating dipoles is thus described by a potential energy $-A/r^6$, where A is a suitable constant.

Repulsion forces

The repulsion forces between two atoms or molecules is due to the Pauli exclusion principle. The behaviour of the potential energy is characterised by a steep negative slope as a function of the distance r; various analytic expressions have been suggested to approximate this behaviour, one of the most frequently used is B/r^{12}, where B is a suitable constant.

The Lennard-Jones potential and the rigid sphere approximation

The total potential energy (repulsive + attractive) is conveniently expressed by the Lennard-Jones potential

$$E_p = \frac{B}{r^{12}} - \frac{A}{r^6}\,. \tag{24.24}$$

If the rigid spheres approximation is assumed, the repulsive term of the potential energy is approximated by an infinite value.

24.5.2 The Van der Waals equation

The Van der Waals state equation for real gases is obtained by phenomenologically modifying the state equation (24.23) of ideal gases, for which the pressure is $p = RT/v$, taking into account

- the finite volume of molecules, due to the repulsion forces and schematised by the rigid spheres model;
- the attractive inter-molecular forces.

Finite volume of molecules

The actual volume accessible to the molecules is modified, with respect to the volume appearing in the equation of state (24.23) of ideal gases, according to:

$$v \to v - b\,, \qquad V \to V - nb\,, \tag{24.25}$$

where b is a phenomenological parameter, called "excluded volume" (for one mole), whose value is determined experimentally.

Example: Let us consider a model of rigid spheres of diameter d. The presence of molecule 1 prevents the center of molecule 2 from assuming the positions within a volume $4\pi d^3/3$ centred on molecule 1. For one mole, neglecting the surface effects on the vessel walls, trascurando l'effetto di superficie sulle pareti del recipiente, one obtains $b = (1/2)N_0(4/3)\pi d^3 = 4N_0 v_{\rm mol}$, where $v_{\rm mol} = \pi d^3/6$ is the volume of one molecule and N_0 is the Avogadro number. The excluded volume b is four times larger than the total volume of molecules. Actually, the model is quite rough: the real molecules are not rigid spheres; the excluded volume b depends, particularly at high pressures, on the peculiar form of repulsive forces.

Taking into account the excluded volume, the pressure is expressed (for one mole or for n moles) by

$$p \;=\; \frac{RT}{v-b}\,, \qquad p \;=\; \frac{nRT}{V-nb} \tag{24.26}$$

Attractive inter-molecular forces

The resultant of the inter-molecular attractive forces is non-zero for the molecules close to the vessel walls (within the range of the inter-molecular forces). The effect is a reduction of the pressure exerted on the vessel walls with respect to the ideal gas pressure.
The reduction is proportional to the product of two factors:

1. the frequency of the collisions of the molecules with the walls, proportional to the density $1/v$,
2. the resultant of the forces acting on each molecule, again proportional to the density $1/v$.

The expression of the density for the ideal gas has to be modified and becomes (for one mole or for n moles)

$$p \;=\; \frac{RT}{v-b} - \frac{a}{v^2}\,, \qquad p \;=\; \frac{nRT}{V-nb} - \frac{n^2 a}{V^2}\,, \tag{24.27}$$

where a is a phenomenological constant, whose value is determined experimentally.

The equation of state

By readjusting (24.27), one obtains the Van der Waals equation of state; for one mole,

$$\boxed{\left(p + \frac{a}{v^2}\right)(v-b) \;=\; RT} \tag{24.28}$$

For n moles,

$$\left(p + \frac{n^2 a}{V^2}\right)(V-nb) \;=\; nRT \tag{24.29}$$

The Van der Waals equation has been derived from quite rough assumptions; its interest based on the qualitative agreement with experimental results.

24.5.3 Statistical derivation of the Van der Waals equation

An alternative derivation of the Van der Waals equation, whose range of application is more general, is based on a statistical approach. It is again convenient to start from the ideal gas case and to introduce suitable modifications.

Statistics of the ideal monatomic gas

In the ideal monatomic gas the energy of each particle is purely kinetic and the particles can be considered as independent. The single-particle partition function is

$$z \;=\; \sum_i g_i e^{-\epsilon_i/kT} \simeq \int_0^\infty g(\epsilon) e^{-\epsilon/kT} d\epsilon \,, \tag{24.30}$$

where $k = k_B$ (Boltzman constant) and the distribution of discrete values has been approximated by a continuous distribution. The density of states $g(\epsilon)$ depends on the energy ϵ and on the volume V according to

$$g(\epsilon)\, d\epsilon = \frac{2\pi}{h^3}\,(2m)^{3/2}\, V\, \sqrt{\epsilon}\, d\epsilon \,, \tag{24.31}$$

so that the single-particle partition function is

$$z \;=\; \frac{V(2\pi mkT)^{3/2}}{h^3} = \frac{V}{\Lambda^3}\,, \tag{24.32}$$

where $\Lambda = h/(2\pi mkT)^{1/2}$ is called "De Broglie thermal wavelength".

Note: We can resort to the quantum statistics in the classical limit, that is we can use the Maxwell-Boltzmann statistics (§ 16.4) for indistinguishable particles, because $n_i \ll g_i$.

The partition function for a system of N identical indistinguishable particles is, according to (16.31),

$$Z = z^N/N! \tag{24.33}$$

Using the Helmholtz function $F = -kT\, \ln Z$, the pressure can be expressed as

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{kTN}{V} = \frac{nRT}{V}\,. \tag{24.34}$$

We have thus recovered the equation of state of the ideal gas.

Statistics of the Van der Waals gas

For a real gas, the inter-molecular interaction can be represented, in the rigid spheres approximation of diameter d, by the potential energy

$$u(r) \;=\; \begin{cases} \infty & \text{for } r < d \\ -\epsilon'(d/r)^6 & \text{for } r \geq d \end{cases} \tag{24.35}$$

The finite size of molecules is taken into account by substituting the volume V in the expression of the partition function (24.32) of the ideal gas by

$$V - Nb'\,, \qquad b' = 2\pi d^3/3\,, \tag{24.36}$$

where N is the total number of molecules and $b' = 4v_{\rm mol}$ is the contribution of each molecule to the excluded volume.

Due to the presence of attractive forces, the molecules are not independent. This difficulty can be overcome by supposing that each molecule moves in a *mean field*, that is a field of constant potential energy generated by the average interaction with all the other molecules:

$$\phi \;=\; \int_d^\infty u(r)\,\frac{N}{V}\,4\pi r^2\, dr \;=\; -2\,\frac{N}{V}\,\epsilon' b' \;=\; -2a'\frac{N}{V}\,. \tag{24.37}$$

In the mean field approximation the particles can be considered as independent. The single-particle partition function (24.32) is modified by the addition of the Boltzmann factor $\exp(-\phi/2kT)$ (the factor 2 in the denominator is due to the fact that the interaction energy is shared by two molecules)

$$z \;=\; \frac{(V - Nb')\, e^{Na'/VkT}}{\Lambda^3}\,, \tag{24.38}$$

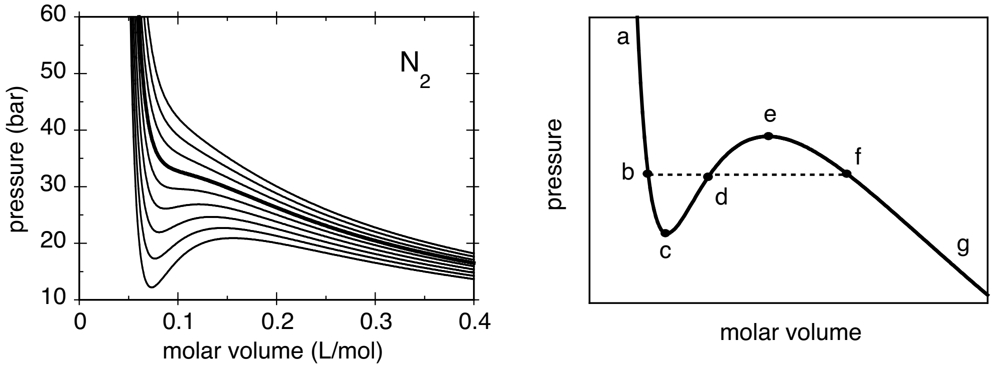


Figure 24.6: Left: Van der Waals isotherms for nitrogen; the thick line is the critical isotherm ($T_c = 126\,\mathrm{K}$). Right: an isotherm for temperature lower than the critical temperature T_c (continuous line); the dashed line represents the experimental behaviour between the points b and f.

and the partition function of the system is again $Z = z^N/N!$
One can easily check that the pressure is

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{kTN}{V - Nb'} - \frac{N^2 a'}{V^2} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \tag{24.39}$$

as in (24.27).

24.5.4 The Van der Waals isotherms

For a given value of temperature T, (24.27) is the equation of the corresponding isotherm:

$$p \;=\; \frac{RT}{v-b} - \frac{a}{v^2}\,. \tag{24.40}$$

The typical behaviour of the Van der Waals isotherms is shown in Fig. 24.6, left.

At high temperatures, the second term in the right member of (24.40) can be neglected, and the graph of the equation reduces to an hyperbola, as for the ideal gas, with the difference that v è is substituted by $v - b$.

A low temperatures the graph is more complicated; the behaviour of the isotherms is oscillating. In Fig. 24.6, right, the behaviour of a low-temperature Van der Waals isotherm $a{-}b{-}c{-}d{-}e{-}f{-}g$ is compared with the corresponding experimental isotherm $a - b - f - g$:

- line $a{-}b$: the Van der-Waals isotherm corresponds to the experimental isotherm of the liquid in stable equilibrium;
- line $b - c$: the Van der-Waals isotherm reproduces the possible experimental behaviour for a superheated liquid;
- line $c{-}d{-}e$: this part of the Van der-Waals isotherm corresponds to states thermodynamically unstable (with negative compressibility), that cannot be experimentally reproduced;
- line $e - f$: the Van der-Waals isotherm reproduces the possible experimental behaviour for a supersaturated vapour;
- line $f{-}g$ the Van der-Waals isotherm corresponds to the experimental isotherm of the vapour in stable equilibrium.

Between the point b and the point f, in the region of liquid–vapour coexistence below the bell-shaped curve, the Van der Waals isotherm and the experimental isotherm are significantly different.

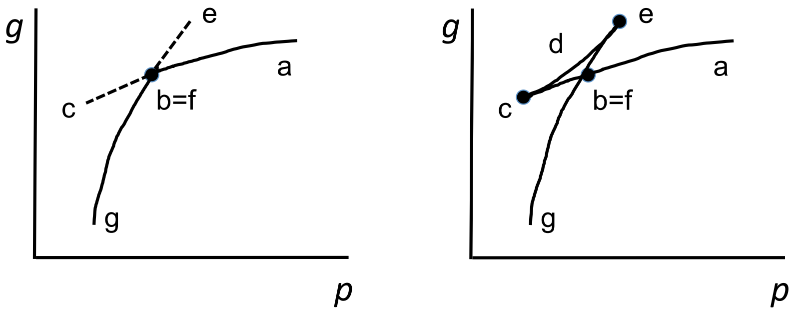


Figure 24.7: Dependence of the molar Gibbs free energy on the pressure at constant temperature. Left: experimental behaviour. Right: for a Van der Waals isotherm. The letters a to g correspond to the points of Fig. 24.6.

24.5.5 Gibbs free energy

The meaning of the Van der Waals isotherms at low temperatures can be better understood by considering the dependence of the molar Gibbs free energy g on the pressure p at constant temperature (see the Fig. 23.2 of § 23.1).
We consider here, in Fig. 24.7, the liquid and vapour phases.
Experimentally (left) the line $a-b$ corresponds to the liquid phase, the line $f-g$ corresponds to the vapour phase. The dashed lines correspond to the metastable phases of the superheated liquid $(b-c)$ and of the supersaturated vapour $(e-f)$.
For the Van der Waals isotherms (fright) the line $c-d-e$ is present too.

Considerations on stability

The isothermal compressibility

$$\chi_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\frac{1}{v}\left(\frac{\partial^2 g}{\partial p^2}\right)_T \tag{24.41}$$

- is positive, $\chi_T > 0$, for stable or metastable states
  lines $(a-b-c)$ and $(e-f-g)$ in Fig. 24.6 and Fig. 24.7
- is negative, $\chi_T < 0$, for unstable states
  line $(c-d-e)$ in Fig. 24.6 and Fig. 24.7

Connection between theory and experiment

The Van der Waals theory doesn't provide the saturated vapour pressure at a given temperature (given by the experimental isobaric dashed line in Fig. 24.6, right).
The position of the isobaric line can be determined, in the Van der Waals theory, from considerations on the Gibbs free energy. As a matter of fact, from the relation

$$dg = -s\,dT + v\,dp \tag{24.42}$$

one deduces that for any isotherm line

$$\Delta g = \int_1^2 v\,dp\,. \tag{24.43}$$

On the closed path $b-c-d-e-f-d-b$ in Fig. 24.6 the variation of any function of state is zero, so that

$$\Delta g = \oint v\,dp = 0\,. \tag{24.44}$$

As a consequence, the areas of the two regions enclosed by the curves ($b-c-d-b$) and ($d-e-f-d$) must be equal. Otherwise stated, once a Van der Waals isotherm has been calculated, the isobaric line of liquid–vapour equilibrium is univocally determined by the condition (24.44).

24.5.6 The critical state

Let us rewrite the equation of the Van der Waals (24.28) isotherms in the form

$$pv^3 \; - (bp + RT)\, v^2 \; + \; a\,v \; - \; ab \; = \; 0\,. \tag{24.45}$$

If a pressure value $p = p_0$ is imposed, the left member of (24.45) becomes a polynomial of third degree in the variable v. Th third-degree polynomial has thee real roots, distinct or coincident, corresponding to the intersections of the Van der Waals isotherms with the isobaric line $p = p_0$.
For the high-temperature isotherms, the polynomial has one single root v_0 for any value of pressure p_0.
For the low-temperature isotherms, values of pressure p_0 exist for which the polynomial has three distinct roots, v_1, v_2, v_3. As it was seen above, it is experimentally consistent the value p_0 that fulfils equation (24.44).
When the temperature increases, the three roots v_1, v_2, v_3 move closer and, at the critical temperature $T_{\rm cr}$, become coincident. Equation (24.45) becomes, at the critical temperature,

$$p_{\rm cr}\,(v - v_{\rm cr})^3 \; = \; 0\,, \tag{24.46}$$

where $p_{\rm cr}$ is the corresponding critical temperature.
Let us now rewrite (24.45) with $p = p_{\rm cr}$ and $T = T_{\rm cr}$ and compare it with the expansion of (24.46):

$$\begin{array}{llllll} p_{\rm cr}\,v^3 & -\,(bp_{\rm cr} + RT_{\rm cr})\,v^2 & +\,a\,v & -\,ab & = & 0\,, \\ p_{\rm cr}\,v^3 & -\,3p_{\rm cr}v_{\rm cr}\,v^2 & +\,3p_{\rm cr}v_{\rm cr}^2 v & -\,p_{\rm cr}v_{\rm cr}^3 & = & 0\,. \end{array} \tag{24.47}$$

By equating the coefficients of the corresponding terms, one obtains the critical values of molar volume, pressure and temperature as functions of the Van der Waals parameters a, b:

$$v_{\rm cr} = 3b\,, \qquad p_{\rm cr} = \frac{a}{27b^2}\,, \qquad T_{\rm cr} = \frac{8a}{27Rb} \tag{24.48}$$

The same result can be obtained by imposing an inflection point to the critical isotherm at the critical point,

$$\left(\frac{\partial p}{\partial v}\right)_T = 0\,, \qquad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0\,, \tag{24.49}$$

where the pressure p is given by (24.40).

The Van der Waals theory can thus foresee the existence of the critical point.
According to the Van der Waals theory (24.48) holds, from which the critical values are connected by the relation

$$\frac{RT_{\rm cr}}{p_{\rm cr}v_{\rm cr}} \; = \; K_{\rm cr} \; = \; 2.67\,, \tag{24.50}$$

where the $K_{\rm cr}$ constant is called critical coefficient. Experimentally, values of $K_{\rm cr}$ larger that the theoretical are obtained, for example 3.03 for H_2 and 4.49 for CO_2.

Law of corresponding states

The qualitative behaviour of the Van der Waals isotherms is equal for all real gases. The parameters a and b appearing in (24.28) are different for different gases.
One can eliminate the parameters a and b from the Van der Waals equation by introducing the three reduced parameters:

$$\pi = \frac{p}{p_{\rm cr}}\,, \qquad \omega = \frac{v}{v_{\rm cr}}\,, \qquad \tau = \frac{T}{T_{\rm cr}}\,. \tag{24.51}$$

By substituting $p = \pi p_{\rm cr}, v = \omega v_{\rm cr}, T = \tau T_{\rm cr}$ in the Van der Waals equation(24.28), one obtains

$$\left(\pi p_{\rm cr} + \frac{a}{\omega^2 v_{\rm cr}^2}\right)(\omega v_{\rm cr} - b) \;=\; R\tau T_{\rm cr}\,. \tag{24.52}$$

By further substituting the values $p_{\rm cr}, v_{\rm cr}, T_{\rm cr}$ of (24.48) one obtains the reduced equation of state, approximately valid for all real gases:

$$\left(\pi + \frac{3}{\omega^2}\right)\left(\omega - \frac{1}{3}\right) \;=\; \frac{8}{3}\,\tau\,. \tag{24.53}$$

24.5.7 Thermodynamical properties of the Van der Waals gas

Internal energy

The differential of the molar internal energy as a function of temperature T and volume V is:

$$\begin{aligned} du &= T\,ds - p\,dv \;=\; T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv - p\,dv \\ &= c_v\,dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv \end{aligned} \tag{24.54}$$

For the *ideal gas*,

$$p = \frac{RT}{v}; \qquad \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v} = \frac{p}{T} \tag{24.55}$$

so that (24.54) becomes

$$du \;=\; c_v\,dT\,. \tag{24.56}$$

The internal energy only depends on temperature.
For a *Van der Waals gas*

$$p = \frac{RT}{v-b} - \frac{a}{v^2}; \qquad \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b} \tag{24.57}$$

so that (24.54) becomes

$$du \;=\; c_v\,dT + \left[\frac{TR}{v-b} - p\right] dv \;= c_v\,dT + \frac{a}{v^2}\,dv\,. \tag{24.58}$$

For a Van der Waals gas the internal energy depends on volume too, because the intensity of the attraction forces depends on volume: when the molar volume increases, the average distances between the molecules increase and the interaction potential energy increases.

Joule effect: free expansion

Let us consider the free expansion introduced in § 10.4.
IAccording to (24.54), the Joule coefficient is

$$\eta \;=\; \left(\frac{\partial T}{\partial v}\right)_u \;=\; -\frac{1}{c_v}\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] \tag{24.59}$$

For the *ideal gas*, taking into account (24.55), one obtains

$$\eta \;=\; 0\,. \tag{24.60}$$

For a *Van der Waals gas*, taking into account (24.57), one obtains

$$\eta \;=\; -\frac{1}{c_v}\frac{a}{v^2} \;< 0\,; \tag{24.61}$$

the Joule free expansion always gives rise to a cooling of a Van der Waals gas. Actually, when the volume increases at constant internal energy, the potential energy increases, so that the average kinetic energy, which is connected to the temperature, must decrease.

Enthalpy

The differential of the molar enthalpy as a function of T and p is

$$\begin{aligned} dh &= T\,ds + v\,dp \;=\; T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp + v\,dp \\ &= c_p\,dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp\,. \end{aligned} \tag{24.62}$$

Effetto Joule-Thomson

Let consider the Joule-Thomson expansion, introduced in § 10.5.
According to (24.62), the Joule-Thomson coefficient is

$$\mu_J \;=\; \left(\frac{\partial T}{\partial p}\right)_h \;=\; \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \tag{24.63}$$

For the *ideal gas*, taking into account the equation of state, one can easily verify that $\mu_J = 0$.

Let us now consider a *Van der Waals gas.* Since it is difficult to calculate the derivative of v with respect to T for the Van der Waals equation, it is convenient to substitute, using the identity (7.51),

$$\left(\frac{\partial v}{\partial T}\right)_p \;=\; -\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v \tag{24.64}$$

and express the Joule-Thomson coefficient as

$$\mu_J \;=\; -\frac{1}{c_p}\,\frac{T\left(\dfrac{\partial p}{\partial T}\right)_v + v\left(\dfrac{\partial p}{\partial v}\right)_T}{\left(\dfrac{\partial p}{\partial v}\right)_T}\,. \tag{24.65}$$

By substituting, in the denominator of (24.65),

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}\,, \qquad \left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} \tag{24.66}$$

and approximating the derivative in the denominator with the ideal gas expression

$$\left(\frac{\partial p}{\partial v}\right)_T \simeq -\frac{RT}{v^2} \tag{24.67}$$

one obtains

$$\begin{aligned} \mu_J &\simeq \frac{1}{c_p}\,\frac{v^2}{RT}\left[\frac{RT}{v-b} - \frac{RTv}{(v-b)^2} + \frac{2a}{v^2}\right] \\ &\simeq \frac{1}{c_p}\left[\frac{2a}{RT} + \frac{v^2}{v-b} - \frac{v^3}{(v-b)^2}\right] \\ &\simeq \frac{1}{c_p}\left[\frac{2a}{RT} - b\right]\,. \end{aligned} \tag{24.68}$$

From (24.68) one can conclude that

- if $2a/RT > b$ the expansion causes cooling
- if $2a/RT < b$ the expansion causes heating

Lt us consider two limiting cases, in the rigid spheres approximation:

1. Dimensionless molecules, that is $b = 0$; the Joule-Thomson expansion causes cooling: $\mu_J \simeq 2a/c_pRT$.
2. Absence of inter-molecular forces, that is $a = 0$; the Joule-Thomson expansion causes heating: $\mu_J \simeq -b/c_p$.

Chapter 25

Many-components systems

In § 23.2, to evaluate the maximum number of phases that can coexist in one-component systems, we introduced the Gibbs phase rule (23.11)

$$f \;=\; 2-(\phi-1) \qquad \text{cioè} \qquad \boxed{f \;=\; 3-\phi}\,, \tag{25.1}$$

where f is the number of free variables, 2 are the available variables (typically T and p), ϕ is the number of coexistent phases.
For a system with c components where no chemical reactions take place, the phase rule becomes (23.12)

$$f \;=\; 2+c\phi-c(\phi-1)-\phi\,, \quad \text{that is} \quad \boxed{f=2+c-\phi} \tag{25.2}$$

In this chapter we will study in more detail the problem of phase equilibrium for systems containing more than one component.
We will start with some simple systems (§ 25.1). We will then give a demonstration of the Gibbs phase rule for systems where no chemical reactions take place (§ 25.2).
At last, we will deal in more detail with two-components solid systems (§ 25.3).

25.1 Examples

Let us start, as in § 23.2, from the general expression

$$(\text{free variables}) \;=\; (\text{available variables}) \;-\; (\text{constraints})\,, \tag{25.3}$$

and see how this expression suits to some significant cases.

Example 1

Let us consider a system containing c=4 components that form a single phase, ϕ=1, and in which no chemical reactions take place.
The available variables are:

- $>$ the two state variables p, T
- $>$ the c=4 values of the molar fractions x_i of the four components

The unique constraint is represented by the sum over the molar fractions, $\sum x_i = 1$.
Therefore the number of free variables (degrees of freedom) is

$$f \;=\; 2+4-1 \;=\; 5\,. \tag{25.4}$$

Temperature, pressure and three of the four molar fractions can be arbitrarily varied.

Example 2

Let us again consider, as in the Example 1, a system containing c=4 components that form a single phase, ϕ=1. Let us however suppose that the following chemical reaction can take place

$$-\nu_1 A_1 - \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4 \,, \tag{25.5}$$

where A_i are the chemical species and ν_i are the stoichiometric coefficients, according to the nomenclature of § 11.4.
The chemical equilibrium requires that (11.53) is fulfilled:

$$\sum_i \mu_i \nu_i \;=\; 0\,, \tag{25.6}$$

where μ_k are the chemical potentials of the four components.
Equation (25.6) represents a further constraint on the system, in addition to the constraint already considered in Example 1.
Therefore the number of free variables (degrees of freedom) is now

$$f \;=\; 2+4-2 \;=\; 4\,. \tag{25.7}$$

Example 3

Let us now consider a system containing c=3 components that form ϕ=2 phases, and in which no chemical reactions take place. The available variables are:

> the two state variables p, T
> the $c \times \phi$=6 values of the molar fractions of the three components in each one of the two phases

There are 5 constraint equations:

> ϕ=2 constraints on the molar fractions of the three components, $\sum x_i = 1$, in each one of the two phases
> 3=$c(\phi-1)$ equations of equilibrium between the ϕ=2 phases for each one of the c=3 components

Therefore the number of free variables (degrees of freedom) is

$$f \;=\; 2 + c\phi - \phi - c(\phi-1) \;=\; 2+6-2-3 \;=\; 3 \tag{25.8}$$

25.2 Demonstration of the phase rule

We give now a general demonstration of the phase rule (25.2) for a many-component closed system in which no chemical reactions take place.

25.2.1 Total number of variables

The calculation of the total number of variables is relatively simple, as shown by the previous examples. For a system with c components forming a number ϕ of phases, the total number of variables is $2 + c\phi$:

> 2 are the state variables p, T
> $c\phi$ are the values of the molar fractions of the c components in each one of the ϕ phases

25.2.2 Number of constraints

The evaluation of the number of constraints is more complicated, and is based on two distinct considerations.

1.

The equilibrium condition for a system maintained at constant temperature and pressure ($dT = 0, dp = 0$) is characterised by the minimum of the Gibbs free energy, that is, according to (8.45), by

$$dG \;=\; \sum_k \mu_k^\alpha dn_k^\alpha \;+\; \sum_k \mu_k^\beta dn_k^\beta + \ldots \sum_k \mu_k^\phi dn_k^\phi \;=\; 0\,, \tag{25.9}$$

where each sum concerns a different phase ($\alpha, \beta, \ \ldots$) and the index k labels the different components.

The differentials dn_k in (25.9) cannot have arbitrary values. The amounts of each component can be exchanged by the different phases but cannot vary in the entire closed system. There are thus c constraints on the differentials dn:

$$\sum_{\text{fasi}} dn_1 = 0\,, \quad \sum_{\text{fasi}} dn_2 = 0\,, \quad \ldots \quad \sum_{\text{fasi}} dn_c = 0\,. \tag{25.10}$$

The problem of constrained minimum for the Gibbs function can be solved by the method of Lagrange multipliers. The c equations (25.10), each one multiplied by a different factor λ_k, are summed to (25.9). By this procedure, the differentials dn_k become independent. One easily finds that the equilibrium condition is expressed by the c equations:

$$\begin{aligned} -\lambda_1 &= \mu_1^\alpha = \mu_1^\beta = \ldots = \mu_1^\phi \\ -\lambda_2 &= \mu_2^\alpha = \mu_2^\beta = \ldots = \mu_2^\phi \\ &\ldots \\ -\lambda_c &= \mu_c^\alpha = \mu_c^\beta = \ldots = \mu_c^\phi \end{aligned} \tag{25.11}$$

According to the equations (25.11), in an equilibrium state the chemical potentials of each one of the c components are equal in the different phases. Each one of the c equations (25.11) contains $\phi - 1$ equalities. Therefore, the condition that the Gibbs function be minimum, gives rise to a number $c\,(\phi - 1)$ of constraints.

2.

A further number of constraints is due to the fact that the system characteristics cannot change if the number of moles of each one of the c components is multiplied by a scale factor within a single phase.

There are thus ϕ equations (one for each phase)

$$\sum_k x_k^\alpha = 1\,, \quad \sum_k x_k^\beta = 1\,, \quad \ldots \sum_k x_k^\phi = 1\,, \tag{25.12}$$

where x_k are the molar fractions of the k component within each phase. The condition on the scale factors gives rise to a number of I ϕ constraints.

25.2.3 Final results

In conclusion, for a closed system with c components and ϕ phases, where no chemical reactions take place, the number f of free variables is, as anticipated in (23.12),

$$f = \underbrace{2 + c\phi}_{\text{total variables}} \quad \underbrace{-c(\phi-1) - \phi}_{\text{constraints}} \qquad \text{that is} \quad \boxed{f = \; 2 + c - \phi}\,. \tag{25.13}$$

Note: If chemical reactions take place, the number of constraints increases. The treatment of chemical reactions is however in general far from trivial, and will be not considered here.

25.3 Two-components solid systems

Let us now study in more detail the case, already briefly considered in § 22.6, of systems with $c = 2$ components, that will be identified as A and B. We will consider the important case of binary solid systems, such as the metal alloys, for example steel (alloy iron–carbon).
For a two-components system the phase rule (25.13) reduces to $f = 4 - \phi$.
The maximum number of free variables f is 3, when only one phase exists, so that ϕ=1. When only one phase exists, the independent variables are the temperature T, the pressure p and the molar fraction of one of the two components, for example x_A.

25.3.1 Enthalpy, entropy and Gibbs function

To understand the behaviour of the two-components solid systems, it is necessary to study the role of the enthalpy H, of the entropy S and of the Gibbs function G, whose molar amounts are connected by the relation

$$g \;=\; h \;- Ts\,. \tag{25.14}$$

In this § 25.3.1 we consider simple systems maintained at constant temperature T and pressure p, so that the only free variable is the molar fraction of one of the two components, for example x_A (obviously $x_B = 1 - x_A$).
The behaviour of the two-components solid systems depends on the relation between the three possible pair interactions between the constituents: AA, BB and AB. We have thus to consider three possible cases. For each case, we will consider the graphs of h, s, g as a function of the molar fraction x_A, variable from 0 to 1.

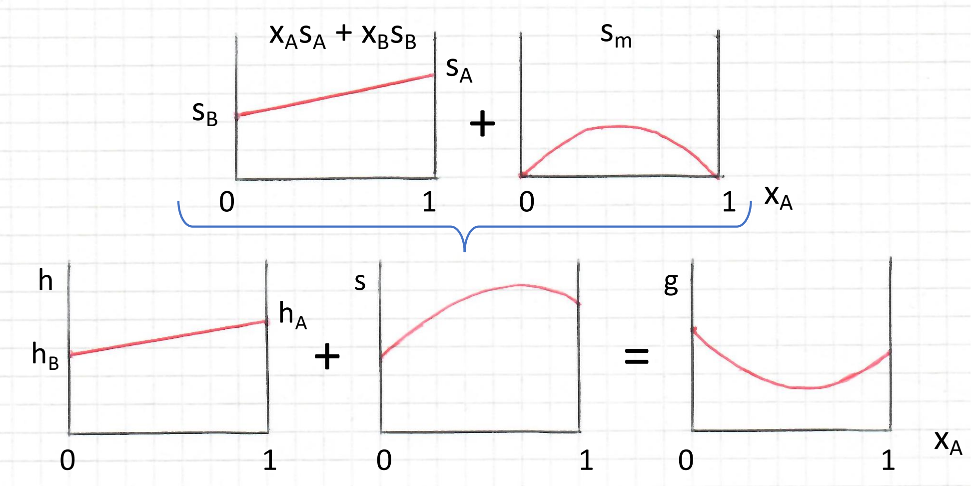


Figure 25.1: Bottom row: behavior of the three functions h, s, and g as a function of the molar fraction x_A for an *ideal* binary solid solution maintained at constant temperature and pressure. In the top row the two contributions to the entropy are separated.

Case 1 - Ideal solution: equal AA, BB and CC interactions.

If the different interactions are of equal force, the *molar enthalpy* $h - u + pv$ linearly depends on concentration (Fig. 25.1, bottom left):

$$h \;=\; x_A h_A + x_B h_B \;=\; h_B + (h_A - h_B)\, x_A\,. \tag{25.15}$$

The *molar entropy* is the sum of two contributions (Fig. 25.1, top): the weighted sum of the entropies of the components, that linearly depends on concentration, and the entropy of mixing

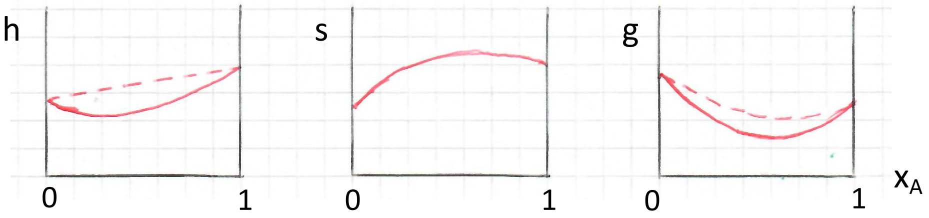


Figure 25.2: Behaviour of the three quantities h, s, and g as a function of the molar fraction x_A for a solid binary solution, maintained at constant temperature and pressure, for which the interaction AB is *stronger* than the interactions AA e BB. The dashed lines correspond to the behaviour of an ideal solution.

s_m, that is zero for $x_A = 0$ and for $x_A = 1$:

$$\begin{aligned} s &= x_A s_A + x_B s_B \; + \; s_m \\ &= s_B + (s_A - s_B), x_A \; - \; R\,(x_A \ln x_A + x_B \ln x_B) \end{aligned} \tag{25.16}$$

The resulting behaviour of the molar entropy is shown in Fig. 25.1, bottom center.

The molar *Gibbs free energy*, $g = h - Ts$, is represented by an upward concave (Fig. 25.1, bottom right).

Note: The expression (25.16) of the molar entropy of mixing corresponds to the expression (11.21) for the mixing of ideal gases (§ 11.2). The expression for ideal gases is valid also for the ideal solutions, and is a satisfactory approximation for the non-ideal solutions considered below.

Case 2 - Non-ideal solution, with AB interaction stronger than AA and BB.

If the interaction AB between different components is stronger than the interactions AA and BB between equal components, the functions h, s and g exhibit the behaviour of Fig. 25.2.
The behaviour of the molare enthalpy $h = u + pv$ is different from the behaviour for an ideal solution (dashed line): because of the stronger intensity of the interaction AB, the molar enthalpy is smaller than for an ideal solution.
As a consequence, also the behaviour of the molar Gibbs free energy is different from the behaviour of an ideal solution: the graph, even if qualitatively similar, is characterised by a deeper concavity.

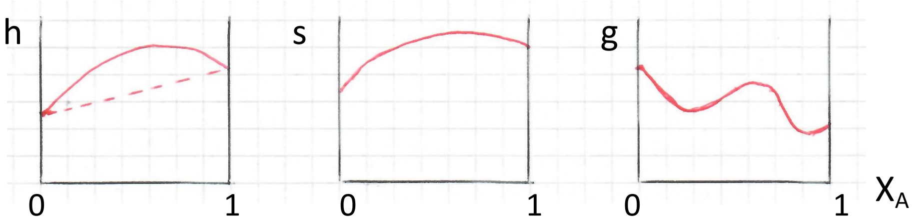


Figure 25.3: Behaviour of the three quantitiesh, s, and g as a function of the molar fraction x_A for a solid binary solution, maintained at constant temperature and pressure,for which the interaction AB is *weaker* than the interactions AA e BB. The dashed lines correspond to the behaviour of an ideal solution.

Case 3 - Non-ideal solution, with interaction AB weaker that AA and BB.

If the interaction AB between different components is weaker than the interactions AA and BB between equal components, the typical behaviour of h and s is shown in Fig. 25.3, left and centre.

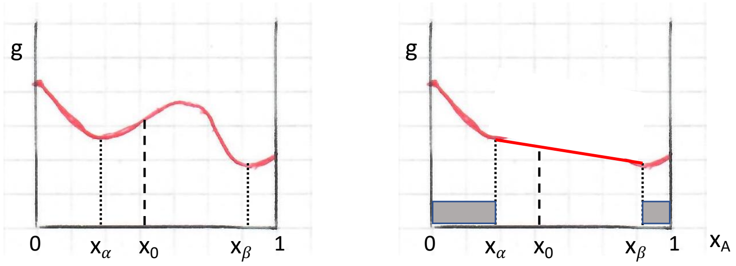


Figure 25.4: Molar Gibbs function g for a binary solid solution, maintained at constant temperature and pressure, for which the interaction AB is much weaker than the interactions AA and BB.

Due to the weaker AB interaction, the molar enthalpy is larger that the enthalpy of an ideal solution: the mixture is energetically less convenient.
For sufficiently large deviations of the behaviour of h from linearity, the behaviour of the molar Gibbs function can assume a shape such as the one of Fig. 25.3, right: the g function is characterised by a maximum separated by two minima.
Let us better analyse in Fig. 25.4 the consequences of the peculiar behaviour of the molar Gibbs function g.
Let x_α and x_β be the concentrations corresponding to the two minima of the molar Gibbs function g. For concentrations $x_A \leq x_\alpha$ and $x_A \geq x_\beta$, the mixture is homogeneous as in the previous cases: there is a unique phase.
The situation is more complicated in the intermediate region $x_\alpha < x_A < x_\beta$. Let us consider a generic concentration x_0 in the intermediate region (Fig. 25.4, left). The corresponding value of g is larger than the values of the two homogeneous phases of concentrations x_α and x_β. For the system it is energetically more convenient to split in two different phases of concentrations x_α and x_β, respectively.
The molar quantities of the two phases are given by the lever rule (Fig. 25.4, right):

$$n_\beta = \frac{x_0 - x_\beta}{x_\beta - x_\alpha}\, n_0\,, \qquad n_\alpha = \frac{x_0 - x_\alpha}{x_\beta - x_\alpha}\, n_0\, .1b \tag{25.17}$$

There are thus two phases, ϕ=2, of fixed composition. According to the phase rule, since temperature and pressure are fixed, the number of free variables is zero.

25.3.2 Influence of temperature

Up to now, we only considered the effect on the molar Gibbs function g of the concentration, at constant temperature and pressure. We want now to inquire on the effect of temperature variations, still maintaining a constant pressure. Let us again consider a mixture of two components A and B, and suppose that at sufficiently low temperatures the solid solution can exhibit two different phases, α and β, while at sufficiently high temperatures the mixture is a homogeneous liquid.
Fig. 25.5 shows the graphs of the molar Gibbs free energy g as a function of concentration x_A at different temperatures.

A.
At sufficiently high temperature, T_4 in Fig. 25.5, the free energy g of the liquid phase L is smaller that the free energies of the two solid phases α and β for all values of concentration x_A.
There is only the liquid phase for each value x_A. According to the phase rule, the number of free variables is $f = 4 - \phi = 3$. Since the pressure is maintained constant, the number of free variables reduces to $f' = 2$, temperature and concentration x_A.

B.
At the temperature T_3 in Fig. 25.5, the situation is more complicated. For different values of x_A the system exhibits two mono-phasic cristalline regions (α and β), a mono-phasic liquid region (L) and two two-phasic regions ($L\,\alpha$ and $L\,\beta$).

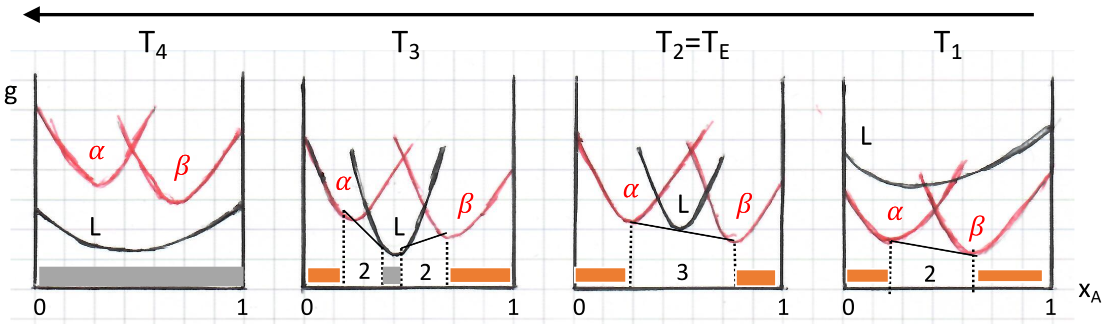


Figure 25.5: Molar Gibbs free energy g for a binary mixture AB at different temperatures (decreasing from left to right). The liquid phase L is represented by a black curve, the solid phases α and β are represented by red curves.

In the mono-phasic regions the free are $f' = 2$: temperature T and concentration x_A.
In the two-phasic regions, $f' = 1$, there is only one free variable, the temperature.

C.

At the temperature $T_2 = T_E$ in Fig. 25.5, for different values of x_A the system exhibits two cristalline mono-phasic regions (α and β) and one three-phasic region, in which the two crystalline phases coexist with the liquid phase.
In the three-phasic region, $f' = 0$, there are no free variables, the temperature is uniquely determined. The temperature T_E at which the three phases coexist is caled “eutectic” (from the Greek “eu-tektos” = well melted).

D.

At sufficiently low temperatures (T_1 in Fig. 25.5), only the solid phases are present, the free energy of the liquid phase being larger in the entire range of concentration.
In two concentration ranges the single phases α and β are present, in the central range the two solid phases coexist.

25.3.3 Diagrammi di stato

As it was shown above, for a two-components systemAB maintained at constant pressure the maximum number of free variables is two, that is the temperature T and the concentration x_A.
Therefore, the state diagrams can be drawn with concentration x_A in abscissa and temperature T in ordinate. Fig. 25.6 shows a possible state diagram for the binary mixture AB considered above. The pressure is considered constant.
The diagram includes:

- Three mono-phasic regions, the liquid phase L and the two solid phases α and β, in which there are two free variables, temperature T and concentration x_A (pressure is fixed).
- Three regions of coexistence of two phases, $\alpha - L$, $\beta - L$ and $\alpha - \beta$, in which there is only one free variable, the temperature; for different values of x_A the relative proportions of the two phases in each region are determined by the lever rule.
- A line, at the eutectic temperature T_E, corresponding to the coexistence of the three phases L, α and β.
  In the eutectic state there are no free variables. The temperature is fixed. For different values of x_A the relative proportions of the three phases are uniquely determined.

It is interesting to study the process of solidification of a binary alloy such as the one represented in Fig. 25.6. Starting from the liquid phase and decreasing the temperature, the phase transition to the solid phase doesn't take place at a well determined temperature. The system first enters in a region of liquid–solid coexistence (for example $\alpha + L$), and at the temperature T_E also the β phase appears.

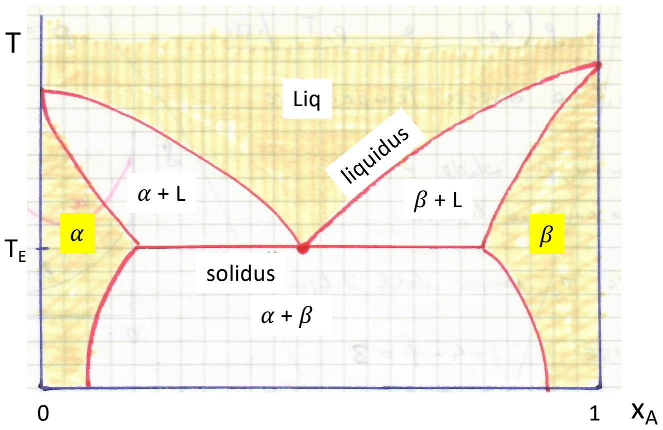


Figure 25.6: Temperature.vs.concentration phase diagram for a binary mixture AB for which two solid phases α and β and the liquid phase L are possible.

Example

A simple example of binary solid solution is given by brass, an alloy formed by copper Cu and zinc Zn. The phase diagram of the Cu-Zn alloy is shown in Fig. 25.7.
For different values of temperature and of pressure, different phases can form: the high-temperature liquid phase or single crystalline phases of different structure $(\alpha, \beta, \gamma, \delta)$. In some regions of the diagram, two phases can coexist, both crystalline or one crystalline and one liquid.

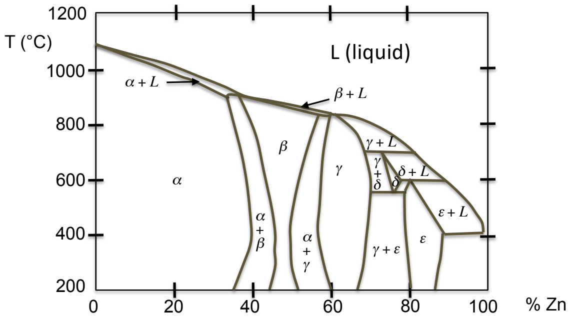


Figure 25.7: Phase diagram of brass (Cu-Zn alloy) at atmospheric pressur as a function of composition (horizontal axis, % Zn) and of temperature (veryical axis).

Chapter 26

Non-crystalline solids. The glass transition

In § 22.4 we mentioned the possibility that some solid substances are not characterised by the microscopic crystalline structure. Such substances are classified as non-crystalline solids or amorphous solids.

Among crystalline solids, particularly relevant from the thermodynamical point of view are the glasses, that are formed when a liquid is so fast cooled that the formation of a regular crystalline structure is prevented by the high value of viscosity.

In this chapter the difference between crystalline and non-crystalline solids is studied in some detail (§ 26.1); the attention is then focused on glasses and on the phenomenological aspects of the glass transition which takes place when a cooled liquid transforms to a glass (§ 26.2).

The glass transitions exhibits some peculiar thermodynamical characteristics, that are studied in § 26.3; in particular, the difference between system in stable and metastable equilibrium and out of equilibrium will be stressed, and the thermal and configurational contributions to the system entropy will be singled out.

26.1 Microscopic structure of solids

At the atmospheric pressure, all substances (excepted helium) at sufficiently low temperatures are solid, that is characterised by well defined volume and shape.

The great variety of possible interatomic interactions for different substances gives rise to different microscopic structures.

From the thermodynamical point of view, the stable equilibrium state is characterised by

1. minimum of the Gibbs free energy $G = U + pV - TS$ for a system maintained at constant temperature T and pressure p;
2. minimum of the Helmholtz free energy $F = U - TS$ for a system maintained at constant temperature T and volume V.

Therefore, the condition of stable equilibrium at $T = 0$ is the minimum of the enthalpy $H = U + pV$ or of the internal energy U.

26.1.1 Crystalline solids

Thermodynamical considerations lead to the conclusion that the stable equilibrium state of solids at $T = 0$ corresponds to a microscopic crystalline structure, characterised by a long-range geometrically ordered arrangement of atoms (Fig. 26.1). Actually, the minimum value of the energy (or of the enthalpy) of an enire system require that the energy (or the enthalpy) be minimum in all its constituent part. The possibility that any part of a solid system be in the same state of stable equilibrium can only be guaranteed by the presence of a long-range crystalline order.

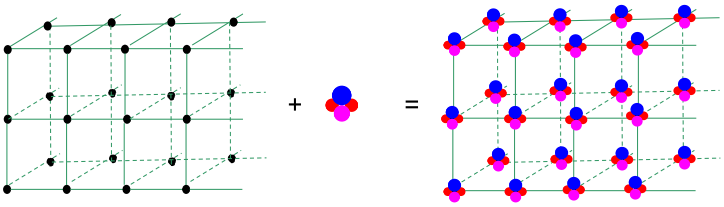


Figure 26.1: A crystal structure (on the right) is made by a regular lattice of points (such as the one on the left) and a base of atoms (such as the one in centre) repeated at each lattice point. There are 14 different types of lattices, differing for their symmetry properties. A base can be made by a single atom or by a larger number of atoms (up to some thousands, as in the case of protein crystals).

Note: The crystal structure of a solid refers to the average positions of the atoms, around which the atoms oscillate as a consequence of the zero point quantum energy and of the thermal vibrations. It has to be anyway noted that crystals with a perfect average structure don't exist; the presence of defects (vacancies, interstitials, dislocations, stoichiometric defect) is unavoidable, if it were not for statistical reasons.

In § 22.4 we have seen that some crystals can assume and maintain equilibrium states that don't correspond to the absolute minimum of the free energy. These metastable states correspond to relative minima of the free energy. A typical example is carbon, whose stable state at ambient temperature and pressure is graphite, while diamond is a metastable phase.

26.1.2 Non-crystalline solids

Solids without a microscopic crystalline structure can be found in nature (for example the solidified volcanic lava) or can per artificially produced (for example glasses, amorphous metal alloys, amorphous semiconductors). In non-crystalline solids, often called amorphous solids, there is no long-range order.
From the thermodynamical standpoint, non-crystalline solids correspond to non-equilibrium states, that can be maintained for extremely long times at relatively low temperatures. A short introduction to non-crystalline solids has already been made in § 22.4.

Production methods

To obtain a non-crystalline solid, the production methods must prevent the attainment of a thermodynamic equilibrium state (crystalline at the microscopic level). A number of substances, such as silica SiO_2 or germanium Ge, can assume both the crystalline and the non-crystalline forms. The choice between the crystalline and the non-crystalline forms is influenced by a number of factors, such as the type of chemical bond and the velocity of the formation process.

The preparation methods can be classified in three main categories; starting point can be a disordered phase (liquid or gaseous) or an ordered crystalline phase.

1. *Fast cooling of a liquid phase.*
   The formation of a cristalline phase at the solidification temperature requires the birth of small crystalline nuclei and their progressive growth. However, when the liquid phase is progressively cooled, its viscosity progressively increases. If the cooling process is sufficiently fast, the atomic kinetics that gives rise to the processes of nucleation and growth is hindered by the increasing viscosity, so that the liquid can become undercooled and at last frozen in a solid disordered structure (the glass structure).

2. *Vapour condensation of a cold surface.*
   Atoms of an element or of a mixture of elements, present as a vapour, can be deposited on a solid substrate maintained at a sufficiently low temperature to prevent the formation of an ordered crystalline structure. By this procedure, thin non-crystalline films (amorphous films) can be obtained. If the substrate temperature is instead sufficiently high and the deposition velocity sufficiently low, a crystalline film can be formed.
   Different methods have been devised to obtain the vapours to be deposited from solid sources: from the heating by Joule effect to the bombardment with ion beams ("sputtering").

3. *Introduction of disorder in a crystalline phase.*
   The creation of an amorphous structure in an initially crystalline solid can be obtained by different methods, for example by collision of ions or fast neutrons ("radiation damage"), by mechanical friction, by shock waves.

Influence of the chemical bond

Although no rigorous rule exist, some general considerations can be made on the relation between the type of chemical bond and the easiness to solidification in a non-crystalline structure.

The non-directional bonds (such as the metallic bond) represent a very weak constraint for the kinetics of atomic rearrangement, so that the liquids of materials with isotropic bonds become crystalline very easily even if the cooling velocity is high.

Viceversa, the directional covalent bonds represent an effective constraint for the atomic rearrangement necessary for the crystallisation of a liquid. Therefore the liquids with covalent bonds require reduced cooling velocity in order to crystallise, and can give rise to non-crystalline solids even for relatively low cooling velocities.

26.1.3 Glasses

Glasses are non-crystalline solids obtained from a liquid phase through a peculiar process called *glass transition.*

If the cooling process is sufficiently fast (the speed depends on the type of material), the liquid of a glass-forming substance can be cooled below the solidification temperature T_m, avoiding crystallisation and becoming a supercooled liquid. If the supercooled liquid is further cooled, its viscosity progressively increases and definitively prevents crystallisation. When the viscosity reaches the typical value of 10^{13} poise (1 poise = $0.1\,\mathrm{N\,s/m^{-2}}$), the substance is frozen in a state of thermodynamic non-equilibrium, in which it maintains the topological microscopic disorder of the liquid but appears as a solid from the macroscopic point of view.

Note: The dynamic viscosity of a liquid is defined as follows. Let us consider a layer of a fluid included between two parallel horizontal planes moving in the horizontal x direction at constant but different velocities. The horizontal shear foce per unit area A to be applied in order to maintain the relative motion of the two planes can be expressed as

$$\frac{F}{A} = \eta \frac{dv_x}{dz}\,, \tag{26.1}$$

where dv_x/dz is the vertical gradient of the horizontal velocity and η is the viscosity coefficient, measured in $\mathrm{N\,s\,m^{-2}}$. The old cgs unit *poise* is frequently used too: $1\,\mathrm{poise} = 0.1\,\mathrm{N\,s\,m^{-2}}$.

In § 26.2 the phenomenology of the glass transition will be described. In § 26.3 the peculiar thermodynamical aspects of the glass transition will be considered.

Here below same examples of non-crystalline solids are presented.

Oxide glasses

A number of oxides can easily form glasses. Among the different oxides one can distinguish

- glass formers oxides, such as silica SiO_2 or boron oxide B_2O_3, that can form glasses by themselves,
- modifier oxides, such as Na_2O, that can be added to the former oxides in order to modify the chemical and physical properties of the resulting glass.

Let us consider two important oxide glasses.

1. Silica SiO_2 is perhaps the most common glass former.
   Silica can exhibit a number of crystal structures (α and β quartz, α and β tridimite, etc). All crystal structure are based on regular tetrahedra Si–O_4 joined at the corners in different configurations. Each silicon atom is coordinated to four oxygen atoms nearest neighbours and each oxygen atom is coordinated to two silicon atoms nearest neighbours.
   In the glassy state, the structure of silica is again based on Si–O_4 tetrahedra connected at the corners. However, the tetrahedra are not perfectly regular and are randomly connected. The glass structure is generally represented as a continuous random network (CRN, see Fig. 26.2).
   Silica SiO_2 is the main component of many commercial glasses, from windowpanes to bottles. The glass transition temperature of the pure silica is quite high, about 1500 K. To reduce the transition temperature as well as to improve the time duration of the glass properties, modifier oxides are added, such as Na_2O, CaO, etc. A typical composition of a commercial glass could be: 70 SiO_2, 20 Na_2O,10 CaO.

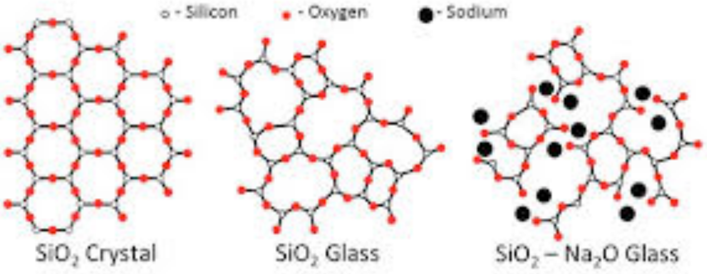


Figure 26.2: Two-dimensional schematic representation of the crystal structure of silica SiO_2 (left), of a continuous random network (CRN) of silica in the glassy state (centre) and of the modified continuous random network of the glass SiO_2-Na_2O (right).

2. Boron oxide B_2O_3, already considered in § 22.4, is probably the most effective glass former oxide. Actually, it is very difficult to obtain boron oxide B_2O_3 in crystalline form.
   In the glassy structure of boron oxide, each boron atom is coordinated to three oxygen atoms nearest neighbours and each oxygen atom is coordinate to two boron atoms nearest neighbours. Often the BO_3 triangles, joined at the corners, give rise to hexagonal rings, called boroxol rings.
   Boro-silicate glasses, containing both boron and silicon oxides, are characterised by a small coefficient of thermal expansion and are thus used to produce instrumentation for chemistry laboratories as well as heat-resistant kitchenware. A typical composition is: 80.6 SiO_2, 12.6 B_2O_3, 4.2 Na_2O, 2.2 Al_2O_3, 0.04 Fe_2O_3, 0.1 CaO, 0.05 MgO, 0.1 Cl.

Metal glasses

The first metal glasses have been obtained as a thin ribbon in 1960 by very the fast cooling (about 10^6 K/s) of a $Au_{75}Si_{25}$ alloy. A very fast cooling is necessary in order to prevent the formation of a crystal structure, that is facilitated by the isotropy of the metal bond. The presence of two different metals in the alloy slows down the crystallisation process and facilitates the glass formation.
In the subsequent years, new glassy alloys have been produced, the cooling speeds have been reduced in some cases down to 1 K/s and now some bulk metallic glasses(BMG) are available too;

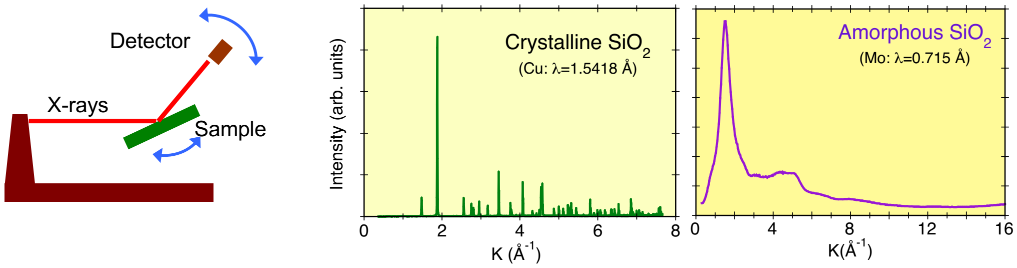


Figure 26.3: X-ray powder diffraction patterns of crystalline silica SiO_2 (centre) and silica glass (right). The quantity in abscissa is the modulus of the scattering vector $K = 4\pi \sin\theta/\lambda$, where θ is the angle of incidence of the X-rays on the sample and λ is the X-ray wavelength (different for the two patterns).

in general, the presence in an alloy of a large number of atomic species favours a sort of "confusion effect", that hinders the formation of a regular crystalline structure.
Amorphous metals can be obtained also by vapour deposition (always through fast cooling) or by bombardment of crystalline samples.
Among the possible advantages of amorphous metals there is the absence of micro-crystals and of interstitials between the micro-crystals, which guarantees a better resistance to corrosion.

26.1.4 Amorphous semiconductors

Non-crystalline solids are classified as glasses when characterised by the glass transition (§ 26.2). Not all non-crystalline solids can be classified as glasses. A relevant example is given by amorphous semiconductors, such as amorphous silicon, a-Si, and amorphous germanium, a-Ge. The production of amorphous semiconductors is generally based on vapour deposition. The extent of structural disorder so obtained depends on the substrate temperature; a relatively high temperature facilitates the movements of adsorbed atoms and the formation of crystalline structures.

26.1.5 Experimental information of the structure

The macroscopic distinction between a crystalline and a non-crystalline solid is made possible by the diffraction of X-rays (or of neutrons).
In Fig. 26.3 the diffraction patterns of crystalline and amorphous silica are compared.
The diffraction patterns of crystals are characterised by very sharp intensity peaks (Bragg peaks), due to the interference of the X-rays scattered by the atoms arranged in a regular lattice structure. The degree of crystallinity of a sample is measured by the presence and intensity Bragg peaks.
In diffraction patterns of non-crystalline solids, such as glasses, Bragg peaks are absent, substituted by broad continuous structures.

For crystalline solids, a suitable analysis of Bragg peaks generally allows the reconstruction of the three-dimensional structure (lattice + base).
For non-crystalline solids (and for liquids) the analysis of diffraction patterns only allows a unidimensional statistical description of the structure in terms of a radial distribution function (RDF) of the inter-atomic distances (Fig. 26.4).

It has anyway to be noticed that in non-crystalline solids, even if long-range order is lacking, some sort of short-range order is always present. The short-range corresponds to the correlation between nearest-neighbour atoms, caused by the bond directionality in covalent structures or by the close packing in metallic structures. The short-rage order is responsible for the first peak in the radial distribution function (Fig. 26.4, left). The structures of the RDF beyond the first peak are due to possible medium-range correlations.

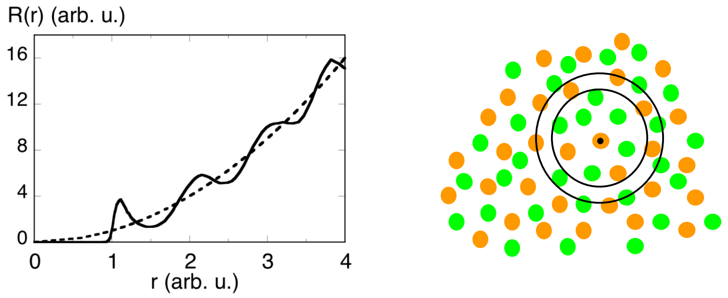


Figure 26.4: Left: a typical radial distribution function (RDF) obtained from the analysis of the diffraction spectrum of a non-crystalline sample; the dashed line corresponds to $4\pi r^2\rho$, where ρ is the average density of the substance. The RDF function measures the average density fluctuations in the environment of each atom due to the presence of the other atoms (two-dimensional projection on the right).

26.2 Phenomenology of the glass transition

The glass transition, that is the transition from the liquid state to the glassy state, exhibits experimental characteristics well distinguished from those of the first-order transition from the liquid state to the crystalline state.

In Fig. 26.5 the main differences between the glass transition an the transition to the crystal state are schematically summarised; the attention is focused on the dependence on temperature of the volume V, of the enthalpy H and on their first derivatives.

Let us start from the liquid phase and progressively decrease the temperature (from right to left in ig. 26.5).

First-order liquid→crystal transition

If the cooling speed is sufficiently low, the liquid phase transforms to the solid crystalline phase at the solidification (melting) temperature T_m. It is a first-order phase transition (§ 23.4) between two phases in thermodynamical equilibrium, represented by dashed lines in Fig. 26.5.
The volume V undergoes a discontinuity at the temperature T_m (corresponding to a decrease of volume for most substances), to which a divergence of the thermal expansion coefficient β corresponds.
Also the enthalpy H undergoes a discontinuity at the temperature T_m; the variation ΔH corresponds to the latent heat, that is to the heat emitted y the substance in passing from the liquid to the solid state. To the discontinuity of H it corresponds a divergence of the heat capacity C_p.

Glass transition

If the cooling speed is sufficiently high, the liquid can go across the temperature T_m without solidifying. The undercooled liquid is in a state of metastable equilibrium: the $V(T)$ and $H(T)$ curves of the undercooled liquid are a continuation of the curves of liquid above T_m.
The decrease of the temperature is accompanied by an increase of the liquid viscosity (Fig. 26.6), that progressively hinders the movement of the liquid molecules.
The glass transition from the undercooled liquid state to the glassy state takes place at the temperature T_g, lower than the solidification temperature T_m. In correspondence of T_g, the volume V and the enthalpy H don't undergo any discontinuity (continuous lines in Fig. 26.5), but suddenly reduce their slope with respect to temperature; in correspondence of T_g, the thermal expansion coefficient β and the heat capacity C_p exhibit discontinuities.
The glass transition is characterised by the absence of the latent heat typical of first-order transitions and corresponding to a strong modification of the microscopic structure.

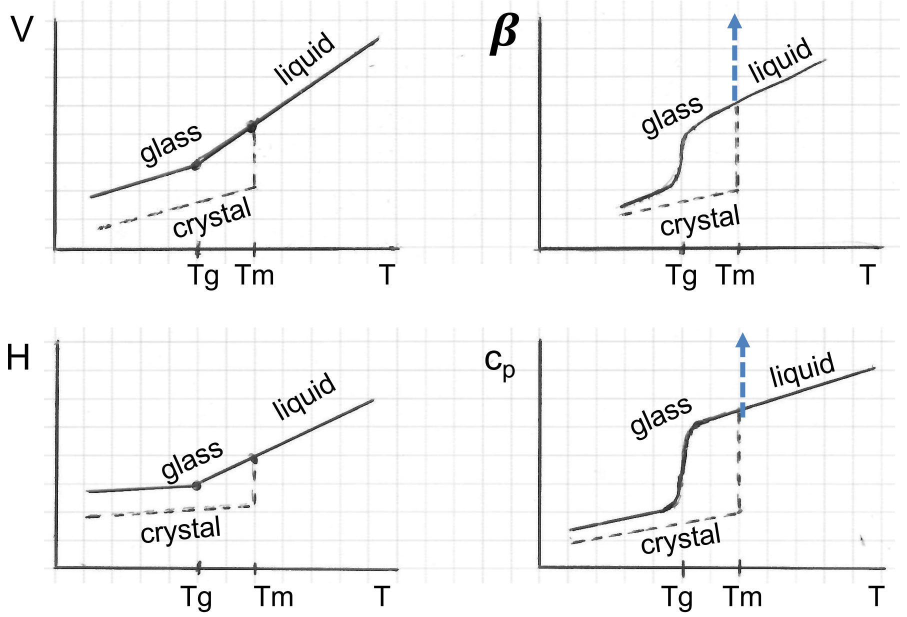


Figure 26.5: Schematic comparison between the glass transition (continuous lines) and the liquid→crystal transition (dashed lines). The graphs have to be considered for decreasing temperature (from right to left). T_g and T_m are the temperatures of glass transition and of solidification (melting), respectively. Top: to the left the volume V, to the right the thermal expansion coefficient $\beta = (\partial V/\partial T)_p/V$. Bottom: to the left the enthalpy H, to the right the constant-pressure heat capacity $C_p = (\partial H/\partial T)_p$.

The discontinuity of the heat capacity (and of other response functions) at T_g attests anyway that a substantial difference exists between the undercooled liquid state and the glassy state. The discontinuous reduction of the specific heat at T_g suggests the following interpretation of the glass transition. In the undercooled liquid state the mobility of the molecules is sufficiently high to allow the storing of energy not only in the vibrations with respect to equilibrium positions but also in the translational motion. The undercooled liquid is in a state of thermodynamical equilibrium, even if metastable (below T_m the stable equilibrium state is the crystalline state). At the temperature T_g the viscosity becomes sufficiently high to prevent the relative translational motion of molecules; in the glass, the energy can only be stored in the local vibrational motion. The glassy state can be considered as the state of a liquid frozen in a particular microscopic configuration, not univocally defined; the glass state is thus not a state of thermodynamical equilibrium.

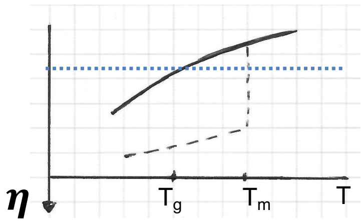


Figure 26.6: Schematic behaviour of the viscosity η as a function of the temperature (notice that the vertical axis is here down-directed). The dashed line refers to the liquid→crystal transition, characterised by a sharp increase of viscosity. The continuous line refers to the glass transition. The dotted line corresponds to the value 10^{13} poise.

Glass transition interval

The glass transition temperature T_g is not uniquely defined for a given substance, as is instead the solidification temperature T_m. Actually, the value of T_g depends on the cooling speed of the initial liquid. The lower is the cooling speed, the lower is the transition temperature T_g from the undercooled liquid state to the glassy state.

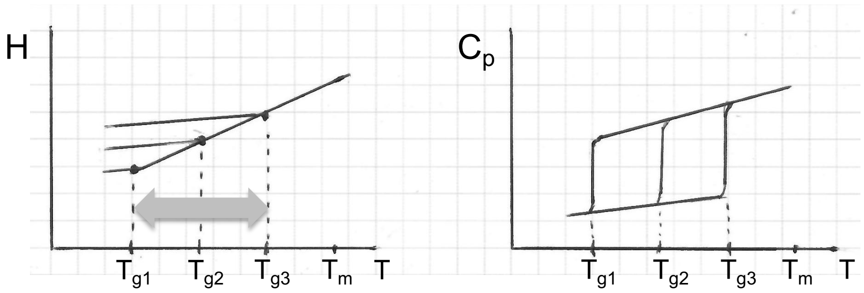


Figure 26.7: Glass transition interval. Left: behaviour of the enthalpy H for three different values of T_g (the behaviour of the volume is similar). Right: behaviour of the heat capacity.

The dependence on temperature of the enthalpy H (or of the volume V or of the viscosity η) is thus to be represented as in Fig. 26.7. The glass transition interval is the interval between the minimum and maximum values of T_g for which the glass transition can be experimentally observed.
The glass transition interval can be very different for different substances. Some examples are listed in Table 26.1.

Substance	Transition interval (K)
SiO_2	1500-2000
Windowpane	800-820
B_2O_3	470-530
Se	302-308
Ethanol	90-96

Table 26.1: Glass transition interval (in kelvin) for selected substances.

26.3 Thermodynamics of the glass transition

The glassy state is a non-equilibrium thermodynamical state Actually, a glass can be in thermal and mechanical equilibrium, so that its temperature T can be defined. The absence of thermodynamical equilibrium concerns the configurational aspect, that is the fact that the spatial disposition of the elementari constituents (atoms or molecules) is not uniquely determined and doesn't correspond to a minimum (absolute or relative) of the free energy.
The situation is for some respects similar to that encountered for chemical reactions, for which a thermodynamical treatment is possible even if there is no chemical equilibrium, provided the system is in thermal and mechanical equilibrium (§ 11.4). The progress of a chemical reactions has been described in terms of the degree of advancement ξ and of the affinity A and it has been possible to calculate the variations dS of entropy. Anticipating the language of the Thermodynamics of irreversible processes (Part VI), one calculated the contribution $d_iS = n_0\,(A/T)\,d\xi$ to the total entropy variation due to the creation of entropy in an irreversible chemical reaction.
For glasses, the irreversible process of modification of the molecular configuration is slowed down and practically frozen by the high viscosity of the system, so that even more so one can resort to

the thermodynamical quantities defined for equilibrium states, such as entropy S and enthalpy H.

Comparison between the entropy of glass and crystal

Starting point for a better understanding of the glass Thermodynamics is the comparison between the entropy of the glassy state and of the crystal state for a given substance.
Experimentally, the information can be obtained by measuring the heat capacity as a function of temperature (Fig. 26.5, bottom right, and Fig. 26.8), from which one can recover the entropy variations by means of the relation

$$dS \;=\; \frac{C_p(T)\,dT}{T} \;=\; C_p(T)\,d(\ln T)\,. \tag{26.2}$$

Let us focus our attention on a substance that can solidify as a crystal or as a glass depending on the cooling speed. Let us consider a temperature T^* at which the substance is in the liquid state and calculate the entropy $S(T^*)$ of the liquid along two different paths which lead the substance from the temperature $T = 0\,\mathrm{K}$ to the temperature $T = T^*$.

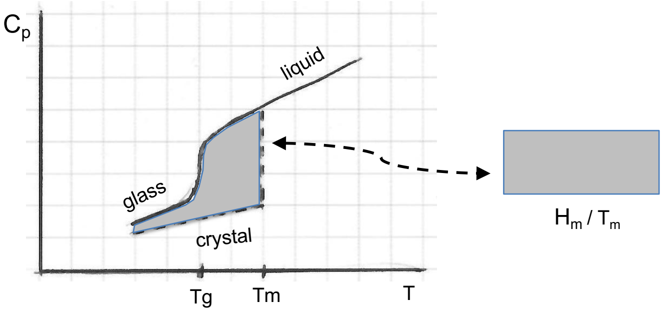


Figure 26.8: Evaluation of the difference between the entropy of the glass and of the crystal t zero kelvin from the measurement of the heat capacities. The horizontal temperature scale has to be considered as logarithmic. The entropy difference corresponds to the grey regions. The grey rectangle on the right represents the entropy variation due to the first-order transition liquid→crystal, $\Delta S = H_m/T_m$, where H_m is the latent heat of the transformation.

In the first case, at $T = 0\,\mathrm{K}$ the substance is in the crystalline state, with entropy S_0^c, and the entropy at T^* can be calculated as:

$$S(T^*) \;=\; S_0^c \;+\; \int_0^{T_m} C_p^c\,\frac{dT}{T} \;+\; \frac{H_m}{T_m} \;+\; \int_{T_m}^{T*} C_p^{liq}\,\frac{dT}{T}\,. \tag{26.3}$$

The entropy variation is the sum of three terms, due to three different processes: the heating of the crystal up to he melting temperature T_m, the phase transition to the liquid phase with latent heat H_m and the heating of the liquid from the melting temperature T_m fup to the temperature T^*.

In the second case, at $T = 0\,\mathrm{K}$ the substance is in a glass state, with entropy S_0^v, there is no first-order phase transition to the liquid state and therefore there is no contribution of latent heat to the entropy variation. The entropy variation can again be considered as the sum of two contributions, one below and one above the melting temperature T_m, taking however into account that below T_m the heat capacity of the glass and of the superheated liquid C_p^{vl} is different from the one of the crystal. The entropy at T^* can thus be calculated as:

$$S(T^*) \;=\; S_0^v \;+\; \int_0^{T_m} C_p^{vl}\,\frac{dT}{T} \;+\; \int_{T_m}^{T*} C_p^{liq}\,\frac{dT}{T}\,. \tag{26.4}$$

By subtracting (26.3) from (26.4) one finds that the difference between the entropy of the glass and of the crystal at $T = 0\,\mathrm{K}$ is

$$S_0^v - S_0^c \;=\; \frac{H_m}{T_m} \;-\; \int_0^{T_m} (C_p^{vl} - C_p^c)\,\frac{dT}{T}\,. \tag{26.5}$$

One finds experimentally that the difference (26.5) is larger than zero, $S_0^v - S_0^c > 0$. According to the Third Principle (Chapter 20), at zero kelvin the entropy of crystals is zero or negligible. The glass entropy is larger than the entropy of the crystal, thus it is larger than zero.

26.3.1 The excess entropy

The difference (26.5) between the glass and the crystal entropies is called "excess entropy". Let us inquire on the meaning of the excess entropy.

In the *liquid state* the entropy is the sum of two contributions:

1. a thermal contribution, due to the vibration of atoms with respect to their equilibrium positions,
2. a configurational contribution, due to the mobility of atoms or molecules, that gives origin to different possible microscopic configurations.

The *transition to the crystalline state* at the temperature T_m entails an abrupt reduction of the entropy, connected to the latent heat of transformation by $\Delta S = H_m/T_m$. Such an entropy reduction corresponds to the cancellation (or sometimes to a strong reduction) of the configurational contribution in the transition from the liquid disordered structure to the crystal structure.

The heat capacity of the crystalline solid, only determined by the thermal (vibrational) contribution is smaller than the heat capacity of the superheated liquid.

Between T_m and T_g the *undercooled liquid* maintains the configurational disorder of the liquid, although progressively reduced, and its heat capacity remains significantly larger than the heat capacity of the crystal. Therefore the entropy reduction of the undercooled liquid between T_m and T_g is larger than the one of the crystal.

At the *glass transition* at T_g, the variable microscopic configuration of the undercooled liquid is frozen viene congelata, so that the corresponding contribution to the entropy is strongly reduced. The heat capacity of the glass is slightly larger than the heat capacity of the crystal, so that slightly larger is its entropy reduction below the temperature T_g.

Globally, in going from the liquid state at high temperature to the solid state at $T = 0\,\mathrm{K}$, both the crystal and the glass undergo a strong reduction of the configurational entropy, but at different temperatures. The experimental result is however that at $T = 0\,\mathrm{K}$ the entropy of the glass is larger than the entropy of the crystal.

Part VI

Thermodynamics of irreversible processes

Chapter 27

Introduction to Thermodynamics of irreversible processes

27.1 Equilibrium Thermodynamics, a remainder

Thermodynamical functions (temperature, internal energy, entropy) are defined only for system in equilibrium states (Chapter 1.3). In macroscopic Thermodynamics, that has been studied in Parts **??** and II, particular relevance is assumed by reversible transformations, in which the thermodynamical systems transform without friction through states that negligibly differ from equilibrium states.

Spontaneous natural processes are actually irreversible, and in many cases cannot be approximated by reversible transformations. However, also in the equilibrium Thermodynamics one can obtain relevant pieces of information on irreversible processes, provided the initial and final states are equilibrium states. In this § 27.1 some relevant results of the equilibrium Thermodynamics are summarised.

Criteria of spontaneous evolution

For an isolated system, the fundamental principle of the macroscopic Thermodynamics represents an evolution criterion: the irreversible transformation from an initial state of constrained equilibrium to a final state of non constrained equilibrium is characterised by an increase of the state function entropy S (§ 5.3). The entropy variation ΔS between the initial and final states can be calculated by integration along whichever reversible transformation connecting the initial and final states (§ 4.4).

The evolution criterion can be recast in the energy representation (§ 6.3) as well as tailored to different experimental situations making use of the different thermodynamical functions that can be obtained through the Legendre transforms: internal energy, enthalpy, Helmholtz function, Gibbs function (Chapters 7 and 8). Anyway, the evolution criteria for non isolated systems can be traced back to the increase of the entropy of the thermodynamical universe, that is of the sum of the system and of its environment.

It is worth noting that in the equilibrium Thermodynamics the *time* never explicitly appears.

Stability of thermodynamical equilibrium

A fundamental property of thermodynamical equilibrium is its intrinsic stability (§ 9.6). Anyway, thermodynamical systems, even if isolated, are subject to local fluctuations of energy and density. A peculiar property of thermodynamic equilibrium is that the fluctuations are always reabsorbed by the system. Only fluctuations of very large extent can lead to instabilities and phase transitions (§ 23.5).

The stability of thermodynamical equilibrium is connected to the curvature of the thermodynamical functions with respect to extensive or intensive variables (§ 9.6). In particular, the stability requires the positivity of specific heats and of compressibilities.

Entropy variations: Gibbs formula

The entropy S is a function of state. Its differential dS is expressed by the Gibbs formula (6.10)

$$T\,dS = dU + p\,dV - \sum \mu_i\,dn_i\,, \tag{27.1}$$

that has a great importance also in the Thermodynamics of irreversible processes. Let us recall some simple applications of the Gibbs formula. Ricordiamo alcuni semplici esempi di applicazione della formula di Gibbs.

Example 1: For a closed system where no chemical reactions or phase transitions take place,

$$T\,dS \;=\; dU + p\,dV \;=\; đQ_{\rm rev}\,. \tag{27.2}$$

Example 2: For a one-component open system (§ 11.3),

$$T\,dS \;=\; dU + p\,dV - \mu\,dn \;=\; đQ_{\rm rev} + Ts\,dn\,. \tag{27.3}$$

Example 3: For a closed system in whih chemical reactions take place (§ 11.4),

$$T\,dS \;=\; dU + p\,dV + n_0 A\,d\xi \;=\; đQ_{\rm rev} + n_0 A\,d\xi\,, \tag{27.4}$$

where A is the affinity and ξ is its degree of advancement.

In the first two examples, the entropy variation of the system is connected to reversible exchanges of heat and/or of molar enthalpy with the surroundings. In the third example, the variation of entropy also depends on chemical processes taking place *within* the system; let us recall that a chemical reaction can be thermodynamically described also in the absence of chemical equilibrium, provided the thermal and mechanical equilibria are guaranteed (§ 11.4).

Note: The Gibbs formula (27.1) refers to a system described only by the extensive variables U, V, n_i. The formula can however easily tailored to systems which require further extensive variables , such as magnetic, dielectric, elastic systems, and so on. For example, for a magnetic system with one component the Gibbs formula can be obtained by inverting equation (17.10).

27.2 Macroscopic non-equilibrium Thermodynamics

In this Part VI we will study the possibility of a more detailed description of irreversible processes, not limited to considerations based only on the initial and final equilibrium states.

Main aims of the Thermodynamics of irreversible processes are the following.

- To define evolution criteria, always based on the increase of entropy, for irreversible processes in which one of the to state, the initial one or the final one, is a no-equilibrium state (see Example 1 below).
- To establish an entropy balance for stationary non-equilibrium states (see Example 2 below).
- To define stability criteria for stationary non-equilibrium statesand possibly to establish a connection between the instability and the evolution, for example for biological systems.
- To mathematically describe the coupling of two different irreversible processes, in which one of the two processes takes place against its natural direction.

To this aim, it is necessary to define and measure the entropy and its variations also for non-equilibrium states.

Basic concepts

The possibility of a thermodynamical description of irreversible processes is based on the following concepts.

a) One assumes that the system undergoing an irreversible process can be divided in a large number of sub-systems, sufficiently small to be considered in states of local quasi-equilibrium but sufficiently large to be macroscopically described. For each one of the sub-systems, supposed to be in an equilibrium state, one considers the *local* entropy variation dS.
b) The entropy variation of a system and of its sub-systems is decomposed as the sum of two contributions: $dS = d_eS + d_iS$, where
   - d_eS is the entropy variation due to the exchanges between the system and its ambient
   - d_iS is the entropy variation due to processes taking place within the system
c) The local character of the entropy variations d_eS and d_iS allows one to focus the attention only on the entropy, independent of the system conditions. There is thus no need to resort to thermodynamical potentials (enthalpy, Helmoltz and Gibbs functions, etc)
d) Different formalisms are required for discrete and continuous systems. The largest interest concerns continuous systems.
e) The *time* is now relevant. One focus the attention on the *entropy production*, defined as d_iS/dt. The unique evolution criterion, valid for whichever system, is represented by the positivity of the entropy production, I

$$\boxed{\frac{d_iS}{dt} > 0\,.} \tag{27.5}$$

f) The entropy production (27.5) can be expressed as the product of a *thermodynamical force* (the cause of the irreversible process) and a *thermodynamical flux* (effect of the thermodynamical force).

We conclude this introductory chapter with two examples, suitable to clarify the two basic concepts of local equilibrium and of non-equilibrium stationary state. The expressions of the entropy production for different cases will be considered in detail in Chapter 28. In Chapter 29 the coupling of irreversible processes will be studied. In Chapter **??** we will consider system maintained in non-equilibrium stationary states by external constraints.

27.2.1 Example 1: local equilibrium

Let us consider a homogeneous metal bar of length ℓ.
Initially the two ends of the bar are in thermal contact with two reservoirs maintained at the temperatures T_1 and T_2, respectively, with $T_2 > T_1$ (Fig. 27.1). The bar is in a state of thermal non-equilibrium, where heat flows from the hot to the cold reservoir; this situation will be analysed in detail in the Example 2 below.
At a given time, the bar is isolated from the two reservoirs. At this time, to be considered as initial time, the bar is out of thermal equilibrium. An irreversible process is triggered, leading the bar in a final equilibrium state at the temperature

$$T_f = \frac{T_1 + T_2}{2}\,. \tag{27.6}$$

Our goal is now to calculate the entropy variation $\Delta S = S_f - S_i$ from the initial to the final state.

The initial state is a non-equilibrium state, so that the initial entropy of the entire bar is in principle undefined. However, the difficulty can be overcome as follows.
Let us consider a section of the bar of infinitesimal width dx at the distance x from the hotter end. Let us assume that any section of infinitesimal width dx can be considered in a state of *local*

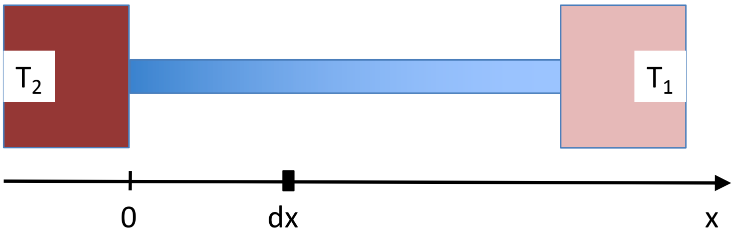


Figure 27.1: MBar of length ℓ connected at its ends with two reservoirs at the temperatures T_1 and T_2, with $T_2 > T_1$.

equilibrium. In the initial state the temperature of the bar in the position x can thus be defined and can be calculated as:

$$T_i(x) \;= T_2 \;-\; \frac{T_2 - T_1}{\ell}\, x\,. \tag{27.7}$$

During the transformation from the initial to the final state, the section dx modifies its temperature from the value $T_i(x)$ to the value $T_f(x)$. It we approximate the transformation as a quasi-static one, the variation of its entropy can be calculated as

$$dS(x) \;=\; \int_{T_i(x)}^{T_f} \frac{C_p \lambda\, dx}{T}\, dT \;=\; C_p\, \lambda\, dx\, \ln \frac{T_f}{T_i(x)}\,, \tag{27.8}$$

where λ is the linear density and C_p the heat capacity per unit mass. The variation $dS(x)$ is positive or negative according to whether the temperature increases or decreases during the irreversible process.

For the entire bar, the entropy variation is

$$\Delta_i S \;=\; C_p\, \lambda \int_0^{\ell} \ln \frac{T_f}{T_i(x)}\, dx \;>\; 0\,, \tag{27.9}$$

where the index i means that $\Delta_i S$ corresponds to entropy creation.

To easily verify that the value of the integral (27.9) is actually positive, one can consider two sections dx in symmetrical positions with respect to the central point of the bar, $x = \ell/2$, for which $T_i = T_f$. The initial temperatures of the two sections are $T_f + \Delta T$ and $T_f - \Delta T$. The contribution of the two sections to the integral in (27.9) is proportional to

$$\ln T_f - \ln(T_f - \Delta T) + \ln T_f - \ln(T_f + \Delta T) \;>\; 0\,.$$

One can generalise the previous example as follows. In many systems out of equilibrium one can often assume that their single parts, small with respect to the entire system but still macroscopic, can be considered in a state of local equilibrium. The local equilibrium can take place if microscopic collisions are sufficiently intense to guarantee the local uniformity of the thermal state.

The local equilibrium can be conceived as obtained through a suitable number of ideal constraints imposed to the system, able to frozen the instantaneous local situation.

In this example, the system (the bar) is isolated during the irreversible process. Its entropy variation (27.9) corresponds to the entropy produced during the irreversible process.

27.2.2 Example 2: non-equilibrium stationary states

Let us again consider the homogeneous metal bar of length ℓ connected at the two ends with two reservoirs at the temperatures T_1 and T_2, with $T_2 > T_1$ (Fig. 27.1). Contrary to the previous example, the bar is now indefinitely maintained in contact with the two reservoirs, so that heat flows continuously from the hot to the cold reservoir.

The state of the bar is

- *out of equilibrium*, with a distribution of temperature values along its length,
- *stationary*, because the distribution of temperatures along the bar is invariable as time goes on.

A flux of heat

$$I_Q = \frac{đQ}{dt} \tag{27.10}$$

takes place along the bar, propagating from the reservoir 2 to the reservoir 1. The amounts of heat leaving the reservoir 2 and absorbed by the reservoir 1 in a given time interval are equal,

$$|Q_1| = |Q_2|\,. \tag{27.11}$$

Let us separately analyse the entropy variations of the reservoirs and of the bar. Since the process is stationary, instead of arbitrarily considering an initial state and a final state, it is more convenient to refer to the entropy variations in unit time.

Entropy variations of the reservoirs

The two reservoirs can be considered in thermodynamical equilibrium, so that their entropy variations per unit time can be easily calculated:

$$\frac{dS_2}{dt} = \frac{1}{T_2}\frac{đQ_2}{dt} < 0\,, \qquad \frac{dS_1}{dt} = \frac{1}{T_1}\frac{đQ_1}{dt} > 0\,. \tag{27.12}$$

Since for the reservoirs $Q_2 < 0, Q_1 > 0$ and $T_1 < T_2$, the entropy variation per unit time of the system composed by the two reservoirs is positive.

Entropy variation of the bar

In each element dx of the bar the entropy S remains unchanged in time, because the state of local equilibrium, s defined in the previous Example 1, remains unchanged in a stationary irreversible process. Therefore, the entropy of the entire bar remains unchanged too:

$$\frac{dS}{dt} = 0\,. \tag{27.13}$$

On the other hand, an irreversible heat transport takes place in the bar and produces entropy. However, the entropy production within the bar doesn't modify its total entropy, because the bar in in a stationary state.
To understand the entropy balance of the bar, it is convenient to split its entropy variation per unit time as the sum of three contributions:

1) Incoming entropy flux, opposite to the outgoing flux from the reservoir 2

$$\frac{dS_{\text{in}}}{dt} = -\frac{dS_2}{dt} > 0\,. \tag{27.14}$$

2) Outgoing flux, opposite to the incoming flux in the reservoir 1

$$\frac{dS_{\text{out}}}{dt} = -\frac{dS_1}{dt} < 0\,. \tag{27.15}$$

3) Entropy creation within the bar

$$\frac{d_iS}{dt}\,. \tag{27.16}$$

The sum of the entropy fluxes incoming in and outgoing from the bar is negative, its value being opposite to the to the sum of the fluxes incoming in and outgoing from the reservoirs:

$$\frac{d_eS}{dt} = \frac{dS_{\text{in}}}{dt} + \frac{dS_{\text{out}}}{dt} < 0\,. \tag{27.17}$$

The amount of entropy outgoing from the bar per unit time is larger than the entering amount. The bar is in a stationary state, for which there is no total entropy variation

$$0 = \frac{dS}{dt} = \frac{d_eS}{dt} + \frac{d_iS}{dt}, \quad \text{so that} \quad \frac{d_iS}{dt} > 0 \tag{27.18}$$

The stationary irreversible process of the system bar + reservoirs is characterised by the *creation of entropy* within the bar ($dS_i/dt > 0$), caused by the flux of heat under a temperature gradient. Locally, for each element of the bar, the outgoing flux is larger that the incoming flux, due to the local entropy production.

In this example, the irreversible process causes an increase of entropy in the isolated system made by the bar and the two reservoirs. The bar by itself is not an isolated system; since the irreversible process is stationary, its entropy doesn't change in time. The irreversibility is characterised by the neat production of entropy along the entire bar, but the produced entropy is continuously transferred to the colder reservoir.

The positive production of entropy per unit time characterises the irreversible processes also in non-isolated systems.

Chapter 28

Entropy production

The evolution criterion for irreversible processes expressed by the fundamental axiom of the macroscopic equilibrium Thermodynamics, $\Delta S > 0$ (§ 5.2), only holds for isolated systems. For non-isolated systems, different evolution criteria have been introduced, based on different thermodynamical functions (Chapter 8).

In the Thermodynamics of irreversible processes, the attention is focussed on the entropy production. A unique evolution criterion is assumed, valid for all systems (isolated or non isolated):

$$\frac{d_i S}{dt} > 0\,, \tag{28.1}$$

where $d_i S/dt$ represents the entropy production per unit time. In this rspect, it is convenient to consider the two examples of § 27.2.

In the present chapter our goal is to learn how the entropy production (28.1) can be calculated for various types of thermodynamical systems. We will first consider discrete systems, formed by a finite little number of homogeneous systems (§ 28.1). We will then consider continuous systems (§ 28.2), whose practical interest is larger. In conclusion, we will discuss the concepts of generalised fluxes and forces (§ 28.4).

28.1 Entropy production in discrete systems

Studying discrete systems allows an easy understanding of the mechanisms of entropy production in terms of finite differences of intensive quantities and fluxes of extensive quantities.

It should anyway be considered that le concept of local equilibrium, introduced in § 27.2 and essential for the thermodynamical treatment of irreversible phenomena, is more problematic for discrete systems than for continuous systems, such as the metal bar of the examples in § 27.2.

28.1.1 Closed and isolated systems

Let us consider again some simple cases studied in § 6.2, where the intensive coordinates have been introduced to characterise the thermal, mechanical and chemical equilibria. Let us now focus the attention on the irreversible processes.

Example 1: two sub-systems with different temperatures

Let us consider an isolated system, divided in two sub-systems by a fixed wall, which can slowly transmit heat. The temperatures of the two sub-systems are different, $T^{(1)}$ and $T^{(2)}$, respectively, with $T^{(1)} < T^{(2)}$ (Fig. 28.1, left).

The entropy variation dS due to the irreversible transfer of energy $dU = đQ$ from the hotter to the colder subsystem can be evaluated by means of equation (6.7), if the process if so slow that the

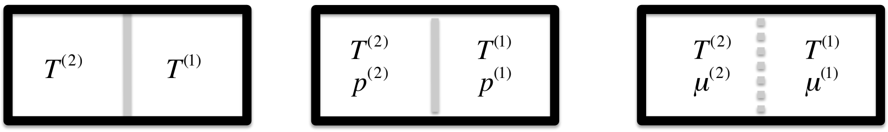


Figure 28.1: An isolated systems divided in two sub-systems: at different temperatures (left), at different temperatures and pressures (centre), at different temperatures and chemical potentials (right).

two sub-systems remain homogeneous, that is if the two sub-systems can be considered in local quasi-equilibrium:

$$dS = \frac{1}{T^{(1)}}\, dU^{(1)} + \frac{1}{T^{(2)}}\, dU^{(2)} = \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] dU^{(1)} \;>\; 0\,. \tag{28.2}$$

Since the entropy variation dS is due only to heat exchanges within the system, $dS = d_iS$. The irreversible process is characterised by entropy production within the system:

$$\frac{d_iS}{dt} \;=\; \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] \frac{dU^{(1)}}{dt} \;>\; 0\,. \tag{28.3}$$

The expression (28.3) of the entropy production can be considered as the product of a generalised force, that is the finite difference of an intensive quantity (here the inverse temperature), times the flux of the conjugate extensive quantity (here the internal energy):

$$\frac{d_iS}{dt} \;=\; \left[\text{generalised force } \Delta\left(\frac{1}{T}\right)\right] \;\times\; \left[\text{flux } \frac{dU}{dt}\right]\,. \tag{28.4}$$

Note 1: It should be noticed that the generalised force conjugate to the energy flux is the difference of the inverse temperatures, $\Delta(1/T)$, not the temperature difference ΔT.

Note 2: In the particular example here considered, the energy flux dU/dt corresponds to the heat flux $đQ/dt$.

Example 2: two subsystems with different temperatures and pressures

Let us now consider an isolated system, divided in two homogeneous sub-systems by a movable wall, which can again slowly transmit heat. The two sub-systems are at different temperatures $T^{(1)}$ and $T^{(2)}$, respectively, with $T^{(1)} < T^{(2)}$, and different pressures $p^{(1)}$ and $p^{(2)}$, respectively, with $p^{(1)} < p^{(2)}$ (Fig. 28.1, centre).

The entropy variation dS due to the irreversible exchange of energy dU and volume dV between the two subsystems is, in the hypothesis that the process is sufficiently slow to maintain the sub-systems homogeneous (local quasi-equilibrium),

$$dS \;=\; \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] dU^{(1)} \;+\; \left[\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}}\right] dV^{(1)} \;>\; 0\,. \tag{28.5}$$

The entropy production

$$\frac{d_iS}{dt} \;=\; \Delta\left(\frac{1}{T}\right) \frac{dU}{dt} \;+\; \Delta\left(\frac{p}{T}\right) \frac{dV}{dt} \tag{28.6}$$

can be again expressed as the sum of products of generalised forces times conjugated fluxes:

$$\frac{d_iS}{dt} \;=\; \sum_k \left[(\text{generalised force})_k \;\times\; (\text{flux})_k\right]\,. \tag{28.7}$$

Note: Here, contrary to the previous Example 1, $dU = T\,dS - p\,dV \neq đQ$; the entropy production, calculated through (27.2), depends on the heat flux $đQ = dU + p\,dV$.

Electro-chemical potential

Given an electrical potential ϕ, the work on a charge dq is

$$\phi\, dq \;=\; \phi z F\, dn\,. \tag{28.8}$$

In the second member of (28.8), n is the number of moles of elementary constituents, $F = 96485\,\mathrm{C/mol}$ is the Faraday constant and z is the number of elementary charges on the elementary constituent.
The energy balance is

$$dU \;=\; T\,dS - p\,dV + (\mu + \phi z F)\,dn \;=\; T\,dS - p\,dV + \tilde{\mu}\,dn\,, \tag{28.9}$$

where $\tilde{\mu} = \mu + \phi z F$ is called electro-chemical potential (the two contributions, electrical and chemical, cannot be experimentally separated).
The entropy variation is

$$dS \;=\; \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\tilde{\mu}}{T}\,dn\,. \tag{28.10}$$

Example: Let us consider an isolated system divided in two sub-systems with temperatures, electrical potentials and chemical potentials, $T^{(1)}, \phi^{(1)}, \mu^{(1)}$ and $T^{(2)}, \phi^{(2)}, \mu^{(2)}$, respectively. The entropy production due to the energy and matter transport is

$$\frac{d_iS}{dt} \;=\; \Delta\left(\frac{1}{T}\right)\frac{dU}{dt} \;+\; \Delta\left(-\frac{\tilde{\mu}}{T}\right)\frac{dn}{dt}\,, \tag{28.11}$$

where $\tilde{\mu}^{(k)} = \mu^{(k)} + \phi^{(k)} z F$, with $k = 1, 2$.
The entriopy production expressed by (28.11) is amenable to the general expression (28.7).

28.1.2 Closed non-isolated systems

Let us now consider the case of *non-isolated* discrete and closed systems, in which the entropy production is not solely amenable to processes internal to the system, but is due also to energy exchanges with the ambient.

Only thermal exchange with the ambient

Let us consider a system enclosed in fixed walls, able to slowly transmit heat, divided in two homogeneous sub-systems by a fixed wall, as well able to slowly transmit heat. The energy variation dU of both sub-systems can be due to the exchange of heat not only between the two sub-systems ($\text{đ}Q_i$) but also between the sub-systems and the surrounding ambient ($\text{đ}Q_e$).
The differential entropy variation of the entire system, in the hypothesis of local quasi-equilibrium of the sub-systems, can be expressed by separately considering the two sub-systems (first line of the following equation) or by separating the exchange of heat with the ambient from the exchange between the two sub-systems (second line of the following equation):

$$\begin{aligned} dS \;=\; dS^{(1)} + dS^{(2)} \;&=\; \left[\frac{\text{đ}Q_e^{(1)}}{T^{(1)}} + \frac{\text{đ}Q_i^{(1)}}{T^{(1)}}\right] + \left[\frac{\text{đ}Q_e^{(2)}}{T^{(2)}} + \frac{\text{đ}Q_i^{(2)}}{T^{(2)}}\right] \\ &=\; \underbrace{\frac{\text{đ}Q_e^{(1)}}{T^{(1)}} + \frac{\text{đ}Q_e^{(2)}}{T^{(2)}}}_{d_eS} + \underbrace{\text{đ}Q_i^{(1)}\left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right]}_{d_iS} \end{aligned} \tag{28.12}$$

One can thus single out two contributions to the entropy variation dS:

– the entropy flux d_eS/dt due to the heat exchange between the sub-systems and the ambient, whose contribution can be both positive or negative;

– the entropy production $d_iS/dt > 0$ due to the exchange of heat $đQ = dU$ induced by the temperature difference between the two sub-systems:

$$\frac{d_iS}{dt} = \Delta\left(\frac{1}{T}\right) \times \frac{dU}{dt}\,. \tag{28.13}$$

The entropy production is again amenable to the general expression (28.7).

Chemical reaction at constant temperature and pressure

Let us now consider a homogeneous system, closed but not isolated, within which a chemical reaction takes place.

A generic chemical reaction can be expressed (§ 11.4) as

$$-\,\nu_1\,A_1 - \nu_2\,A_2 \;\rightleftharpoons\; \nu_3\,A_3 + \nu_4\,A_4\,, \tag{28.14}$$

where A_k are reagents and products and ν_k are the stoichiometric coefficients.

The variations dn_k of reagents and products can be expressed in terms of a unique parameter, the degree of advancement ξ, as

$$dn_k = \nu_k\,d\xi \tag{28.15}$$

and the affinity A is defined as

$$A = -\sum\nolimits_k \mu_k\nu_k\,, \tag{28.16}$$

where μ_k are the chemical potentials of reagents and products. If $A > 0$, the reaction (28.14) goes forward; if $A < 0$, the reaction goes backwards; in equilibrium, $A = 0$ (Fig. 11.5).

Let us suppose that the reaction takes place at constant temperature and pressure, so that the most suitable thermodynamical potential is the Gibbs function $G = H - TS$. The evolution criterion § 11.4 is

$$dG = -n_0\,A\,d\xi < 0\,, \tag{28.17}$$

where n_0 is a scale factor. In conditions of equilibrium, $A = 0$ and the Gibbs function is minimal.

The entropy variation (§ 11.4) is

$$\begin{aligned} dS &= \frac{1}{T}\,dU + \frac{p}{T}\,dV - \sum_k \frac{\mu_k}{T}\,dn_k \\ &= \frac{1}{T}đQ + n_0\,\frac{A}{T}\,d\xi \\ &= d_eS + d_iS\,. \end{aligned} \tag{28.18}$$

The first term corresponds to the entropy variation due to the exchange of heat with the ambient, and can be both positive or negative. The second term corresponds to the entropy production due to the irreversible development of the reaction and is necessarily positive (when $A > 0$, also $d\xi > 0$, and viceversa).

The evolution criterion (28.17) can be recast in terms of entropy production:

$$\frac{d_iS}{dt} = n_0\,\frac{A}{T}\,\frac{d\xi}{dt} = n_0\,\frac{A}{T}\,v > 0\,; \tag{28.19}$$

the quantity $v = d\xi/dt$ is the reaction speed.

Also (28.19) has the form of the product of a thermodynamical force (A/T) times a thermodynamical flux (v). In this case both force and flux are scalar quantities, without directional properties.

Coupled chemical reactions

Different chemical reactions can take place contemporarily within the same vessel. The entropy production is expressed as the sum of the contributions of single reactions:

$$\frac{d_iS}{dt} = \frac{1}{T}\sum_\rho A_\rho\, v_\rho > 0\,. \tag{28.20}$$

The total entropy production (28.20) is positive. It can however be that single reactions take place in the direction of a negative production of entropy.
The coupling of irreversible processes can make possible that one or more processes take place in the direction of entropy reduction at the expenses of a larger entropy production in other coupled processes.

28.1.3 Open systems

An open system can exchange matter with its environment (§ 11.3). We have already shortly considered open systems in § 11.3. By generalising (11.34) and (11.35) to the case of systems with more than one component, the energy balance of an open system is written as

$$\begin{aligned} dU &= T\,dS - p\,dV + \sum\nolimits_k \mu_k\,dn_k \\ &= T\sum\nolimits_k n_k\,ds_k - p\,dV + \sum\nolimits_k h_k\,dn_k \\ &= đQ - p\,dV + \sum\nolimits_k h_k\,dn_k\,, \end{aligned} \tag{28.21}$$

where h_k is the molar enthalpy of the k-th component.
Often the energy variation (28.21) is written as

$$dU = d\Phi - p\,dV\,, \tag{28.22}$$

where the term

$$d\Phi = T\sum n_k\,ds_k + \sum h_k\,dn_k = đQ + \sum h_k\,dn_k$$

is the total energy exchanged by conduction (thermal contact) $đQ$ and by convection (matter transport) $\sum h_k\,dn_k$.
By substituting dU from (28.22) in the Gibbs equation, the entropy variation becomes

$$\begin{aligned} dS &= \frac{1}{T}\,dU + \frac{p}{T}\,dV - \sum\nolimits_k \frac{\mu_k}{T}\,dn_k \\ &= \frac{1}{T}\,d\Phi - \sum\nolimits_k \frac{\mu_k}{T}\,dn_k\,, \end{aligned} \tag{28.23}$$

where the first term in the last line is the entropy variation due to the energy flux (conduction + convection), the second term is the entropy variation due to the exchange of matter. The entropy variation is only due to exchanges of energy and matter between the system and its ambient, $dS = d_eS$; there is no entropy production.

Two sub-systems divided by a permeable wall

Let us now consider an isolated system, divided in two homogeneous divided by a permeable wall, that can slowly transmit heat. The two sub-systems are at different temperatures, pressures and chemical potentials, with $T^{(1)} < T^{(2)}$, $p^{(1)} < p^{(2)}$ and $\mu^{(1)} < \mu^{(2)}$ (Fig. 28.1, right).
The two sub-systems can be considered as two open systems with one single component. The internal energy variation of each one of the two sub-systems can be expressed in the form (28.22), where $d\Phi = đQ + h\,dn$ is the thermal energy exchanged by both conduction and convection.
The entropy variation of each one of the two sub-systems is given by (28.23):

$$dS = \frac{1}{T}\,d\Phi - \frac{\mu}{T}\,dn\,. \tag{28.24}$$

The entropy variation dS of the entire system is due to the irreversible exchange of energy dU and matter dn between the two sub-systems. If the process is sufficiently slow so as to maintain the two sub-systems homogeneous,

$$dS \;=\; \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] d\Phi^{(1)} \;-\; \left[\frac{\mu^{(1)}}{T^{(1)}} - \frac{\mu^{(2)}}{T^{(2)}}\right] dn^{(1)} \;>\; 0\,. \tag{28.25}$$

The entropy production

$$\frac{d_iS}{dt} \;=\; \Delta\left(\frac{1}{T}\right)\,\frac{d\Phi}{dt} \;+\; \Delta\left(-\frac{\mu}{T}\right)\,\frac{dn}{dt} \tag{28.26}$$

can again be expressed as the sum of products

$$\frac{d_iS}{dt} \;=\; \sum_k \,[(\text{generalised force})_k \,\times\, (\text{flux})_k]\;. \tag{28.27}$$

Chemical reaction in an open system

If a chemical reaction takes place within an open system, that can reversibly exchange reagents and products with its ambient, the entropy variation contains both the term (28.23), due to the exchange of energy and matter with the ambient, and the term due to the irreversible development of the reaction

$$dS \;=\; \underbrace{\frac{1}{T}\,d\Phi - \sum\nolimits_k \frac{\mu_k}{T}\,dn_k}_{d_eS} \;+\; \underbrace{\frac{A}{T}\,d\xi}_{d_iS}\;. \tag{28.28}$$

The entropy production per unit time due to the development of the reaction is again expressed by (28.19), as for closed systems.

28.2 Continuous systems: fluxes and forces

In the discussion of irreversible processes in discrete systems of § 28.1 the concepts of thermodynamical force and flux have been introduced. Those concepts can be more rigorously defined for continuous systems, whose properties are continuous functions of spatial coordinates and of time. Continuous systems are more interesting for practical purposes.

28.2.1 Thermodynamical fluxes

In § 28.1 two types of thermodynamical fluxes have been introduced:

- scalar fluxes, such as the velocity of chemical reactions $v = d\xi/dt$;
- vector fluxes, characterised by a direction, such as the energy or matter fluxes.

Both scalar and vector fluxes are here considered for continuous systems too. It is convenient to distinguish the fluxes of conservative quantities (such as mass and energy) from the fluxes of non-conservative quantities (such as entropy).

28.2.2 Fluxes of conservative quantities

Our first step is to express the First Law of Thermodynamics (conservation of energy, Chapter 3) in local terms, suited to the treatment of irreversible processes in continuous systems. Otherwise stated, we want to give an analytic form the the law of local energy conservation. For a continuous system it is necessary to give a local expression to the conservation of matter too, for one-component systems as well as for many-component systems.

The time variation of a conservative quantity G (for example the internal energy U or the mass m) contained in a given volume V takes place through the transport of the quantity G across the surface A forming the boundary of the volume:

$$\frac{dG}{dt} = \int_A \vec{J}_G \cdot \hat{n}\, dA\,, \tag{28.29}$$

where $\vec{J}_G$ is the flux of the quantity G outgoing from the volume V per unit of time and surface and $\hat{n}$ is the unit vector perpendicular to the surface dA.
The integral form (28.29) of the law of conservation of the quantity G can be transformed into a local form by introducing the density ρ_G of G, such that

$$G = \int_V \rho_G(\vec{r})\, dV\,, \tag{28.30}$$

and one uses the Gauss theorem for the flux

$$\int_A \vec{J} \cdot \hat{n}\, dA = \int_V \vec{\nabla} \cdot \vec{J}\, dV\,. \tag{28.31}$$

One can thus obtain the differential continuity equation

$$\frac{\partial \rho_G}{\partial t} = -\vec{\nabla} \cdot \vec{J}_G\,, \tag{28.32}$$

Mass conservation (one component)

The local conservation of the mass is expressed in terms of the continuity equation (28.32) for the mass density $\rho = dm/dV$:

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot \vec{J}_m\,, \tag{28.33}$$

where $\vec{J}_m$ is the flux of mass.

Mass conservation (many components)

For a many-component system in which no chemical reactions take place, it is convenient to refer to the continuity equation for the numerical density $c_i = dn_i/dV$:

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla} \cdot \vec{J}_i\,, \tag{28.34}$$

where $\vec{J}_i$ is the flux of moles of the i-th component.

Energy conservation

The continuity equation for the energy density ρ_e is

$$\frac{\partial \rho_e}{\partial t} = -\vec{\nabla} \cdot \vec{J}_e\,, \tag{28.35}$$

where$\vec{J}_e$ is the energy flux.
Equation (28.35) is the local expression of the First Law of Thermodynmics.

28.2.3 Fluxes of non-conservative quantities

Let us now consider two relevant cases of non-conservative quantities: the reagents and product of a chemical reaction and the entropy.

Chemical reactions

Within a system which hosts a chemical reaction, the number n_i of moles of the i-th component can vary as an effect of two mechanisms: transport of matter (t) and chemical reaction (r); for a finite volume V,

$$\frac{\partial n_i}{\partial t} = \frac{\partial_t n_i}{\partial t} + \frac{\partial_r n_i}{\partial t} = -\int_V \vec{\nabla} \cdot \vec{J}_i \, dV + \int_V \nu_i \, \frac{d\xi}{dt} \, dV \,. \tag{28.36}$$

The amounts of reagents and products are left unchanged by the transport processes, are modified by the chemical reaction.
The integral form of (28.36) can be transformed into the differential form of a modified continuity equation

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla} \cdot \vec{J}_i + \nu_i \, J_{\mathrm{ch}} \,. \tag{28.37}$$

wherec_i are the concentrations of reagents and products, $\vec{J}_i$ are their incoming and outgoing fluxes, and $J_{\mathrm{ch}} = v = d\xi/dt$ is a form of generalised flux connected to the chemical reaction.
In (28.37) two types of flux thus appear appear,

- a vector flux of matter$\vec{J}_i$, which describes the matter transport processes,
- a scalar flux $J_{\mathrm{ch}} = v = d\xi/dt$, which describes the advancement of the chemical reaction, within which the amounts of reagents and products are not conserved..

28.2.4 Entropy flux and entropy production

The concept of flux can be considered also for non-conservative quantities, such as entropy. However, the conservation equation (28.29) doesn't hold; anyway, as we will see below, if can be conveniently modified to take into account the processes of entropy production.

Let us define the local entropy density s_v (entropy per volume unit) by means of the equations

$$S = \int_V s_v \, dV \,, \qquad \frac{dS}{dt} = \int_V \frac{\partial s_v}{\partial t} \, dV \,. \tag{28.38}$$

Note: For the study of irreversible processes in continuous systems one refers to the densities per volume unit rather than to the molar quantities.

Let us consider the entropy S contained in a volume V within the surface A. Let us decompose the variation of entropy for unit time in two contributions, due to flux and production, respectively:

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} = -\int_A \vec{J}_s \cdot \hat{n} \, dA + \frac{d_i S}{dt} \,, \tag{28.39}$$

where $\vec{J}_s$ is the entropy flux outgoing from the surface A. Making use of the divergence theorem, we can introduce the volume integrals:

$$\frac{dS}{dt} = -\int_V \vec{\nabla} \cdot \vec{J}_s \, dV + \int_V \sigma \, dV \,, \tag{28.40}$$

where σ is the local entropy production (entropy production per volume unit).
The differential equation corresponding to the integral equation (28.40) is

$$\frac{\partial s_v}{\partial t} = -\vec{\nabla} \cdot \vec{J}_s + \sigma \,. \tag{28.41}$$

The general evolution criterion for continuous systems consists in the positivity of the local entropy production,

$$\boxed{\sigma > 0} \tag{28.42}$$

28.2.5 Thermodynamical forces

In § 28.1 two types of forces, of scalar and vector character, have been introduced for discrete systems. Also for continuous systems two types of thermodynamical forces (also called generalised forces or affinities) can be distinguished:

- *scalar* thermodynamical forces; for example, for chemical reactions, the affinity divided by the temperature, $\mathcal{F}_{\rm ch} = A/T$;
- *vector* thermodynamical forces, characterised by a given direction; for discrete systems they consist in finite differences, for continuous systems they consist in gradients of intensive quantities; for example:

$$\vec{\mathcal{F}}_Q \;=\; \vec{\nabla}\left(\frac{1}{T}\right), \quad \vec{\mathcal{F}}_i \;=\; \vec{\nabla}\left(-\frac{\mu_i}{T}\right) \tag{28.43}$$

28.3 Local entropy production

Let us consider the Gibbs equation for the reversible entropy variation for a macroscopic system:

$$T\,dS \;=\; dU + p\,dV - \sum\nolimits_i \mu_i dn_i \,. \tag{28.44}$$

For irreversible processes, the Gibbs equation (28.44) can still be used, provided the volume V of the system can be contemporarily considered

- sufficiently small that the intensive quantities can be considered as uniform,
- sufficiently large that the statistical fluctuations can be neglected.

Otherwise stated, the the system enclosed in the volume V shouldn't be too far from thermodynamical equilibrium.

If the quantities per volume unit are introduced,

$$s_v = S/V\,, \quad u_v = U/V\,, \quad c_i = n_i/V\,, \tag{28.45}$$

equation (28.44) becomes

$$T\,d(s_vV) \;=\; d(u_vV) + p\,dV - \sum\nolimits_i \mu_i d(c_iV)\,, \tag{28.46}$$

whence

$$V\left[T\,ds_v - du_v + \sum\nolimits_i \mu_i dc_i\right] \;=\; dV\left[-T\,s_v + u_v + p - \sum\nolimits_i \mu_i c_i\right] \tag{28.47}$$

The expression in square parentheses in the second member of (28.47) is identically zero; for a demonstration, it is sufficient to multiply by V and compare with the Euler relation (7.24), $G = U + pV - TS = \sum \mu_i n_i$.

As a consequence, the expression in square parentheses in the first member of (28.47) is identically zero too.

Local Gibbs equation

Equating to zero the expression in square parentheses in the first member of (28.47), one obtains the local Gibbs equation, which doesn't contain the volume V:

$$T\,ds_v \;=\; du_v - \sum\nolimits_i \mu_i\,dc_i \tag{28.48}$$

From (28.48) one obtains in turn the time variation of the local entropy:

$$T\,\frac{\partial s_v}{\partial t} \;=\; \frac{\partial u_v}{\partial t} - \sum\nolimits_i \mu_i \frac{\partial c_i}{\partial t}\,. \tag{28.49}$$

Local entropy production

If the continuity equations (28.41), (28.35) and (28.37)

$$\frac{\partial s_v}{\partial t} = -\vec{\nabla}\cdot\vec{J}_s + \sigma\,, \qquad \frac{\partial u_v}{\partial t} = -\vec{\nabla}\cdot\vec{J}_u\,, \qquad \frac{\partial c_i}{\partial t} = -\vec{\nabla}\cdot\vec{J}_i + \nu_i J_{\text{ch}}\,, \tag{28.50}$$

are inserted in (28.49), after some steps of vector calculus (see the demonstration below), one obtains the following expression for the local entropy production

$$\boxed{\sigma \;=\; \vec{J}_u\cdot\vec{\nabla}\left(\frac{1}{T}\right) \;-\; \sum\nolimits_i \vec{J}_i\cdot\vec{\nabla}\left(\frac{\mu_i}{T}\right) \;+\; J_{\text{ch}}\,\frac{A}{T}\,,} \tag{28.51}$$

that corresponds to a sum of terms, each one of which is the product of a generalised flux times a thermodynamical force:

$$\boxed{\sigma \;=\; \sum\nolimits_k J_k\,\mathcal{F}_k} \tag{28.52}$$

Demonstration

By inserting the continuity equations (28.50) in (28.49), one obtains

$$-\vec{\nabla}\cdot\vec{J}_s + \sigma \;=\; -\frac{1}{T}\vec{\nabla}\cdot\vec{J}_u - \sum \frac{\mu_i}{T}\left[-\vec{\nabla}\cdot\vec{J}_i + \nu_i J_{\text{ch}}\right]. \tag{28.53}$$

Making use of the vector calculus rule

$$\vec{\nabla}\cdot(a\vec{v}) = a\vec{\nabla}\cdot\vec{v} + \vec{v}\cdot\vec{\nabla}a \quad\Rightarrow\quad a\vec{\nabla}\cdot\vec{v} = \vec{\nabla}\cdot(a\vec{v}) - \vec{v}\cdot\vec{\nabla}a \tag{28.54}$$

the factor $1/T$ can be transferred under the $\vec{\nabla}$ operator, so that one obtains

$$\sigma \;=\; \vec{\nabla}\cdot\vec{J}_s - \vec{\nabla}\cdot\frac{\vec{J}_u}{T} + \vec{J}_u\cdot\vec{\nabla}\left(\frac{1}{T}\right) + \sum\nolimits_i \vec{\nabla}\cdot\frac{\mu_i\vec{J}_i}{T} - \sum\nolimits_i \vec{J}_i\cdot\vec{\nabla}\left(\frac{\mu_i}{T}\right) \;+\; J_{\text{ch}}\,A\,. \tag{28.55}$$

The first, second and fourth terms on the right of (28.55) can be eliminated, because

$$\begin{aligned} \vec{\nabla}\cdot\left[\vec{J}_s - \frac{\vec{J}_u}{T} + \sum\frac{\mu_i}{T}\,\vec{J}_i\right] \quad &= \\ \vec{\nabla}\cdot\left[\frac{1}{A}\frac{d}{dt}\left(dS - \frac{dU}{T} + \sum\frac{\mu_i}{T}\,dn\right)\hat{n}\right] \quad &= \quad \vec{\nabla}\cdot 0 \;=\; 0\,, \end{aligned} \tag{28.56}$$

where $\hat{n}$ is the flux direction and A is the normal surface.
Equation (28.51) is then obtained.

28.3.1 Non-equilibrium stationary states

A system is said to be in a stationary state if its local properties are time independent. For example, for a stationary system

$$\frac{\partial\rho}{\partial t} = 0\,, \qquad \frac{\partial c_i}{\partial t} = 0\,, \qquad \frac{\partial\rho_e}{\partial t} = 0\,, \qquad \frac{\partial s_v}{\partial t} = 0\,. \tag{28.57}$$

Let us focus here our attention on the non-equilibrium stationary states already encountered in one example of § 27.2 (Example 2).
By inserting the stationary conditions (28.57) in the continuity equations (28.50) one obtains different conditions for conservative and for non-conservative quantities.

Conservative quantities

For conservative quantities, according to the continuity equations, for example (28.33), (28.34) and (28.35) for the mass and the energy, the divergence of the fluxes is zero in the stationary state,

$$\vec{\nabla} \cdot \vec{J_i} \; = \; 0 \, . \tag{28.58}$$

Example: In the one-dimensional case, (28.58) becomes

$$\frac{dJ}{dx} \; = \; 0 \, , \quad \text{that is} \quad J \text{ independent of } x \, . \tag{28.59}$$

The condition (28.58) for non-equilibrium stationary state, is less demanding than the condition $\vec{J_i} = 0$, which holds in the case of thermodynamical equilibrium.

Non-conservative quantities

For non-conservative quantities in a stationary non-equilibrium state, the divergence of the fluxes is not zero.
Let as consider, as a first example, a *chemical reaction*, in which reagents and products are not conserved. In a stationary state, the first member of (28.37) is null, $\partial c_i / \partial t = 0$, so that

$$\vec{\nabla} \cdot \vec{J_i} = \nu_i \, J_{\text{ch}} \, . \tag{28.60}$$

The divergences of the fluxes $\vec{J_i}$ of the different components (reagents and products) are not null, but equal to the chemical flux of the reaction $J_{\text{ch}} = v = d\xi/dt$ multiplied by the stoichiometric coefficients ν_i.

As a second example of non-conservative quantity , let us consider the *entropy.* In a stationary state, the the molar entropy doesn't vary. Therefore, if one imposes $\partial s_v / \partial t$=0, equation (28.41) becomes

$$\vec{\nabla} \cdot \vec{J_s} = \sigma \, . \tag{28.61}$$

The divergence of the entropy flux is equal to the local production of entropy σ.
The entropy created in a stationary state has to be transferred to the ambient, in order to maintain the entropy density of the system constant. Therefore, non-equilibrium stationary states cannot be established in adiabatic systems, that is in systems that cannot exchange entropy with the ambient.

The properties of non-equilibrium stationary states will be considered in more detail in Chapter **??**.

28.4 Properties of thermodynamical forces and fluxes

It has been established above that the entropy production can be expressed in terms of products of generalised fluxes (or velocities) J times generalised forces (or affinities) $\mathcal{F}$.
For discrete systems, the entropy production per unit time is

$$\frac{d_i S}{dt} \; = \; \sum\nolimits_k J_k \, \mathcal{F}_k \, . \tag{28.62}$$

For continuous systems (see for example 28.51) the local entropy production per unit time is

$$\sigma \; = \; \sum\nolimits_k J_k \, \mathcal{F}_k \, . \tag{28.63}$$

28.4.1 Equivalent systems of forces and fluxes

The choice of generalised forces $\mathcal{F}$ and generalised fuxes J is not unique. For example if in the expression (28.51) of the local entropy production σ, one substitutes

$$\vec{\nabla}\left(\frac{1}{T}\right) = \frac{1}{T^2}\,\vec{\nabla}\,(-T)\;, \quad \vec{\nabla}\left(-\frac{\mu}{T}\right) = \frac{1}{T}\,\vec{\nabla}\,(-\mu) - \frac{\mu}{T^2}\,\vec{\nabla}(-T)\,, \tag{28.64}$$

one obtains the equivalent expression

$$\begin{aligned} \sigma \;&=\; \frac{1}{T}\left(\frac{\vec{J}_u}{T} - \frac{\sum \mu_i \vec{J}_i}{T}\right)\cdot\vec{\nabla}(-T) \;+\; \frac{1}{T}\sum \vec{J}_i\cdot\vec{\nabla}(-\mu_i) \;+\; J_{\text{ch}}\,\frac{A}{T} \\ &=\; \frac{1}{T}\,\vec{J}_s\cdot\vec{\nabla}(-T) \;+\; \frac{1}{T}\sum \vec{J}_i\cdot\vec{\nabla}(-\mu) \;+\; \frac{1}{T}\,J_{\text{ch}}\,A\,, \end{aligned} \tag{28.65}$$

where $\vec{J}_s$ is the entropy flux.
The product $T\sigma$ is sometimes called *dissipation function.*
Different choices of forces and fluxes can simplify the mathematical treatment of some problems, like the choice of reference frames in Mechanics.

Conjugated forces and fluxes

By comparing (28.51) with (28.65), one can distinguish two different systems of conjugated forces and fluxes:

$$\begin{array}{c|c} J & \mathcal{F} \\ \hline \vec{J}_u & \vec{\nabla}(1/T) \\ \vec{J}_i & \vec{\nabla}(-\mu/T) \\ J_{\text{ch}} & A/T \end{array} \qquad\qquad \begin{array}{c|c} J' & \mathcal{F}' \\ \hline \vec{J}_s/T & \vec{\nabla}(-T) \\ \vec{J}_i/T & \vec{\nabla}(-\mu) \\ J_{\text{ch}}/T & A \end{array} \tag{28.66}$$

28.4.2 Relations between generalised forces and generalised fluxes

To calculate the local entropy production per unit time σ by means of (28.63), it is necessary to know the fluxes J_k conjugated to the thermodynamical forces $\mathcal{F}_k$. Thermodynamical forces and fluxes are not independent, but are connected by cause-effect relations. The knowledge of the relations between thermodynamical forces and fluxes, as well as of the properties of these relations, plays o relevant role in the Thermodynamics of irreversible processes.

Phenomenological relations between thermodynamical forces and fluxes

In many cases, the dependence of flux J on its conjugated force $\mathcal{F}_k$, experimentally determined, can assume, to a good approximation, a relatively simple form. Let us consider some examples.

a) The *heat flux* is connected to the temperature gradient by the Fourier law:

$$\vec{J}_Q \;=\; -K_{\text{th}}\,\vec{\nabla}T \tag{28.67}$$

where K_{th} is te thermal conductivity. One can easily verify that the relation between the heat flux $\vec{J}_Q = \vec{J}_u$ and the conjugated generalised force$\vec{\nabla}(1/T)$ is

$$\vec{J}_Q \;=\; K_{\text{th}}\,T^2\,\vec{\nabla}\left(\frac{1}{T}\right)\,. \tag{28.68}$$

b) The *matter flux* is connected to the gradient of the concentration c_i (Fick first law) or to the gradient of the chemical potential:

$$\vec{J}_i \;=\; -D\,\vec{\nabla}c_i \;=\; -\frac{D}{\mu_{ii}}\,\vec{\nabla}\mu_i\,, \tag{28.69}$$

where D is the diffusion coefficient and $\mu_{ii} = \partial\mu_i/\partial c_i$.

c) The *flux of electrical charge* is connected to the gradient of the electric potential:

$$\vec{J}_{\rm el} \;=\; -\sigma_{\rm el}\,\vec{\nabla}\phi_{\rm el}\,, \tag{28.70}$$

where $\sigma_{\rm el}$ is the electrical conductivity (don't mistake with σ = entropy production) and $\phi_{\rm el}$ is the electrical potential.

Coupling of non-conjugated fluxes and forces

One finds experimentally that some relations can exist also between non-conjugated fluxes and forces. In those cases, one speaks of coupling between irreversible processes that take place simultaneously. For example:

- In *thermo-electrical* effects an electromotive force is generated at the junction of two metals maintained at different temperatures.
- In *thermo-mechanical* effects, a matter flux is generated in the direction of the pressure gradient as an effect of a temperature gradient.

The study of the couplings between non-conjugated fluxes and forces is one of the main applications of the Thermodynamics of irreversible processes and is treated in Chapter 29.

Purely resistive systems and linear systems

For a number of systems, the values of generalised fluxes at a given time only depend on the values of the generalised forces at the same time. Such systems are said to be "purely resistive", in analogy with purely resistive electrical circuits, where no memory effects, due to capacitance and inductance, are present.

A general expression of the relation between fluxes and forces for purely resistive systems in a state not too far from equilibrium can be given by a series expansion with respect to the equilibrium state (where $\mathcal{F}_i = 0, J_k = 0$):

$$J_k \;=\; \sum_i \left(\frac{\partial J_k}{\partial \mathcal{F}_i}\right)_0 \mathcal{F}_i \;+\; \frac{1}{2}\sum_{ij}\left(\frac{\partial^2 J_k}{\partial \mathcal{F}_i\,\partial \mathcal{F}_j}\right)_0 \mathcal{F}_i\mathcal{F}_j \;+\cdots \tag{28.71}$$

If the state of a system is sufficiently near to the equilibrium state, the expansion (28.71) can be limited to the first order (linear approximation), so that

$$J_k \;=\; \sum\nolimits_i L_{ik}\mathcal{F}_i \tag{28.72}$$

where the factors

$$L_{ik} \;=\; \left(\frac{\partial J_k}{\partial \mathcal{F}_i}\right)_0 \tag{28.73}$$

are called *kinetic coefficients*.

Since a given flux can depend not only on its conjugated force but also on other forces, one distinguishes two types of kinetic coefficients:

1. direct coefficients L_{ii}
2. coupling coefficients $L_{ik} (i \neq k)$

Equations (28.68) , (28.69) and (28.70), concerning heat flux, matter flux and electric charge flux, respectively, hold for purely resistive systems in linear approximation and contain only direct kinetic coefficients.

Chapter 29

Coupled linear processes

In this Chapter we deal with the coupling of linear irreversible processes, already shortly introduced in § 28.4. The coupling of irreversible processes can give rise to some important effects, such as the thermoelectric phenomena. In some cases, the coupling makes possible that in one of the processes the entropy production be negative, provided the negative production be overcome by the positive production in another process, coupled to the first one.

As it was shown in Chapter 28, the local entropy production can be expressed, for continuous systems, by (28.52):

$$\sigma \;=\; \sum\nolimits_k J_k \mathcal{F}_k \,, \tag{29.1}$$

where J_k and $\mathcal{F}_k$ are fluxes and thermodynamical forces, respectively.

For purely resistive systems, in the linear approximation the relation between fluxes and thermodynamical forces is given by (28.72):

$$J_k \;=\; \sum\nolimits_i L_{ik} \mathcal{F}_i \,, \tag{29.2}$$

where the L_{ik} factors are the kinetic coefficients, directed if $i = k$, coupling if $i \neq k$.

In this Chapter we will introduce some constraints imposed on the linear coefficients $L_{ii}(i \neq k)$ and L_{ij} by the Curie pronciple, that concerns the symmetry properties of physical systems (§ 29.1), by the Onsager reciprocal relations (§ 29.2) and by the requirement that the overall entropy production cannot be negative (§ 29.3). The demonstration of the Onsager reciprocal relations, based on the microscopic symmetry of physical laws, is sketched in § 29.4.

The practical example of thermoelectric phenomena is treated in Chapter 28.4.

29.1 Curie principle and its consequences

A first constraint on the relations between fluxes and thermodynamical forces depends on the symmetry properties of the physical systems.

The fluxes J and the thermodynamical forces $\mathcal{F}$ can be classified according to their different character as

- scalars (rank 0 tensors); example: chemical reaction
- vectors (rank 1 tensors); example: transport phenomena
- tensors (rank 2 tensors); example: phenomena connected to viscosity

As in previous chapters, we treat here only scalar and vector fluxes and forces .

In principle, in (29.2) the sum index k can label the single cartesian components of vector forces and fluxes, so that one could expect the possibility of whichever coupling between forces and fluxes, independent of their scalar or vector character.

Actually, symmetry considerations expressed by the Curie principle imply that, at least for isotropic systems, the coupling is possible only between forces and fluxes of the same tensor character (scalar with scalar, vectors with vectors). The local entropy production is thus better expressed by separating the two types of forces and fluxes:

$$\sigma \;=\; \sum\nolimits_i J_i^s\,\mathcal{F}_i^s \;+\; \sum\nolimits_j \vec{J}_j^v \cdot \vec{\mathcal{F}}_j^v\,, \tag{29.3}$$

where the apex s means scalar, the apex v means vector.
For isotropic systems, the phenomenological relations have to be separately expressed for scalar and vector forces and fluxes:

$$J_i^s \;=\; \sum_i L_i^{ss}\,\mathcal{F}_i^s\,, \qquad \vec{J}_j^v \;=\; \sum_j \mathsf{L}_j^{vv}\,\vec{\mathcal{F}}_j^v\,, \tag{29.4}$$

where the kinetic coefficients L^{ss} are scalar quantities and the kinetic coefficients L^{vv} are diagonal tensors of rank two, with equal diagonal elements

$$\mathsf{L}^{vv} \;=\; L^{vv}\mathsf{U}\,, \tag{29.5}$$

where L^{vv} is a scalar quant andity U is the unit tensor.

Demonstration

In 1894, the French physicist Pierre Curie proposed a principle, whose simples formulation is that "the symmetries of the causes of a physical phenomenon must be present in the effects too". In our case, the causes are the thermodynamical forces, the effects are the fluxes.
To simplify the notation, let us consider only a scalar flux J^s nd a vector flux $\vec{J}^v$ connected to a scalar force $\mathcal{F}^s$ and to a vector force $\vec{\mathcal{F}}^v$.
Let us suppose that phenomena of different tensor rank (scalar and vector) could be in any case coupled, so that the phenomenological relations should be

$$\left\{\begin{array}{lclclclcl}
J^s & = & L^{ss}\,\mathcal{F}^s & + & L_x^{sv}\,\mathcal{F}_x^v & + & L_y^{sv}\,\mathcal{F}_y^v & + & L_z^{sv}\,\mathcal{F}_z^v \\
J_x^v & = & L_x^{vs}\,\mathcal{F}^s & + & \mathsf{L}_{xx}^{vv}\,\mathcal{F}_x^v & + & \mathsf{L}_{xy}^{vv}\,\mathcal{F}_y^v & + & \mathsf{L}_{xz}^{vv}\,\mathcal{F}_z^v \\
J_y^v & = & L_y^{vs}\,\mathcal{F}^s & + & \mathsf{L}_{yx}^{vv}\,\mathcal{F}_x^v & + & \mathsf{L}_{yy}^{vv}\,\mathcal{F}_y^v & + & \mathsf{L}_{yz}^{vv}\,\mathcal{F}_z^v \\
J_z^v & = & L_z^{vs}\,\mathcal{F}^s & + & \mathsf{L}_{zx}^{vv}\,\mathcal{F}_x^v & + & \mathsf{L}_{zy}^{vv}\,\mathcal{F}_y^v & + & \mathsf{L}_{zz}^{vv}\,\mathcal{F}_z^v
\end{array}\right. \tag{29.6}$$

where the coefficient L^{ss} is a scalar quantity, the coefficients $\vec{L}^{sv}$ and $\vec{L}^{vs}$ are vectors, and the coefficient L^{vv} is a tensor of rank two.

For an isotropic system, owing to symmetry (Curie principle), the kinetic coefficients must be invariant with respect to the direction of the cartesian axes.
Polar vectors are not invariant with respect to axes inversions, so that the Curie principle is fulfilled only if $\vec{L}^{sv} = \vec{L}^{vs} = 0$, that is the scalar-vector coupling coefficients are zero.
Concerning the vector-vector coupling, the invariance with respect to the axes rotations requires that the L^{vv} tensor be diagonal, with equal diagonal elements.

29.2 Onsager reciprocal relations

A second constraint of the kinetic coefficients is represented by the Onsager relations.
Let the fluxes, both scalar and vector, be connected to the forces, both scalar and vector, by the relations

$$J_k \;=\; \sum\nolimits_i L_{ik}\,\mathcal{F}_i\,, \tag{29.7}$$

where the indices k, i span the cartesian components of fluxes and forces of the same tensor rank.
The reciprocal Onsager relations assert that

- if no magnetic fields are present

$$L_{ik} \;=\; L_{ki} \tag{29.8}$$

- if an external magnetic field $\vec{\mathcal{H}}$ is present

$$L_{ik}(\vec{\mathcal{H}}) \;=\; L_{ki}(-\vec{\mathcal{H}}) \tag{29.9}$$

The reciprocal Onsager relations can be demonstrated on the base of statistical considerations for systems not too far from equilibrium (see below, § 29.4). They are experimentally verified for a larger set of situations, so that one sometimes refers to them as a Fourth Law of Thermodynamics.

Example: thermal conduction

Let us consider the irreversible process of thermal conduction and study the coupling between the different cartesian components of forces and fluxes. The linear relation between the thermodynamical force (the temperature gradient) and the heat flux is

$$J_i \;=\; \sum\nolimits_j \mathsf{L}_{ij}\, \frac{\partial}{\partial x_j}\left(\frac{1}{T}\right), \tag{29.10}$$

where $i, j = 1, 2, 3$ label the three cartesian components of the gradient and flux vectors.

a) For an *isotropic* system, $\mathsf{L}_{ij} = L\mathsf{U}$, where L is a scalar quantity and U is the unit tensor. The flux has the same direction of the force.
The heat flux is connected to the temperature gradient by the relation Il flusso di calore è legato al gradiente di temperatura dalla relazione $\vec{J} = -K_{\text{th}}\vec{\nabla}T$, where K_{th} is the thermal conductivity. As a consequence

$$\vec{J} \;=\; L\,\vec{\nabla}\left(\frac{1}{T}\right) \;=\; -L\,\frac{1}{T^2}\,\vec{\nabla}T \;=\; -K_{\text{th}}\vec{\nabla}T\,, \tag{29.11}$$

so that the kinetic coefficient is $L = K_{\text{th}}T^2$.

b) If the system is *non isotropic*, the flux direction is not necessarily equal to the direction of the thermodynamical force. The thermal conductivity is a now tensor K_{ij}, instead of a scalar quantity. The relation between cartesian components of fluxes and forces is

$$J_i \;=\; \sum\nolimits_j \mathsf{L}_{ij}\, \frac{\partial}{\partial x_j}\left(\frac{1}{T}\right) \;=\; \sum\nolimits_j -\mathsf{L}_{ij}\,\frac{1}{T^2}\,\frac{\partial T}{\partial x_j} \;=\; \sum\nolimits_j -\mathsf{K}_{ij}\,\frac{\partial T}{\partial x_j}\,. \tag{29.12}$$

The Onsager theorem asserts that $\mathsf{L}_{ij} = \mathsf{L}_{ji}$, so that also $\mathsf{K}_{ij} = \mathsf{K}_{ji}$ for each pair of values ij.

29.3 Further constraints on the kinetic coefficients

A third constraint on the kinetic coefficients depends on the requirement that the local entropy production be non negative.
Let us consider two coupled processes; for simplicity let us assume two fluxes and two forces in a one-dimensional system:

$$\begin{cases} J_1 = L_{11}\,\mathcal{F}_1 + L_{12}\,\mathcal{F}_2 \\ J_2 = L_{21}\,\mathcal{F}_1 + L_{22}\,\mathcal{F}_2 \end{cases} \tag{29.13}$$

The local entropy production has to be globally positive for the two coupled processes:

$$\sigma \;=\; \sum\nolimits_k J_k\,\mathcal{F}_k \;=\; L_{11}\,\mathcal{F}_1^2 + (L_{12}+L_{21})\,\mathcal{F}_1\mathcal{F}_2 + L_{22}\,\mathcal{F}_2^2 \;>\; 0\,. \tag{29.14}$$

The sum is thus a positive quadratic form. As a consequence:

- Since $\sigma > 0$ even if $\mathcal{F}_1 = 0$, then $L_{22} > 0$

- Since $\sigma > 0$ even if $\mathcal{F}_2 = 0$, then $L_{11} > 0$
- The determinant of the quadratic form has to be positive, so that

$$L_{12}\, L_{21} < L_{11}\, L_{22}\,. \tag{29.15}$$

Taking into account the Onsager relation $L_{12} = L_{21}$, one has

$$L_{12}^2 < L_{11}\, L_{22} \tag{29.16}$$

(The coupling coefficients L_{12} e L_{21} can be positive or negative).

In the general case of more than two coupled processes, one has

$$L_{ii} > 0\,, \qquad \det[L_{ij}] > 0\,. \tag{29.17}$$

29.4 Statistical demonstration of the Onsager relations

The statistical demonstration of the Onsager relations $L_{ik} = L_{ki}$ is based on the symmetry of the physical laws, at the *microscopic level*, with respect to time inversion.
We will first study the effect of time-inversion symmetry on the unavoidable microscopic fluctuations of extensive quantities in a system in thermodynamical (macroscopic) equilibrium.
We will then liken the decay of a spontaneous fluctuation to an irreversible process in which the thermodynamical forces and the fluxes of extensive quantities are connected by linear phenomenological relations.

29.4.1 Fluctuations and correlation

Let us consider an isolated thermodynamical system and focus our attention on two of its extensive coordinates, X_j and X_k.
In a state of macroscopic equilibrium, fluctuations of the extensive coordinates X_j and X_k take continuously place, caused by their fast transfers between sub-systems of the isolated system.
Let δX_j and δX_k be the instantaneous fluctuations in a given sub-system, that is the deviations of the coordinates X_j and X_k with respect to their average values.
Th average values of the fluctuations are zero,

$$\langle \delta X_j \rangle = 0\,, \quad \langle \delta X_k \rangle = 0\,. \tag{29.18}$$

The average values of the quadratic terms are instead non zero,

$$\langle (\delta X_j)^2 \rangle\,, \quad \langle (\delta X_k)^2 \rangle\,, \quad \langle \delta X_j\, \delta X_k \rangle\,. \tag{29.19}$$

In particular, let us focus our attention on the retarded correlation momenta

$$\langle \delta X_j\, \delta X_k(\tau) \rangle\,, \tag{29.20}$$

that measure the correlation between the fluctuation δX_j at a given time and the fluctuation δX_k at a time retarded by τ.
The symmetry with respect to time inversion requires that

$$\langle \delta X_j\, \delta X_k(\tau) \rangle \;=\; \langle \delta X_j\, \delta X_k(-\tau) \rangle\,, \tag{29.21}$$

that is that

$$\langle \delta X_j\, \delta X_k(\tau) \rangle \;=\; \langle \delta X_j(\tau)\, \delta X_k \rangle\,. \tag{29.22}$$

By subtracting $\langle \delta X_j \delta X_k \rangle$ from both members of (29.22) and dividing the result by τ, one obtains

$$\left\langle \delta X_j\; \frac{\delta X_k(\tau) - \delta X_k}{\tau} \right\rangle \;=\; \left\langle \frac{\delta X_j(\tau) - \delta X_j}{\tau}\; \delta X_k \right\rangle\,. \tag{29.23}$$

For $\tau \to 0$, equation (29.23) becomes

$$\left\langle \delta X_j \, \frac{d(\delta X_k)}{dt} \right\rangle \;=\; \left\langle \frac{d(\delta X_j)}{dt} \, \delta X_k \right\rangle . \tag{29.24}$$

According to (29.24), the moment of correlation between the fluctuation δX_j and the velocity of the fluctuation δX_k is equal to the moment of correlation between the fluctuation δX_k and the velocity of the fluctution δX_j.

29.4.2 Fluctuations and phenomenological laws

Let us now liken the decay of a fluctuation to an irreversible process described by a linear relation between forces and fluxes, so that

$$\frac{d(\delta X_k)}{dt} \;=\; \sum\nolimits_i L_{ki} \, \mathcal{F}_i \, , \qquad \frac{d(\delta X_j)}{dt} \;=\; \sum\nolimits_i L_{ji} \, \mathcal{F}_i \, . \tag{29.25}$$

By inserting equations (29.25) in (29.24) one obtains

$$\sum\nolimits_i L_{ki} \, \langle \delta X_j \, \mathcal{F}_i \rangle \;=\; \sum\nolimits_i L_{ij} \, \langle \mathcal{F}_i \, \delta X_k \rangle \, . \tag{29.26}$$

The statistical fluctuation theory shows that (if magnetic fields are absent) the fluctuation of a thermodynamical force is only correlated to the fluctuation of the conjugated extensive parameter, according to

$$\langle \delta X_j \, \mathcal{F}_i \rangle \;=\; -k_B \, \delta_{ij} \, . \tag{29.27}$$

By inserting (29.27) into (29.26) one obtains the Onsager reciprocal relations.

Note: While the fluctuations of different extensive quantities can be correlated, the thermodynamical forces can be correlated only to the conjugate fluctuations.

Demonstration of (29.27)

Let us consider an isolated system in thermodynamical equilibrium, so that

$$S_0 \;=\; k_B \, \ln \Omega_0 \, . \tag{29.28}$$

A fluctuation δX_k of an extensive quantity X_k gives rise to an entropy reduction

$$\Delta S \;=\; S - S_0 \;=\; k_B \, \ln \frac{\Omega}{\Omega_0} \; < 0 \, . \tag{29.29}$$

The probability of the fluctuation is

$$\mathcal{P}(\delta X_k) \;=\; C \, \frac{\Omega}{\Omega_0} \;=\; C \, \exp(\Delta S / kB) \, , \tag{29.30}$$

where C is a normalisation constant.

1.

Let us consider the entropy variation ΔS due to simultaneous fluctuations of a number of extensive quantities. If the fluctuations are not too large, the entropy variation ΔS can be expanded as

$$\Delta S \;=\; \sum_i \left(\frac{\partial S}{\partial(\delta X_i)} \right)_0 \delta X_i \;+\; \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 S}{\partial(\delta X_i) \partial(\delta X_j)} \right)_0 \delta X_i \, \delta X_j \;+\; \ldots \tag{29.31}$$

The first term on the right of (29.31) is zero (equilibrium condition for isolated systems). Equation (29.31) can thus be re-written, limited to the second order term, as

$$\Delta S \;=\; -\sum_{ij} g_{ij} \, \delta X_i \, \delta X_j \, , \qquad \text{where} \quad g_{ij} = -\frac{1}{2} \left(\frac{\partial^2 S}{\partial(\delta X_i) \partial(\delta X_j)} \right)_0 . \tag{29.32}$$

As a generalisation of (29.30), the probability density of the fluctuation $\delta X_1, \delta X_2, \ldots = \{\delta X_k\}$ can be expressed as

$$\mathcal{P}(\{\delta X_k\}) \;=\; C\;\exp\left(-\frac{1}{k_B}\sum_{ij} g_{ij}\,\delta X_i\,\delta X_j\right)\,. \tag{29.33}$$

2.
The fluctuation δX_i gives rise to a counteracting thermodynamical force

$$\mathcal{F}_i \;=\; \frac{\partial \Delta S}{\partial(\delta X_i)} \;=\; -\sum_j g_{ij}\,\delta X_j \;=\; k_B\,\frac{\partial \ln \mathcal{P}}{\partial(\delta X_i)} \;=\; \frac{k_B}{\mathcal{P}}\,\frac{\partial \mathcal{P}}{\partial(\delta X_i)}\,. \tag{29.34}$$

3.
One can now calculate the average value of the left member of (29.27) by integrating, over the space spanned by by all te fluctuations $\{\delta X_n\}$, the product $\delta X_j\,\mathcal{F}_i$ multiplied by the probability density:

$$\langle \delta X_j \mathcal{F}_i\rangle \;=\; \int\cdots\int \delta X_j\,\mathcal{F}_i\;\mathcal{P}(\{\delta X_n\})\;d(\{\delta X_n\})\,. \tag{29.35}$$

Let us substitute in (29.35) $\mathcal{F}_i$ as expressed by the last member of (29.34),

$$\langle \delta X_j \mathcal{F}_i\rangle \;=\; k_B\int\cdots\int \delta X_j\;\frac{\partial \mathcal{P}}{\partial(\delta X_i)}\;d(\{\delta X_n\})\,, \tag{29.36}$$

and calculate by parts the integral with respect only to the variable δX_j:

$$\begin{aligned}\int \delta X_j\;\frac{\partial \mathcal{P}}{\partial(\delta X_i)}\;d(\delta X_j) \;&=\; |\,\delta X_j\,\mathcal{P}|_{-\infty}^{+\infty} \;-\; \int_{-\infty}^{+\infty} \mathcal{P}\,\frac{\delta X_j}{\delta X_i}\,d(\delta X_j)\\ &=\; 0 \;-\; \delta_{ij}\int_{-\infty}^{+\infty} \mathcal{P}\,d(\delta X_j)\,.\end{aligned} \tag{29.37}$$

By re-inserting the integral in (29.36) one obtains

$$\langle \delta X_j \mathcal{F}_i\rangle \;=\; -k_B\,\delta_{ij}\int\cdots\int \mathcal{P}(\{\delta X_n\})\;d(\{\delta X_n\}) \;=\; -k_B\,\delta_{ij}\,. \tag{29.38}$$

Part VII

Complements and applications

Chapter 30

Kinetic model of ideal gases

Ideal gases (the monatomic ideal gas and the bi- and many-atomic ideal gases) are particularly interesting thermodynamical systems. All real gases, when their density decreases, approach the same ideal behaviour, represented by the simple equation of state $pV = nRT$. It has already been stressed (§ 2.3) that the ideal gas plays a fundamental role in thermometry.

In this chapter, after a short summary of the main thermodynamical properties of ideal gases (§ 30.1), we will present the kinetic model, first introduced by J.K. Maxwell in the middle of the XIX Century, that interprets the thermodynamical properties in terms of microscopic structure at the molecular level. We will separately consider the monatomic ideal gas (§ 30.2) and the many-atomic gases (§ 30.3). The distributions of energy and velocity of the gas molecules will be considered in § 30.4. The chapter is concluded with a short account of the limits of the model (§ 30.5)

A more complete statistical approach to the ideal gas Thermodynamics will be introduced in the next Chapter 31.

30.1 Thermodynamical properties of the ideal gases

For gases, as for all simple substances, the three coordinates pressure p, volume V and temperature T are connected by an equation of state, the thermal equation of state,(§ 2.4).

All real gases, when the pressure decreases and the temperature increases, approach the so-called "ideal gas" behaviour and their thermodynamical coordinates are connected by the same equation of state, called the ideal gas equation of state:

$$pV = nRT = NkT \,, \tag{30.1}$$

where T is the absolute thermodynamical temperature introduced in Chapter 4. In the first equality n is the number of moles, $R \simeq 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is the universal gas constnt. In the second equality, N is the number of moleules, $k \simeq 1.38 \times 10^{-23}$ J/K $\simeq 8.6 \times 10^{-5}$ eV/K is the Boltzmann constant (§ 13.3, § 15.3).

Note: When the ideal gas approximation is not sufficient, the thermodynamical state of real gases is described by more complex equation of state, such as the Van der Waals eqution (24.29) introduced in § 24.5.

30.1.1 Specific heats and internal energy of ideal gases

While the same equation of state (30.1) is valid for all gases, in the low pressure and/or high temperature approximation, other properties can be different for different types of gas, depending on the number of atoms that make up a molecule. It is thus necessary to distinguish the monatomic ideal gas, the biatomic ideal gas, and so on.

Specific heats

Specific heats are particularly important quantities (§ 9.1). For constant-volume and constant-pressure transformations (isochore and isobare, respectively) the molar specific heats of ideal gases, c_v and c_p, respectively, are largely independent of temperature and atomic species, but depend on the number of atoms per molecule. In particular:

	c_v	c_p
Monatomic gas (noble gases, metal vapours ...)	$(3/2)\ R$	$(5/2)\ R$
Biatomic gases (O_2, H_2, N_2, ...)	$(5/2)\ R$	$(7/2)\ R$

Internal energy

One can experimentally verify (for example by studying the free expansion) that the internal energy of ideal gases only depends on temperature: $U = U(T)$. The transformations of ideal gases taking place at constant temperature (isothermal) are thus iso-energetic.

Let us consider an isochoric transformation. Since the volume is constant, the work performed on the system is null; therefore, according to the First Law,

$$dU \;=\; đQ \;=\; n\, c_v\, dT; \qquad\qquad \Delta U \;=\; Q \;=\; n\, c_v\, \Delta T.$$

Since both the temperature T and the internal energy U are function of state, for whichever transformation of an ideal gas

$$dU \;=\; n\, c_v\, dT; \qquad\qquad \Delta U \;=\; n\, c_v\, \Delta T\,.$$

The variation of the internal energy is always connected to the temperature variations through the constant-volume specific heat c_v.

It is worth remembering that the actual form of the $U(T)$ function cannot be deduced by purely thermodynamical considerations.

30.1.2 Thermodynamical transformations of ideal gases

Let us now summarise the characteristics of some transformations of ideal gases from an initial state i to a final state f.

Reversible isochores (V=cost.)

The work made on the system is

$$W \;=\; -\int_i^f p\, dV \;=\; 0\,.$$

According to the First Law the heat absorbed by the system is thus

$$Q \;=\; \Delta U \;=\; n\, c_v\, (T_f - T_i) \;=\; \frac{c_v}{R}\, V\, (p_f - p_i)\,.$$

Reversible isobares (p=cost.)

The work made on the system is

$$W \;=\; -\int_i^f p\, dV \;=\; p\, (V_f - V_i) \;=\; nR\, (T_f - T_i)\,.$$

The heat absorbed by the system is

$$Q \;=\; n\, c_p\, (T_f - T_i)\,.$$

The variation of internal energy is

$$\Delta U \;=\; n\, c_v\, (T_f - T_i)\,.$$

Since $\Delta U = Q + W$, from the previous equations one can easily deduce that the following relation between specific heats holds for ideal gases:

$$c_p \;=\; c_v \;+\; R\,.$$

Reversible isotherms (T=cost.)

The graph of a reversible isotherm of an ideal gas in the pV plane is an equilateral hyperbole $pV = nRT = \text{cost.}$
The work made on the system is

$$W \;=\; -\int_i^f p\, dV \;=\; -nRT \int_i^f \frac{dV}{V} \;=\; -nRT\, \ln\frac{V_f}{V_i} \;=\; -nRT\, \ln\frac{p_i}{p_f}\,.$$

The interna energy doesn't vary, because $\Delta U = nc_v \Delta T = 0$.
As a consequence, the absorbed heat is $Q = -W$.

Reversible adiabats (Q=0)

The variation of internal energy is

$$\Delta U \;=\; n\, c_v\, (T_f - T_i)\,.$$

According to the First Law, since $Q = 0$, the work made on the system is

$$W \;=\; \Delta U \;=\; n\, c_v\, (T_f - T_i)\,.$$

From the First Law,

$$dU \;-\; đW \;=\; 0 \qquad \Rightarrow \qquad n\, c_v\, dT \;+\; p\, dV \;=\; 0\,.$$

By using the equation of state $pV = nR\theta$ one can obtain the equation of the reversible adiabat in the pV plane pV:

$$p\, V^{\gamma} \;=\; \text{cost.} \qquad\qquad \text{where} \qquad \gamma \;=\; \frac{c_p}{c_v}.$$

For monatomic gases $\gamma = 1.67$.
For biatomic gases $\gamma = 1.4$.

Again, by using the equation of state on can verify that, for reversible adiabatic transformations,

$$\theta\, V^{\gamma-1} \;=\; \text{cost.}; \qquad\qquad \theta\, p^{(1-\gamma)/\gamma} \;=\; \text{const.}$$

30.2 Kinetic model for the monatomic ideal gas

The kinetic model, introduced by J.K. Maxwell, allowed the interpretation of the pressure and temperature of the ideal gases in terms of microscopic behaviour, that is of the behaviour at the atomic level.
Let us first consider the model for the monatomic ideal gas. Let us assume, to simplify the calculations, that the gas is contained in a cubic vessel is side ℓ and vlume $V = \ell^3$ (one can demonstrate that this condition is actually not restrictive, and that the conclusions of the calculations hold si for whichever shape of the vessel).
Besides, let the cube edges be parallel to the cartesian axes of the reference system $Oxyz$.

The hypotheses at the base of the model are the following

a) the atoms are punctiform, so that they cannot collide
b) the motion of atoms is continual and chaotic
c) there are no forces of interaction between the atoms
d) the collisions of atoms with the vessel walls are perfectly elastic

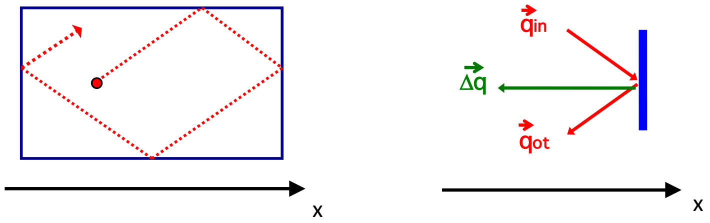


Figure 30.1: A sinistra: traiettoria di un atomo. A destra: variazione della quantità di moto di un atomo a seguito dell'urto elastico con una parete del recipiente.

Pressure

The linear momentum of an atom and its projection along the x axis are, respectively,

$$\vec{q} \;=\; m\,\vec{v}\,; \qquad\qquad q_x \;=\; m\,v_x\,. \tag{30.2}$$

Due to the elastic collision with a wall of the vesses perpendicular to the x axis, the x component of the linear momentum of an atom inverts its sign, $\Delta q_x = -2mv_x$ (Fig. 30.1), and the wall undergoes an impulse of x component

$$J_x \;=\; -\Delta q_x \;=\; 2\,m\,v_x\,. \tag{30.3}$$

The pressure of the gas on the wall is the ratio between the x component of the force F_x and the surface A of the wall, $p = F_x/A$.

The kinetic model explains the pressure as due to the collisions of the atoms with the wall. Let $J_{x,\Delta t}$ be the total impulse exerted on the wall by the collisions in the time interval Δt.

Let us suppose, for the moment, that all atoms have the same velocity v_x. On can then express the pressure as

$$p \;=\; \frac{F}{A} \;=\; \frac{J_{x,\Delta t}}{\Delta t\,A} \;=\; \frac{N_{\rm coll}}{J_x}\Delta t\,A\,. \tag{30.4}$$

The number of collisions $N_{\rm coll}$ in the time interval Δt can be expressed as a function of the velocity v_x

$$N_{\rm coll} \;=\; \frac{v_x\,\Delta t\,A}{V}\,\frac{N}{2}\,, \tag{30.5}$$

where the first factor is the fraction of the total volume adjacent to the wall and of thickness $v_x\,\Delta t$, the second factor $N/2$ is the number of atoms with velocity $v_x > 0$.

By substituting $N_{\rm coll}$ one can find

$$p \;=\; \frac{F}{A} \;=\; \frac{N}{V}\,m\,v_x^2\,. \tag{30.6}$$

Actually, the velocity is not the same for all atoms. The value v_x^2 has to be substituted with the average value $\langle v_x^2\rangle$. Since the three directions x, y, z are equivalent, one can calculate the average value as $\langle v_x^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle = 3v_x^2$, so that

$$p \;=\; \frac{1}{3}\,\frac{N}{V}\,m\,\langle v^2\rangle \;=\; \frac{2}{3}\,\frac{N}{V}\,\langle E_k\rangle \tag{30.7}$$

where $\langle E_k\rangle = m\,\langle v^2\rangle/2$ is the average kinetic energy of atoms.

Temperature and average kinetic energy

Let us now compare the thermal equation of state for the ideal gas with the expression of the pressure calculated aby the kinetic model:

$$pV \;=\; nRT \;=\; NkT \qquad \Leftrightarrow \qquad pV \;=\; \frac{2}{3}\,N\,\langle E_k\rangle \tag{30.8}$$

There is a relation of direct proportionality between temperature and average kinetic energy:

$$\langle E_k\rangle \;=\; \frac{3}{2} k_B\, T\,, \tag{30.9}$$

where N is the number of atoms and k_B is the Boltzmann constant.
Taking into account that the three directions xyz are equivalent, for each one of the directions one has

$$\langle E_{k,x}\rangle \;=\; \frac{1}{3}\langle E_k\rangle \;=\; \frac{1}{2} k_B\, T\,. \tag{30.10}$$

This equation corresponds to the classical principle of *equipartition of energy*: the average energy of a system is equally distributed among all the degrees of freedom. In the present case of the monatomic ideal gas there are three degrees of freedom, corresponding to the three independent quadratic terms that contribute to the total kinetic energy.

30.3 Non-monatomic ideal gases

For the monatomic ideal gas there is a relation of direct proportionality between temperature and average kinetic energy. One could conclude that temperature and energy are two equivalent quantities Actually, this equivalence holds only for the monatomic ideal gas, where the kinetic energy is purely translational.
In non-monatomic gases, the energy can be stored also in rotational and vibrational degrees of freedom of the molecules, and this fact is responsible for the difference of specific heats.
The connection between pressure and collisions on the walls of the vessel holds also for non-monatomic gases. The velocities of the molecules are connected only to the kinetic energy of translation, not to the total energy stored in the molecules.
In non-monatomic gases the temperature is thus proportional only to the translational component of the kinetic energy of the molecules. In classical physics, the principle of equipartition of energy is anyway valid: to each degree of freedom rotational or vibrational of molecules it corresponds an average energy equal to $kT/2$.

30.4 Distribuzioni delle velocità e delle energie

The molecules of a gas in equilibrium at a given temperature and pressure have different velocities.
A fundamental result of the kinetic model for ideal gases is the derivation of the distributions of the velocities and the kinetic energies of the center of mass of the molecules (that have been here already calculated in § 16.4 through a more general statistical approach).
The Maxwell-Boltzmann distribution of the translational energies of the center of mass is given by the probability density of (16.39)

$$f_{E_k}(E_k) = \frac{2\pi}{(\pi kT)^{3/2}}\,\sqrt{E_k}\, e^{-E_k/kT}. \tag{30.11}$$

The distribution of the energies of the center of mass doesn't depend on the type of gas (Fig. 30.2, center).
Let us stress two characteristics of the distribution:

a) when the temperature increases, also the average value $\langle E_k\rangle$ of the distribution increases,
b) when the temperature increases, the distribution broadens.

In addition to the distribution of energies $f_\epsilon(\epsilon)$, it is interesting to consider also the distribution of velocities (16.40):

$$f_v(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{-mv^2/2kT}\,. \tag{30.12}$$

The distribution of velocities depends on the mass, that is on the type of gas (Fig. 30.2,right).

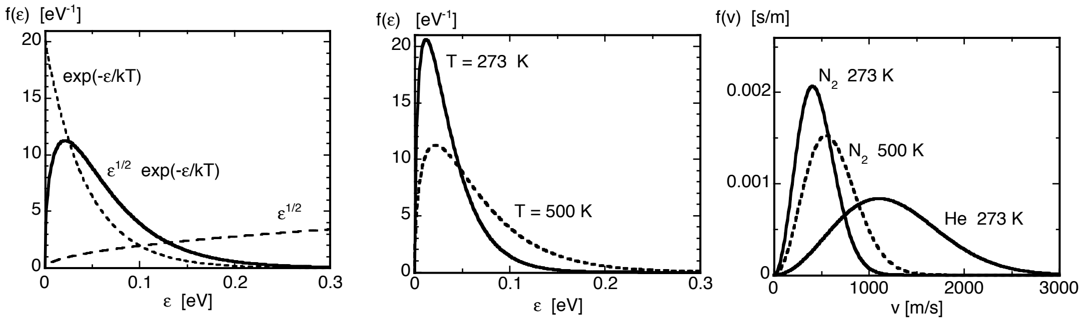


Figure 30.2: Ideal gases (same as Fig. 16.3). Left: comparison among the density of states $\propto \sqrt{\epsilon}$, the exponential factor $\exp(-\beta\epsilon)$ and their product. Center: Maxwell-Boltzmann distribution of the energies for an ideal gas at two different temperatures. Right: Maxwell-Boltzmann distribution of the velocities for different gases at different temperatures.

30.5 Limits of the kinetic model and of the classical approach

The kinetic model is based on a set of approximations, listed at the beginning of § 30.2, and on the classical Mechanics.

In order to explain the behaviour of real gases, it is necessary to take into account the finite sizes of atoms and the forces of interaction between atoms or molecules. The Van der Waals theory (§ 24.5) was devised to this aim and leads to an equation of state more complex than the one of the ideal gas. In particular, owing to the presence of interaction forces between atoms or molecules, the pressure p inside the gas is larger the pressure exerted by the collisions on the walls of the vessel.

The proportionality between the temperature T and the average kinetic energy of translation is based on the thermal equation of state of the ideal gas, and leads to the idea that the temperature is a measure of the thermal motion. The very meaning of temperature is actually more subtle and is better clarified by the statistical theory considered in Part III and by the statistics of magnetic systems considered in Part IV.

Lastly, one should stress the difficulties of the kinetic model in the interpretation of the behaviour of non-monatomic gases, where the energy can be stored also in the rotational and vibrational degrees of freedom of molecules, for whose treatment a quantum approach is necessary and the classical equipartition of energy is not necessarily verified. The quantum approach is conveniently taken into account by the statistical treatment, to which te next Chapter 31 is dedicated.

Chapter 31

Statistics of ideal gases

This chapter is dedicated to the statistics of ideal gases, already shortly introduced in Part III .
We will first consider the statistics of the monatomic ideal gas, in which the energy of the atoms is purely kinetic (§ 31.1) and will give the statistical interpretation of the thermodynamical quantities § 31.2.
We will then, in § 31.3, consider the biatomic gases, in which the vibrational and rotational contributions to the total energy of molecules are present ; the statistical approach will allow us to take into account the quantum aspects of the rotational and vibrational contributions.

31.1 Ideal monatomic gas: statistics

The main characteristics of the monatomic ideal gas, relevant for the statistical approach, are the following.

- The atoms of the monatomic gas are indistinguishable particles; however, the ideal gas approximation corresponds to a dilution sufficiently high that the occupation number of the energy levels be much smaller than their degeneracy, $n_i/g_i \ll 1$; as a consequence, one can resort to the classical limit (§ 16.3), corresponding to the Maxwell-Boltzmann statistics (§ 16.4).
- The atoms of a highly diluted gas are weakly interacting; the connection between the molecular partition function z and the partition function Z of the entire system is thus very simple (§ 16.4); a residual weak interaction is anyway necessary to guarantee the achievement of thermodynamical equilibrium.
- Only the kinetic energy of translation of the atoms has to be taken into account; at the typical temperatures of present interest, the degrees of freedom internal to the atoms (such as the electronic or nuclear ones) cannot be excited.

31.1.1 Quantisation of the kinetic energy

Even within the classical limit, it is convenient to start from the quantisation of the linear momentum $\vec{p} = \hbar\vec{k}$ and of the kinetic energy ϵ of the gas atoms. Let us consider, for simplicity, a cubic vessel of side L. The components of the linear momentum $\vec{p}$ are quantised:

$$p_x = \hbar k_x = \frac{h}{2L}\,n_x\,, \quad p_y = \hbar k_y = \frac{h}{2L}\,n_y\,, \quad p_z = \hbar k_z = \frac{h}{2L}\,n_z\,, \tag{31.1}$$

where n_x, n_y, n_z are non-negative integer numbers. As a consequence, the kinetic energy ϵ is quantised too:

$$\epsilon_x = \frac{p_x^2}{2m} = \frac{h^2}{8mL^2}\,n_x^2 \qquad \epsilon = \frac{p^2}{2m} = \frac{h^2}{8mL^2}\,(n_x^2 + n_y^2 + n_z^2)\,. \tag{31.2}$$

Example: Let us consider one litre of helium, $L = 0.1\,\mathrm{m}$, $m = 6.68 \times 10^{-27}\,\mathrm{kg}$. From the kinetic model of ideal gases one gets $\langle\epsilon_x\rangle = k_BT/2$. For $T = 300\,\mathrm{K}$, $\epsilon_x \simeq 2{\times}10^{-21}$ J $\simeq 1.25{\times}10^{-2}$ eV. In correspondence of the average value $\langle\epsilon_x\rangle$, the integer number $n_x \simeq 1.5{\times}10^{18}$. For heavier gases at the same temperature T, the integer number n_x increases proportionally to $\sqrt{m}$.

The energy levels are very close. I livelli di energia sono estremamente vicini. For Δn_x=1, the energy variation $\Delta\epsilon_x \ll k_BT$ for whichever temperature of practical interest.

31.1.2 Degeneracy of levels

The terns of integer values (n_x, n_y, n_z) represent a lattice of points within the first octant of the three-dimensional cartesian space.
To each energy interval $\epsilon_i \pm d\epsilon_i$ there correspond the points (n_x, n_y, n_z) included within the octant of a spherical shell of radius $R_i \pm dR_i$. Since $R^2 = n_x^2 + n_y^2 + n_z^2$, the kinetic energy values can be expressed as

$$\epsilon_i = \frac{h^2}{8mL^2}\,R_i^2\,. \tag{31.3}$$

The number g' of states whose energy is $\epsilon \le \epsilon'$ is given by the number of points (n_x, n_y, n_z) enclosed by the spherical surface in the positive octant:

$$g' \;=\; \frac{4\pi V(2m\epsilon')^{3/2}}{3h^3}. \tag{31.4}$$

For a diluted gas, typically $n_i \ll g_i$.

Example: Let us again consider a litre of helium gas (L = 0.1 m, T = 300 K); the number of levels whose energy is smaller than the average value$\langle\epsilon\rangle = 3\langle\epsilon_x\rangle = 6{\times}10^{-21}$ J i$g' \simeq 10^{27}$, to be compared with the total number of atoms, $N \simeq 10^{22}$.

31.1.3 Density of states

The energy levels ϵ_i are very close, so that it is convenient to approximate the distribution of discrete values with a continuous distribution

$$\epsilon = \frac{h^2}{8mL^2}\,R^2\,. \tag{31.5}$$

Let us consider a spherical shell of radius R and thickness dR, corresponding to energy values included between ϵ and $\epsilon + d\epsilon$, where

$$d\epsilon = \frac{h^2}{8mL^2}\,2R\,dR. \tag{31.6}$$

The volume of the spherical shell, limited to the first octant, is

$$v = \frac{1}{8}\,4\pi R^2\,dR. \tag{31.7}$$

The number of states included within the shell is equal to the shell volume and is proportional to the thickness $d\epsilon$; it can be expressed as:

$$g(\epsilon)\,d\epsilon = \frac{1}{8}\,4\pi\,R^2\,dR\,, \tag{31.8}$$

where the quantity $g(\epsilon)$ is called *density of states*.
By substituting $R^2 = 8mL^2\epsilon/h^2, dR = \sqrt{2m}\,L\,d\epsilon/h\sqrt{\epsilon}$, one obtains

$$g(\epsilon)\,d\epsilon = \frac{2\pi}{h^3}\,(2m)^{3/2}\,V\,\sqrt{\epsilon}\,d\epsilon. \tag{31.9}$$

The density of states $g(\epsilon)$ increases proportionally to the square root of the energy value ϵ. It is worth noting the difference with the density o states of a macroscopic systems, that increases much more rapidly when the energy increases (§ 15.1).

31.1.4 Molecular partition function

Since $n_i \ll g_i$, one can resort to the Maxwell-Boltzmann statistics for indistinguishable particles at the classical limit (§ 16.4). The energy levels are very close, so that the molecular partition function of (16.23) can be expressed through an integral

$$z \;=\; \sum_i g_i\, e^{-\epsilon_i/kT} \qquad \rightarrow \qquad z \;=\; \int_0^\infty g(\epsilon)\, e^{-\epsilon/kT}\, d\epsilon. \tag{31.10}$$

By substituting the expression of $g(\epsilon)$ from (31.9) in (31.10), one obtains

$$z \;=\; \frac{4\pi V\,(2m)^{3/2}}{h^3} \int_0^\infty \sqrt{\epsilon}\, e^{-\epsilon/kT}\, d\epsilon. \tag{31.11}$$

By substituting $y^2 = \epsilon/kT$, so that $\epsilon = kTy^2$, $d\epsilon = 2kTy\,dy$ and taking advantage of the known value of the integral

$$\int_0^\infty y^2\, e^{-y^2}\, dy \;=\; \frac{\sqrt{\pi}}{4} \tag{31.12}$$

one can obtain the final expression of the molecular partition function for the monatomic ideal gas:

$$z \;=\; \frac{V\,(2\pi mkT)^{3/2}}{h^3}. \tag{31.13}$$

Example: For one litre of helium gas at $T=$ 300 K: $z \simeq 10^{27}$.

Since the atoms are weakly interacting, the partition function Z of the entire system can be connected to the molecular partition function z La funzione di partizione Z del sistema, poiché gli atomi sono debolmente interagenti, può essere collegata alla funzione di partizione molecolare z (31.13) by the relation

$$Z \;=\; \sum_j e^{-E_j/kT} \;=\; \frac{1}{N!}\, z^N\,, \tag{31.14}$$

where the sum is now over all the states j (no more over the levels), so that the degeneracy factor is absent

31.1.5 Energy and velocity distributions

Th distribution of atoms as a function of their kinetic energy is

$$\frac{dn}{d\epsilon} \;=\; \frac{N}{z}\, e^{-\epsilon/kT}\, g(\epsilon)\, d\epsilon \;=\; \frac{2\pi N}{(\pi kT)^{3/2}}\, \sqrt{\epsilon}\, e^{-\epsilon/kT}. \tag{31.15}$$

The probability density that the energy of an atoms be ϵ is

$$f_\epsilon(\epsilon) = \frac{1}{N}\,\frac{dn}{d\epsilon} \;=\; \frac{2\pi}{(\pi kT)^{3/2}}\, \sqrt{\epsilon}\, e^{-\epsilon/kT}. \tag{31.16}$$

The energy distribution depends on temperature, but is independent of mass: actually, the factor $m^{3/2}$ of (31.9) is present in both the numerator, in the expression of $g(\epsilon)$, and in the denominator, in the expression of z. One can easily verify that the average energy value is

$$\langle\epsilon\rangle = \int_0^\infty \epsilon\, f_\epsilon(\epsilon)\, d\epsilon = \frac{3}{2} k_B T\,. \tag{31.17}$$

The statistical theory for the monatomic ideal gas replicates the result of the kinetic model: the average kinetic energy is proportional to the temperature; the proportionality constant is the same too.

The velocity distribution is easily obtained from the energy distribution, because

$$\epsilon = \frac{1}{2} m v^2 \quad \text{and} \quad \frac{dn}{dv} = \frac{dn}{d\epsilon}\,\frac{d\epsilon}{dv} = mv\,\frac{dn}{d\epsilon}. \tag{31.18}$$

By substituting (31.18) in (31.16) one obtains the probability density that the magnitude of the velocity of an atom be v:

$$f_v(v) = \frac{1}{N}\frac{dn}{dv} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{-mv^2/2kT}\,. \tag{31.19}$$

The $f_v(v)$ distribution depends on both the temperature and the mass of toms.

The maximum of the distribution corresponds to the most probable velocity v_{mp}:

$$\frac{df_v}{dv} = 0 \quad \to \quad v_{mp} = \sqrt{\frac{2kT}{m}} \simeq 1.41 \sqrt{\frac{kT}{m}}\,. \tag{31.20}$$

The average velocity $\langle v \rangle$ is easily obtained:

$$\langle v \rangle = \int_0^\infty v\, f_v(v)\, dv \quad \to \quad \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \simeq 1.59 \sqrt{\frac{kT}{m}}\,. \tag{31.21}$$

The mean square velocity $\sqrt{\langle v^2 \rangle}$ is easily obtained too:

$$\langle v^2 \rangle = \int_0^\infty v^2\, f_v(v)\, dv \quad \to \quad \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} \simeq 1.73 \sqrt{\frac{kT}{m}}\,. \tag{31.22}$$

Obviously

$$\langle \epsilon \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T. \tag{31.23}$$

Examples of energy and velocity distributions are shown in Fig. 30.2.

31.2 Ideal monatomic gas: thermodynamical quantities

Let us now see how the main thermodynamical quantities of the monatomic ideal gas can be obtained from the statistical approach, according to the method introduced in Chapter 15.

Internal energy

From (15.36), with $Z = z^N/N!$, one obtains the expression for the internal energy U:

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V = NkT^2 \left(\frac{\partial \ln z}{\partial T}\right)_V = NkT^2 \frac{\partial}{\partial T}\left(\frac{3}{2}\ln T\right)_V = \frac{3}{2} NkT. \tag{31.24}$$

Note: For the monatomic ideal gas only the translational kinetic energy, proportional to T, is taken into account. As already mentioned above, the electronic contribution to the total energy is here not considered since the electronic excitations are of the order of $\Delta\epsilon \simeq 1$ eV, that is much larger than the value of kT at ambient temperature.

Heat capacity

The constant-volume heat capacity is

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{3}{2} Nk. \tag{31.25}$$

Entropy

For the entropy, it is convenient to start from the general expression (15.43) of S as a function of the canonical partition function Z. Since $Z = z^N/N!$ and making use of the Stirling approximation $\ln(N!) \simeq N\ln(N) - N$, one obtains

$$S \;=\; \frac{U}{T} + k\ln Z \;=\; \frac{U}{T} + Nk\ln\frac{z}{N} + kN. \tag{31.26}$$

By substituting in (31.26) the value of U from (31.24) and of z from (31.13), one obtains

$$S \;=\; Nk\ln\frac{V}{N} \;+\; \frac{3}{2}Nk\ln T \;+\; \underbrace{\frac{3}{2}Nk\ln\frac{2\pi mk}{h^3} \;+\; \frac{5}{2}Nk}_{\text{indep. of } V \text{and } T} \tag{31.27}$$

Note: When the temperature is progressively reduced, say for $T \to 0$, all gases become *real*, liquify and possibly solidify. At low temperatures, the partition function Z cannot be approximated by the value for the ideal gas; the expressions of S and U are different from the ones of the ideal gas. In particular, the ideal gas expression (31.27) wouldn't give $S \to 0$ for $T \to 0$.

Pressure and equation of state

From (15.50), substituting $Z = z^N/N$ and the value (31.13) of z, one obtains

$$p \;=\; kT\left(\frac{\partial\ln Z}{\partial V}\right)_T \;=\; NkT\left(\frac{\partial\ln z}{\partial V}\right)_T \;=\; NkT\left(\frac{\partial\ln V}{\partial V}\right)_T \;=\; \frac{NkT}{V}\,. \tag{31.28}$$

The equation of state is thus

$$pV \;=\; NkT \qquad \text{thatis} \qquad pV \;=\; nRT. \tag{31.29}$$

31.3 Ideal bi-atomic gases

Let us now consider bi-atomic gases, whose molecules contain two atoms (for example H_2, O_2, NO, etc.).

Four are the possible contributions to the energy of each molecule (neglecting nuclear contributions): translational, rotational, vibrational and electronic. For each energy level, the energy value is the sum of four contributions:

$$\epsilon \;=\; \epsilon^{tr} + \epsilon^{rot} + \epsilon^{vib} + \epsilon^{el} \tag{31.30}$$

and the degeneracy of each level is the product of four factors

$$g \;=\; g^{tr}\,g^{rot}\,g^{vib}\,g^{el}. \tag{31.31}$$

The typical spacings between the energy levels are

translational	$\Delta\epsilon^{\mathrm{tra}}$	$\simeq 0$		(as for the monatomic gas)
rotational	$\Delta\epsilon^{\mathrm{rot}}$	$\simeq 10^{-3}$	eV	
vibrational	$\Delta\epsilon^{\mathrm{vib}}$	$\simeq 0.1$	eV	
electronic	$\Delta\epsilon^{\mathrm{el}}$	≥ 1	eV	

The translational contribution is treated in the same way as for the monatomic gas.

Again, as for the monatomic gas, the electronic contributions can be neglected, since they can be activated only at temperatures higher than the ones of our interest here.

31.3.1 Classical approach and its inadequacy

Rotational energy

A bi-atomic molecule can rotate around an axis containing its center of mass. The rotation can be described by the angular momentum $\vec{L} = I\vec{\omega}$, where I is the moment of inertia and $\vec{\omega}$ is the angular velocity. The angular momentum $\vec{L}$ can be decomposed along two directions a and b mutually perpendicular and perpendicular to the line joining the two atoms, so that $L^2 = L_a^2 + L_b^2$ (the component along the line joining the two atoms is negligible, since the corresponding moment of inertia is practically null).
The rotational energy is purely kinetic and its value $\epsilon^{\rm rot} = L^2/2I$ can be decomposed as the sum of two equivalent terms $\epsilon^{\rm rot} = L_a^2/2I + L_b^2/2I$.
There are thus two independent rotational degrees of freedom, to each one of whom it corresponds a quadratic contribution to the total energy, $L_a^2/2I$ and $L_b^2/2I$.

Vibrational energy

The vibration takes place along the direction joining the two atoms. Within the harmonic approximation, the energy is the sum of two terms, a kinetic one and a potential one: $\epsilon^{\rm vib} = \mu v^2/2 + \kappa x^2/2$, where μ is the reduced mass, κ is the elastic constant and v is the relative velocity.
Also for vibrations there are thus two quadratic contributions to the energy, one kinetic and the other potential.

Equipartition of energy

According to a fundamental theorem of classical statistics, the total energy of a system is equally distributed among all its quadratic contributions.
For a bi-atomic molecule there are seven quadratic contributions to the energy, three translational, two rotational and two vibrational

$$\epsilon^{\rm tot} = \epsilon^{\rm tra} + \epsilon^{\rm rot} + \epsilon^{\rm vib} = \frac{mv_x^2}{2} + \frac{mv_y^2}{2} + \frac{mv_z^2}{2} + \frac{L_a^2}{2I} + \frac{L_b^2}{2I} + \frac{\mu v^2}{2} + \frac{\kappa x^2}{2} \qquad (31.32)$$

According to the classical equipartition theorem, to each quadratic term of the energy it would correspond a contribution to the internal energy $NkT/2 = nRT/2$, proportional to the temperature (k is the Boltzmann constant, R is the gas constant, N is the number of molecules, n is the number of moles). Actually, for a monatomic gas, where the translational kinetic energy contains three quadratic terms, according to 31.24 the internal energy is $U = 3NkT/2$, in agreement with the classical equipartition of energy.
One should thus expect that for a bi-atomic gas the internal energy U be the sum of seven terms of equal extent, each one proportional to the temperature: $U = 7NkT/2 = 7nRT/2$.

Experimental specific heats

Direct experimental information on the internal energy of a system can be obtained by the measurement of specific heats.
According to the classical equipartition theorem, one would expect that the molar specific heat of a bi-atomic gas by $c_v = 7R/2$.
However, for whichever bi-atomic gas, the experimental behaviour of the specific heat as a function of temperature doesn't agree with the classical equipartition theorem. As an example, Fig.31.1 shows the specific heat of molecular H_2 as a function of the temperature.
Only for very high temperatures the value of the specific heat is the one expected according to the equipartition theorem, that is $c_v = 7R/2$. At low temperatures $c_v = 3R/2$ and at intermediate temperatures $c_v = 5R/2$.
This behaviour is common to all bi-atomic gases, even if for different temperature intervals.
The discrepancy between the experimental values of the specific heats of bi-atomic gases and the expectations of the equipartition theorem is due to the inadequacy of the classical statistical

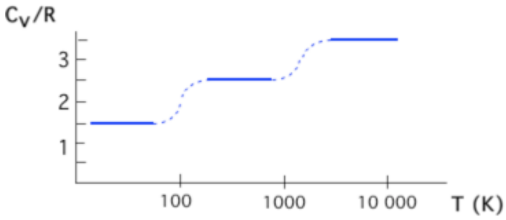


Figure 31.1: Constant-volume specific heat, divided by R, of the molecular hydrogen H_2 as a function of the temperature. Notice the logarithmic scale of the temperature axis.

approach. The experimental behaviour of the temperature dependence of the specific heats of bi-atomic gases (as well as of many-atomic gases and of crystals) could be satisfactorily explained only after the advent of the quantum mechanics. Actually, the peculiar behaviour of the specific heats is due to the quantisation of the rotational and vibrational energy levels, as is shown below.

31.3.2 Quantum approach

The gas molecules are indistinguishable particles. As already stated above, for an ideal gas one can resort to the approximation for indistinguishable particles at the classical limit (§ 16.4).
The molecular partition function is the product of the partition functions corresponding to the three contributions, translational, rotational and vibrational:

$$z \;=\; z^{\rm tra}\, z^{\rm rot}\, z^{\rm vib} \;=\; \left(\sum_i g_i^{\rm tra}\, e^{-\epsilon_i^{\rm tra}/kT}\right)\left(\sum_J g_J^{\rm rot}\, e^{-\epsilon_J^{\rm rot}/kT}\right)\left(\sum_s g_s^{\rm vib}\, e^{-\epsilon_s^{\rm vib}/kT}\right). \qquad (31.33)$$

One has seen above that, for the translational motion in a diluted gas, $n_i \ll g_i$. Even more so for the rotational and vibrational contributions, so that $n_i \ll g^{\rm tra}\, g^{\rm rot}\, g^{\rm el}$.

Below we will deal with the rotational and vibrational contributions, for which the quantum approach is necessary. The translational contribution to the total energy and to the specific heat is anyway shown, for comparison, in the left graphs of Fig. 31.3.

Rotational energy

Starting point is the expression of the rotational kinetic energy $\epsilon^{\rm rot} = L^2/2I$, where L is the magnitude of the angular momentum and I is the moment of inertia with respect to the rotation axis.
The quantisation of the squared magnitude of the angular momentum, L^2, entails the quantisation of the rotational energy, according to the expression

$$\epsilon_J^{\rm rot} \;=\; \frac{L^2}{2I} \;=\; \frac{\hbar^2 J(J+1)}{2I} \;=\; J(J+1)\,\theta_r\,k, \qquad (J=0,1,2,\ldots) \qquad (31.34)$$

where J is a non-negative integer number called azimuthal quantum number, k is the Boltzmann constant and

$$\theta_r \;=\; \frac{\hbar}{2kI} \qquad (31.35)$$

is the *characteristic rotational temperature*, inversely proportional to the moment of inertia I.
The energy of the lowest level, corresponding to $J=0$, is $\epsilon_0^{\rm rot} = 0$. The distance between neighbouring levels linearly increases when the quantum number J increases. The levels of rotational energy for molecular hydrogen H_2 and for molecular oxygen O_2 are compared in Fig. 31.2. The distance between neighbouring levels is much larger for hydrogen than for oxygen.
The rotational levels are degenerate; the degeneracy of the J-th level is

$$g_J^{\rm rot} \;=\; 2J+1. \qquad (31.36)$$

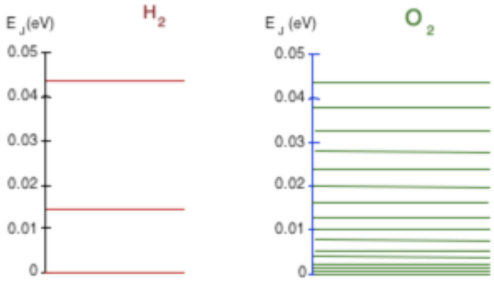


Figure 31.2: Rotational energy levels for the molecules of hydrogen (left) and oxygen (right).

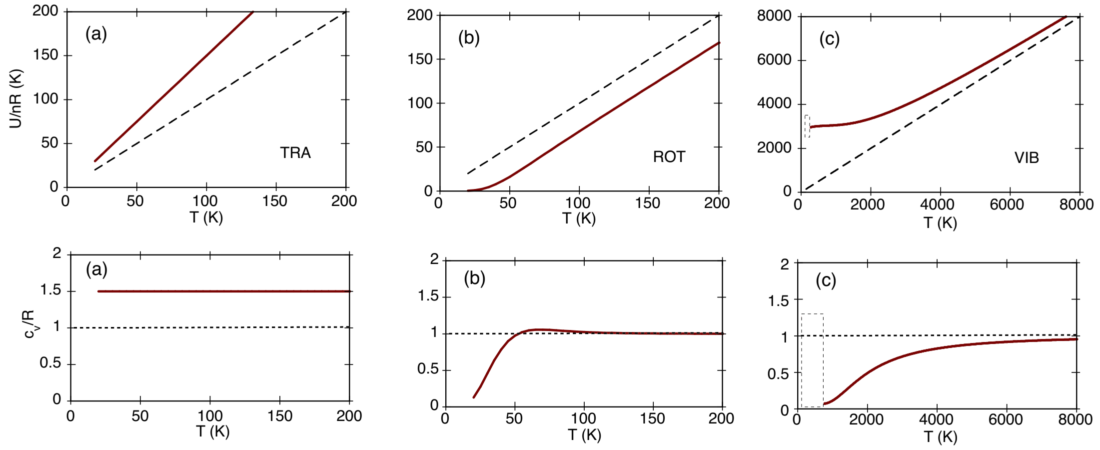


Figure 31.3: Continuous lines: contributions to the reduced internal energy U/nR (top) and to the reduced molar specific heat c_v/R (bottom) of a bi-atomic molecule due to translation (left), rotation (center) e vibrational (right). The particular case for which θ_r=85.5 K and θ_v= 6140 K (as for molecular hydrogen) has been considered. The dashed lines correspond to $U = nRT$ and $c_v = nR$. Notice the different scales of the axes.

The rotational **partition function** is thus

$$z^{\text{rot}} \;=\; \sum_{J=0}^{\infty} g_J^{\text{rot}}\, e^{-\epsilon_J^{\text{rot}}/kT} \;=\; \sum_{J=0}^{\infty} (2J+1)\, e^{-J(J+1)\theta_r/T} . \tag{31.37}$$

The weight of the different terms of the sum is given by the ratio θ_r/T in the exponential factors. If the temperature T is much lower than the rotation characteristic temperature θ_r, the value of the exponentials is negligible for any value $J > 0$. When the temperature T increases, the rotational levels are progressively populated, starting from the levels with the smallest J values. According to the Maxwell-Boltzmann distribution (16.24), the population of the level with quantum number J,

$$n_J^{\text{rot}} \;=\; \frac{N}{z^{\text{rot}}}\,(2J+1)\,\exp\left[-\frac{\hbar^2 J(J+1)}{2IkT}\right] \;=\; \frac{N}{z^{\text{rot}}}\,(2J+1)\,\exp\left[-\frac{J(J+1)\,\theta_r}{T}\right] , \tag{31.38}$$

increases when the temperature T increases.
To rotational contribution to the **internal energy** can be calculated from (16.41),

$$U^{rot} \;=\; NkT^2\,\frac{d}{dT}\left(\ln z^{\text{rot}}\right) , \tag{31.39}$$

by introducing the values of the rotational partition function given by (31.37). The rotational energy as a function of temperature for θ_r=85.5 K is shown in Fig. 31.3, top center: at low temperature, the rotational levels are not populated and the rotational energy is smaller that the one expected from the classical equipartition theorem (dashed line). When the temperature increases, the slope of the curve approaches the classical behaviour. Correspondingly, the molar specific heat (Fig. 31.3, center bottom) attains the classical value $c_v = R$ only at sufficiently high temperatures.

The classical limit of the quantum behaviour at high temperatures can be explained as follows. When $T \gg \theta_r$ (classical limit), an exceedingly large number of levels are occupied and the sum in (31.37) extends to very large values of J, so that $2J+1 \simeq 2J$ and $J(J+1) \simeq J^2$; the sum over the J values can be approximated by the integral

$$z^{rot} \;=\; \int_{J=0}^{\infty} 2J\, e^{-\theta_r J^2/T}\, dJ \;=\; \frac{T}{\theta_r}\,. \tag{31.40}$$

Within the approximation (31.40), the limit of the rotational energy is given by

$$U^{rot} \;=\; NkT^2\,\frac{d}{dT}\left(\ln z^{\text{rot}}\right) \;\xrightarrow[T\gg\theta_r]{}\; NkT\,. \tag{31.41}$$

Examples: The characteristics rotational temperatures θ_r of some gases are: for H_2, θ_r=85.5 K; for CO, θ_r= 2.77 K; for O_2, θ_r=2.09 K.
For CO and O_2, the θ_r temperature is much lower than the ambient temperature, so that at the ambient temperature the classical limit is verified, $U^{\text{rot}} = NkT$, $U = U^{\text{rot}} + U^{\text{tra}} = 5NkT/2$ and $c_v/R = 5/2$.
On the contrary, for hydrogen θ_r is of the same order of the ambient temperature 300 K: therefore, at 300 K the behaviour of hydrogen is not classical, the rotational contributions to the internal energy and to the specific heat is smaller than the one expected according to the classical theory (Fig. 31.1).

Note: The behaviour shown in Fig. 31.3, center column, has been calculated from (31.38) and (31.39) assuming θ_r=85.5 K, which is the rotational temperature of moleular hydrogen. Actually, the real behaviour of molecular hydrogen is slightly different, for the following reason. The hydrogen molecule has two distinct forms, depending on the relative orientation of the nuclear spins of the two atoms: 25% of the molecules are para-hydrogen (anti-parallel spins, singlet state) and 75% are orto-hydrogen (parallel spins, triplet state). To fulfil the requirements of wave-functions symmetry, in the sum (31.37) of the rotational partition function, only odd values of j have to be considered for orto-hydrogen, only even values for para-hydrogen.

Vibrational energy

In the quantum mechanical approach, one cannot distinguish the kinetic and potential contributions to the vibrational energy, as a consequence of the uncertainty principle. Fro a harmonic oscillator of angular frequency $\omega = 2\pi\nu$ the quantised vibrational energy is expressed as

$$\epsilon_s \;=\; \left(s+\frac{1}{2}\right)\hbar\omega \;=\; \left(s+\frac{1}{2}\right)\theta_v k \tag{31.42}$$

where s is a non-negative integer number and

$$\theta_v \;=\; \frac{\hbar\omega}{k} \tag{31.43}$$

is the *vibrational characteristic temperature.*
The levels of vibrational energy are equally spaced and non degenerated.
The **vibrational partition function** is

$$z^{\text{vib}} \;=\; \sum_{s=0}^{\infty} e^{-(s+1/2)\theta_v/T} \;=\; e^{-\theta_v/2T}\sum_s e^{-s\theta_v/T} \;=\; \frac{e^{-\theta_v/2T}}{1-e^{-\theta_v/T}}\,. \tag{31.44}$$

(In the last equality one has taken into account that $\sum_s x^s = 1/(1-x)$, where here $x = \exp(-\theta_v/T) < 1$.)

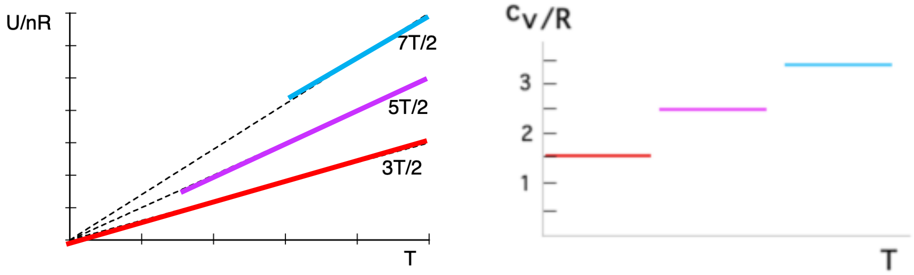


Figure 31.4: Schematic representation of the behaviour of the internal energy (left) and of the specific heat (right) for an ideal bi-atomic gas.

According to the Maxwell-Boltzmann distribution (16.24), the population of the level with quantum number s is

$$n_s^{vib} = \frac{N}{z^{vib}}\, e^{-(s+1/2)\theta_v/T} = \frac{N}{z^{vib}}\, e^{-(s+1/2)\theta_v/T}. \tag{31.45}$$

The vibrational contribution to the **internal energy** is

$$U^{vib} = NkT^2 \frac{d}{dT}\left(\ln z^{vib}\right) = kN\theta_v \left[\frac{1}{2} + \frac{1}{e^{\theta_v/T}-1}\right] \tag{31.46}$$

where the first term $kN\theta_v/2$ is the *zero point energy*, that, being independent of temperaure, doesn't contribute to the specific heat (Fig. 31.3, right).
Because of the energy quantisation, the percent contribution of the vibrational energy to the total internal energy progressively increases when the temperature increases.
Only at sufficiently high temperatures, that is for $T \gg \theta_v$, the following approximation holds,

$$U^{vib} = kN\theta_v \left[\frac{1}{2} + \left(e^{\theta_v/T}-1\right)^{-1}\right] \simeq kN\theta_v \left[\frac{1}{2} + \left(1+\frac{\theta_v}{T}+\frac{\theta_v^2}{2T^2}-1\right)^{-1})\right] \tag{31.47}$$

$$\simeq Nk\theta_v \left[\frac{1}{2} + \frac{T}{\theta_v}\left(1+\frac{\theta_v}{2T}\right)^{-1}\right] \simeq Nk\theta_v \left[\frac{1}{2} + \frac{T}{\theta_v}\left(1-\frac{\theta_v}{2T}\right)\right] = NkT \tag{31.48}$$

and the classical result of the equipartition theorem is recovered.

Examples: The characteritstics vibrational temperatures of some gases are: for H_2, θ_v= 6140 K; for Cl_2, θ_v= 810 K; for Na_2, θ_v= 230 K. The characteristics vibrational temperatures are generally much higher than the ambient temperature, Le temperature caratteristiche di vibrazione sono generalmente molto maggiori della temperatura ambiente, so the vibrational levels are not excited at the ambient temperature and don't contribute to the specific heat (Fig. 31.1).

31.3.3 Internal energy and specific heat of bi-atomic gases

The results obtained above are schematised in Fig. 31.4, where the three contributions, translational, rotational and vibrational to the total internal energy and to the specific heat are plotted as a function of temperature.
At low temperatures, only the translational energy is relevant; at intermediate temperatures the rotational contribution adds on; at high temperatures the vibrtional contribution adds on. A bassa temperatura contribuisce solo l'energia traslazionale, a temperature intermedie si aggiunge l'energia rotazionale, ad alte energie si aggiunge l'energia vibrazionale.
The direct proportionality between internal energy U and temperature T, that is verified for the monatomic ideal gas, doesn't hold for other gases and for other systems. Internal energy and temperature are not equivalent thermodynamical quantities.

Part VIII

Appendices

Chapter 32

Tables

32.1 Greek alphabet

Table 32.1: The Greek alphabet

Name	*Lower-case*	*Uppe-rcase*	*Name*	*Lower-case*	*Uppe-rcase*
Alfa	α	A	Ni (nu)	ν	N
Beta	β	B	Xi	ξ	$\mathit{\Xi}$
Gamma	γ	$\mathit{\Gamma}$	Omicron	o	O
Delta	δ	$\mathit{\Delta}$	Pi	π	$\mathit{\Pi}$
Epsilon	ϵ, ε	E	Rho	ρ	P
Zeta	ζ	Z	Sigma	σ	$\mathit{\Sigma}$
Eta	η	H	Tau	τ	T
Theta	θ, ϑ	$\mathit{\Theta}$	Upsilon	υ	$\mathit{\Upsilon}$
Iota	ι	I	Phi	ϕ	$\mathit{\Phi}$
Kappa	κ	K	Chi	χ	X
Lambda	λ	$\mathit{\Lambda}$	Psi	ψ	$\mathit{\Psi}$
Mi (mu)	μ	M	Omega	ω	$\mathit{\Omega}$

32.2 Constants of Physics

The fundamental constants of Physics are measure in different laboratories by different techniques. An international committee, the CODATA (Committee on Data for Science and Technology), periodically gathers and compares the results obtained by the different laboratories. The values of some fundamental constants, taken from the CODATA compilation of 2018, are listed in Table 32.2.

The values of the first seven constants since May 2019 are assumed as exact and represent the defining constants of the International System of units (SI). The uncertainties of the other constants are expressed in a form particularly suited to very accurate measures. The significant digits that represent the uncertainty δX (typically two digits) are contained in parentheses after the central value; for example esempio,

$$m_e = 9.109\,383\,7015(28)\times 10^{-31}\,\text{kg}$$

means

$$m_e = (9.109\,383\,7015 \pm 0.000\,000\,0028)\times\ 10^{-31}\,\text{kg}.$$

The complete list of fundamental constants can be found in the website of NIST, at the address `https://pml.nist.gov/cuu/Constants/`.

Approximate values of some quantities relevant for Thermodynamics are listed in Table 32.2 .

Table 32.2: Values of some constants of Physics

Constant	*Symbol*	*Value*	*Unit*
Frequency of the hyperfine d ^{133}Cs transition	$\Delta\nu_{Cs}$	$9\,192\,631\,770$	Hz
Velocity of light in vacuum	c	$299\,792\,458$	m s^{-1}
Planck constant	h	$6.626\,070\,15\times10^{-34}$	J s
Elementary charge	e	$1.602\,176\,634\times10^{-19}$	C
Boltzmann constant	k_B	$1.380\,649\times10^{-23}$	J K^{-1}
Avogadro constant	N_A	$6.022\,140\,76\times10^{23}$	mol^{-1}
Luminous efficacy	K_{cd}	683	lm W^{-1}
Vacuum permeability	μ_0	$4\pi\cdot10^{-7}$	H m^{-1}
Vacuum permittivity	$\epsilon_0 = 1/\mu_0 c^2$	$8.854\,187\,817...\cdot10^{-12}$	F m^{-1}
Gravitational constant	G	$6.674\,30(15)\cdot10^{-11}$	m^{3}kg^{-1}s^{-2}
Electron mass	m_e	$9.109\,383\,7015(28)\cdot10^{-31}$	kg
Proton mass	m_p	$1.672\,621\,923\,69(51)\cdot10^{-27}$	kg
Neutron mass	m_n	$1.674\,927\,498\,04(95)\cdot10^{-27}$	kg
Atomic mass unit	u	$1.660\,539\,066\,60(50)\cdot10^{-27}$	kg
Fine structure constant	α	$7.297\,352\,5693(11)\cdot10^{-3}$	
Rydberg constant	R_∞	$10\,973\,731.568\,160(21)$	m^{-1}
Bohr radius	a_0	$0.529\,177\,210\,903(80)\cdot10^{-10}$	m
Bohr magneton	μ_B	$9.274\,010\,0783(28)\cdot10^{-24}$	J T^{-1}
Nuclear magneton	μ_N	$5.050\,783\,17(20)\cdot10^{-27}$	J T^{-1}
Gas constant	$R = N_A\,k_B$	$8.314\,462\,618...$	J mol^{-1} K^{-1}

Table 32.3: Approximate values of some quantities relevant for Thermodynamics

Quantity	*Symbol*	*Value*	*Unit*
Elettronvolt	eV	$1.602\cdot10^{-19}$	J
Planck constant	h	$6.626\cdot10^{-34}$	J s
		$4.136\cdot10^{-15}$	eV s
Reduced Planck constant	$\hbar = h/2\pi$	$1.055\cdot10^{-34}$	J s
		$6.583\cdot10^{-16}$	eV s
Atomic mass unit	u	$1.660\cdot10^{-27}$	kg
Avogadro number	N_A	$6.022\cdot10^{23}$	mol^{-1}
Gas constant	R	8.314	J mol^{-1} K^{-1}
Boltzmann constant	k_B	$1.381\cdot10^{-23}$	J K^{-1}
		$8.617\cdot10^{-5}$	eV K^{-1}

32.3 Temperature scales

Table 32.4: Most important temperature scales

		Absolute zero	*Ice melting* (at 1 bar)	*Water boiling* (at 1 bar)	*Notes*
Centigrade scales	Celsius	-273.15	0	100	
	Kelvin	0	273.15	373.15	
Other scales	Fahrenheit	-459.67	32	212	(1)
	Rankine	0	491.67	671.67	(2)
	Réaumur	-218.52	0	89	(3)

(1) The Fahrenheit scale, still in use in Anglo-Saxon countries, was first proposed in 1724 by the physicist Gabriel Fahrenheit (Dantzig 1686 - the Hague 1736). Born in Poland, Fahrenheit worked in U.K. and in Holland; in 1714 he built the first mercury thermometer.
The Fahrenheit scale (symbol °F) assigns the values 32 °F to the ice melting point at atmospheric pressure and 212 °F to the water boiling point at atmospheric pressure. The interval between the two values is thus 180 °F.

(2) The Rankine scale, proposed around 1860 by the Scottish physicist W.J. Rankine and no longer in use, is an absolute scale referred to the Fahrenheit scale (as the absolute Kelvin is referred to the Celsius scale).

(3) The Réaumur scale was proposed in 1732 by the French physicist R. A. Ferachault de Réaumur.

Table 32.5: Conversions between different scales

Fahrenheit → Celsius	T [°C] = 5 T[°F]/9 - 17.78
Fahrenheit → Kelvins	T [K] = 5 T[°F]/9 + 255.37
Celsius → Fahrenheit	T [°F] = 9 T[°C]/5 + 32
Kelvin → Fahrenheit	T [°F] = 9 T[K]/5 - 459.6

Chapter 33

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