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Antonio Saggion Rossella Faraldo Matteo Pierno

# Thermodynamics 

Fundamental Principles and Applications

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## Thermodynamics

Fundamental Principles and Applications

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[^0]> Antonio Saggion dedicates his contribution to the memory of Nicolo Dallaporta, former Professor of Theoretical Physics of the University of Padova and renowned scientist.

## Preface

In order to explain what pushed us to write this book on thermodynamics, and to help the reader understand how to approach it, it seems appropriate to begin with the following quote:

In November 1919, the London Times published an article by A. Einstein entitled "My Theory." We have copied here a section of the article:

There are several kinds of theory in physics. Most of them are constructive. These attempt to build a picture of complex phenomena out of some relatively simple proposition. The kinetic theory of gases, for instance, attempts to refer to molecular movement the mechanical, thermal, and diffusional properties of gases. When we say that we understand a group of natural phenomena, we mean that we have found a constructive theory which embraces them.

But in addition to this most weighty group of theories, there is another group consisting of what I call theories of principle. These employ the analytic, not the synthetic method. Their starting point and foundation are not hypothetical constituents, but empirically observed general properties of phenomena, principles from which mathematical formulae are deduced of such a kind that they apply to every case which presents itself. Thermodynamics, for instance, starting from the fact that perpetual motion never occurs in ordinary experience, attempts to deduce from this, by analytic processes, a theory which will apply in every case. The merit of constructive theories is their comprehensiveness, adaptability, and clarity; that of the theories of principle, their logical perfection, and the security of their foundation.

Along with special relativity, thermodynamics is a theory of principle, according to Einstein's categorization. This means that it is a theory based upon a universally accepted assumption, starting from which the analytic method is used to deduce constraints or correlations within all natural phenomena. As with relativity, its fundamental property consists in generality.

Other macroscopic theories such as mechanics or electromagnetism bring together many experimental observations in an abstract mathematical formulation. This allows for precise predictions, which, however, are constrained to the field of phenomena within which they were synthesized.

Thermodynamics is also based on an abstract mathematical formulation, but this produces two types of results: inequalities and general relations between quantities which appear independent from each other at first sight. This is why thermodynamics is so often carried out by engineers and is so important for biologists.

Another very important aspect, which symbolizes the cultural choices made in this work, regards the connection with statistical mechanics. It is often believed that, for example, the concept of temperature is, essentially, absorbed within "preexisting" concepts in mechanics, like that of kinetic energy in its various forms. In these cases, there may be the conviction that, after the "discovery of atoms," mechanics, developing an opportune probabilistic language, can make thermodynamics obsolete, as happened for optics, which had its "own laws" and ended up becoming a chapter of electromagnetism.

In the previous quote, Einstein brings the problem clearly into focus: Kinetic theory (and statistical mechanics) represents an attempt to attribute some so-called thermal phenomena to the movement of molecules. This reductionist attitude can provide results which may agree, more or less, with observations but cannot represent a "true" law in the sense to which Einstein refers:

> The example I saw before me was thermodynamics. The general principle was there given in the statement: the laws of nature are such that it is impossible to construct a perpetuum mobile.

For these reasons, thinking about our students, it seemed necessary to us to highlight the distinction between the two areas: that of thermodynamics and that of statistical mechanics. Differently from the choices made in many of the more recent treatises, in which the two aspects are mixed, partly for reasons of didactical completeness and partly to show how the two aspects support each other reciprocally, in this work we have avoided referring, even if only to make analogies, to kinetic theories (or of statistical mechanics in general). The work on thermomechanical effects in Part III is no exception to this. The relations obtained with the general methods of thermodynamics of irreversible processes have been covered again in the Knudsen gas case using a classic mechanical-statistical modeling tool. This is a very informative comparison which provides a "hands-on approach" to understanding the amount of particular hypotheses that need to be satisfied in order to obtain the same result.

Thermodynamics nowadays is based upon a set of concepts and on the choice of a mathematical structure which has undergone significant evolutions, starting from the first theorizations of the second half of the nineteenth century but despite this, the conceptual and formal original structure is often maintained. Examples of this are the persistence of the calorimeter definition of "heat" and the establishment of the second law according to the original formulation of Lord Kelvin or R. Clausius. The first example (which risks keeping alive the old idea of "caloric,"
meaning a fluid that flows from one body to another) faces the student with two substantial difficulties bordering on real conceptual errors. On the one hand, the concept of heat is persistently associated with variations in temperature ${ }^{1}$; on the other hand, it creates the necessity to "demonstrate" the heat-work equivalence (which further reinforces the idea of caloric) in order to then "demonstrate" that energy is a function of state.

Commenting on the second example (the Second Principle) is more demanding. One arrives at the concept of entropy, which is the theorization, meaning the translation into a mathematical form, of the fundamental postulate on the impossibility of perpetual motion, after a long, strenuous and mathematically questionable process.

Whatever the solution of the first and second principles, their formulation is always dependent on the definition of the amount of heat transferred in an interaction. This represents a limitation that has to be overcome, and this can only be obtained through further postulation. The problem lies in the fact that the concept of the amount of heat transferred only makes sense for closed systems, meaning systems which do not exchange mass, therefore leaving out all of those systems (open systems) which are of primary interest to biology and to applications in engineering. This further step is carried out by generalizing the relation between energy and entropy, that the first and second principles indicated as for closed systems.

The final postulation, which brings everything together, consists in establishing, for every macroscopic system, the existence of the so-called Fundamental Relation.

This contains all of the properties of a macroscopic system: the conditions of stability (i.e., of observability) of states of equilibrium and the responses that the system provide to any external perturbation. All the thermomechanical properties of materials can be expressed with partial derivatives of the Fundamental Relation of that material. The fact that these relations are verified by experimental observation allows us to understand that the existence of this relation expresses that value of generality as Einstein sees it, and therefore has that characteristic of "true," meaning not linked to modelings.

In conclusion, together with the formulation of the first law, which defines energy and postulates its conservation, the existence and the geometric properties of the Fundamental Relation constitute the complete and all-inclusive formulation of the postulate "according to which perpetual motion is impossible." The Fundamental Relation and its differential expression (which is sometimes called the Fundamental Equation) also constitute the starting point for the study of the dynamics of irreversible processes. It is from this differential expression that the "forms" of the flows describing the dynamics of the processes in action, and of the forces which put these processes into motion, are identified.

[^1]
## Outline of This work

- Part I is dedicated to the fundamental principles that, as in Feynman's methodological approach, we can call the "Toolbox." In conformity with Einstein's statement, the student will focus on "... the principles that give rise to mathematically formulated criteria" which will be used to expand their knowledge of natural phenomena. Knowledge of nature will be reflected in complete and clear descriptions based on the certainty of foundations.
- The First Principle is expressed according to M. Born's formulation given in 1921 in an article published in Physikalische Zeitschrift 22(21), 224. The most relevant part of this approach is his definition of amount of heat as an all-inclusive amount which sums up the energy transferred to the system by all the interactions not controlled by the observer. The Second Principle consists in the definition of entropy. There are various excellent formulations, but we have chosen that adopted by E. A. Guggenheim in his celebrated treatise on thermodynamics first published in 1949. In this formulation, entropy and temperature are defined as two fundamental, complementary quantities (as in other formulations), but the core point consists in the separation of the variation in entropy, in any infinitesimal process, into the sum of two contributions: one due to the processes which occur within the system and one due to the interaction with the outside. This subdivision into two contributions, which has to be done for the variation of any extensive quantity, is of fundamental importance because it clearly shows the role of the interactions in the transfer of entropy from the outside world. This choice will prove to have been very advantageous when studying irreversible processes: The contributions from interactions with the outside will make up the flows whose dynamics constitute our description of the processes underway. In Part I, we have also included a chapter on Maxwell's relations. The reason for situating this topic, which would appear to be more technical, in the part dedicated to fundamental principles lies in the need to show how knowledge of the Fundamental Relation is equivalent to the knowledge (in general, it will be a knowledge gained from experimental measures) of the coefficients of compressibility, of thermal expansion, and of a specific heat of the system under consideration.
- In Part II, named "Applications," we apply the fundamental principles to a series of generalized situations which are frequently to be found. The various topics are listed in the index, but two of them may be highlighted. One concerns the particular attention devoted to the law of corresponding states, a topic which, in our opinion, should always form part of the specific training. The other concerns the relation between radiation, relativity and thermodynamics; it contains a summary of the route by which Planck was able to extract the correct expression of spectral density of radiation in thermal equilibrium and which peaked in his famous article at the end of 1900 . The reason for this choice is that we consider it necessary to remember the fundamental role thermodynamics had in obtaining
the result which provided him with a Nobel Prize and all of us with one fundamental step in the advancement of knowledge.
- Part III is dedicated to the study of configurations outside equilibrium and of the dynamics of natural processes. We have kept separate in this work the case of discontinuous systems, that is the case of those configurations that are formed by systems each in internal equilibrium but not in equilibrium among themselves, from the case of continuous systems, meaning those configurations in which the intensive state variables can be considered continuous functions of the coordinates. While for the discontinuous systems the starting point will be the fundamental equation valid for states of equilibrium, the case of continuous systems requires, to some extent, a reformulation of the thermodynamic equations within this new light. Throughout all this Part, the centrality of the production of entropy (which measures the speed with which the processes make entropy increase) emerges as the physical quantity which governs the dynamics of the processes. It is invariant with respect to the different descriptions the observer may opt for, and it enables the identification of the generalized forces which determine the establishment of the flows and the study of the interference between different processes. Due attention is reserved for the study of stationary states and the role the production of entropy has in establishing the evolution criteria toward stationary states. In this context, the principles due to Le Chatelier and to Le Chatelier-Braun, still used both in physics and in chemistry, find their explanation.
- In Part IV, the L. Szilard's version of the Maxwell paradox is discussed together with solution proposed by Bennet in order "to save" the Second Principle. This establishes a profound link between thermodynamics and the theory of information, giving rise to a new branch of science where the two disciplines are deeply merged. It changes our point of view on the relation between observer and observed and opens the way to proposals of new paradigms.
- Two appendices have been added at the end. The first is of technical nature in the sense that we provide some mathematical formulae useful throughout the book and a clear discussion concerning the notations we adopted to describe small and infinitesimal processes. The other is devoted to the mechanical interpretation of pressure. In it we obtain some general relations between pressure and energy density for isotropically distributed molecules.


## Concluding Remark

This book contains, in an extended and in-depth version, the topics that have been treated in the course of thermodynamics held, for several years, at the Department of Physics and Astronomy of the University of Padua. The choice of specific topics may vary from year to year, but the conceptual structure, consisting of half the course devoted to the thermodynamics of equilibrium states and half to the thermodynamics of irreversible processes, is kept constant.

For the part concerning the thermodynamics of equilibrium states, the chosen approach was the one well defined by E. A. Guggenheim in his famous treatise, and this has already been previously commented in this introduction.

Regarding the study of irreversible processes, there may be two levels of approach. A complete approach, for advanced students, which must include the development of the formalism related to continuous systems. Another approach, simpler but more intuitive, concerns the study of the irreversible processes that develop between systems in internal equilibrium (we call it discontinuous systems approximation). This part has always been carried out by adopting, as a reference text, the excellent little book Thermodynamics of Irreversible Processes by I. Prigogine and published in 1961 by John Wiley \& Sons, by I. Prigogine but no longer easily available in the libraries.

The great merit of this short monograph consists in providing the undergraduate student with a complete picture of the so-called Onsager Theory on the definition and the interference of irreversible processes.

Both Guggenheim's and Prigogine's treatises have in common the fundamental starting point of dividing the variation of any extensive quantity in the two contributions related, respectively, to interactions with the external world and to processes occurring internally to the system.

For this reason, they formed a coherent and solid didactical tool.

Padua, Italy<br>May 2019<br>Antonio Saggion<br>Rossella Faraldo<br>Matteo Pierno

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## Acronyms

| $\theta$ | Empirical temperature |
| :---: | :---: |
| $T$ | Thermodynamic or absolute temperature |
| W | Amount of work done on the thermodynamic system by the external world |
| $U$ | Energy of a system |
| $\vec{F}$ | Force (mechanical) |
| $\vec{P}$ | Momentum |
| $\vec{v}$ | Velocity |
| $m_{0}$ | Rest mass |
| $\gamma_{L}$ | Lorentz factor |
| $U_{\mathrm{K}}$ | Kinetic energy |
| $\psi$ | Electrostatic potential |
| $q$ | Electric charge |
| $\vec{E}, E$ | Electrostatic field (vector, modulus) |
| $Q$ | Amount of heat given to a system in a finite transformation |
| $\Delta$ | Finite difference of a quantity |
| d | Differential of a function |
| $\hat{d}$ | Infinitesimal amount, not an exact differential |
| $\hat{d}_{\text {i }}$ | Infinitesimal variation of an extensive quantity, due to internal processes |
| $\hat{d}_{\text {e }}$ | Infinitesimal variation of an extensive quantity, due to the interaction with the external world |
| $S$ | Entropy |
| $\mathcal{E}$ | Generic extensive quantity |
| $x$ | Generic intensive quantity |
| $\eta$ | Efficiency of a thermal engine |
| $\Omega$ | Available energy |
| $\Lambda$ | Available work |
| $\Phi_{\Lambda}$ | Availability |
| $n$ | Number of moles |
| $n_{\gamma}$ | Number of moles of component $\gamma$ |


| $p$ | Pressure |
| :---: | :---: |
| $\mu_{\gamma}$ | Chemical potential of component $\gamma$ |
| $F$ | Free energy or Helmholtz potential |
| H | Enthalpy or heat function |
| G | Gibbs potential or free enthalpy |
| $\xi$ | Internal degree of freedom of a constrained system. Degree of advancement of a chemical reaction. In a generalized sense, degree of advancement of a generic process |
| $\chi_{T}$ | Coefficient of isothermal compressibility |
| $\chi_{S}$ | Coefficient of adiabatic compressibility |
| $C_{p}$ | Heat capacity at constant pressure |
| $C_{V}$ | Heat capacity at constant volume |
| $\alpha$ | Coefficient of thermal expansion |
| $\gamma$ | Ratio between the heat capacities at constant pressure and at constant volume |
| $G_{\text {m }}$ | Molar Gibbs potential |
| $U_{\mathrm{m}}$ | Molar energy |
| $V_{\mathrm{m}}$ | Molar volume |
| $S_{\text {m }}$ | Molar entropy |
| $H_{\text {m }}$ | Molar enthalpy |
| $A, B, C$ | First, second, and third virial coefficient |
| $C_{H}$ | Joule-Thomson coefficient |
| $T_{\text {cr }}$ | Critical temperature |
| $p_{\text {cr }}$ | Critical pressure |
| $V_{\text {cr }}$ | Critical volume |
| $\tilde{t}$ | Reduced temperature |
| $\tilde{p}$ | Reduced pressure |
| $\tilde{v}$ | Reduced volume |
| $f$ | Number of microscopic degrees of freedom |
| $\sigma$ | Surface tension |
| $\mathcal{S}_{\text {eq }}$ | Spreading parameter |
| $\vartheta_{\text {eq }}$ | Equilibrium contact angle |
| $q_{\text {fr }}$ | Free charge |
| $\rho_{\text {fr }}$ | Free charge density |
| $\epsilon$ | Electric permittivity of a material |
| $\chi$ | Electric susceptibility of a material |
| $\mu$ | Magnetic permeability of a material |
| $\chi_{m}$ | Magnetic susceptibility |
| $\vec{D}$ | Electric displacement |
| $\vec{P}$ | Electric polarization |
| $\vec{B}$ | Magnetic field |
| $\vec{H}$ | Magnetizing field |
| $\vec{M}$ | Magnetization vector |
| $\theta_{\mathrm{CW}}$ | Curie-Weiss Temperature |


| $\mathcal{W}$ | Emittance |
| :---: | :---: |
| $\mathcal{W}_{0}$ | Emittance of a black body |
| $\mathcal{B}$ | Emissivity |
| $\mathcal{B}_{0}$ | Emissivity of a black body |
| $\mathscr{A}$ | Absorptivity |
| $\mathscr{A}_{0}$ | Absorptivity of a black body |
| $\mathcal{S}_{0}$ | Spectral emissivity of entropy for a black body |
| $u_{v}$ | Spectral energy density |
| $\varepsilon$ | Energy of a particle or, in general, of an elementary constituent. |
| $\hat{d} \Phi$ | Infinitesimal energy transferred to an open system |
| $\mathcal{P}$ | Production of entropy |
| $X$ | Generalized force |
| $J$ | Generalized flux |
| $\nu_{\gamma}$ | Stoichiometric coefficient of the component $\gamma$ |
| $\nu_{\gamma}^{\rho}$ | Stoichiometric coefficient of the component $\gamma$ in the $\rho$-th chemical reaction |
| v | Velocity of the reaction or reaction rate |
| $\xi_{\rho}$ | Degree of advancement of the $\rho$-th chemical reaction |
| $\mathrm{v}_{\rho}$ | Reaction rate of the $\rho$-th chemical reaction |
| $\mathcal{A}$ | Affinity of the chemical reaction |
| $\mathcal{A}^{\prime}$ | Affinity of the $\rho$-th chemical reaction |
| $X_{\rho}$ | Generalized force of $\rho$-th chemical reaction |
| $J_{U}$ | Flux of energy in discontinuous systems |
| $X_{U}$ | Generalized force relative to the flux of energy in discontinuous systems |
| $J_{\gamma}$ | Generalized flux of component $\gamma$ in discontinuous systems |
| $X_{\gamma}$ | Generalized force relative to the flux of component $\gamma$ in discontinuous systems |
| $z_{\gamma}$ | Electric valence or electrovalency of component $\gamma$ |
| $\tilde{\mathcal{A}}_{\gamma}$ | Electrochemical affinity of component $\gamma$ |
| $\tilde{\mu}_{\gamma}$ | Electrochemical potential of component $\gamma$ |
| $J_{\text {th }}$ | Thermal flux |
| $X_{\text {th }}$ | Generalized force relative to the thermal flux |
| $J_{\rho}$ | Generalized flux of the $\rho$-th process in discontinuous systems |
| $L_{\rho \rho^{\prime}}$ | Linear phenomenological coefficient describing the interference between process $\rho$ and $\rho^{\prime}$ |
| $j_{\text {ch }}$ | Rate per unit volume of the chemical reaction |
| $\pi$ | Production of entropy per unit volume |
| K | Equilibrium constant of a chemical reaction |
| $\mathrm{v}^{+}$ | Forward reaction rate |
| $\mathrm{v}^{-}$ | Backward reaction rate |
| $k^{+}$ | Forward kinetic constant of a chemical reaction |
| $k^{-}$ | Backward kinetic constant of a chemical reaction |
| $\tau$ | Relaxation time of a process or of a system |
| $J_{m}$ | Generalized flux of matter in discontinuous systems |

$X_{m} \quad$ Generalized force relative to the flux of matter in discontinuous systems
$\tilde{Q} \quad$ Heat of transfer
$\varepsilon \quad$ Energy of a single particle
$J^{+} \quad$ Generalized flux in the forward direction in discontinuous systems
$J^{-} \quad$ Generalized flux in the backward direction in discontinuous systems
$J_{U}^{+} \quad$ Energy flux in the forward direction in discontinuous systems
$J_{U}^{-} \quad$ Energy Flux in the backward direction in discontinuous systems
$\tilde{U} \quad$ Energy of transfer
$X_{I} \quad$ Generalized force relative to the electric current, in discontinuous systems
$\alpha_{\rho} \quad$ Fluctuation of the $\rho$-th state parameter
$\varrho \quad$ Mass density
$\varrho_{\gamma} \quad$ Mass density of the component $\gamma$
$C_{\gamma} \quad$ Molar concentration of the component $\gamma$
$c_{\gamma} \quad$ Mass concentration of the component $\gamma$
$c_{\gamma} \quad$ Mole fraction of the component $\gamma$
$e \quad$ Density of a generic extensive quantity
$\mathcal{E}^{*} \quad$ Specific value (per unit mass) of a generic extensive quantity
$v_{\gamma}^{\prime} \quad$ Stoichiometric number times the molecular weight $v_{\gamma}^{\prime}=v_{\gamma} M_{\gamma}$
$M_{\gamma} \quad$ Molecular weight of the component $\gamma$
$\vec{v}_{\gamma} \quad$ Local velocity of the component $\gamma$
$\vec{v} \quad$ Local velocity of the center of mass of the fluid
$\vec{J}_{\gamma} \quad$ Diffusion flux density of the component $\gamma$
$\vec{F}_{\gamma} \quad$ Force per unit mass acting on the component $\gamma$
$U^{*} \quad$ Specific (per unit mass) energy
$\vec{J}_{u} \quad$ Energy flux density in continuous systems
$\vec{J}_{q} \quad$ Heat flux density in continuous systems
$S^{*} \quad$ Specific (per unit mass) entropy
$V^{*} \quad$ Specific (per unit mass) volume
$\mu_{\gamma}^{*} \quad$ Specific chemical potential of component $\gamma$
$\vec{J}_{s}^{\prime} \quad$ Entropy flux density deprived of the convective term
$\vec{J}_{s, \text { tot }} \quad$ Total entropy flux density (including the convective term)
$\vec{J}_{\gamma}^{a} \quad$ Diffusion flux density of the component $\gamma$ respect to a generic velocity $\vec{a}$
$\mu_{\mathrm{d}} \quad$ Mobility or mobility coefficient
$\mathcal{D} \quad$ Diffusion coefficient
$\lambda \quad$ Heat conductivity of a material
$\sigma_{\mathrm{el}} \quad$ Electric conductivity of a material
$\omega_{A} \quad$ Absolute thermoelectric power of metal A
$\omega_{B} \quad$ Absolute thermoelectric power of metal B
$\omega_{A B} \quad$ Absolute thermoelectric power of metal AB
$\Pi_{A B} \quad$ Peltier coefficient of a thermocouple AB
$\tau_{A}^{\mathrm{Th}} \quad$ Thomson coefficient of metal A
$q_{\mathrm{el}}^{*} \quad$ Charge per unit mass of the electron
$\vec{J}_{\mathrm{el}} \quad$ Diffusion flux of electrons (momentum density)

| $m_{\text {el }}$ | Electron's mass |
| :---: | :---: |
| $\tilde{\mu}_{\text {el }}^{*}$ | Specific electrochemical potential of the electron |
| $\mathcal{D}_{T}$ | Thermodiffusion coefficient |
| $\mathrm{S}_{T}$ | Soret's coefficient |
| $\mathcal{D}_{\text {F }}$ | Dufour's coefficient |
| $w$ | Number of microscopic states which correspond to the same macroscopic state |
| $\underline{I}$ | Amount of Information possessed by a message in the case of equiprobable symbols |
| $\mathbb{H}$ | Amount of information possessed by a message in the general case |
| $S_{\text {bit }}$ | Entropy for 1 bit of Information |
| $\langle\mathbb{I}\rangle$ | Average information per symbol |
| $\mathbb{H}_{\text {st }}$ | Statistical entropy |
| $\tilde{\rho}$ | Density matrix |
| $\mathbb{K}$ | Algorithmic entropy |
| $\vec{g}$ | Momentum density of electromagnetic fields |
| $\vec{S}$ | Density of energy flux |
| AMO | Accurate macroscopic observer |
| COP | Coefficient of performance |
| IGUS | Information gathering and using system |
| LMO | Low-accuracy macroscopic observer |
| LTE | Local thermodynamic equilibrium |

## List of Some Useful Constants

$c \quad$ Speed of light in vacuum, $c=2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
$\epsilon_{0} \quad$ Electric permittivity or electric constant in vacuum, $\epsilon_{0}=8.854 \times 10^{-12} \mathrm{Cm}^{-1} \mathrm{~V}^{-1}$
$N_{\mathrm{A}} \quad$ Avogadro number, $N_{\mathrm{A}}=6.022 \times 10^{23}$
$k_{B} \quad$ Boltzmann constant, $k_{B}=1.381 \times 10^{-23} \mathrm{JK}^{-1}$
$R \quad$ Gas constant, $R=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}=1.987 \mathrm{calmol}^{-1} \mathrm{~K}^{-1}$
$e \quad$ Electric charge, $e=1.602 \times 10^{-19} \mathrm{C}$
$\mathfrak{F} \quad$ Faraday constant, $\mathfrak{F}=N_{A} e=0.965 \times 10^{5} \mathrm{C}$
$\mu_{0} \quad$ Magnetic permeability in vacuum, $\mu_{0}=4 \pi \times 10^{-7} \mathrm{NA}^{-2}$
$a \quad$ Stefan-Boltzmann constant, $a=7.56 \times 10^{-16} \mathrm{Jm}^{-3} \mathrm{~K}^{-4}$
$\sigma \quad$ Radiation constant, $\sigma=5.67 \mathrm{~s}^{-1} \mathrm{~m}^{-2} \mathrm{~K}^{-4}$
$\mathscr{S}_{\odot} \quad$ Solar constant, $\mathscr{S}_{\odot}=1366 \mathrm{Wm}^{-2}$
$h \quad$ Planck constant, $h=6.626 \times 10^{-34} \mathrm{~m}^{2} \mathrm{~kg} \mathrm{~s}^{-1}$

# Formulation of the Theory 

# Chapter 1 <br> Macroscopic Systems and Empirical Temperature 


#### Abstract

The definitions of the macroscopic system and of empirical temperature are discussed. At the first step of the theory, a definition of the state of equilibrium must be given for isolated systems and the definition of mutual equilibrium between closed systems put in contact comes as a consequence. The property of being in mutual equilibrium is, by definition, denoted by saying that the two systems have the same temperature. Empirical observation shows that the property of having the same temperature, i.e., of being in mutual equilibrium, is transitive and this statement is assumed to be true in general. This is the content of the Zeroth Principle of Thermodynamics, and it is the necessary postulation which allows us to define the concept of empirical temperature as a physical quantity.


Keywords Macroscopic systems • Macroscopic observer • Thermodynamic state $\cdot$ Empirical temperature $\cdot$ Zeroth principle

### 1.1 Macroscopic Systems

The need to use the adjective macroscopic came about at the beginning of the twentieth Century, with the discovery of Quantum Physics and the development of the atomic-molecular theory of matter. Since the desire to extend the laws of Classical Physics to the atomic world proved to be destined to failure, it was necessary to create a new theoretical context for the phenomena which take place in the atomicscale world; these phenomena define what we normally call the microscopic world. Conversely, those phenomena that we can study within the theoretical context of Classical Physics are normally called the macroscopic world.

Since we know that the size of an atom is very small, we could define as a macroscopic system a physical system which is made up of a large number of elementary systems (e.g., atoms or molecules). This could be considered an acceptable definition of a macroscopic system and this is precisely what we currently do when we want to apply kinetic theories to the description of macroscopic systems. However, when it comes to the physics of continuous systems this leaves us empty-handed. In this case, we do not have the alternative of the microscopic system but we continue to use the
theoretical context of Classical Physics (pre-quantum). It is preferable, therefore, to change the point of view and decide that being macroscopic or microscopic is not a property of the object being observed but indeed $a$ way of observing and processing on the part of the observer. A macroscopic system is, therefore, any physical system which is observed, and studied, by a macroscopic observer.

### 1.2 Macroscopic Observer

A macroscopic observer is an observer, who works with tools having timescales and spatial resolutions that we define as macroscopic. In the first instance, these spatial and temporal resolutions are determined by our senses, meaning that they are linked to our physiology. Starting from this first means of contact with the outside world, the observer has created other research tools which, even though they work on space and timescales that are very distant from those accessible to our sensory apparatus (both much smaller or much larger), are, however, based on the Physics devised from sensory observations. In this way we have created a theoretical context, i.e., a collection of theories and of observation tools that we now define as classic or macroscopic: it is for this reason and only in these cases, that we may correctly make reference to an extension (or sometimes a strengthening) of our sensory apparatus.

The need to characterize the macroscopic observer rises from the failure, as we have seen, of the attempt to extend the classical theoretical context to atomic phenomena. This made it necessary to establish a new mechanics and new electromagnetism and new observation tools, that is a new theoretical context.

We know that a mole of gas in normal conditions occupies a volume of 22.4 L , and we know that it is composed of $\sim 6 \times 10^{23}$ molecules. We can associate with each molecule a share of the occupied volume and from this extract the order of magnitude of the average distance between two molecules. We can also refer to the first experiments in the diffraction of X-rays in a crystal to get a measure of the order of magnitude of the interatomic distance in solids. In the various cases we obtain that the typical dimension of the so-called "microscopic world" is

$$
\begin{equation*}
d_{\text {micro }} \sim 10^{-9}-10^{-10} \mathrm{~m} . \tag{1.1}
\end{equation*}
$$

Likewise, the elementary models of the atomic structure suggest that the movement of electrons on the atomic scale is carried out with a periodicity whose timescale is of the order of magnitude of the inverse of the frequency of the radiation emitted in the transitions and therefore of the order:

$$
\begin{equation*}
\tau_{\text {micro }} \sim 10^{-15} \mathrm{~s} . \tag{1.2}
\end{equation*}
$$

The same can be said for the oscillation of atoms in crystal structures. These are of the orders of magnitude that characterize the world we call microscopic.

Things are very different for the macroscopic world. We know that the resolving power, $d$, of an optical instrument, that is, the minimum distance at which we can distinguish two point sources is of the order of the wavelength used in the instrument. If we use visible light, we have

$$
\begin{equation*}
d_{\text {macro }} \sim 5 \times 10^{-7} \mathrm{~m} \tag{1.3}
\end{equation*}
$$

so approximately a factor 1000 greater than the interatomic scale. This means that in a volume that we can (with a certain amount of effort) distinctly see as macroscopic observers, there are around $\sim 10^{9}$ elementary objects characterizing the microscopic world.

Likewise, for the time duration of the measurements, we can compare the order of magnitude of the duration of the macroscopic observations that are of the order of $\tau_{\text {macro }} \sim 10^{-2}-10^{-3} \mathrm{~s}$, with the timescale of the motions on the atomic scale as provided by our theories.

We can see that in the time taken to carry out a macroscopic observation, the elementary constituents of the microscopic world complete an enormous number of elementary oscillations. That is, in the time interval of our observation, we can only take in configurations that in the atomic scale are static configurations (i.e., average configurations).

An inexperienced reader, reading in a hurry might say: with the development of atomic physics we discovered that the macroscopic way of observing provides, in reality, a very loose vision of the real world; why do we continue with it now that we have much more refined observation tools? Behind the question lies the non-stated conviction that from a detailed knowledge of the microscopic world we can, sooner or later, become aware of the behavior on the larger scale of the macroscopic world. This conviction, which is called reductionism, is flawed, and the failure is not due to difficulties with calculations, which one day could be slowly overcome, but is of a conceptual nature. We can agree that there is one reality but that it appears in different forms through the different instruments we use to observe it.

Naturally, a very interesting problem arises of finding the link between macroscopic appearance and microscopic appearance. For example, interpreting pressure in terms of the average value of the momentum transferred to the surface per unit of time or temperature in terms of average kinetic energy of the molecules can certainly be functional in a certain (very limited) number of situations. As we will see, pressure and temperature are quantities which express the speed with which energy changes with a change of volume or of entropy and they have, therefore, a much more general meaning than that which can appear from the examples that we can extract from kinetic theories.

### 1.3 Thermodynamic State

With the term thermodynamic state we mean the set of the values of all the macroscopic properties of the system under consideration. Mass, volume, coefficient of viscosity, index of refraction, density, chemical composition, energy, electrical resistivity, etc., are examples of state parameters. The number of properties adds up to several dozens, but from our experimental investigation we have discovered many laws describing mutual dependencies. A lower number will, therefore, be necessary to know all the others. We will call the set of all the properties useful for describing the system's response to any stimulus, thermodynamic state. The minimum number of appropriate properties required to define the state completely is a question that cannot be answered now but that must be postponed until the theory has developed sufficiently. This will be defined in Sect.4.2. As we will see later, all of the properties of the system, which we will also call state parameters, are defined in situations that we will call states of equilibrium. For further details on this definition, we refer the reader to Sect. 1.6.1.

### 1.4 The Concept of Empirical Temperature

The need to introduce a new state variable, the empirical temperature, derives from the tactile perception of hotness and coldness and the finding that some physical properties change accordingly. The introduction of an empirical temperature scale makes it possible to determine whether two systems put in contact, are or not in a condition of mutual equilibrium. In order for this condition to be objectively certified, it is necessary that the relationship of mutual equilibrium between various bodies enjoys the property of being transitive. This is confirmed in empirical observations but must be assumed to be of general validity. This postulate is called the Zeroth Principle of Thermodynamics. The choice of this classification is due to the fact that this Principle should precede the First Principle. We refer shortly to the Celsius scale as the most familiar example of the empirical temperature scale.

### 1.5 The Perception of Hotness and Coldness

Among our primitive sensory experiences, shared by all individuals, are the experiences of hotness and coldness. They are experiences that every person, from childhood, obtains through tactile contact with the object under observation. During this contact, the observer registers a change in their psychological-physical being and attributes this change to an interaction with the observed object. The classification in terms of "hot" or "cold" reveals itself to be, in some cases, completely personal and dependent upon the circumstances that the observer learns to consider as external
to the observer-observed object relationship. In certain cases, on the other hand, there is a general consensus between different individuals and an almost complete independence from the external circumstances (in the sense that the evaluation is identically repeated whatever change there might be to the external circumstances). All of this drives us to investigate the laws which regulate such phenomena and to set out new fields of research in the area of human physiology and psychophysiology. However, this is not the aspect we want to deal with here because, as a first step, it is useful to separate the observer from the observed, that is to attribute to the observed object its own, as it were, objectivity. In the end, we will mention briefly the most recent developments in Thermodynamics in which we will see that this separation needs to be seriously reconsidered.

It is a common experience that different properties (physical quantities, state parameters...) of an object change their value depending on whether is it hot or cold. Let us look at some examples.

In studying the laws according to which some solid bodies change shape when subject to outside stimuli or disturbances, we developed the theory of elasticity. With weak disturbances, we see that the entity of the deformations is proportional to the intensity of the force applied: a simple and often-mentioned case is that of the dynamometer which, when suitably calibrated, can be used to measure the intensity of forces applied in static situations. Remaining within the area of linear deformations, we have defined a very important state parameter named elastic constant which sets out, indeed, the law of proportionality between the intensity $F$ of the applied force and the extension of the deformation $\Delta \ell$,

$$
\begin{equation*}
F=-k \Delta \ell . \tag{1.4}
\end{equation*}
$$

The value of the elastic constant depends on the type of material the dynamometer was built with and on its size. It can easily be seen in the laboratory that the value of the elastic constant changes visibly depending on whether the spring (which basically makes up the dynamometer) is hot or cold.

Likewise, let us consider the phenomenon of the conduction of electric current in metals. If we consider wires (so that the problem can be treated as one dimensional) we see that, within wide limits, the intensity of current $I$ is proportional to the difference in applied potential:

$$
\begin{equation*}
\psi=R I . \tag{1.5}
\end{equation*}
$$

This is the well-known Ohm's Law. We remark that it is referred to dynamic equilibrium configurations. Specifically, when the potential difference $\psi$ is applied to a conductor, its electrons in the conduction energy band experience an electric field, and therefore a force. As a consequence they are accelerated but, as their average velocity increases, the collisions with the ionic structure of the conductor manifest themselves, on average, as a dissipative viscous force whose intensity increases as the (average) velocity increases. When the two forces, the one due to the electric field and the one due to dissipation, balance, the average velocity will be constant, and it
will be called drift velocity. This is the situation named as "dynamic equilibrium"1 and this is the case in which Ohm's law applies. We also know that $R$, which is called electric resistance of that wire, depends on the material chosen, and that, for the same material, it is proportional to the length $l$ and inversely proportional to the area $A$ of the cross-section of the wire:

$$
\begin{equation*}
R=\varrho l / A, \tag{1.6}
\end{equation*}
$$

where $\varrho$ is called resistivity of the conductor and depends on the material used and not on its geometric form. We can easily observe that $\varrho$ takes on a different value depending on whether the metal is hot or cold. In the same way, we can verify that many other properties of bodies change depending on whether they are hot or cold such as the volume of a body, for example, the refractive index of a material, the coefficient of viscosity, etc. Therefore, being hot or cold does not only concern the physiology of the human body or, at the most, the tactile human body-object interaction, but in general, we should expect some properties of the objects external to us to have different values. In other words, the thermodynamic state of the system is different depending on whether it is hot or cold. Therefore, being hot or cold reveals the presence of an internal extra degree of freedom. ${ }^{2}$

### 1.6 The Empirical Temperature and the Zeroth Principle of Thermodynamics

This section is devoted to the definition of empirical temperature. The concept of temperature will find its complete formulation in Chap. 4 where it will be defined as a physical quantity complementary to entropy but it is necessary to proceed step by step. In this way not only the historical process is respected but also the conceptual difference between empirical temperature and temperature will appear more clearly.

### 1.6.1 Equilibrium State

When two bodies are put into contact we notice, in general, that both of them undergo some sort of modification; we see, that is, that some properties (or state parameters) of each body vary. If the two bodies form an isolated system, meaning that they interact amongst themselves but not with other bodies. This can be reasonably certified by considering that we do not see any changes in the surrounding objects ascribable to

[^2]an interaction with the first two. ${ }^{3}$ We can observe that the amplitude of these changes decreases in time until it becomes imperceptible to measuring instruments. We will say, then, that the two systems have reached a state of mutual equilibrium. To denote this relational situation between the two systems we will also use the expression: the two given systems have the same temperature. Be aware though that this simply denotes a relationship (that is if they are put into contact nothing happens) between the two systems but the temperature, as a physical quantity, has not yet been defined. This definition would not be possible without the formulation of a fundamental principle, called the Zeroth Principle of Thermodynamics.

### 1.6.2 The Zeroth Principle

This principle is suggested by empirical observations, whose results are then generalized. It confirms the transitive property of being in mutual equilibrium, that is, of the property of having the same temperature. This states the following:
(1) Let us suppose that body $\mathscr{B}_{1}$ is in mutual equilibrium with body $\mathscr{B}_{2}$ (that is, it has the same temperature as body $\mathscr{B}_{2}$ ). This means that when $\mathscr{B}_{1}$ and $\mathscr{B}_{2}$ are put into contact, no change occurs;
(2) Let us suppose that the same body $\mathscr{B}_{1}$ is in mutual equilibrium with body $\mathscr{B}_{3}$ (has the same temperature as body $\mathscr{B}_{3}$ ). This means that when $\mathscr{B}_{1}$ and $\mathscr{B}_{3}$ are put into contact, no change occurs;
(3) Then body $\mathscr{B}_{2}$ is in mutual equilibrium with body $\mathscr{B}_{3}$ (that is, it has the same temperature as body $\mathscr{B}_{3}$ ) that is, if we put $\mathscr{B}_{2}$ and $\mathscr{B}_{3}$ into contact no change occurs.
This principle is necessary to be able to define the function of the thermometer and therefore an empirical temperature scale as physical quantity.

To define one empirical temperature scale one proceeds in this way: a body is chosen as a sample and one of its properties, whose value (on the scale on which it has been defined) changes when the body goes from being hot to being cold, is selected. The changes in this property are recorded on a new scale, which is arbitrarily defined.

For example, one can observe the change in volume of a certain mass of mercury. To make even a small variation in volume easily appreciable we will limit the free surface of the mercury to the section of a capillary, that is, a small tube of constant section with a very small area; in that way, a small variation in volume will manifest itself through a noticeable change in the position of the surface of the mercury within the capillary.

We will put this body in contact with a body $\mathscr{B}_{2}$, we will wait for mutual equilibrium to be established and we will observe the position of the meniscus of the mercury. Then, we will put the sample body in contact with body $\mathscr{B}_{3}$ and will carry

[^3]out the same procedure. If the position, in the capillary, of the free surface of the mercury coincides with the position previously observed, we will say that bodies $\mathscr{B}_{2}$ and $\mathscr{B}_{3}$ have the same temperature, that is, that if they are put into contact no change will occur.

It is clear that the value of the volume (that is its measurement in $\mathrm{cm}^{3}$, for example) in that state is not important but serves only to certify a relationship of equilibrium, therefore, the different positions are noted by a number which orders them according to an arbitrarily chosen convention. In this way we attribute, for the sake of convenience, a numerical value to the different positions of the meniscus and we define an empirical temperature scale. We thought it appropriate to order the different positions with numbers increasing from cold toward hot. The instrument created and employed in this way is to be called a thermometer. ${ }^{4}$

As is well known, the most common empirical temperature scale is the Celsius scale. In the example briefly described earlier, the capillary is fixed carefully to a rigid, rectilinear support and then the procedure is as follows: this object is put in contact with boiling water at the pressure of one atmosphere, it will be seen that the position of the meniscus moves. When the position of the meniscus does not move anymore, meaning that the volume of the mercury does not change anymore, we can say that the mercury and the boiling water are in mutual equilibrium, so have the same temperature, and therefore we mark the position of the meniscus on the support and we write the number 100. Then we bring the same object into contact with ice in equilibrium with water in a liquid state at the pressure of one atmosphere. We wait for the position of the meniscus to become stable and we mark its position on the same support. In that position, we write the number 0 (zero) and then we divide the straight segment between the two positions into 100 intervals of equal length and we number them. We will call the instrument created in this way a thermometer and the numerical scale the Celsius scale.

Obviously, we can create a large number of different empirical scales and the property observed in order to define the empirical temperature scale can be a volume, a length, an electrical resistance, a potential difference etc.

Naturally, all of these possible empirical temperature scales are different from each other and equally acceptable. Some are more convenient than others depending on the different conditions in which they work; for example, in very cold or very hot situations mercury is impossible to use, so something else will need to be invented and then the different segments linked up. Furthermore, the choice will need to be made with respect to practicality (costs, cumbersomeness, etc.), to functionality (speed of readiness, extent of the scale, etc.) and to reliability (durability and relative lack of sensitivity to changes in external environment).

From now on, when we put the thermometer in contact with any body we will see that after a certain amount of time the level of the meniscus will no longer change. We will read the number that corresponds to its position and we will say that, in that

[^4]moment, the thermal state of the body, understood as the heat level ${ }^{5}$ of the body corresponds to that of the thermometer (mutual equilibrium) and this is recorded by the number read. We can say that, in that state, the temperature of the body in question has the numerical value read on the scale of the thermometer. In this way, the property of being hot or cold, that changes the value of some properties of the bodies, has been placed outside of our sensory apparatus and been made independent of it. In other words, objective.

We will indicate the value of the empirical temperature, measured on an arbitrary scale, with the letter $\theta$ while we will keep the denomination of temperature, and it will be indicated with the symbol $T$, for the scale of temperatures which will be defined when formulating the Second Principle. By pointing out this detail, we wish to reiterate a fact: any $\theta$ scale serves only to establish whether two systems (let us say $\mathcal{S}_{1}$ and $\mathcal{S}_{2}$ ) are in mutual equilibrium, that is, whether $\theta_{\mathcal{S}_{1}}=\theta_{\mathcal{S}_{2}}$. If $\theta_{\mathcal{S}_{1}} \neq \theta_{\mathcal{S}_{2}}$ then we should expect that, once an interaction has been created (for example, putting them into contact with each other), changes in the states are produced but the numerical values of $\theta$ cannot give us any other information, except in the few cases where a purely empirical cataloging has already occurred.

[^5]
## Chapter 2 <br> The First Principle of Thermodynamics


#### Abstract

The first Principle defines, for every system, a property named energy which is a conserved quantity and this means that its variations in a process, can be due only to the interaction with the external world. The latter interactions are divided into two groups. On one side, we consider all the interactions which are described within some theoretical contexts developed up to now. We say that these are the interactions controlled by the observer. In the second group, we place all those interactions which are unknown to the observer or which are treated as such. The cumulative effect of these unknown interactions gives rise to one term which is currently called quantity of heat. After having defined the meaning of adiabatic transformation, experimental evidence shows that in the latter case the amount of work delivered by the interactions controlled by the observer in a change of state depends only on the initial and final states and does not depend on the transformation used. This defines energy and, as a consequence, the contribution of the unknown interactions in a generic transformation, that is the amount of heat, is defined by the difference between the variation of energy and the amount of work carried out in that transformation. All this needs to be formulated for closed (with respect to mass) systems.


Keywords First principle • Adiabatic systems • Energy • Heat (quantity of)

### 2.1 Introduction

The first Principle of Thermodynamics consists of the definition of two quantities, fundamental for Physics: (i) energy, which will be indicated using the symbol $U$ and the (ii) quantity of heat, which will be indicated by $\hat{d} Q$ or $Q$ for infinitesimal or finite transformations, respectively. While the energy is, by definition, a function of the state of the system and therefore contributes to defining the state of the system, the quantity of heat describes, in part, the type of interaction with the external world to which the system is submitted and therefore, in general, its value depends on the particular transformation carried out.

### 2.2 Closed Systems

We define closed systems as those systems that do not exchange mass with the outside world. Unless stated otherwise, we will take into consideration only closed systems.

Let us consider a closed system that is initially in a state of equilibrium indicated with A. To induce a change of state on this, we (the observer) have to carry out actions on it, meaning that we have to interact with it. By interacting we will destroy the state of equilibrium in which the system finds itself and, when the interaction is over, the system will settle itself into a new state of equilibrium, which we will call B. We can say that we have carried out the transformation from the initial state A to the final state B.

There are some types of interaction for which we have a sufficient theoretical context, meaning that we have theories within which we are able to completely describe the interactions that we carry out.

We will say that these interactions are controlled by the observer.
We can apply forces and do this, basically, in two ways: by applying forces distributed over the surface of the boundary, or forces distributed in the volume of the system. We can also modify the state of the system creating or changing external fields that might be electrical fields, magnetic fields, or gravitational fields. In these latter cases, to carry out these actions, we have to move electric charges, switch on or change electrical currents or move masses.

To quantify our actions, we have theories available that we consider adequate and so we can say that these are the actions that we control. We can generalize what we have learned studying mechanics and calculate, or measure, the amount of work required to move the charges, change the intensities of the currents, move masses or do work with other types of forces such as friction forces or surface forces, pressure forces in particular.

### 2.3 Adiabatic Walls and Adiabatic Transformations

Let us consider the following example. Let us suppose, on a normal summer day, we have a receptacle containing water and some ice cubes. We can put a whisk with suitable blades into the water in the receptacle to mix the liquid in a very efficient way. Note that if we mix the water energetically ice will melt fairly quickly. In this situation, we can even find a correlation between the amount of work carried out on the blades to make them turn and the corresponding quantity of ice which will have melted.

We can measure this quantity of work measuring the moment of the forces applied to the whisk, the angular velocity with which it turns, and the time interval during which we made the blades turn, multiplying these three numbers. Therefore, we attribute the change of state of the system to the action carried out and we quantify the
latter by measuring the amount of work carried out. This is an example of interactions controlled by the observer.

We can also not do anything and leave the receptacle on the table and come back an hour later. We will see that a certain amount of the ice has melted just the same.

The observer will say that other interactions of the system with the outside world exist that he does not control, i.e., that are not within any of the theoretical contexts he created.

The need to be able to establish a stable connection between the actions carried out by the observer and the changes in state seems destined to failure.

We can observe, however, that changing the material we made the receptacle with, we can slow down the speed with which these uncontrolled interactions occur. If we substitute a receptacle made of thin metal with one made of glass the time required for a certain amount of ice to melt becomes significantly longer. If we then use a Dewar flask (or even a normal thermos flask), the melting time becomes much longer. The development of appropriate technologies has reduced the percentage of ice melted after some days to a negligible amount.

Therefore, these materials have the property of slowing down, in an ever more efficient way, the intensity of these unknown interactions. Imagining that we take these empirical observations to the limit, we will call those (ideal) materials that are completely impervious to these new interactions, adiabatic.

If a system is surrounded by adiabatic walls, the only way the external world can interact and cause changes in state of the system (processes), is through using electromagnetic or gravitational fields (volume and long-range forces) or by changing the boundary with forces distributed over the surface that is by interactions controlled by the experimenter (observer).

### 2.4 The Definition of Energy

Let us consider a closed and adiabatic system in a state of equilibrium A. We carry out certain operations on the system and we see that, once these are completed, the system is taken to another state of equilibrium, B. Obviously, once one way has been found to reach state B , an infinite number of ways can be found to reach the same result. Experience shows that once A and B are fixed, the total quantity of work that the observer carries out, operating in different ways, always has the same value. This quantity is indicated by with the symbol $W_{\mathrm{A}, \mathrm{B}}^{\mathrm{ad}}$. We will assume that this result has universal value.

The formal expression which fixes this statement is the following: for every closed and adiabatic system, a function exists which depends only on the state, called Energy, that we will indicate with the symbol $U$, and that is defined by the following relation:

$$
\begin{equation*}
U(\mathrm{~B})-U(\mathrm{~A})=W_{\mathrm{A}, \mathrm{~B}}^{\mathrm{ad}} . \tag{2.1}
\end{equation*}
$$

From the definition we can see that energy, as a function of state, is defined except for an arbitrary additive constant or, in other words, only the variations in energy between two states of equilibrium are defined. In Sect.2.4.1, we review the definition of energy in situations resulting in familiar to any undergraduate in Physics.

### 2.4.1 Energy of Familiar Adiabatic Systems

The following examples are well known from Mechanics and Electrostatics. Here we want to pick them up again using the language which characterizes the thermodynamic context, in which the concept of state and of the actions that the observer (i.e., the "external world") carries out on the system to induce a change in state are brought to the forefront.

## Energy of a Point Mass

It is the simplest system. It consists of what is normally called "point mass" and that, in our language, can be described as follows: a point mass is a physical system which is completely determined solely by the value of its mass $m_{0}$ and by the values of its position and of its instantaneous velocity, respectively, $\mathbf{r}, \mathbf{v}$. Changes in state will be determined by changes in some of the (six) state coordinates $\mathbf{r}, \mathbf{v}$. Let us suppose that it is initially in the state $\mathrm{A} \equiv\left(\mathbf{r}_{\mathrm{A}}, \mathbf{v}_{\mathrm{A}}\right)$ and that the desire is to take the system to the predetermined final state $B \equiv\left(\mathbf{r}_{B}, \mathbf{v}_{B}\right)$, as shown in Fig. 2.1.

To obtain this change of state, we will have to apply appropriate forces on the point whose resultant, in every instant, we shall indicate with $\mathbf{F}$. By definition, the total amount of work we will have to carry out will be given by


Fig. 2.1 Change of state for a point mass, from an initial state $A \equiv\left(\mathbf{r}_{A}, \mathbf{v}_{A}\right)$ to a final state $B \equiv\left(\mathbf{r}_{\mathrm{B}}, \mathbf{v}_{\mathrm{B}}\right)$ along the path $\Gamma$

$$
\begin{equation*}
W_{\mathrm{A}, \mathrm{~B}}=\int_{\substack{\mathrm{A} \\ \text { path } \Gamma}}^{\mathrm{B}} \mathbf{F} \cdot \mathbf{v} \mathrm{~d} t, \tag{2.2}
\end{equation*}
$$

where the integral is a curvilinear integral calculated along the specific trajectory $\Gamma$ described by the system under the action of the forces we applied.
(a) Newtonian case.

In the Newtonian context, that is, if the law of motion is

$$
\begin{equation*}
\mathbf{F}=\frac{\mathrm{d} \mathbf{P}}{\mathrm{~d} t}=m_{0} \frac{\mathrm{~d} \mathbf{v}}{\mathrm{~d} t}, \tag{2.3}
\end{equation*}
$$

$\mathbf{P}$ being the momentum of the point of mass $m_{0}$, it can be shown that

$$
\begin{equation*}
W_{\mathrm{A}, \mathrm{~B}}=\frac{1}{2} m_{0} v_{2}^{2}-\frac{1}{2} m_{0} v_{1}^{2} . \tag{2.4}
\end{equation*}
$$

We can carry out this change of state in an infinite number of ways by appropriately modifying the dependence of the value of the applied force $\mathbf{F}$ from the position occupied instantaneously by the point mass. As can be seen, the total amount of work carried out by us always takes on the same value, and this depends solely on the values of the state variables in A and in B. Or rather, this depends only on the moduli of the initial and final velocities, therefore on one state variable out of six. In the Newtonian context, the total amount of work carried out is given by the variation, between the final state and the initial state, of the function $U$ :

$$
\begin{equation*}
U=\frac{1}{2} m_{0} v^{2}+\text { constant } \tag{2.5}
\end{equation*}
$$

which is defined for any arbitrary constant. This means that there are infinite functions $U$, which have the property of providing, with their variation, the right value for $W$. These infinite functions differ among themselves due to the differing value of the constant, but this is irrelevant because we are only interested in variations in $U$. The quantity Eq. (2.5) is called energy of the point mass. Commonly, this is also called kinetic energy but in this case the adjective sends us off track: it makes sense to use adjectives when you want to distinguish between different forms of energy but in this particularly simple case, the energy of the system is completely described by that term in itself. Generally, the value of the constant is set to zero, since it is natural to think that the kinetic energy is null when the velocity is zero (point mass at rest). This has the same value as choosing to set the potential energy equal to zero at infinity.
(b) Relativistic case.

In this case, the law of motion is a little different because it has to be expressed in a four-dimensional form. It can be seen that

$$
\begin{equation*}
\mathbf{F} \cdot \mathbf{v}=m_{0} c^{2} \frac{\mathrm{~d} \gamma_{L}}{\mathrm{~d} t} \tag{2.6}
\end{equation*}
$$

$c$ being the light speed in vacuum, $\gamma_{L}=\left(1-v^{2} / c^{2}\right)^{-1 / 2}$ the Lorentz factor ${ }^{1}$ and $m_{0}$ the rest (Newtonian) mass. Therefore

$$
\begin{equation*}
W_{\mathrm{A}, \mathrm{~B}}=\int_{\substack{\mathrm{A} \\ \text { path } \Gamma}}^{\mathrm{B}}(\mathbf{F} \cdot \mathbf{v}) \mathrm{d} t=m_{0} c^{2} \gamma_{L_{2}}-m_{0} c^{2} \gamma_{L_{1}}, \tag{2.7}
\end{equation*}
$$

$\gamma_{L_{2}}$ and $\gamma_{L_{1}}$ being the values that the Lorentz factor of the point mass takes on in the final state and in the initial state, respectively. In the relativistic context, the same can be said in an almost identical fashion for the variation in energy: the work is independent of the trajectory and is equal to the difference of the function $U$ :

$$
\begin{equation*}
U=m_{0} \gamma_{L} c^{2}+\text { constant } \tag{2.8}
\end{equation*}
$$

Even in the relativistic context, the energy is defined within an arbitrary constant. In the last work of the annus mirabilis 1905, Einstein overcomes the uncertainty in the expression of energy due to the arbitrary additive constant and fixes an absolute value of energy in the form:

$$
\begin{equation*}
U=m_{0} \gamma_{L} c^{2} \tag{2.9}
\end{equation*}
$$

In doing this, he sets the energy of a body as equal to the sum of the energy at rest $m_{0} c^{2}$ and of the kinetic energy $U_{K}=U-m_{0} c^{2}$. Obviously, the variations in this last quantity (that now deserves the adjective kinetic) coincide with the values of the quantity of work carried out, but Einstein's postulation has many other implications that we do not wish to discuss in this context.

## Energy of a Condenser in Vacuum

Let us consider a plane, parallel plate empty capacitor in vacuum with electric permittivity $\epsilon_{0}$. We will indicate with $\Sigma$ the area of the plates, their distance with $h$ and with $q$ the amount of charge deposited on them in a certain moment. We will operate in order to change the state, assuming that the plates are non-deformable

[^6]and, specifically, at a constant distance from each other. In that case, the state is solely determined by the value of the charge or, equivalently, by the intensity of the electric field between the two plates. Let us suppose that the capacitor is in the initial state $q_{\mathrm{A}}$ and that we want to take it to the final state $q_{\mathrm{B}}$. In order to calculate the amount of work, the observer will have to carry out to move an appropriate amount of charge from one plate to the other we have to proceed via infinitesimal transformations. The infinitesimal amount of work that the outside world carries out to move an infinitesimal quantity of charge $\mathrm{d} q$ is
\[

$$
\begin{equation*}
\hat{d} W=\psi \mathrm{d} q, \tag{2.10}
\end{equation*}
$$

\]

where

$$
\begin{equation*}
\psi=\frac{1}{\epsilon_{0}} q \frac{h}{\Sigma} \tag{2.11}
\end{equation*}
$$

is the potential difference when the charge is $q$. The transition between $q_{\mathrm{A}}$ to $q_{\mathrm{B}}$ can be carried out following many different procedures but the total work that we will have to carry out will always have the value

$$
\begin{equation*}
W_{\mathrm{A}, \mathrm{~B}}=\frac{1}{2 \epsilon_{0}} \frac{h}{\Sigma}\left(q_{\mathrm{B}}^{2}-q_{\mathrm{A}}^{2}\right)=\frac{1}{2} h \Sigma \epsilon_{0}\left(E_{\mathrm{B}}^{2}-E_{\mathrm{A}}^{2}\right) . \tag{2.12}
\end{equation*}
$$

In calculating this result, we made some assumptions: (a) that the charge on the plates is distributed uniformly, which is equivalent to disregard the so-called edge effects; (b) that inside is a vacuum; (c) that the capacitor is not deformed during the process; (d) that the different charging processes are slow enough.

Having expressed the amount of work as a function of the intensity of the electric field allows us to describe the same result in different terms: if we consider as our physical system the region of space, of volume $V_{C}=h \Sigma$, internal to the capacitor, and consider as initial and final states the intensity of the electric field $E_{\mathrm{A}}$ and $E_{\mathrm{B}}$, we can state that that region of space contains a certain the quantity of energy $U_{\text {es }}(E)$ associated only with the creation of the electrostatic field $E$ which, therefore, we will call energy of the electric field. Its expression is

$$
\begin{equation*}
U_{\mathrm{es}}(E)=\frac{1}{2} \epsilon_{0}(h \Sigma) E^{2}+\text { constant } \tag{2.13}
\end{equation*}
$$

within an arbitrary additive constant (which is generally set null, like for kinetic energy).

Furthermore, since the field is perfectly homogeneous within the volume under consideration, the energy too will be considered uniformly distributed in it with density:

$$
\begin{equation*}
u=\frac{1}{2} \epsilon_{0} E^{2} . \tag{2.14}
\end{equation*}
$$

## Energy of Point Charges at Rest

This example, at first glance similar to the previous one, will be dealt with in quite a different way. Before, our system was a region of space within which we created an electric field; the state variable was the intensity of the field itself and so we defined the energy of the field. In this case, the system is made up of a specific distribution of point charges $q_{i}$ at rest, and the state of the system is defined by their positions $\mathbf{r}_{i}$. To modify the space distributions of the charges, we have to apply forces and calculate the total amount of work we have to carry out. The positions of the various charges in the initial configuration A are indicated by $\mathbf{r}_{i}^{\mathrm{A}}$ and in the final configuration B by $\mathbf{r}_{i}^{\mathrm{B}}$. We can demonstrate that the total amount of work carried out by the external world to change the configuration from $A$ to $B$ equals

$$
\begin{equation*}
W_{\mathrm{A}, \mathrm{~B}}=\frac{1}{2} \frac{1}{4 \pi \epsilon_{0}}\left[\sum_{i, j} \frac{q_{i} q_{j}}{r_{i, j}^{\mathrm{B}}}-\sum_{i, j} \frac{q_{i} q_{j}}{r_{i, j}^{\mathrm{A}}}\right], \tag{2.15}
\end{equation*}
$$

where

$$
\begin{equation*}
\frac{1}{r_{i, j}^{\mathrm{A}}}=\frac{1}{\left|\mathbf{r}_{i}^{\mathrm{A}}-\mathbf{r}_{j}^{\mathrm{A}}\right|} \text { and } \frac{1}{r_{i, j}^{\mathrm{B}}}=\frac{1}{\left|\mathbf{r}_{i}^{\mathrm{B}}-\mathbf{r}_{j}^{\mathrm{B}}\right|} \tag{2.16}
\end{equation*}
$$

are the same for the final configuration $B$. In a similar way to the previous examples, we can see that the amount of work carried out by us is given by the difference between the final and the initial configurations of the function:

$$
\begin{equation*}
U=\frac{1}{2} \frac{1}{4 \pi \epsilon_{0}} \sum_{i, j} \frac{q_{i} q_{j}}{r_{i, j}}+\text { constant } \tag{2.17}
\end{equation*}
$$

The function $U$ is called energy of the configuration of charges. Since this function depends only on the positions of the different charges, it is normally called potential energy. Likewise, the same reasoning can be used for other frequently encountered cases such as spring force and the energy in the Earth's gravitational field. However, getting back to the case of electrostatics, an important consideration needs to be made. One particular, and very familiar, case of Eq. (2.17) occurs when, as the starting configuration A you take the one where all the charges are at infinity and a value for the energy $U(\infty)=0$ is attributed. With the arbitrary additive constant thus determined, the expression for the energy of a given configuration becomes

$$
\begin{equation*}
U=\frac{1}{2} \frac{1}{4 \pi \epsilon_{0}} \sum_{i, j} \frac{q_{i} q_{j}}{r_{i, j}} \tag{2.18}
\end{equation*}
$$

To demonstrate this result, it is assumed that the force that we apply in every moment to take each charge from infinity to the prescribed position is practically equal and opposite to the electrostatic force carried out by the other charges already settled
into their final positions. Only in this condition will the integral which provides the total amount of the work carried out by us (and which will have an equal and opposite value to the work carried out by the electrostatic forces) be independent of the trajectories traveled by the charges on their paths from infinity. It is obviously an asymptotic procedure, which is carried out only ideally with practically zero velocity and which, therefore, takes place over an infinite lapse of time. In any procedure conceived as realistic, in order to create the configuration in a finite period of time, we would have to start from a system of charges set, at rest, far apart and submit them to accelerations to take them to their final positions at rest. In a realistic situation, therefore, we would not be able to ignore radiative phenomena and these would make the amount of work carried out by us certainly dependent on the trajectory traveled by the charges and on the way in which this trajectory is traveled. The same could be said for the example of charging the capacitor: the process of charging has to take place very slowly to be able to consider the electromagnetic field and the distribution of the charges in an electrostatic configuration in every moment. As we well know, in all real processes in which movements of charges are involved, magnetic fields are formed, radiation is generated, and the electrostatic approach is seen for what it is, that is a model conceived with a passage to the limit. We are reflecting on an abstract situation that we consider the asymptotic situation towards which we have real phenomena tend. This happens in all fields of Physics, however this procedure is correct because the theoretical context enables us to estimate how much the imagined process differs from the real process.

### 2.5 Definition of Heat (Quantity of)

We always consider a closed system in a state of equilibrium A and we operate upon it in order to take it to a new state of equilibrium B. We will now operate in a more general way, without a restriction of adiabatic walls. Experience shows that the amount of work carried out by us depends on the particular transformation that we have brought forth. We define as the amount of heat provided by the outside world to the system, in that particular transformation, the difference between the change of energy and the amount of work carried out by us in that particular transformation. Formally, indicating this new quantity with the symbol $Q_{\mathrm{A}, \mathrm{B}}$ we have

$$
\begin{equation*}
Q_{\mathrm{A}, \mathrm{~B}}=[U(\mathrm{~B})-U(\mathrm{~A})]-W_{\mathrm{A}, \mathrm{~B}}=\Delta U_{\mathrm{A}, \mathrm{~B}}-W_{\mathrm{A}, \mathrm{~B}} . \tag{2.19}
\end{equation*}
$$

From now on, the symbol $\Delta$ applied to a state function will always indicate the difference of the values of that function between the final and the initial state, so Eq. (2.19) can usefully be written as

$$
\begin{equation*}
\Delta U_{\mathrm{A}, \mathrm{~B}}=W_{\mathrm{A}, \mathrm{~B}}+Q_{\mathrm{A}, \mathrm{~B}} . \tag{2.20}
\end{equation*}
$$

In this expression, we can see that the variation of energy of a closed system in a certain process is given by the sum of two contributions, quite distinct among themselves, due to two distinct modalities of the interaction of the outside world with the system. The first term ( $W_{\mathrm{A}, \mathrm{B}}$ ) describes the interactions controlled by the observer, therefore those which fall within part of a known theoretical context, referring to which the observer is able to determine the amount of work carried out. The second term, $Q_{\mathrm{A}, \mathrm{B}}$ brings together all of those modes of interaction of the outside world on the system that are not controlled by the observer. It is useful to read Eq. (2.20) in this way: in a transformation from a state A to a state B , both of equilibrium, a certain quantity of energy is transferred from the outside world to the system and this happens in the two ways we described. While the first one represents known ways, i.e., connected to known theoretical contexts, the second includes all the other types of interactions and therefore describes our deficit, or in other words our ignorance, in understanding interactions. It should be noted that this definition of quantity of heat includes the already known definition which comes from simple calorimetry but represents the maximum generalization of it. In particular, it separates the concept of quantity of heat transferred to the system from the concept of change of temperature. This connection, on the other hand, is a constituent part of the calorimetric definition and often causes much ambiguity and even errors in the study of successive developments in Thermodynamics. This definition of quantity of heat is due to [2].

### 2.6 Infinitesimal Transformations

The definitions of energy Eq. (2.1) and of quantity of heat Eq. (2.19) were given for finite transformations in which the initial and final states are states of equilibrium. We can get these two states closer and closer together and so the quantities at play will be smaller and smaller. We will call infinitesimal transformations the transformation between very close states of equilibrium, though seen from the point of view of a passage to the limit for zero amplitude of the transformation. In this sense, we will consider the states of equilibrium of a macroscopic system as defined by continuous variables and the relations between these quantities will define the functions to which we will apply the theory of continuous and differentiable functions.

Both the First and the Second Principles will be formulated for infinitesimal transformations and therefore the fundamental equations for Thermodynamics are differential equations, as occurs for the fundamental equations of both Mechanics and Electromagnetism. This procedure is necessary so that the definition of work, as we have seen from the study of Mechanics, is given for infinitesimal transformations. The main consequence of taking on this approach is that considering the balance equation between variations in energy, amount of work, and amount of heat in a very small change of state, is equivalent to considering this equation as the projection of a differential equation. In that case, the property of energy as a function of state will be formally expressed, requiring that the differential of the function which expresses energy in function of the other state variables is an exact differential. As we will see
throughout this whole work, it is from this property and from the analogous property for entropy that a large quantity of results of absolute generality will be obtained. On the other hand, for the work and the amount of heat they are just infinitesimal quantities but they are not the differentials of a state function.

It is clear that the infinitesimal quantities which will appear in the differential equations must be represented by different symbols according to whether they are exact differentials or not. In Appendix A. 5 we will summarize the different cases in which different symbols will be necessary.

### 2.7 Formulation of the First Principle of Thermodynamics

For infinitesimal transformations, we will indicate the infinitesimal quantities of work and of heat provided by the external world to the system with the symbols $\hat{d} W$ and $\hat{d} Q$, respectively. We will use the symbol d to indicate an infinitesimal quantity, which represents the variation of a function of state and therefore an exact differential. For the First Principle of Thermodynamics, we can write the following conclusive statement:

$$
\begin{equation*}
\mathrm{d} U=\hat{d} W+\hat{d} Q . \tag{2.21}
\end{equation*}
$$

One last, but very important, comment. The definition of energy given in Eq. (2.1) has to guarantee that it is defined for every possible state of equilibrium. The value of energy in state X is defined as follows: you choose a reference state O and assign an arbitrary value for energy to this state, for example, the value 0 (zero). In this way, the value of the energy in state $X$ will be defined by the measure (or calculation) of the quantity of work that we carry out to take the system from the reference state O to the generic state X in an adiabatic way. For this to be a good definition of energy, it is necessary that any state X can be reached from the reference state O in an adiabatic way. A careful reader might observe that it would be enough to be sure that the two states $O$ and $X$ can be linked, in one sense or the other, by an adiabatic transformation. In this case, by measuring the quantity of work carried out we could either measure

$$
\begin{equation*}
[U(\mathrm{X})-U(\mathrm{O})] \text { or }[U(\mathrm{O})-U(\mathrm{X})] . \tag{2.22}
\end{equation*}
$$

As it stands now, we cannot answer this question and therefore this definition of energy is not solid. The Second Principle of Thermodynamics will answer this question.

## Chapter 3 <br> The Second Principle of Thermodynamics


#### Abstract

The impossibility of realizing the perpetual motion is universally accepted as a fundamental principle of Physics. This postulate defines two main categories, where physical processes can be placed: natural processes and unnatural processes. The former includes all the observed processes and the hypothesized processes that do not violate the fundamental principle and are, therefore, possible. The latter includes all the hypothesized processes that violate the principle of the impossibility of perpetual motion, and therefore they cannot occur. This is the starting point for formulating an evolutionary criterion for all-natural processes. To achieve this, a suitable mathematical tool must be developed. The fundamental step is the definition of entropy and of absolute temperature. These are complementary quantities and constitute the basis of the Second Principle, which must be formulated, first, in the frame of closed systems. Before the extension of the fundamental equations of Thermodynamics to continuous systems, the approximation of discontinuous systems and the problem of the conversion of heat into work both for reversible and irreversible engines are discussed. The coefficients of performance of refrigerators and of heat pumps are defined and the problem of the maximum work obtainable from a given configuration immersed in a given environment is briefly treated.


Keywords Natural processes • Unnatural processes • Quasi-static processes • Reversible processes $\cdot$ Second principle $\cdot$ Entropy $\cdot$ Temperature $\cdot$ Absolute temperature $\cdot$ Thermal engines $\cdot$ Efficiency of an engine $\cdot$ Carnot cycles $\cdot$ Endoreversible engines • Coefficient of performance • Heat pumps • Refrigerators • Maximum work • Availability

### 3.1 Introduction

The Second Principle, which constitutes a fundamental principle of Physics, is often referred to as the principle, which states "the impossibility of realizing the perpetual motion." ${ }^{11}$ Let us comment briefly on the origin of this denomination. Realizing perpetual motion means to build a device that, once set in motion, would continue

[^7]forever. In the past centuries, but also in our days, various attempts to realize perpetual motion have been accomplished. In purely mechanical systems, one has to compensate for the energy dissipated by friction forces and then some energy must be supplied. Therefore, either one does not believe any longer in the principle of energy conservation or, if energy conservation is maintained, the device would stop running when the energy source has been exhausted as it happens, for instance, with familiar pendulum clocks. Such a formulation of the impossibility of perpetual motion would not lead, then, to any element of novelty with respect to the principle of energy conservation already established. In other words, the acceptance that in real physical world friction cannot be eliminated might, at most, suggest some metaphysical meditation but does not constitute any sort of introduction to a new fundamental principle of physics.

The debate about the impossibility of creating perpetual motion changed profoundly in the nineteenth century when the issue of converting heat into mechanical motion became of the utmost importance, at least initially, for practical reasons. It was proved that we can extract heat from a source, use it to make a body to expand, and use the expansion to produce mechanical work. Evidently, this opened the way to a new perspective: use heat transfer as a positive work producer instead of considering it as a negative energy-wasting interaction (friction is one kind of heat interaction).

Immediately "the economic question" arose: how much work can we produce per Joule extracted from a heat source?

It is understood that this question refers to a repetitive, i.e., cyclical, way of producing work. Indeed it is well known, for example, that by expanding isothermally an ideal gas we can obtain 1 joule of work per each Joule of extracted heat but this could not last forever because the expansion could not continue indefinitely. It was soon realized that an entire conversion of heat into work was not obtainable in a repetitive (cyclical) way even for an ideal, frictionless engine. This statement was assumed to constitute a basic law, which regulates the heat-work transformation and was formulated in two different but equivalent forms one by Rudolf Clausius and the other by Lord Kelvin (William Thomson).

The former statement, by R. Clausius, is: Heat can never pass from a colder to a warmer body without some other change, connected therewith. The latter, by Lord Kelvin, is: It is impossible to construct an engine (cyclically working device), which can produce work by absorbing energy in the form of heat from a single thermal reservoir.

It is easy to prove that if one of the two formulations is falsified then the other is falsified too, then the two formulations are equivalent.

In the new technical-scientific context that the Industrial Revolution determined, the question of the impossibility of perpetual motion can be put in this way:

If we could construct an engine (cyclic transformation) with $100 \%$ efficiency, i.e., in which the amount of produced work equals the amount of heat supplied to the engine, we could return to the heat source that we used to operate the engine, exactly the same amount of energy consumed to make the machine work and so it could be kept running for eternity. Someone could observe, with reason, that this device still needs the absence of friction but now the argument is quite different. The
conservation of energy is not under discussion but we wonder whether the existence of an ideal, frictionless device, which could realize perpetual motion, as proposed above and to which real devices could approach indefinitely, can be conceived. The postulation about the impossibility of realizing perpetual motion is equivalent to stating the impossibility of obtaining a $100 \%$ efficiency engine even in the absence of friction, and this fact changes the situation in a radical way:

It prescribes the impossibility that a particular class of processes can take place in nature (either in the form of Clausius's or in that of Kelvin's statements for instance). If this prohibition were confined into the particular field of the construction of thermal machines, we could speak of an empirical law valid in a particular field of Physics but it is immediately obvious that if a certain class of hypothetical processes are not allowed then this could be the signature of the existence of a fundamental principle that governs the feasibility of any process in nature.

Then, the compact expression impossibility of realizing perpetual motion well represents this fundamental principle to which any (constructive) theory of Physics must be submitted. For instance, it makes a reason for the fact that
(i) The macroscopic states of equilibrium we observe must resist against unavoidable perturbations, i.e., they must possess a form of stability in order to be observable by a macroscopic observer;
(ii) A macroscopic system responds in a predictable way to external perturbations;
(iii) Apparently independent phenomena are deeply connected;
(iv) The chemical reactions proceed in certain directions;
(v) Matter and/or energy must flow with certain modalities according to the configuration determined in that instant;
(vi) The properties of the electromagnetic radiation in equilibrium with matter do not depend from the properties of matter anywhere in the universe and so on ...

As we shall see in Chap. 17, the Principle concerning the impossibility of realizing perpetual motion is so vastly and deeply founded in Physics that the need to explain the Maxwell-Szilard paradox, which tries to falsify it will push us to change our view on the observer-observed relation. To make a conjecture become a Principle of Physics, it is necessary that it be expressed in a complete way with a formal mathematical language and this will be developed in this chapter. There are several possible formulations but we will adopt the one given by E. A. Guggenheim in [3].

### 3.2 Natural and Unnatural Processes

We will call natural processes those processes, finite or infinitesimal, which can take place in nature. Obviously, all the observed processes belong to this group. Similarly, we will call unnatural processes those processes, finite or infinitesimal, which cannot take place in nature. The Second Principle of Thermodynamics establishes the criterion, which allows us to fit any hypothetical process into one of these two categories. In order to do this, we have to identify which is the property all-natural
processes hold in common and, on the other side, the property all-unnatural processes have in common. To be able to create the tool which allows us to decide whether an imagined infinitesimal process should belong to one or the other of these two main categories, it is necessary to conceive of, by abstraction, a third category of processes called quasi-static processes.

### 3.3 Quasi-static Processes

Quasi-static processes are infinitesimal processes, imagined abstractly, that do not fit either in the group of natural processes or in that of unnatural processes but, we could say, they fit in the border between the two previously defined categories.

An example will help us to understand this categorization. Let us consider a cylindrical receptacle placed vertically and containing water in a liquid state in the bottom part and in the top part water vapor. The top part of the cylinder is closed by a movable piston without friction. Furthermore, the water and the water vapor are at the same uniform temperature.

By changing the load on the piston, we can change the pressure inside the receptacle as we please, within certain limits, indicating the value with $p$. Furthermore, we will indicate the value of the vapor pressure of water at that temperature with $p_{\mathrm{s}}$.

Now, let us imagine the process which consists of transferring a small quantity of matter from the liquid state to the vapor state.

If $p<p_{\mathrm{s}}$, the hypothesized process will be a natural process. This process is called evaporation and could actually be observed. The opposite process, which consists of a small quantity of water vapor turning into a liquid state, is called condensation and cannot take place under the supposed conditions: it will be classified as an unnatural process. Vice versa, if $p>p_{\mathrm{s}}$ the formerly hypothesized process, that is the evaporation, will be considered an unnatural process and, naturally, the opposite process will be considered natural. If we get the condition $p=p_{\mathrm{s}}$ the hypothesized process can be considered, at its limit, a natural process, but its opposite (that is, an infinitesimal condensation) can also be considered, at its limit, a natural process. Therefore, the hypothesized process can be considered as belonging, as an extreme situation, both to the natural and the unnatural processes.

The infinitesimal processes which have this property are called quasi-static processes. We can say that these ideal processes are both natural and unnatural at the same time because also their opposite (that is, the same infinitesimal process with a "change of sign") is both a unnatural and natural process. For this reason, we can affirm that they are abstract processes which fit in the border between natural and unnatural processes. This example can be generalized. Let us consider an isolated system which is prepared, initially, in a certain configuration. Generally, this system will not be in a stationary state and we will observe some modifications, that is, some processes, until all the properties of the system will have reached values that are constant in time. We will say that the system is in a state of equilibrium and that the processes that we have observed have made the system move from the initial
nonequilibrium configuration toward the state of equilibrium compatible with the constraints. In an isolated system, natural processes move a configuration toward the equilibrium state. Conversely, once this state has been reached, a process which moves the system away from the state of equilibrium is to be considered an unnatural process.

An infinitesimal process which moves from a state of equilibrium will be, by definition, a quasi-static process.

### 3.4 Reversible Processes

Let us return to the example of the evaporation or condensation of a small mass we considered in Sect. 3.3 to define a quasi-static process. We know that the process of evaporation or of condensation requires that a certain amount of heat is provided to or removed from the cylinder by the outside environment, for example through the bottom of the receptacle. If the temperature outside the cylinder is equal to the temperature inside, the necessary transfer of the small quantity of heat will be, in turn, a process which occurs between two systems in mutual equilibrium and therefore will be a quasi-static process. In this case the hypothesized process of evaporation (or likewise of condensation) will be called a reversible process. In conclusion, a quasi-static process is an infinitesimal process which occurs in a system in a state of equilibrium. If the system is also in equilibrium with the outside world, then the process will be called reversible.

### 3.5 Formulation of the Second Principle: Definition of $S$ and $T$

If we consider a change of state, we can observe that this can come about both because of interactions with the external world (that is, interactions in which the external world transfers some energy by doing work and/or exchanging heat) and because of modifications that happen inside the system but that are not linked to interactions with the outside. As an example of the latter consider an isolated system in which some internal constraint is removed. The distinction between transformations due to interaction with the outside, and transformations due to internal processes are extremely important for the formulation of the Second Principle which we chose to write about here. ${ }^{2}$ The Second Principle also has to be formulated for closed systems and infinitesimal transformations.

[^8]For every physical system, a state variable called Entropy is defined and noted with the symbol $S$, which has the following properties:
(1) $S$ is a function of state.
(2) $S$ is an extensive quantity.
(3) In an infinitesimal process, the variation of $S$ is always given by the sum of two contributions $\mathrm{d} S=\hat{d}_{\mathrm{e}} S+\hat{d}_{\mathrm{i}} S$.
(4) $\hat{d}_{\mathrm{e}} S$ measures the contribution to the variation of entropy, due to the interaction of the system with the outside world. This term is given by

$$
\begin{equation*}
\hat{d}_{\mathrm{e}} S=\frac{\hat{d} Q}{T} \tag{3.1}
\end{equation*}
$$

where $\hat{d} Q$ is the infinitesimal amount of heat transferred from the outside world to the system and $T$ is a new, intensive, state variable which depends only on the empirical temperature of the system and therefore can be considered a new temperature scale. This last statement requires a more in-depth explanation, which we will pick up on again later.
(5) $\hat{d}_{\mathrm{i}} S$ represents the contribution to the variation of entropy due to processes which occur inside the system. For this term, we have

$$
\begin{cases}\hat{d}_{\mathrm{i}} S>0 & \text { for natural processes }  \tag{3.2}\\ \hat{d}_{\mathrm{i}} S<0 & \text { for unnatural processes } \\ \hat{d}_{\mathrm{i}} S=0 & \text { for quasi-static and for reversible processes. }\end{cases}
$$

Let us examine each point in more detail.

### 3.5.1 State Functions

Being a state function means that $S$ is defined only for equilibrium states and that its variation in an infinitesimal process is expressed by an exact differential. Its variation in a finite process, like for energy, depends only on the values of the state parameters in the initial and final states A and B and not on the particular choice of the process which took the system from A to B , but differently from energy, entropy is not a conserved quantity. This means that it can also change because of internal processes (i.e., without any causal connection with the external world). For example, if a system is isolated and an internal boundary exists, for example, a wall dividing the system into two volumes with different densities or temperatures, removing this internal restriction brings about a repositioning of the system into a new state of equilibrium but this happens without the outside world "realizing it". As we will see in Chap.7,
the same occurs if inside an isolated system a phase ${ }^{3}$ transition occurs. This will bring about, in general, a change (in this case an increase) in the value of the entropy but certainly not of the energy. Like in the case of Energy, only the variations of Entropy in a process are defined, so a reference state A can be chosen to assign an arbitrary value of Entropy to, after which the value of $S$ for any other state of equilibrium can be determined.

### 3.5.2 Extensive and Intensive Quantities

Often, the property of extensiveness of a physical quantity is referred to with the term additiveness. The intention with this choice is to highlight the rule: "the value of the whole is equal to the sum of the values of the parts." It is necessary to specify what is meant by "whole" and "parts".

The definition is the following: let us have a system and let $V$ be the volume occupied by it. Let us consider an arbitrary partition of the volume into two volumes $V_{1}$ and $V_{2}$ such that $V=V_{1}+V_{2}$. A property $\mathcal{E}$ is said to be extensive if its value relative to the volume $V$ is

$$
\begin{equation*}
\mathcal{E}=\mathcal{E}_{1}+\mathcal{E}_{2}, \tag{3.3}
\end{equation*}
$$

where $\mathcal{E}_{1}$ and $\mathcal{E}_{2}$ are the values of the quantity $\mathcal{E}$ calculated on $V_{1}$ and $V_{2}$, respectively, for any subdivision of the volume $V$. As we will see better in Chap. 16 this means that $\mathcal{E}$ can be written as

$$
\begin{equation*}
\mathcal{E}(t)=\int_{V} e(\mathbf{r}, t) \mathrm{d} V \tag{3.4}
\end{equation*}
$$

where $e$ will be called "density" of $\mathcal{E}$ at the point $\mathbf{r}=(x, y, z)$ and at the instant $t .{ }^{4}$ The property called "being additive" should be understood as referring to the additiveness of volumes. For example, the energy of a system, the entropy, the mass, the electrical charge are extensive quantities. ${ }^{5}$

Intensive quantities are quantities defined in every point of the system such as pressure, density, temperature, velocity, etc. Normally, it is a nonsense to talk about temperature of a system or of density of a system unless we know from the start that the temperature or the density is uniform. The same is true for velocity. As we will see further on, all the intensive quantities are always defined as partial derivatives of an extensive quantity with respect to another extensive quantity. In general, given an intensive quantity $x$, it will be

[^9]\[

$$
\begin{equation*}
x=\left(\frac{\partial \mathcal{E}}{\partial \mathcal{E}^{\prime}}\right)_{(\ldots)} \tag{3.5}
\end{equation*}
$$

\]

where $x(\mathbf{r}, t)$ is a function of spatial coordinate and time, while (...) means that the partial derivatives are taken keeping constant some extensive variables other than $\mathcal{E}^{\prime}$.

### 3.5.3 Measuring $S$

Like for energy, also for entropy only the variations in a transformation are defined, therefore entropy is defined with an indetermination of arbitrary additive constant. As far as measuring variations in entropy is concerned, we can observe that the term $\hat{d}_{\mathrm{i}} S$ is quantitatively defined only for quasi-static transformations (for which it will be equal to zero). Therefore, if we refer to the definition, to measure a variation in entropy we have to carry out a finite transformation made up of infinitesimal quasistatic transformations, that is, transformations made up of a continuous succession of states of equilibrium:

$$
\begin{equation*}
S(\mathrm{~B})-S(\mathrm{~A})=\int_{\mathrm{A}}^{\mathrm{B}} \hat{d}_{\mathrm{e}} S=\int_{\mathrm{A}}^{\mathrm{q} . \mathrm{s} .} \mathrm{B} \frac{\hat{d} Q}{T}, \tag{3.6}
\end{equation*}
$$

where the integral is carried out along any quasi-static transformation. In this case, and only in this case

$$
\left\{\begin{array}{l}
\hat{d}_{\mathrm{i}} S=0  \tag{3.7}\\
\hat{d}_{\mathrm{e}} S=\frac{\hat{d} Q}{T}=\mathrm{d} S
\end{array}\right.
$$

so that $\hat{d}_{\mathrm{e}} S$ becomes the exact differential d $S$. As we have seen, the term $\hat{d}_{\mathrm{e}} S$ determines quantitatively the value of the increase of entropy in the system caused by an interaction with the outside world. This contribution is proportional to the quantity of energy that the external world puts into the system by means of interactions which are not controlled by the observer. An increase in entropy can, therefore, be associated with the increase in our ignorance of the overall state of the system, that the process has determined. Naturally, so that Eq.(3.6) can be considered, at least in principle, an operative definition of entropy, it is necessary to have an instrument to measure the temperature $T$ independently. In any case, Eq. (3.6) constitutes an exemplary "operative definition" from a conceptual point of view but quite dissatisfactory from a truly operational side, i.e., experimental in the real sense of the word. We will see in Chap. 5 how that problem will find an adequate solution.

### 3.5.4 The Absolute, or Thermodynamic, Temperature T

It is necessary, however, to highlight that the Second Principle postulates the existence of two new state parameters, $S$ and $T$. The coefficient of proportionality between the change in entropy and the amount of injected heat is given by the reciprocal of the value of a new physical quantity, $T$, whose denomination will be fully explained in Sect.3.6. Each is complementary to the other in the sense that we cannot define one without defining the other also but the development of the theory must ensure that at least one can be measured independently. Furthermore, while $S$ is, like energy, volume, mass, etc., an extensive state parameter and therefore representative of the state of the system, $T$ is an intensive parameter. Its reciprocal $1 / T$ provides information on how rapidly the entropy of the system changes according to the energy transferred from the outside world at a constant volume.

The necessity remains, however, for an operative definition of $T$ which is independent of the measure of $S$. In Sect.3.8, Chaps. 6 and 12 we will see how this can be resolved in different ways, and, in particular, we will see that the ratio $T_{2} / T_{1}$ is determined in an absolute way, leaving us, therefore, with one degree of freedom only: we can choose one reference state and assign to this an arbitrary value of $T$, after which the scale will be completely defined.

### 3.6 Discontinuous Systems Approximation

We have seen that energy $U$ and entropy $S$ are defined for states of equilibrium like, on the other hand, all the state parameters. It might seem, therefore, that thermodynamics is unable to deal with systems not in equilibrium and, as a consequence, with natural processes. The following example, though extremely simple, shows the way often used to overcome this difficulty. The other possible way is passing to continuous systems, but this requires new formal instruments which will be carried out in Chap. 16.

Let us consider two isolated systems, schematically represented in Fig.3.1, that we will identify using Suffixes I and II, each one in a state of internal equilibrium. The state variables that interest us, here, will have the values $U^{\mathrm{I}}, U^{\mathrm{II}}, S^{\mathrm{I}}, S^{\mathrm{II}}, T^{\mathrm{I}}, T^{\mathrm{II}}$. Now we will allow them to come into contact, with a small part of their surfaces, for example, linking them using a metal wire which allows for a small exchange of heat among them. We will suppose that this slight interaction will not significantly alter the state of equilibrium in which they find themselves in that particular moment. This means, in other words, that we are able to estimate the error we make by maintaining this supposition. Let us consider an infinitesimal process in which system I receives, from the external world, an infinitesimal quantity of heat which we will indicate with $\hat{d}^{\mathrm{I}} Q$. Likewise for system II.

Let us now apply all the propositions defining Entropy. For System I, we will have

$$
\begin{equation*}
\mathrm{d} S^{\mathrm{I}}=\hat{d}_{\mathrm{e}} S^{\mathrm{I}}+\hat{d}_{\mathrm{i}} S^{\mathrm{I}}=\frac{\hat{d}^{\mathrm{I}} Q}{T^{\mathrm{I}}} \tag{3.8}
\end{equation*}
$$



Fig. 3.1 Two homogeneous systems (i.e., phases) each in a state of internal equilibrium. The thin connection between the two represents a weak interaction between them. It is weak enough to permit the maintenance of internal equilibria. The regions in each system, in which the state variables vary significantly are small enough to be disregarded. For simplicity, let's suppose that the overall system is isolated
with $\hat{d}_{\mathrm{i}} S^{\mathrm{I}}=0$ because system I is in a state of equilibrium and therefore the infinitesimal transformation is quasi-static. ${ }^{6}$

Likewise, we can write for system II:

$$
\begin{equation*}
\mathrm{d} S^{\mathrm{II}}=\hat{d}_{\mathrm{e}} S^{\mathrm{II}}+\hat{d}_{\mathrm{i}} S^{\mathrm{II}}=\frac{\hat{d}^{\mathrm{II}} Q}{T^{\mathrm{II}}}, \tag{3.9}
\end{equation*}
$$

with $\hat{d}_{\mathrm{i}} S^{\mathrm{II}}=0$. Now let us consider the composite system formed by I and II together. This system will have an entropy $S=S^{\mathrm{I}}+S^{\mathrm{II}}$ due to extensiveness and as a consequence for the entropy change of the composite system we will have

$$
\begin{equation*}
\mathrm{d} S=\mathrm{d} S^{\mathrm{I}}+\mathrm{d} S^{\mathrm{II}}=\frac{\hat{d}^{\mathrm{I}} Q}{T^{\mathrm{I}}}+\frac{\hat{d}^{\mathrm{II}} Q}{T^{\mathrm{II}}} . \tag{3.10}
\end{equation*}
$$

Furthermore, since the global system is an isolated one (each of the two can only interact with the other and not with third system), we will have $\hat{d} Q=\hat{d}^{\mathrm{I}} Q+\hat{d}^{\mathrm{II}} Q=$ 0 from which it will be $\hat{d}^{\mathrm{I}} Q=-\hat{d}^{\mathrm{II}} Q$. Then

$$
\begin{equation*}
\mathrm{d} S=\hat{d}^{\mathrm{II}} Q\left(\frac{1}{T^{\mathrm{II}}}-\frac{1}{T^{\mathrm{I}}}\right) . \tag{3.11}
\end{equation*}
$$

Also, for system I + II the relation

$$
\begin{equation*}
\mathrm{d} S=\hat{d}_{\mathrm{e}} S+\hat{d}_{\mathrm{i}} S \tag{3.12}
\end{equation*}
$$

will, obviously, be true. This system is isolated and therefore

$$
\begin{equation*}
\hat{d}_{\mathrm{e}} S=0 . \tag{3.13}
\end{equation*}
$$

[^10]Hence

$$
\begin{equation*}
\mathrm{d} S=\hat{d}_{\mathrm{i}} S=\hat{d}^{\mathrm{II}} Q\left(\frac{1}{T^{\mathrm{II}}}-\frac{1}{T^{\mathrm{I}}}\right) . \tag{3.14}
\end{equation*}
$$

From the propositions 5 in Sect.3.5, we have $\hat{d}_{\mathrm{i}} S>0$ if the imagined process is a natural one, while if the result is $\hat{d}_{\mathrm{i}} S<0$ the imagined process will be unnatural. In the first case (natural process), we will have the following two possibilities:

$$
\begin{array}{r}
\text { either } \hat{d}^{\mathrm{II}} Q>0 \text { and } T^{\mathrm{I}}>T^{\mathrm{II}} \\
\text { or } \hat{d}^{\mathrm{II}} Q<0 \text { and } T^{\mathrm{II}}>T^{\mathrm{I}} \tag{3.15}
\end{array}
$$

In both cases, we can see that heat flows from the body with higher $T$ to the body with lower $T$.

If $T^{\mathrm{I}}=T^{\mathrm{II}}$ instead, the imagined process will have as a consequence $\hat{d}_{\mathrm{i}} S=0$. This means, by definition, that the overall state of the system is a state of internal equilibrium against heat transfer. So, in the same way as the empirical temperature $\theta, T$ certifies the state of mutual equilibrium between two systems and, for this reason, it may be called "temperature" but, while this completes the meaning of the empirical temperatures, the absolute scale has the predictive function assigned to it by the Second Principle.

### 3.6.1 Resume

The points which deserve to be highlighted are the following:
(1) We have neglected the properties of the border zone, which allows the interaction between the two systems. For example, we could reasonably assume that the temperature changes continuously through that zone (along the wire in our example) but if its mass is much smaller than the masses of the two systems, we will be able to estimate the error that we commit in assuming a discontinuous variation of the intensive parameters.
(2) We could, then, calculate for the overall system the contribution $\hat{d}_{\mathrm{i}} S$ (the term whose value is not quantitatively determined by the Second Principle) by turning into internal, those contributions which, for the individual systems, were external.
(3) The Second Principle states that if two systems I and II are in mutual equilibrium with respect to the transfer of a small quantity of heat, $T^{\mathrm{I}}=T^{\mathrm{II}}$ (and vice versa) must be true. For this reason, we are allowed to name as "temperature" the new intensive quantity $T$ which is introduced together with $S$ by the Second Principle. Remember that the concept of empirical temperature preexisted the Second Principle and was created just to describe a relation of mutual thermal equilibrium. The new scale of temperatures $T$ covers the same function but tells much more.
(4) From Eq. (3.14) and by virtue of the Second Principle, we see that the new quantity $T$ prescribes the direction of the process. To be more precise, it is just $1 / T$ that has this general predictive power. No empirical temperature can cover this role. Henceforth we shall call $T$ simply "temperature" or "absolute temperature". When we need to refer to an empirical scale of temperatures we will make explicit mention of.
(5) This example is a paradigmatic example: we had to call on all the propositions that define the Second Principle. The idea of considering a nonequilibrium system as a composite system consisting of subsystems each in internal equilibrium and weakly interacting will allow us to find a large amount of results. The alternative to this is a theory in the continua (see Chap. 16. For this reason, we call this first modeling "Approximation of discontinuous systems".

### 3.7 On the Predictive Power of Thermodynamics

The First Principle sets a relationship of balance, which must be respected, and which therefore contributes to the predictive ability of Thermodynamics in the same way that conservation of the momentum or of the angular momentum contribute to the predictive power of Mechanics.

In the case of Thermodynamics, the evolution criterion is completely contained in the Second Principle and, following the formulation given to it in this text, is explicitly expressed by proposition (5) where it is stated that $\hat{d}_{\mathrm{i}} S>0$ for all the natural processes and $\hat{d}_{\mathrm{i}} S<0$ for all the unnatural processes. Further, the separation into processes internal to the system and processes due to interaction with the outside is very functional towards the study of irreversible processes.

Within the approximation of discontinuous systems, it is essential to proceed in two stages: first, the quantitative expressions of the variation in entropy are written for each of the different interacting systems. In this way, the amounts of extensive quantities exchanged in the interactions can be accounted for as terms of the $\hat{d}_{\mathrm{e}} S$ type.

Afterward, the variation in entropy for the overall system is written, making use of the property of extensiveness of the entropy and some terms that, for each part, described interactions with the outside, now become internal processes to which we will apply proposition (5), which contains the evolution criterion.

There are, basically, two types of predictions: on the direction of the processes and on the strength of their mutual interference. They are completely general predictions meaning that they are not linked to any type of modeling.

An isolated system can be formed by simple parts, each one in a state of internal equilibrium but not necessarily in a state of equilibrium among themselves. In this case we will call our system a "composite system." So that the composite system can be formed by simple parts in internal equilibrium but not in equilibrium among themselves, it is necessary for there to be an adequate number of internal constraints between the various simple parts that our system is the union of (for example, these
could be fixed or mobile, adiabatic or diathermic walls, that might separate areas that are not homogeneous among themselves or have different compositions, etc.). If any of these internal restrictions are removed then processes that the restriction did not allow before, become possible and will be active until a new state of equilibrium is reached.

The predictive ability of thermodynamics stands in the ability to predict what new state of equilibrium will be reached following the removal of an internal constraint in an isolated system. Obviously, these will be natural processes so the value of the total entropy of the system in the new state of equilibrium will have to be higher than the value of the entropy at the beginning of the process. Let us now try to turn the problem upside down: let us suppose that we have an isolated system that has reached a state of internal equilibrium. If, for some reason, we imagine that a different composite configuration is created (that we could always imagine creating by adding some kind of internal constraint, for example, by creating a structure made out of small cells), we will obtain a configuration in which the total entropy (which for the property of extensiveness is the sum of the values of the entropy in each small cell) will be lower than when we started. In this case, the Second Principle states that the transition from the state of equilibrium to a composite state of equilibrium would be an unnatural process.

This is the meaning of the current affirmation according to which "entropy has a maximum". Naturally, this is a relative maximum. This provides a fundamental criterion of stability of the states of equilibrium: in an isolated system, the stable or metastable states of equilibrium occur at the configurations corresponding to a (relative) maximum entropy.

This reasoning can be generalized to systems, which are not isolated but subject to a number of external constraints which is equal to the number of macroscopic degrees of freedom. For example, in the environment in which we live, it is very common to impose on the system restrictions on the temperature (constant temperature transformations), on the external pressure (isobaric transformations) or on the total volume (isochoric transformations) etc. In these cases, the stable or metastable states of equilibrium correspond to points of minimum of other thermodynamic potentials such as Free Energy, Enthalpy, or the Gibbs potential (naturally, which of these is chosen depends on the nature of the external restrictions). Therefore, in a certain sense, we can affirm that the Second Principle justifies the existence of the macroscopic states that we observe.

One last comment, of a very general nature, comes from studying the relationships relative to proposition (5) in Sect. 3.5 The only case in which the theory allows us to create precise quantitative predictions is in the case of quasi-static, or reversible, transformations. Therefore, in all of the transformations that actually take place, that is in the natural ones, the theory only predicts inequalities. Therefore, the expected value for a physical quantity in a natural process will have to be of the type: it cannot be higher than or it cannot be lower than. This could be considered a limitation such as to make thermodynamics less "useful" compared to other theories, but a careful examination of the question will turn the situation on its head.

Is it possible to get specific quantitative predictions from thermodynamics? It certainly is possible, but this would imply either treating the processes as quasi-static or "modeling" in some way the system. The latter, for example, could involve a particular treatment of the physical properties of the boundaries, a particular modelization of the flow of the state parameters through the boundaries (for example, in a discontinuous approximation, or assuming that the flows occur, in the transition regions, according to profiles which "make sense"), the assumption of certain state equations, and so on.

This is exactly what we would carry out when we operate in the fields of mechanics or electromagnetism, or in any other theoretical context which enables us to make specific predictions. Even from a statistical mechanics point of view, we can make certain predictions but, in this case, we are dealing with a discipline which is intrinsically a modelization. As one moves away from the peculiarities of a model and one starts investigating the dynamics of the processes in a general sense, the possibility to make specific predictions diminishes and one arrives, in the most general situation, at inequalities to which all of the modelizations will have to submit themselves.

### 3.8 Efficiency of Thermal Engines

Let's now turn our attention, in an overall view, to the problem of the efficiency of a thermal engine that is an engine that uses the energy drawn in the form of heat transfer from external sources and produces mechanical work. The latter can be used immediately or can be accumulated in a "work reservoir", for example, by lifting a weight or putting a flywheel in rotation. With a very rough expression, we will say that this machine has turned a certain amount of heat into work. Sometimes, we talk about transformation of heat into work improperly. If we refer to Eq. (2.20), for a transformation from the initial state A to the final state B we have

$$
\begin{equation*}
\Delta U_{\mathrm{A}, \mathrm{~B}}=W_{\mathrm{A}, \mathrm{~B}}+Q_{\mathrm{A}, \mathrm{~B}} . \tag{3.16}
\end{equation*}
$$

Then, we may speak safely of transformation of heat into work only when $\Delta U_{\mathrm{A}, \mathrm{B}}=0$ because only in these cases we have the quantitative definite relation $Q_{\mathrm{A}, \mathrm{B}}=-W_{\mathrm{A}, \mathrm{B}}$. In general, the two situations in which the required condition occurs, are either in a cyclic transformation or in a nonequilibrium steady state. In this section, we will deal only with thermal engines, that is tools that perform transformations that can be repeated indefinitely and are, therefore, cyclical changes while the latter case will be treated in Sect. 15.2. Obviously, we are interested only in those cyclical transformations for which

$$
\begin{equation*}
W_{\mathrm{tot}, \mathrm{cyc}}<0, \tag{3.17}
\end{equation*}
$$

i.e., in engines which supply external world with positive work which can be used or stored somewhere. Suppose we have $n$ bodies, that we call thermostats or heat sources, of very large heat capacities and relaxation times short compared to the
timescales of the processes and let $T_{i}$ with $i=1 \ldots n$ be their temperatures. Let us accept the constraint that our thermal engine performs cyclic transformations in which it exchanges heat only with these thermostats (all of them or only some of them) so that the cycle will be composed by isotherms with the sources at $T_{i}$ and adiabatic transformations. In some of the isotherms, the engine will receive positive quantities of heat from the sources and in the remaining ones negative quantities of heat. Let us enumerate the former with index $i$ and the latter with index $j$. We define efficiency of the engine the quantity

$$
\begin{equation*}
\eta=\frac{-W_{\mathrm{tot}, \mathrm{cyc}}}{\sum_{i} Q_{i}}, \tag{3.18}
\end{equation*}
$$

where $-W_{\text {tot, cyc }}$ is the total amount of work done by the engine in one cycle (that is the algebraic sum of all the amounts of work done in every single transformation) and the sum of the heat quantities $Q_{i}$ is extended only to the transformations of type $i$. As we numbered with the index $j$ those transformations in which the machine absorbs a negative quantity of heat from the respective sources, let's denote, for convenience, with $Q_{j}$ the absolute value of these quantities of heat and then we will write $-W_{\text {tot, cyc }}=\sum_{i} Q_{i}-\sum_{j} Q_{j}$ and the expression for the efficiency will be

$$
\begin{equation*}
\eta=1-\frac{\sum_{j} Q_{j}}{\sum_{i} Q_{i}} . \tag{3.19}
\end{equation*}
$$

We want to find which one is the cyclic transformation to which corresponds the maximum efficiency consistent with the assigned constraint. We begin with one cycle which produces positive work and let us see how it can be modified in order to increase the efficiency. Consider the composite system formed by the $n$ sources and by the engine. By hypothesis, this constitutes a thermally isolated system. Consider a transformation in which the engine has completed a cycle and calculate the variation in total entropy of the composite system. We will have

$$
\begin{equation*}
\Delta S^{\mathrm{comp}}=\Delta S^{\mathrm{eng}}+\Delta S^{\text {sour }} \tag{3.20}
\end{equation*}
$$

In our case $\Delta S^{\text {eng }}=0$ (cyclic transformation) and

$$
\begin{equation*}
\Delta S^{\text {sour }}=-\sum_{i} \frac{Q_{i}}{T_{i}}+\sum \frac{Q_{j}}{T_{j}} \tag{3.21}
\end{equation*}
$$

As the composite system is an adiabatic system (no part of it exchanges heat with the outside world) the transformation is a transformation due solely to internal processes so, for the cyclic transformation, we can write

$$
\begin{equation*}
\Delta S^{\mathrm{comp}}=-\sum_{i} \frac{Q_{i}}{T_{i}}+\sum \frac{Q_{j}}{T_{j}} \geq 0 \tag{3.22}
\end{equation*}
$$

or

$$
\begin{equation*}
\sum \frac{Q_{j}}{T_{j}} \geq \sum_{i} \frac{Q_{i}}{T_{i}} \tag{3.23}
\end{equation*}
$$

where we shall have the sign of inequality for all engines running natural transformations and the sign of equality if the cyclic transformation is a completely reversible transformation. We modify the initial cycle and make all the transformations quasistatic (running them very slowly) and taking care to modify them so that the heat exchanges take place at the same temperature. Of course, by modifying the transformations in this way, the amplitude of them (both for the adiabatic and the isothermal ones), will change and the amounts of heat exchanged, will change. So, Eq. (3.23) will become

$$
\begin{equation*}
\sum_{j} \frac{Q_{j}}{T_{j}}=\sum_{i} \frac{Q_{i}}{T_{i}} \tag{3.24}
\end{equation*}
$$

The changes in the heat quantities will be such that either some $Q_{j}$ will be lower or some $Q_{i}$ will be higher or both. In all these cases, the efficiency Eq. (3.19) will increase.

The first result is that whatever the cycle is, it will be convenient to perform it reversibly. The efficiency can be improved further if we modify the adiabats in such a way to substitute the various transformations of type $j$, in such a way that we use only the source with the lowest temperature among those denoted with $T_{j}$. Let's denote by $T_{j, \min }$ its temperature. In Eq. (3.24) the summation on the left will be replaced by a single term we indicate by $Q_{\text {out }} / T_{j, \min }$ and write

$$
\begin{equation*}
\frac{Q_{\mathrm{out}}}{T_{j, \min }}=\sum_{j} \frac{Q_{j}}{T_{j}} \tag{3.25}
\end{equation*}
$$

with

$$
\begin{equation*}
Q_{\mathrm{out}}=\sum_{j} T_{j, \min } \frac{Q_{j}}{T_{j}} . \tag{3.26}
\end{equation*}
$$

Since for all $j$, we shall have

$$
\begin{equation*}
\frac{T_{j, \min }}{T_{j}}<1 \tag{3.27}
\end{equation*}
$$

except the case in which the ratio of the temperatures is 1 , we shall have

$$
\begin{equation*}
Q_{\mathrm{out}}<\sum_{j} Q_{j} \tag{3.28}
\end{equation*}
$$

In the expression of the efficiency, the summation $\sum_{j} Q_{j}$ will be replaced by the single term $Q_{\text {out }}$ and, hence, the efficiency will increase.

Similarly we can use, among the sources of type $i$, only the one that has the highest temperature $T_{i, \max }$. Then, we will have

$$
\begin{equation*}
\sum_{i} \frac{Q_{i}}{T_{i}}=\frac{Q_{\mathrm{in}}}{T_{i, \max }} \tag{3.29}
\end{equation*}
$$

with

$$
\begin{equation*}
Q_{\mathrm{in}}=\sum_{i} T_{i, \max } \frac{Q_{i}}{T_{i}} \tag{3.30}
\end{equation*}
$$

and we shall have

$$
\begin{equation*}
Q_{\mathrm{in}}>\sum_{i} Q_{i} \tag{3.31}
\end{equation*}
$$

After inserting this result in Eq.(3.19), we see that the efficiency will rise again becoming

$$
\begin{equation*}
\eta=1-\frac{T_{j, \min }}{T_{i, \max }} \tag{3.32}
\end{equation*}
$$

The last possible step will be to choose as $T_{j, \text { min }}$ and as $T_{i, \text { max }}$, respectively, the lowest and the highest temperatures among the available ones and the maximum efficiency will be:

$$
\begin{equation*}
\eta=1-\frac{T_{\min }}{T_{\max }} \tag{3.33}
\end{equation*}
$$

As we see the maximum efficiency will be achieved by using only the extreme temperatures and will be given by Eq. (3.33). It must also be emphasized that in this demonstration there is no trace of the peculiar nature of the material used for running the engine. This reversible cycle is, therefore, composed of two isotherms and two adiabats and is called Carnot cycle operating between the two given temperatures.

### 3.9 Carnot Cycles

Let's consider a thermal engine operating a Carnot cycles between $T_{1}$ and $T_{2}$ with $T_{1}>T_{2}$, as shown in Fig. 3.2. Let AB be the reversible isothermal expansion at $T_{1}$, BC the reversible adiabatic expansion from state B at $T_{1}$ to state C at the intercept with the isotherm at $T_{2}$, the remaining state D is consequently defined. The four transformations are completely defined if we specify two of the four states A, B, C and D.

From the point of view of the performance of the engine, having fixed the two temperatures, it is enough to choose either the amount of heat $Q_{1}$ absorbed by the engine from the source at $T_{1}$ or the amount of heat $Q_{2}$ given off at $T_{2}$, or the amount of work $W$ produced in one cycle. In general, we may write


Fig. 3.2 A reversible Carnot cycle is represented. Solid lines show that every intermediate state is an equilibrium state and then the four transformations are quasi-static. Transformations $A B$ and $C D$ represent an isothermal expansion and compression, respectively, only if the coefficient of thermal expansion of the substance employed by the engine is positive. For this latter comment see Eq. (5.14) and Problems 5.2 and 5.3

$$
\begin{align*}
W & =Q_{1}-Q_{2},  \tag{3.34}\\
\Delta S_{\text {univ }} & =-\frac{Q_{1}}{T_{1}}+\frac{Q_{2}}{T_{2}} . \tag{3.35}
\end{align*}
$$

If the cycle is reversible (Carnot cycle) we shall have $\Delta S_{\text {univ }}=0$ and

$$
\begin{align*}
& \frac{Q_{1}}{T_{1}}=\frac{Q_{2}}{T_{2}},  \tag{3.36}\\
& \eta=1-\frac{T_{2}}{T_{1}} . \tag{3.37}
\end{align*}
$$

If the cycle is, for any reason, not completely reversible we shall have

$$
\begin{align*}
& \Delta S_{\text {univ }}>0  \tag{3.38}\\
& Q_{2}>Q_{1}\left(\frac{T_{2}}{T_{1}}\right) . \tag{3.39}
\end{align*}
$$

Since the work performed per cycle is $W=Q_{1}-Q_{2}$, we have

$$
\begin{align*}
& W<Q_{1}\left(1-\frac{T_{2}}{T_{1}}\right),  \tag{3.40}\\
& \frac{W}{Q_{1}}=\eta<\left(1-\frac{T_{2}}{T_{1}}\right) . \tag{3.41}
\end{align*}
$$

As we can see, given the two temperatures, the relevant quantities are $Q_{1}$ and $Q_{2}$ or one of the two amounts of heat and the amount of work $W$ produced, while in the Carnot case only one is independent owing to entropy conservation. Both for reversible and irreversible cycles, we may look at the engine just as a device which absorbs some entropy from source $T_{1}$ and transfers some other amount of entropy to source $T_{2}$ regardless the particular nature of the fluid used to operate them.

In a Carnot cycle, these two amounts of entropy are just equal while if some processes in the engine are not reversible, the engine transfers to the colder source more entropy then the one taken from the hotter one. This can be described by saying that the engine must expel toward the colder source the entropy taken from $T_{1}$, plus the entropy that it produces in each cycle owing to the irreversibility of some of its processes.

Let us call $\Delta S_{\text {prod }}$ the amount of entropy produced by the irreversibilities in the engine, per cycle. Since the entropy variation of the engine per cycle has to be zero, we have to impose that, in every cycle, the entropy injected into the engine by source $T_{1}$ plus the entropy generated by the engine itself must be expelled to the outside (i.e., the source at $T_{2}$ ). Let's write the expressions of the entropy input per cycle $\Delta S_{\text {in }}=Q_{1} / T_{1}$ and of the entropy output $\Delta S_{\text {out }}=Q_{2} / T_{2}$ and require

$$
\begin{equation*}
\Delta S_{\mathrm{out}}=\Delta S_{\mathrm{in}}+\Delta S_{\mathrm{prod}} \tag{3.42}
\end{equation*}
$$

which leads to

$$
\begin{equation*}
\frac{Q_{2}}{T_{2}}=\frac{Q_{1}}{T_{1}}+\Delta S_{\mathrm{prod}} \tag{3.43}
\end{equation*}
$$

To some extent, this relation anticipates the key point in the theory of irreversible processes which will be based on the quantitative study of the entropy produced by irreversible processes. In the reversible case $\Delta S_{\text {prod }}=0$ and the previous formulas are recovered. In the irreversible case, the details of the particular engine are irrelevant and what matters is just the entropy produced per cycle. Since the latter must be positive (this is equivalent to the condition $\hat{d}_{\mathrm{i}} S>0$ ) we see from Eq. (3.43) that the efficiency has to decrease in natural engines. For instance, if we keep $Q_{1}$ fixed the quantity of heat given off to the low temperature will be given by

$$
\begin{equation*}
Q_{2}=Q_{1}\left(\frac{T_{2}}{T_{1}}\right)+T_{2} \Delta S_{\text {prod }} \tag{3.44}
\end{equation*}
$$

Since the product $Q_{1}\left(T_{2} / T_{1}\right)$ is the amount of heat that would be released to the low-temperature source by a reversible engine, we see that $Q_{2}$ increases by the amount $T_{2} \Delta S_{\text {prod }}$. It follows that the amount of work produced by the irreversible engine $W_{\text {irr }}$ decreases:

$$
\begin{equation*}
W_{\mathrm{irr}}=W_{\mathrm{rev}}-T_{2} \Delta S_{\mathrm{prod}} \tag{3.45}
\end{equation*}
$$

Similarly, if we keep $Q_{2}$ (i.e., the quantity of heat given away to the refrigerator at $T_{2}$ ) fixed, the quantity of heat extracted per cycle from the hot source must decrease to the value $Q_{1}$ given by

$$
\begin{equation*}
Q_{1}=Q_{2}\left(\frac{T_{1}}{T_{2}}\right)-T_{1} \Delta S_{\text {prod }} \tag{3.46}
\end{equation*}
$$

and the quantity of work per cycle decreases. In all cases, the efficiency $\eta$ decreases. For instance, if we keep $Q_{1}$ fixed the efficiency will be

$$
\begin{equation*}
\eta=\left(1-\frac{T_{2}}{T_{1}}\right)-\frac{T_{2} \Delta S_{\mathrm{prod}}}{Q_{1}} \tag{3.47}
\end{equation*}
$$

Notice that while for Carnot (reversible) cycles the efficiency depends on the two temperatures only, in the case of irreversible (say natural) cycles the efficiency depends, in general, also on the extent of the isotherms.

### 3.10 On the Determination of the New Scale of Temperature $T$

The measurement of the efficiency of a Carnot cycle provides a possible measurement of the ratio between the two temperatures in the absolute scale. As we have seen in Sect.3.8, this ratio is independent of the nature of the material used to operate the machine as long as it is operated reversibly and, therefore, it is determined in an absolute way. We can say that the efficiency of a Carnot engine is a universal function of the working temperatures provided that these are measured in the particular scale defined by the Second Principle. There are other ways to define experimentally this scale of temperature and we will consider, as examples, the case of the black-body radiation and the measurement of the virial coefficients of a gas. The latter is a practical way that can be realized in laboratory with great accuracy. As we will see in both cases, it is the ratio $T_{1} / T_{2}$ that is determined, in nature, in an absolute manner and may be measured experimentally. For the complete definition of the scale, we have the freedom to choose, arbitrarily, the scale value at one point and then the absolute scale is completely defined.

### 3.11 The Carnot Engine and Endoreversible Engines

Consider the case in which we have only two heat sources at temperatures $T_{1}$ and $T_{2}$ with $T_{1}>T_{2}$. The thermal engine with the maximum efficiency will operate with two isotherms at the given temperatures and with two adiabats, all them being reversible and its efficiency is

$$
\begin{equation*}
\eta=1-\frac{T_{2}}{T_{1}} \tag{3.48}
\end{equation*}
$$

To ensure that the transformations in the engine are close to the corresponding reversible transformations, we will have to "put to zero" the friction in the mechanical parts, realize expansions and compressions in a timescale very long compared to the relaxation time of the fluid and make sure that the heat exchanges always occur between bodies at the same temperature (or very near to it). This implies that the time taken to complete one cycle will become very long. In the limit of a reversible cycle, the time taken will be infinite and therefore the power of the machine will be zero. The issue concerning the maximum efficiency, raised in Sect. 3.9, has now to be changed: we want to design an engine not with the highest efficiency but which has the maximum power for the same boundary conditions. This problem has been treated by H. Callen in [4] and we report briefly his results. For a more extensive treatment, see also [5]. The boundary condition will be the same as in the Carnot engine case that is the use of the same two thermostats, but it is easy to convince ourselves that the main problem has to do with the isothermal transformations that is with those interactions in which the engine exchanges heat with the two sources at $T_{1}$ and $T_{2}$.

Indeed, while the relaxation times of the fluid can be made relatively very short ${ }^{7}$ and the mechanical parts can be suitably lubricated, the characteristic times for heat exchanges face severe limitations. We shall assume that the mechanical interactions are reversible and that the changes of state of the fluid can be treated as a succession of internal equilibrium states, while the irreversibility of the cycle can be confined to the processes of heat exchange. More precisely, we assume that the heat exchanges with two given sources at $T_{1}$ and $T_{2}$ are realized when the engine is at the temperatures $T_{\mathrm{w}}$ and $T_{\mathrm{c}}$, respectively, such that

$$
\begin{equation*}
T_{1}>T_{\mathrm{w}}>T_{\mathrm{c}}>T_{2} . \tag{3.49}
\end{equation*}
$$

Here $T_{\mathrm{w}}$ stands for "warm temperature" and is chosen to be lower than $T_{1}$ in order to speed up the transfer of $Q_{1}$ from the source to the engine and similarly for $T_{\mathrm{c}}$ which stands for "cold temperature".

If we want to accelerate the processes of heat exchange, we must lower $T_{\mathrm{w}}$ and increase $T_{\mathrm{c}}$ as much as possible but, in doing so, the efficiency will tend rapidly to zero.

Let us look for the best compromise between the rapidity and the efficiency of operation. Let $\kappa_{\mathrm{w}}$ and $\kappa_{\mathrm{c}}$ be the thermal conductances of the devices exchanging heat with $T_{1}$ and $T_{2}$, respectively:

$$
\begin{equation*}
\kappa=\frac{[\text { conductivity }] \times[\text { area }]}{[\text { thickness }]} . \tag{3.50}
\end{equation*}
$$

Then, the time intervals $\Delta t_{\mathrm{w}}$ and $\Delta t_{\mathrm{c}}$, spent by the engine to exchange the required amounts of heat with the given sources at $T_{1}$ and $T_{2}$, are given, respectively, by

[^11]\[

$$
\begin{align*}
\frac{Q_{1}}{t_{\mathrm{w}}} & =\kappa_{\mathrm{w}}\left(T_{1}-T_{\mathrm{w}}\right)  \tag{3.51}\\
\frac{Q_{2}}{t_{\mathrm{c}}} & =\kappa_{\mathrm{c}}\left(T_{\mathrm{c}}-T_{2}\right) \tag{3.52}
\end{align*}
$$
\]

If we neglect the time intervals relative to the adiabats, the time required per cycle will be

$$
\begin{equation*}
\Delta t=\Delta t_{\mathrm{w}}+\Delta t_{\mathrm{c}}=\frac{Q_{1}}{\kappa_{\mathrm{w}}\left(T_{1}-T_{\mathrm{w}}\right)}+\frac{Q_{2}}{\kappa_{\mathrm{c}}\left(T_{\mathrm{c}}-T_{2}\right)} \tag{3.53}
\end{equation*}
$$

The entropy variations $\Delta S_{\mathrm{w}}$ and $\Delta S_{\mathrm{c}}$ of the engine in the two isotherms at $T_{\mathrm{w}}$ and $T_{\mathrm{c}}$ are, respectively:

$$
\begin{align*}
& \Delta S_{\mathrm{w}}=\frac{Q_{1}}{T_{\mathrm{w}}}  \tag{3.54}\\
& \Delta S_{\mathrm{c}}=\frac{-Q_{2}}{T_{\mathrm{c}}} \tag{3.55}
\end{align*}
$$

and since $\Delta S_{\text {cyc }}=0$ and $\Delta S_{\text {ad }}=0$ we get

$$
\begin{equation*}
Q_{2}=Q_{1} \frac{T_{\mathrm{c}}}{T_{\mathrm{w}}} . \tag{3.56}
\end{equation*}
$$

The time interval per cycle can be written as follows:

$$
\begin{equation*}
\Delta t=Q_{1}\left[\frac{1}{\kappa_{\mathrm{w}}\left(T_{1}-T_{\mathrm{w}}\right)}+\frac{T_{\mathrm{c}} / T_{\mathrm{w}}}{\kappa_{\mathrm{c}}\left(T_{\mathrm{c}}-T_{2}\right)}\right] . \tag{3.57}
\end{equation*}
$$

In fact, the engine performs a Carnot cycle (reversible) between the temperatures $T_{\mathrm{w}}$ and $T_{\mathrm{c}}$ and will produce, in each cycle, the amount of work:

$$
\begin{equation*}
W=Q_{1}-Q_{2}=Q_{1}\left(1-\frac{T_{\mathrm{c}}}{T_{\mathrm{w}}}\right) \tag{3.58}
\end{equation*}
$$

Then, after substitution of $Q_{1}$ from Eq. (3.58) in Eq. (3.57), we can write the following expression for the time $t$ spent in each cycle and for the power $P$ of the engine:

$$
\begin{equation*}
\Delta t=W \frac{T_{\mathrm{w}}}{T_{\mathrm{w}}-T_{\mathrm{c}}}\left[\frac{1}{\kappa_{\mathrm{w}}\left(T_{1}-T_{\mathrm{w}}\right)}+\frac{T_{\mathrm{c}} / T_{\mathrm{w}}}{\kappa_{\mathrm{c}}\left(T_{\mathrm{c}}-T_{2}\right)}\right] \tag{3.59}
\end{equation*}
$$

and

$$
\begin{equation*}
P=\frac{W}{\Delta t}=\left[\frac{T_{\mathrm{w}}}{\kappa_{\mathrm{w}}\left(T_{1}-T_{\mathrm{w}}\right)\left(T_{\mathrm{w}}-T_{\mathrm{c}}\right)}+\frac{T_{\mathrm{c}}}{\kappa_{\mathrm{c}}\left(T_{\mathrm{c}}-T_{2}\right)\left(T_{\mathrm{w}}-T_{\mathrm{c}}\right)}\right]^{-1} . \tag{3.60}
\end{equation*}
$$

Now the problem is to choose the temperatures $T_{\mathrm{w}}$ and $T_{\mathrm{c}}$ so as to maximize the power of the engine. H. Callen finds [4]

$$
\begin{gather*}
\left\{\begin{array}{l}
T_{\mathrm{w}}=c \sqrt{T_{1}}, \\
T_{\mathrm{c}}=c \sqrt{T_{2}},
\end{array}\right.  \tag{3.61}\\
c=\frac{\sqrt{\kappa_{\mathrm{w}} T_{1}}+\sqrt{\kappa_{\mathrm{c}} T_{2}}}{\sqrt{\kappa_{\mathrm{w}}}+\sqrt{\kappa_{\mathrm{c}}}} . \tag{3.62}
\end{gather*}
$$

Then, the maximum power will be

$$
\begin{equation*}
P_{\max }=\kappa_{\mathrm{w}} \kappa_{\mathrm{c}} \frac{\sqrt{T_{1}}-\sqrt{T_{2}}}{\sqrt{\kappa_{\mathrm{w}}}+\sqrt{\kappa_{\mathrm{c}}}} . \tag{3.63}
\end{equation*}
$$

The efficiency of this endoreversible engine maximized in power will be

$$
\begin{equation*}
\eta_{\mathrm{end}}=1-\frac{T_{\mathrm{c}}}{T_{\mathrm{w}}}=1-\sqrt{\frac{T_{2}}{T_{1}}} . \tag{3.64}
\end{equation*}
$$

Resuming:

- The Carnot engine has maximum efficiency but zero power. The most critical points in the operation of engines are in heat transfer along the isotherms.
- Endoreversible engines perform transformations which may be considered internally quasi-static. Irreversibility is confined in the heat exchanges with the sources at $T_{1}$ and $T_{2}$. In order to accelerate the heat exchanges ,the isotherms are performed when the engine is at $T_{\mathrm{w}}$ and $T_{\mathrm{c}}$ according to Eq. (3.49).
- The temperatures which maximize the power of the engine are given by Eq. (3.61)
- The time per cycle is given by Eq. (3.59). It decreases if the conductance increases hence it is convenient to use fluids with large thermal conductivity and large surfaces for heat exchange.
- The (maximum) power is given by Eq. (3.60). It increases with increasing thermal conductances.
- The efficiency is given by Eq. (3.64). It is always less then the efficiency of a Carnot engine working between the same sources, but it is remarkable that the efficiency is independent from the thermal conductances of the heat exchangers.


### 3.12 Coefficient of Performance (COP)

In Sect.3.8, we considered engines designed to produce some positive work and for this purpose they have to absorb heat from the hot source and deliver a part of it to the cold one. In this section, we want to consider the reversed situation in which the
engine is operated in order to absorb some heat from a cold source and transfer it, together with some amount of mechanical work, to a hot source. Let $T_{\mathrm{c}}$ and $T_{\mathrm{h}}$ be the temperatures of the cold and of the hot source, respectively, $\left(T_{\mathrm{h}}>T_{\mathrm{c}}\right)$. Moreover, we denote with $Q_{\mathrm{c}}$ and $Q_{\mathrm{h}}$ the absolute values of the quantities of heat exchanged with the cold and with the hot source, respectively, and with $W$ the amount of work supplied to the engine in one cycle. From the First Principle, we have

$$
\begin{equation*}
Q_{\mathrm{h}}=Q_{\mathrm{c}}+W \tag{3.65}
\end{equation*}
$$

and if the processes are all reversible the Eq. (3.36) between $Q_{\mathrm{c}}$ and $Q_{\mathrm{h}}$ holds

$$
\begin{equation*}
\frac{Q_{\mathrm{c}}}{T_{\mathrm{c}}}=\frac{Q_{\mathrm{h}}}{T_{\mathrm{h}}} . \tag{3.66}
\end{equation*}
$$

The Coefficient Of Performance, shortly denoted by COP, is defined by the ration of the effect we want to produce and the amount of work required.

### 3.12.1 Refrigerator

The engine working in the above manner is called <<refrigerator>> when the purpose is to take away heat from the cold source in order to maintain it at a given temperature $T_{\mathrm{c}}$. It is the case of a freezer where the cold source is the cell whose temperature, owing to non-perfect insulation, tends to raise its temperature and the hot source is, for instance, the kitchen. The refrigerator can also be used in order to keep the room fresh and deliver heat outside (hot source in summer). In these cases, the effect we want to obtain is the removal from the cold source of as much $Q_{\mathrm{c}}$ as we can per joule of work employed. The COP is defined by

$$
\begin{equation*}
\mathrm{COP}_{\text {refr }}=\frac{Q_{\mathrm{c}}}{W} . \tag{3.67}
\end{equation*}
$$

In the case of an ideal refrigerator we can use Eq. (3.36) and express the COP just in terms of the two temperatures:

$$
\begin{equation*}
\mathrm{COP}_{\text {refr } ; \mathrm{id}}=\frac{Q_{\mathrm{c}}}{Q_{\mathrm{h}}-Q_{\mathrm{c}}}=\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}-T_{\mathrm{c}}} . \tag{3.68}
\end{equation*}
$$

### 3.12.2 Heat Pump

The same engine can be used in order to take heat from the cold source, for instance, the exterior of a house in wintertime, and deliver it, together with the work supplied
to the engine, to the "hot source" which is the interior of the house. In this case, the effect we aim at is to obtain as much $Q_{\mathrm{h}}$ as we can for a given $W$ so that the COP of a heat of pump is defined by

$$
\begin{equation*}
\mathrm{COP}_{\mathrm{hp}}=\frac{Q_{\mathrm{h}}}{W} . \tag{3.69}
\end{equation*}
$$

For the ideal heat pump, we have

$$
\begin{equation*}
\mathrm{COP}_{\mathrm{hp}, \mathrm{id}}=\frac{T_{\mathrm{h}}}{T_{\mathrm{h}}-T_{\mathrm{c}}} \tag{3.70}
\end{equation*}
$$

In both cases for real refrigerators or heat pumps, the COP is less then the COP of the corresponding ideal engine. To show this it is sufficient to look at the Second Principle. The composite system formed by the two sources together with the engine is a thermally isolated system (the source of work is considered reversible) and then in every cycle the total entropy must increase. The entropy variation for the engine is zero and for the two heat sources we have:

$$
\begin{equation*}
\Delta S=-\frac{Q_{\mathrm{c}}}{T_{\mathrm{c}}}+\frac{Q_{\mathrm{h}}}{T_{\mathrm{h}}}>0 \tag{3.71}
\end{equation*}
$$

If we make use of Eqs. (3.69) and (3.70) in Eq. (3.71), it is straightforward to prove that for both the refrigerators and the heat pumps, the COP relative to real engines is smaller than the corresponding ideal one.

Example 3.1 The use of heat pumps is generally encouraged by Governments as part of an energy-saving policy. Suppose that a house is subjected to a heat dispersion to the outside due to imperfect thermal insulation. If you want to keep it at a constant temperature, you have to introduce an amount of energy, within the hour, equal to the quantity that is dissipated outside of the same time interval.

If we use an electric heater it is clear that for each joule introduced in the house we will have to consume $W_{\text {eh }}=1 \mathrm{~J}$ of electricity. Let's see what can be the energy consumption of a heat pump for each joule introduced. If the room is kept at a temperature of $22^{\circ} \mathrm{C}$ and if the external environment is at a temperature of $6^{\circ} \mathrm{C}$, in the case of an ideal heat pump the energy consumption, $W_{\mathrm{hp}, \mathrm{id}}$ for each joule produced, will be

$$
\begin{equation*}
W_{\mathrm{hp}, \mathrm{id}}=\frac{1 \mathrm{~J}}{\mathrm{COP}_{\mathrm{hp}, \mathrm{id}}}=\frac{16}{295.15}=0.054 \mathrm{~J} . \tag{3.72}
\end{equation*}
$$

For commercial heat pumps, the $C O P$ ranges between 3 and 5 . If we assume the value $\mathrm{COP} \simeq 4$ for every joule consumed the heat pump delivers 4 J into the house.

We may consider the electric heater as a heat pump with COP $=1$ or, in other words, a heat pump working with a hypothetical environment at $T=0 \mathrm{~K}$.

### 3.13 Availability and Maximum Work

We discuss, in the light of the First and Second Principles of thermodynamics, the following problem. Let us consider a system $\mathscr{S}$, which is closed and undergoes a transformation from the initial A to the final state B. We impose the constraint that in this transformation the system exchanges heat only with one external body $\mathscr{B}$ and does work on a mechanical system $\mathscr{M}$. The body $\mathscr{B}$ is characterized by a relaxation time very short with respect to the interactions timescale so the changes of state to which it is subjected can be considered quasi-static. Similarly, the mechanical system will be virtually without friction in all its moving parts so that each process would be considered to be reversible. This change of state can be realized through many different operations so that we want to calculate the maximum amount of work obtainable in this change of state of the system with the constraints that we have specified.

## Maximum Work and Available Energy

Given the initial and final states A and B, the energy and entropy changes have the same values for the different possible processes and let $\Delta U$ and $\Delta S$ be their values, respectively. Let us begin by choosing one process as starting point and denote by $W$ the amount of work done by the System $\mathscr{S}$ on $\mathscr{M}$ and by $Q$ the quantity of heat supplied by the system $\mathscr{S}$ to the body $\mathscr{B}$ ( $\hat{d} W$ and $\hat{d} Q$ for infinitesimal process, respectively). From the First Principle, we get

$$
\begin{equation*}
-\Delta U=W+Q \tag{3.73}
\end{equation*}
$$

Since $\Delta U$ is fixed, if we want to obtain the maximum value for $W$ we have to look for the process with the minimum value for $Q$. Assume, in the first instance, that the body $\mathscr{B}$ has a very large heat capacity, that is, it behaves as a thermostat and be $T_{0}$ its temperature. Since $\mathscr{S}$ and $\mathscr{B}$ do not exchange heat with other systems, the composite system $\mathscr{S}+\mathscr{B}$ is a thermally isolated system. Then the change in entropy of the composite system will be

$$
\begin{equation*}
\Delta S_{\text {tot }}=\Delta S+\Delta S_{\mathscr{B}} \tag{3.74}
\end{equation*}
$$

which becomes

$$
\begin{equation*}
\Delta S_{\mathrm{tot}}=\Delta S+\frac{Q}{T_{0}} \geq 0 \tag{3.75}
\end{equation*}
$$

From (3.75)

$$
\begin{equation*}
Q \geq-T_{0} \Delta S \tag{3.76}
\end{equation*}
$$

so that the minimum value for $Q$ will be $Q=-T_{0} \Delta S$ and this occurs when the interaction between $\mathscr{S}$ and $\mathscr{B}$ will be reversible. In this case, the amount of work done by S on the mechanical system $\mathscr{M}$ will be

$$
\begin{equation*}
W_{\max }=-\Delta U+T_{0} \Delta S \tag{3.77}
\end{equation*}
$$

Therefore, all transformations from the state A to the state B carried reversibly and with the above constraint will provide the same amount of work given by Eq. (3.77) and this is the maximum value. Note that in this case also the system $\mathscr{S}$, in its interaction with $\mathscr{B}$, will have the same temperature $T_{0}$.

Under the above hypothesis, Eq. (3.77) can be written in the following form:

$$
\begin{align*}
W_{\max }=-\Delta U+T_{0} \Delta S & =-\left(U_{\mathrm{B}}-U_{\mathrm{A}}\right)+T_{0}\left(S_{\mathrm{B}}-S_{\mathrm{A}}\right), \\
& =-\left(U_{\mathrm{B}}-T_{0} S_{\mathrm{B}}\right)+\left(U_{\mathrm{A}}-T_{0} S_{\mathrm{A}}\right), \\
& =-\Omega_{\mathrm{B}}+\Omega_{\mathrm{A}},  \tag{3.78}\\
& =-\Delta \Omega,
\end{align*}
$$

where we set

$$
\begin{equation*}
\Omega=U-T_{0} S \tag{3.79}
\end{equation*}
$$

In this form, the maximum work appears as the difference of a property (state function) of the system $\mathscr{S}$ relative to an environment with a certain temperature and is called available energy.

## Available Work

In many applications, environments have also the characteristic property of acting a constant pressure $p_{0}$ on $\mathscr{S}$. In these cases, the system $\mathscr{S}$ will do work on $\mathscr{M}$ but also against the pressure of the environment. The latter contribution is equal to

$$
\begin{equation*}
W_{\mathrm{env}}=p_{0}\left(V_{\mathrm{B}}-V_{\mathrm{A}}\right), \tag{3.80}
\end{equation*}
$$

then the maximum amount of work that will be done on $\mathscr{M}$ will be

$$
\begin{align*}
W_{\max }^{\prime}=W_{\max }-p_{0}\left(V_{\mathrm{B}}-V_{\mathrm{A}}\right) & =-\Delta \Omega-p_{0}\left(V_{\mathrm{B}}-V_{\mathrm{A}}\right) \\
& =-\Delta\left(U-T_{0} S+p_{0} V\right)  \tag{3.81}\\
& =-\Delta \Lambda,
\end{align*}
$$

where we posed

$$
\begin{equation*}
\Lambda=U+p_{0} V-T_{0} S \tag{3.82}
\end{equation*}
$$

This is a property (state function) of the system $\mathscr{S}$ but relatively to an environment characterized by values $p_{0}$ and $T_{0}$ of pressure and temperature and is called available work of the system in a given environment.

## Availability

As a corollary to what we discussed above, we can now answer the following question: given a system $\mathscr{S}$ set at a certain initial state A, inside an environment characterized by $p_{0}$ and $T_{0}$, what is the maximum amount of work that we can get from $\mathscr{S}$ and net of the work done on the environment? The starting point is to recognize that if $\mathscr{S}$ is in complete equilibrium with the environment we can no longer get any work; This state of the system $\mathscr{S}$ is called dead state. Then if we denote by $U_{0}, V_{0}, S_{0}, p_{0}$, respectively, the values of energy, volume, entropy, and pressure of the system in the dead state we shall have

$$
\begin{equation*}
W_{\max }=-\left(U_{0}-U+p_{0} V_{0}-p_{0} V-T_{0} S_{0}+T_{0} S\right)=\Lambda-\Lambda_{0} . \tag{3.83}
\end{equation*}
$$

Let us put

$$
\begin{equation*}
\Phi_{\Lambda}=\Lambda-\Lambda_{0}, \tag{3.84}
\end{equation*}
$$

$\Phi_{\Lambda}$ being called availability and it depends on the initial state of the system and on the choice of the environment in which it is immersed.

## Problems

3.1 A refrigeration unit keeps a freezer cell at temperature $T_{1}=250 \mathrm{~K}$ and transfers heat to the environment at temperature $T_{2}=300 \mathrm{~K}$. The compressor is situated outside the cell and produces useful work at the rate of $90 \%$ of the energy absorbed from electricity while the remaining $10 \%$ is dissipated by heat transfer to the environment. The freezer cell is separated from the environment by imperfect walls, which allow the quantity $Q_{1}=4.2 \times 10^{7} \mathrm{~J}$ of heat to enter the cell every hour. The coefficient of performance of the unit is $\mathrm{COP} \simeq 3$. Find
(i) The power of the compressor;
(ii) The total quantity of heat transferred to the environment per hour;
(iii) The entropy variation, per hour, of the cell and of the environment;
(iv) The power of the compressor if the refrigerator worked as a reversible engine.
3.2 A thermal engine operates having heat interactions with two thermostats at temperatures $T_{1}=470 \mathrm{~K}$ and $T_{2}=300 \mathrm{~K}$. In each cycle, the increase of the entropy of the Universe is $\Delta S_{\text {univ }}=0.14 \mathrm{cal} \mathrm{K}{ }^{-1}$ and the engine transfers to the lower temperature source $Q_{2}=200 \mathrm{cal}$. Determine the quantity of work produced by the engine per cycle and its efficiency.
3.3 A thermal engine operates Carnot cycles between $T_{1}$ and $T_{2}$ with $T_{1}>T_{2}$. Let AB be the reversible isothermal expansion at $T_{1}, \mathrm{BC}$ the reversible adiabatic expansion from state B at $T_{1}$ to state C at the intercept with the isotherm at $T_{2}$.

The engine absorbs $Q_{1}=400 \mathrm{~kJ}$ per cycle from the source at high temperature and releases $Q_{2}=300 \mathrm{~kJ}$ to the one at low temperature.
(a) Calculate the efficiency $\eta_{\text {rev }}$.

At a certain moment during the adiabatic expansion BC, the engine exhibits a malfunction which causes this transformation to be irreversible and the consequence is that the isotherm $T_{2}$ is intercepted at another point say $\mathrm{C}^{\prime}$. The rest of the cycle proceeds reversibly as before. Show that the the efficiency must be lower. In particular, if in order to reach state C from state $\mathrm{C}^{\prime}$ the engine gives off to the source an additional quantity of heat $Q_{\mathrm{C}^{\prime} \mathrm{C}}=40 \mathrm{~kJ}$.
(b) Calculate the efficiency of the engine in these new conditions.
3.4 An engine operates exchanging heat with three thermostats at temperatures $T_{1}$, $T_{2}$ and $T_{3}$ with $T_{1}>T_{2}>T_{3}$. The engine releases heat only to the heat source at $T_{3}$ and absorbs heat from the other two.
(a) Find the maximum work produced as a function of the amounts of heat withdrawn from $T_{1}$ and $T_{2}$.
(b) Show that the maximum efficiency depends only on the ratio $Q_{1} / Q_{2}$ of the quantities of heat withdrawn from the two sources at $T_{1}$ and $T_{2}$.
3.5 An engine operates exchanging heat with three thermostats at temperatures $T_{1}$, $T_{2}$ and $T_{3}$ with $T_{1}>T_{2}>T_{3}$. The engine releases heat only to the heat source at $T_{2}$ and absorbs heat from the other two. Let's denote with $Q_{1}, Q_{2}$ and $Q_{3}$ the absolute values of the heat quantities exchanged, per cycle, with the three sources respectively. Determine the maximum value of the work done by the engine, and, in the case of a reversible engine, for which value of the ratio $\xi=Q_{3} / Q_{1}$ the amount of work produced is zero.
3.6 An engine operates exchanging heat with three thermostats at temperatures $T_{1}$, $T_{2}$ and $T_{3}$ with $T_{1}>T_{2}>T_{3}$. The engine releases heat only to the heat source at $T_{1}$ and absorbs heat from the other two. Let's denote with $Q_{1}, Q_{2}$ and $Q_{3}$ the absolute values of the heat quantities exchanged, per cycle, with the three sources respectively.
(a) Prove that the work done by the engine is always negative.
(b) The engine is then used as a heat pump. Determine its COP.
3.7 Two bodies with thermal capacities $C_{1}$ and $C_{2}$, supposed to be constant in the temperature intervals we are considering, have initial temperatures $T_{1}$ and $T_{2}$ respectively $\left(T_{1}>T_{2}\right)$. Determine the maximum amount of work that can be produced by an engine working in a "cyclic mode". By "cyclic mode" we mean that at the beginning and at the end of the operations the engine is in the same state.
3.8 A reversible engine operates between two thermostats at temperatures $T_{1}=$ 500 K and $T_{2}$ with $T_{2}<T_{1}$. In every cycle, the engine absorbs $10^{3} \mathrm{~kJ}$ from $T_{1}$ and produces 600 kJ in mechanical work.
(a) Determine the temperature $T_{2}$ of the second thermostat and the amount of heat given to it per cycle $Q_{2}$.
(b) Suppose, that due to aging the engine works with an efficiency equal to 0.75 times its maximum value but still we want to extract from the hot source at $T_{1}$ the same amount of heat and to produce the same amount of work per cycle. At what temperature should the engine transfer the amount of heat $Q_{2}$ ?
3.9 A reversible engine operates between a source at $T_{1}=500 \mathrm{~K}$ and a body with constant heat capacity $C=10^{4} \mathrm{~J} \mathrm{~K}^{-1}$ at the initial temperature $T_{\mathrm{i}}$. Overall, the engine absorbs $Q_{1}=10^{3} \mathrm{~kJ}$ from the source at $T_{1}$ and produces $W=600 \mathrm{~kJ}$ as mechanical work after having completed an integer number of cycles. Determine the amount of heat $Q_{2}$ released to the body and its initial temperature $T_{\mathrm{i}}$.
3.10 Find the maximum amount of work that can be extracted from one ton of water at a temperature of $80^{\circ} \mathrm{C}$ in an environment at $20^{\circ} \mathrm{C}$. Neglect changes in water volume and in the specific heat of water.
3.11 An endoreversible engine operates between two heat reservoirs at $T_{1}=480 \mathrm{~K}$ and $T_{2}=300 \mathrm{~K}$ in the maximum power modality. The entropy of the Universe increases in proportion to the work produced. Determine the entropy increase per joule produced.
3.12 Let's have two identical vessels each one containing 10 L of water at $\theta \simeq 20^{\circ} \mathrm{C}$. A refrigerator operates between the two vessels cooling one of the two and heating the other. The vessels have a negligible heat capacity. The machine is kept operating for 10 minutes and we see that the temperature of the cold body is $\theta \simeq 8^{\circ} \mathrm{C}$. Determine the power of the machine.
3.13 A reversible engine operates using three heat reservoirs at temperatures $T_{1}=$ $1000 \mathrm{~K}, T_{2}=500 \mathrm{~K}$ and $T_{3}=200 \mathrm{~K}$. In every cycle, the engine absorbs $Q_{1}=1000 \mathrm{~J}$ from reservoir at $T_{1}$ and produces on the environment a quantity of work $W=600 \mathrm{~J}$. Find the quantities of heat absorbed by the engine from the other two reservoirs.
3.14 A system undergoes an isothermal, quasi-static transformation from the state A to the final state B , at the temperature $\theta=150^{\circ} \mathrm{C}$. In this transformation the work done on the system amounts to $W_{\mathrm{I}}=212 \mathrm{~J}$. Then the system is brought back from state B to state A by means of an adiabatic transformation in which the system gives back a quantity of work $\left|W_{\text {II }}\right|=100 \mathrm{~J}$. Determine
(a) The variation of entropy $S_{\mathrm{B}}-S_{\mathrm{A}}$ in the first transformation;
(b) Is the second process quasi-static?
3.15 A reversible engine operates between a thermostat at temperature $T_{1}=600 \mathrm{~K}$ and a vessel containing ice and water in mutual equilibrium at the pressure of one atmosphere. The initial masses of water and of ice are, respectively, $m_{\mathrm{w}}=210 \mathrm{~g}$ and $m_{\text {ice }}=30 \mathrm{~g}$. The heat of fusion of ice is $\Lambda \simeq 334 \mathrm{~J} \mathrm{~g}^{-1}$. After some time, we stop the engine and we see that in the vessel we have water at the temperature $T_{2}=293.16{ }^{\circ} \mathrm{C}$. Determine the amount of work delivered by the engine (neglect water evaporation).

# Chapter 4 <br> The Fundamental Relation and the Thermodynamic Potentials 


#### Abstract

For each thermodynamic system, it is possible to determine a relation between energy, entropy, and the work parameters (the volume only in the case of simple systems) that is called the Fundamental Relation of the system. We start first with closed systems with no chemical reactions for which the Equilibrium State Postulate determines, in general, the number of degrees of freedom and then it is generalized to open systems with variable chemical composition. The Fundamental Relation describes the set of all stable and metastable equilibrium states that the system can reach and the geometrical properties of the surface described by it determines the conditions of stability of equilibrium states. It can be represented in various forms according to the external constraints. The representations commonly used, in addition to that of Energy and of Entropy, are the Free Energy, the Enthalpy, and the Gibbs Potential and the general properties of isothermal, isobaric and isochoric transformations are discussed. The definition of the chemical potential is given and its physical meaning as the thermodynamic potential responsible of phase equilibria is shown.


Keywords State postulate • Fundamental relation of thermodynamics • Open systems • Free energy • Enthalpy $\cdot$ Gibbs potential $\cdot$ Stability of equilibrium states • Isothermal compressibility

### 4.1 Introduction

In the previous chapter, we defined the first three Principles of Thermodynamics and, in particular, we defined two fundamental quantities such as energy $U$ and entropy $S$. Their fundamental property is that they are both state functions (the former is a conserved state function while the latter is a non conserved one) and we have seen, in some examples, the relevance of this. In order to construct a solid formal assessment it is necessary, at this point, to go deeper into the concepts of "equilibrium state" and of "degrees of freedom" for a macroscopic system. Until now we could manage with a primitive definition of an equilibrium state as the stationary macroscopic configuration which is spontaneously reached in an isolated system. Every macroscopic
quantity that the observer determines experimentally, is defined for equilibrium states and then the set of all macroscopic properties was assumed as the formal definition of the state of a macroscopic configuration. We deal with a set of numbers, some referring to extensive quantities and some to intensive quantities as, for example, volume, temperature, mass, pressure, energy, entropy, coefficient of viscosity, electrical conductivity, magnetic permeability, chemical composition, and many others. In general, the state is composed of several tens of numbers depending on the system we are considering, but we know, partly from experimental observations and partly owing to the theoretical context we are using, that many state parameters are linked among themselves by quantitative relations. It follows that a much lower number of parameters is sufficient to define the state, since the other quantities are deducible by means of well-known relations. The reduction of the number of parameters necessary to identify the state could appear, at a first glance, merely dictated by a reason of practical convenience but, on the contrary, is a matter of fundamental interest. It is necessary to establish a criterion for determining:

1. The number of degrees of freedom of a system and that is, how many state parameters are necessary and sufficient to uniquely determine the thermodynamic state;
2. What is one possible choice of independent parameters. Once we have found one possible choice, this will not be unique but the identification of at least one of them is necessary and the mutual independence among these state parameters must be guaranteed. Obviously, it will not be enough that we do not know the existence of mutual dependencies.

All this must be possible regardless of the fact that our knowledge of the different properties of the system and of the relationships between them is complete or not. This result is guaranteed by the so-called Equilibrium State Postulate of more briefly State Postulate [6]. We start limiting ourselves to consider closed systems without chemical reactions. The general formulation will be given in Sect.4.3.1.

### 4.2 The Equilibrium State Postulate for Closed Systems with No Chemical Reactions

We consider an equilibrium state $A$ and an infinitesimal transformation. From the First Principle, we have

$$
\begin{equation*}
\mathrm{d} U=\hat{d} W+\hat{d} Q . \tag{4.1}
\end{equation*}
$$

It is necessary to carry out some considerations about the term $\hat{d} W$ which represents the amount of work that we do on the system (that is the term that we control). The definition comes from Mechanics where we have seen that, for a small displacement of the point where a force $\mathbf{F}$ is applied, the amount of work done is defined by

$$
\begin{equation*}
\hat{d} W=\mathbf{F} \cdot \mathrm{d} \mathbf{s} . \tag{4.2}
\end{equation*}
$$

From this, it is immediate to define the amount of work done in a small deformation of an extended body and, with subsequent generalizations, we write the expression for compressible fluids. In the latter case, under the conditions required by hydrostatics and fluid dynamics, we can write the expression for the work done in the form

$$
\begin{equation*}
\hat{d} W=-p \mathrm{~d} V, \tag{4.3}
\end{equation*}
$$

where $p$ is the value of the pressure of the fluid and $V$ its volume. For the moment, as we consider a fluid in a state of equilibrium, the value of the pressure of the fluid will coincide with the value of the equivalent pressure ${ }^{1}$ exerted from the outside world. Let us consider other contexts in which we can determine the amount of work we do on the system for small changes of state.

We have previously seen that the amount of work done in order to vary the intensity of the electric field within the plates of a capacitor is given by

$$
\begin{equation*}
\hat{d} W=\psi \mathrm{d} q, \tag{4.4}
\end{equation*}
$$

where $\psi$ is the potential difference between the plates and $q$ is the free charge deposited on the plates.

If we consider a surface layer (the topic will be discussed in a dedicated Chap. 9), in order to vary, by an infinitesimal amount, the area of the surface we will have to do the work

$$
\begin{equation*}
\hat{d} W=\sigma \mathrm{d} \Sigma, \tag{4.5}
\end{equation*}
$$

where $\sigma$ is the surface tension and $\Sigma$ the area of the surface. In all the examples that we can cite, it emerges a common feature: the amount of work we have to do, by means of different modes of action, in order to produce a small change of state in the system is always given by the product of the small change of an extensive quantity times the value of an associated intensive quantity. In general, the amount of work we (external world) have to do on the system will be written in the form

$$
\begin{equation*}
\hat{d} W=\sum_{i=1}^{k} x_{i} \delta \mathcal{E}_{i}, \tag{4.6}
\end{equation*}
$$

where $\mathcal{E}_{i}$ is the $i$ th extensive quantity on which the observer operates creating interactions and $x_{i}$ is the associated intensive quantity. Indeed, as we shall demonstrate in Chap. 14 where irreversible processes will be extensively treated, it is the difference of these intensive quantities between systems not in mutual equilibrium, that will play the role of generalized forces. In this context, the extensive quantities $\mathcal{E}_{i}$ will be called "quasi-static work parameters" and they represent the $k$-independent

[^12]modes the observer adopts to interact with the system in a controlled manner and produce changes on it. As we know there are other ways of interaction, not controlled by the observer. All of them are grouped in one general term designated by $\hat{d} Q$ and then for any small change in a closed system we have
\[

$$
\begin{equation*}
\mathrm{d} U=\hat{d} Q+\sum_{i=1}^{k} x_{i} \mathrm{~d} \mathcal{E}_{i} \tag{4.7}
\end{equation*}
$$

\]

We know that, for quasi-static transformation, the $\hat{d} Q$ term can be expressed as the product of an intensive quantity times the infinitesimal variation of an appropriate extensive quantity. In this case, we write

$$
\begin{equation*}
\hat{d} Q=T \mathrm{~d} S . \tag{4.8}
\end{equation*}
$$

We can conclude that for quasi-static transformations or for small transformations starting from a state of equilibrium, we can write

$$
\begin{equation*}
\mathrm{d} U=T \mathrm{~d} S+\sum_{i=1}^{k} x_{i} \mathrm{~d} \mathcal{E}_{i} \tag{4.9}
\end{equation*}
$$

or the equivalent form

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U-\frac{1}{T} \sum_{i=1}^{k} x_{i} \mathrm{~d} \mathcal{E}_{i} \tag{4.10}
\end{equation*}
$$

These arguments suggest the following statement.

## Statement of the Equilibrium State Postulate

Observable equilibrium states are determined by all interactions of the system with the outside world. If the interactions with the outside world take place by means of $k$ independent work parameters $\mathcal{E}_{i}$ with $i=1,2 \ldots, k$, the equilibrium states (stable or metastable) will be uniquely determined by the $k$ quasi-static work parameters and the energy $U$. As a consequence, the number of degrees of freedom is ${ }^{2}(k+1)$.

### 4.2.1 Simple Systems

We call simple system a system in which the interaction with the external world occurs only via one single work parameter.

[^13]The most frequent case for us is the case of a compressible fluid in which the only form of work can be written as $\hat{d} W=-p \mathrm{~d} V$. In this case, Eq. (4.9) becomes

$$
\begin{equation*}
\mathrm{d} U=T \mathrm{~d} S-p \mathrm{~d} V \tag{4.11}
\end{equation*}
$$

Equivalently, we can express the small entropy change that follows a small change of volume and energy, in a quasi-static process:

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V \tag{4.12}
\end{equation*}
$$

This shows that a simple system is provided with two degrees of freedom, in other words that, given the values for the volume and energy, entropy and all the other properties, are uniquely determined.

### 4.3 The Fundamental Relation

Relations given by Eqs. (4.9) and (4.10) are expressed in terms of small variations of extensive quantities. Now, we transform this relation among small quantities into a differential equations. Formally, this is equivalent to say that for every macroscopic system there is a function, called the Fundamental Relation for that system and that we will write in the form

$$
\begin{equation*}
U=U\left(S, \mathcal{E}_{i}\right) \tag{4.13}
\end{equation*}
$$

or equivalently

$$
\begin{equation*}
S=S\left(U, \mathcal{E}_{i}\right) \tag{4.14}
\end{equation*}
$$

whose differential forms are, respectively:

$$
\begin{equation*}
\mathrm{d} U=T \mathrm{~d} S+\sum_{i} x_{i} \mathrm{~d} \mathcal{E}_{i} \tag{4.15}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U-\frac{1}{T} \sum_{i=1}^{k} x_{i} \mathrm{~d} \mathcal{E}_{i} \tag{4.16}
\end{equation*}
$$

Thanks to the State Postulate we know that the system has $(k+1)$ degrees of freedom and that one possible choice of independent parameters is provided by the $k$ work parameters $\mathcal{E}_{i}$ plus the energy $U$. If we write the Fundamental Equation ${ }^{3}$ in the form Eqs. (4.13) and (4.15), we will say that we are in the energy representation, whereas if we write it in the form Eqs. (4.14) and (4.16) we will say that we have adopted the

[^14]entropy representation. All informations on the properties of the system under our observation, are contained, as we shall see, in its Fundamental Relation.

The State Postulate and its formalizations Eq. (4.15) or Eq. (4.16) lead us to state the fundamental thermodynamic point of view:

- The state of the system is determined by a set of extensive quantities.
- The number of necessary and sufficient extensive quantities (i.e. degrees of freedom of the system) is set by the Equilibrium State Postulate and is equal to the number $k$ of independent work parameters, plus one. The mutual independence of the work parameters is due to the attitude of the observer, in other words is established by the choice, made by the experimenter, on how to operate.
- The outside world induces changes in the state of the system by transferring to it extensive quantities. This is a general criterion for characterizing the interactions.
- These interactions can take place in "controlled" modes, that is, within known theoretical contexts. These modes are realized operating with (i.e. transferring from the outside to the system) the extensive parameters $\mathcal{E}_{i}$.
- These interactions also occur through modes different than those characterized in the previous point and which are not controlled by the observer. They are all included in transfer of entropy $S$; Now we understand that this is consistent with our definition of the transferred amount of heat as the mode of interaction that includes all those who are not covered by the predefined theoretical contexts.
- In the light of what we have seen in this subsection, we see that it would be more correct to speak of entropy transfer instead of heat transfer because entropy is possessed by the systems and can, therefore, be exchanged (in contrast to heat). In spite of this, there remains in the language of physics the heat transfer expression born with calorimetry at a time when the terms "heat" and "energy" indicated substantially different quantities. This expression is still so deeply rooted both in the natural and in the specific (scientific) languages, that we will continue to use it solely for reasons of functionality.

Among the extensive quantities that systems exchange during interactions (i.e. $\mathcal{E}_{i}$ and $S$ ), some are conserved quantities some are non conserved quantities.

In addition the required condition that the state parameters are extensive quantities implies that the Fundamental Relation is a homogeneous function of degree one. Formally

$$
\begin{equation*}
U\left(\lambda S, \lambda \mathcal{E}_{i}\right)=\lambda U\left(S, \mathcal{E}_{i}\right) \tag{4.17}
\end{equation*}
$$

where $\lambda$ is an arbitrary, real positive number. By using the Euler's theorem (see Appendix A.3) for homogeneous functions of first degree, it is possible to rewrite the Fundamental Relation in the integral form

$$
\begin{equation*}
U\left(S, \mathcal{E}_{i}\right)=\left(\frac{\partial U}{\partial S}\right)_{\mathcal{E}_{i}} S+\sum_{i=1}^{k}\left(\frac{\partial U}{\partial \mathcal{E}_{i}}\right)_{S, \mathcal{E}_{j \neq i}} \mathcal{E}_{i} \tag{4.18}
\end{equation*}
$$

By considering Eqs. (4.13) and (4.11), then Eq. (4.18) becomes

$$
\begin{equation*}
U(S, V)=T S-p V \tag{4.19}
\end{equation*}
$$

with

$$
\begin{align*}
T & =\left(\frac{\partial U}{\partial S}\right)_{V},  \tag{4.20}\\
p & =-\left(\frac{\partial U}{\partial V}\right)_{S} . \tag{4.21}
\end{align*}
$$

The relation given in Eq. (4.20) represents the definition of temperature, which has been extensively detailed from Sect.3.5 to Sect.3.10. Conversely, Eq. (4.21) needs to be properly commented. The term $p$ was introduced in Mechanics as the expression of "force per unit area". In Eq. (4.21), $p$ stands for a partial derivative but will still be called "pressure". As we did for temperature, it will be necessary to justify this denomination, and this will be done in Sect.4.3.3. These are the most general definitions of the variables known under the names temperature and pressure, respectively, and of course their definition will be the same also in the more general case in which the work parameters are in any number provided they are kept constant.

### 4.3.1 The General Case for Open Systems with Variable Composition: The Chemical Potential

The principles of Thermodynamics have been formulated for closed systems in the absence of chemical reactions. We recall that the definition of amount of heat would be meaningless for an open system but within this limitation the experimental observations have provided an abundant quantity of direct indications that led the observer to the formulation that we have discussed up to this moment. In the case of open systems or otherwise of variable composition, the observer will operate generalizations and only after, empirical observations will show whether there are contradictions. Let us suppose that there are $m$ components and that $k$ of them, with $k \leq m$ are independent. For example, if there are no chemical reactions it will be $k=m$, while if there are $p$ chemical reactions it will be $k=m-p$. In general the choice of the $k$ independent components to be taken as independent, is not unique. In order to describe the quantity of matter for each component we could use the mass $m_{\gamma}$ or the mole number $n_{\gamma}$. In this treatise we will use the latter. ${ }^{4}$

From now on, for simplicity of writing, we shall limit ourselves to the case in which there is only one work parameter and that this is the volume $V$. The Fundamental Relation for each system will now be written, in its most general form in the energy representation, as

[^15]\[

$$
\begin{equation*}
U=U\left(S, V, n_{1}, n_{2}, \ldots, n_{k}\right) \tag{4.22}
\end{equation*}
$$

\]

and the Fundamental Equation will be written in the form

$$
\begin{equation*}
\mathrm{d} U=T \mathrm{~d} S-p \mathrm{~d} V+\sum_{\gamma=1}^{k} \mu_{\gamma} \mathrm{d} n_{\gamma} \tag{4.23}
\end{equation*}
$$

where

$$
\begin{align*}
T & =\left(\frac{\partial U}{\partial S}\right)_{V, n_{\gamma}}  \tag{4.24}\\
p & =-\left(\frac{\partial U}{\partial V}\right)_{S, n_{\gamma}} \tag{4.25}
\end{align*}
$$

as in Eqs. (4.20) and (4.21) of closed systems without chemical reactions. The new term that is now being introduced is

$$
\begin{equation*}
\mu_{\gamma}=\left(\frac{\partial U}{\partial n_{\gamma}}\right)_{S, V, n_{\gamma^{\prime}} \neq \gamma} \tag{4.26}
\end{equation*}
$$

and it is called the chemical potential of component $\gamma$. This is an intensive state function and, as we shall see Chaps. 7 and 14, plays a very important role in regulating both phase transitions and chemical reactions.

It must be pointed out that Eq. (4.26) is a definition of chemical potential which is unquestionable from the formal point of view but absolutely poor from the physical (i.e. operational) point of view. Indeed if we had to measure such a thermodynamic potential following its definition we should measure the fraction $\Delta U / \Delta n_{\gamma}$ keeping constant the volume and the abundance of the other components and this is, in principle, easy but we should do the same also for entropy which is an extensive quantity as $n_{\gamma}$ and this is, in principle, quite complicated.

We will see that it will be more appropriate to adopt different definitions for $\mu_{\gamma}$ that do not suffer from this difficulty by referring to thermodynamical potentials different from energy (Free Energy or the Gibbs potential). In the more general case we will have, for the Fundamental Relation in the energy representation, the expression $U=U\left(S, \mathcal{E}_{i}, n_{\gamma}\right)$ where $\mathcal{E}_{i}$ are the work parameters as previously defined. Some authors prefer to use the same notation for the work parameters $\mathcal{E}_{i}$, and the mole numbers $n_{\gamma}$ (in any case they are all extensive quantities). In that case the terms of type $\mu_{\gamma} \mathrm{d} n_{\gamma}$ are called "chemical work" to standardize the naming to the terms of the type $x_{i} \mathrm{~d} \mathcal{E}_{i}$. In this way the chemical potentials acquire the function of "generalized forces" (as the $x_{i}$ ) and this is correct as we will see in the study of phase equilibria and chemical reactions.

### 4.3.2 Other Thermodynamic Potentials

The thermodynamic point of view, outlined in this section, and according to which the interaction of the observer with the systems (and thus also of the systems with each other) can be viewed as transfers of extensive quantities, is conceptually correct, elegant and provide the fundamental point of view for the study of irreversible processes. It will be just the variations of extensive quantities that will be interpreted as generalized flows and that will give the name to individual processes and among which we will study the modes of mutual interference. However, in the study of the thermodynamics of equilibrium states it is appropriate to define new extensive quantities such that they express explicitly the constraints imposed by observer in the laboratory. For instance we can easily control the temperature or the pressure of a system ${ }^{5}$ but we will have the need for new representations of the Fundamental Equation, which explicitly take into account the constraints on the temperature and/or pressure.

One possibility could be to express the Fundamental Relation, both in the energy and in the entropy representations, as functions of temperature and pressure but, in order to do that, we have to express, for instance, the volume as a function of temperature and pressure i.e. we have to introduce the equation of state. In other words we must introduce informations on the particular system we are dealing with and so, while Eq. (4.22) is a relation of absolute generality, its expression as a function of a different choice of independent variables would be of particular validity.

From this comes the opportunity to introduce new thermodynamic potentials which have the same power of the Fundamental Relation but that they are expressed in a natural way as a function of the state of $T$ and $p$ variable. Potentials that serve the purpose are

$$
\begin{align*}
& F=U-T S,  \tag{4.27}\\
& H=U+p V,  \tag{4.28}\\
& G=U+p V-T S, \tag{4.29}
\end{align*}
$$

where $F$ is the Free Energy or Helmoltz Potential, $H$ is the Enthalpy or Heat Function, and $G$ the Gibbs Potential or Free Enthalpy. Their utility is clear if we write the changes in an infinitesimal process

$$
\begin{align*}
& \mathrm{d} F=-S \mathrm{~d} T-p \mathrm{~d} V+\sum_{\gamma=1}^{k} \mu_{\gamma} \mathrm{d} n_{\gamma},  \tag{4.30}\\
& \mathrm{d} H=T \mathrm{~d} S+V \mathrm{~d} p+\sum_{\gamma=1}^{k} \mu_{\gamma} \mathrm{d} n_{\gamma}, \tag{4.31}
\end{align*}
$$

[^16]\[

$$
\begin{equation*}
\mathrm{d} G=-S \mathrm{~d} T+V \mathrm{~d} p+\sum_{\gamma=1}^{k} \mu_{\gamma} \mathrm{d} n_{\gamma} \tag{4.32}
\end{equation*}
$$

\]

From their differential expressions we see that each of the three potentials is associated in a natural way to a suitable choice of the state variables and precisely:

$$
\begin{align*}
& F=F\left(T, V, n_{\gamma}\right),  \tag{4.33}\\
& H=H\left(S, p, n_{\gamma}\right),  \tag{4.34}\\
& G=G\left(T, p, n_{\gamma}\right) \tag{4.35}
\end{align*}
$$

These associations, that we called "natural", mean that the differential Eqs. (4.30)(4.32) are of general validity exactly as Eq. (4.22) and, consequently, also Eqs. (4.33)(4.35) have the same rank of the Fundamental Relations. They are the Fundamental Relation of the system under observation but in different representations. From the previous relations we can write different, but equivalent, definitions of the chemical potential:

$$
\begin{align*}
\mu_{\gamma} & =\left(\frac{\partial F}{\partial n_{\gamma}}\right)_{T, V, n_{\gamma^{\prime}} \neq \gamma},  \tag{4.36}\\
& =\left(\frac{\partial H}{\partial n_{\gamma}}\right)_{S, p, n_{\gamma^{\prime}} \neq \gamma},  \tag{4.37}\\
& =\left(\frac{\partial G}{\partial n_{\gamma}}\right)_{T, p, n_{\gamma^{\prime} \neq \gamma}} . \tag{4.38}
\end{align*}
$$

As we see the definitions of the chemical potential in the Free Energy and in the Gibbs potential representations, do not suffer the "defect", only on the operational level, it is suffering from the original definition in the Energy representation. We will see how the examination of the main properties of these new thermodynamic potentials can permanently solve this aspect and, above all, allow an understanding of the physical meaning of the chemical potential.

### 4.3.3 The Free Energy and Isothermal Processes in Closed Systems

From the Second Principle

$$
\begin{equation*}
\hat{d} Q=T \mathrm{~d} S-T \hat{d}_{\mathrm{i}} S \tag{4.39}
\end{equation*}
$$

and for an isothermal transformation:

$$
\begin{equation*}
\hat{d} Q=\mathrm{d}(T S)-T \hat{d}_{\mathrm{i}} S . \tag{4.40}
\end{equation*}
$$

Therefore, in the case of isothermal transformations the Second Principle establishes that, for all natural isothermal transformations:

$$
\begin{equation*}
\hat{d} Q<\mathrm{d}(T S) . \tag{4.41}
\end{equation*}
$$

We go back to the First Principle for closed systems and without chemical reactions and for an infinitesimal transformation:

$$
\begin{equation*}
\mathrm{d} U=\hat{d} W+\hat{d} Q \tag{4.42}
\end{equation*}
$$

we get, for natural isothermal transformations:

$$
\begin{equation*}
\mathrm{d} U<\hat{d} W+\mathrm{d}(T S) \tag{4.43}
\end{equation*}
$$

and then

$$
\begin{array}{ll}
\mathrm{d} F<\hat{d} W & \text { (natural isotherms) } \\
\mathrm{d} F>\hat{d} W & \text { (unnatural isotherms) } \\
\mathrm{d} F=\hat{d} W & \text { (quasi-static isotherms) } \tag{4.46}
\end{array}
$$

The previous relations mean that if we operate on a system to make it perform a isothermal transformation, the amount of work that we have to spend is equal to the change in free energy for quasi-static transformations or larger. The free energy change is, therefore, the minimum value of the amount of work required. If $\hat{d} W=0$, as it may happens for a system maintained at constant volume, Eqs. (4.44)-(4.46) become

$$
\begin{array}{ll}
\mathrm{d} F<0 & \text { (natural processes) } \\
\mathrm{d} F>0 & \text { (unnatural processes) } \\
\mathrm{d} F=0 & \text { (quasi-static processes) } \tag{4.49}
\end{array}
$$

We can say that Eqs. (4.44)-(4.46) represent the Second Principle limited to isothermal transformations.

## Why $\boldsymbol{p}$ Can Be Called Pressure?

Consider a cylinder subdivided into two parts by a piston which can move without friction. This cylinder is held at a constant temperature $T$ and at a constant (total) volume $V$. The piston divides the system into two compartments inside each of which is contained a homogeneous fluid (phase). The quantities for each compartment will be indicated with symbols $\alpha$ and $\beta$. We shall have: $V^{\alpha}+V^{\beta}=V$ and $T^{\alpha}=T^{\beta}=T$. We consider an infinitesimal process which consists in a displacement of the piston
by an infinitesimal amount. For each compartment, we will have

$$
\begin{align*}
\mathrm{d} F^{\alpha} & =-p^{\alpha} \mathrm{d} V^{\alpha}  \tag{4.50}\\
\mathrm{d} F^{\beta} & =-p^{\beta} \mathrm{d} V^{\beta} \tag{4.51}
\end{align*}
$$

Since the volume of the whole cylinder has a constant value, it will be $\mathrm{d} V^{\alpha}=-\mathrm{d} V^{\beta}$, and we have

$$
\begin{equation*}
\mathrm{d} F=\mathrm{d} F^{\alpha}+\mathrm{d} F^{\beta}=\left(-p^{\alpha}+p^{\beta}\right) \mathrm{d} V^{\alpha} \tag{4.52}
\end{equation*}
$$

The hypothesized process will be a quasi-static process if $\mathrm{d} F=0$ and this means that the overall system $(\alpha+\beta)$ will be in equilibrium with respect to that process. This happens if

$$
\begin{equation*}
p^{\alpha}=p^{\beta} \tag{4.53}
\end{equation*}
$$

The hypothesized process will be a natural one if

$$
\begin{equation*}
\left(-p^{\alpha}+p^{\beta}\right) \mathrm{d} V^{\alpha}<0 \tag{4.54}
\end{equation*}
$$

and this leads to the two possible conditions

$$
\begin{array}{r}
\text { either } \mathrm{d} V^{\alpha}>0 \text { and } p^{\alpha}>p^{\beta} \\
\text { or } \mathrm{d} V^{\alpha}<0 \text { and } p^{\alpha}<p^{\beta} . \tag{4.56}
\end{array}
$$

The condition given by Eq. (4.53) is called hydrostatic equilibrium. The two cases described by Eqs. (4.55) and (4.56) are summed up in the rule: the compartment at higher pressure increases in volume. This seems obvious if we limit ourselves to the mechanical definition of pressure, and this proves that the intensive quantity defined in Eq. (4.25) deserves the name "pressure".

## Physical Meaning of the Chemical Potential

Consider two phases (homogeneous systems) denoted by the symbols $\alpha$ and $\beta$. The two phases are kept at the same temperature $T^{\alpha}=T^{\beta}=$ constant but they are not necessarily at the same pressure as would be, for example, if they were separated by a membrane which allows for the flow of some component while maintaining a pressure difference. In addition we suppose that chemical reactions are absent and that the two phases are in a state of internal equilibrium. They are not necessarily in mutual equilibrium in the sense that they can exchange matter between them and only between them (the overall system is a closed system). Imagine that an infinitesimal amount of matter migrates from phase $\alpha$ to phase $\beta$. We want to know under what conditions this process is allowed (natural process) or forbidden (unnatural process). Since this is an isothermal process we write the Free Energy change for the different systems in play. For systems $\alpha$ and $\beta$ we have respectively:

$$
\begin{align*}
\mathrm{d} F^{\alpha} & =-p^{\alpha} \mathrm{d} V^{\alpha}+\sum_{\gamma=1}^{k} \mu_{\gamma}^{\alpha} \mathrm{d} n_{\gamma}^{\alpha}  \tag{4.57}\\
\mathrm{d} F^{\beta} & =-p^{\beta} \mathrm{d} V^{\beta}+\sum_{\gamma=1}^{k} \mu_{\gamma}^{\beta} \mathrm{d} n_{\gamma}^{\beta} . \tag{4.58}
\end{align*}
$$

This writing is justified because both systems undergo a quasi-static transformation as they are in a state of internal equilibrium. Now, consider the system consisting in the union of the two systems $\alpha$ and $\beta$, and denote with $F$ its Free Energy. We shall have

$$
\begin{gather*}
F=F^{\alpha}+F^{\beta}  \tag{4.59}\\
\mathrm{d} F=-p^{\alpha} \mathrm{d} V^{\alpha}+\sum_{\gamma=1}^{k} \mu_{\gamma}^{\alpha} \mathrm{d} n_{\gamma}^{\alpha}-p^{\beta} \mathrm{d} V^{\beta}+\sum_{\gamma=1}^{k} \mu_{\gamma}^{\beta} \mathrm{d} n_{\gamma}^{\beta} . \tag{4.60}
\end{gather*}
$$

For the overall system the total work done on it from the outside will be the sum of the amount of work performed on the $\alpha$ system plus the amount of work done on the $\beta$ system. Furthermore, since it is closed we will have

$$
\begin{gather*}
n_{\gamma}^{\alpha}+n_{\gamma}^{\beta}=\text { const },  \tag{4.61}\\
\mathrm{d} n_{\gamma}^{\alpha}+\mathrm{d} n_{\gamma}^{\beta}=0 . \tag{4.62}
\end{gather*}
$$

Then Eq. (4.60) becomes

$$
\begin{equation*}
\mathrm{d} F=\hat{d} W+\sum_{\gamma=1}^{k}\left(\mu_{\gamma}^{\alpha}-\mu_{\gamma}^{\beta}\right) \mathrm{d} n_{\gamma}^{\alpha} \tag{4.63}
\end{equation*}
$$

If the two systems are in equilibrium with respect to the hypothetical transfer of matter, it must be

$$
\begin{equation*}
\mathrm{d} F=\hat{d} W \tag{4.64}
\end{equation*}
$$

and then

$$
\begin{equation*}
\sum_{\gamma=1}^{k}\left(\mu_{\gamma}^{\alpha}-\mu_{\gamma}^{\beta}\right) \mathrm{d} n_{\gamma}^{\alpha}=0 \tag{4.65}
\end{equation*}
$$

Since the sum is extended only to a set of independent components, and as the equilibrium condition must hold for any virtual process, then for every $\gamma$ it must be

$$
\begin{equation*}
\mu_{\gamma}^{\alpha}=\mu_{\gamma}^{\beta} . \tag{4.66}
\end{equation*}
$$

If the transformation is assumed to be a natural process

$$
\begin{align*}
& \mathrm{d} F<\hat{d} W  \tag{4.67}\\
& \sum_{\gamma=1}^{k}\left(\mu_{\gamma}^{\alpha}-\mu_{\gamma}^{\beta}\right) \mathrm{d} n_{\gamma}^{\alpha}<0, \tag{4.68}
\end{align*}
$$

and this for every $\gamma$

$$
\begin{equation*}
\left(\mu_{\gamma}^{\alpha}-\mu_{\gamma}^{\beta}\right) \mathrm{d} n_{\gamma}^{\alpha}<0 . \tag{4.69}
\end{equation*}
$$

The expression given by Eq. (4.66) defines the physical meaning of the chemical potential $\mu_{\gamma}$ of a specific component: it expresses the equilibrium condition with respect to the transfer of matter between the two systems. As we will see in greater detail below, the chemical potential rules all those processes that involve changes in the composition for example the chemical reactions. The chemical potential is an intensive quantity, is defined point by point, and therefore depends on intensive quantities. In general it will be written in the form

$$
\begin{equation*}
\mu_{\gamma}=\mu_{\gamma}\left(T, p, C_{1} C_{2}, \ldots, C_{k}\right), \tag{4.70}
\end{equation*}
$$

where $\left\{C_{i}=n_{i} / n\right\}_{i=1,2, \ldots, k}$ are the molar concentrations of the $i$ th component, being $n_{i}, n$ the number of moles of $i$ th the component and the total number of moles in the mixture, respectively. We point out that in general the chemical potential of a specific component depends also on the presence of the other components. From Eq. (4.69) we see that if for component $\gamma$ the condition of equilibrium is not satisfied, then we may have one of the two possibilities:

$$
\begin{align*}
& \text { either } \mu_{\gamma}^{\alpha}>\mu_{\gamma}^{\beta} \text { and } \mathrm{d} n_{\gamma}^{\alpha}<0 \text {, }  \tag{4.71}\\
& \text { or } \mu_{\gamma}^{\alpha}<\mu_{\gamma}^{\beta} \quad \text { and } \quad \mathrm{d} n_{\gamma}^{\alpha}>0 \text {. } \tag{4.72}
\end{align*}
$$

In any case, the rule is that component $\gamma$ migrates from the phase with higher chemical potential towards the one with lower chemical potential. We see now that the chemical potential gradient acts, in some way, to "force" the process of mass transfer. Something very similar happens, as we shall see in greater detail below, for chemical reactions and this justifies the choice of the name.

### 4.3.4 The Enthalpy and Isobaric Processes

The situation in which we observe transformations at constant pressure is frequent in nature and easy to realize in the laboratory. The Fundamental Relation in the Enthalpy representation for closed systems, with constant composition and for isobaric transformations reads

$$
\begin{equation*}
\mathrm{d} H=T \mathrm{~d} S \tag{4.73}
\end{equation*}
$$

so if we transfer a small amount of heat to a system that is initially in a state of equilibrium, and we do this at a constant pressure, we will have:

$$
\begin{equation*}
\hat{d} Q=\mathrm{d} H \tag{4.74}
\end{equation*}
$$

This means that the amount of heat supplied to the system gives the measure of the enthalpy change. For example if we supply heat by the use of an electrical resistance. We can measure the current intensity $I$ and the potential difference $\psi$ across the resistance. The amount of heat given off by the resistance in a time interval $t$ is easily obtained after multiplication of these three numbers so we can write:

$$
\begin{equation*}
\psi I \mathrm{~d} t=\mathrm{d} H \tag{4.75}
\end{equation*}
$$

and we see, then, that the measure of the enthalpy change at constant pressure may be is relatively simple in some cases, and this justifies the designation (little used now) of heat function. If we have a closed system at constant composition, in a state of equilibrium and consider an infinitesimal (quasi-static) transformation at constant pressure, we observe, in correspondence to the supply of a small quantity of heat $\delta Q$, a temperature variation which we will denote with $\delta T$. From Eq. (4.74) we have

$$
\begin{equation*}
\frac{\delta Q}{\delta T}=C_{p}=\left(\frac{\partial H}{\partial T}\right)_{p} \tag{4.76}
\end{equation*}
$$

The quantity $C_{p}$ is called heat capacity at constant pressure. It will be called specific heat at constant pressure or molar heat at constant pressure if we refer to the unit mass or to one mole, respectively.

### 4.3.5 The Gibbs Potential and Isothermal and Isobaric Processes

Let us go back to the Fundamental Relation in the energy representation $U=$ $U\left(S, V, n_{\gamma}\right)$. For Euler's theorem on homogeneous functions of first degree (see Appendix A.3), we can write

$$
\begin{gather*}
U=T S-p V+\sum_{\gamma=1}^{k} \mu_{\gamma} n_{\gamma}  \tag{4.77}\\
G=\sum_{\gamma=1}^{k} \mu_{\gamma} n_{\gamma} \tag{4.78}
\end{gather*}
$$

Recalling Eq. (4.32), for an infinitesimal transformation at constant $p$ and $T$ we may write

$$
\begin{equation*}
\mathrm{d} G=\sum_{\gamma=1}^{k} \mu_{\gamma} \mathrm{d} n_{\gamma} \tag{4.79}
\end{equation*}
$$

While the chemical potentials are properties of the individual components, the Gibbs potential is a property of the overall system and hence we cannot speak of the chemical potential of the overall system. The measurement of $G$ is reconducted to the measurement of the energy $U$ and of the entropy $S$ and, in principle, this is assured by the two principles that define these quantities. For a chemically pure phase, i.e., composed of a single component, Eq. (4.78) simply becomes

$$
\begin{align*}
& G=\mu n,  \tag{4.80}\\
& G_{\mathrm{m}}=\mu, \tag{4.81}
\end{align*}
$$

that is, the chemical potential coincides with the value of the Gibbs potential per mole. It is useful, for further applications, to differentiate Eq. (4.81)

$$
\begin{equation*}
\mathrm{d} \mu=-S_{\mathrm{m}} \mathrm{~d} T+V_{\mathrm{m}} \mathrm{~d} p . \tag{4.82}
\end{equation*}
$$

From (4.82) we obtain two important relations which give us a deeper insight on the structure of the chemical potential for chemically pure substances or for ideal solutions

$$
\begin{equation*}
\left(\frac{\partial \mu}{\partial T}\right)_{p}=-S_{\mathrm{m}} \tag{4.83}
\end{equation*}
$$

and

$$
\begin{equation*}
\left(\frac{\partial \mu}{\partial p}\right)_{T}=V_{\mathrm{m}} . \tag{4.84}
\end{equation*}
$$

The measurement of the Gibbs potential does not allow us to go back to the values of the individual chemical potentials in a mixed system however, the phase equilibrium condition (4.66) gives us an indication of how to proceed, as shown e.g. in Fig. 4.1.

We put the composed system in contact, through a membrane permeable only to component $\gamma$, with a small cylinder. We know that, at equilibrium, the chemical potential of the component $\gamma$ in the composed system will be equal to that of the substance contained in the small cylinder. The latter is a chemically pure phase and, in principle, we could measure

$$
\begin{equation*}
G_{\mathrm{m}}=U_{\mathrm{m}}+p V_{\mathrm{m}}-T S_{\mathrm{m}} . \tag{4.85}
\end{equation*}
$$

In practice we need only to measure the pressure of equilibrium inside the small cylinder (the temperature will be the same).


Fig. 4.1 A way to measure the chemical potential of one component, when it is part of a mixture when we know the Gibbs potential of that component when it is a pure substance, is depicted. The mixture is kept at a fixed pressure and temperature in cylinder A . The small cylinder B communicates with A through a membrane permeable only to the component we are interested in, and a small sample of it is extracted. When the equilibrium with the mixture is established the chemical potential in the two cylinders will be the same. In $B$ we have a pure substance and by measuring the pressure of the sample in B we can find the value of $G_{\mathrm{m}}$ for the pure substance and then the chemical potential of the component in the mixture

### 4.3.6 The Stability Problem in a Thermodynamical System

In the study of Mechanics we have already encountered the problem of the stability of equilibrium states. In that context, after defining what is meant by equilibrium state through the equations of motion, we first distinguish between stable, metastable and unstable equilibrium situations. For the stable and metastable states, the requirement is that there exists a neighborhood of the equilibrium configuration, of non-zero radius, such that for any perturbation of the configuration that is maintained within this neighborhood, the system returns towards the equilibrium configuration. Conversely, the state of equilibrium will be unstable if there is at least one type of disturbance, of whatsoever small amplitude, which causes the abandonment of the equilibrium configuration by the system.

In the thermodynamical context, the problem can be put in similar terms, from a formal point of view, but the outcome of this analysis will be a little different.

In Mechanics we consider an equilibrium configuration and we apply the principle of virtual work in order to test the stability condition. Similarly in the Thermodynamical theory we consider a hypothetical equilibrium state and we require that every "small" transformation, moving from it, should be an unnatural process.

The relevance of carrying on an exhaustive treatment on the stability conditions of thermodynamical states of equilibrium is twofold. On one side we know that some equilibrium states can be foreseen by equations of state obtained from some models, then it is important to discriminate between stable and therefore observable states and unstable, non-observable states. As an example consider the van der Waals equation of state which will be treated in Chap. 8.

On the other the stability conditions dictate the geometrical structure of the Fundamental Relation and this allows absolute general predictions about the physical properties of the system.

In this subsection, we shall be concerned with closed systems, in the absence of chemical reactions and, for simplicity of writing, let's consider phases (homogeneous systems) with only one work parameter $V$.

Consider the system in an equilibrium state $A$. As we know from the State Principle, the system has two degrees of freedom and then, any equilibrium state needs two constraints to be determined. It is natural to consider as external constraints the ones we normally encounter in our observations or in the laboratory experiments that is constraints on volume, pressure, temperature and on the adiabaticity of the walls.

Fixed two of these constraints, one corresponding thermodynamic configuration called state $A$, candidate to be a stable state, is determined by the set of values of the extensive quantities and by their distribution point by point.

Suppose that this configuration suffers a "small" modification, respectful of externally imposed constraints, due to some spontaneous fluctuation or to some external disturbance. In all generality we can describe the onset of the perturbed configuration, assuming that it is determined by a small flux of some extensive quantity between different regions within the system, and let's call this new configuration, i.e. the perturbed state, state $A^{\prime}$.

If the transition from the perturbed state $A^{\prime}$ to state $A$ is a natural one, internal processes will set on and bring back the perturbed state to the original one. If this happens for every perturbed state within a neighborhood of state $A$, the latter will be a stable or metastable equilibrium state.

Equivalently we can say that the stability conditions require that the transition from state $A$ to the perturbed state $A^{\prime}$ is an unnatural process for every state $A^{\prime}$ within a non null neighborhood of state A.

The classification of the virtual process regarded as a natural or unnatural process is always determined by the Second Principle and, ultimately, we can say in short by the rule " $\hat{d}_{\mathrm{i}} S>0$ " but, as we shall see, the formal expression of this rule is different depending on the different constraints that we will consider. ${ }^{6}$

Of course depending on the nature of external constraints it will be appropriate to express the Fundamental Relation in the most suitable representation according to the constraints.

We shall proceed in this way: first we select a pair of external constraints and we will find which pair of state variables must be kept constant in order to give a formal expression to the constraints. Let us describe a variety of perturbed states A' around state $A$ by means of a parameter $\xi$ which we will call "internal degree of freedom" and define $\xi$ so that the equilibrium state $A$ corresponds to the value $\xi^{e}=0$. With this formalism the Fundamental Relation in the entropy representation may be written

$$
\begin{equation*}
S=S(U, V, \xi) \tag{4.86}
\end{equation*}
$$

[^17]When the Fundamental Relation will be written in other representations, the perturbed states will be described by a continuous internal degree of freedom $\xi$ in a similar way.

### 4.3.7 Adiabatic Systems

We examine two possibilities for the second constraint: at constant volume or at constant pressure.

## Adiabatic Systems with Constant Volume

The mathematical expression of these two constraints is

$$
\begin{align*}
\mathrm{d} U & =0  \tag{4.87}\\
\mathrm{~d} V & =0 . \tag{4.88}
\end{align*}
$$

The requirement that all states in a neighborhood of the state $A$ are not reachable by a natural process is that for all of them the contribution due to internal processes $\hat{d}_{\mathrm{i}} S<0$ and then, as $\hat{d}_{\mathrm{e}} S=0$, it will be $\mathrm{d} S<0$. State $A$ must be a state of relative maximum entropy

$$
\begin{equation*}
S=S_{\max } . \tag{4.89}
\end{equation*}
$$

## Adiabatic Systems at Constant Pressure

Let's find the mathematical expression for these two constraints. We may write the infinitesimal work as

$$
\begin{equation*}
\hat{d} W=-p \mathrm{~d} V=-\mathrm{d}(p V) \tag{4.90}
\end{equation*}
$$

and then

$$
\begin{equation*}
\hat{d} Q=\mathrm{d} U-\hat{d} W=\mathrm{d} U+\mathrm{d}(p V) \tag{4.91}
\end{equation*}
$$

Therefore, the formal expression will be

$$
\begin{align*}
& \mathrm{d} H=0  \tag{4.92}\\
& \mathrm{~d} p=0 \tag{4.93}
\end{align*}
$$

and, as in the previous case, the stability will be ensured if the state $A$ will be a point of relative maximum for the entropy:

$$
\begin{equation*}
S=S_{\max } \tag{4.94}
\end{equation*}
$$

### 4.3.8 Systems at Constant Temperature

As we have demonstrated, Eqs. (4.44)-(4.46) are equivalent to the Second Principle restricted to the case of isothermal transformations. From these, we will derive the stability conditions after we have also specified the second constraint.

## Systems at Constant Temperature and Volume

Given the constraints $\mathrm{d} T=0$ and $\mathrm{d} V=0$, for any infinitesimal transformation it will be $\hat{d} W=0$. Therefore, the requirement that all small transformations from state $A$ to the perturbed state $A^{\prime}$ should be unnatural transformations, will be ensured by the condition (see Eqs. (4.47)-(4.49))

$$
\begin{equation*}
\delta F>0 \text { (unnatural transformations). } \tag{4.95}
\end{equation*}
$$

Alternatively, the condition of stability requires that the state A is a point of relative minimum for the free energy

$$
\left.\begin{array}{l}
\mathrm{d} T=0  \tag{4.96}\\
\mathrm{~d} V=0 \\
F=F_{\min }
\end{array}\right\} \text { stable equilibrium at constant } T, V
$$

## Systems at Constant Temperature and Pressure

If the external pressure is maintained at the constant value $p$ the infinitesimal amount of work done by external world on the system will be

$$
\begin{equation*}
\hat{d} W=-p \mathrm{~d} V=-\mathrm{d}(p V) \tag{4.97}
\end{equation*}
$$

In this case Eqs. (4.44)-(4.46) will be written as

$$
\begin{align*}
& \mathrm{d} F<-\mathrm{d}(p V),  \tag{4.98}\\
& \mathrm{d} F>-\mathrm{d}(p V),  \tag{4.99}\\
& \mathrm{d} F=-\mathrm{d}(p V) \tag{4.100}
\end{align*}
$$

or, alternatively:

$$
\begin{array}{ll}
\mathrm{d}(F+p V)<0 & \text { (natural transformations) } \\
\mathrm{d}(F+p V)>0 & \text { (unnatural transformations) } \\
\mathrm{d}(F+p V)=0 & \text { (quasi-static transformations ). } \tag{4.103}
\end{array}
$$

Then, the requirement that all infinitesimal transformations that move from the state of equilibrium A are unnatural implies that it always must be $\mathrm{d} G>0$. The expression of the condition of stability, in this case, is

$$
\left.\begin{array}{l}
\mathrm{d} T=0  \tag{4.104}\\
\mathrm{~d} p=0 \\
G=G_{\min }
\end{array}\right\} \text { stable equilibrium at constant } T, p
$$

Therefore, $G$ must exhibit a relative minimum in correspondence of the stable equilibrium state.

### 4.3.9 Systems at Constant Entropy

Previously we saw that the stability condition for adiabatic systems is ensured by points with relative maximum for entropy. In this subsection we want to complete the scheme of possible different choices of external constraints imposing the condition that the system is constrained to have constant entropy. From the point of view of the experimental counterpart this is certainly an abstract issue because while we can easily imagine building tools to regulate the volume, pressure, temperature or energy, we do not have instruments that can be considered good entropy regulators. In spite of this it is certainly interesting to complete the scheme of possible pairs of parameters to keep constant (among those we have chosen at the beginning of this section as the most significant). In fact, these two possible new choices will convert a point of maximum entropy into a point of minimum energy or enthalpy.

To obtain this result we consider Eq. (4.86) and we apply identity Eq. (A.8) keeping the volume constant, we have

$$
\begin{equation*}
\left(\frac{\partial S}{\partial U}\right)_{V, \xi}\left(\frac{\partial U}{\partial \xi}\right)_{V, S}\left(\frac{\partial \xi}{\partial S}\right)_{V, U}=-1 \tag{4.105}
\end{equation*}
$$

which, by considering Eq. (4.24), may be written as

$$
\begin{equation*}
\left(\frac{\partial U}{\partial \xi}\right)_{V, S}=-T\left(\frac{\partial S}{\partial \xi}\right)_{V, U} \tag{4.106}
\end{equation*}
$$

This relation shows that in the points where the member on the right, $(\partial S / \partial \xi)_{V, U}$, is zero, also the member on the left, $(\partial U / \partial \xi)_{V, S}$ is null, and that the two derivatives have always opposite sign. By recalling Sect.4.3.7, this implies that, if the entropy is maximum in the point $\xi=0$ at constant $U$, in the same point, at constant $S$, we have:

$$
\left.\begin{array}{l}
\mathrm{d} S=0  \tag{4.107}\\
\mathrm{~d} V=0 \\
U=U_{\mathrm{min}}
\end{array}\right\} \text { stable equilibrium at constant } S, V
$$

that is, if one fixes the volume and the entropy then the stability is ensured by a point of minimum energy. In this way we recover the criterion that is most familiar from Mechanics. To complete the picture, we fix the values of entropy and pressure. The Fundamental Relation, written in natural variables entropy and pressure is the Enthalpy and the stable state will be characterized by a minimum of such thermodynamic potential.

$$
\left.\begin{array}{l}
\mathrm{d} S=0  \tag{4.108}\\
\mathrm{~d} p=0 \\
H=H_{\min }
\end{array}\right\} \text { stable equilibrium at constant } S, p
$$

All of these relations show the geometric properties the Fundamental Relation. These properties involve the existence of symmetries, which may be investigated experimentally.

Let us consider some important consequences deriving from the stability requirements of equilibrium states.

### 4.3.10 The Isothermal Compressibility

Consider a phase maintained at constant temperature and volume $V$. Its Fundamental Relation will be properly written in the Free Energy representation

$$
\begin{equation*}
F=F(T, V) . \tag{4.109}
\end{equation*}
$$

We consider this system as the composed of two parts I and II with equal volume $V^{\mathrm{I}}=V^{\mathrm{II}}=V / 2$. The Free Energy for each part will be

$$
\begin{equation*}
F^{\mathrm{I}}\left(T, \frac{V}{2}\right)=F^{\mathrm{II}}\left(T, \frac{V}{2}\right)=\frac{1}{2} F(T, V) . \tag{4.110}
\end{equation*}
$$

Now imagine that an internal disturbance occurs in such a way that the volume of one of the two halves, for example, the part I, increases by a small amount $\delta V$ at the expense of the volume of the second part. As the total volume is constrained to a constant value the volume of the second part will decrease by the same amount; we could say that a small amount of volume is transferred from the second half to the first. The Free Energies of the two parties will vary accordingly:

$$
\begin{align*}
F^{\mathrm{I}}\left(T, \frac{V}{2}+\delta V\right) & =F^{\mathrm{I}}\left(T, \frac{V}{2}\right)+\left(\frac{\partial F}{\partial V}\right) \delta V+\frac{1}{2}\left(\frac{\partial^{2} F}{\partial^{2} V}\right)(\delta V)^{2}+\cdots \\
F^{\mathrm{II}}\left(T, \frac{V}{2}-\delta V\right) & =F^{\mathrm{II}}\left(T, \frac{V}{2}\right)-\left(\frac{\partial F}{\partial V}\right) \delta V+\frac{1}{2}\left(\frac{\partial^{2} F}{\partial^{2} V}\right)(\delta V)^{2}+\cdots \tag{4.111}
\end{align*}
$$

In the perturbed state the total Free Energy will have the value

$$
\begin{equation*}
F^{\prime}=F^{\mathrm{I}}\left(T, \frac{V}{2}+\delta V\right)+F^{\mathrm{II}}\left(T, \frac{V}{2}-\delta V\right) \tag{4.113}
\end{equation*}
$$

If the initial state $V^{\mathrm{I}}=V^{\mathrm{II}}=V / 2$ was a state of stable or metastable equilibrium, the Free Energy of the perturbed state will be increased:

$$
\begin{equation*}
\left[F^{\mathrm{I}}\left(T, \frac{V}{2}+\delta V\right)+F^{\mathrm{II}}\left(T, \frac{V}{2}-\delta V\right)\right]-\left[F^{\mathrm{I}}\left(T, \frac{V}{2}\right)+F^{\mathrm{II}}\left(T, \frac{V}{2}\right)\right]>0, \tag{4.114}
\end{equation*}
$$

hence

$$
\begin{equation*}
\left(\frac{\partial^{2} F}{\partial^{2} V}\right)_{T}>0 \tag{4.115}
\end{equation*}
$$

and, recalling (4.21) we will have

$$
\begin{equation*}
\left(\frac{\partial p}{\partial V}\right)_{T}<0 \tag{4.116}
\end{equation*}
$$

We define Coefficient of Isothermal Compressibility $\chi_{T}$ the quantity

$$
\begin{equation*}
\chi_{T}=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T} \tag{4.117}
\end{equation*}
$$

This coefficient measures the percentage change in volume caused by a unit pressure change when all is made at a constant temperature.

By virtue of inequality Eq. (4.116), which as we have seen is absolutely general, the coefficient of isothermal compressibility is always positive for all states of stable or metastable equilibrium. If a theoretical model gives negative values for $\chi_{T}$ for some equilibrium states those states cannot be observable (see the case of the van der Waals model in Chap. 8). We define $\chi_{S}$ Coefficient of adiabatic compressibility as:

$$
\begin{equation*}
\chi_{S}=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S} . \tag{4.118}
\end{equation*}
$$

As it can be seen this coefficient measures the percentage of volume change per unit pressure change when this is done adiabatically. As in the case of the coefficient of isothermal compressibility, the inequality

$$
\begin{equation*}
\left(\frac{\partial p}{\partial V}\right)_{S}<0 \tag{4.119}
\end{equation*}
$$

shows that the coefficient $\chi_{S}$ will always be a positive number for all stable or metastable equilibrium states.

### 4.3.11 The Dependence of Entropy on Temperature

Another important consequence that derives from the application of the stability conditions of equilibrium states for closed phases with no chemical reactions, concerns the way in which the entropy changes as the temperature varies. Technically the operations to be performed are similar to those illustrated in the previous case but here we will change the constraints imposed from outside. As in the previous case suppose to divide the system "halfway" with respect to some extensive quantity and we will imagine a disturbance where a small (infinitesimal) transfer of the extensive quantity between the two parties takes place.

In this case, we consider a phase with total entropy and volume fixed, at the values $S$ and $V$, in the equilibrium state $A$. We know that if the state $A$ is a stable or metastable state, energy should have, locally, a minimum value. Imagine to divide the system into two parts of volume $V / 2$. All values of the extensive quantities will, in the unperturbed state $A$, will be $1 / 2$ of their values for the entire system (energy and entropy). Now imagine to be a small transformation in which one part transfers to the other a small amount of entropy (for example, suppose that we realize the transfer of a small amount of heat between the two parties).

The entropy of the first half will pass from the value $S / 2$ to the value $(S / 2+\delta S)$ while that of the second part will go to the value $(S / 2-\delta S)$ thus keeping constant the total entropy.

This virtual process will change the total energy value (we use the same notation used in the previous case):

$$
\begin{align*}
U^{\mathrm{I}}\left(\frac{V}{2}, \frac{S}{2}+\delta S\right) & =U^{\mathrm{I}}\left(\frac{V}{2}, \frac{S}{2}\right)+\left(\frac{\partial U}{\partial S}\right)_{V} \delta S+\frac{1}{2}\left(\frac{\partial^{2} U}{\partial^{2} S}\right)_{V}(\delta S)^{2}+\cdots \\
U^{\mathrm{II}}\left(\frac{V}{2}, \frac{S}{2}-\delta S\right) & =U^{\mathrm{II}}\left(\frac{V}{2}, \frac{S}{2}\right)-\left(\frac{\partial U}{\partial S}\right)_{V} \delta S+\frac{1}{2}\left(\frac{\partial^{2} U}{\partial^{2} S}\right)_{V}(\delta S)^{2}+\cdots \tag{4.120}
\end{align*}
$$

The sum of these two quantities will give us the new value of the total energy and this will have to be higher than $U(V, S)$ i.e. the one corresponding to the initial stable equilibrium state: This leads to the condition

$$
\begin{equation*}
\left(\frac{\partial^{2} U}{\partial^{2} S}\right)_{V}>0 \tag{4.122}
\end{equation*}
$$

Recalling Eq. (4.20), we get

$$
\begin{equation*}
\left(\frac{\partial S}{\partial T}\right)_{V}>0 \tag{4.123}
\end{equation*}
$$

This condition is very general and descends from the stability properties of the equilibrium states. The importance of this result is immediately visible because, as we shall see later, this derivative is immediately connected to the heat capacity at constant volume.

### 4.3.12 Other Consequences from the Stability Conditions

We can follow the same path made in the two previous cases, by varying the type of constraints and the extensive quantity that is transferred between the two parties in which one imagines to divide the system. For example if the constraint is on pressure, we may refer to the Fundamental Relation in the Enthalpy representation and to imagine a small transfer of entropy between one half and the other. It's easy to verify that the condition that in the initial state the Enthalpy has a minimum value leads to the result

$$
\begin{equation*}
\left(\frac{\partial^{2} H}{\partial^{2} S}\right)_{p}>0 \tag{4.124}
\end{equation*}
$$

which implies

$$
\begin{equation*}
\left(\frac{\partial S}{\partial T}\right)_{p}>0 . \tag{4.125}
\end{equation*}
$$

Similarly to the previous case this partial derivative is closely linked to the thermal capacity at constant pressure $C_{p}$. This condition is not, however, independent of the preceding one because, as it will be proved later, it will always be

$$
\begin{equation*}
C_{p}>C_{V} \tag{4.126}
\end{equation*}
$$

By analogy with the previous examples, it is easy to prove that

$$
\begin{equation*}
\left(\frac{\partial p}{\partial V}\right)_{S}<0 \tag{4.127}
\end{equation*}
$$

## Chapter 5 <br> Maxwell Relations


#### Abstract

All information we have concerning a thermodynamical system, including the equation of state, is contained in its Fundamental Relation. This Relation depicts, in the space of thermodynamical configurations, a hypersurface which is formed by all the equilibrium states of the system. The fact that in any transformation the initial and the final points (at least) must belong to this surface poses several correlations among the variations of the state parameters of the system. Therefore the existence of the Fundamental Relation allows us to predict the response of the system to any external perturbation and this can be achieved by writing the differentials of the Fundamental Relation in its various representations. We call Maxwell's Relations the relations we obtain by applying the Schwarz theorem to the partial derivatives of the Fundamental Relation. As an example, the general relation between the specific heats at constant volume and pressure is obtained together with the general relations between isothermal and adiabatic compressibilities. It can be shown that the Fundamental Relation is completely determined by the knowledge of three independent parameters like, for instance, the specific heat at constant pressure, the coefficient of isothermal compressibility and the coefficient of thermal expansion. Measuring the latter three parameters the dependence of entropy on temperature, pressure and volume is known, and the same applies to other representations of the Fundamental Relation.


Keywords Maxwell relations - Heat capacities at constant volume and constant pressure $\cdot$ Coefficients of compressibility $\cdot$ Coefficient of thermal expansion $\cdot$ Entropy $\cdot$ Measuring entropy

### 5.1 Introduction

As we have seen in Chap. 4 every system has an associated Fundamental Relation and this defines the $k+1$ dimensional surface ( $k$ is the number of independent work parameters) in the space of thermodynamic configurations, formed by all the states in stable or metastable equilibrium. This implies that any thermodynamic process may be represented by a connection between two points of this surface that represent
the initial and final configurations (which are, necessarily, equilibrium states). This connection will, in turn, be representable by a continuous solid line on this surface if the transformation is a quasi-static transformation, otherwise may be represented by small disconnected continuous segments on this surface if there are only some quasi-static parts, or by isolated points or, as frequently happens, only by the initial and final points.

Whatever the situation is, the need for the points to belong to a given surface determines quantitative relations among the changes of the system properties that have general validity and are, in fact, a consequence of the existence of a determined Fundamental Relation.

In order to explore, at least partially, such a very large amount of correlations it is convenient to start considering infinitesimal transformations that move from equilibrium states (quasi-static). To do this we will write the differentials of the Fundamental Relation in its most significant representations.

Since the differentials we are going to write are exact differentials, we will be able to apply the Schwarz theorem on the equality of the cross partial derivatives.

Maxwell relations are the relations that we can get from the application of Schwarz's theorem. The number of relations that we can obtain in this way, is very large and not all of them will be of immediate utility. We will just examine some.

### 5.2 Some Properties of Materials

In this section, we define some parameters of materials which are very important both for immediate technological applications and, as we shall see, to achieve a complete knowledge of the Fundamental Relation of each system.

Certainly, we can say that the Second Principle operationally defines the entropy but it is equally true that the measurement of its variation through the integral

$$
\begin{equation*}
\int_{\text {q.s. }} \frac{\hat{d} Q}{T} . \tag{5.1}
\end{equation*}
$$

along a quasi-static transformation, acceptable in principle, is always of very little practical use.

Conversely, it is relatively easy and certainly very useful to measure how much the volume of a body expands or decreases when its temperature is increasing at constant pressure, or to what extent its volume decreases when the pressure acting on it increases. The same can be said for the heat capacities i.e. for the measure of the temperature increase caused by the transfer of a certain amount of heat under certain restrictions. We'll see how the knowledge of these parameters (we could call them "technological parameters") provides complete information on the entropy of each macroscopic system and then on all the thermodynamic potentials and this is equivalent to the knowledge of the Fundamental Relation of the system.

From the Fundamental Relation, we can get the so-called Equation of State, that is the relation among pressure, volume, and temperature which holds at equilibrium states and which can, in all generality, be written in the form

$$
\begin{equation*}
V=V(p, T) \tag{5.2}
\end{equation*}
$$

or, by making pressure explicit

$$
\begin{equation*}
p=p(V, T) \tag{5.3}
\end{equation*}
$$

After differentiating Eq. (5.2), we have

$$
\begin{equation*}
\mathrm{d} V=\left(\frac{\partial V}{\partial p}\right)_{T} \mathrm{~d} p+\left(\frac{\partial V}{\partial T}\right)_{p} \mathrm{~d} T \tag{5.4}
\end{equation*}
$$

We define the coefficient of isothermal compressibility $\chi_{T}$ by the quantity:

$$
\begin{equation*}
\chi_{T}=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T} \tag{5.5}
\end{equation*}
$$

and the coefficient of thermal expansion $\alpha$

$$
\begin{equation*}
\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p} . \tag{5.6}
\end{equation*}
$$

The differential expression of the equation of state Eq. (5.2) becomes

$$
\begin{equation*}
\frac{\mathrm{d} V}{V}=-\chi_{T} \mathrm{~d} p+\alpha \mathrm{d} T \tag{5.7}
\end{equation*}
$$

and similarly for Eq. (5.3) we get

$$
\begin{equation*}
\mathrm{d} p=-\frac{1}{\chi_{T}} \mathrm{~d}(\ln V)+\frac{\alpha}{\chi_{T}} \mathrm{~d} T \tag{5.8}
\end{equation*}
$$

The first example of Maxwell Relations can be obtained by cross-differentiating Eq. (5.7):

$$
\begin{equation*}
\left(\frac{\partial \chi_{T}}{\partial T}\right)_{p}=-\left(\frac{\partial \alpha}{\partial p}\right)_{T} \tag{5.9}
\end{equation*}
$$

from which we see that the compressibility and the thermal expansion coefficients are not completely independent of each other.

### 5.3 The Volume and Pressure Dependance of Entropy

When dealing with isothermal transformations it is convenient to express the Fundamental Relation in the representation of the Free Energy and in that of the Gibbs potential:

$$
\begin{align*}
& \mathrm{d} F=-S \mathrm{~d} T-p \mathrm{~d} V  \tag{5.10}\\
& \mathrm{~d} G=-S \mathrm{~d} T+V \mathrm{~d} p, \tag{5.11}
\end{align*}
$$

and by using the Schwarz's theorem we get

$$
\begin{align*}
& \left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial p}{\partial T}\right)_{V}  \tag{5.12}\\
& \left(\frac{\partial S}{\partial p}\right)_{T}=-\left(\frac{\partial V}{\partial T}\right)_{p} \tag{5.13}
\end{align*}
$$

From Eqs. (5.8) and (5.6), we obtain the general relations:

$$
\begin{align*}
& \left(\frac{\partial S}{\partial V}\right)_{T}=\frac{\alpha}{\chi_{T}}  \tag{5.14}\\
& \left(\frac{\partial S}{\partial p}\right)_{T}=-\alpha V \tag{5.15}
\end{align*}
$$

If we select one suitable reference state at a given temperature and we assign to that state an arbitrary value $S_{0}$ to the entropy, if we know, even merely graphically, the values of $\alpha$ and of $\chi_{T}$ we know the value of entropy in any other state at the same temperature. In order to obtain a complete knowledge of entropy we need to know its dependence on temperature.

### 5.4 The Heat Capacities and the Temperature Dependance of Entropy

An elementary and intuitive definition of heat capacity of a body, or of specific heat of a material, was given in thermology and was bound to a particular choice of a scale of empirical temperature, usually the Celsius scale. It is defined as the ratio of the quantity of heat transferred to the body and the consequent temperature increase. Most frequently this process is conceived either at constant volume or at constant pressure:

$$
\begin{equation*}
C_{V, p}=\left(\frac{\delta Q}{\delta \vartheta}\right)_{V, p} \tag{5.16}
\end{equation*}
$$

This definition can be useful for some special technical applications but is totally inadequate from the thermodynamic point of view where we are interested in reaching, through the measures of these parameters, a complete knowledge of the Fundamental Relation and this result will be achieved after we will have a comprehensive knowledge of entropy.

For this purpose, after Eqs. (5.14) and (5.15) that provide us with the knowledge of entropy at constant temperature, the thermal capacity will give us the temperature dependence.

We will consider, for the moment, only the two cases of processes: at constant pressure and constant volume.

### 5.4.1 The Heat Capacity at Constant Pressure

If a system is maintained at constant pressure, we know that the quantity of heat supplied in an infinitesimal process produces a change of enthalpy given by the relation:

$$
\begin{equation*}
\hat{d} Q=\mathrm{d} H=T \mathrm{~d} S . \tag{5.17}
\end{equation*}
$$

We define $C_{p}$, heat capacity at constant pressure by the relation:

$$
\begin{equation*}
C_{p}=\left(\frac{\partial H}{\partial T}\right)_{p}=T\left(\frac{\partial S}{\partial T}\right)_{p} \tag{5.18}
\end{equation*}
$$

From the definition (5.18), it is clear that the energy transferred in the form of heat will be distributed partly on the increase of the energy of the system and in part will be used to do work against the mechanism that ensures constant pressure. For example, as we shall see, the so-called latent heat in a phase transition (that occurs at a constant pressure) is shared between these two items. If we refer to a unit mass system, $C_{p}$ will be called specific heat at constant pressure; if we will refer to one mole it will be called molar heat at constant pressure.

### 5.4.2 The Heat Capacity at Constant Volume

If the system is constrained to maintain a constant volume, the supply of a small amount of heat will result in an equivalent increase of its energy. Then, we define as heat capacity at constant volume the quantity:

$$
\begin{equation*}
C_{V}=\left(\frac{\partial U}{\partial T}\right)_{V}=T\left(\frac{\partial S}{\partial T}\right)_{V} \tag{5.19}
\end{equation*}
$$

As before $C_{V}$ will be called specific heat at constant volume or molar heat at constant volume depending on whether it refers to the unit mass or to one mole, respectively.

Generally, the mechanical-statistical models provide predictions for the specific heat at constant volume because they allow to calculate the total energy of the system. The comparison with the experiment, to validate the model, is, however, quite complicated because it is difficult to vary the temperature of a body and to maintain the volume constant while it is much easier to vary its temperature while maintaining the pressure constant. It is generally preferred to measure the specific heat at constant pressure and recover from it the specific heat at constant volume. We, therefore, need a general, i.e., independent of the modeling, relationship between the two.

### 5.4.3 The Relation Between $C_{p}$ and $C_{V}$

We have to find the relationship between the derivative of the entropy with respect to temperature made at constant pressure and that made at constant volume. We simply apply Eq.(A.15) with $w=S, x=T, y=V$ and $z=p$ and we obtain

$$
\begin{equation*}
\left(\frac{\partial S}{\partial T}\right)_{p}=\left(\frac{\partial S}{\partial T}\right)_{V}+\left(\frac{\partial S}{\partial V}\right)_{T}\left(\frac{\partial V}{\partial T}\right)_{p} \tag{5.20}
\end{equation*}
$$

From Eqs. (5.14) and (5.6) we obtain

$$
\begin{equation*}
\left(\frac{\partial S}{\partial T}\right)_{p}=\left(\frac{\partial S}{\partial T}\right)_{V}+V \frac{\alpha^{2}}{\chi_{T}} \tag{5.21}
\end{equation*}
$$

and after multiplying by $T$ we obtain the relation we were looking for

$$
\begin{equation*}
C_{p}=C_{V}+\frac{\alpha^{2} V T}{\chi_{T}} \tag{5.22}
\end{equation*}
$$

This relation is of absolute generality. Since we know that for states in stable or metastable equilibrium $\chi_{T}>0$ we will always have

$$
\begin{equation*}
C_{p}>C_{V} . \tag{5.23}
\end{equation*}
$$

As can be seen the two specific heats, the coefficient of compressibility and the coefficient of thermal expansion are mutually bound by one general relation and then only three of these may be chosen as independent. From the knowledge of three of these, we have a complete knowledge of the dependence of the entropy on the pressure, volume and temperature, and then we can say we have a complete knowledge of the Fundamental Relation.

### 5.4.4 The Adiabatic Compressibility Coefficient

Another parameter, very important in applications, is the coefficient of adiabatic compressibility $\chi_{S}$. It measures the percentage change in volume following a unit change of pressure when this is done adiabatically. Formally

$$
\begin{equation*}
\chi_{S}=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S} \tag{5.24}
\end{equation*}
$$

It is rather easy to show that, in all generality, the coefficient of adiabatic compressibility is related in a simple way to the coefficient of isothermal compressibility and the specific heats.

We have just to apply Eq. (A.8) once with the variables $(p, V, T)$ and, again, with the variables $(p, V, S)$ :

$$
\begin{align*}
& \left(\frac{\partial V}{\partial p}\right)_{T}=-\frac{\left(\frac{\partial V}{\partial T}\right)_{p}}{\left(\frac{\partial p}{\partial T}\right)_{V}}  \tag{5.25}\\
& \left(\frac{\partial V}{\partial p}\right)_{S}=-\frac{\left(\frac{\partial S}{\partial p}\right)_{V}}{\left(\frac{\partial S}{\partial V}\right)_{p}} \tag{5.26}
\end{align*}
$$

and hence

$$
\begin{equation*}
\frac{\left(\frac{\partial V}{\partial p}\right)_{T}}{\left(\frac{\partial V}{\partial p}\right)_{S}}=\frac{\left(\frac{\partial S}{\partial V}\right)_{p}\left(\frac{\partial V}{\partial T}\right)_{p}}{\left(\frac{\partial S}{\partial p}\right)_{V}\left(\frac{\partial p}{\partial T}\right)_{V}}=\frac{\left(\frac{\partial S}{\partial T}\right)_{p}}{\left(\frac{\partial S}{\partial T}\right)_{V}} \tag{5.27}
\end{equation*}
$$

If we recall Eqs. (5.18) and (5.19) we obtain

$$
\begin{align*}
& \frac{\chi_{T}}{\chi_{S}}=\frac{C_{p}}{C_{V}}  \tag{5.28}\\
& \chi_{S}=\frac{C_{V}}{C_{p}} \chi_{T} \tag{5.29}
\end{align*}
$$

As we see the coefficient of adiabatic compressibility is always smaller than the one at constant temperature and is always positive for states of stable or metastable equilibrium.

### 5.4.5 The Equations of the Adiabatic Transformations

The result given in Eq. (5.29) is of the utmost generality. In order to find the equation of an adiabatic (quasi-static) transformation we have to integrate the following differential equation:

$$
\begin{equation*}
\frac{1}{V} \frac{\mathrm{~d} V}{\mathrm{~d} p}=-\frac{C_{V}}{C_{p}} \chi_{T} \tag{5.30}
\end{equation*}
$$

where the symbol of total derivative denotes the derivative taken along the adiabatic curve. This relation can be used to calculate any small changes in volume for small variations of pressure if we know $C_{V} / C_{p}$ and $\chi_{T}$ for a given value of the pressure and temperature. In order to integrate Eq. (5.30) we need to know the dependence of $C_{p}$, $C_{V}$ and $\chi_{T}$ on $p$ and on $V$. For a system in which $\chi_{T} \simeq p^{-1}$ with good approximation (e.g. dilute gases above the critical temperature Chap.6), we may write Eq. (5.30) as

$$
\begin{equation*}
\frac{\mathrm{d}(\ln V)}{\mathrm{d}(\ln p)}=-\frac{C_{V}}{C_{p}} \tag{5.31}
\end{equation*}
$$

and if, in the temperature and pressure intervals we are considering, we may treat $C_{p}$ and $C_{V}$ as constants, we get

$$
\begin{equation*}
p V^{\gamma}=\text { constant } \tag{5.32}
\end{equation*}
$$

where with the symbol $\gamma$ we have denoted the ratio $C_{p} / C_{V}$.

### 5.5 Concluding Remarks and the Role of $C_{p}, \alpha, \chi_{T}$

We have defined five parameters which describe the response of a system to the two most frequent stresses, i.e., to heating and compression under the different conditions which usually occur in the laboratory.

We saw that only three of these coefficients are independent of each other and the general agreement is to choose as independent coefficients $C_{p}, \alpha$ and $\chi_{T}$.

When we tabulated these three parameters, the Fundamental Relation, and then all thermodynamic potentials, are known and we can easily make predictions about what will be the response of the system to any external disturbance.

Consider, for example, to be interested in knowing what will be the increase of pressure in a system held at constant volume, if the temperature is increased by $\mathrm{d} T$ (of course we are always talking about closed systems). Formally, we are looking for

$$
\begin{equation*}
\mathrm{d} p=\left(\frac{\partial p}{\partial T}\right)_{V} \mathrm{~d} T \tag{5.33}
\end{equation*}
$$

We can answer the question because we have seen from Eq. (5.8) that

$$
\begin{equation*}
\left(\frac{\partial p}{\partial T}\right)_{V}=\frac{\alpha}{\chi_{T}} \tag{5.34}
\end{equation*}
$$

but this gives us the opportunity for a further comment.
In any problem like this in which we want to predict the effect of a certain action performed from outside, and in accordance with certain assigned constraints, the solution requires the knowledge of the partial derivatives of a parameter with respect to another parameter given some constraints.

We can see that any partial derivative can be expressed in terms of the three independent coefficients $C_{p}, \alpha$ and $\chi_{T} .{ }^{1}$ We will not develop a general technique to bring any partial derivative to the above three but let it be sufficient, in order to support the above statement, to have a look to the expression of all the thermodynamic potentials as a function of these three factors.

First, as already seen in Eqs. (5.14), (5.15) and (5.18), or equivalently Eq. (5.19), we can consider the entropy completely determined apart from an additive constant (this will, in turn, be determined by the Third Law). As for the other potentials we will just consider Energy and Free Energy; for the others, it will be a question of a little gymnastics with the partial derivatives.

Separating the dependence on the pressure and that on temperature and volume, for Energy we may write

$$
\begin{gather*}
\left(\frac{\partial U}{\partial p}\right)_{T}=V\left(\chi_{T} p-\alpha T\right)  \tag{5.35}\\
\mathrm{d} U=C_{V} \mathrm{~d} T+\left(\frac{\alpha T}{\chi_{T}}-p\right) \mathrm{d} V \tag{5.36}
\end{gather*}
$$

from which we write the dependence of the Energy $U$ from the volume at constant temperature:

$$
\begin{equation*}
\left(\frac{\partial U}{\partial V}\right)_{T}=\left(\frac{\alpha T}{\chi_{T}}-p\right) \tag{5.37}
\end{equation*}
$$

For Free Energy $F$ we have

$$
\begin{gather*}
\left(\frac{\partial F}{\partial p}\right)_{T}=\chi_{T} p V  \tag{5.38}\\
\mathrm{~d} F=-S \mathrm{~d} T-p \mathrm{~d} V \tag{5.39}
\end{gather*}
$$

Let's see some examples where we may determine the response of a system under certain external stresses.

[^18]
### 5.5.1 Isothermal Processes

A closed system goes through an isothermal transformation from the initial pressure $p_{\mathrm{i}}$ to the final pressure $p_{\mathrm{f}}$. Write the expressions for the amount of heat that it absorbs and the amount of work that must be made on the system in this process.

For an infinitesimal process where the variation in the pressure is $\mathrm{d} p$ the two quantities will be given by the following expressions:

$$
\begin{align*}
& \hat{d} Q=T\left(\frac{\partial S}{\partial p}\right)_{T} \mathrm{~d} p=-\alpha T V \mathrm{~d} p  \tag{5.40}\\
& \hat{d} W=-p \mathrm{~d} V=-p\left(\frac{\partial V}{\partial p}\right)_{T} \mathrm{~d} p=p V \chi_{T} \mathrm{~d} p \tag{5.41}
\end{align*}
$$

where in the first equation we made use of Eq. (5.15) (as we can see, by adding the two results we get, how it should happen, Eq. (5.35). For the same quantities but in a process in which the pressure change is not small enough, we have to write the integral expression, if we suppose the process to be quasi-static:

$$
\begin{align*}
& Q=-T \int_{\substack{p_{i} \\
\text { isoth }}}^{p_{\mathrm{f}}} \alpha V \mathrm{~d} p  \tag{5.42}\\
& W=\int_{\substack{p_{\mathrm{i}} \\
\text { isoth }}}^{p_{\mathrm{f}}} p V \chi_{T} \mathrm{~d} p \tag{5.43}
\end{align*}
$$

Obviously in order to use these relations we need to know the dependence of $\alpha, \chi_{T}$ and the volume as a function of pressure at the given temperature. If we consider the average values of the coefficient of thermal expansion and the coefficient of isothermal compressibility in the range of pressure we are considering we may write

$$
\begin{align*}
& Q=-\langle\alpha\rangle T \int_{\substack{p_{\mathrm{i}} \\
\text { isoth }}}^{p_{\mathrm{f}}} V \mathrm{~d} p,  \tag{5.44}\\
& W=\left\langle\chi_{T}\right\rangle \int_{\substack{p_{\mathrm{i}} \\
\text { isoth }}}^{p_{\mathrm{f}}}(p V) \mathrm{d} p . \tag{5.45}
\end{align*}
$$

### 5.5.2 Free Expansion

If we consider a rigid container divided into two parts by a septum. One part, of volume $V$, contains $n$ moles of gas at temperature $T$ while the other side is empty. The septum is removed and the gas expands freely to occupy the entire volume
and reach a new state of equilibrium at a new temperature and pressure. Further, we suppose that the process is fast enough to be considered adiabatic. This is what generally is meant by free expansion and, for instance, we know that for an ideal gas the temperature will remain constant and the pressure can be obtained from the equation of state. It is interesting to ask what is the final temperature in the case of a real gas.

Since, in general, the coefficients of thermal expansion, the molar heats and the adiabatic compressibility depend on pressure and temperature, we cannot give the answer for finite transformations but if we consider an infinitesimal transformation in which the volume varies by a quantity a small amount $\mathrm{d} V$, we can get some interesting indications.

For the assumed conditions (free and adiabatic expansion) energy will maintain a constant value. The temperature variation can be written as

$$
\begin{equation*}
\mathrm{d} T=\left(\frac{\partial T}{\partial V}\right)_{U} \mathrm{~d} V \tag{5.46}
\end{equation*}
$$

Making use of Eq. (A.8) we can express the partial derivative we are interested in, in the form:

$$
\begin{equation*}
\left(\frac{\partial T}{\partial V}\right)_{U}=-\frac{1}{C_{V}}\left(\frac{\partial U}{\partial V}\right)_{T} \tag{5.47}
\end{equation*}
$$

where $C_{V}$ is the heat capacity at constant volume. From Eq. (5.37) we obtain

$$
\begin{equation*}
\mathrm{d} T=\frac{1}{C_{V}}\left(p-\frac{\alpha}{\chi_{T}} T\right) \mathrm{d} V \tag{5.48}
\end{equation*}
$$

This result is valid for small transformations, that is, transformations which can be treated as infinitesimal and quasi-static i.e. starting from an equilibrium state, but can not be used for finite transformations when these may not be treated as quasi-static. For a dilute gas above the critical temperature (i.e., an ideal gas approximation) we may put

$$
\begin{align*}
\alpha & \simeq \frac{1}{T}  \tag{5.49}\\
\chi_{T} & \simeq \frac{1}{p} \tag{5.50}
\end{align*}
$$

and we find that the temperature remains constant.

### 5.5.3 Pressure Drop in Free Expansion

A system is subject to a small free expansion and we measure the temperature variation $\mathrm{d} T$. Let us find the pressure variation. Of course the answer can be given provided that we know the Fundamental Relation of the system and this is equivalent to know
$\alpha, \chi_{T}, C_{p}$. Similarly to what was done in Sect. 5.5.2. We express the quantity we are looking for in the following way:

$$
\begin{equation*}
\mathrm{d} p=\left(\frac{\partial p}{\partial T}\right)_{U} \mathrm{~d} T \tag{5.51}
\end{equation*}
$$

We have to express the partial derivative as a function of the "technical parameters". With reference to Eq. (A.8) we have

$$
\begin{equation*}
\left(\frac{\partial p}{\partial T}\right)_{U}=-\frac{\left(\frac{\partial U}{\partial T}\right)_{p}}{\left(\frac{\partial U}{\partial p}\right)_{T}} \tag{5.52}
\end{equation*}
$$

The denominator is given by Eq. (5.35) while, for the numerator, it is necessary to take a further step. By using the identity $U=H-p V$, and calculating the derivative, we obtain

$$
\begin{equation*}
\left(\frac{\partial U}{\partial T}\right)_{p}=n C_{p}-p V \alpha \tag{5.53}
\end{equation*}
$$

Following the same procedure as in the previous examples we obtain

$$
\begin{equation*}
\mathrm{d} p=-\frac{n C_{p}-p V \alpha}{V\left(\chi_{T} p-\alpha T\right)} \mathrm{d} T . \tag{5.54}
\end{equation*}
$$

### 5.5.4 Temperature-Pressure Variations in Adiabatic Transformations

In a situation in a certain sense "complementary" to that treated in the previous cases, we consider the temperature variation in an adiabatic process as a function of the pressure variation. For infinitesimal processes, we may write

$$
\begin{equation*}
\mathrm{d} T=\left(\frac{\partial T}{\partial p}\right)_{S} \mathrm{~d} p \tag{5.55}
\end{equation*}
$$

and, making use of Eqs. (A.8) and (5.15) that gives us the dependence of entropy on pressure at constant temperature, we get

$$
\begin{equation*}
\mathrm{d} T=\frac{V}{n C_{p}} \alpha T \mathrm{~d} p \tag{5.56}
\end{equation*}
$$

### 5.5.5 Temperature-Volume Variations in Adiabatic Transformations

A system is subject to a volume variation $\mathrm{d} V$ along an adiabatic transformation, starting from a given equilibrium state. Determine the variation of the temperature:

$$
\begin{equation*}
\mathrm{d} T=\left(\frac{\partial T}{\partial V}\right)_{S} \mathrm{~d} V \tag{5.57}
\end{equation*}
$$

and with reference to Eqs. (A.8) and (5.12) we have

$$
\begin{equation*}
\left(\frac{\partial T}{\partial V}\right)_{S}=-\frac{\left(\frac{\partial S}{\partial V}\right)_{T}}{\left(\frac{\partial S}{\partial T}\right)_{V}}=-\frac{\alpha T}{\chi_{T} C_{V}} \tag{5.58}
\end{equation*}
$$

and finally we obtain

$$
\begin{equation*}
\mathrm{d} T=-\frac{\alpha T}{\chi_{T} C_{V}} \mathrm{~d} V \tag{5.59}
\end{equation*}
$$

It easy to verify that for an ideal gas the above Eq. (5.59), after integration, leads to

$$
\begin{equation*}
T V^{\frac{R}{C_{V}}}=\text { constant } \tag{5.60}
\end{equation*}
$$

Taking into account that, for dilute gases

$$
\begin{equation*}
C_{p}-C_{V}=R \tag{5.61}
\end{equation*}
$$

and posing

$$
\begin{equation*}
\gamma=\frac{C_{p}}{C_{V}} \tag{5.62}
\end{equation*}
$$

the Eq. (5.60) is often written as

$$
\begin{equation*}
T V^{(\gamma-1)}=\text { constant } \tag{5.63}
\end{equation*}
$$

## Problems

5.1 The specific heat of Platinum at constant pressure may be expressed by the empirical formula

$$
C_{p}=a+b T+\frac{d}{T^{2}}
$$

with $a=123 \mathrm{~J} \mathrm{Kg}^{-1} \mathrm{~K}^{-1}, b=28.7 \times 10^{-3} \mathrm{~J} \mathrm{Kg}^{-1} \mathrm{~K}^{-2}$ and $d=2.15 \mathrm{~J} \mathrm{Kg}^{-1} \mathrm{~K}$. Determine the enthalpy and the entropy variations in an isobaric transformation from the initial temperature $T_{1}=280 \mathrm{~K}$ to the final temperature $T_{2}=1370 \mathrm{~K}$. The mass is 0.1 Kg .
5.2 Let us consider 100 g of water at a temperature of $20^{\circ} \mathrm{C}$, undergoing an isothermal transformation in which the pressure varies from an initial value $p_{\mathrm{i}}$ to the final value $p_{\mathrm{f}}$. At this temperature and in this range of pressures we have the following average values: $\left\langle\chi_{T}\right\rangle=0.48 \times 10^{-4} \mathrm{~atm}^{-1}$ and $\langle\alpha\rangle=0.2 \times 10^{-3} \mathrm{~K}^{-1}$. We are interested in calculating the amount of work done by the outside, the amount of heat supplied to the water and the variation of energy of the water. Consider the special case where the water expands passing from the pressure $p_{i}=40 \mathrm{~atm}$ to the final pressure $p_{\mathrm{f}}=1 \mathrm{~atm}$.
5.3 In analogy with the case treated in the previous problem, 100 g of water are brought to the temperature $\vartheta \simeq 0.2^{\circ} \mathrm{C}$, and undergo an isothermal compression from the initial pressure 1 atm to the pressure 40 atm . In this condition the coefficient of isothermal compressibility is, on average, $\left\langle\chi_{T}\right\rangle=0.46 \times 10^{-4} \mathrm{~atm}^{-1}$ and the average coefficient of thermal expansion $\langle\alpha\rangle=-0.64 \times 10^{-4} \mathrm{~K}^{-1}$. Determine the amount of heat absorbed by the water from the external world.
5.4 A homogeneous solid with mass $m=0.5 \mathrm{Kg}$ is compressed at constant temperature $T_{0}=100 \mathrm{~K}$ and quasi-statically from the initial pressure $p_{0}=1 \mathrm{bar}$ to the final pressure $p_{\mathrm{f}}=5 \times 10^{3}$ bar. The equation of state can be approximated by $V^{*}=$ $V_{0}^{*}-a p+b T$ where $V^{*}$ is the specific volume, with $a=8 \times 10^{-16} \mathrm{~m}^{4} \mathrm{Kg}^{-2} \mathrm{~s}^{2}$ and $b=3.5 \times 10^{-9} \mathrm{~m}^{3} \mathrm{Kg}^{-1} \mathrm{~K}^{-1}$. Its specific energy is given by $U^{*}=U_{0}^{*}+c T-b p T$. Determine the amount of heat $Q$ and the amount of work $W$ transferred to the solid by the external world in this transformation.
5.5 The same solid considered in the previous exercise is subject to a rapid compression in the same pressure interval. The transformation can be treated as an irreversible adiabatic compression and at the end of the transformation the temperature of the solid is $T_{\mathrm{f}}=300 \mathrm{~K}$. The constant $c$ in the equation for the specific energy is $c=20 \mathrm{~J} \mathrm{Kg}^{-1} \mathrm{~K}^{-1}$. Determine: (a) the amount of work done on the solid; (b) the specific heats of the solid at constant volume $C_{V}$ and at constant pressure $C_{p}$ and (c) the entropy variation of the solid.
5.6 A cube made of Copper is compressed reversibly and isothermally from the initial pressure $p_{1}=1$ bar to the final pressure $p_{2}=10^{3}$ bar. The temperature is $T=300 \mathrm{~K}$. Determine: (i) the amount of work done on the solid; (ii) the amount of heat given to the solid; (iii) the free energy and the energy variations of the copper. The following data can be used: Coefficient of thermal compressibility $\alpha=$ $5.0 \times 10^{-5} \mathrm{~K}^{-1}$, Coefficient of isothermal compressibility $\chi_{T}=8.6 \times 10^{-12} \mathrm{~Pa}^{-1}$ and Specific volume $V^{*}=1.14 \times 10^{-4} \mathrm{~m}^{3} \mathrm{Kg}^{-1}$ and the mass is $m=3 \mathrm{Kg}$.

## Part II <br> Applications

## Chapter 6 <br> General Properties of Gaseous Systems


#### Abstract

This chapter deals with the general properties of gases starting from their isothermal behavior and the definition of the virial coefficients. The Joule-Thomson experiment (throttling experiment) is discussed together with the subsequent calorimetric measurements which prove the proportionality of the first virial coefficient to the absolute temperature $T$. The latter fact allows us to have a further tool for defining the absolute scale once an arbitrary value for $T$ at one reference state is chosen. The Joule-Thomson coefficient and the inversion curve are defined and the problem of gases liquefaction is shortly outlined. The expression of the chemical potential for dilute gases is also shown. The heat capacities of gases are widely discussed starting from the theorem of energy equipartition.


Keywords Gases • Virial coefficients • Throttling • Temperature scale • Joule-Thomson coefficient • Inversion temperature • Liquefaction • Low temperatures • Chemical potential of gases • Heat capacities • Energy equipartition

### 6.1 Isothermal Behavior of Gases

It is convenient to start from the Boyle-Mariotte's law. We take a certain amount of some gas contained in a cylinder with a movable piston. We keep the temperature constant and measure the volume for different values of the pressure. Boyle-Mariotte have verified that, for every gas maintained at a given temperature, the product ( $p V$ ) tends to a constant value when the pressure becomes lower and lower. We set this law with the formula:

$$
\begin{equation*}
\lim _{p \rightarrow 0}(p V)=A(T) \tag{6.1}
\end{equation*}
$$

The quantity $A(T)$ depends on the temperature but also depends on the type of selected gas. We can also state that it will be proportional to the quantity of gas because if we double the amount of gas at the same temperature and pressure, the volume will double. Keeping the temperature to a fixed value, we can expand the product $(p V)$ in a power series of the pressure $p$ :

$$
\begin{equation*}
p V=A(T)+B(T) p+C(T) p^{2}+\cdots \tag{6.2}
\end{equation*}
$$

The quantities $A(T), B(T), C(T)$ are named first, second, third virial coefficients respectively. As we have already seen for the first coefficient $A$, they all depend on the temperature and on the type of gas; similarly they are proportional to the amount of gas. The latter could be measured by weight or by number of moles for instance. For the moment we are interested in highlighting their temperature dependence.

### 6.2 The First Virial Coefficient for Gases

Experimentally, it can be shown that the first virial coefficient is proportional to the (absolute) temperature $T$. This fact is of fundamental importance and therefore it is necessary, in the following, to examine with some detail how it is possible, by means of experimental observations, to establish this relation of proportionality. The possibility of using gases in the so-called "perfect gas thermometers", still used in many treaties, is based on this result.

The experimental evidence derives from the combination of two experiments: the first is the Joule-Thomson experiment which is preparatory to a second calorimetric measurement.

### 6.2.1 The Joule-Thomson Experiment

The Joule-Thomson experiment, also called throttling experiment, consists of forcing a certain amount of gas to pass, adiabatically, from an initial state $p_{1}, V_{1}, \theta_{1}$ to a final state $p_{2}, V_{2}, \theta_{2}$ flowing through a capillary or a porous separator (throttle). The initial and final temperatures are denoted, in this particular case, by their values measured in some empirical scale $\theta$ because the experimental observations we are discussing here are devoted to define, operationally, the absolute scale.

Two cylinders communicate through a throttle as shown schematically in Fig. 6.1. Initially the gas is in cylinder 1 and is prepared at arbitrary pressure $p_{1}$, and temperature $\theta_{1}$ while cylinder 2 is empty and the piston is regulated in such a way to maintain a constant arbitrary pressure $p_{2}$ (with $p_{2}<p_{1}$ ) when the gas flows in. The two cylinders are thermally insulated and the gas is forced to pass from cylinder 1 to cylinder 2 under the described conditions. In this experiment we have three free parameters: $p_{1}, \theta_{1}$, that is the initial state of the gas, and $p_{2}$. We measure the final temperature $\theta_{2}$. In this way, for every given initial state we can represent on a $(\theta, p)$ plane the value of the final temperature $\theta_{2}$ as a function of the final pressure $p_{2}$.

The reason for adopting this device (throttle) is to ensure a pressure jump between the gases in the two cylinders so that the intermediate states traversed by the gas during the process, can always be described as composed by two parts each one in internal
(a)

(b)

(c)


Fig. 6.1 Two cylinders communicate by means of a throttle. a Initially, the gas is in container 1 and is pushed toward container 2 acting with a constant pressure $p_{1}$. The gas is prepared at an initial temperature $\theta_{1}$ and occupies the volume $V_{1}$. b In container 2 the piston is moved ensuring a constant pressure $p_{2}$ and the gas is pushed to flow into container 2. c After the throttling, the gas is all in container 2 where it occupies a volume $V_{2}$ at temperature $\theta_{2}$. The two cylinders are thermally insulated
equilibrium with a discontinuous variation of pressure. In this way the amount of work done on the gas in the whole process can be easily calculated.

If we denote by $W_{1}$ and $W_{2}$ the amount of work performed, on cylinder 1 and 2 respectively, we can easily write $W_{1}=p_{1} V_{1}$ and $W_{2}=-p_{2} V_{2}$ where $V_{1}$ and $V_{2}$ are, the volumes occupied by the gas when it is all in cylinder 1 (beginning) and in
cylinder 2 (end of the throttling). The total amount of work done on the gas in this process is

$$
\begin{equation*}
W=W_{1}+W_{2}=p_{1} V_{1}-p_{2} V_{2} . \tag{6.3}
\end{equation*}
$$

The transformation

$$
\begin{equation*}
\left(p_{1}, V_{1}, \theta_{1}\right) \rightarrow\left(p_{2}, V_{2}, \theta_{2} .\right) \tag{6.4}
\end{equation*}
$$

is an adiabatic transformation and then, by he First Principle, we have $\Delta U=W$. This means that $U\left(p_{2}, \theta_{2}\right)-U\left(p_{1}, \theta_{1}\right)=p_{1} V_{1}-p_{2} V_{2}$ and then:

$$
\begin{equation*}
H\left(p_{1}, \theta_{1}\right)=H\left(p_{2}, \theta_{2}\right) \tag{6.5}
\end{equation*}
$$

For every initial state $\left(p_{1}, \theta_{1}\right)$, we can draw the curve $\theta=\theta(p)$ by measuring the final temperature $\theta_{2}$ for different values of the final pressure $p_{2}$. We obtain a curve which is the locus of the states having the same enthalpy as the initial state $\left(p_{1}, \theta_{1}\right)$.

The construction of these isoenthalpic curves constitute a preparatory stage to the calorimetric measurements that will show the proportionality of the first virial coefficient to the temperature.

### 6.2.2 Some Thermodynamic Potentials for Gases

From the equation of state Eq. (6.2), we can get some relevant information on the thermodynamic potentials of a gas. We start from the general relations:

$$
\begin{align*}
V & =\left(\frac{\partial G}{\partial p}\right)_{T}  \tag{6.6}\\
H & =G+T S=G-T\left(\frac{\partial G}{\partial T}\right)_{p} \tag{6.7}
\end{align*}
$$

If we make use of Eq. (6.2) written in the form $V=(A / p)+B+C p+\ldots$ we can write the variation of the Gibbs between two states at the same temperature. By integrating Eq.(6.6) at constant temperature we obtain

$$
\begin{align*}
& \Delta G=G(p, \theta)-G\left(p^{\dagger}, \theta\right)= \\
& =A(T) \ln \frac{p}{p^{\dagger}}+B(T)\left(p-p^{\dagger}\right)+\frac{1}{2} C(T)\left(p^{2}-p^{\dagger}\right)+\ldots \tag{6.8}
\end{align*}
$$

From Eq. (6.7), the Enthalpy difference $\Delta H$ between two states at the same temperature can be written in form

$$
\begin{equation*}
\Delta H=H(p, \theta)-H\left(p^{\dagger}, \theta\right)=\Delta G-T\left(\frac{\partial \Delta G}{\partial T}\right) \tag{6.9}
\end{equation*}
$$

By substituting Eq.(6.8) in Eq. (6.9) and differentiating respect to the temperature we obtain

$$
\begin{align*}
& H(p, \theta)-H\left(p^{\dagger}, \theta\right)=\left[A(T)-T \frac{\mathrm{~d} A(T)}{\mathrm{d} T}\right] \ln \frac{p}{p^{\dagger}}+ \\
& +\left[B(T)-T \frac{\mathrm{~d} B(T)}{\mathrm{d} T}\right]\left(p-p^{\dagger}\right)+\frac{1}{2}\left[C(T)-T \frac{\mathrm{~d} C(T)}{\mathrm{d} T}\right]\left(p^{2}-p^{\dagger}\right)+\ldots \tag{6.10}
\end{align*}
$$

the last expression the total derivatives of the virial coefficients appear because are a function of temperature only.

### 6.2.3 Calorimetric Measurements for the Determination of the First Virial Coefficient

In order to obtain more information about the virial coefficients and, in particular, on their dependence on temperature, we will measure the enthalpy change Eq. (6.10) through simple calorimetric measurements.

We know that the measurement of the quantity of heat supplied to a system in a transformation is equal to its enthalpy change only if the transformation is at constant pressure while in Eq. (6.10) we have the expression of the enthalpy variation between two states at the same temperature and at different pressures. It is at this point that the experiment of Joule-Thomson comes to the aid.

Suppose that in the Joule-Thomson expansion the gas becomes colder i.e. $\theta_{2}<\theta_{1}$. Let's take the gas in cylinder 2 and raise its temperature to the initial temperature $\theta_{1}$ at the constant pressure $p_{2}$. If we denote with $Q$ the amount of heat supplied to the gas in this transformation, we will have

$$
\begin{equation*}
Q=H\left(p_{2}, \theta_{1}\right)-H\left(p_{2}, \theta_{2}\right), \tag{6.11}
\end{equation*}
$$

and, by making use of the isoenthalpic curves Eq.(6.5) obtained by the JouleThomson experiment, we will get

$$
\begin{equation*}
Q=H\left(p_{2}, \theta_{1}\right)-H\left(p_{1}, \theta_{1}\right) . \tag{6.12}
\end{equation*}
$$

If, on the contrary, the gas in the Joule-Thomson expansion becomes hotter i.e. $\theta_{2}>\theta_{1}$, then we may take back the gas to the initial state and then raise, at constant pressure $p_{1}$, its temperature to the measured value $\theta_{2}$. In such a case the amount of heat delivered to the gas will be equal to the following enthalpy difference:

$$
\begin{equation*}
Q=H\left(p_{1}, \theta_{2}\right)-H\left(p_{1}, \theta_{1}\right), \tag{6.13}
\end{equation*}
$$

and by using, once again, the isoenthalpic curves of Eq. (6.5) we get

$$
\begin{equation*}
Q=H\left(p_{1}, \theta_{2}\right)-H\left(p_{2}, \theta_{2}\right) \tag{6.14}
\end{equation*}
$$

In both cases, the measurement of the quantity of heat provides us with an experimental measurement of the expression given in Eq. (6.10).

The relevant fact is the presence of the logarithmic term in this expression and this means that, for a given temperature, the amount of heat $Q$ must exhibit a divergence when the final pressure tends to zero. This divergence is not manifested and the experimental data are soon arranged, for each temperature, at a constant value.

This fact has the consequence that the logarithmic term must be absent in the power expansion and this implies that the coefficient of the logarithmic term must be identically zero at all temperatures, i.e.,

$$
\begin{equation*}
A=T \frac{\mathrm{~d} A}{\mathrm{~d} T} \tag{6.15}
\end{equation*}
$$

and this is equivalent to state that the first virial coefficient must be proportional to the absolute temperature:

$$
\begin{equation*}
A(T) \propto T \tag{6.16}
\end{equation*}
$$

### 6.3 Definition of the Temperature Scale by Means of Gases

To completely define the scale of absolute temperature, we proceed follows: we select a certain amount of a given gas, and we measure the volume at different pressures keeping it at a constant temperature whose value is denoted by $\theta_{1}$ in some empirical scale as, for instance, the Celsius scale. We calculate the product ( $p V$ ) for different pressures and we extrapolate the value of this product to pressures tending to zero. This extrapolated value will give us a measurement of the first virial coefficient $A_{1}$ of that gas at the empirical temperature $\theta_{1}$

$$
\begin{equation*}
A_{1}=\lim _{p \rightarrow 0}(p V)_{\theta_{1}} \tag{6.17}
\end{equation*}
$$

We proceed in a similar way along another isotherm at the empirical temperature $\theta_{2}$. We shall obtain the new value for the first virial coefficient:

$$
\begin{equation*}
A_{2}=\lim _{p \rightarrow 0}(p V)_{\theta_{2}} \tag{6.18}
\end{equation*}
$$

Then the ratio of the two first virial coefficients will be

$$
\begin{equation*}
\frac{A_{1}}{A_{2}}=\frac{T_{1}}{T_{2}} . \tag{6.19}
\end{equation*}
$$

Since this ratio does not depend either on the amount or on the kind of the selected gas, we may state that it is determined in nature in an absolute way. We are left with
the freedom to set the value of the temperature in an arbitrary state after which the scale will be completely determined. As we know, we agreed to assign the value $T=273.15 \mathrm{~K}$ at the melting point of distilled water at the pressure $p_{0}=1 \mathrm{~atm}$. More rigorously, we choose the value:

$$
\begin{equation*}
T=273.16 \mathrm{~K} \tag{6.20}
\end{equation*}
$$

in correspondence to the triple point of water (see Sect.7.3). The latter formulation is much preferable because the triple point is a configuration with zero degrees of freedom while the liquid-solid equilibrium temperature depends on the pressure.

## Why Have We Adopted This Convention?

Before understanding the deeper meaning of the concept of absolute temperature, there was a general consensus about the use of the empirical temperature defined by the Celsius scale. Indeed much work on the measurement of specific heats, thermal expansion coefficients and, in general, a large amount of calorimetric measurements had been cataloged using that empirical temperature scale. It was therefore convenient that the translation of the experimental data in the new temperature scale was as simple as possible.

For this purpose, it is convenient to make sure that the unit change in temperature, i.e., the degree, was the same in passing from one scale to another. Since the unit in the Celsius scale is defined as the hundredth part of the mercury volume change between the boiling point and the melting point of water at atmosphere, it is clear that the best choice was to manage so that even in the new scale the difference of the values of $T$ between the same two reference states, was equal to 100 .

In order to obtain this result, we measure the first virial coefficient for a certain amount of a certain gas at a temperature $\theta_{1}=100^{\circ} \mathrm{C}$ and the temperature $\theta_{2}=0^{\circ} \mathrm{C}$. We will get two values that we denote, respectively, with $A_{1}$ and $A_{2}$.

The ratio between the two experimentally measured values is

$$
\begin{equation*}
\frac{A_{1}}{A_{2}} \simeq 1.366 \tag{6.21}
\end{equation*}
$$

and then from Eq.(6.19) we set

$$
\begin{equation*}
\frac{T_{1}}{T_{2}}=1.366 \tag{6.22}
\end{equation*}
$$

This number is absolute in the sense that it does not depend on any convention. Now we impose that the difference between the two values is

$$
\begin{equation*}
T_{1}-T_{2}=100 . \tag{6.23}
\end{equation*}
$$

The solution of the system composed by the two Eqs. (6.22) and (6.23) gives the values:

$$
\begin{equation*}
T_{1}=373.15 \quad T_{2}=273.15 \tag{6.24}
\end{equation*}
$$

We have imposed that the temperature difference between the boiling point of water and the ice melting point at the pressure of 1 atmosphere, is equal to 100 both in absolute scale and in the Celsius scale and that is all.

For instance, if we say (as we currently do) that the difference in absolute temperature between, for instance, $\theta_{1}=53^{\circ} \mathrm{C}$ and $\theta_{2}=20^{\circ} \mathrm{C}$ is $\Delta T=33 \mathrm{~K}$, this means that we neglect the temperature dependence of the coefficient of thermal expansion of mercury in the interval $0^{\circ} \mathrm{C} \leq \theta \leq 100^{\circ} \mathrm{C}$. Having this in mind we may write

$$
\begin{equation*}
T=273.15+\theta \tag{6.25}
\end{equation*}
$$

and this is the most convenient relationship between the Celsius scale and the absolute scale but it is subject to the approximation mentioned before. It is clear that the further we move away from the range in which the Celsius scale was defined, i.e. the range $0-100^{\circ} \mathrm{C}$, the more meaningless relationship Eq. (6.25) becomes.

The current assertion that "absolute zero is -273.15 Celsius degrees" is a statement that might make sense only if we consider Eq. (6.25) as the relation that defines the Celsius scale out of the interval in which it was initially defined, otherwise it makes no sense.

### 6.3.1 Other Determinations of the Temperature Scale

There are different routes to determine the absolute temperature scale but the one previously discussed is the closest to the so-called "perfect gas thermometer".

An alternative route was already considered when we discussed the issue of the maximum efficiency of a heat engine. On that occasion we have demonstrated, as a consequence of the Second Principle, that the maximum efficiency of a heat engine that operates between two thermostats is given by

$$
\begin{equation*}
\eta_{\max }=1-\frac{T_{2}}{T_{1}} \tag{6.26}
\end{equation*}
$$

where $T_{1}$ and $T_{2}$ are the values of the temperatures (respectively, of the "hot" source and of the "cold" source) measured in the new absolute scale and hence, if we measure (asymptotically) this maximum efficiency, we obtain a measure of the ratio $\left(T_{2} / T_{1}\right)$.

Another way would be to measure the energy density of the black-body radiation or, equivalently, the measurement of the radiation pressure at thermodynamic equilibrium. From thermodynamics, it results that these quantities are proportional to the fourth power of the temperature measured in absolute scale, as it will be shown in Sect. 12.4:

$$
\begin{equation*}
\frac{p_{1}}{p_{2}}=\frac{T_{1}^{4}}{T_{2}^{4}} . \tag{6.27}
\end{equation*}
$$

Also, in this case, the measurement of the ratio between the pressures at two different temperatures will provide an absolute measure of the ratio between the absolute temperature values. It remains then to make use of the arbitrariness that is left to us, in analogy with the procedure outlined in the case of the gas thermometer, in order to determine the scale completely.

### 6.4 The Universal Constant of Gases

We have seen, with a solid experimental evidence, that the first virial coefficient $A$ for gases is proportional to the absolute temperature.

Since the volume is an extensive quantity, the first virial coefficient must also be proportional to the quantity of gas contained in the vessel. If we choose to measure the amount of gas through the number of moles $n$ we can write

$$
\begin{equation*}
A=n R T . \tag{6.28}
\end{equation*}
$$

The practice shows that, with this choice, the proportionality coefficient $R$ has the same value for all gases. For this reason, it is called the universal gas constant. The value of the universal gas constant is

$$
\begin{equation*}
R=8.31 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}=0.082{\mathrm{~atm} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}=1.987 \mathrm{cal} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} . . . . ~}_{\text {. }} \tag{6.29}
\end{equation*}
$$

### 6.5 The Joule-Thomson Coefficient

The Joule-Thomson experiment reproduces, under controlled conditions, the adiabatic expansion of a gas against a constant pressure (as it could be, e.g., the expansion of a gas contained in a cylinder or the expansion of steam at high pressure in a turbine, against the atmospheric pressure). In general the temperature of the gas undergoing such an adiabatic expansion will change. It may increase or decrease depending on the initial state as it will discussed in Sect. 6.6. For instance, given the initial temperature, if the density of the gas is high enough the temperature will increase under expansion while for relatively low initial pressure the temperature will decrease and this technique can be used to lower the gas temperature as described in Sect.6.6.1.

We have seen that this process can be well approximated by an expansion at constant enthalpy, then it is appropriate to define the so called Joule-Thomson coefficient as the change in temperature per unit change of pressure in a isoenthalpic process. Making use of Eq. (A.8) applied to the function $H=H(p, T)$ we get

$$
\begin{equation*}
\left(\frac{\partial T}{\partial p}\right)_{H}=-\left(\frac{\partial H}{\partial p}\right)_{T}\left(\frac{\partial T}{\partial H}\right)_{p} \tag{6.30}
\end{equation*}
$$

Let's use Eq. (6.7) to calculate $(\partial H / \partial p)_{T}$ in the second member of Eq. (6.30):

$$
\begin{equation*}
\left(\frac{\partial H}{\partial p}\right)_{T}=\left(\frac{\partial G}{\partial p}\right)_{T}-T\left(\frac{\partial^{2} G}{\partial p \partial T}\right)=V-T \alpha V=V(1-\alpha T) \tag{6.31}
\end{equation*}
$$

where $\alpha$ is the coefficient of thermal expansion. Recalling the definition of heat capacity at constant pressure $C_{p}=(\partial H / \partial T)_{p}$ we obtain the expression for the Joule-Thomson coefficient:

$$
\begin{equation*}
C_{H}=\left(\frac{\partial T}{\partial p}\right)_{H}=\frac{T V}{C_{p}}\left(\alpha-\frac{1}{T}\right) . \tag{6.32}
\end{equation*}
$$

As we can easily see $C_{H}$ is an intensive quantity positive or negative according to the sign of the quantity $(\alpha-1 / T)$. In the former case the gas under expansion cools, in the latter it becomes hotter.

In general, to be able to make predictions about the behavior of a gas in this kind of expansion, it is necessary to assume a particular equation of state. For a gas which obeys the equation of state $p V=R T$ (ideal gas), one immediately obtains

$$
\begin{equation*}
\alpha=\frac{1}{T}, \tag{6.33}
\end{equation*}
$$

and it follows that in this case the Joule-Thomson coefficient is identically zero. For such a gas, the temperature will not change in the isoenthalpic expansion and this implies that $p_{1} V_{1}=p_{2} V_{2}$. Since we must have $H_{1}=H_{2}$, it follows that

$$
\begin{equation*}
U_{1}=U_{2} \tag{6.34}
\end{equation*}
$$

This shows that, for a system with this equation of state, the energy depends only on the temperature.

We see then that the cooling or heating of a gas in response to an expansion depends on being

$$
\begin{equation*}
\alpha \gtrless \frac{1}{T} \tag{6.35}
\end{equation*}
$$

If we adopt a phenomenological equation of state as shown in Eq.(6.43) it will be the second virial coefficient $B(T)$, or more precisely its temperature dependence, to decide the matter (calling into play also the third virial coefficient, the algebra is complicated a little bit, and the condition will also depend on pressure). In this approximation we see that we can write in all generality

$$
\begin{equation*}
\alpha V=\left(\frac{\partial V}{\partial T}\right)_{p} \simeq n\left(\frac{R}{p}+\frac{\mathrm{d} B}{\mathrm{~d} T}\right) \tag{6.36}
\end{equation*}
$$

where $B=B(T)$ is the second virial coefficient per mole. Replacing the previous expression in Eq. (6.32) we write

$$
\begin{equation*}
C_{H} C_{p}=n T\left[\frac{R}{p}+\frac{\mathrm{d} B}{\mathrm{~d} T}\right]-n \frac{R T}{p}-n B(T)=-n B+n T \frac{\mathrm{~d} B}{\mathrm{~d} T} \tag{6.37}
\end{equation*}
$$

obtaining at the end

$$
\begin{equation*}
C_{H}=\frac{n}{C_{p}} T^{2} \frac{\mathrm{~d}\left(\frac{B}{T}\right)}{\mathrm{d} T} . \tag{6.38}
\end{equation*}
$$

### 6.6 The Inversion Curve

From the general introductory discussion made in the previous section, we have seen that for all gases, if we represent the thermodynamic states in a plane $(p, T)$, the equation

$$
\begin{equation*}
\alpha(p, T)=\frac{1}{T} \tag{6.39}
\end{equation*}
$$

defines the locus of the points (thermodynamic states) in which the Joule-Thomson coefficient is zero. This means that, if we prepare the gas in an initial state at a given temperature, $(\alpha-1 / T)$ and therefore $C_{H}$ change sign while the pressure varies. The discussion may be somehow detailed after we have made a choice on the equation of state to be adopted but in general we expect that, at a given temperature, $C_{H}$ will be negative for the high pressures and positive for the lower pressures. Indeed at high pressures, that is at relatively high densities, the repulsion between nuclei dominates in the sense that the average potential energy between the molecules is positive as it is made clear in Fig. 8.1 which shows the two essential features of intermolecular interactions (at short and large distance) valid for every equation of state. We expect that, under expansion, the average distance between molecules increases and then the average potential energy decreases in favor of an increase of the average kinetic energy.

Conversely, at low pressure, the intermolecular potential energy is dominated by the attractive part of the interaction and the average potential energy will be negative. Under expansion, the potential energy will increase at the expense of average kinetic energy.

At ordinary temperatures and pressures for hydrogen and, more in general, for the noble gases, the attractive interaction is very weak and the deviation from the ideal gas equation of state is due mainly to the repulsive part.

The curve described by Eq. (6.39) is the locus of the points where the behavior of the gas, subject to an isoenthalpic expansion, changes sign and for this reason it is called inversion curve.


Fig. 6.2 a States at constant enthalpy downstream the throttling of the gas starting from the state $p_{1}, T_{1}$ before throttling. The maximum of the curve defines the inversion temperature $T_{\mathrm{i}}$, and pressure $p_{\mathrm{i}}$, at a fixed enthalpy $H$. b Dashed line is the inversion curve of a given gas obtained by the collection of different inversion temperatures and pressures for different enthalpies (different initial states). According to the definition of $C_{H}$ given in Eq. (6.32), positive (negative) derivative $(\partial T / \partial p)_{H}$ accounts for gas cooling (heating)

In Fig. 6.2a it is outlined the procedure to determine the inversion temperature. For a given initial state ( $p_{1}, T_{1}$ ) upstream the throttling, we select different final pressures $p_{2}, p_{2}^{\prime}, p_{2}^{\prime \prime}, \cdots<p_{1}$ downstream the throttling, and we measure $T_{2}, T_{2}^{\prime}, T_{2}^{\prime \prime}, \ldots$ The collection of these final states determines a curve $T=T(p)$ which is at constant enthalpy showing a maximum value at $\left(p_{\mathrm{i}}, T_{\mathrm{i}}\right)_{H}$. At this specific state both [ $\alpha(p, T)-1 / T]$ and $C_{H}(p, T)$ change sign. By repeating the procedures for different initial states, we obtain a family of curves. Each of them being at constant $H$ whose value is fixed by the choice of the initial state. Hence, we determine a collection of different inversion points ( $p_{\mathrm{i}}, T_{\mathrm{i}}$ ) forming the inversion curve either in the ( $T, p$ ) or ( $p, T$ ) plane (see Fig. 6.2b).

### 6.6.1 Liquefaction of Gases and the Attainability of Low Temperatures

For every gas, there is a temperature $T_{\mathrm{cr}}$, known as critical temperature, so that the liquefaction of a gas is possible only below $T_{\text {cr }}$. This argument will be treated extensively in Chap. 7. To liquify the gas it is necessary to bring it below the critical temperature and then compress it isothermally. If we already possess bodies at a sufficiently low temperature there is no problem at least in principle, but if the lowest available temperature is above the critical temperature of the gas, the latter cannot be liquefied by a simple isothermal compression. It is necessary to lower further its temperature, and this can be done with an isoenthalpic expansion according to the procedure outlined in Sect.6.5. In general, for obvious technical reasons, it will be convenient to expand the gas against the atmospheric pressure $p_{0}$ then our problem can be set in this way: given the initial temperature $T_{0}$, how shall we select the initial
pressure $p$ such that we obtain the maximum temperature drop in one isoenthalpic expansion against the atmospheric pressure? If we denote by $T$ the value of the temperature of the gas after the expansion, we may write

$$
\begin{equation*}
T-T_{0}=\int_{p}^{p_{0}}\left(\frac{\partial T}{\partial p}\right)_{H} \mathrm{~d} p \tag{6.40}
\end{equation*}
$$

In the above Eq.(6.40), $p_{0}$ and $T_{0}$ are given and then we may consider the value of the final temperature as a function only of the initial pressure $p$ chosen for expansion, formally $T=T(p)$. The derivative of this function with respect to $p$ leads to

$$
\frac{\mathrm{d} T}{\mathrm{~d} p}=-\left(\frac{\partial T}{\partial p}\right)_{H}
$$

and then the minimum value for $T$ will be obtained if we choose the initial value of the pressure $p$ in such a way to have $\mathrm{d} T / \mathrm{d} p=0$. In other words in such a way that

$$
\begin{equation*}
\left(\frac{\partial T}{\partial p}\right)_{H}=0 \tag{6.41}
\end{equation*}
$$

This means that the maximum effect will be obtained if we start from the inversion curve at the given temperature $T_{0}$. Let us consider, as an example, the following gases:

## Example 6.1

Nitrogen. The critical temperature of Nitrogen is about 126.2 K so it was possible to liquefy it by using thermostats at relatively higher temperatures.

Hydrogen. The critical values for Hydrogen are $p_{\text {cr }} \simeq 13 \mathrm{~atm}$ and $T_{\mathrm{cr}} \simeq 33.18 \mathrm{~K}$. In Fig. 6.3, the inversion curve for Hydrogen is represented in a plane ( $p, T$ ) and we see that the maximum pressure drop is obtained at a temperature of about $64-65 \mathrm{~K}$ which is almost twice its critical temperature. At this temperature, the pressure on the inversion curve of Hydrogen is about 160 atm and this would be the situation for maximum cooling effect in one single expansion. In practice, it is convenient to work at $T \simeq 72 \mathrm{~K}$ and $p \simeq 140 \mathrm{~atm}$. This temperature can be reached by evaporating liquid nitrogen at low pressure. ${ }^{1}$

Helium. The gas with the lowest critical temperature is Helium (He) with $T_{\text {cr }} \simeq$ 5.3 K and $p_{\text {cr }} \simeq 2.26 \mathrm{~atm}$.

Resuming the mechanism to obtain low temperatures is the following: we start from easily accessible temperatures and we liquefy a gas having a relatively high critical temperature. By evaporating the obtained liquid below the saturation pressure, we can lower its temperature and then liquefy other gases having a lower critical temperature. By iterating the process, we arrive at liquid Helium. With this technique,

[^19]Fig. 6.3 Inversion curve for Hydrogen. Data are taken from Sommerfeld, Thermodynamics and Statistical Mechanics-Lectures on Theoretical Physics, [7]

we can reach temperatures of the order of a fraction of one degree. To proceed further toward the attainment of lower temperatures it is necessary to resort to the adiabatic demagnetization of some paramagnetic substances. The issue will be briefly discussed in Sect. 11.7.

### 6.7 A Simple Approximation of the Isothermal Behavior of Gases

Let's start from the virial expansion given by Eq. 6.2 and let us write an expansion for the volume, in the form:

$$
\begin{equation*}
V=A p^{-1}+B+C p+\cdots \tag{6.42}
\end{equation*}
$$

For temperatures well below the critical temperature (roughly $T \lesssim 0.65 T_{\text {cr }}$ ), the contribution of the third virial coefficient is negligible up to pressures of more than 100 atmospheres and then, for our purposes, it will be sufficiently accurate to consider the equation of state up to the second virial coefficient:

$$
\begin{equation*}
V_{\mathrm{m}}=\frac{R T}{p}+B(T) \tag{6.43}
\end{equation*}
$$

As regards the temperature dependence of the second virial coefficient experimental observations agree well with a relationship of the type:

$$
\begin{equation*}
B(T)=b-\frac{a}{R T} \tag{6.44}
\end{equation*}
$$

in which $a$ and $b$ are phenomenological constants depending on the particular gas. This choice of the symbols $a, b$ to indicate these two constants is not accidental but find explanation when we discuss the properties of the van der Waals equation of state in Chap. 8.

Meanwhile, we note that for every gas there is a temperature, called "Boyle temperature" $T_{\mathrm{B}}$, at which the second virial coefficient vanishes. If the pressure is not too high, so that Eq. (6.43) holds, we obtain the following expression for the Boyle temperature in terms of the two phenomenological constants $a$ and $b$ :

$$
\begin{equation*}
T_{\mathrm{B}}=\frac{a}{R b} . \tag{6.45}
\end{equation*}
$$

At this temperature the gas seems to be optimally described by the equation of ideal gases but we must be aware that many important properties of the gas depend also on the derivative with respect to temperature of the second virial coefficient and the latter is by no means zero. One example is the Joule-Thompson coefficient.

### 6.8 The Chemical Potential in Diluted Gases

It is convenient treat the case of a single component gas separately from the general case of a gas mixture.

## Case of One Component Gas

Recalling that the Gibbs function per mole of a chemically pure phase coincides with the chemical potential of that component, we may integrate Eq. (6.6) with the approximated equation of state discussed in Eq. (6.43). Since Eq. (6.6) is a partial differential equation, it may be integrated by choosing first a reference pressure $p^{\dagger}$ and then integrate at constant temperature. We obtain

$$
\begin{equation*}
\mu(p, T)=R T \ln \frac{p}{p^{\dagger}}+B(T)\left(p-p^{\dagger}\right)+\mu^{\dagger}(T) \tag{6.46}
\end{equation*}
$$

where $\mu^{\dagger}(T)$ is the chemical potential at the reference pressure $p^{\dagger}$ is a function of temperature only to be determined. If we take the reference pressure $p^{\dagger}$ low enough, the product $B(T) p^{\dagger}$ will be very small and can be neglected so that a very good approximation for the chemical potential of a gas can be written as

$$
\begin{equation*}
\mu(p, T)=R T \ln \frac{p}{p^{\dagger}}+B(T) p+\mu^{\dagger}(T) \tag{6.47}
\end{equation*}
$$

In this expression, the term $B(T) p$ describes fairly well the correction to the chemical potential of an ideal gas due to the second virial coefficient $B(T)$.

As far as the function $\mu^{\dagger}(T)$ is concerned, if the reference pressure $p^{\dagger}$ is low, it can be modeled fairly well. It depends on the microscopic nature of the gas and it results that different gases can be grouped into four categories: monoatomic molecules, diatomic molecules, linear polyatomic and nonlinear polyatomic molecules (the same grouping which is very appropriate in the study of the heat capacities of gases treated in Sect. 6.9). The subject is dealt with in an exhaustive way in [3] to which the reader is addressed for a complete and in-depth discussion of the topic.

For an ideal gas, the chemical potential may written as

$$
\begin{equation*}
\mu(p, T)=\mu^{\dagger}(T)+R T \ln \frac{p}{p^{\dagger}} \tag{6.48}
\end{equation*}
$$

## Case of a Multi Component Gas

Suppose that the gas is formed by a mixture of several components $\gamma$ which are present with a molar concentration $C_{\gamma}$, given by

$$
C_{\gamma}=\frac{n_{\gamma}}{\Sigma_{\rho} n_{\rho}}
$$

and let's limit ourselves to the case of gases whose equation of state, when considered individually, can be well described by the ideal gas equation. Moreover, if the different gases are weakly interacting with each other, the Dalton law holds and the partial pressure $p_{\gamma}$ of each component is

$$
\begin{equation*}
p_{\gamma}=C_{\gamma} p \tag{6.49}
\end{equation*}
$$

and for each component $\gamma$ we can write the chemical potential in the form:

$$
\begin{equation*}
\mu_{\gamma}(p, T)=\mu_{\gamma}^{\dagger}(T)+R T \ln \frac{p_{\gamma}}{p^{\dagger}} \tag{6.50}
\end{equation*}
$$

By making use of Eq. (6.50) we obtain

$$
\begin{equation*}
\mu_{\gamma}(p, T)=\mu_{\gamma}^{\dagger}(T)+R T \ln \frac{p}{p^{\dagger}}+R T \ln C_{\gamma} \tag{6.51}
\end{equation*}
$$

The above Eq. (6.51) can also be written in the following form:

$$
\begin{equation*}
\mu_{\gamma}(p, T)=\eta_{\gamma}(p, t)+R T \ln C_{\gamma} \tag{6.52}
\end{equation*}
$$

which will be used in the following chapters. This relation is important because it highlights the dependence of the chemical potential of each component on its (molar) concentration.

### 6.9 Molar Heat at Constant Volume for Dilute Gases

The study of the molar heats of dilute gases offers an important opportunity to verify in what way and to what level of depth the measurements by the macroscopic observer offer fundamental information on the structure of the microscopic world.

The bridge between macroscopic observations and the atomic-molecular theory of matter is based on the mechanical-statistical model. In particular it is rooted on the theorem of equipartition of energy which shall be briefly discussed shortly after. First of all it is appropriate to start from the definition of the heat capacity given in Eq. (5.19) and let us assume that the gas is sufficiently diluted that the mutual interaction between different molecules can be disregarded. In this approximation, the total energy of the system can be written as the sum of the energies of the individual particles

$$
\begin{equation*}
U=\sum_{i=1}^{N} \varepsilon^{(i)}, \tag{6.53}
\end{equation*}
$$

where $\varepsilon^{(i)}$ is the total energy of one of the $N$ elementary constituents of the gas (atoms or molecules). Within this approximation, in a small transformation at constant volume, the amount of energy injected into the system in order to produce an increase of temperature, will be distributed among the elementary constituents. It is, then, necessary to examine the structure of $\varepsilon^{(i)}$ from the point of view of its capability of absorbing energy.

### 6.9.1 Microscopic Degrees of Freedom

Along the entire section, in order to describe the structure of $\varepsilon^{(i)}$, we will use the Hamiltonian formalism because this is useful both for an introduction to the energy equipartition theorem and for a discussion of the role of quantum mechanics. Let us consider, first, the simplest case of monoatomic molecules for which the total energy is entirely given by the kinetic energy of a point mass

$$
\begin{equation*}
\varepsilon^{(i)}=\varepsilon_{\text {tra }}^{(i)}=\frac{p_{x}^{2}}{2 m}+\frac{p_{y}^{2}}{2 m}+\frac{p_{z}^{2}}{2 m} \tag{6.54}
\end{equation*}
$$

where $m$ is the mass of the molecule and $p_{x}, p_{y}$ and $p_{z}$ are the three components of the momentum.

As a next step toward the more general case, let's consider a rigid polyatomic molecule. By "rigid" we mean that the individual atoms form a rigid structure or, in other words, we assume that oscillations of atoms near their equilibrium positions are absent.

In this case, the total kinetic energy of the molecule can be split into the sum of the translation term analogous to that in Eq. (6.54), where the velocity is the center of
mass (c.m.) velocity, plus the kinetic energy in the c.m. frame which can be written as

$$
\begin{equation*}
\varepsilon_{\mathrm{rot}}^{(i)}=\frac{L_{1}^{2}}{2 I_{1}}+\frac{L_{2}^{2}}{2 I_{2}}+\frac{L_{3}^{2}}{2 I_{3}}, \tag{6.55}
\end{equation*}
$$

where $L_{1}, L_{2}$, and $L_{3}$ are the projection of the angular momentum along three principal axes of inertia and $I_{1}, I_{2}$, and $I_{3}$ are the corresponding three principal moments of inertia. Obviously, for a one-dimensional molecule, as, for instance, diatomic molecules, the moment of inertia along the molecular axis will be considered null and then the energy stored in the rotational modes in Eq. (6.55) will consist of only two terms.

More in general, if the rigidity assumption is released, we have to take into account oscillatory motions of the atoms around their equilibrium positions. If the amplitude of these oscillations is not too large, they can be described as harmonic oscillations. In the simple case of a diatomic molecule we have only one oscillatory mode, along the line connecting the two atoms, with a given fundamental pulsation $\omega_{0}$. The energy of the oscillatory motion, $\varepsilon_{\mathrm{vib}}^{(i)}$, can be written as

$$
\begin{equation*}
\varepsilon_{\mathrm{vib}}^{(i)}=\frac{1}{2}\left(p_{q}^{2}+\omega_{q}^{2} q^{2}\right) \tag{6.56}
\end{equation*}
$$

where $q$ is called normal coordinate of oscillation (in the simplest model of two oscillating masses, as we are considering here as a starting point, it is the distance between them), $p_{q}=\dot{q}$ is the corresponding generalized momentum and $\omega_{q}$ is the harmonic oscillation frequency relative to the $q$ coordinate. In general, for polyatomic molecules, the description of the oscillatory motions is a little bit more complicated and deserves some careful discussion. In general, for any structure subject to possible oscillating motions, it is possible to identify a set of $k$ fundamental modes, each having an energy:

$$
\varepsilon_{\alpha}=\frac{1}{2}\left\{p_{q, \alpha}^{2}+\omega_{q, \alpha}^{2} q_{\alpha}^{2}\right\}_{\alpha=1,2, \ldots, k}
$$

with the following properties:
(a) Every possible oscillatory motion can be expressed as a linear combination of these fundamental modes;
(b) The fundamental modes are mutually independent.

The choice of these fundamental modes is not unique but their number is univocally determined; it depends on the number of atoms and defines the so-called number of oscillatory degrees of freedom of the molecule. However, it can also depend on the spatial form of the molecule. For example, for the same number of atoms, the number of fundamental oscillatory modes for a linear molecule exceeds by one unit the number of oscillatory degrees of freedom for a nonlinear molecule. The reason for this is the following: the number of coordinates necessary and sufficient to determine the spatial configuration of a set of $n$ points is $3 n$. Three of them are used for the
position of the center of mass and, for a nonlinear structure, three more are used for the angular coordinates of the "quasi-rigid" configuration. The oscillatory degrees of freedom left are then $3 n-6$. If the molecule is linear only two angular coordinates are required and then $3 n-5$ oscillatory modes are necessary for a complete description. As we shall see in Sect. 6.9.3, this significantly changes the macroscopic property we are discussing in this section.

Let us consider the case of water $\mathrm{H}_{2} \mathrm{O}$, a polyatomic non linear molecule with $n=3$. For this molecule the number of vibrational degrees of freedom is $k=3$. Two main vibrational modes can be identified: stretching and bending vibrations. Within the stretching modes it is the length of the bonds to be changed. This can occur either by symmetric stretching (ss) where the hydrogen bonds change their length in phase (both bonds vibrate in and out together) or asymmetric stretching (as) in which one bond is shortened as the other bond elongated. Conversely, within bending modes it is the angle between the hydrogen bonds to be changed, as if they would be the blades of a scissor. For this reason bending modes of water molecule are commonly referred as scissoring modes. By infrared spectroscopy it is possible to measure the energy of these vibrational modes in terms of the modes' wavenumber $\tilde{v}=1 / \lambda$, $\lambda$ being the wavelength of a given mode. Both the stretching modes are found at $\tilde{v}_{\mathrm{ss}, \mathrm{as}} \simeq 4000 \mathrm{~cm}^{-1}$ corresponding to $\hbar \omega_{\mathrm{ss}, \mathrm{as}}=h c / \lambda_{\mathrm{ss}, \mathrm{as}} \simeq 0.5 \mathrm{eV}$. Conversely, the bending mode (scissoring) is found at $\tilde{v}=2000 \mathrm{~cm}^{-1}$ corresponding to an energy of $\hbar \omega_{\text {bend }} \simeq 0.25 \mathrm{eV}$. Compared to the thermal energy $k_{B} T \simeq 1 / 40 \mathrm{eV}$ at $T=300 \mathrm{~K}$, the energy of all these vibrational modes $\hbar \omega_{\mathrm{ss}, \mathrm{as}}, \hbar \omega_{\text {bend }}$ are greater at least by one order of magnitude. Therefore, at room temperature the vibrational modes of the water molecule results to be essentially frozen. In general the contribution of oscillations to the total energy of the molecule will be written as

$$
\begin{equation*}
\varepsilon_{\mathrm{vib}}^{(i)}=\frac{1}{2} \sum_{\alpha=1}^{k}\left(p_{q, \alpha}^{2}+\omega_{q, \alpha}^{2} q_{\alpha}^{2}\right), \tag{6.57}
\end{equation*}
$$

where the summation is performed over the selected fundamental oscillatory modes, designed by the index $\alpha$ according to the brief discussion above [8].

Summing up, in general, for polyatomic molecules and in the absence of external fields, the total energy of the single elementary constituent may be written as

$$
\begin{equation*}
\varepsilon^{(i)}=\varepsilon_{\mathrm{tra}}^{(i)}+\varepsilon_{\mathrm{rot}}^{(i)}+\varepsilon_{\mathrm{vib}}^{(i)} \tag{6.58}
\end{equation*}
$$

and if we make use of Eqs. (6.54), (6.55) plus the appropriate number of oscillatory terms like those described in Eq. (6.56), we see that $\varepsilon^{(i)}$ is the sum of terms in which the generalized coordinates and the conjugate momenta appear quadratically and for this reason they are called also harmonic.

The brief discussion carried out to this point aims at exploring all the possible relevant contributions to the expression of the total energy of a molecule, coming from the analysis of its atomic structure. Indeed, we know that also the single atom, in turn, is a system endowed with an internal structure and this would give rise to further
terms in the expression of the total energy. These further internal degrees of freedom, are linked to the existence of the electronic component but their contribution to the variations of energy, becomes significant when the temperatures, and therefore the amount of energy involved in the intermolecular collisions, are close to the energy of dissociation of the molecules. We shall confine ourselves to much lower temperatures and their contribution to the total energy will be considered as a constant. It follows that, for temperature variations in the interval we are interested in here, they will not contribute to energy variations.

### 6.9.2 Energy Equipartition

The theorem of energy equipartition constitutes a milestone in the mechanicalstatistical theory of matter and allows us to establish a very important connection between the molar heat capacities at constant volume and the number of microscopic modes among which the energy of the molecule can be distributed. This important result is valid provided that the following conditions are satisfied:
(1) The terms in Eq. (6.58) must be harmonic, meaning that they all depend quadratically from the hamiltonian conjugated coordinates $p, q$. In Eq. (6.58), we have written the energy as the sum of different contributions each depending either on one coordinate or on one conjugated momentum. For instance, the term $\varepsilon_{\text {tra }}^{(i)}$ depends quadratically on the three momenta $p_{x}, p_{y}$ and $p_{z}$ and, similarly, $\varepsilon_{\text {rot }}^{(i)}$ depends quadratically on the components of the angular momentum. They do not depend on the conjugated coordinates as would happen if the system were immersed in an external field. In this case, the energy would depend on the position or the orientation of the molecule as we shall see in Sect. 10.5 for polarized systems. Indeed, in the latter case the energy depends on the cosine of an angular coordinate and not quadratically and this term is not harmonic according to our definition. In the case of $\varepsilon_{\mathrm{vib}}^{(i)}$, the contribution depends quadratically both on the coordinate $q_{\alpha}$ and on the conjugated momentum as shown in Eq. (6.57) and they are both harmonic.
(2) The energy contributions are treated classically. This is the second fundamental requirement. Consider, as an example, one term relative to the energy of rotation. In the quantum description, the energy levels are distributed according to a discrete spectrum whose fundamental energy level is of the order

$$
\begin{equation*}
E_{0}^{\mathrm{rot}} \sim \frac{h^{2}}{I} \tag{6.59}
\end{equation*}
$$

where $h$ is the Planck constant, and $I$ the molecule's moment of inertia. Let us introduce a characteristic temperature $T_{\text {rot }}$, defined by

$$
\begin{equation*}
k_{\mathrm{B}} T_{\mathrm{rot}} \sim \frac{h^{2}}{I} \tag{6.60}
\end{equation*}
$$

For $T<T_{\text {rot }}$, the energy transferred in molecular collisions will not be sufficient to excite higher rotational energy levels. In this case, the rotational degrees of freedom are said to be frozen in the sense they are unable to absorb their share of energy when the temperature is mildly increased. On the contrary, at temperature $T>T_{\text {rot }}$ the rotation energy levels are populated. When high quantum numbers are reached, the spacing between adjacent energy levels is very small compared to $k_{\mathrm{B}} T$, the density of states appears as continuously distributed and hence will behave classically. With the same argument, it is possible to define another characteristic temperature $T_{\text {vib }}$ such that temperature below which the vibrational modes are frozen:

$$
\begin{equation*}
k_{\mathrm{B}} T_{\mathrm{vib}} \sim \frac{\hbar^{2} \omega_{q}}{2} \tag{6.61}
\end{equation*}
$$

The theorem of energy equipartition states that, if conditions (1) and (2) stated at the beginning of Sect. 6.9.2 are fulfilled, then at thermodynamic equilibrium every term in Eq. (6.58) contributes with (1/2) $k_{\mathrm{B}} T$ to the average energy of the single molecule $\left\langle\varepsilon^{(i)}\right\rangle$.

Since in the thermodynamical context the total macroscopic energy $U$ is given by the sum of the average energies of the single molecules at equilibrium:

$$
U=\langle U\rangle=\sum_{i}^{N}\left\langle\varepsilon^{(i)}\right\rangle
$$

the total molar energy will be given by

$$
\begin{equation*}
U_{\mathrm{m}}=N_{\mathrm{A}}\left(\frac{1}{2} f k_{\mathrm{B}} T\right)=\frac{1}{2} f R T \tag{6.62}
\end{equation*}
$$

where $f$ is the number of terms appearing in Eq. (6.58) and defines the number of microscopic degrees of freedom of the gas. From Eq. (6.62) we obtain the molar heat at constant volume:

$$
\begin{equation*}
C_{V}=\frac{1}{2} f R \tag{6.63}
\end{equation*}
$$

Equation (6.63) is described by saying that every microscopic degree if freedom contributes $(1 / 2) R$ to the molar heat at constant volume of the gas.

### 6.9.3 On the Temperature Dependence of Molar Heats

We shall discuss only the molar heat at constant volume which comes entirely from the internal energy of the gas, the one at constant pressure being given by Eq. (5.22).

In Fig. 6.4, we schematically report the behavior of molar heat capacity at constant volume as a function of temperature. For a monoatomic molecule, the energy is
completely described by the three translational terms if we disregard the electronic contributions. The three microscopic degrees of freedom lead to

$$
\begin{align*}
& \left\langle\varepsilon^{(i)}\right\rangle=\left\langle\varepsilon_{\text {tra }}^{(i)}\right\rangle=\frac{3}{2} k_{\mathrm{B}} T,  \tag{6.64}\\
& U_{\mathrm{m}}=N_{\mathrm{A}}\left\langle\varepsilon^{(i)}\right\rangle=\frac{3}{2} R T,  \tag{6.65}\\
& C_{\mathrm{V}}=\left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_{\mathrm{V}}=\frac{3}{2} R . \tag{6.66}
\end{align*}
$$

being Eq. (6.64) the average energy of a single molecule, Eq. (6.65) the energy of one mole and Eq. (6.66) the molar heat capacity at constant volume.

For diatomic molecules, the number of degrees of freedom depends on temperature. At low temperatures, any gas behaves as if it were a monoatomic gas as already discussed in Sect.6.9.2. At increasing temperatures, the rotational terms start to absorb energy and then the molar heat increases. When the rotational energy levels behave classically, all the microscopic degrees of freedom are fully classical and the energy equipartition holds. Then, the average energy of a molecule and the molar heat at constant volume become

$$
\begin{align*}
& \left\langle\varepsilon^{(i)}\right\rangle=\left\langle\varepsilon_{\text {tra }}^{(i)}\right\rangle+\left\langle\varepsilon_{\text {rot }}^{(i)}\right\rangle=\frac{5}{2} k_{\mathrm{B}} T  \tag{6.67}\\
& C_{\mathrm{V}}=\left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_{\mathrm{V}}=\frac{5}{2} R \tag{6.68}
\end{align*}
$$

By increasing the temperature, the molar heat of diatomic molecules remains constant to $C_{\mathrm{V}}=(5 / 2) R$ until the energy levels of the oscillatory motion of the molecule begin to be excited and this happens at temperatures higher than the char-


Fig. 6.4 Qualitative representation of the molar heat at constant volume $C_{\mathrm{V}}$ as a function of temperature for a dilute gas

Table 6.1 Rotational and vibrational temperatures for some substances

| Substance | $T_{\text {rot }} / \mathrm{K}$ | $T_{\text {vib }} / \mathrm{K}$ |
| :--- | :--- | :--- |
| $\mathrm{H}_{2}$ | 85 | 6215 |
| $\mathrm{D}_{2}$ | 43 | 4394 |
| $\mathrm{O}_{2}$ | 2.1 | 2256 |
| $\mathrm{~N}_{2}$ | 2.9 | 3377 |
| CO | 2.8 | 3103 |
| HCl | 15 | 4227 |

acteristic temperature $T_{\text {vib }}$ defined in Eq. (6.61). Then the molar heat will increase again with temperature. When the vibrational mode is excited at high quantum numbers, it behaves classically and the energy equipartition applies again. In this range of temperatures the average energy of the molecule and the molar heat are respectively

$$
\begin{align*}
& \left\langle\varepsilon^{(i)}\right\rangle=\left\langle\varepsilon_{\text {tra }}^{(i)}\right\rangle+\left\langle\varepsilon_{\text {rot }}^{(i)}\right\rangle+\left\langle\varepsilon_{\text {vib }}^{(i)}\right\rangle=\frac{7}{2} k_{\mathrm{B}} T,  \tag{6.69}\\
& C_{\mathrm{V}}=\left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_{\mathrm{V}}=\frac{7}{2} R . \tag{6.70}
\end{align*}
$$

For polyatomic molecules, we have to distinguish between linear molecules and nonlinear molecules. In the former case the situation is similar to that of the diatomic molecule as far as the rotational degrees of freedom are concerned, but it differs in the counting of vibrational degrees of freedom. In our simplified model, the molar heat capacity at constant volume at increasing temperatures will assume the values $(3 / 2) R$, $(5 / 2) R$ plus the contributions of the vibrational modes whose number depends on the number of atoms according to the discussion in Sect. 6.9.1.

For nonlinear molecules, the values of the molar heat capacity at constant volume, at increasing temperature, will range with values $(3 / 2) R,(3 R)$ plus the contributions of the vibrational modes whose number depends on the number of atoms according to the discussion in Sect. 6.9.1 as before. It is important to highlight the sharp difference, at intermediate temperatures, which depend only on the different spatial shape.

It is interesting to consider the order of magnitude of the rotational and vibrational characteristic temperatures defined for some substances.

As it results from Table 6.1, at ordinary temperatures we are typically in the interval $T_{\mathrm{rot}}, T_{\mathrm{vib}}$ for several substances. Therefore, the vibrational modes can be considered frozen, while the rotational degrees of freedom can be treated as classical.

At temperatures $T>T_{\text {vib }}$ the molar heat increases. However, it is hard to describe the vibrational degrees as classical since dissociation or ionization processes begin to take place. The eventual contribution of the electronic transitions to the molar heat requires temperature even higher and is not be considered here.

## Chapter 7 Phase Transitions


#### Abstract

In this chapter, we introduce the study of phase equilibria and phase transitions. Phenomenological phase diagrams are showed and linked to the equations of phase equilibrium Clausius-Clapeyron's equations obtained from the application of the general principles of thermodynamics. The latent heats and the conditions for solid-liquid, solid-vapor, and liquid-vapor equilibrium are briefly discussed together with the temperature dependence of latent heats. Finally, the continuity of gaseous and liquid states is presented and continuous phase transitions are discussed on the basis of the Ehrenfest relations to be applied to those phase changes in which there is no evidence of latent heats.


Keywords Phase • Latent heats • Triple point • Critical point • Continuous phase transitions $\cdot$ Phase diagrams $\cdot$ Melting point

### 7.1 Phases Equilibrium

All substances show the property of appearing in different states of aggregation when they are in suitable combinations of pressure and temperature. According to the discussion in Sect.3.5.1 different states of aggregation, which at equilibrium are considered as homogeneous parts, are different phases of the system and the transformations of matter from one state of aggregation to another, is called phase transition. In Chap. 4, we have proved that Eq. (4.66) is the general condition which ensures the equilibrium with respect to the transfer of matter between the two phases. In general, the chemical potential of one component is a function of pressure, temperature, and the concentrations $\left\{C_{i}\right\}_{i=1, \ldots, k}$ of all the other independent components, as we have seen in Eq. (4.70).

Let us consider, for simplicity, two chemically pure phases, i.e., two phases composed of only one component ${ }^{1}$ and let the two phases be in thermal and mechanical

[^20]equilibrium (i.e. at the same pressure and temperature). For each component, we write the equilibrium condition, with respect to the transfer of matter, in the following form:
\[

$$
\begin{equation*}
\mu_{1}(p, T)=\mu_{2}(p, T) \tag{7.1}
\end{equation*}
$$

\]

The equality set by Eq. (7.1) provides a relation between pressure and temperature at phase equilibrium. Given one of the two intensive variables, the value of the other variable for maintaining the phase equilibrium is determined by Eq. (7.1). For this reason, a system of two phases in mutual equilibrium constitutes a system with only one degree of freedom. Since we aim to obtain the dependence $p=p(T)$ for two phases at equilibrium, let us differentiate both sides of Eq.(7.1):

$$
\begin{equation*}
\left(\frac{\partial \mu_{1}}{\partial p}\right)_{T} \mathrm{~d} p+\left(\frac{\partial \mu_{1}}{\partial T}\right)_{p} \mathrm{~d} T=\left(\frac{\partial \mu_{2}}{\partial p}\right)_{T} \mathrm{~d} p+\left(\frac{\partial \mu_{2}}{\partial T}\right)_{p} \mathrm{~d} T \tag{7.2}
\end{equation*}
$$

According to Chap. 5, we have

$$
\begin{align*}
& \left(\frac{\partial \mu}{\partial p}\right)_{T}=V_{\mathrm{m}}  \tag{7.3}\\
& \left(\frac{\partial \mu}{\partial T}\right)_{p}=-S_{\mathrm{m}} \tag{7.4}
\end{align*}
$$

$V_{\mathrm{m}}, S_{\mathrm{m}}$ being the molar volume and molar entropy respectively. By using Eqs. (7.3) and (7.4), the expression in Eq. (7.2) may be written in the familiar form:

$$
\begin{equation*}
V_{\mathrm{m}}^{(1)} \mathrm{d} p-S_{\mathrm{m}}^{(1)} \mathrm{d} T=V_{\mathrm{m}}^{(2)} \mathrm{d} p-S_{\mathrm{m}}^{(2)} \mathrm{d} T \tag{7.5}
\end{equation*}
$$

that is

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{S_{\mathrm{m}}^{(2)}(p, T)-S_{\mathrm{m}}^{(1)}(p, T)}{V_{\mathrm{m}}^{(2)}(p, T)-V_{\mathrm{m}}^{(1)}(p, T)}=\frac{\Delta S}{\Delta V} \tag{7.6}
\end{equation*}
$$

where $\Delta$ denotes the change of either $V$ or $S$ between the final state $(2, p, T)$ and the initial state $(1, p, T)$. These two states have the same pressure and the same temperature but differ only in the states of aggregation. In the last member of Eq. (7.6), the index that refers to the molar quantities has been abandoned because both the volume and entropy are proportional to the number of moles.

This equation is well known with the name of Clapeyron's equation. It allows us to calculate the change in the equilibrium pressure due to a small change in temperature.

### 7.2 Latent Heat

Since the transition $(1, p, T) \rightarrow(2, p, T)$ connects two states having the same temperature, in Eq. (7.6) for the entropy change we may write

$$
\begin{equation*}
\Delta S=T Q_{1 \rightarrow 2} \tag{7.7}
\end{equation*}
$$

where $Q_{1 \rightarrow 2}$ is the amount of heat supplied to the overall system $(1+2)$ in the phase transition. Since the transformation occurs also at constant pressure we will have

$$
\begin{equation*}
Q_{1 \rightarrow 2}=\Delta H \tag{7.8}
\end{equation*}
$$

The quantity $\Delta H$ is called latent heat of the transformation. The latent heat is given by the enthalpy variation between the two states and represents the quantity of heat that have to be supplied to the overall system when a certain quantity of matter undergoes a phase transition remaining in phase equilibrium with the other. If the specific volumes of the two phases differ, some work must be done in the phase transition. Hence the latent heat differs from the energy difference $\Delta U$ by this amount.
Introducing the latent heats, the Clapeyron's equation can be written in the common form

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{\Delta H}{T \Delta V} \tag{7.9}
\end{equation*}
$$

### 7.2.1 Liquid-Vapor Equilibrium

In this case, we set phase 1 as the liquid phase and phase 2 as the vapor phase. For temperatures $T \lesssim 0.65 T_{\text {cr }}$ (see Sect. 8.3.2) the second molar virial coefficient of the vapor, as expressed by Eq. (6.2), is of the order of $10^{-3}-10^{-4}$ relative to ( $R T / p$ ) and then it is well described by the equation of state of an ideal gas. In addition, with good approximation, we can, neglect the volume of the liquid relative to that of the vapor:

$$
\begin{equation*}
V_{\mathrm{m}}^{\mathrm{vap}}-V_{\mathrm{m}}^{\mathrm{liq}} \simeq \frac{R T}{p} \tag{7.10}
\end{equation*}
$$

then the Clapeyron's equation becomes

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{\Delta H_{\mathrm{m}}}{R} \frac{p}{T^{2}} \tag{7.11}
\end{equation*}
$$

that is

$$
\begin{equation*}
\frac{\mathrm{d} \ln p}{\mathrm{~d}\left(\frac{1}{T}\right)}=-\frac{\Delta H_{\mathrm{m}}}{R} \tag{7.12}
\end{equation*}
$$

In a temperature range in which the latent heat of evaporation may be considered practically constant, Eq. (7.12) can be integrated and we obtain:

$$
\begin{align*}
& \ln \frac{p}{p^{\dagger}}=-\frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T}-\frac{1}{T^{\dagger}}\right)  \tag{7.13}\\
& p=p^{\dagger} \exp \left[-\frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T}-\frac{1}{T^{\dagger}}\right)\right] \tag{7.14}
\end{align*}
$$

where $p^{\dagger}$ is the saturated vapor pressure at a reference temperature $T^{\dagger}$. The relation given in Eq. (7.13) may be used to measure the molecular weight of a substance. We measure the saturated vapor pressure at different temperatures and we plot ( $\ln p$ ) versus $(1 / T)$. The angular coefficient of the straight line will be equal (in absolute value) to $\Delta H_{\mathrm{m}} / R$. Then, if we supply a quantity of heat equal to the latent heat thus obtained, the decrease in weight of the quantity of liquid expressed in grams will be equal to the molecular weight.

### 7.2.2 Equilibrium Between Condensed Phases: Solid-Liquid

In this case the Clapeyron's equation will be

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{\Delta H_{\mathrm{m}}}{T\left(V_{\mathrm{m}}^{\mathrm{liq}}-V_{\mathrm{m}}^{\text {sol }}\right)} \tag{7.15}
\end{equation*}
$$

With few exceptions, the molar volume of the liquid is larger than the molar volume of the solid in mutual equilibrium and the latent heat of fusion is always positive (indeed you have to provide heat to melt a solid). Then, in general, we have

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}>0 \tag{7.16}
\end{equation*}
$$

and this means that if you increase the pressure on a solid the melting point, i.e. the temperature at which the solid starts to melt, increases.

It is well known that water is an exceptional case. In fact, for water $V_{\mathrm{m}}^{\text {liq }}<V_{\mathrm{m}}^{\text {sol }}$ as evidenced by the fact that ice floats on water and therefore $(\mathrm{d} p / \mathrm{d} T)<0$. This means that if you increase the pressure on the ice the melting point decreases.

This accounts for the motion of glaciers: the bedrock which supports the masses of ice is very uneven and so locally, on very small areas, you can develop extremely high pressures; consequently the melting point can be considerably lower, the ice locally melts and then refreezes as soon as the irregularity is overcome and the pressure locally decreases.

Example 7.1 Remaining on the case of water, if we consider the solid-liquid transition at atmospheric pressure, the latent heat of fusion $\left(\right.$ at $\left.\theta=0^{\circ} \mathrm{C}\right)$ is $\lambda_{\text {fus }} \simeq 333.5 \mathrm{~J} / \mathrm{g}$ and hence $\Delta H_{\mathrm{m}} \simeq 6003 \mathrm{~J} / \mathrm{mole}$. Concerning the variation of molar volume we have $V_{\mathrm{m}}^{\text {sol }} \simeq 19.6 \mathrm{~cm}^{3} /$ mole and $V_{\mathrm{m}}^{\text {liq }} \simeq 18.0 \mathrm{~cm}^{3} /$ mole and then

$$
\begin{align*}
\frac{\mathrm{d} p}{\mathrm{~d} T} & =\frac{6003}{273.16 \times(18.0-19.6) \times 10^{-6}} \frac{\mathrm{~J}}{\mathrm{~m}^{3} \mathrm{~K}}= \\
& =-13.7 \times 10^{6} \frac{N}{\mathrm{~m}^{2} \mathrm{~K}} \simeq-136 \frac{\mathrm{~atm}}{\mathrm{~K}} \tag{7.17}
\end{align*}
$$

### 7.2.3 Solid-Vapor Equilibrium

The solid-vapor transition process is called sublimation and for many aspects can be treated similarly to the liquid-vapor transition. In particular, let us notice that in this case equilibrium occurs at lower temperatures with respect to liquid-vapor equilibrium but also the sublimation pressure is lower than the saturation pressure. The discussion in Sect. 7.3 shows that, in general, the temperature is lower by a factor of order 2 while the sublimation pressure is lower by a factor of order 100 with respect to the liquid-vapor case. This means that the molar volume of the vapor is much, much larger than that of the solid and that the approximations leading to Eq. (7.12) are better fulfilled.

As an example, let us calculate the sublimation pressure $p_{2}$ of water at $\theta \simeq$ $-60^{\circ} \mathrm{C}$. We know that at $\theta \simeq-36^{\circ} \mathrm{C}$ the sublimation pressure is $p_{1} \simeq 0.02 \mathrm{kPa}$ and the heat of sublimation is $\Delta H \simeq 2839.1 \mathrm{~kJ} \mathrm{Kg}^{-1}$. We see experimentally that the heat of sublimation is fairly constant in that temperature interval. First, we have to calculate the molar heat of sublimation. Get

$$
\begin{equation*}
\Delta H_{\mathrm{m}}=18 \times 10^{-3} \times \Delta H \simeq 51.1 \mathrm{~kJ} \tag{7.18}
\end{equation*}
$$

Then, with reference to Eq. (7.13), in our case we have

$$
\begin{equation*}
\ln \frac{p_{2}}{p_{1}}=-\frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)=-\frac{5.1 \times 10^{3}}{8.31} \times\left(\frac{1}{213.16}-\frac{1}{237.16}\right) \simeq-2.95 \tag{7.19}
\end{equation*}
$$

leading to

$$
\begin{equation*}
p_{2} \simeq 1.06 \times 10^{-3} \mathrm{kPa} \tag{7.20}
\end{equation*}
$$

### 7.3 Triple Point

Equation (7.1) defines a curve in the $(p, T)$ plane where two phases of a substance, labelled as 1 and 2 , are in mutual equilibrium. If the same substance may appear in another state of aggregation, say in the phase 3, the equation

$$
\begin{equation*}
\mu_{1}(p, T)=\mu_{3}(p, T) \tag{7.21}
\end{equation*}
$$

defines the curve in which phases 1 and 3 are in mutual equilibrium. If the curves defined by Eqs. (7.1) and (7.21) intersect, in the point of intersection the three phases are in mutual equilibrium.

Denoting by $\mu_{3}=\mu_{3}(p, T)$ the chemical potential of the substance in the phase 3 , the coordinates of the point of mutual equilibrium among the three phases are found by solving the system:

$$
\begin{equation*}
\mu_{1}(p, T)=\mu_{2}(p, T)=\mu_{3}(p, T) \tag{7.22}
\end{equation*}
$$

This is a system of two equations in the two unknowns $p$ and $T$ whose solution gives one value for each variable that we denote with $p_{\mathrm{tr}}$ and $T_{\mathrm{tr}}$. At this pressure and temperature, the three phases are in mutual equilibrium and this state is called triple point.

Three phases in mutual equilibrium constitute a system with zero degrees of freedom and this is the reason why, to fix the absolute scale, we choose the triple point of water instead of other possible alternatives such as, for instance, the melting point at a pressure of one atmosphere.

### 7.4 Phase Diagrams

Starting from the triple point (TP), we may integrate Eq. (7.6) for the solid-liquid, liquid-vapor, solid-vapor equilibrium. We obtain three curves as shown in Fig. 7.1a, b. As a result, the $(p, T)$ plane is divided into three main regions ${ }^{2}$ within which only one state of aggregation (phase) is present except for the points in the curves where the substance can coexist in two different states of aggregation in mutual equilibrium. These representations are known as phase diagrams. As anticipated in Sect.7.2.2, the difference between Fig. 7.1a, b concerns the slope of the solid-liquid equilibrium line as discussed in Sect.7.2.2. Most substances behave as showed in Fig.7.1a. Conversely, Fig. 7.1b refers to the case of water and few other substances, like antimony and bismuth, as far as the slope of the melting line is concerned.

Example 7.2 Dry ice. Let us consider, for example, the case of carbon dioxide. The triple point is at $p_{\text {tr }}=5.1 \mathrm{~atm}$ and $T_{\mathrm{tr}}=216.6 \mathrm{~K}$ and hence it is not possible to have liquid $\mathrm{CO}_{2}$ at atmospheric pressure where only the solid and gaseous phases are present. Following the sublimation line, we see that the solid-gas equilibrium at atmospheric pressure occurs at the temperature $T=194.7 \mathrm{~K}$. If we denote by $\theta_{\text {sub }}$ the sublimation temperature, in Celsius scale, at one atmosphere we see that $\theta_{\text {sub }} \simeq$

[^21]

Fig. 7.1 a Sketch of a typical phase diagram for a generic substance. TP and CP are the triple point and the critical point, respectively. The box around CP is replotted in Fig. 7.3 in terms of the ( $p, V$ ) variables. b Semi-qualitative phase diagram for water. At variance with most substances, water exhibits a solid-liquid equilibrium line with negative slope

Fig. 7.2 In this phase diagram two transformation at constant pressure are described: one is occurring between $p_{\text {tr }}$ and $p_{\text {cr }}$, an other below $p_{\text {tr }}$

$-78.5^{\circ} \mathrm{C}$ and then, at normal condition, solid $\mathrm{CO}_{2}$ sublimates quite abundantly. At atmospheric pressure solid $\mathrm{CO}_{2}$ is well known as "dry ice" because it cannot exist in the liquid phase.

Example 7.3 Isobaric transformation. It may be useful, for didactic reasons, to describe the various steps in a process in which a pure substance undergoes a wide temperature change at constant pressure and in which phase transitions are involved. With reference to Fig. 7.2, let us start from the initial state A whose pressure and temperature are denoted, respectively, by $p_{\mathrm{A}}$ and $T_{\mathrm{A}}$. Let us choose the pressure in the interval $p_{\text {tr }}<p_{\mathrm{A}}<p_{\text {cr }}, p_{\text {tr }}$ and $p_{\text {cr }}$ being respectively the triple point and the critical point pressures (see Sect. 8.3.2) and the temperature $T_{\mathrm{A}}$ low enough so that A is well inside the solid-state region.

1. We start from state A (low temperature) and supply heat at constant $p$ until we reach the solid-liquid equilibrium curve at state $B$, along the transformation $A B$. In this transformation, the amount of heat supplied is equal to the product of the heat capacity of the solid times the increase in temperature (if the heat capacity can be considered a constant, otherwise we have to integrate over temperature).
2. When we reach state $B$, phenomenologicallly we can see that, while we continue to supply heat to the system, the temperature remains at the constant value $T_{\mathrm{B}}$ of state B. The solid-liquid change is taking place and this transformation occurs at constant pressure and temperature. The supplied heat is equal to the latent heat of fusion.
3. When the phase transition at $B$ has been completed the point will be in the region named "liquid" and further heating will cause the temperature increase according to the heat capacity of the liquid, up to the temperature $T_{\mathrm{C}}$ at state C . Similarly to what occurred at state B, the temperature does not increase despite the heat being supplied to the system. A second phase transition from the liquid phase to the vapor phase is taking place. Also this phase transition occurs at a constant temperature and the amount of heat supplied is equal to the latent heat of evaporation.
4. Beyond the state C , the temperature increase under heating is regulated by the $C_{p}$ of the vapor.

Similarly, in Fig. 7.2, an isobaric transformation at a pressure lower than $p_{\text {tr }}$ is represented. If we start from state D in the solid phase region, we shall cross only one phase change in state E and the analysis of the transformations is analogous to the melting and the boiling cases just discussed.

### 7.4.1 ( $p, V)$ Diagrams

Together with the phase diagrams in the plane $(p, T)$ it is useful to consider similar diagrams on the plane ( $p, V$ ) where curves at constant temperature will be described. Let us first consider a small region in the $(p, V)$ plane, around the critical point, as marked in Fig. 7.1a by the box around CP. It is useful to consider a certain amount of substance confined in a cylinder with a movable piston and maintained at constant temperature during the transformations. The pressure is measured and the volume variable, in the $(p, V)$ diagram, is the volume of the cylinder. Inside the cylinder one or two phases in mutual equilibrium, will be present according to the value of pressure, temperature and volume as shown qualitatively in Fig. 7.4.

From Fig. 7.3, we see that, at relatively high temperatures, the shape of the curves is very similar to the equilateral hyperbolas which describe, as is well known, the ideal gas isotherms.

At decreasing temperatures, the "equilateral hyperbolas" deform showing an increasing deviation from the behavior expected for an "ideal" gas. If we further decrease the temperature we arrive at a well-determined temperature at which the isotherm shows the presence of a horizontal inflection point. This is called "critical

Fig. 7.3 Qualitative isotherms of a given substance close to the critical point


Fig. 7.4 Cylinders at different volume at constant $p, T$ for an expansion of the liquid in equilibrium with its vapor (or a compression of the vapor in equilibrium with the liquid) according to Fig. 7.3

constant $p_{\mathrm{s}}<p_{\mathrm{cr}}, \quad$ constant $T<T_{\mathrm{cr}}$
isotherm" the value of the temperature $T_{\text {cr }}$ is called the critical temperature and the corresponding value for pressure $p_{\text {cr }}$ is called the critical pressure.

For temperatures below the critical value in the cylinder, we may observe a phase separation. If we go along the isotherm starting from large volumes we see, inside the cylinder, only the vapor phase with the same properties of the gas observed at "high temperatures" (that is well above the critical temperature).

When the volume reaches the point B whose volume is denoted by $V_{\mathrm{B}}$, as shown in Fig. 7.3, a further decrease in the volume occurs at a constant pressure and we are observing the formation of liquid (see Fig. 7.4). The fraction of liquid increases and the portion of the gas phase decreases accordingly, until the isotherm reaches the point A whose volume is $V_{\mathrm{A}}$, in which there is only liquid inside the cylinder. From that point, a further decrease of volume requires a huge increase of pressure as is the case for all liquids, i.e., the coefficient of isothermal compressibility defined in Eq. (5.5) is very small, as it is the case of all liquids, and more generally of the condensed phases.

Then, we see that the formation of liquid takes place only at temperatures below the critical temperature. For this reason, the gaseous phase at these temperatures is called vapor. Differently from what happens at temperatures above the critical temperature, where the gaseous phase is called simply "gas", here the vapor is potentially on the way to become a liquid. The vapor at volume $V_{\mathrm{B}}$ is called "saturated vapor". This designation is to indicate that the state has all the properties of a gas (at fairly low temperatures, the equation of state is very close to the equation of state of ideal gases) but if inside the cylinder there was the formation of a small amount of liquid the two phases would be in mutual equilibrium. Symmetrically in the zone of the liquid, the liquid in the state indicated by the value $V_{\mathrm{A}}$ of the volume is in a state of equilibrium with its vapor that is, if it were in the presence of a small amount of steam the two phases would be in mutual equilibrium.

If the temperature further decreases the volume of the saturated vapor, that we generically indicated with the symbol $V_{\mathrm{B}}$ increases while the volume of the liquid in equilibrium with the vapor, $V_{\mathrm{A}}$ decreases.

The points in which there is only one phase but in equilibrium with the other, trace a curve which has the shape of an asymmetric bell called "Andrews bell".

It is necessary to note that the experimental isotherms below the critical temperature, both in the points of type A and in those of type B , are continuous but with discontinuous derivatives.

### 7.4.2 Molar Heat at Equilibrium

Consider two phases in mutual equilibrium in the conditions examined so far and let us vary, by an infinitesimal amount, the temperature of the two phases but operating so as to maintain the phase equilibrium. Let us ask the amount of heat to be supplied to each phase in this process. If we refer to one mole (or to a unit mass), we are led to define, for each phase, a new kind of molar (specific) heat.

This will be neither a transformation at constant volume nor at constant pressure but will need to change the external pressure by the right amount so as to preserve the phase equilibrium. From the Clapeyron's equation, we have immediately

$$
\begin{equation*}
\mathrm{d} p=\frac{\Delta S}{\Delta V} \mathrm{~d} T \tag{7.23}
\end{equation*}
$$

The amount of heat that must be supplied to one mole in one phase in order to increase its temperature by one degree keeping it in the phase equilibrium with the other one, is called molar heat at equilibrium. Obviously, the molar heat at equilibrium is a property not only of the phase we are considering but also depends on which is the other phase with which it is in phase equilibrium.

If we denote this molar heat, for each phase, with the symbol $C_{\text {eq }}^{(1,2)}$, we may write

$$
\begin{align*}
\hat{d} Q & =C_{\mathrm{eq}}^{(1,2)} \mathrm{d} T  \tag{7.24}\\
& =T \frac{\mathrm{~d} S_{\mathrm{m}}^{(1,2)}}{\mathrm{d} T} \mathrm{~d} T, \tag{7.25}
\end{align*}
$$

where the symbol of total derivative indicates the directional derivative along an infinitesimal transformation that preserves the phase equilibrium. Formally, we have

$$
\begin{align*}
C_{\mathrm{eq}}^{(1,2)} & =T\left[\left(\frac{\partial S_{\mathrm{m}}^{(1,2)}}{\partial T}\right)_{p}+\left(\frac{\partial S_{\mathrm{m}}^{(1,2)}}{\partial p}\right)_{T} \frac{\mathrm{~d} p}{\mathrm{~d} T}\right]=  \tag{7.26}\\
& =C_{p}^{(1,2)}-\alpha^{(1,2)} V_{\mathrm{m}}^{(1,2)} \frac{\Delta H_{\mathrm{m}}}{\Delta V} . \tag{7.27}
\end{align*}
$$

In going from Eq. (7.26) to Eq. (7.27), we must recall the general expression of the derivative of entropy with respect to pressure at constant temperature given in Eq. (5.15).

An interesting case concerns the liquid-vapor equilibrium. In this case the molar heats at equilibrium are called "molar heats of saturation" (both for the steam and the liquid). We have already seen that for sufficiently low temperatures ( $T \lesssim 0.65 T_{\text {cr }}$ ) the saturated vapor is well described by the equation of ideal gases and, also, that the molar volume of the steam is much greater than that of the liquid. In these conditions we can assume with good approximation, for the steam, $\alpha \simeq 1 / T$ and then, for the saturated steam we will have

$$
\begin{equation*}
C_{\mathrm{sat}}^{\mathrm{vap}} \simeq C_{p}^{\mathrm{vap}}-\frac{\Delta H_{\mathrm{m}}}{T} \tag{7.28}
\end{equation*}
$$

Example 7.4 In the case of water at one atmosphere, we know that the boiling point is $T=373 \mathrm{~K}$ and that the latent heat amounts to $\Delta H_{\mathrm{m}} \simeq 40896 \mathrm{~J} \mathrm{~mol}^{-1}$. If, for the molar heat at constant pressure, we take the experimental value $C_{p}^{\text {vap }} \simeq$ $34.9 \mathrm{~J} \mathrm{~mole}^{-1} \mathrm{~K}^{-1}$ (note that this value is very close to the expected value for an ideal gas with 6 degrees of freedom), we obtain

$$
\begin{equation*}
C_{\mathrm{sat}}^{\mathrm{vap}} \simeq 34.9-\frac{40896}{373}=34.9-109.6=-74.7 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \tag{7.29}
\end{equation*}
$$

The negative value indicates that to increase the temperature of saturated steam keeping it in saturation conditions, we need to remove heat. As regards the heat at equilibrium of the liquid phase Eq.(7.27) gives

$$
\begin{equation*}
C_{\mathrm{sat}}^{\mathrm{liq}} \simeq C_{p}^{\mathrm{liq}}-\alpha^{\mathrm{liq}} V_{\mathrm{m}}^{\mathrm{liq}} \frac{\Delta H_{\mathrm{m}}}{V_{\mathrm{m}}^{\mathrm{vap}}} . \tag{7.30}
\end{equation*}
$$

Since the coefficient of thermal expansion of the liquid is much lower than that of the steam and the molar volume of the liquid it is less than that of the steam by, at least, a factor of $10^{3}-10^{4}$ (while $C_{p}$ is of the same order of magnitude) it is correct to write

$$
\begin{equation*}
C_{\mathrm{sat}}^{\mathrm{liq}} \simeq C_{p}^{\mathrm{liq}} \tag{7.31}
\end{equation*}
$$

i.e., for the condensed phases is correct to speak of one single molar heat (the same also applies to the solid phase) if we can allow for a small error that we are able to estimate with some precision.

### 7.4.3 Temperature Dependence of the Latent Heats

In order to evaluate the temperature dependence of latent heats (they are frequently indicated with the Greek letter $\lambda$ ) let's recall that, by definition, they are given by $\lambda=\Delta H_{\mathrm{m}}$ and that, since the phase transition also occurs at a constant temperature, we have $\Delta H_{\mathrm{m}}=T \Delta S_{\mathrm{m}}$. Then we may write

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{~d} T}\left[\frac{\Delta H_{\mathrm{m}}}{T}\right]=\frac{\mathrm{d}}{\mathrm{~d} T}\left[S_{\mathrm{m}}^{(2)}(p, T)-S_{\mathrm{m}}^{(1)}(p, T)\right]=\frac{\mathrm{d} S_{\mathrm{m}}^{(2)}(p, T)}{\mathrm{d} T}-\frac{\mathrm{d} S_{\mathrm{m}}^{(1)}(p, T)}{\mathrm{d} T} \tag{7.32}
\end{equation*}
$$

where the total derivative notation is used, also in this case, because they have to calculated along the equilibrium curves between the two phases. With this condition, we have

$$
\begin{equation*}
C_{\mathrm{eq}}=T \frac{\mathrm{~d} S_{\mathrm{m}}}{\mathrm{~d} T} \tag{7.33}
\end{equation*}
$$

and then

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{~d} T}\left(\frac{\Delta H_{\mathrm{m}}}{T}\right)=\frac{C_{\mathrm{eq}}^{(2)}-C_{\mathrm{eq}}^{(1)}}{T} \tag{7.34}
\end{equation*}
$$

from which we obtain

$$
\begin{equation*}
\frac{\mathrm{d} \Delta H_{\mathrm{m}}}{\mathrm{~d} T}=C_{\mathrm{eq}}^{(2)}-C_{\mathrm{eq}}^{(1)}+\frac{\Delta H_{\mathrm{m}}}{T} \tag{7.35}
\end{equation*}
$$

In the case of the liquid-vapor equilibrium, if we remember Eqs.(7.28) and (7.31) we have

$$
\begin{equation*}
\frac{\mathrm{d} \Delta H_{\mathrm{m}}^{\text {evap }}}{\mathrm{d} T}=C_{p}^{\mathrm{vap}}-C_{p}^{\mathrm{liq}} \tag{7.36}
\end{equation*}
$$

and this allows us to estimate the error committed when we use the integrated Eq. (7.13) for describing the temperature dependence of the saturated steam.

### 7.5 Continuity of States

We come back to Fig. 7.1 and we notice that the condensation line is the only line in the phase diagram ending on a specific state, that we are able to measure, at least in principle. In fact, while the condensation line"ends" on the critical point, the melting line is not limited unless we consider practical constraints concerning the effective possibility of realizing states at high pressure. Conversely, when moving along the sublimation line, the third principle of thermodynamics (see Chap. 13) prevents to reach states at $T=0 \mathrm{~K}$, no matter how low $T$ may be pushed. Therefore, we may wonder whether would happen within a transformation turning around the critical point. In fact, accordingly to Fig. 7.1 the system is expected to pass from the vapor (liquid) phase to the liquid (vapor) phase without crossing a phase equilibrium line, as the ones described by the Clapeyron's equation Eq.(7.6).

In practice, with reference to the isotherms of Fig. 7.3, this transformation can be practically realized by taking the vapor phase in a given initial state and raising the temperature of the vapor phase above the critical temperature, by keeping the volume always greater than the critical volume. Then, the vapor can be compressed up to the liquid state below the critical volume, by keeping the temperature above the critical temperature, and finally cool the liquid to its original temperature, in a final state keeping the volume sufficiently below the critical volume. At the end of this transformation we brought the substance from the gaseous phase to the liquid phase having the same temperature of the gas, by a continuous change throughout which there is never more than one phase present. This apparently contrasts to what described by the Clapeyron's equation. We will address this point in the following Sect.7.6. The possibility to pass from vapor to liquid state (and vice versa) without observing coexistence of two states of aggregation (phases) has been first realized by Thomson in 1871 and later discussed by van der Waals in 1873 within his Ph.D. titled "On the Continuity of the Gaseous and Liquid States".

### 7.6 Continuous-Phase Transitions

The Clapeyron's equation provided by Eq.(7.9) transforms the equilibrium condition of Eq.(7.1) between chemical potentials into a relation between pressure and temperature for two or more phases in equilibrium.

This relation can be visualized by equilibrium lines in ( $p, T$ ) phase diagrams, as showed in Fig. 7.1. Every time that we cross the equilibrium curves a system passes from one phase to an other by experiencing jumps in the molar volume and molar entropy as given by Eqs. (7.3) and (7.4). However, it results that the condensation line ends with the critical point, so that, for a given substance, the passage of vapor (or liquid) to the supercritical state can no longer be described by using Eqs. (7.3) and (7.4). This situation can be also understood in terms of the isotherms: indeed, the jump of Eq. (7.3) for the molar volume, represented in the ( $p, V$ ) plane by couples
of states at the same temperature and same pressure on the coexisting bell around the critical point, vanishes as the temperature of the vapor (or liquid) phase is raised to or above the critical temperature. In parallel, the same applies to the jumps of molar entropy, causing the vanishing of the latent heat in the passage to the supercritical state.

As a consequence, around the critical point the Clapeyron's equation does not provide any information on pressure and temperature at the equilibrium between two phases, since $\mathrm{d} p / \mathrm{d} T$ is reduced to an indeterminacy of the form $0 / 0$. To address a description of these phase changes, let us call $\Delta \mu$ the jump of the chemical potential when one mole of a substance is passing from the phase 1 to the phase 2 at given pressure and temperature:

$$
\begin{equation*}
\Delta \mu(T, p)=\mu_{2}(T, p)-\mu_{1}(T, p) \tag{7.37}
\end{equation*}
$$

Similarly to what we performed in Sect. 7.1, let us denote with $\mathrm{d}(\Delta \mu)$ the differential of the chemical potential difference in Eq. (7.37)

$$
\begin{equation*}
\mathrm{d}(\Delta \mu)=\mathrm{d}\left(\mu_{2}-\mu_{1}\right) \tag{7.38}
\end{equation*}
$$

Then, we expand Eq. (7.38) accurate in $\mathrm{d} P$ and $\mathrm{d} T$ to the second-order terms:

$$
\begin{align*}
& \mathrm{d}(\Delta \mu)=\Delta\left(\frac{\partial \mu}{\partial p}\right)_{T} \mathrm{~d} p+\Delta\left(\frac{\partial \mu}{\partial T}\right)_{p} \mathrm{~d} T+\frac{1}{2} \Delta\left(\frac{\partial^{2} \mu}{\partial p^{2}}\right)_{T}(\mathrm{~d} p)^{2}+ \\
& +\Delta\left(\frac{\partial^{2} \mu}{\partial p \partial T}\right) \mathrm{d} p \mathrm{~d} T+\frac{1}{2} \Delta\left(\frac{\partial^{2} \mu}{\partial T^{2}}\right)_{p}(\mathrm{~d} T)^{2} \tag{7.39}
\end{align*}
$$

Accordingly to Eqs. (7.3) and (7.4), the expression Eq. (7.39) becomes

$$
\begin{align*}
& \mathrm{d}(\Delta \mu)=\Delta V_{\mathrm{m}} \mathrm{~d} p+\Delta S_{\mathrm{m}} \mathrm{~d} T+\frac{1}{2} \Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_{T}(\mathrm{~d} p)^{2}+ \\
& +\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_{p} \mathrm{~d} p \mathrm{~d} T-\frac{1}{2} \frac{\Delta C_{p}}{T}(\mathrm{~d} T)^{2} \tag{7.40}
\end{align*}
$$

$\Delta C_{p}=C_{p}^{(2)}-C_{p}^{(1)}$ being the (finite) difference of the heat capacities, at constant pressure, between phases 1 and 2 .

In the continuous phase transitions the first two terms of the expansion Eq. (7.40) are clearly null, since $V_{\mathrm{m}}^{(1)}=V_{\mathrm{m}}^{(2)}$ and $S_{\mathrm{m}}^{(1)}=S_{\mathrm{m}}^{(2)}$. Therefore

$$
\begin{equation*}
\mathrm{d}(\Delta \mu)=\frac{1}{2} \Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_{T}(\mathrm{~d} p)^{2}+\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_{p} \mathrm{~d} p \mathrm{~d} T-\frac{1}{2} \frac{\Delta C_{p}}{T}(\mathrm{~d} T)^{2} \tag{7.41}
\end{equation*}
$$

Along the phase equilibrium line $\Delta \mu$ is identically null, so that Eq. (7.41) becomes

$$
\begin{equation*}
\frac{1}{2} \Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_{T}(\mathrm{~d} p)^{2}+\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_{p} \mathrm{~d} p \mathrm{~d} T-\frac{1}{2} \frac{\Delta C_{p}}{T}(\mathrm{~d} T)^{2}=0 \tag{7.42}
\end{equation*}
$$

Dividing both the members of Eq. (7.42) by $(\mathrm{d} T)^{2}$ we get

$$
\begin{equation*}
\frac{1}{2} \Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_{T}\left(\frac{\mathrm{~d} p}{\mathrm{~d} T}\right)^{2}+\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_{p}\left(\frac{\mathrm{~d} p}{\mathrm{~d} T}\right)-\frac{1}{2} \frac{\Delta C_{p}}{T}=0 \tag{7.43}
\end{equation*}
$$

The relation given by Eq. (7.43) provides the differential equation for the equilibrium curve. By regarding Eq. (7.43) as a quadratic equation, for the value $\mathrm{d} p / \mathrm{d} T$ to be unique, the discriminant in Eq. (7.43) must be equal to zero:

$$
\begin{equation*}
\Delta C_{p}\left\{\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_{T}\right\}+T\left\{\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_{p}\right\}^{2}=0 \tag{7.44}
\end{equation*}
$$

The condition set by Eq. (7.44) can be used to provide two equivalent expressions for the derivative $\mathrm{d} p / \mathrm{d} T$ along the phase equilibrium curve. The solution of the second degree Eq. (7.43) leads to

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=-\frac{\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_{p}}{\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_{T}} \tag{7.45}
\end{equation*}
$$

By using the Eq.(7.44) the solution in Eq.(7.45) can be written in the equivalent form:

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{\Delta C_{p}}{\Delta\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_{p}} \tag{7.46}
\end{equation*}
$$

The set of Eqs. (7.45) and (7.46) is referred to as Ehrenfest's equations, generalizing the Clapeyron's equation provided by Eqs. (7.3) and (7.4) to the case of continuous phase transitions.

In general, it possible to describe continuous phase transitions in terms of a discontinuity in the heat capacity $C$, with continuity of $H, S, G$, at a certain temperature, with neither latent heats nor a discontinuity in volume. The temperature at which these transitions take place are usually known as lambda point $T_{\lambda}$ or critical point, and this generalizes the concept of critical point introduced in Sect. 7.4.2 for the gas-liquid transition. Strictly speaking, the expression "lambda point" has been first applied to the transition normal fluid-superfluid occurring in liquid ${ }^{4} \mathrm{He}$ for the lambda shape assumed by $C$ in this transition. Conversely, a critical point $T_{\mathrm{c}}$ is used not only for gases but also for normal conductor-superconductor transition. In general, the discontinuity in $C$ may have finite or non finite jumps depending on the specific lambda point. The first lambda point was discovered by Curie and therefore
it is called the Curie point, below which a ferromagnetic material (as e.g., iron) has permanent magnetization and above which it has not, and behave as a paramagnetic substance.

Many other lambda points are known to occur in crystals and are usually associated with a sudden change in the extent to which the molecules in the crystal can rotate freely.

Phase transitions described by Eqs. (7.45), (7.46) are also known as transition of the second order. The reason for this denominations can be easily understood in the classification provided by Ehrenfest. In detail, for an ordinary phase change, which we may call a transition of the first order, we have

$$
\left.\begin{array}{l}
G  \tag{7.47}\\
S=-\frac{\partial G}{\partial T}
\end{array} \begin{array}{l}
\text { continuous } \\
\text { discontinuous }
\end{array}\right\} \text { first-order phase transitions. }
$$

In the transitions of the second order, which we have been discussing, we have

$$
\left.\begin{array}{ll}
G, \frac{\partial G}{\partial T} & \text { continuous }  \tag{7.48}\\
C=-\frac{T \partial^{2} G}{\partial T^{2}} & \text { discontinuous }
\end{array}\right\} \text { second-order phase transitions. }
$$

We point out that the expression phase change (or phase transition) of the second order has been the subject of a large debate and criticism in the past and led to a considerable confusion. For this reason, it would be better to avoid this nomenclature.

To conclude, we just notice that it is possible to iterate the procedure outlined above and introduce a transition of the higher order by

$$
\left.\begin{array}{ll}
G, \frac{\partial G}{\partial T}, \frac{\partial^{2} G}{\partial T^{2}} & \text { continuous }  \tag{7.49}\\
\frac{\partial^{3} G}{\partial T^{3}} & \\
\text { discontinuous }
\end{array}\right\} \text { third-order phase transitions, }
$$

and so on.

### 7.6.1 Differences Between Continuous- and Discontinuous-Phase Transitions

We would now focus on the deep difference between continuous (or second-order) and discontinuous (or first-order) phase transitions.

Within the latter case, each phase is stable by itself on both sides of the transition point. This follows from the fact that the chemical potential of a "phase 1 " $\mu_{1}(p, T)$ and the chemical potential of a "phase 2 " $\mu_{2}(p, T)$ are determined on both sides of the phase-transition point, either a pressure or a temperature, where they mutually
intersect. However, while one of them corresponds to the absolute minimum (i.e., to the absolutely equilibrium state), the curve with the larger value of $\mu$ corresponds to the metastable state of a substance. Accordingly, during discontinuous phase transitions superheating and supercooling phenomena are possible. Conversely, metastable states (like superheating and supercooling) are impossible within continuous phase transitions.

This aspect can also be understood on a different way: within a given phase we should consider the possibility of the appearance of a rather small quantity of a new phase whose properties differ strongly from the properties of the old phase, or of the appearance of a new phase in the entire volume of the substance, but with properties differing but little from the properties of the old phase. The first case takes place during discontinuous phase transitions, when the new phase originates in small nuclei and has molar volume and molar entropy differing from the corresponding quantities of the old phase. As it is shown in Sect. 9.6, the phase transition may be delayed due to the existence of surface energy, and metastable states appear. The second case takes place during continuous phase transitions, when a new phase, the phase with symmetry differing from that of the initial phase, appears at once in the entire volume and not in small nuclei. Therefore, no phase interface appears between the phases and delay of phase transition is impossible. With continuous phase transition the dependence of the chemical potential on temperature and pressure is represented by a single smooth curve, and not by the intersection of two curves, as is the case with first-order phase transitions. It is clear, however, that some thermodynamic functions exhibit a sort of singularity on the phase transition line, because the second derivatives of the chemical potential undergo a discontinuity jump on that line. This is the case, for example, of the specific heats.

### 7.7 Exercises

7.1 Treating the saturated as an ideal gas, prove Eq. (7.28)
7.2 For Ammonia $\left(\mathrm{NH}_{3}\right)$, experiments report the following expressions for the saturated vapor:

$$
\begin{aligned}
& \ln p_{\mathrm{s}}=23.03-\frac{3754}{T} \text { at solid-vapor equilibrium } \\
& \ln p_{\mathrm{s}}=19.49-\frac{3063}{T} \text { at liquid-vapor equilibrium }
\end{aligned}
$$

where the saturation pressure $p_{\mathrm{s}}$ is expressed in torr.

1. Determine the temperature of the triple point.
2. Determine the latent heats of vaporization and sublimation near the triple point.
3. Determine the latent heat of fusion near the triple point.
7.3 From the steam tables (see [4]) we see that the saturation pressures at $\theta_{1}=$ $100^{\circ} \mathrm{C}, \theta_{2}=90^{\circ} \mathrm{C}$ and $\theta_{3}=80^{\circ} \mathrm{C}$ are, respectively, $p_{1}=1.01 \times 10^{5} \mathrm{~Pa}, p_{2}=$ $0.701 \times 10^{5} \mathrm{~Pa}$ and $p_{3}=0.474 \times 10^{5} \mathrm{~Pa}$. Determine the latent heat of vaporization Din the temperature intervals $\left(\theta_{1}, \theta_{2}\right),\left(\theta_{2}, \theta_{3}\right)$ and $\left(\theta_{1}, \vartheta_{3}\right)$.

## Chapter 8 <br> van der Waals Equation


#### Abstract

The van der Waals equation of state is obtained as the first- order correction to the ideal gas equation and some observational consequences are discussed: the correlation of the critical parameters, the Joule-Thomson coefficient, the inversion curve, and the determination of the vapor pressure. The Law of Corresponding States is formulated and discussed in several aspects. The notion of generalized charts is introduced with particular reference to the compressibility chart. The behavior in the proximity of the critical point is briefly examined.


Keywords van der Waals equation of state • Critical point • Boyle temperature • Thermal expansion • Molar heats • Inversion curve • Vapor pressure • Corresponding states $\cdot$ Compressibility factor $\cdot$ Compressibility charts $\cdot$ Triple point

### 8.1 Introduction

Johannes Diderik van der Waals was born in Leiden on November 23, 1837 and died in Amsterdam on March 8, 1923. He was awarded the Nobel Prize in 1910 "for his work on the equation of state of gases and liquids". Despite being a "dated" equation of state, it is still very widely referred to both in research articles and in Physics textbooks. In the face of an extreme simplicity, it provides a large amount of results, some accurate enough others less accurate but, in all cases, the qualitative course of experimental observations is well foreseen. Evidently, a state equation that depends on only two parameters is already sufficient to highlight the essential features of the behavior of gases including the phase transitions and the inversion curve.

### 8.2 A Simple Modification to the Equation of State for Ideal Gases

For each temperature, at very low pressure, the equation of state Eq. (6.43), for one mole, tends to form

$$
\begin{equation*}
p V_{\mathrm{m}}=R T \tag{8.1}
\end{equation*}
$$

which is well known as the "ideal gas" equation of state. A simple exercise in classical kinetic theory shows that this equation of state can be obtained by a model in which we take:

1. The molecules have zero size (point-like molecules);
2. The molecules do not interact with each other;
3. The collisions of the molecules with the walls are perfectly elastic.

It is clear that such a model is inherently contradictory because if the molecules do not interact with each other when they are relatively far and if they do not collide at small distances (such as a gas of hard spheres of non zero dimension), they cannot exchange energy among themselves. Moreover, if they cannot exchange energy, in some way, with the walls (that is they cannot become "thermalized" by the walls as it happens, for instance, with the radiation field), they can never reach a thermodynamic equilibrium distribution: each molecule will retain its energy at a constant value.

The first step toward the construction of a real gas model, can be done by abandoning or modifying, some of the three assumptions that underlie the "ideal gas model". van der Waals has maintained the hypothesis on elastic collisions with the walls (otherwise, the gas properties would be dependent on the properties of the walls) and amended the first two.

Regarding the first assumption (in item 1), van der Waals envisages that the molecules are comparable to rigid spheres, impenetrable and with constant volume. The justification for this hypothesis is based on the consideration that the strong electrostatic repulsive interaction on the part of the nuclei is completely shielded by the electronic clouds at medium distances. It will suddenly become effective when the nuclei are at a relatively short distance, i.e., below the size of the electronic clouds.

As regards to the second hypothesis (in item 2), he assumes that at large distances, the molecules are subject (on average) to an attractive force as suggested by classical electrodynamics. If we refer to the form of the interaction potential ${ }^{1}$ between two molecules, these two assumptions are two constraints on the form of this potential that can be displayed, qualitatively, in Fig. 8.1. The behavior at small and at large distances is underlined. In the former case, the derivative of the potential with respect to the mutual distance is negative, being the absolute value extraordinarily large. This is typical of strong repulsive forces. At large distance, the derivative of the potential is positive and decreases with increasing distance. This indicates attractive forces with rapidly decreasing intensity, as it is the case of dipole-dipole interactions [9].

At a very simple level of approximation, it is not necessary to specify the shape of this force, but we can limit ourselves to take into account average effects as we shall see.

If we denote with $b$ the total "proper" volume of the molecules (i.e., of the rigid spheres) then the volume available for each molecule will be $V_{\mathrm{m}}^{\prime}=V_{\mathrm{m}}-b$ then the

[^22]

Fig. 8.1 Qualitative description of the interaction potential $\mathcal{U}$ between pairs of molecules $i, j$ as a function of the mutual distance $r=r_{i j}=\left|\mathbf{r}_{i}-\mathbf{r}_{j}\right|$. Only the short-range interactions (nuclear, short distance, electrostatic repulsion) and long-range interactions (attractive, dipole-dipole, van der Waals interactions, proportional to $r^{-6}$ ) are shown
kinetic model will lead to the equation of state.

$$
\begin{equation*}
p_{\mathrm{id}}\left(V_{\mathrm{m}}-b\right)=R T . \tag{8.2}
\end{equation*}
$$

Here, the term marked with the symbol $p_{\text {id }}$ is the pressure calculated from the "ideal gas" kinetic model in which no interaction has been introduced between molecules at large distances. Concerning the latter part of the interaction, we will not go into discussions on detailed models but certain general features can be introduced with simple arguments. The interaction, whatever the particular form is, will be rapidly decreasing with the relative distance between the molecules: in the case of electric dipole forces, the intensity decreases with the sixth power of the distance, then we can characterize its effect by means of a parameter, called "radius of action" $r_{0}$, which defines the distance beyond which the mutual interaction can safely be neglected.

If a molecule is located in an "internal" part of the gas, that is, at a point which is distant from the walls for more than $r_{0}$, this molecule will be surrounded symmetrically (on average) by the other molecules and the average force that will act on it will be null.

If the molecule is located "near the wall" that is, at a distance less than the radius of action, it will experience, on average, an attractive force toward the internal part of the gas by the surrounding molecules. The effect of this force, whose average intensity will increase as the molecule is approaching the boundary, will produce a reduction of the momentum of the molecule which is about of being reflected by the wall. This Bremsstrahlung effect will reduce the momentum transferred by the molecule to the wall. Since the pressure measures the momentum transferred to the wall per unit area and per unit time, we expect that the recorded pressure will be less than the one calculated in the "ideal gas" model. It is reasonable to assume that the average Bremsstrahlung effect on the single molecule will be proportional to the molecular number density. Also, the number of impacts with the walls, per
second and per unit area is proportional to the molecular number density, then it is reasonable to assume the deficit of pressure will be proportional to the molecular number density squared.

The above argument can be put a little more clearly. Referring to the mechanical interpretation of pressure, as developed in Appendix B.1, the value of the measured pressure is given by the total momentum exchanged by the gas molecules normal to the wall, per unit area, and per unit time. If we consider one single molecule, its contribution to the measured pressure is given by $2 P_{z}$ where $P_{z}$ is the component of its momentum perpendicular to the wall in the instant of the collision. After integrating over all the directions of motions and over the velocity distribution of the impinging molecules, let us define the average value of $P_{z}$ and denote it with the symbol $\left\langle P_{z}\right\rangle$. For a given velocity distribution, the rate of collisions per unit area will be proportional to the molecular number density and then, for the measured pressure $p$ we may safely affirm that

$$
\begin{equation*}
p \propto \frac{1}{V_{\mathrm{m}}}\left\langle P_{z}\right\rangle, \tag{8.3}
\end{equation*}
$$

where we made use of the fact that the molecular number density is proportional to the inverse of the molar volume of the gas $V_{\mathrm{m}}$.

If we neglect molecular interactions, the value of $\left\langle P_{z}\right\rangle$ will be denoted with $\left\langle P_{z}\right\rangle_{0}$ and will lead us to the ideal gas pressure according to the calculations performed in Appendix B.1.

If we allow for an attractive interaction between molecules, the value of $\left\langle P_{z}\right\rangle$ for each molecule impinging the wall, will be lower (Bremsstrahlung effect) then the ideal gas case. Let us write the relation

$$
\begin{equation*}
\left\langle P_{z}\right\rangle=\left\langle P_{z}\right\rangle_{0}-\left\langle\Delta P_{z}\right\rangle \tag{8.4}
\end{equation*}
$$

where $\left\langle\Delta P_{z}\right\rangle$ denotes the average value of the decrease of $P_{z}$ due to the Bremsstrahlung effect exerted on the impinging molecule by the internal ones.

The Bremsstrahlung effect, on the single molecule, can be safely assumed to be, in its turn, proportional to the molecular number density, i.e., we may write

$$
\begin{equation*}
\left\langle\Delta P_{z}\right\rangle \propto \frac{1}{V_{\mathrm{m}}} \tag{8.5}
\end{equation*}
$$

then, putting together Eqs. (8.3)-(8.5) we have

$$
\begin{equation*}
p \propto \frac{1}{V_{\mathrm{m}}}\left\langle P_{z}\right\rangle \propto \frac{1}{V_{\mathrm{m}}}\left[\left\langle P_{z}\right\rangle_{0}-\left\langle\Delta P_{z}\right\rangle\right] \tag{8.6}
\end{equation*}
$$

From Eq. (8.6), we see that the Bremsstrahlung effect on the measured pressure is well described by one term proportional to

$$
\begin{equation*}
\propto \frac{1}{V_{\mathrm{m}}}\left\langle\Delta P_{z}\right\rangle \propto \frac{1}{V_{\mathrm{m}}^{2}}, \tag{8.7}
\end{equation*}
$$

which is proportional to the molecular number density squared regardless the details of the attractive interactions between pairs of molecules. This explains, in part, the success and the utility of the van der Waals equation in spite of the simplicity of the arguments on which it is based.

In conclusion, the pressure $p$ recorded on the wall will be linked to the pressure provided by the kinetic model of the ideal gas (that we have denoted by $p_{\text {id }}$ ) by a relation of the type

$$
\begin{equation*}
p=p_{\mathrm{id}}-\frac{a}{V_{\mathrm{m}}^{2}}, \tag{8.8}
\end{equation*}
$$

where $a$ is a positive constant that summarizes, in the first approximation, the average effect of Bremsstrahlung due to the attractive part of the intermolecular forces.

After these simple arguments, the equation of state of "the ideal gas", that comes from a classical kinetic model ("absurd" according to our discussion in Sect. 8.2 but functional) will be changed, into a certainly more realistic one, becoming

$$
\begin{equation*}
\left(p+\frac{a}{V_{\mathrm{m}}^{2}}\right)\left(V_{\mathrm{m}}-b\right)=R T . \tag{8.9}
\end{equation*}
$$

The parameter $b$ accounts for the "non-zero size of the molecules" in the most crude way. It is the way to enter in the model the existence, as a first approximation, of a very strong repulsive force between molecules at small distances.

The $a$ parameter expresses, in the first approximation, the effect (on pressure) of the attractive forces between molecules, at large distances.

In the case of $n$ moles, it is straightforward to write $V_{\mathrm{m}}=(V / n)$ and, after replacing in Eq. (8.9), we obtain

$$
\begin{equation*}
\left(p+\frac{a n^{2}}{V^{2}}\right)(V-n b)=n R T . \tag{8.10}
\end{equation*}
$$

For different values of the temperature, the equation of van der Waals provides a family of isotherms whose shape is shown in Fig. 8.2.

## Mean Field Approximation

We conclude this section with an important comment: at low density, the molecular interactions can be well described by pair interactions and then only the two extreme parts of the interaction potential, described in Fig. 8.1 are relevant. At higher densities, this approximation may be improved by introducing the so-called mean field approximation. Briefly, each molecule is treated individually, subjected to an "effective force" which takes into account the average effect of the interactions with all the other molecules. Within this approximation, each molecule can be regarded as a probe of the overall field generated by all the others. Therefore, we can write the total potential energy of the system as

Fig. 8.2 Isotherms for a van der Waals gas in terms of reduced pressure and volume, $\tilde{p}=p / p_{\text {cr }}$ and $\tilde{v}=V / V_{\text {cr }}$, around the critical isotherm. From bottom to top, isotherms correspond to $\tilde{t}=T / T_{\text {cr }}$ $=0.85,0.90,1.00,1.05$, 1.10 , respectively


$$
\begin{equation*}
U_{\mathrm{pot}}=\frac{1}{2} \sum_{i=1}^{N} \mathcal{U}_{\mathrm{eff}}\left(\mathbf{r}_{i}\right) \tag{8.11}
\end{equation*}
$$

being $\mathbf{r}_{i}$ the position of each "probe particle" and the factor $1 / 2$ is used to avoid double counting the number of interaction when using pair potentials. Also in a mean-field perspective, density fluctuations of the gas are neglected when we take the average density in place of the local density. However, it is well known that the presence of attractive forces enhances the amplitude of the density fluctuations and the mean-field approximation becomes a useful tool for dealing with the issue. Any equation of state is conceived for describing states of equilibrium. As we will see in Sect. 15.3.1 macroscopic states must be thought as average states if we take into account the existence of fluctuations and the quantitative treatment of the phenomenon in isolated systems, is limited to linear deviations (small fluctuations). However, this approximation is expected to fail in the attempts to describe the phenomenology associated with the approach of the critical point, where fluctuations are definitely not negligible.

### 8.3 Successes and Failures of the van der Waals Equation

The shape of the isotherms, which can be seen in Fig. 8.2, shows the following relevant behaviors:

1. For high values of the temperature, the isotherm has a hyperbola-like shape and this shows that the gas behavior is very close to that of the ideal gas. This agrees with what is observed experimentally;
2. As temperature falls, the isotherms show a deformation, compared to the form of "equilateral hyperbolas", in the area of relatively high pressures;
3. At a temperature, whose value depends on the $a$ and $b$ constants that characterize the particular gas, the isotherms show a horizontal inflection. The temperature at which this occurs is called the "critical temperature" and is indicated by $T_{\text {cr }}$;

For temperatures below $T_{\mathrm{cr}}$, the behavior of the isotherm changes markedly:

1. For large volumes, i.e., for low values of the pressure, the isotherms maintain the form of equilateral hyperbolas, in the $(p, V)$ plane, clearly showing the shape that is expected for ideal gases;
2. For small values of the volume, and therefore relatively high pressure, the van der Waals's isotherms deviate significantly from the hyperbola taking a much steeper slope. The derivative $(\partial p / \partial V)_{T}$ assumes very large absolute values and this shows that in that area the equation describes a fluid with a very small coefficient of isothermal compressibility. This property is characteristic of liquids;
3. In the intermediate zone that is the one between the large volumes (hyperbola) and small volumes (liquid), the behavior shows a region in which $(\partial p / \partial V)_{T}>0$. If we refer to Eq. (4.116), this part of the isotherm is formed by unstable states of equilibrium and cannot be considered as observable states. However, that part of the isotherm will be used in Sect.8.3.7 in order to determine the vapor pressure, at that temperature, as provided by the van der Waals equation of state.

### 8.3.1 van der Waals Equation and the Boyle Temperature

The Boyle temperature of a gas, was defined in Sect. 6.7 as the temperature at which the second virial coefficient $B(T)$ vanishes. If we recall the van der Waals equation for one mole, we may write as Eq. (8.9) retaining only linear terms in the two small constants $a$ and $b$ and obtain the:

$$
\begin{equation*}
V_{\mathrm{m}}=\frac{R T}{\left(p+\frac{a}{V_{\mathrm{m}}^{2}}\right)}+b \simeq \frac{R T}{p}\left(1-\frac{a}{p V_{\mathrm{m}}^{2}}\right)+b \tag{8.12}
\end{equation*}
$$

where me made use of the fact that $a / p V_{\mathrm{m}}^{2} \ll 1$. Hence,

$$
\begin{equation*}
V_{\mathrm{m}} \simeq \frac{R T}{p}+b-\frac{a}{R T} \tag{8.13}
\end{equation*}
$$

where we used the approximation:

$$
R T \frac{a}{p^{2} V_{\mathrm{m}}^{2}} \simeq \frac{a}{R T} .
$$

If we remember the definition of the second virial coefficient given by Eq. (6.2), we recover Eq. (6.44), in which the second virial coefficient was introduced on empirical basis, while Eq. (8.13) is derived from an equation of state.

### 8.3.2 The Critical Point

Empirical observations show that when we compress a gas at constant temperature, we see that at relatively high temperatures, the fluid maintains the properties of a gas at any pressure, while at relatively low temperatures the compression process leads to the formation of the liquid phase.

The temperature below which compression leads to the formation of the liquid phase and above which the fluid remains in the gaseous state is called critical temperature and is denoted with the symbol $T_{\mathrm{cr}}$.

In Sect. 8.3, where we briefly discussed the behavior of the isotherms of van der Waals in the $(p, V)$ plane, we had already introduced the concept of critical temperature as the temperature at which the function $p=p(V)$ exhibits a horizontal inflection. Now, we have one opportunity of using the experimental measurements of the critical parameters to determine the constants $a$ and $b$ which characterize the specific gas. The inflection point identifies a specific value of the volume and of the pressure that will be called critical volume $V_{\mathrm{cr}}$, and critical pressure $p_{\mathrm{cr}}$. A horizontal inflection point satisfies the following two conditions:

$$
\begin{align*}
& \left(\frac{\partial p}{\partial V}\right)_{T}=0  \tag{8.14}\\
& \left(\frac{\partial^{2} p}{\partial V^{2}}\right)_{T}=0 \tag{8.15}
\end{align*}
$$

Let us write the equation of state in the form

$$
\begin{equation*}
p=\frac{R T}{V_{\mathrm{m}}-b}-\frac{a}{V_{\mathrm{m}}^{2}}, \tag{8.16}
\end{equation*}
$$

and after some simple calculations we obtain

$$
\begin{align*}
& V_{\text {cr }}=3 b  \tag{8.17}\\
& p_{\text {cr }}=\frac{1}{27} \frac{a}{b^{2}}  \tag{8.18}\\
& R T_{\text {cr }}=\frac{8}{27} \frac{a}{b} \tag{8.19}
\end{align*}
$$

It seems that if we measure accurately the critical parameters, we may obtain the values of the two parameters $a$ and $b$ which define the van der Waals equation of state of that particular gas.

Here a problem arises. We measure three numbers, namely volume, pressure, and temperature at the critical point and determine two parameters $a$ and $b$. This case of overdetermination can be resolved only if the three parameters that define the critical point are not mutually independent.

If we make use of the van der Waals equation, we find that between the volume, pressure and temperature at the critical point the following relation applies:

Table 8.1 Observed values of the adimensional ratio defined in Eq. (8.21) for some gases. Measured values show that the Law of Corresponding States (see Sect. 8.4) is rather well observed

| Gas | $\left(p_{\text {cr }} V_{\text {cr }} / R T_{\text {cr }}\right)_{\exp }$ |
| :--- | :--- |
| Ne | 0.305 |
| Ar | 0.292 |
| Kr | 0.290 |
| Xe | 0.278 |
| $\mathrm{~N}_{2}$ | 0.292 |
| $\mathrm{O}_{2}$ | 0.292 |
| CO | 0.294 |
| $\mathrm{CH}_{4}$ | 0.289 |

$$
\begin{equation*}
\left(\frac{p_{\mathrm{cr}} V_{\mathrm{cr}}}{R T_{\mathrm{cr}}}\right)_{\mathrm{vdW}}=\frac{3}{8}=0.375 \tag{8.20}
\end{equation*}
$$

for every gas. The idea that the ratio Eq. (8.20) has the same value for all substances is undoubtedly of the utmost importance but this should not be attributed to one of the successes of the van der Waals equation of state in particular but, rather, to a consequence of the fact that the equation of state depends, mainly, on just two macroscopic parameters or, in other words, two parameters are sufficient to characterize, in the first instance, the diverse substances.

Phenomenological observations (some examples are given in Table 8.1) support the prediction that actually the ratio ( $p_{\text {cr }} V_{\text {cr }} / R T_{\text {cr }}$ ) assumes a constant value for all gases or, more precisely, one can identify groups of substances such that within each group the ratio is constant with some accuracy while going from group to another, the common value changes slightly. The different groups are formed by the molecules which have similarities from the microscopic (molecular) point of view. For molecules with simple structure as the noble gases, and nonpolar diatomic molecules, the observed value is

$$
\begin{equation*}
\left(\frac{p_{\mathrm{cr}} V_{\mathrm{cr}}}{R T_{\mathrm{cr}}}\right)_{\exp }=0.27 . \tag{8.21}
\end{equation*}
$$

The error of the van der Waals equation is in between 25 and $30 \%$. However, it is remarkable that the value of the dimensionless ratio defined in Eq. (8.21) is the same for different substances whithin each group.

Since the value for the ratio ( $p_{\text {cr }} V_{\text {cr }} / R T_{\text {cr }}$ ) provided by the equation of van der Waals is pretty poor if we try to determine $a$ and $b$ by measuring the critical parameters, we will see that choosing different pairs of critical parameters (i.e., $p_{\text {cr }}, V_{\text {cr }}$ or $p_{\text {cr }}, T_{\text {cr }}$ or $V_{\text {cr }}, T_{\text {cr }}$ ) will result in little different values for $(a, b)$.

### 8.3.3 The Dependence of the Energy of a van der Waals Gas on Volume

It is reasonable to expect that the energy dependance of a van der Waals gas is described by the parameter $a$ which takes into account the existence of attractive forces between molecule. Let us begin from the fundamental equation for a closed system written in the entropy representation

$$
\begin{equation*}
\mathrm{d} S=\frac{\mathrm{d} U}{T}+\frac{p}{T} \mathrm{~d} V \tag{8.22}
\end{equation*}
$$

and use Eq. (8.10) for the ratio $p T^{-1}$. Let us express all in the differentials of temperature and volume and obtain

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V} \mathrm{~d} T+\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{T}+\frac{n R T}{V-n b}-\frac{a n^{2}}{V^{2}}\right] \mathrm{d} V \tag{8.23}
\end{equation*}
$$

By applying the Schwarz identity, we cross differentiate and obtain

$$
\begin{equation*}
\frac{1}{T}\left(\frac{\partial^{2} U}{\partial V \partial T}\right)=-\frac{1}{T^{2}}\left(\frac{\partial U}{\partial V}\right)_{T}+\frac{1}{T}\left(\frac{\partial U}{\partial T \partial V}\right)+\frac{1}{T^{2}} \frac{a n^{2}}{V^{2}} \tag{8.24}
\end{equation*}
$$

and then

$$
\begin{equation*}
\left(\frac{\partial U}{\partial V}\right)_{T}=\frac{a n^{2}}{V^{2}} \tag{8.25}
\end{equation*}
$$

and this term depends on the parameter $a$ only as was expected.
Moving from the result in Eq. (8.25), it is interesting to write the expression for the energy of a van der Waals gas in the variables temperature and volume:

$$
\begin{equation*}
\mathrm{d} U=n C_{V} \mathrm{~d} T+\frac{a n^{2}}{V^{2}} \mathrm{~d} V \tag{8.26}
\end{equation*}
$$

In Eq. (8.32), we shall prove that $C_{V}$ depends on temperature only ( $\left.C_{V}=C_{V}(T)\right)$ and, moreover, if we assume $C_{V}$ constant, in some interval of temperature, we may integrate Eq. (8.26) and obtain energy as a function of the state:

$$
\begin{equation*}
U-U_{0}=n C_{V}\left(T-T_{0}\right)-n^{2} a\left(\frac{1}{V}-\frac{1}{V_{0}}\right) \tag{8.27}
\end{equation*}
$$

### 8.3.4 The Coefficient of Thermal Expansion for a van der Waals Gas

Let us write the van der Waals equation state in the form

$$
\begin{equation*}
p=\frac{R T}{V_{\mathrm{m}}-b}-\frac{a}{V_{\mathrm{m}}^{2}}, \tag{8.28}
\end{equation*}
$$

and, by differentiating and posing $\mathrm{d} p=0$, we can easily derive the coefficient of thermal expansion and the quantity $(\alpha-1 / T)$ which shows the difference from the ideal gas behavior. We obtain:

$$
\begin{equation*}
\alpha-\frac{1}{T}=\frac{\left[\frac{2 a}{R T}\left(\frac{V_{\mathrm{m}}-b}{V_{\mathrm{m}}}\right)^{2}-b\right]}{\left[V_{\mathrm{m}} T-\frac{2 a}{R}\left(\frac{V_{\mathrm{m}}-b}{V_{\mathrm{m}}}\right)^{2}\right]} \tag{8.29}
\end{equation*}
$$

A coarser expression can be written if we consider the terms containing the constants $a$ o $b$ small and we neglect the terms in which they appear either to the second power or as a product of the two:

$$
\begin{equation*}
\alpha-\frac{1}{T}=\frac{\left(\frac{2 a}{R T}-b\right)}{V_{\mathrm{m}} T} \tag{8.30}
\end{equation*}
$$

These expressions will be very useful for qualitative arguments about the inversion curve of the gas as provided by the equation of van der Waals. Quantitative forecasts are not very good, but the trend of the dependence on pressure and temperature is quite satisfactory.

### 8.3.5 The Molar Heats at Constant Volume and at Constant Pressure in a van der Waals Gas

From the result Eq. (8.25), we can write the expression of the molar energy of a van der Waals gas as a function of temperature and volume:

$$
\begin{equation*}
\mathrm{d} U_{\mathrm{m}}=C_{V} \mathrm{~d} T+\frac{a}{V_{\mathrm{m}}^{2}} \mathrm{~d} V_{\mathrm{m}} \tag{8.31}
\end{equation*}
$$

and applying the Schwarz identity to Eq. (8.31):

$$
\begin{equation*}
\frac{\partial C_{V}}{\partial V_{\mathrm{m}}}=\frac{\partial\left(\frac{a}{V_{\mathrm{m}}^{2}}\right)}{\partial T}=0 \tag{8.32}
\end{equation*}
$$

and this shows that the molar heat at constant volume is a function of temperature only. As for the molar heat at constant pressure, we may refer to Eq. (5.22):

$$
\begin{equation*}
C_{p}=C_{V}+\frac{\alpha^{2} V T}{\chi_{T}} \tag{8.33}
\end{equation*}
$$

From Eq. (5.8) we get

$$
\begin{equation*}
\frac{\alpha}{\chi_{T}}=\left(\frac{\partial p}{\partial T}\right)_{V} \tag{8.34}
\end{equation*}
$$

and then for a van der Waals gas we obtain

$$
\begin{equation*}
\frac{\alpha}{\chi_{T}}=\frac{R}{V_{\mathrm{m}}-b} \tag{8.35}
\end{equation*}
$$

In order to complete the calculation of $C_{p}$ we have to recover Eq. (8.29) for the expression of $\alpha$. After some easy calculations we obtain

$$
\begin{equation*}
C_{p}-C_{V}=\frac{R}{\left[1-\frac{2 a}{R T} \frac{\left(V_{\mathrm{m}}-b\right)^{2}}{V_{\mathrm{m}}^{3}}\right]} \tag{8.36}
\end{equation*}
$$

The above relation can be approximated neglecting all the terms but those which are first order in $a$ or in $b$ :

$$
\begin{equation*}
C_{p}-C_{V}=\frac{R}{\left[1-\frac{2 a}{R T V_{\mathrm{m}}}\right]} \tag{8.37}
\end{equation*}
$$

### 8.3.6 The Joule-Thomson Coefficient and the Inversion Curve for a van der Waals Gas

Let us remember the definition of Joule-Thomson coefficient given by the general definition given in Eq. (6.32). Here, the Joule-Thomson coefficient is related to the coefficient of thermal expansion $\alpha$ given by Eq. (8.29) or by the simplified expression Eq. (8.30). Combining the two we obtain, respectively:

$$
\begin{equation*}
C_{H}=\frac{1}{C_{p}} \frac{\left[\frac{2 a}{R T}\left(\frac{V_{\mathrm{m}}-b}{V_{\mathrm{m}}}\right)^{2}-b\right]}{\left[1-\frac{2 a}{R T} \frac{\left(V_{\mathrm{m}}-b\right)^{2}}{V_{\mathrm{m}}^{3}}\right]} \tag{8.38}
\end{equation*}
$$

and

$$
\begin{equation*}
C_{H}=\frac{V_{\mathrm{m}} T}{C_{p}} \frac{\left(\frac{2 a}{R T}-b\right)}{V_{\mathrm{m}} T}=\frac{\left(\frac{2 a}{R T}-b\right)}{C_{p}} \tag{8.39}
\end{equation*}
$$

The expression of the inversion curve is obtained setting $(\alpha-1 / T)=0$, and in our case we get

$$
\begin{equation*}
\frac{2 a}{R T}\left(\frac{V_{\mathrm{m}}-b}{V_{\mathrm{m}}}\right)^{2}=b \tag{8.40}
\end{equation*}
$$

This expression can be written in the variables ( $p, T$ ) with some calculations, reusing the equation of state. We shall come back to this topic in connection with our discussion about the Law of Corresponding States.

If we are satisfied with the approximate expression Eq. (8.39) we find, in the simplest expression, the inversion temperature:

$$
\begin{equation*}
T_{i}=\frac{2 a}{R b} \tag{8.41}
\end{equation*}
$$

corresponding to

$$
\begin{equation*}
T_{i}=2 T_{\mathrm{B}} \tag{8.42}
\end{equation*}
$$

We see, then approximately, that the inversion temperature is double the Boyle temperature.

### 8.3.7 Determination of Vapor Pressure from the van der Waals Equation

From the van der Waals equation of state we can determine the value of the vapor pressure, at each temperature, with a graphic method.

Consider an isotherm at a temperature below the critical temperature and represent graphically the curve obtained from the van der Waals equation of state at that temperature.

We want to superimpose on this representation the horizontal portion that describes the phase separation whose position gives the value of the pressure of the saturated vapor. Let us denote with A and B, respectively, the states at which this


Fig. 8.3 Maxwell construction for the determination of the vapor pressure using the van der Waals equation of state. States A and B represent saturated liquid and vapor, respectively. The integral of the molar volume, as a function of pressure and at constant temperature, is carried out from A to B along the van der Waals curve, as described by Eqs. (8.44), (8.45). As a representative example, in the figure we refer to the van der Waals isotherm at $\tilde{t}=T / T_{\text {cr }}=0.9$. As a result, the equal area condition gives a vapor pressure $\tilde{p}_{\mathrm{s}}=p_{\mathrm{s}} / p_{\text {cr }}=0.65$
horizontal portion intersects the isotherm on the part of the liquid and on that of the vapor (see Fig. 8.3).

Since the points $A$ and $B$ represent two states in mutual equilibrium, the chemical potentials must be equal. We can formally calculate the value of the chemical potential in $\mathrm{B}, \mu_{\mathrm{B}}$, starting from its value in $\mathrm{A}, \mu_{\mathrm{A}}$, by integrating along the van der Waals isotherm:

$$
\begin{equation*}
\mu_{\mathrm{B}}=\mu_{\mathrm{A}}+\int_{\mathrm{A}}^{\mathrm{B}}\left(\frac{\partial \mu}{\partial p}\right)_{T} \mathrm{~d} p, \tag{8.43}
\end{equation*}
$$

Since it must be $\mu_{\mathrm{A}}=\mu_{\mathrm{B}}$ and $p_{\mathrm{A}}=p_{\mathrm{B}}$ we obtain

$$
\begin{equation*}
\int_{\mathrm{A}}^{\mathrm{B}}\left(\frac{\partial \mu}{\partial p}\right)_{T} \mathrm{~d} p=0 . \tag{8.44}
\end{equation*}
$$

If we denote by C the point at which the isotherm intersects the horizontal portion, we can decompose the integral Eq. (8.44) into the sum of the two integrals:

$$
\begin{equation*}
\int_{\mathrm{A}}^{\mathrm{C}}\left(\frac{\partial \mu}{\partial p}\right)_{T} \mathrm{~d} p+\int_{\mathrm{C}}^{\mathrm{B}}\left(\frac{\partial \mu}{\partial p}\right)_{T} \mathrm{~d} p=0 . \tag{8.45}
\end{equation*}
$$

Remembering that $(\partial \mu / \partial p)_{T}=V_{\mathrm{m}}$ the previous relation can be written in a form that can be more easily interpreted:

$$
\begin{equation*}
\int_{\mathrm{A}}^{\mathrm{C}} V_{\mathrm{m}} \mathrm{~d} p+\int_{\mathrm{C}}^{\mathrm{B}} V_{\mathrm{m}} \mathrm{~d} p=0 \tag{8.46}
\end{equation*}
$$

This relation shows that the areas of the two surfaces marked in the figure must be equal. The procedure for deriving graphically the value of the vapor pressure from the van der Waals equation of state, is the following: draw the isotherm corresponding to the chosen temperature and determine the position of the horizontal line in such a way that the two areas are equal. The number red on the ordinate provides the value of the vapor pressure we were looking for.

### 8.3.8 Free Energy in a van der Waals Gas

According to item 3 of Sect.8.3, the condition for stability implicates a positive curvature for the free energy $F$ as a function of the gas volume $V$ :

$$
\begin{equation*}
\left(\frac{\partial^{2} F}{\partial V^{2}}\right)_{T}=-\left(\frac{\partial p}{\partial V}\right)_{T}>0 \tag{8.47}
\end{equation*}
$$

In parallel, the equilibrium condition in terms of $F$ is usually stated as

$$
\begin{equation*}
\left(\frac{\partial F}{\partial V}\right)_{T}=0 \tag{8.48}
\end{equation*}
$$

At a fixed temperature $T<T_{\text {cr }}$, let us consider a state $\mathrm{A}=\left(p_{\mathrm{A}}, V_{\mathrm{A}}\right)$ in the liquid phase and a state $\mathrm{B}=\left(p_{\mathrm{B}}, V_{\mathrm{B}}\right)$ in the vapor phase. Let $N=N_{\text {liq }}+N_{\text {vap }}$ be the total number of molecules at any volume $V$ between $V_{\mathrm{A}}, V_{\mathrm{B}}, N_{\text {liq }}, N_{\text {vap }}$ being the number of molecules in the liquid phase and the vapor phase, respectively. Clearly, as shown in Fig. 7.4) the total volume $V$ of the system, when $V_{\mathrm{A}}<V<V_{\mathrm{B}}$, is given by

$$
\begin{equation*}
V=\frac{N_{\text {liq }}}{N} V_{\text {liq }}+\frac{N_{\text {vap }}}{N} V_{\text {vap }} \tag{8.49}
\end{equation*}
$$

In parallel, let us indicate with $F_{\text {vap }}$ and $F_{\text {liq }}$ the free energy of the liquid phase and the vapor phase, respectively. Conversely, let $F_{\text {lv }}$ be the free energy of the system within $V_{\mathrm{A}}<V<V_{\mathrm{B}}$ when both liquid and vapor phases are present. Recalling that

Fig. 8.4 Free energy of a van der Waals gas below the critical temperature. Line connecting the states $\mathrm{A}, \mathrm{B}$ is the free energy corresponding to two phases according to Eq. (8.51). $\mathrm{A}^{\prime}, \mathrm{B}^{\prime}$ are states on the spinodal curve

$F$ is an extensive quantity, we can write

$$
\begin{equation*}
F_{\text {lv }}=\frac{N_{\text {liq }}}{N} F_{\text {liq }}+\frac{N_{\text {vap }}}{N} F_{\text {vap }} . \tag{8.50}
\end{equation*}
$$

By substituting in Eq. (8.50) the expressions $N_{\text {liq }} / N$ and $N_{\text {vap }} / N$ obtained from Eq. (8.49) we get

$$
\begin{equation*}
F_{\mathrm{lv}}=F_{\mathrm{A}}+\frac{V-V_{\mathrm{A}}}{V_{\mathrm{B}}-V_{\mathrm{A}}}\left(F_{\mathrm{B}}-F_{\mathrm{A}}\right) \tag{8.51}
\end{equation*}
$$

where $F_{\mathrm{A}}=F_{\text {liq }}(\mathrm{A}), F_{\mathrm{B}}=F_{\text {vap }}(\mathrm{B}), V_{\mathrm{A}}=V_{\text {liq }}(\mathrm{A})$, and $V_{\mathrm{B}}=V_{\text {vap }}(\mathrm{B})$. Therefore, from Eq. (8.51), it results that the free energy of the system enclosing both liquid and vapor phase is a straight line in the $(F, V)$ diagram, connecting the two states A and $B$ where the system is entirely in the liquid and gas state, respectively.

So, below $T_{\text {cr }}$, the van der Waals isotherms report a region where the stability condition is violated and $\partial^{2} F / \partial V^{2}<0$. For any $T<T_{\text {cr }}$, this happens between the minimum and the maximum of the van der Waals isotherm as shown in Fig. 8.4 where they are denoted by $\mathrm{A}^{\prime}$ and $\mathrm{B}^{\prime}$. In this region, the free energy for a biphasic system connecting the states $\mathrm{A}^{\prime}$ and $\mathrm{B}^{\prime}$ is always below the corresponding free energy of a single phase. Considering the analytical form of the van der Waals isotherms below the critical temperature, for any $T<T_{\text {cr }}$, it is possible to find a couple of states enclosing an instability region specific of each $T$. By iterating this construction for different $T<T_{\text {cr }}$, we individuate a curve enclosing the instability states of the van der Waals isotherms, known as the spinodal curve, as shown in Fig. 8.5.

Therefore, the coexistence curve results always larger than the spinodal curve. These curve "touch" one each other only at the critical point ( $p_{\text {cr }}, V_{\text {cr }}, T_{\text {cr }}$ ). It is important to remark that, at variance with unstable states inside the spinodal curve, it is possible to observe only one phase just inside the coexisting curve, even if the free energy of these states is larger than the one corresponding to a mixture of two phases coexisting at the thermodynamic equilibrium with $V$ and $F$ given by Fig. 8.4. The states falling just inside the coexisting curve are therefore metastable and correspond

Fig. 8.5 Isotherms for a van der Waals gas. For $T<T_{\text {cr }}$ isotherms are dashed within the coexistence region showed by Fig. 7.3 since they are connecting either metastable states as the superheated liquid (a) and the supersaturated vapor (c), or unstable states (b) which are bounded by the spinodal curve. Lines at constant pressure within the coexistence region are the equilibrium vapor pressure according to the Maxwell construction given by Eq. (8.46) for a van der Waals gas

to superheated liquid and supersaturated vapor whether the corresponding pressure is just below, or just above $p_{\mathrm{s}}$, respectively. In Sect. 9.4 phase changes occurring in the metastability region will be described.

### 8.4 The Law of Corresponding States

In the above discussion on the van der Waals equation of state, we highlighted the fact that an equation of state that depends only on two parameters, has the consequence that the three critical parameters are not independent of each other and that the dimensionless ratio ( $p_{\text {cr }} V_{\text {cr }} / R T_{\text {cr }}$ ) has the same value for different fluids. This fact is well confirmed by empirical observations even if the accuracy of the numerical result suggests the existence of different groups of substances.

Each equation of state for a particular fluid, which we denote with the index $\gamma$, can be formally written as

$$
\begin{equation*}
\varphi_{\gamma}(p, V, T)=0 \tag{8.52}
\end{equation*}
$$

and from that we are able to calculate the critical parameters.
We define the reduced variables the adimensional state variables:

$$
\begin{equation*}
\tilde{p}=\frac{p}{p_{\mathrm{cr}}}, \quad \tilde{v}=\frac{V}{V_{\mathrm{cr}}}, \quad \tilde{t}=\frac{T}{T_{\mathrm{cr}}}, \tag{8.53}
\end{equation*}
$$

and let us express the equation of state, formally, as a function of these reduced variables:

$$
\begin{equation*}
\tilde{\varphi}_{\gamma}(\tilde{p}, \tilde{v}, \tilde{t})=0 . \tag{8.54}
\end{equation*}
$$

The equations of state so expressed, for each $\gamma$, must give the same result for the critical point that is

$$
\begin{equation*}
\tilde{\varphi}_{\gamma}(1,1,1)=0 \tag{8.55}
\end{equation*}
$$

This argument concerning the critical point and, more important, several empirical evidences suggest the following hypothesis: different fluids have the same equation of state if it is expressed in reduced variables. In other words there exists one equation of state, in reduced variables $\tilde{\varphi}(\tilde{p}, \tilde{v}, \tilde{t})=0$ for every $\gamma$ :

$$
\begin{equation*}
\tilde{\varphi}_{\gamma}(\tilde{p}, \tilde{v}, \tilde{t})=\tilde{\varphi}(\tilde{p}, \tilde{v}, \tilde{t})=0 \tag{8.56}
\end{equation*}
$$

The assumption given in Eq. (8.56) is known as the Law of Corresponding States and has many observable consequences. Let us consider some of these consequences in the followings sections.

### 8.4.1 Corresponding States for the Second Virial Coefficient

The second virial coefficient $B=B(T)$ has the dimension of a volume. If, for each gas, we measure $B$ at various temperatures and we plot $B / V_{\mathrm{cr}}$ as a function of $T / T_{\mathrm{cr}}$ we see that the experimental data, for different gases, overlap along the same curve with great accuracy. In particular, the Boyle temperature for different gases has the same value if it is expressed in units of their critical temperature:

$$
\begin{equation*}
\frac{T_{\mathrm{B}}}{T_{\mathrm{cr}}} \simeq 2.6 \tag{8.57}
\end{equation*}
$$

### 8.4.2 The Compressibility Factor and the Generalized Compressibility Chart

The discussion in the previous subsections, concerning the second virial coefficient will be better understood if it is seen within a more general argument that we are going to mention here. ${ }^{2}$

As we have seen the virial coefficients $B(T), C(T), \ldots$ describe how far the fluid is considered to deviate from the so-called "ideal gas" which is properly described by the first coefficient $A(T)$.

[^23]If we maintain, as a reference situation for a gas the one of the "ideal gas", the "closeness", or the "remoteness" of the equation of state of a real fluid is currently described by a single comprehensive parameter called compressibility factor. ${ }^{3}$

It is generally denoted with the symbol $Z=Z(p, T)$ and is defined by the ratio:

$$
\begin{equation*}
Z=\frac{p V_{\mathrm{m}}}{R T} \tag{8.58}
\end{equation*}
$$

Clearly for an ideal gas the function $Z(p, T)$ maintains the constant value $Z=1$ while, for real gases, its value depends on the state. The graphic representation of this function is equivalent to the knowledge of the equation of state of that particular substance. In technical applications, this parameter is represented in a plane ( $Z, p$ ) by a family of curves one for each temperature and the graphical representation of these curves is named compressibility chart. If, at a given pressure and temperature, the compressibility factor $Z(p, T)$ remains close to 1 along a transformation, then the gas may be treated as an ideal gas but if $Z$ differs substantially from unity, the equation of state departs significantly, the compressibility charts must be used and then the compressibility factor is a good indicator of proximity of the gas to the ideal behavior.

Compressibility charts can be prepared for any pure substance of particular interest or may be calculated from an equation of state like, for instance, the van der Waals equation or some other more accurate ones. In both cases, having in mind to make use of the Law of Corresponding States, the chart is represented in reduced variables and in this case we draw, in a plane ( $Z, \tilde{p}$ ), the family of curves bearing as an index the reduced temperature $\tilde{t}$. In this case, we speak of a generalized compressibility chart.

In Fig. 8.6, the represented compressibility chart is the one obtained from the Lee-Kesler equation of state [11]. This is a quite accurate equation of state based on 12 parameters and details can be found in [12].

Following exactly the same procedure, other generalized charts are constructed as, for instance, the generalized chart for entropy and generalized chart for enthalpy particularly important in engineering applications. These generalized charts allow quickly finding a variation of entropy or enthalpy in certain changes of state for substances of which we know the critical point. Let us consider the following example.
Example 8.1 Let us consider a cylinder containing 5 kg of Carbon Dioxide $\left(\mathrm{CO}_{2}\right.$, Molecular Weight $M_{\mathrm{CO}_{2}} \simeq 44$ ) at the temperature $\theta_{1} \simeq 122.5^{\circ} \mathrm{C}$ and at the pressure $p_{1} \simeq 221.4$ bar. Determine the volume of the cylinder and compare the result with the value obtained treating the gas as an ideal gas. The gas is then heated, at constant pressure, up to the temperature $\theta_{2} \simeq 183.4^{\circ} \mathrm{C}$. We aim to determine the amount of work done on the gas. The critical pressure and temperature of carbon dioxide are, respectively, $p_{\text {cr }}=73.7$ bar and $T_{\text {cr }}=304.36 \mathrm{~K}$.

The number of moles is $n \simeq 5000 / 44 \simeq 113.6$ and then we may calculate the initial volume from the ideal gas state equation:

[^24]

Fig. 8.6 Generalized compressibility chart. Reproduced with permission from Van Wylen et al., Fundamentals of Classical Thermodynamics [12]

$$
V_{1_{\mathrm{id}}}=\frac{n R T_{1}}{p_{1}} \simeq \frac{113.6 \times 8.31 \times 395.6}{221.4 \times 10^{5}} \simeq 0.017 \mathrm{~m}^{3}=17 \mathrm{~L} .
$$

The value of the volume we obtain from the compressibility chart is

$$
V_{1}=\frac{n Z R T}{p}=Z V_{1_{\mathrm{id}}}
$$

The correct value for $Z$ is obtained from the compressibility chart provided that we calculate first the reduced pressure and temperature of the initial state. We get, respectively

$$
\begin{aligned}
& \tilde{p}_{1} \simeq \frac{221.4}{73.7} \simeq 3 \\
& \tilde{t}_{1} \simeq \frac{395.6}{304.36} \simeq 1.3
\end{aligned}
$$

From the compressibility chart shown in Fig. 8.6, we find that the compressibility factor is (in the initial state)

$$
Z_{1} \simeq 0.635
$$

then

$$
V_{1}=Z_{1} V_{1_{\mathrm{id}}} \simeq 0.635 \times 17 \simeq 10.8 \mathrm{~L}
$$

The amount of work, $W$, done on the gas in the isobaric transformation to the final state is

$$
W=-p\left(V_{2}-V_{1}\right)
$$

We need the final volume $V_{2}$. In order to determine it we have to refer, once again, to the compressibility chart and then we need the reduced pressure and temperature of the final state. The former takes the same constant value as in the initial state $\tilde{p}_{2}=\tilde{p}_{1} \simeq 3$ while the latter is $\tilde{t}_{2}=456.5 / 304.36 \simeq 1.5$. From the compressibility chart the compressibility factor results

$$
Z_{2} \simeq 0.79
$$

The final volume is

$$
V_{2}=n Z_{2} \frac{R T_{2}}{p_{2}} \simeq 113.6 \times 0.79 \times \frac{8.31 \times 456.5}{221.4 \times 10^{5}} \simeq 15.38 \mathrm{~L}
$$

The amount of work is

$$
W \simeq-221.4 \times 10^{5} \times(15.38-10.8) \simeq-1.01 \times 10^{5} \mathrm{~J}
$$

### 8.4.3 Vapor Pressure and Latent Heat of Vaporization

At sufficiently low temperature, which in our case means $T \lesssim 0.65 T_{\text {cr }}$, the vapor, though in the state of saturated vapor, is well described by the ideal gas equation of state ${ }^{4}$ and the vapor pressure, according to Eq. (7.13), is well described by

$$
\begin{equation*}
\ln \frac{p}{p^{\dagger}}=-\frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T}-\frac{1}{T^{\dagger}}\right) \tag{8.59}
\end{equation*}
$$

where $p^{\dagger}$ and $T^{\dagger}$ refers to a reference state. From this relation, we see that logarithm of $p$ is a linear function of $(1 / T)$, i.e., may be written in the form

$$
\begin{equation*}
\ln \frac{p}{p^{\dagger}}=c_{1}-c_{2}\left(\frac{T^{\dagger}}{T}\right) \tag{8.60}
\end{equation*}
$$

where $c_{1}$ and $c_{2}$ are two phenomenological constants. According to the Law of Corresponding States, let's write

$$
\begin{equation*}
\ln \left(\frac{p}{p_{\mathrm{cr}}}\right)=\Gamma_{1}-\Gamma_{2}\left(\frac{T_{\mathrm{cr}}}{T}\right), \tag{8.61}
\end{equation*}
$$

with $\Gamma_{1}$ and $\Gamma_{2}$ being two adimensional phenomenological constants which are the same for every gas. From the comparison between Eq. (8.59) and Eq. (8.61) we get an important relation which provides us with the value of latent heat of vaporization:

$$
\begin{equation*}
\Gamma_{2}=\frac{\Delta H_{\mathrm{m}}}{R T_{\mathrm{cr}}} \tag{8.62}
\end{equation*}
$$

From this relation and from the experimental value for the constant $\Gamma_{2}$ we get the interesting relationship for the latent heat:

$$
\begin{equation*}
\Delta H_{\mathrm{m}}=5.21 R T_{\mathrm{cr}} \tag{8.63}
\end{equation*}
$$

Relations given by Eqs. (8.61) and (8.63) have a theoretical basis, as we have seen in Eq. (8.59), which is based on the assumption that the saturated vapor is very close to an ideal gas and that the latent heat of vaporization is practically constant (at least in the temperature interval used to integrate the Clapeyron's equation). At "high" temperatures that is $0.65 T_{\text {cr }} \lesssim T \lesssim T_{\text {cr }}$ the saturated vapor is not well represented by the ideal gas law and the latent heat of vaporization decreases to become zero at the critical temperature. For this reason it is preferable to characterize the gaseous and liquid phases in mutual equilibrium by means of their densities and the latter are measured in units of the respective critical density (reduced densities). These

[^25]

Fig. 8.7 Reduced density of the liquid and the gaseous phases in mutual equilibrium, as a function of the reduced temperature for a group of substances. Data show that the Law of Corresponding States holds with appreciable accuracy. Figure reproduced with permission from Guggenheim, Thermodynamics: An Advanced Treatment for Chemists and Physicists [3]
reduced densities of the phases in mutual equilibrium are measured for a group of substances and the results are shown in Fig. 8.7 as a function of the respective reduced temperature. As reported by [3], the data are well described by the very simple relations:

$$
\begin{align*}
& \frac{\varrho^{L}+\varrho^{G}}{2 \varrho_{\mathrm{cr}}}=1+\frac{3}{4}(1-\tilde{t}),  \tag{8.64}\\
& \frac{\varrho^{L}-\varrho^{G}}{\varrho_{\mathrm{cr}}}=\frac{7}{2}(1-\tilde{t})^{1 / 3} . \tag{8.65}
\end{align*}
$$

The reader is referred to the discussion contained in [3] for a more in-depth examination of the problem.

Table 8.2 The ratios $T_{\text {tr }} / T_{\text {cr }}$ and $p_{\text {tr }} / p_{\text {cr }}$ are shown for some elements

| Substance | $\left(T_{\text {tr }} / T_{\text {cr }}\right)_{\text {exp }}$ | $\left(p_{\text {tr }} / p_{\text {cr }}\right) \times 100$ |
| :--- | :--- | :--- |
| Ne | 0.549 | 1.58 |
| Ar | 0.557 | 1.42 |
| Kr | 0.553 | 1.33 |
| Xe | 0.557 | 1.40 |

### 8.4.4 Triple Point and the Law of Corresponding States

If the Law of Corresponding States, according to which the equation of state expressed in reduced variables is the same for all substances (or, at least, for some groups of substances), holds we expect that the phase diagram represented in reduced variables is the same for various components. One particular consequence would be that the ratio of the critical values to the homologous values at the triple point are the same value for different substances.

From Table 8.2 it is found that for the various substances the ratio of the temperature at the triple point to the critical temperature is maintained close to the value

$$
\begin{equation*}
\frac{T_{\mathrm{tr}}}{T_{\mathrm{cr}}} \simeq 0.555 \tag{8.66}
\end{equation*}
$$

Similarly, for the ratio of the triple point pressure to the critical point pressures:

$$
\begin{equation*}
\frac{p_{\mathrm{tr}}}{p_{\mathrm{cr}}} \simeq 1.4 \times 10^{-2} \tag{8.67}
\end{equation*}
$$

### 8.4.5 The Inversion Curve and the Law of Corresponding States

In Sect. 6.6, we discussed briefly the definition of inversion curve as formed, in a ( $p, T$ ) plane, by the points in which the Joule-Thomson coefficient is zero and, in general, this is equivalent to Eq. (6.39). Every gas will be described by its own inversion curve. However, the Law of Corresponding States suggests that Eq. (6.39), written in terms of reduced variable, gives

$$
\begin{equation*}
\tilde{\alpha}(\tilde{p}, \tilde{t})=\frac{1}{\tilde{t}} \tag{8.68}
\end{equation*}
$$

Therefore, from Eq. (8.68), the specific inversion curve for each gas can be obtained. The degree of accuracy of such a rule can be estimated by looking at Fig. 8.8. Here, the experimental data for the inversion curves of different substances are shown together with the extrapolated results obtained from [13]. We do not enter into the problem of choosing the most adequate equation of state but we emphasize the fact


Fig. 8.8 Generalized inversion curves in reduced variables for different fluids. Reproduced with permission from Hendricks et al., Joule-Thomson inversion curves and related coefficients for several simple fluids [14]
that the experimental data overlap on a single sharply defined curve and this shows to what extent the Law of Corresponding States is supported by experimental data.

Fig. 8.9 The inversion curve in reduced variables, obtained from Eq. (8.70) is shown. For comparison, the inversion curve of hydrogen showed in Fig. 8.8 is also reported in reduced variables


### 8.4.6 The Law of Corresponding States and the van der Waals's Equation

The van der Waals equation is an example of an equation of state which can, in a natural way, be written in reduced variables. It is a useful example because, even if the accuracy of the numerical results is sometimes a little poor, nevertheless the qualitative trends are easily and correctly reproduced.

Going back to Eqs. (8.17)-(8.19) with some calculations we get

$$
\begin{equation*}
\left(\tilde{p}+\frac{3}{\tilde{v}^{2}}\right)(3 \tilde{v}-1)=8 \tag{8.69}
\end{equation*}
$$

This is the van der Waals equation written for all gases. If we refer to Sect. 8.3.6, we can write the expression of the inversion curve in reduced variables having adopted this equation of state.

In [7], it is quoted the result obtained with some calculations:

$$
\begin{equation*}
\tilde{p}=24 \sqrt{3 \tilde{t}}-12 \tilde{t}-27 \tag{8.70}
\end{equation*}
$$

The graphical representation of this curve with superimposed the experimental results are shown in Fig. 8.9. Both the experimental curve and the curve obtained from the van der Waals equation of state has "bell-like" shape and at the points under the bell the coefficient Joule-Thomson is positive. This means that if the initial state is in this region, the expansion will lead to a cooling of the gas. The maximum temperature drop is obtained with the maximum expansion pressure jump starting from the peak of the inversion curve.

### 8.5 Power Laws at the Critical Point in a van der Waals Gas

From van der Waals Eq. (8.9) we see that the critical isotherm exhibits a horizontal change of curvature, where $(\partial p / \partial V)_{T_{\text {cr }}}=0$. Therefore

$$
\chi_{T} \propto\left(\frac{\partial V}{\partial p}\right)_{T} \rightarrow \infty \quad \text { for } T \simeq T_{\mathrm{cr}} .
$$

In this section, we aim at exploring how the compressibility diverges. More generally, we would explore the behavior of thermodynamic quantities relevant for the van der Waals gas, in the vicinity of the critical point. To this aim let use introduce the variables $\hat{t}, \hat{v}, \hat{p}$ :

$$
\left\{\begin{array}{l}
\hat{t} \equiv\left(\frac{T-T_{\mathrm{cr}}}{T_{\mathrm{cr}}}\right)=\tilde{t}-1  \tag{8.71}\\
\hat{v} \equiv\left(\frac{V-V_{\mathrm{cr}}}{V_{\mathrm{cr}}}\right)=\tilde{v}-1 \\
\hat{p} \equiv\left(\frac{p-p_{\mathrm{cr}}}{p_{\mathrm{cr}}}\right)=\tilde{p}-1
\end{array}\right.
$$

Within these change of state variable, the van der Waals equation becomes:

$$
\begin{equation*}
1+\hat{p}=\frac{4(1+\hat{t})}{1+(3 / 2) \hat{v}}-\frac{3}{(1+\hat{v})^{2}} \tag{8.74}
\end{equation*}
$$

By expanding the denominators of Eq. (8.74) close to the critical point, so that $\hat{v} \ll 1$, we get:

$$
\begin{equation*}
1+\hat{p}=4(1+\hat{t})\left(1-\frac{3}{2} \hat{v}+\frac{9}{4} \hat{v}^{2}+\frac{27}{8} \hat{v}^{3}+\ldots\right)-3\left(1-2 \hat{v}+3 \hat{v}^{2}-4 \hat{v}^{3}+\ldots\right) \tag{8.75}
\end{equation*}
$$

After some simple algebra, Eq. (8.75) may be approximated as

$$
\begin{equation*}
\hat{p} \simeq 4 \hat{t}-6(\hat{t} \hat{v})-\frac{3}{2} \hat{v}^{3} \tag{8.76}
\end{equation*}
$$

## Compressibility

By taking the derivative of Eq. (8.76) respect to $\hat{v}$ we get

$$
\begin{equation*}
\left(\frac{\partial \hat{p}}{\partial \hat{v}}\right)=-6 \hat{t}-\frac{9}{2} \hat{v}^{2} \tag{8.77}
\end{equation*}
$$

At the critical point $V=V_{\text {cr }}, T=T_{\text {cr }}$ :

$$
\begin{equation*}
\chi_{T}=-\frac{1}{V_{\mathrm{cr}}}\left(\frac{\partial V}{\partial p}\right)_{T=T_{\mathrm{cr}}} \propto-\left(\frac{\partial \hat{p}}{\partial \hat{v}}\right)_{\hat{t}=0}^{-1} \propto \hat{t}^{-1}=\left(\frac{T}{T_{\mathrm{cr}}}-1\right)^{-1}, \tag{8.78}
\end{equation*}
$$

so that

$$
\begin{equation*}
\chi_{T} \sim\left(T-T_{\mathrm{cr}}\right)^{-1} . \tag{8.79}
\end{equation*}
$$

## Density Mismatch Between the Vapor and Liquid Phase

The equilibrium condition $\mu_{1}=\mu_{2}$ for the chemical potential of two coexisting phases labeled 1 and 2, implies that

$$
\begin{equation*}
\int_{1}^{2} V \mathrm{~d} p=0 \Rightarrow \int_{1}^{2} \hat{v} \mathrm{~d} \hat{p}=0 \tag{8.80}
\end{equation*}
$$

Correspondingly, the differential of Eq. (8.76) at constant $T$ results to be

$$
\begin{equation*}
\mathrm{d} \hat{p}=-\left(6 \hat{t}+\frac{9}{2} v^{2}\right) \mathrm{d} \hat{v} \tag{8.81}
\end{equation*}
$$

By substituting Eq. (8.81) in Eq. (8.80) we get

$$
\begin{equation*}
\int_{1}^{2} \hat{v} \mathrm{~d} \hat{p}=-3 \hat{t}\left(\hat{v}_{2}^{2}-\hat{v}_{1}^{2}\right)-\frac{9}{8}\left(\hat{v}_{2}^{4}-\hat{v}_{1}^{4}\right)=0 . \tag{8.82}
\end{equation*}
$$

Therefore, slightly below $T_{\text {cr }}$, or equivalently when $\hat{t} \rightarrow 0^{-}$

$$
\begin{equation*}
\left|\hat{v}_{2}\right|=\left|\hat{v}_{1}\right| \Rightarrow\left|V_{2}-V_{\mathrm{cr}}\right|=\left|V_{1}-V_{\mathrm{cr}}\right| . \tag{8.83}
\end{equation*}
$$

This implies that the "bell" enclosing coexisting phases is symmetric respect to the critical point ( $p_{\text {cr }}, V_{\text {cr }}$ ). Therefore, we can write Eq. (8.76) in both phases with $\hat{p}_{1}=\hat{p}_{2}$ and $\hat{v}_{1}=-\hat{v}_{2}:$

$$
\begin{equation*}
4 \hat{t}-6 \hat{t} \hat{v}_{1}-\frac{3}{2} \hat{v}_{1}^{3}=4 \hat{t}+6 \hat{t} \hat{v}_{2}-\frac{3}{2} \hat{v}_{2}^{3}, \tag{8.84}
\end{equation*}
$$

which implies that

$$
\begin{equation*}
\hat{v}_{1} \propto(-\hat{t})^{1 / 2} \Leftrightarrow\left(V_{1}-V_{\mathrm{cr}}\right) \propto\left(T_{\mathrm{cr}}-T\right)^{1 / 2} . \tag{8.85}
\end{equation*}
$$

For the density difference around the critical point we can easily derive that

$$
\begin{equation*}
\varrho_{l}-\varrho_{g} \propto\left(T_{\mathrm{cr}}-T\right)^{1 / 2} \tag{8.86}
\end{equation*}
$$

## Critical Isotherm

For $\hat{t} \simeq 0$ we observe that $\hat{p}(\hat{v}) \simeq \hat{v}^{3}$. Therefore,

$$
\begin{align*}
& \left(V-V_{\mathrm{cr}}\right) \propto\left(p-p_{\mathrm{cr}}\right)^{1 / 3}  \tag{8.87}\\
& \quad \text { equivalently: } \\
& \left(\varrho-\varrho_{\mathrm{cr}}\right) \propto\left(p-p_{\mathrm{cr}}\right)^{1 / 3} \tag{8.88}
\end{align*}
$$

Summarizing, close to the critical point, the compressibility and the density difference between the vapor and liquid phase can be expressed as power laws with respect to $\Delta T=\left|T-T_{\text {cr }}\right|$. The corresponding exponents are known as critical exponents $\beta, \gamma$, respectively, being $\beta=1$ and $\gamma=1 / 2$ in the van der Waals model.

### 8.6 Exercises

8.1 A cylinder with rigid and adiabatic walls is divided, by a septum, in two parts A and B whose volume are, respectively, $V_{\mathrm{A}}=20 \mathrm{~L}$ and $V_{\mathrm{B}}=2 \mathrm{~L}$. Part B is empty while part A is filled by ten moles of carbon dioxide the pressure $p=10$ bar. The gas is well described by the van der Waals equation where the two constants are $a=$ $363.96 \times 10^{-3} \mathrm{~m}^{6} \mathrm{~Pa} \mathrm{~mole}^{-2}, b=0.0427 \times 10^{-3} \mathrm{~m}^{3} \mathrm{~mole}^{-1}$ and the molar heat at constant volume is $C_{V} \simeq 28.85 \mathrm{~J} \mathrm{~mole}^{-1} \mathrm{~K}^{-1}$. The septum is removed and the gas suffers a free expansion to the final volume. Estimate the temperature variation.
8.2 Carbon dioxide is expanded against atmospheric pressure in a throttling experiment. The initial state is $p_{0}=20 \mathrm{bar}$ and $T_{0}=270 \mathrm{~K} . \mathrm{CO}_{2}$ can be treated using the van der Waals equation of state with parameters $a=363.96 \times 10^{-3} \times \mathrm{m}^{6} \mathrm{~Pa} \mathrm{~mole}^{-2}$ and $b=0.0427 \times 10^{-3} \mathrm{~m}^{3} \mathrm{~mole}^{-1}$. The molar heat at constant pressure is $C_{p}=$ $40.225 \mathrm{~J} \mathrm{~mole}^{-1} \mathrm{~K}^{-1}$. Estimate the final temperature.
8.3 The critical temperature and pressure for Nitrogen are, respectively, $T_{\mathrm{cr}}=$ 126.2 K and $p_{\text {cr }}=33.95 \mathrm{bar}$. In the initial state we have 3 kg of Nitrogen at $T=164 \mathrm{~K}$ and at $p_{1} \simeq 67.9 \mathrm{bar}$. The system undergoes an isothermal transformation in which pressure is increased by a factor 2.12 to the final value $p_{2} \simeq 143.9$ bar. We observe that the volume has decreased by the same ratio. Does this mean that the gas in this region of operation behaves very nearly like an ideal gas? Determine the two volumes.
8.4 In an isothermal process of a gas from the initial pressure $p_{1}$ to the final pressure $p_{2}$, the compressibility factor changes from the initial value $Z_{1}$ to the final value $Z_{2}$. Prove that $Z_{2}<Z_{1}\left(p_{2} / p_{1}\right)$.
8.5 Calculate the coefficient of thermal expansion of a real gas as a function of the compressibility factor.
8.6 The vapor pressure of Neon $(\mathrm{Ne})$ is well described by the relation:

$$
\begin{equation*}
\log p=8.75-0.0437 T-\frac{127}{T} \tag{8.89}
\end{equation*}
$$

in which $p$ is the vapor pressure expressed in torr. The critical point of Ne is $p_{\mathrm{cr}}^{(\mathrm{Ne})}=$ 27 atm . and $T_{\mathrm{cr}}^{(\mathrm{Ne})}=44 \mathrm{~K}$. For Argon (Ar) the critical point is $p_{\mathrm{cr}}^{(\mathrm{Ar})}=48 \mathrm{~atm}$ and $T_{\text {cr }}^{(\mathrm{Ne})}=151 \mathrm{~K}$. Find the Argon vapor pressure at $T=135 \mathrm{~K}$.
8.7 The critical point for carbon dioxide is $T_{\text {cr }}=304.20 \mathrm{~K}, p_{\text {cr }}=7.39 \mathrm{MPa}$ and $V_{\text {cr }}=94 \times 10^{-3} \mathrm{~m}^{3} \mathrm{~kg}^{-1}$. Determine the volume occupied by $44 \mathrm{~kg}\left(10^{3} \mathrm{~mole}\right)$ of carbon dioxide at pressure $p=48$ bar and temperature $\theta=122.3^{\circ} \mathrm{C}$.
8.8 A adiabatic cylinder whose total volume is $V_{0}=1.2 \mathrm{~m}^{3}$ is divided into two parts by a partition. One part, whose volume is $V_{1}=470 \mathrm{~L}$ is filled by 44 kg of carbon dioxide at the temperature $T_{0}=600 \mathrm{~K}$ while the other part is empty. The partition is removed and the gas will settle in a new state of equilibrium with final temperature $T$. Supposing that in this temperature interval the molar heat at constant volume is constant and is $C_{V} \simeq 28.85 \mathrm{~J} \mathrm{~mole}^{-1} \mathrm{~K}^{-1}$ and that the gas is well described by the van der Waals equation with $a=363.96 \times 10^{-3} \mathrm{~m}^{6} \mathrm{~Pa} \mathrm{~mole}^{-2}$, estimate the final temperature.

## Chapter 9 <br> Surface Systems


#### Abstract

In this chapter, the general principles of Thermodynamics are applied to two-dimensional systems in which extensiveness is referred to areas of surfaces instead of volumes. The boundary between a liquid and its vapor is considered and is treated, as the first approximation, as a surface system possessing its own energy and entropy which contribute, additively, to the overall energy and entropy of the two phases. The surface tension is defined and the thermodynamical potentials of the surface layer are obtained. Consequently, the general properties of thermodynamical transformations and of specific heat of the surface system are briefly discussed. In particular, the influence of the surface tension on the chemical potential and hence on phase equilibrium is explored and this allows us to treat, with some approximation, the problem of the stability of supersaturated vapor.


Keywords Surface systems • Surface tension • Interface systems • Stability of equilibrium states • Curvature effects - Kelvin's relation • Nucleation in supersaturated vapor $\cdot$ Spinodal decomposition $\cdot$ Corresponding states

### 9.1 Introduction

In the approximation of discontinuous systems, the different phases are considered separated by ideal surfaces of zero thickness such that the intensive properties (for example, the density and therefore the energy density, entropy, etc.) are described as variants, in a discontinuous manner on passing from one phase to the other. In addition even if we assign the transition region a very small thickness, the contribution of all extensive quantities held by it, may often be considered irrelevant in determining the overall state of the system. In some cases, however, this cannot be accepted, and we have to increase the level of complexity of the description. The first step is to consider the transition zone as a third system which possesses its own amount of thermodynamic potentials, some of which cannot be neglected.

To have a more precise idea of how to treat this transition zone, we consider the case of the surface tension which manifests itself in the zone of separation between two phases. In particular we shall consider, in a simplified version, a liquid and its vapor, in mutual equilibrium.

Fig. 9.1 A liquid in equilibrium with its vapor at a given temperature $T$. The interaction among molecules are supposed to be, on average, attractive $r_{0}$ denotes the interaction range. The two molecules A and B are characterized by their distance from the phase separation surface


### 9.2 Surface Tension

Consider a vessel containing a liquid in equilibrium with its vapor all at uniform temperature as outlined in Fig. 9.1. Then, consider a molecule $A$ located in an inner part of the liquid. ${ }^{1}$ Let's denote by $r_{0}$ the range of the intermolecular forces that will be supposed to be attractive. A sphere with radius $r_{0}$ centered on the molecule $A$ will be populated by the other molecules in a statistically homogeneous way, and then the net forces they exert on the molecule will, on average, balance. If we now consider a molecule B close enough to the surface of separation between the two phases, the symmetrical situation no longer exists and, as the density of the vapor is less than that of the liquid, the resultant force acting on it will be directed normally to the surface of separation and directed toward the inside. This allows us to give a first-approximation definition of the surface layer. The closer is the molecule to the surface layer, the more intense is the attractive force. The first consequence of this qualitative argument, is that if we want to bring a molecule from the internal zone (molecule A) to the surface layer, we must do some positive work and, therefore, if we want to increase the area of the surface of separation between the two phases, we must make positive work to bring an adequate number of molecules from the inside the surface zone.

This amount of work is proportional to the increase of the surface area and, in a first approximation, depends only on temperature. ${ }^{2}$

If we denote with $\Sigma$ the area of the separation surface and with $\hat{d} W_{\Sigma}$ the infinitesimal amount of work done to increase the area of the separation surface by the infinitesimal amount $\mathrm{d} \Sigma$, we write:

[^26]\[

$$
\begin{equation*}
\hat{d} W_{\Sigma}=\sigma(T) \mathrm{d} \Sigma . \tag{9.1}
\end{equation*}
$$

\]

The quantity $\sigma(T)$ is called surface tension or interfacial tension. Remembering the meaning of the thermodynamic potentials we see that, if we vary the area of the separation surface in an isothermal process, it is possible to define the surface tension as the increase of free energy $\mathrm{d} F$ per unit area increase $\mathrm{d} \Sigma$. Within the more general context of open systems, by using the Fundamental Relation for the free energy of Eq. (4.30) and the expression in Eq. (9.1), we can write

$$
\begin{equation*}
\sigma=\left(\frac{\partial F}{\partial \Sigma}\right)_{T, V, N} \tag{9.2}
\end{equation*}
$$

$F, T, V, N$ being, for the two-phase system, the total free energy, the temperature, the total volume, and the number of particles (molecules), respectively. A dimensional analysis of $\sigma$ leads to the following identity:

$$
\begin{equation*}
[\sigma]=\frac{[\text { energy }]}{[\text { area }]}=\frac{[\text { force }]}{[\text { length }]} . \tag{9.3}
\end{equation*}
$$

In other words, for any line one can imagine to draw on the surface $\Sigma$, the surface tension $\sigma$ may also be interpreted as the force per unit length acting perpendicularly to that line in order to keep the surface separating two phases in a stable equilibrium state. ${ }^{3}$ For this reason, it is common to report measures of the surface tension either in $\mathrm{J} / \mathrm{m}^{2}$ or $\mathrm{N} / \mathrm{m}$.

The surface tension is a property of the two phases in mutual equilibrium. It depends on the difference in number density of molecules in the two phases which, in turn, depends on the temperature. At "sufficiently low" temperatures ( $\lesssim 0.65 T_{c}$ ), where the molecular density of the vapor is small compared to that of the liquid, the surface tension depends very little on the presence of the vapor and in this case we may speak simply of "surface tension of the liquid". It depends only on the number density of the molecules of the liquid, and, therefore, we expect that its temperature dependence is connected in a simple way to the coefficient of thermal expansion.

More generally, the coefficient of surface tension can also be defined when the liquid is in contact with other materials but in this case, it also depends on the specific nature of these materials. We will come back on this aspect at the end of the chapter in Sect. 9.6.4.

[^27]
### 9.3 Properties of Surface Layers

Consider a portion of the surface layer between two phases, of area $\Sigma$, at the temperature $T$ and with very small thickness in order to consider the volume of the layer negligible. For this system the fundamental equation, in differential form, will be written as

$$
\begin{equation*}
\mathrm{d} U=T \mathrm{~d} S+\sigma \mathrm{d} \Sigma \tag{9.4}
\end{equation*}
$$

and in finite form $S=S(U, \Sigma)$ or $U=U(S, \Sigma)$.
The extensive nature of energy and entropy will be expressed by the relationships:

$$
\begin{equation*}
U=u_{\Sigma} \Sigma, \quad S=s_{\Sigma} \Sigma \tag{9.5}
\end{equation*}
$$

where $u_{\Sigma}=u_{\Sigma}(T)$ and $s_{\Sigma}=s_{\Sigma}(T)$ are, respectively, the surface energy density and the surface entropy density and they depend only on temperature. Then

$$
\begin{align*}
u_{\Sigma} & =\left(\frac{\partial U}{\partial \Sigma}\right)_{T}  \tag{9.6}\\
s_{\Sigma} & =\left(\frac{\partial S}{\partial \Sigma}\right)_{T} \tag{9.7}
\end{align*}
$$

These quantities depend only on the value of surface tension and can be determined in the following way.

Regarding $s_{\Sigma}$ let us refer to Eq. (9.4) and express the latter as a function of temperature and surface area. To do this, we express the differential of the entropy in the differentials of the area and of temperature:

$$
\begin{equation*}
\mathrm{d} S=s_{\Sigma} \mathrm{d} \Sigma+\frac{\mathrm{d} s_{\Sigma}}{\mathrm{d} T} \Sigma \mathrm{~d} T \tag{9.8}
\end{equation*}
$$

and we obtain

$$
\begin{equation*}
\mathrm{d} U=T \frac{\mathrm{~d} s_{\Sigma}}{\mathrm{d} T} \Sigma \mathrm{~d} T+\left(\sigma+T s_{\Sigma}\right) \mathrm{d} \Sigma \tag{9.9}
\end{equation*}
$$

and then applying the Schwarz theorem we get

$$
\begin{equation*}
s_{\Sigma}=-\frac{\mathrm{d} \sigma}{\mathrm{~d} T} \tag{9.10}
\end{equation*}
$$

Similarly, we write Eq. (9.4) putting in evidence the differential of the entropy and express the differential of the energy in terms of surface and temperature variables:

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \frac{\mathrm{~d} u_{\Sigma}}{\mathrm{d} T} \Sigma \mathrm{~d} T+\left(\frac{1}{T} u_{\Sigma}-\frac{\sigma}{T}\right) \mathrm{d} \Sigma . \tag{9.11}
\end{equation*}
$$

As before, equating the cross derivatives, we get

$$
\begin{equation*}
u_{\Sigma}=\left(\sigma-T \frac{d \sigma}{d T}\right) \tag{9.12}
\end{equation*}
$$

We can now write the expressions for the energy and entropy:

$$
\begin{align*}
& U=\left(\sigma-T \frac{\mathrm{~d} \sigma}{\mathrm{~d} T}\right) \Sigma  \tag{9.13}\\
& S=-\frac{\mathrm{d} \sigma}{\mathrm{~d} T} \Sigma \tag{9.14}
\end{align*}
$$

(we recell that $\mathrm{d} \sigma / \mathrm{d} T \leq 0$ ). Having written the expressions for the energy and, the entropy for a surface layer we can obtain other relevant properties. For instance, the heat capacity at constant area, $C_{\Sigma}$ and the specific (per unit area) heat, $c_{\Sigma}$, will be

$$
\begin{align*}
& C_{\Sigma}=T\left(\frac{\partial S}{\partial T}\right)_{\Sigma}=-T \frac{\mathrm{~d}^{2} \sigma}{\mathrm{~d} T^{2}} \Sigma  \tag{9.15}\\
& c_{\Sigma}=T\left(\frac{\partial s_{\Sigma}}{\partial T}\right)_{\Sigma}=-T \frac{\mathrm{~d}^{2} \sigma}{\mathrm{~d} T^{2}} \tag{9.16}
\end{align*}
$$

The free energy, which is defined as $F=U-T S$, will be

$$
\begin{equation*}
F=\sigma \Sigma \tag{9.17}
\end{equation*}
$$

and this could be obtained directly from the definition of surface tension Eq. (9.1) and from the assumption that it depends on temperature only. In the following example we estimate the order of magnitude of the thermal effects occurring in coalescence.

Example 9.1 Consider, as an example, the energy balance in a process of coalescence of a certain number of small drops in one larger drop. Suppose to have very small drops of water at the temperature $\theta=25^{\circ} \mathrm{C}$ with radius $r \simeq 1 \mu \mathrm{~m}$ and suppose that they merge to form one drop with radius $R \simeq 1 \mathrm{~mm}$. If we denote by $N$ the number of small drops involved, from volume conservation (incompressible liquid) we have

$$
\begin{equation*}
N=\left(\frac{R}{r}\right)^{3} \simeq 10^{9} \tag{9.18}
\end{equation*}
$$

If we denote by $\Sigma$ the surface area of the large drop and by $\Sigma_{0}$ the total surface area of the $N$ small drops, we have

$$
\begin{equation*}
\Sigma=4 \pi N^{2 / 3} r^{2}=N^{-1 / 3} \Sigma_{0} \tag{9.19}
\end{equation*}
$$

and hence, the variation of the total surface area in the process is

$$
\begin{equation*}
\Delta \Sigma=\Sigma-\Sigma_{0}=-\Sigma_{0}\left(1-N^{-1 / 3}\right) \tag{9.20}
\end{equation*}
$$

Let us refer to the energy possessed by the surface layers in the two configurations. If we denote by $\Delta U_{\Sigma}$ the variation of this part of the total energy of the system in the coalescence process, we may write

$$
\begin{equation*}
\Delta U_{\Sigma}=\sigma \Delta \Sigma=-\sigma \Sigma_{0}\left(1-N^{-1 / 3}\right) \simeq-\sigma \Sigma_{0} \tag{9.21}
\end{equation*}
$$

where the approximate value is due to the very large value of $N$ in this example. Taking for the surface tension of water at $\theta=25^{\circ} \mathrm{C}$, the approximate value $\sigma\left(\theta=25^{\circ} \mathrm{C}\right) \simeq 72 \times 10^{-3} \mathrm{~J} \mathrm{~m}^{-2}$, we have:

$$
\begin{equation*}
\Delta U_{\Sigma} \simeq-72 \times 10^{-3} \times 10^{9} \times 4 \pi 10^{-12} \simeq 9.05 \times 10^{-4} \mathrm{~J} \tag{9.22}
\end{equation*}
$$

Due to energy conservation, the final drop will experience an increase of temperature $\Delta T$ given by

$$
\begin{equation*}
\Delta T=\frac{-\Delta U_{\Sigma}}{C_{\mathrm{drop}}} \tag{9.23}
\end{equation*}
$$

where $C_{\text {drop }}$ is the heat capacity of the final drop. The mass of the drop is approximately $m \simeq 4.18 \times 10^{-6} \mathrm{~kg}$ and hence $C_{\text {drop }} \simeq 4.18 \times 10^{3} \times 4.18 \times 10^{-6} \simeq 1.75 \times$ $10^{-2} \mathrm{~J} \mathrm{~K}^{-1}$. The temperature variation is obtained from Eq. (9.23):

$$
\begin{equation*}
\Delta T \simeq \frac{9.05 \times 10^{-4} \mathrm{~J}}{1.75 \times 10^{-2} \mathrm{~J} \mathrm{~K}^{-1}} \simeq 5.2 \times 10^{-2} \mathrm{~K} \tag{9.24}
\end{equation*}
$$

Similarly let us consider Mercury. The surface tension is $\sigma\left(\theta \simeq 20^{\circ} \mathrm{C}\right) \simeq$ $0.559 \mathrm{~J} \mathrm{~m}^{-2}$ and then, for the energy variation in the process we have

$$
\begin{equation*}
\Delta U_{\Sigma} \simeq-559 \times 10^{-3} \times 10^{9} \times 4 \pi 10^{-12} \simeq 7.03 \times 10^{-3} \mathrm{~J} \tag{9.25}
\end{equation*}
$$

For the heat capacity we need the density and the specific heat of Mercury. We have, respectively, for the density $\varrho \simeq 1.34 \times 10^{4} \mathrm{~kg} \mathrm{~m}^{-3}$ and for the specific heat $C_{\mathrm{Hg}}^{*} \simeq 0.14 \times 10^{3} \mathrm{~J} \mathrm{~kg}^{-1}$ and hence for the heat capacity:

$$
\begin{equation*}
C_{\mathrm{Hg}}^{*} \simeq 4.188 \times 10^{-9} \times 1.34 \times 10^{4} \times 0.14 \times 10^{3} \simeq 0.785 \times 10^{-2} \mathrm{~J} \mathrm{~K}^{-1} \tag{9.26}
\end{equation*}
$$

Then the temperature variation results

$$
\begin{equation*}
\Delta T \simeq \frac{7.03 \times 10^{-3} \mathrm{~J}}{0.785 \times 10^{-2} \mathrm{~J} \mathrm{~K}}{ }^{-1} \simeq 0.9 \mathrm{~K} \tag{9.27}
\end{equation*}
$$

### 9.3.1 Stability of Equilibrium States

The stability criteria for equilibrium states derive directly from the fundamental Principles of Thermodynamics as we have already widely discussed in Sect. (4.3.6). Let's take a surface layer with total area $\Sigma$ and consider it as composed by two arbitrary subsystems 1 and 2 with areas $\Sigma_{1}$ and $\Sigma_{2}$, respectively. The extensivity of extensive quantities implies

$$
\begin{align*}
& \Sigma=\Sigma_{1}+\Sigma_{2}  \tag{9.28}\\
& U_{\Sigma}=U_{1}+U_{2}  \tag{9.29}\\
& S_{\Sigma}=S_{1}+S_{2} \tag{9.30}
\end{align*}
$$

Let the system be isolated, with constant area, and consider a virtual, infinitesimal transformation in which the area of one subsystem changes by an infinitesimal amount and let's denote with $T_{1}$ and $T_{2}$ the temperatures of the two subsystems. For this infinitesimal process we may write

$$
\begin{align*}
& \mathrm{d} \Sigma=0 \Rightarrow \mathrm{~d} \Sigma_{1}=-\mathrm{d} \Sigma_{2}  \tag{9.31}\\
& \mathrm{~d} U_{\Sigma}=0 \Rightarrow \mathrm{~d} U_{1}=-\mathrm{d} U_{2}  \tag{9.32}\\
& \mathrm{~d} S_{\Sigma}=\mathrm{d} S_{1}+\mathrm{d} S_{2} \tag{9.33}
\end{align*}
$$

The entropy variations of the two parts are

$$
\begin{align*}
& \mathrm{d} S_{1}=\frac{1}{T_{1}} \mathrm{~d} U_{1}-\frac{\sigma_{1}}{T_{1}} \mathrm{~d} \Sigma_{1}  \tag{9.34}\\
& \mathrm{~d} S_{2}=\frac{1}{T_{2}} \mathrm{~d} U_{2}-\frac{\sigma_{2}}{T_{2}} \mathrm{~d} \Sigma_{2} \tag{9.35}
\end{align*}
$$

then for the entire system we write

$$
\begin{equation*}
\mathrm{d} S_{\Sigma}=\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right) \mathrm{d} U_{1}-\left(\frac{\sigma_{1}}{T_{1}}-\frac{\sigma_{2}}{T_{2}}\right) \mathrm{d} \Sigma_{1} \tag{9.36}
\end{equation*}
$$

The general stability criteria discussed in Sect.4.3.6 require that a stable (or metastable) configuration, with the given constraints, corresponds to a point in which entropy possess a (relative) maximum. Therefore for every infinitesimal, virtual, transformation we require that $\mathrm{d} S_{\Sigma}=0$ and from this it follows that

$$
\begin{equation*}
\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right) \mathrm{d} U_{1}-\left(\frac{\sigma_{1}}{T_{1}}-\frac{\sigma_{2}}{T_{2}}\right) \mathrm{d} \Sigma_{1}=0 \tag{9.37}
\end{equation*}
$$

Since the variations $\mathrm{d} U_{1}$ and $\mathrm{d} \Sigma_{1}$ can be taken to be independent of each other we derive the conditions:

$$
\begin{align*}
& T_{1}=T_{2},  \tag{9.38}\\
& \sigma_{1}=\sigma_{2} . \tag{9.39}
\end{align*}
$$

So we are led to the conclusion that in a surface layer in a stable equilibrium state, temperature, and surface tension must be uniform.

### 9.4 Interfaces at the Contact Between Two Phases in Equilibrium

We consider now two phases in mutual equilibrium separated by a surface layer with area $\Sigma$. What we can do, now, is to build a first modeling of the surface layer of separation based on one single parameter, i.e., the surface tension, and, as a consequence, we are able to attribute to the surface layer, well-defined expressions for its thermodynamic properties.

In this new context, therefore, we will consider the overall system as a system composed of three subsystems: phase 1 , phase 2 , and the surface layer and their properties will be denoted by the indices 1,2 and $\Sigma$, respectively.

At the surface phase we will assign a null volume and, consequently, a null (negligible) number of moles. For the overall system, the extensive properties will be written as follows:

$$
\begin{align*}
V & =V_{1}+V_{2}  \tag{9.40}\\
n & =n_{1}+n_{2}  \tag{9.41}\\
U & =U_{1}+U_{2}+U_{\Sigma}  \tag{9.42}\\
S & =S_{1}+S_{2}+S_{\Sigma} \tag{9.43}
\end{align*}
$$

The external constraints are the following:
(1) Closed system: $\mathrm{d} n=0$;
(2) Constant volume: $\mathrm{d} V=0$;
(3) Isolated system: $\mathrm{d} U=0$ that is $\mathrm{d} U_{\Sigma}=-\left(\mathrm{d} U_{1}+\mathrm{d} U_{2}\right)$.

The condition for stable or metastable equilibrium is given by the points of maximum entropy, which implies that for each virtual infinitesimal process compatible with the assigned constraints we must have

$$
\begin{equation*}
\mathrm{d} S=0 \tag{9.44}
\end{equation*}
$$

For the two tridimensional phases we may write

$$
\begin{equation*}
\mathrm{d} S_{1,2}=\frac{1}{T_{1,2}} \mathrm{~d} U_{1,2}+\frac{p_{1,2}}{T_{1,2}} \mathrm{~d} V_{1,2}-\frac{\mu_{1,2}}{T_{1,2}} \mathrm{~d} n_{1,2}, \tag{9.45}
\end{equation*}
$$

while for the surface phase:

$$
\begin{equation*}
\mathrm{d} S_{\Sigma}=\frac{1}{T_{\Sigma}} \mathrm{d} U_{\Sigma}-\frac{\sigma}{T_{\Sigma}} \mathrm{d} \Sigma \tag{9.46}
\end{equation*}
$$

After adding and taking into account the constraints we get

$$
\begin{align*}
& \left(\frac{1}{T_{1}}-\frac{1}{T_{\Sigma}}\right) \mathrm{d} U_{1}+\left(\frac{1}{T_{2}}-\frac{1}{T_{\Sigma}}\right) \mathrm{d} U_{2}-\left(\frac{\mu_{1}}{T_{1}}-\frac{\mu_{2}}{T_{2}}\right) \mathrm{d} n_{1}+  \tag{9.47}\\
& +\left(\frac{p_{1}}{T_{1}}-\frac{p_{2}}{T_{2}}\right) \mathrm{d} V_{1}-\frac{\sigma}{T_{\Sigma}} \mathrm{d} \Sigma=0
\end{align*}
$$

It should be observed that the variations of the volume $V_{1}$ (or, it would be the same, for the volume $V_{2}$ ) and the variation of the area of the separation surface, $\mathrm{d} \Sigma$, are not mutually independent. From fundamental geometry we know that

$$
\begin{equation*}
\frac{\mathrm{d} \Sigma}{\mathrm{~d} V}=\frac{1}{r_{1}}+\frac{1}{r_{2}} \tag{9.48}
\end{equation*}
$$

where $r_{1}$ and $r_{2}$ are the two principal radii of curvature of the surface considered, as shown in Fig. 9.2. In the simple case of a spherical surface we have

$$
\begin{equation*}
\frac{\mathrm{d} \Sigma}{\mathrm{~d} V}=\frac{2}{r} \tag{9.49}
\end{equation*}
$$

where $r$ is the radius of the sphere. With this clarification, Eq. (9.47) becomes

$$
\begin{align*}
& \left(\frac{1}{T_{1}}-\frac{1}{T_{\Sigma}}\right) \mathrm{d} U_{1}+\left(\frac{1}{T_{2}}-\frac{1}{T_{\Sigma}}\right) \mathrm{d} U_{2}-\left(\frac{\mu_{1}}{T_{1}}-\frac{\mu_{2}}{T_{2}}\right) \mathrm{d} n_{1}+  \tag{9.50}\\
& +\left[\frac{p_{1}}{T_{1}}-\frac{p_{2}}{T_{2}}-\frac{\sigma}{T_{\Sigma}}\left(\frac{1}{r_{1}}+\frac{1}{r_{2}}\right)\right] \mathrm{d} V_{1}=0 .
\end{align*}
$$

Now all the differentials are mutually independent so Eq. (9.50) implies

Fig. 9.2 Principal radii of curvature of a surface separating two subsystems (e.g., two phases)


$$
\begin{align*}
T_{1} & =T_{\Sigma}  \tag{9.51}\\
T_{2} & =T_{\Sigma}  \tag{9.52}\\
\mu_{1} & =\mu_{2}  \tag{9.53}\\
p_{1} & =p_{2}+\sigma\left(\frac{1}{r_{1}}+\frac{1}{r_{2}}\right) . \tag{9.54}
\end{align*}
$$

Two things need to be highlighted: the first, as seen from Eq. (9.53) the necessary condition for the phase equilibrium is the equality of the chemical potentials but in this case, it should be noted that the two phases will be at the same temperature but at a different pressure. The second consideration is the role played by the curvature of the surface of separation as seen from Eq. (9.54). For a flat surface, that is with $r_{1}, r_{2} \rightarrow \infty$, the pressures on the two phases are equal but in the case of a curved surface, the difference between two pressures may be significant.

In the particular case of a spherical separation surface where $r_{1}=r_{2}=r$, we get

$$
\begin{equation*}
p_{1}=p_{2}+\frac{2 \sigma}{r} \tag{9.55}
\end{equation*}
$$

stop The expression in Eq. (9.55) is known as Laplace equation and the pressure of curvature is also known as Laplace pressure of a droplet or a bubble. We notice that we obtained the Laplace equation by following only a thermodynamic approach. It would be rather easy to recover the same result in a purely mechanical way by treating the surface as an elastic film nevertheless, from the thermodynamical point of view, the two situations are a little different and the analogy between surface tension phenomena and elasticity conceals some dangers.

In order to have the order of magnitude of the pressure difference consider, as an example, the case of a spherical drop of water at the temperature $20^{\circ} \mathrm{C}$ and immersed in a saturated atmosphere. At this temperature the surface tension is approximately $\sigma \simeq 0.073 \mathrm{Nm}^{-1}$ while the pressure of saturated vapor is $p\left(20^{\circ} \mathrm{C}\right) \simeq 17.51 \mathrm{~mm} \mathrm{Hg} \simeq 0.023 \mathrm{~atm}$. For a drop of radius equal to $10 \mu \mathrm{~m}$ the internal pressure that is approximately:

$$
\begin{align*}
& \sigma\left(\frac{1}{r_{1}}+\frac{1}{r_{2}}\right)=\frac{2 \sigma}{r} \simeq 0.146 \mathrm{~atm}  \tag{9.56}\\
& p_{1} \simeq 0.023+0.146 \tag{9.57}
\end{align*}=0.169 \mathrm{~atm} .
$$

### 9.5 Curvature Effect on Vapor Pressure: Kelvin's Relation

According to Eq. (9.55) inside a drop of liquid pressure is enhanced and, if the curvature radius is sufficiently small, the pressure increase may be very high. It follows that the chemical potential of the liquid may change significantly and, as a consequence, the vapor pressure of the surrounding vapor increases accordingly.


Fig. 9.3 A and B represent, respectively, the states in which we have liquid and saturated vapor in mutual equilibrium at the same temperature $T . \mathrm{B}_{1}$ represents the supersaturated vapor at pressure $p_{\text {ss }}$ and $\mathrm{A}_{1}$ the state of the liquid within the droplet at pressure $p_{\text {liq. }}$. They are both at the same temperature $T$. The chemical potential in A and B has the same value

Let us have a pure vapor at temperature $T$, kept constant, and let $p_{\mathrm{s}}$ be the saturation vapor pressure at that temperature as provided by the Clapeyron's equation (7.9). ${ }^{4}$ Suppose that, within the vapor, a spherical drop, of radius $r$, is formed and denote with $p_{\text {liq }}$ the total pressure inside it. In order to reestablish the equilibrium condition between vapor and liquid, the pressure of the vapor phase must be brought to a new value such that the two chemical potentials are equal. Let us denote with $p_{\mathrm{ss}}$ this new value. With reference to Fig. 9.3 let us denote with $A_{1}$ the thermodynamical state of the liquid and with $B_{1}$ the state to which the vapor must be brought so that it is again in equilibrium with the drop. It easy to see that it must be a supersaturated vapor and then its pressure will be denoted by $p_{s s}$ ( $p_{\mathrm{ss}}>p_{\mathrm{s}}$ as will be proved below).

If a spherical drop of radius $r$ is formed then, as we have seen, inside the drop the pressure of the liquid is given by

$$
\begin{equation*}
p_{\mathrm{liq}}=p_{\mathrm{ss}}+\frac{2 \sigma}{r} \tag{9.58}
\end{equation*}
$$

$p_{s s}$ being the pressure external to the drop.
The chemical potential in $\mathrm{A}_{1}$ can be obtained starting from its value in A and by integration along the isotherm to the point $\mathrm{A}_{1}$ :

$$
\begin{equation*}
\mu_{\mathrm{liq}}\left(T, p_{\mathrm{liq}}\right)=\mu_{\mathrm{liq}}\left(T, p_{\mathrm{s}}\right)+\int_{\mathrm{A}}^{\mathrm{A}_{\mathrm{I}}}\left(\frac{\partial \mu}{\partial p}\right)_{T} \mathrm{~d} p \tag{9.59}
\end{equation*}
$$

[^28]Since ${ }^{5}$

$$
\left(\frac{\partial \mu}{\partial p}\right)_{T}=V_{\mathrm{m}}^{\mathrm{liq}}(T, p)
$$

where $V_{\mathrm{m}}^{\mathrm{liq}}(T, p)$ is the molar volume of the liquid at temperature $T$ and at the generic pressure $p$. If we neglect the change of volume of the liquid with pressure then the integral becomes trivial and we get

$$
\begin{equation*}
\mu_{\mathrm{liq}}\left(T, p_{\mathrm{liq}}\right)=\mu_{\mathrm{liq}}\left(T, p_{\mathrm{s}}\right)+V_{\mathrm{m}}^{\mathrm{liq}}(T)\left(p_{\mathrm{ss}}-p_{\mathrm{s}}+\frac{2 \sigma}{r}\right) \tag{9.60}
\end{equation*}
$$

In a similar way, we proceed to determine the chemical potential of supersaturated vapor starting from its value in the state $B$ and integrating along the isotherm to the pressure $p_{\text {ss }}\left(\right.$ state $\left.\mathrm{B}_{1}\right)$ :

$$
\begin{equation*}
\mu_{\mathrm{ss}}\left(T, p_{\mathrm{ss}}\right)=\mu_{\text {vap }}\left(T, p_{\mathrm{s}}\right)+\int_{\mathrm{B}}^{\mathrm{B}_{1}}\left(\frac{\partial \mu}{\partial p}\right)_{T} \mathrm{~d} p . \tag{9.61}
\end{equation*}
$$

In this case $(\partial \mu / \partial p)_{T}=V_{\mathrm{m}}^{\text {vap }}(T, p)$ and, describing the vapor with the equation of state of ideal gases:

$$
\begin{align*}
& \mu_{\mathrm{ss}}\left(T, p_{\mathrm{ss}}\right)=\mu_{\text {vap }}\left(T, p_{\mathrm{s}}\right)+\int_{\mathrm{B}}^{\mathrm{B}_{1}} \frac{R T}{p} \mathrm{~d} p  \tag{9.62}\\
& \mu_{\mathrm{ss}}\left(T, p_{\mathrm{ss}}\right)=\mu_{\text {vap }}\left(T, p_{\mathrm{s}}\right)+R T \ln \left(\frac{p_{\mathrm{ss}}}{p_{\mathrm{s}}}\right) \tag{9.63}
\end{align*}
$$

Since

$$
\begin{equation*}
\mu_{\text {liq }}\left(T, p_{\mathrm{s}}\right)=\mu_{\mathrm{vap}}\left(T, p_{\mathrm{s}}\right) \tag{9.64}
\end{equation*}
$$

let us define

$$
\begin{equation*}
\Delta \mu=\mu_{\mathrm{ss}}\left(T, p_{\mathrm{ss}}\right)-\mu_{\mathrm{liq}}\left(T, p_{\mathrm{liq}}\right)=R T \ln \left(\frac{p_{\mathrm{ss}}}{p_{\mathrm{s}}}\right)-V_{\mathrm{m}}^{\mathrm{liq}}(T)\left(p_{\mathrm{ss}}-p_{\mathrm{s}}+\frac{2 \sigma}{r}\right) . \tag{9.65}
\end{equation*}
$$

The last term, assuming that the logarithmic term is of the order of unity, is of the order $R T \sim p_{\mathrm{s}} V_{\mathrm{m}}^{\text {vap }}$ where $V_{\mathrm{m}}^{\text {vap }}$ is the molar volume of saturated vapor at temperature $T$ and pressure $p_{\mathrm{s}}$. As we supposed to be far enough from the critical temperature to be able to use the approximation of an ideal gas for vapor, we'll have $V_{\mathrm{m}}^{\text {vap }} \gg V_{\mathrm{m}}^{\text {liq }}$ so we can well approximate:

[^29]\[

$$
\begin{equation*}
\Delta \mu \simeq R T \ln \left(\frac{p_{\mathrm{ss}}}{p_{\mathrm{s}}}\right)-V_{\mathrm{m}}^{\mathrm{liq}}(T) \frac{2 \sigma}{r} \tag{9.66}
\end{equation*}
$$

\]

In order to have equilibrium between the drop and the ambient vapor we require

$$
\begin{equation*}
\Delta \mu=0 \tag{9.67}
\end{equation*}
$$

and this allows to determine the saturation pressure for a liquid-vapor system with curved separation surface:

$$
\begin{equation*}
\ln \left(\frac{p_{\mathrm{ss}}}{p_{\mathrm{s}}}\right)=\frac{2 \sigma}{r R T} V_{\mathrm{m}}^{\mathrm{liq}}(T) \tag{9.68}
\end{equation*}
$$

Notice that $r$ is the curvature radius of the liquid and it must be understood as positive if the separating surface is convex, negative if it is concave. For instance if we introduce a capillary in the liquid and the latter does not wet the capillary, then the separation surface seen from the liquid is convex and then the saturation pressure of the vapor in the capillary is higher $p_{s s}>p_{s}$.

If the liquid wets the capillary the surface seen from the liquid is concave, the radius $r$ is negative and the saturation pressure of the vapor is less than the saturation pressure for flat surface (i.e., than that given by Eq. (7.9).

Equation (9.66) which leads to Kelvin's equation (9.68) can be examined from another point of view and this introduces, as a first approximation, the problem of the stability of metastable states. Let us keep the external pressure $p_{s s}$ as fixed and discuss Eq. (9.66) in terms of the size of different drops.

First, let us define a characteristic size, denoted by $r_{e}$, such that the drop is in equilibrium with the ambient vapor. The equilibrium radius is given by

$$
\begin{equation*}
r_{\mathrm{e}} \simeq \frac{2 \sigma V_{\mathrm{m}}^{\mathrm{liq}}}{R T \ln \left(\frac{p_{\mathrm{ss}}}{p_{\mathrm{s}}}\right)} \tag{9.69}
\end{equation*}
$$

Looking at Eq. (9.66) it is immediate to recognize that for drops with size smaller than $r_{e}$ the difference in the chemical potentials will be

$$
\begin{equation*}
\Delta \mu<0 \tag{9.70}
\end{equation*}
$$

and we expect the drop to evaporate. The equilibrium radius given in Eq. (9.69) seems to constitute the criterion that characterizes the dimension of the perturbations that are spontaneously reabsorbed in a supersaturated vapor. The issue will be treated with some rigor in Sect. 9.6 nevertheless it is useful discuss some orders of magnitude.

To this aim, let us consider steam at the temperature of $20^{\circ} \mathrm{C}$. We have seen that at this temperature the surface tension of water amounts to $\sigma \simeq 0.073 \mathrm{Nm}^{-1}$. As regards the molar volume of the liquid, we can approximately take the usual
value $V_{\mathrm{m}}^{\mathrm{liq}} \simeq 18 \mathrm{~cm}^{3}=1.8 \times 10^{-5} \mathrm{~m}^{3}$. As for the logarithmic term let us write the value $p_{\mathrm{ss}}$ of the pressure of the supersaturated steam in the form $p_{\mathrm{ss}}=p_{\mathrm{s}}+\Delta p$, and consider $\Delta p<p_{\mathrm{s}}$. Then, we have

$$
\begin{equation*}
\ln \left(1+\frac{\Delta p}{p_{\mathrm{s}}}\right) \simeq \frac{\Delta p}{p_{\mathrm{s}}} \tag{9.71}
\end{equation*}
$$

The expression for the equilibrium radius Eq. (9.69) can be written in the form

$$
\begin{equation*}
r_{\mathrm{e}} \simeq \frac{V_{\mathrm{m}}^{\mathrm{liq}}}{V_{\mathrm{m}}^{\text {vap }}} \frac{2 \sigma}{\Delta p} \tag{9.72}
\end{equation*}
$$

At the temperature $\theta \simeq 20^{\circ} \mathrm{C}$ is $p_{\mathrm{s}} \simeq 17.51 \mathrm{~mm} \mathrm{Hg} \simeq 2.3 \times 10^{3} \mathrm{~Pa}$ and thus the molar volume of the saturated steam will be

$$
V_{\mathrm{m}}^{\text {vap }}=\frac{R T}{p_{\mathrm{s}}} \simeq \frac{2.44 \times 10^{3} \mathrm{~J}}{2.3 \times 10^{3} \mathrm{~Pa}} \simeq 1.06 \mathrm{~m}^{3}
$$

Let's take for $\Delta p$ the value $\Delta p \sim 4 \mathrm{~mm} \mathrm{Hg} \simeq 5.3 \times 10^{2} \mathrm{~Pa}$ (that is, approximately $23 \%$ of the saturated vapor pressure) for the equilibrium radius we obtain the value

$$
\begin{equation*}
r_{\mathrm{e}} \simeq 4.67 \times 10^{-9} \mathrm{~m} \tag{9.73}
\end{equation*}
$$

We can express this critical size of the fluctuation in terms of the number of molecules involved in the density fluctuation.

The volume of the characteristic droplet is approximately $V_{\text {drop }} \simeq 4.26 \times$ $10^{-25} \mathrm{~m}^{3}$. Since the mass of a molecule of water (equal to about 18 times the mass of the proton) is roughly $m_{\mathrm{H}_{2} \mathrm{O}} \simeq 3 \times 10^{-26} \mathrm{~kg}$ and we assume the approximate value $10^{3} \mathrm{~kg} \mathrm{~m}^{-3}$ for the density of water, we get, for the mass of the droplet, the value $m_{\text {drop }} \simeq 4.26 \times 10^{-22} \mathrm{~kg}$. This corresponds to a drop formed by a number of molecules $N_{\text {molec }}$ of the order of

$$
\begin{equation*}
N_{\mathrm{molec}} \simeq 1.4 \times 10^{4} \tag{9.74}
\end{equation*}
$$

We note that the number of molecules within the critical radius is very sensitive to the pressure difference as we find that

$$
\begin{equation*}
N_{\mathrm{molec}} \propto(\Delta p)^{-3} \tag{9.75}
\end{equation*}
$$

With similar arguments, it is easy to show that Eq. (9.69) can be applied to the formation of a vapor bubble when entering the coexistence region from the state A of Fig.9.3. In this case, the superstaurated pressure $p_{\text {ss }}$ needs to be replaced by the superheated pressure of the liquid, and the molar volume of the liquid droplet with the one of the vapor bubble. The nucleation rate of droplets (or bubbles) formed at $r_{\mathrm{e}}$ by density fluctuations rapidly increases as the system is progressively penetrating
inside the coexistence region. Indeed, before reaching the instability region, it is possible to individuate an intermediate, sharp region, known as fuzzy nucleation line, at which the nucleation and growth of the new phase are in practice instantaneous. As a consequence, the lifetime of the metastable phases inside the coexistence region rapidly decreases as the instability region is approached, and is connected to the nucleation processes.

### 9.6 Nucleation Processes and Metastability in Supersaturated Vapor

Some phase transitions belong to our normal experience. For example, we consider obvious that water, cooled to zero degrees Celsius, solidifies becoming ice. Likewise, the condensation of water vapor in drops of liquid water when the temperature of the steam is lowered, belongs or to everyday experience. Nevertheless, we know that if the water is completely pure and without mechanical disturbances, the cooling may proceed beyond the phase transition points without phase separations (if we operate in an appropriate way). The states we may observe operating in this way are called supersaturated vapor or supercooled liquids and they are metastable states. Indeed if they are perturbed with enough intensity they spontaneously undergo a phase separation which proves to be the more stable configuration. Within this evidence we aim to deepen the knowledge of the mechanism that is responsible for triggering the phase transitions. The theory which explains this very important class of phenomena is called Nucleation Theory of Phase Transitions and is based on the idea that in metastable phases some very small portions of matter form aggregates of more stable phase, called seeds or embryos, which, in their turn, are either reabsorbed or grow and initiate the phase transition.

These embryos may be formed either by stochastic processes in a pure homogeneous phase, or by condensation caused by external agents like, for instance, ions or impurities in the walls. In the former case, we speak of homogeneous nucleation in the latter of heterogeneous nucleation.

Let us now discuss the equilibrium between a small liquid drop and its supersaturated vapor, when the latter is maintained at constant temperature $T_{0}$ and pressure $p_{0}>p_{\mathrm{s}}$ greater than the vapor pressure $p_{\mathrm{s}}$ for the equilibrium liquid-vapor. With reference to Fig. 9.3 the pressure $p_{0}$ corresponds to $p_{\mathrm{ss}}$. The pressure of the liquid inside the drop of radius $r$ is

$$
\begin{equation*}
p_{1}=p_{0}+\frac{2 \sigma\left(T_{0}\right)}{r} \tag{9.76}
\end{equation*}
$$

on account for the surface tension $\sigma=\sigma\left(T_{0}\right)$ at the temperature $T_{0}$. Since the vapor is supersaturated, the equilibrium configuration would be that of the liquid at the saturated pressure in equilibrium with the vapor. However, it is well known that such supersaturated vapor do not immediately change to liquid as far as it is com-
pressed to $p_{\mathrm{s}}$. Rather, if the pressure $p_{0}$ is only slightly greater than $p_{\mathrm{s}}$, the vapor can rest in a metastable equilibrium state for a long time. Ideally, in the absence of any perturbation this metastable state can be kept indefinitely. Let us consider a nucleus of a liquid drop formed due to a spontaneous fluctuation of the vapor density (homogeneous nucleation).

We regard the metastable phase as an external medium at $T_{0}$ and $p_{0}$ containing the nucleus, and we aim to calculate the work necessary to form of the nucleus. The volume $V_{0}$ of the medium is so large compared to volume of the droplet $V_{1}$, that $T_{0}$ and $p_{0}$ can be reasonably considered constant during the nucleation process. Within the constraint of a surrounding medium at constant $p_{0}$ and $T_{0}$, we need to make use of the available work $\Lambda$ introduced in Eq. (3.82) to calculate the work required to form a liquid drop with free energy per unit area $\sigma\left(T_{0}\right)$. By using Eq. (3.84) for the availability $\Phi_{\Lambda}=\Delta \Lambda$, we can write

$$
\begin{equation*}
W=\Phi_{\Lambda}=\Delta \Lambda=\Delta\left(U-T_{0} S+p_{0} V\right) \tag{9.77}
\end{equation*}
$$

Since, in this case, the process occurs at constant temperature equal to the temperature $T_{0}$ of the surrounding vapor, the work in Eq. (9.77) can be written in terms of the free energy:

$$
\begin{equation*}
\Phi_{\Lambda}=\Delta\left(F+p_{0} V\right) \tag{9.78}
\end{equation*}
$$

To calculate the (finite) variation of $F+p_{0} V$ in Eq. (9.78), it is sufficient to consider only the amount $m_{\text {vap }}$ of vapor which enters the liquid phase within the drop. Indeed, the state of the remaining ( $M_{0}-m_{\text {vap }}$ ) vapor in the metastable phase remains unchanged:

$$
\begin{equation*}
\Phi_{\Lambda}=\left[F_{1}\left(p_{1}\right)+p_{0} V_{1}+\sigma \Sigma\right]-\left[F_{0}\left(p_{0}\right)+p_{0} V_{0}\right] \tag{9.79}
\end{equation*}
$$

where $F_{1}$ and $F_{0}$ are the liquid and the vapor free energy, respectively, the former taken at the pressure $p_{1}$ of the liquid phase inside the droplet and latter at the supersaturated pressure $p_{0}$. According to Eq. (9.2), for the liquid nucleus we should also consider the free energy per unit area $\sigma=\sigma\left(T_{0}\right)$ competing to the droplet surface at the temperature $T_{0}$ of the surrounding vapor.

We stress that the available work $\Lambda=U-T_{0} S+p_{0} V$ of the whole system "liquid+ vapor" differs from the Gibbs potential $G(T, p)$ since $T_{0}$ and $p_{0}$ are always referred to the temperature and the pressure of the vapor, remaining constant during any change $\Delta \Lambda$. Therefore, in the change $\Delta \Lambda$ described by Eq. (9.79) the last term corresponds to the Gibbs potential of the vapor $G_{0}\left(T_{0}, p_{0}\right)$. Since $T_{0}$, for the vapor we can write

$$
\begin{equation*}
\Lambda^{\mathrm{vap}}=F_{0}\left(p_{0}\right)+p_{0} V_{0}=G_{0}\left(p_{0}\right) \tag{9.80}
\end{equation*}
$$

Conversely, the first term can be reconsidered as a function of the the Gibbs potential of the liquid $G_{1}\left(T_{0}, p_{1}\right)$ as

$$
\begin{equation*}
\Lambda^{\mathrm{liq}}=F_{1}\left(p_{1}\right)+p_{0} V_{1}=G_{1}\left(p_{1}\right)-\left(p_{1}-p_{0}\right) V_{1} \tag{9.81}
\end{equation*}
$$

given that

$$
\begin{equation*}
\Lambda^{\text {surf }}=\left(u_{\Sigma}-T_{0} s_{\Sigma}\right)=\sigma\left(T_{0}\right) \Sigma \tag{9.82}
\end{equation*}
$$

is the available work contributed by the surface $\Sigma$ with free energy per unit area equal to $\sigma\left(T_{0}\right)=\left(u_{\Sigma}-T_{0} s_{\Sigma}\right), u_{\Sigma}, s_{\Sigma}$ being the energy and the entropy per unit area, respectively, at the temperature $T_{0}$. By combining Eqs. (9.82), (9.81), (9.80), then Eq. (9.78) can be written in terms of the Gibbs potential as

$$
\begin{equation*}
\Phi_{\Lambda}=G_{1}\left(p_{1}\right)-G_{0}\left(p_{0}\right)-\left(p_{1}-p_{0}\right) V_{1}+\sigma \Sigma \tag{9.83}
\end{equation*}
$$

It is useful to notice that, for a nucleus in equilibrium with the metastable phase we should have $G_{1}\left(p_{1}\right)=G_{0}\left(p_{0}\right)$ so that the work to form a nucleus in equilibrium with vapor as expressed by Eq. (9.83) reduces to sum of $\left(p_{1}-p_{0}\right) V_{1}$ which is known as useful work, and the energy $\sigma \Sigma$ accounting for the formation of the surface $\Sigma$. Under the assumptions that the (i) formation of the liquid drop can be treated as a perturbation with respect to the surrounding vapor, and (ii) the liquid can be considered incompressible during a change at constant $T=T_{0}$ from $p_{0}$ to $p_{1}$, the Gibbs potential within the drop can be approximated by

$$
\begin{equation*}
G_{1}\left(p_{1}\right) \simeq G_{1}\left(p_{0}\right)+\left(p_{1}-p_{0}\right) V_{1} \tag{9.84}
\end{equation*}
$$

By replacing Eq. (9.84) in Eq. (9.83) we get

$$
\begin{equation*}
\Phi_{\Lambda} \simeq G_{1}\left(p_{0}\right)-G_{0}\left(p_{0}\right)+\sigma \Sigma=\Delta G+\sigma \Sigma \tag{9.85}
\end{equation*}
$$

where the change of the Gibbs potential $\Delta G=\Delta G\left(T_{0}, p_{0}\right)$ is to be considered at the temperature and the pressure of the surrounding vapor. Since the vapor at the supersaturated pressure $p_{0}$ is found in a metastable state whose equilibrium state would be the liquid phase, the change at constant $p_{0}$, and $T_{0}$ of the Gibbs potential between the liquid and the vapor phase is always negative, according to the equilibrium conditions (4.104)

$$
\begin{equation*}
\Delta G=G_{1}\left(p_{0}\right)-G_{0}\left(p_{0}\right)<0 \tag{9.86}
\end{equation*}
$$

Conversely, the energy $\sigma \Sigma$ competing to the surface is always positive, being the work needed to create a surface $\Sigma$ with energy per unit area equal to $\sigma$. For a nucleus of radius $r$, Eq. (9.85) becomes

$$
\begin{equation*}
\Phi_{\Lambda}(r)=-\frac{4}{3} \pi r^{3} \varrho_{1}\left[G_{0}^{*}\left(p_{0}\right)-G_{1}^{*}\left(p_{0}\right)\right]+4 \pi r^{2} \sigma \tag{9.87}
\end{equation*}
$$

$\varrho_{1}$ being the mass density of the liquid phase, $G_{0}^{*}, G_{1}^{*}$ the specific Gibbs potential of the vapor and the liquid phase, respectively. According to Eq. (9.86) the difference $\left(G_{0}^{*}-G_{1}^{*}\right)>0$ is positive at constant $p_{0}$, and therefore $\Phi_{\Lambda}(r)$ as a function of the

Fig. 9.4 Bulk contribution (dashed dotted line) and surface contribution (dashed line) to the availability $\Phi_{\Lambda}$ for a sphere of radius $r$ (dashed dotted line) according to Eq. (9.87). All curves are plotted as a function of the nucleus size $r$ in units of the critical radius $r_{c}=2 \sigma /\left(\varrho_{1} \Delta g\right)$ according to Eq. (9.88)

nucleus size $r$ is maximum for a "critical" nucleus size $r_{\mathrm{c}}$ given by

$$
\begin{equation*}
r_{\mathrm{c}}=\frac{2 \sigma}{\varrho_{1}\left(G_{0}^{*}-G_{1}^{*}\right)} \tag{9.88}
\end{equation*}
$$

which can be easily obtained by differentiating Eq. (9.87) with respect to $r$ and looking for the roots of the derivative. For $r<r_{\mathrm{c}}$ a decrease of $r$ is a natural (spontaneous) process and the nucleus is absorbed. Conversely, for $r>r_{\mathrm{c}}$ an increase of $r$ is natural and the nucleus grows. The condition $r=r_{\mathrm{c}}$ is an equilibrium condition which is unstable according to the stability of equilibrium states Eq. (4.104) applied to Eq. (9.77):

$$
\begin{equation*}
\Phi_{\Lambda}(r)=\Phi_{\Lambda}^{\max } \quad \text { if } r=r_{\mathrm{c}} \tag{9.89}
\end{equation*}
$$

Concluding, the expression given by Eq. (9.87) can be regarded as the potential barrier which needs to be overcome for the formation of a stable nucleus, as shown in Fig. 9.4.

### 9.6.1 Spinodal Decomposition

In Sect. 9.6 we saw that in liquid-vapor transitions, the formation of the new phase takes place through nucleation of droplets or bubbles depending on the direction of the transformation considered (see Fig. 9.5a, c). The creation of a droplet (bubble) with surface $\Sigma$ requires the energy $\sigma \Sigma$, as introduced in Eq. (9.79). However, from Eq. (9.93) it results that this energy is extremely low in the vicinity of the critical point. Therefore, it is spontaneous to wonder what would happen if one enters in the coexistence region from the critical point. In this case, the system is "pushed" in a


Fig. 9.5 Spinodal decomposition and nucleation of metastable phases in a two- phase system (specifically, liquid and vapor) for transformations (a), (b), (c), respectively, as shown in Fig. 8.5 inside the coexistence region
thermodynamical unstable state and the separation in two phases takes place immediately in the absence of any nucleation step. However, since the interfacial tension between the two phases is zero, there is no need to form droplets. As a consequence, the structure of the interface between the two phases results particularly complex, characterized by a fractal geometry in which the phases are "surrounding" one each other (see Fig. 9.5b). It is relevant that by analyzing the spinodal pattern in the wave vectors domain it is possible to individuate a characteristic length growing in time up to the complete phase separation, corresponding to the equilibrium condition. We point out that the separation process is driven by gravity (a volume force) acting on the density mismatch of the two phases, since the interfacial tension (a surface force) between phases is negligible, and this is the opposite of what happens for metastable states.

### 9.6.2 Temperature Dependence

Since the existence of surface tension is justified, in the atomic-molecular model, by the different number density of the substance in the two phases, we will expect its value to grow with increasing this number density difference. If we remember the typical shape of the "Andrews bell" for a substance below the critical temperature as discussed in Chap. 7, we see that the surface tension must be a decreasing function of temperature and tends to zero if we increase the temperature to the critical point where the two phases are no longer distinguishable.

As the temperature decreases the density difference between the two phases increases, and then $\sigma$ will increase. For water, the dependence on $T$ is shown in Fig.9.6. As we can see the critical temperature is about $374^{\circ} \mathrm{C}$ which is the point in which the surface tension vanishes.

In Table 9.1 the surface tension of some substances at $\theta \simeq 20^{\circ} \mathrm{C}$ is reported. It is interesting to further investigate a little deeper in the temperature dependence of the surface tension. Near the critical point, the experimental data are well described by

Fig. 9.6 Surface tension of water in equilibrium with saturated vapor below the critical point. At the critical temperature ( $\theta=374^{\circ} \mathrm{C}$ ), the surface tension vanishes. Data are taken from Sychev, Complex Thermodynamics Systems [15]


| Substances | $\sigma\left(\mathrm{J} / \mathrm{m}^{2}\right)$ |
| :--- | :--- |
| Ammonia | 0.021 |
| Acetone | 0.024 |
| Benzene | 0.029 |
| Water | 0.073 |
| Glycerol | 0.059 |
| Methyl alcohol | 0.023 |
| Mercury | 0.559 |
| Oil (olive) | 0.032 |

the expression:

$$
\begin{equation*}
\sigma \propto\left(T_{\text {cr }}-T\right)\left(\varrho_{\text {liq }}-\varrho_{\text {vap }}\right)^{\frac{2}{3}} \tag{9.90}
\end{equation*}
$$

(see discussion in [3]) where $\varrho_{\text {liq }}$ and $\varrho_{\text {vap }}$ are, respectively, the mass density of the liquid and that of the vapor in mutual equilibrium at temperature $T$. The dependence of these densities on temperature are very well described by the empirical relations of Eq. (8.65). For our purpose it is useful to point out the dependance of the difference between the liquid and gas densities, at equilibrium, on temperature is given by:

$$
\begin{equation*}
\left(\varrho_{\mathrm{liq}}-\varrho_{\mathrm{vap}}\right) \propto\left(1-\frac{T}{T_{\mathrm{cr}}}\right)^{\frac{1}{3}} \tag{9.91}
\end{equation*}
$$

Putting together Eqs. (9.90) and (9.91) we obtain the following relation for the temperature dependence of the surface tension:

$$
\begin{equation*}
\sigma=\sigma_{0}\left(1-\frac{T}{T_{\text {cr }}}\right)^{1+\frac{2}{9}} \tag{9.92}
\end{equation*}
$$

where $\sigma_{0}$ is a constant (obviously it cannot be named the surface tension at the critical temperature as Eq. (9.92) could erroneously suggest). The reason for writing the exponent in the form $(1+2 / 9)$ is due to the fact that the generally accepted formula is written in the form

$$
\begin{equation*}
\sigma=\sigma_{0}\left(1-\frac{T}{T_{\mathrm{cr}}}\right)^{1+r} \tag{9.93}
\end{equation*}
$$

and the different data set and modelizations differ in the value of the constant $r$.

### 9.6.3 Surface Tension and the Law of Corresponding States

In Eq. (9.92) the constant $\sigma_{0}$ has to be determined empirically for every substance and it has the dimension of a surface tension, that is [energy]/[area]. It follows that the quantity $\left(\sigma_{0} V^{2 / 3} / R T\right)$ is dimensionless. According to the Law of Corresponding States the quantity

$$
\begin{equation*}
\sigma_{0} \frac{V_{c r}^{\frac{2}{3}}}{R T_{\text {cr }}} \tag{9.94}
\end{equation*}
$$

is expected to have the same value for different substances. In [3] the experimental data for Neon, Argon, Xenon, Nitrogen, Oxygen, and Methane. The empirical results are, respectively, $0.487 \times 10^{-7}, 0.517 \times 10^{-7}, 0.505 \times 10^{-7}, 0.541 \times 10^{-7}$, $0.529 \times 10^{-7}$ and $0.528 \times 10^{-7}$. It is remarkable that among Argon, Xenon, Nitrogen, Oxygen and Methane the values are within $2 \%$ while Neon is off by roughly $10 \%$. This suggest, once again, that the Law of Corresponding States may be better verified within subgroups of substances with similar microscopic properties but we shall not go through this argument.

### 9.6.4 Interfaces at Contact Between Three Phases in Equilibrium

We saw in Sect. 9.4 that interfaces separating two phases in mutual equilibrium can be planar or spherical, according to Eq. (9.54) with $r_{1}, r_{2} \rightarrow \infty$ and $r_{1}=r_{2}=r$, respectively. Within the presence of a third phase the equilibrium conditions need to be reconsidered. This is the case of the capillarity, when a liquid is found in simultaneous contact with its vapor and, in addition, to a solid wall. Similarly, at equilibrium, liquid drop deposited on a solid substrate assumes at fixed $T$ different shapes depending on the specific substrate. Indeed, due to the presence of three phases, we need to consider three surface tensions corresponding to the interfaces solid-liquid (SL), liquid-gas (LG), and solid-gas (SG). We already noticed in Sect. 9.4) that the density


Fig. 9.7 Different wetting configurations: a drop partially wetting the solid surface and balancing of the surface tensions, defining equilibrium contact angle; $\mathbf{b}$ liquid film in total wetting; $\mathbf{c}$ drop completely impregnates micro grooves (Wenzel state); d the liquid is suspended on the asperities (Cassie state, or lotus effect)
of a saturated vapor phase is much lower than the one of the corresponding liquid. This applies also to gases or mixtures of gases regardless the specific nature of gas considered. Therefore, for sake of simplicity, let us assume that the "gas" may be either a given substance in the gas phase, including the mixture of gases (e.g., the air), or the saturated vapor of the liquid phase.

Let us introduce the triple line or contact line as the line in simultaneous contact with three phases, liquid (L), solid (S) and gas (G). The equilibrium condition at the contact line was given by Young and Dupré by balancing the forces per unit length acting on the contact line. In other words, considering Eq. (9.3) this force balance is a relation for the surface tensions $\sigma_{\mathrm{SG}}, \sigma_{\mathrm{SL}}, \sigma_{\mathrm{LG}}$ :

$$
\begin{equation*}
\sigma_{\mathrm{LG}} \cos \vartheta_{\mathrm{eq}}=\sigma_{\mathrm{SG}}-\sigma_{\mathrm{SL}}, \tag{9.95}
\end{equation*}
$$

where $\vartheta_{\text {eq }}$, known as the equilibrium contact angle, is the angle formed by the liquid and the solid interface, while $\sigma_{\mathrm{LG}} \cos \vartheta_{\text {eq }}$ is the projection of $\sigma_{\mathrm{LG}}$ on the plane containing $\sigma_{\mathrm{SL}}$ and $\sigma_{\mathrm{SG}}$, i.e., the solid surface (see Fig. 9.7a).

It is clear from Eq. (9.95) that the contact angle depends on the equilibrium conditions of the three coexisting phases. If the "gas" phase is just the saturated vapor of the liquid phase, the contact angle is determined either by the properties of the liquid and its saturated vapor or by the properties of the solid material. It is therefore meaningless to speak of the contact angle simply for a given liquid; it should be always indicated the solid material the liquid is in contact with. In that case, at fixed $T$, the contact angle is thus a constant, depending on the interaction between the liquid and the solid.

For any value of $\vartheta_{\text {eq }}$ satisfying Eq. (9.95), the liquid is said to (partially) wet the solid surface. However, as the difference $\sigma_{\mathrm{SG}}-\sigma_{\mathrm{SL}}$ is increased enough that

$$
\begin{equation*}
\sigma_{\mathrm{SG}}-\sigma_{\mathrm{SL}} \geq \sigma_{\mathrm{LG}}, \tag{9.96}
\end{equation*}
$$

it is more convenient for the system to form two distinct surfaces (LG and SL) respect to have only one SG surface (see Fig. 9.7b.) In other words it "costs" less energy to completely cover the solid surface, than wet one portion. The difference:

$$
\begin{equation*}
U_{\mathrm{dry}}-U_{\mathrm{wet}}=\mathcal{S}_{\mathrm{eq}} \tag{9.97}
\end{equation*}
$$

between the energy of the dry surface $U_{\text {dry }}$ with respect to the energy $U_{\text {wet }}$ of same surface wet by the liquid phase is called spreading parameter. Per unit surface:

$$
\begin{equation*}
\mathcal{S}_{\mathrm{eq}}=\sigma_{\mathrm{SG}}-\left(\sigma_{\mathrm{SL}}-\sigma_{\mathrm{LG}}\right) \tag{9.98}
\end{equation*}
$$

Therefore,

$$
\begin{array}{ll}
\mathcal{S}_{\mathrm{eq}}>0 & \text { complete wetting, } \\
\mathcal{S}_{\mathrm{eq}}<0 & \text { partial wetting. } \tag{9.100}
\end{array}
$$

For $\mathcal{S}_{\text {eq }}>0$, the liquid spreads over the solid surface as a thin film. As far as the spreading proceeds the film becomes progressively thinner, becoming as thin as the molecular thicknesses, at least in principle. In practice, the spreading of the film progressively slows down, being strongly affected by the presence of surface defects, where it easily pins well before tapering to the molecular scale.

In the case of partial wetting $\left(\mathcal{S}_{\mathrm{eq}}<0\right)$, for many solid surfaces, $\vartheta_{\text {eq }}$ can be larger than $90^{\circ}$, leading to drops shaped as spherical caps on the solid surface. When the liquid is water, such surfaces are said hydrophobic. Conversely, if $\vartheta_{\text {eq }}<90^{\circ}$ we speak of hydrophilic surfaces. It is interesting to notice that, within the most hydrophobic surfaces, the contact angle can hardly be larger than $120^{\circ}$. Indeed, the socalled superhydrophobic surfaces, commonly defined as $\vartheta_{\text {eq }} \geq 150^{\circ}$, are definitely not smooth as it happens in nature for lotus leaves. In fact, lotus leaves display a complex micro texturing so that some air remains confined within these structures and hence, behind the liquid drop, we find an heterogeneous, multiphase system ( $\mathrm{S}+\mathrm{G}$ ) composed by air bubbles trapped inside the "micro stings".

Strong water repellence occurs because the roughness imposed on smooth hydrophobic surfaces further decreases the solid-liquid free energy with respect to the gas-liquid free energy, so that the contact angle results increased. Without entering a discussion that is largely out from our scope, we just mention that the equilibrium contact angle denoted by Eq. (9.95) can be defined only locally for rough surfaces. Therefore, it is necessary to introduce a new quantity, the so called apparent contact angle $\vartheta_{\text {ap }}$, accounting for the effective wettability on textured surfaces. The apparent contact angle is well described by the Wenzel's model (just sketched in Fig. 9.7c) for rough, yet chemically homogeneous, surfaces characterized by a ratio $r$ of the real surface area to the apparent surface area:

$$
\begin{equation*}
\cos \vartheta_{\mathrm{ap}}=r \cos \vartheta_{\mathrm{eq}} \tag{9.101}
\end{equation*}
$$

Since $r>1$ the hydrophobicity of smooth surfaces results enhanced by the presence of the roughness.

For hydrophobic rough surfaces (see Fig. 9.7d) preventing the liquid to fill all the rough asperities, air (gas) pockets remain trapped beneath the liquid drop whose
contact line is in simultaneous contact with a the fraction $f_{\mathrm{s}}$ of solid surface at $\vartheta_{\text {eq }}$ and a fraction $\left(1-f_{\mathrm{s}}\right)$ of air (gas) at $\vartheta_{\text {eq }}=\pi$. Within these composite surfaces the apparent contact angle is provided by the Cassie-Baxter's model ${ }^{6}$

$$
\begin{equation*}
\cos \vartheta_{\mathrm{ap}}=-1+f_{\mathrm{s}}\left(\cos \vartheta_{\mathrm{eq}}+1\right) \tag{9.102}
\end{equation*}
$$

that sets the non wetting limit condition at $\theta_{\text {ap }}=180^{\circ}$ obtained when $f_{\mathrm{s}}$ vanishes.
We conclude this section by mentioning that superhydrophobic surfaces have attracted a considerable interest for applications related to self-cleaning, nonsticking, anti-icing, low-friction resistance. With regard to heat exchanges, they have shown excellent capabilities to increase the heat transfer in several engineering processes involving vapor condensation, such as air conditioning, condensers, desalination, and refrigeration. In fact, since the condensation heat transfer is in general proportional of the total surface exposed to the vapor, at least for nonmetal vapors it results enhanced by dropwise condensation occurring in superhydrophobic surfaces, rather than filmwise condensation taking place in the hydrophilic or moderately hydrophobic ones.

[^30]
## Chapter 10 Electrostatic Field


#### Abstract

In this chapter, we discuss the modifications of the thermodynamical potentials of a system when it is immersed in an electrostatic field. The interaction between field and matter is described by the electric susceptibility of the material which is called dielectric constant for linear materials. The correct expressions for energy, free energy, chemical potential, and the other thermodynamic potentials due to the interaction with electrostatic fields is obtained neglecting electrostriction. The dielectric constant for dilute gases is obtained by statistical methods and, as an example, the increase of gas density following the charging of a condenser is calculated. A brief overlook to electrostriction as the second-order effect, is given in the last section.


Keywords Electrostatic field • Electric susceptibility • Dielectric constant • Linear dielectrics • Thermodynamic potentials • Electrostriction • Langevin's function

### 10.1 Introduction

In this chapter, we want to discuss the modifications of the thermodynamic potentials of a macroscopic system when an electrostatic field is created in the region occupied by it. A new work parameter is introduced and the operations performed by the experimenter must be analyzed.

Let us begin considering a capacitor with plane-parallel plates and neglect edge effects. ${ }^{1}$ Consider the capacitor completely immersed in a fluid (liquid or gas) and indicate, respectively, with $V$ the volume of the portion of the fluid in which the capacitor is fully immersed and with $p$ the value of the pressure acting on the part of the fluid that is external to the condenser. ${ }^{2}$

[^31]Further, denote with $q_{\mathrm{fr}}$ the amount of electric charge (free charge) possessed by the positive plate and with $\psi$ the potential difference between the plates. In order to change by an infinitesimal amount the charge of the capacitor, we shall spend the infinitesimal amount of work:

$$
\begin{equation*}
\hat{d} W_{\mathrm{el}}=\psi \mathrm{d} q_{\mathrm{fr}} . \tag{10.1}
\end{equation*}
$$

Be $\Sigma$ the area of the plates and $h$ their distance. We have $\psi=h|\mathbf{E}|$ and, from the first Maxwell equation $q_{\mathrm{fr}}=\Sigma|\mathbf{D}|$ where $\mathbf{E}$ is the electric field inside the capacitor and $\mathbf{D}$ the electric displacement. The infinitesimal amount of work done on the fluid will be written as

$$
\begin{equation*}
\hat{d} W_{\mathrm{el}}=(h \Sigma) \mathbf{E} \cdot \mathrm{d} \mathbf{D}=V_{\text {cond }} \mathbf{E} \cdot \mathrm{d} \mathbf{D} \tag{10.2}
\end{equation*}
$$

where $V_{\text {cond }}$ is the volume of the capacitor.
This is a simple but general relation: it states that in order to modify, by an infinitesimal amount, the electric field within a (small) volume $V_{\text {cond }}$ the infinitesimal amount of work given by Eq. (10.2), has to be spent.

In order to go further and give Eq.(10.2) any practical utility, the functional relationship $\mathbf{E}=\mathbf{E}(\mathbf{D})$ must be known. It will then be useful to recall some basic relations from a treatise on electrostatics.

### 10.2 The Response of Matter

When the experimenter creates an electric field or modifies a pre-existing field in a certain region of space, he has to appropriately move some electrical charges that he controls (i.e., free charges). If in the region is present some dielectric material, the distribution of the elementary charges of which it is made up, changes, i.e., the dielectric responds to the disturbance by changing its electrical configuration. We say that the dielectric is polarized or, more generally, that it changes its polarization state.

The state of polarization of the dielectric is completely described by the polarization vector $\mathbf{P}=\mathbf{P}(\mathbf{r})$. The vector $\mathbf{P}$ is defined by the relation:

$$
\begin{equation*}
\mathrm{d} \mathbf{P}_{\mathrm{dip}}=\mathbf{P}(\mathbf{r}) \mathrm{d} V \tag{10.3}
\end{equation*}
$$

$\mathrm{d} \mathbf{P}_{\text {dip }}$ being the (infinitesimal) dipole moment generated by the polarization charges in the infinitesimal volume $d V$ in the point of coordinates $\mathbf{r}$ and, therefore $\mathbf{P}(\mathbf{r})$ is the density of dipole moment possessed by the material. If the field $\mathbf{P}(\mathbf{r})$ is known, the distribution of the polarization charges is known ${ }^{3}$ The sum of the distribution of the polarization charges and of the charges controlled by the observer, the free charges,

[^32]will be known and this will enable us to determine the electrostatic field in the entire space.

Since $\mathbf{P}$ is an intensive quantity its value will depend on intensive quantities.
In all generality we can assume that it depends on the density (molar) of the material, the temperature and the electric field acting at the point $\mathbf{r}$.

If we now assume that the dielectric is homogeneous and isotropic then the polarization is parallel to the electric field and then we can write:

$$
\begin{equation*}
\mathbf{P}=\epsilon_{0} \chi \mathbf{E} . \tag{10.4}
\end{equation*}
$$

This relation defines the quantity $\chi$ named electric susceptibility of the material. $\epsilon_{0}$ is a constant whose value depends on the adopted unit system, it is called permittivity of free space or permittivity of vacuum and its value is

$$
\begin{equation*}
\epsilon_{0}=8.85410^{-12} \mathrm{C}^{2} \mathrm{~J}^{-1} \mathrm{~m}^{-1} \tag{10.5}
\end{equation*}
$$

As we know from the study of electrostatics, the electric displacement $\mathbf{D}$ is defined by the relation:

$$
\begin{equation*}
\mathbf{D}=\epsilon_{0} \mathbf{E}+\mathbf{P} \tag{10.6}
\end{equation*}
$$

and it is straightforward to prove that the sources of the electric displacement are the free charges, that is exactly the charges that the observer moves. If we use Eq. (10.4) we obtain

$$
\begin{array}{r}
\mathbf{D}=\epsilon_{0}(1+\chi) \mathbf{E}, \\
\epsilon=\epsilon_{0}(1+\chi), \tag{10.8}
\end{array}
$$

where $\epsilon$ is named electric permittivity of the material. From definition Eq.(10.8), we may relate the electric displacement to the electric field:

$$
\begin{equation*}
\mathbf{D}=\epsilon \mathbf{E} \tag{10.9}
\end{equation*}
$$

and this is the functional relationship between $\mathbf{E}$ and $\mathbf{D}$ that allows us to calculate the thermodynamic potentials. As we can see, now the whole problem lies in knowing (or rather in making a good modeling for) the dependence of the dielectric susceptibility $\chi$, and then of the dielectric permittivity $\epsilon$, on the intensive state variables.

As noted earlier, the susceptibility $\chi$ will, in general, be a function of

$$
\begin{equation*}
\chi=\chi(\varrho, T, E), \tag{10.10}
\end{equation*}
$$

where $\varrho$ is the density of the material, $T$ the temperature, and $E$ the intensity of the field in the point of interest (we consider isotropic materials).

### 10.3 The Dielectric Constant

The dependence of the electric susceptibility on the electric field is difficult to model. For small values of the intensity of the applied electric field we can, with good approximation, assume that the response of the material is proportional to the perturbation that is, in our case, we will assume that the polarization vector is proportional to the electric field. In this case, we speak of linear medium, and this means that the susceptibility does not depend on the intensity of the field, therefore, by Eq. (11.22) we can write

$$
\begin{equation*}
\chi=\chi(\varrho, T) \tag{10.11}
\end{equation*}
$$

and for the electric permittivity:

$$
\begin{equation*}
\epsilon=\epsilon(\varrho, T) \tag{10.12}
\end{equation*}
$$

In this case, the ratio of the electric permittivity $\epsilon$ to that of free space $\epsilon_{0}$, is called dielectric constant. ${ }^{4}$

### 10.4 Thermodynamic Potentials for Linear Dielectrics

The thermodynamic potentials for homogeneous, isotropic and linear materials are obtained from the fundamental equation where the elementary amount of work Eq. (10.2) is added:

$$
\begin{align*}
\mathrm{d} U & =T \mathrm{~d} S-p \mathrm{~d} V+V_{\text {cond }} \mathbf{E} \cdot \mathrm{d} \mathbf{D}+\Sigma_{\gamma} \mu_{\gamma} \mathrm{d} n_{\gamma},  \tag{10.13}\\
\mathrm{d} F & =-S \mathrm{~d} T-p \mathrm{~d} V+V_{\text {cond }} \mathbf{E} \cdot \mathrm{d} \mathbf{D}+\Sigma_{\gamma} \mu_{\gamma} \mathrm{d} n_{\gamma},  \tag{10.14}\\
\mathrm{d} G & =-S \mathrm{~d} T+V \mathrm{~d} p+V_{\text {cond }} \mathbf{E} \cdot \mathrm{d} \mathbf{D}+\Sigma_{\gamma} \mu_{\gamma} \mathrm{d} n_{\gamma} . \tag{10.15}
\end{align*}
$$

As for the dependence of the electric susceptibility Eq.(10.11) on the density, it will be enough to consider that, with good approximation, it will be proportional to the molar density of the dielectric and, in a first instance, the density will be treated as dependent on temperature and pressure of the fluid, as expected from its equation of state in zero field conditions.

In our case, in a second approximation, the introduction of the electric field will contribute to a variation of the density and so we have to consider that even the electric field will enter into the equation of state.

We call electrostriction the phenomenon that consists in the variation of the volume of the fluid associated with a change in the intensity of electrostatic field at con-

[^33]stant pressure and temperature. Quantitatively, this effect is measured by $(\partial V / \partial \mathbf{E})_{T, p}$ or, equivalently, by $(\partial V / \partial \mathbf{D})_{T, p}$.

In order to obtain the integrated expressions for the thermodynamic potentials we will, in the first instance, neglect electrostriction. Returning later to the more general formulas Eqs. (10.13)-(10.15) we will be able to assess the extent of the phenomenon that we have neglected.

### 10.4.1 Thermodynamic Potentials for Linear Dielectrics Without Electrostriction

In many experimental situations and particularly for fluids whose compressibility is small, electrostriction will be treated as a phenomenon of the second order. This means that we will assume, in the first instance, that the density is constant and with a second iteration, we will evaluate the change in volume, and therefore in density, for the introduction of the field.

Under these conditions, we will assume, at first, $\epsilon=\epsilon(T)$ and then the amount of electrostatic work to pass from zero field to a field of intensity $E$ can be easily obtained by integrating Eq. (10.2) as long as the charging process takes place along an isothermal process. In fact, only under this condition we can write

$$
\hat{d} W_{\mathrm{el}}^{\mathrm{isot}}=V_{\mathrm{cond}} E \in \mathrm{~d} E
$$

with $\epsilon$ taken as a constant along the process. Then, the amount to create an electrostatic field of intensity $E$ is given by

$$
\begin{equation*}
W_{0, E}^{\mathrm{isot}}=V_{\text {cond }} \frac{1}{2} \epsilon E^{2} . \tag{10.16}
\end{equation*}
$$

Now we can write the new expression for the free energy of the system:

$$
\begin{equation*}
F=F_{0}+V_{\text {cond }} \frac{1}{2} \epsilon E^{2}, \tag{10.17}
\end{equation*}
$$

where $F_{0}$ is the free energy of the system with zero field. The term added to the zero field free energy in Eq. (10.17) can be denoted with

$$
\begin{equation*}
F_{\mathrm{el}}=V_{\mathrm{cond}} \frac{1}{2} \epsilon E^{2}, \tag{10.18}
\end{equation*}
$$

which is defined as "free energy of the electric field". This designation is a coarse designation because the corresponding term does not describe a property of the electrostatic field but of the interaction dielectric-electrostatic field. As the electrostatic field inside the condenser is considered as homogeneous, we can properly imagine
that the free energy (and so will be for energy and other extensive thermodynamic potentials) is uniformly distributed in the volume of the condenser (here is an argument in favor of the definition of extensive quantities based on volume integral of their density) and we can usefully define the free energy density due to the presence of the field $f_{\text {el }}$ as

$$
\begin{equation*}
f_{\mathrm{el}}=\frac{1}{2} \epsilon E^{2} . \tag{10.19}
\end{equation*}
$$

Still within the hypothesis of a linear dielectric and neglecting electrostriction, we can derive an expression for the energy associated with the presence of the field. In Eq. (10.13) we may write

$$
\begin{equation*}
\mathbf{E} \cdot \mathrm{d} \mathbf{D}=\epsilon \mathbf{E} \cdot \mathrm{d} \mathbf{E}+E^{2} \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T} \mathrm{~d} T \tag{10.20}
\end{equation*}
$$

and hence:

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V-\frac{1}{2} V_{\text {cond }} \frac{\epsilon}{T} \mathrm{~d} E^{2}-V_{\text {cond }} \frac{1}{T} \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T} E^{2} \mathrm{~d} T-\sum_{\gamma} \frac{\mu_{\gamma}}{T} \mathrm{~d} n_{\gamma} \tag{10.21}
\end{equation*}
$$

Let us develop the differential of the energy as a function of the differentials of $V, E^{2}, T$ and $n_{\gamma}$

$$
\begin{align*}
\mathrm{d} S=\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)\right. & \left.+\frac{p}{T}\right] \mathrm{d} V+\frac{1}{T}\left[\left(\frac{\partial U}{\partial\left(E^{2}\right)}\right)-\frac{1}{2} V_{\text {cond }} \epsilon\right] \mathrm{d} E^{2}+  \tag{10.22}\\
& +\frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)-V_{\text {cond }} \frac{\mathrm{d} \epsilon}{\mathrm{~d} T} E^{2}\right] \mathrm{d} T-\sum_{\gamma} \frac{\mu_{\gamma}}{T} \mathrm{~d} n_{\gamma}
\end{align*}
$$

Now, by applying the Schwarz identity Appendix A. 4 between the second and the third term of the second member we get

$$
\begin{align*}
-\frac{1}{T^{2}}\left[\left(\frac{\partial U}{\partial\left(E^{2}\right)}\right)-\frac{1}{2} V_{\text {cond }} \epsilon\right] & +\frac{1}{T}\left[\frac{\partial^{2} U}{\partial T \partial\left(E^{2}\right)}-\frac{1}{2} V_{\text {cond }} \frac{\mathrm{d} \epsilon}{\mathrm{~d} T}\right]= \\
& =\frac{1}{T}\left[\left(\frac{\partial^{2} U}{\partial\left(E^{2}\right) \partial T}\right)-V_{\text {cond }} \frac{\mathrm{d} \epsilon}{\mathrm{~d} T}\right] \tag{10.23}
\end{align*}
$$

and hence:

$$
\begin{equation*}
\frac{\partial U}{\partial\left(E^{2}\right)}=\frac{1}{2} V_{\mathrm{cond}}\left(\epsilon+T \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T}\right) \tag{10.24}
\end{equation*}
$$

The second member of this equation does not depend on the intensity of the field so we can easily integrate and get

$$
\begin{equation*}
U=U_{0}+\frac{1}{2} V_{\text {cond }}\left(\epsilon+T \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T}\right) E^{2} \tag{10.25}
\end{equation*}
$$

where $U_{0}$ represents the energy of the system with zero field while the second term is the additive correction due to the presence of the electric field. Similarly to what was said before for the free energy, we can assume that the energy is distributed uniformly throughout the volume of the dielectric and define the intensive quantity

$$
\begin{equation*}
u_{\mathrm{el}}=\frac{1}{2}\left(\epsilon+T \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T}\right) E^{2}, \tag{10.26}
\end{equation*}
$$

which is the correct expression (always within the limits of the adopted approximations) of the variation of the energy density due to the presence of the electrostatic field.

From the definitions of energy and free energy energy given in Eqs.(2.1) and (4.27), we can derive the contribution of the presence of the electrostatic field to the entropy and entropy density starting from the identity

$$
S=\frac{(U-F)}{T},
$$

we get:

$$
\begin{equation*}
S=\frac{U_{0}-F_{0}}{T}+\frac{1}{2} V_{\text {cond }} \frac{1}{T}\left(\epsilon+T \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T}\right) E^{2}-V_{\text {cond }} \frac{1}{T} \frac{1}{2} \epsilon E^{2}, \tag{10.27}
\end{equation*}
$$

which becomes

$$
\begin{equation*}
S=S_{0}+S_{\mathrm{el}}, \tag{10.28}
\end{equation*}
$$

where

$$
S_{0}=\frac{U_{0}-F_{0}}{T}
$$

is the entropy of the system with zero field and

$$
S_{\mathrm{el}}=\frac{1}{2} V_{\text {cond }} \frac{\mathrm{d} \epsilon}{\mathrm{~d} T} E^{2}
$$

is the contribution due to the electrostatic field. Likewise Eq. (12.35) we can write the expression for the entropy density due to the electrostatic field:

$$
\begin{equation*}
s_{\mathrm{el}}=\frac{1}{2} \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T} E^{2} . \tag{10.29}
\end{equation*}
$$

It is important to highlight that, within the theoretical context that we have adopted in this discussion, the entropy due to the interaction with the electric field, depends only on the derivative of the dielectric constant with respect to temperature.

As we will see when we shall treat the problem of the dielectric constant from a statistical point of view, the dependence of $\epsilon$ on the temperature is related with the polar conformation of the molecules while the contribution to the polarization due to the polarizability (that is the term that takes into account the deformation of the molecules) is described by a term independent of the temperature. For nonpolar materials entropy does not depend (in a first approximation) on the presence of electrostatic field. This is consistent with the statistical treatment of entropy, in fact only for polar molecules, the electrostatic field creates a partial orientation of the molecules and thus reduces the volume of the available phase space (it is also said that the presence of the electric field creates some "order"). This leads us to predict a decrease in entropy and indeed, as we shall see, in the statistical model we have adopted we will find $\mathrm{d} \epsilon / \mathrm{d} T<0$.

### 10.5 Dielectric Constant for Ideal Gases

In order to make calculations particularly simple we consider the gas composed by one component. All the molecules are characterized by a polarizability $\alpha$ and by their dipole moment whose absolute value we denote by $\beta$.

In the presence of an electric field $\mathbf{E}$ a mole of gas will acquire a total dipole moment equal to

$$
\begin{equation*}
\mathbf{P}_{\mathrm{mol}}=N_{A} \alpha \mathbf{E}+N_{A}\langle\boldsymbol{\beta}\rangle \tag{10.30}
\end{equation*}
$$

where $N_{A}$ is the Avogadro's number and $\langle\boldsymbol{\beta}\rangle$ is the mean value of the molecular dipole moment in the field $\mathbf{E}$.

To calculate the latter contribution we will assume that each molecule behaves in a completely unrelated manner with the other molecules (low density) and that the dielectric is in a state of thermodynamic equilibrium. Let us take as z -axis a direction parallel to the electric field and denote by $\vartheta$ the angle between the direction of the dipole of the molecule and the direction of the field.

The infinitesimal solid angle subtended by the directions which form with the direction of the field ( $z$-axis) an angle between $\vartheta$ and $\vartheta+\mathrm{d} \vartheta$ is

$$
\begin{equation*}
\mathrm{d} \Omega=2 \pi \sin \vartheta \mathrm{~d} \vartheta \tag{10.31}
\end{equation*}
$$

The potential energy of an electric dipole in an electric field is

$$
\begin{equation*}
U_{\mathrm{pot}}=-\boldsymbol{\beta} \cdot \mathbf{E}=-\beta E \cos \vartheta, \tag{10.32}
\end{equation*}
$$

therefore the probability that a molecule has an orientation which forms with the electric field an angle between $\vartheta$ e $\vartheta+\mathrm{d} \vartheta$ will be

$$
\begin{equation*}
P(\vartheta) \mathrm{d} \vartheta=\frac{2 \pi \exp \left(-U_{\mathrm{pot}} / k_{B} T\right) \sin \vartheta \mathrm{d} \vartheta}{2 \pi \int_{0}^{\pi} \exp \left(-U_{\mathrm{pot}} / k_{B} T\right) \sin \vartheta \mathrm{d} \vartheta} . \tag{10.33}
\end{equation*}
$$

For convenience we write Eq. (10.33) in the form

$$
\begin{equation*}
P(\vartheta) \mathrm{d} \vartheta=-\frac{\exp \left(-U_{\mathrm{pot}} / k_{B} T\right) \mathrm{d}(\cos \vartheta)}{\int_{-1}^{+1} \exp \left(-U_{\mathrm{pot}} / k_{B} T\right) \mathrm{d}(\cos \vartheta)} \tag{10.34}
\end{equation*}
$$

We are interested in the mean values of the three components of the dipole moment of the molecule. It is obvious that the mean values in the directions perpendicular to the electric field ( $z$-axis) are zero and then let us calculate $\left\langle\beta_{z}\right\rangle$ only. Since $\beta_{z}=\beta \cos \vartheta$ we have

$$
\begin{equation*}
\left\langle\beta_{z}\right\rangle=\beta\langle\cos \vartheta\rangle=\beta \int_{0}^{\pi} \cos \vartheta P(\vartheta) \mathrm{d} \vartheta . \tag{10.35}
\end{equation*}
$$

If we use Eq. (10.34) and we place

$$
\begin{equation*}
x=\left(\beta E / k_{B} T\right), \tag{10.36}
\end{equation*}
$$

we obtain

$$
\begin{equation*}
\langle\cos \vartheta\rangle=\frac{\int_{-1}^{+1} \cos \vartheta \exp (x \cos \vartheta) \mathrm{d}(\cos \vartheta)}{\int_{-1}^{+1} \exp (x \cos \vartheta) \mathrm{d}(\cos \vartheta)} \tag{10.37}
\end{equation*}
$$

To calculate these integrals it is convenient to make the variable change $y=x \cos \vartheta$ and notice that the integrand in the numerator can be written as

$$
\begin{equation*}
\cos \vartheta \exp (x \cos \vartheta)=\frac{\mathrm{d}}{\mathrm{~d} x}[\exp (y)] \tag{10.38}
\end{equation*}
$$

Then, for the numerator of Eq. (10.37) we will have

$$
\begin{align*}
& \int_{-1}^{+1} \cos \vartheta \exp (x \cos \vartheta) \mathrm{d}(\cos \vartheta)= \int_{-1}^{+1} \frac{\mathrm{~d}}{\mathrm{~d} x} \exp (x \cos \vartheta) \mathrm{d}(\cos \vartheta)= \\
&=\frac{\mathrm{d}}{\mathrm{~d} x} \int_{-1}^{+1} \exp (x \cos \vartheta) \mathrm{d}(\cos \vartheta)=\frac{\mathrm{d}}{\mathrm{~d} x}\left\{\frac{1}{x} \int_{-x}^{+x} \exp (y) \mathrm{d} y\right\}=  \tag{10.39}\\
&=\frac{\mathrm{d}}{\mathrm{~d} x}\left\{\frac{1}{x}[\exp (x)-\exp (-x)]\right\}
\end{align*}
$$

Similarly, for the denominator Eq. (10.37) :

$$
\begin{equation*}
\int_{-1}^{+1} \exp (x \cos \vartheta) \mathrm{d}(\cos \vartheta)=\frac{1}{x} \int_{-x}^{+x} \exp (y) \mathrm{d} y=\frac{1}{x}(\exp (x)-\exp (-x)) \tag{10.40}
\end{equation*}
$$

Finally, the desired result will be

$$
\begin{equation*}
\langle\cos \vartheta\rangle=\frac{\mathrm{d}}{\mathrm{~d} x} \ln \left\{\frac{1}{x}[\exp (x)-\exp (-x)]\right\} \tag{10.41}
\end{equation*}
$$

The derivative in Eq. (10.41) is known as the "Langevin's function" $\mathscr{L}(x)$ :

$$
\begin{equation*}
\mathscr{L}(x)=\frac{\mathrm{d}}{\mathrm{~d} x} \ln \left\{\frac{1}{x}[\exp (x)-\exp (-x)]\right\}=\frac{\exp (x)+\exp (-x)}{\exp (x)-\exp (-x)}-\frac{1}{x} \tag{10.42}
\end{equation*}
$$

The behavior of $\mathscr{L}(x)$ is shown in Fig. 10.1. It is easy to verify that for the Langevin's function we have the following limiting conditions for very large and for very small values of the variable $x$. For large values:

$$
\begin{equation*}
\lim _{x \rightarrow \infty} \mathscr{L}(x)=1 \tag{10.43}
\end{equation*}
$$

For small values it is convenient to develop $\mathscr{L}(\mathrm{x})$ in power series of the variable $x$. Then for $x \ll 1$ we find

$$
\begin{equation*}
\mathscr{L}(x) \simeq \frac{x}{3}=\frac{\beta E}{3 k_{B} T} . \tag{10.44}
\end{equation*}
$$

If we denote with $(n / V)$ the molar density of the gas, the intensity of the polarization vector (dipole moment per unit volume) will be:

Fig. 10.1 The Langevin's function $\mathscr{L}$ (continuous line). For large values of the argument $x$ the function tends asymptotically to 1 . For small values of $x$ the Langevin's function goes to zero with slope $1 / 3$ (dashed line)


$$
\begin{equation*}
P=\frac{n}{V}\left(\alpha N_{A} E+\frac{\beta^{2} E}{3 k_{B} T} N_{A}\right) \tag{10.45}
\end{equation*}
$$

As it can be seen, the polarization is proportional to the intensity of the field, for weak fields. As it is evident from Eq. (10.36) weak fields means:

$$
\begin{equation*}
E \ll \frac{k_{B} T}{\beta} \tag{10.46}
\end{equation*}
$$

and in this approximation, the polarization can be written as

$$
\begin{equation*}
P=\frac{n}{V}\left(a+\frac{b}{T}\right) E \tag{10.47}
\end{equation*}
$$

with:

$$
\begin{align*}
a & =N_{A} \alpha  \tag{10.48}\\
b & =N_{A} \frac{\beta^{2}}{3 k_{B}} \tag{10.49}
\end{align*}
$$

Finally the dielectric constant, for weak fields, will be expressed by the relation:

$$
\begin{equation*}
\epsilon=\epsilon_{0}+\frac{n}{V}\left(a+\frac{b}{T}\right) \tag{10.50}
\end{equation*}
$$

## Examples

In the following the thermodynamic potentials modified by the presence of an electrostatic field, will be applied in three cases: first, we calculate the increase of concentration of a gas within a charged condenser; second. we estimate the thermal effect in charging or discharging a capacitor and, finally, we calculate the electrostriction as the second-order effect.

Example 10.1 Increase of gas concentration in charged condensers. Consider a capacitor with plane and parallel plates, immersed in a gas in ideal conditions. The volume of the gas is much larger than the volume of the capacitor. In the initial configuration the condenser is uncharged and the gas is in a state of thermodynamical equilibrium at uniform temperature and density. The condenser is charged and let $E$ be the intensity of the electric field (neglect edge effects) and a new equilibrium state is reached. Consider the gas divided into two subsystems: one part is constituted by the gas inside the condenser whose volume is $V=V_{\text {cond }}$ maintained constant, and the other is formed by the gas outside the condenser also maintained at constant volume.

We denote by the superscript "int" and "ext" the values of the thermodynamic quantities of the gas in the internal and in the external zone, respectively. When the new equilibrium state is reached we shall observe:

$$
\begin{align*}
& T^{\mathrm{int}}=T^{\mathrm{ext}}=T,  \tag{10.51}\\
& \mu^{\mathrm{int}}=\mu^{\mathrm{ext}} . \tag{10.52}
\end{align*}
$$

Let us calculate the chemical potentials. For the gas in the outer zone (zero field zone) we have:

$$
\begin{equation*}
\mu^{\mathrm{ext}}=\left(\frac{\partial F^{\mathrm{ext}}}{\partial n^{\mathrm{ext}}}\right)_{T, V^{\mathrm{ext}}}=\left(\frac{\partial F_{0}^{\mathrm{ext}}}{\partial n^{\mathrm{ext}}}\right)_{T, V_{\mathrm{ext}}} \tag{10.53}
\end{equation*}
$$

Let us refer to Eq. (6.52) which was given for dilute gases and in which the dependance on the molar concentration $C$ was put in evidence:

$$
\begin{equation*}
\mu^{\mathrm{ext}}=\eta^{\dagger}+R T \ln C^{\mathrm{ext}} \tag{10.54}
\end{equation*}
$$

As for the gas in the internal zone we refer to Eq.(10.14):

$$
\begin{equation*}
\mu^{\mathrm{int}}=\left(\frac{\partial F^{\mathrm{int}}}{\partial n^{\mathrm{int}}}\right)_{T, V^{\mathrm{int}},(\epsilon E)} \tag{10.55}
\end{equation*}
$$

Making use of Eq. (10.17) for the free energy:

$$
\begin{align*}
\mu^{\mathrm{int}} & =\left(\frac{\partial F_{0}^{\mathrm{int}}}{\partial n^{\mathrm{int}}}\right)_{T, V \mathrm{int}}+\frac{1}{2} V_{\mathrm{cond}}\left(\frac{\partial\left(\epsilon E^{2}\right)}{\partial n^{\mathrm{int}}}\right)_{T, V \mathrm{int},(\epsilon E)}=  \tag{10.56}\\
& =\mu_{0}^{\mathrm{int}}+\frac{1}{2} V_{\mathrm{cond}} \epsilon^{2} E^{2}\left(\frac{\partial(1 / \epsilon)}{\partial n^{\mathrm{int}}}\right)_{T, V, \text { int }}
\end{align*}
$$

In the last passage of Eq. (10.56) we introduced

$$
\begin{equation*}
\mu_{0}^{\mathrm{int}} \equiv\left(\frac{\partial F_{0}^{\mathrm{int}}}{\partial n^{\mathrm{int}}}\right)_{T, V \mathrm{int}} \tag{10.57}
\end{equation*}
$$

as the chemical potential of the gas inside the condenser with zero field, and we performed the derivative of $\left(\epsilon E^{2}\right)$ at constant $(\epsilon E)$. By making use Eq. (6.52) again, Eq. (10.56) becomes:

$$
\begin{equation*}
\mu^{\mathrm{int}}=\eta^{\dagger}+R T \ln C^{\mathrm{int}}-\frac{1}{2} V_{\mathrm{cond}} E^{2}\left(\frac{\partial \epsilon}{\partial n^{\mathrm{int}}}\right)_{T, V \mathrm{int}} \tag{10.58}
\end{equation*}
$$

For the gas inside the condenser we have $V^{\text {int }}=V_{\text {cond }}$ and

$$
\begin{equation*}
\epsilon=\epsilon_{0}+\frac{n^{\mathrm{int}}}{V^{\mathrm{int}}}\left(a+\frac{b}{T}\right) \tag{10.59}
\end{equation*}
$$

then the chemical potential of the gas inside the condenser can be written

$$
\begin{equation*}
\mu^{\mathrm{int}}=\eta^{\dagger}+R T \ln C^{\mathrm{int}}-\frac{1}{2} E^{2}\left(a+\frac{b}{T}\right) \tag{10.60}
\end{equation*}
$$

The condition for phase equilibrium is $\mu^{\text {int }}=\mu^{\text {ext }}$ and we get

$$
\begin{align*}
& R T \ln \frac{C^{\mathrm{int}}}{C^{\mathrm{ext}}}=\frac{1}{2} E^{2}\left(a+\frac{b}{T}\right)  \tag{10.61}\\
& \frac{C^{\mathrm{int}}}{C^{\mathrm{ext}}}=\exp \left[\frac{E^{2}}{2 R T}\left(a+\frac{b}{T}\right)\right] \tag{10.62}
\end{align*}
$$

Since the argument of the exponential function is positive ( $a>0$ and $b \geq 0$ ) we see that the concentration inside the condenser is always greater then the concentration in the external part. When we charge the condenser the gas is always, partially, drawn inside.

Finally, let us conclude with a brief discussion on thermal phenomena which take place when charging or discharging a capacitor and on electrostriction that we have treated as the second-order phenomenon.

Example 10.2 Thermal effects in dielectrics. Let us consider a plane condenser with the same approximations adopted up to now, filled with dielectric material. The condenser is charged and the electric field passes from zero to the final value $E$, keeping the temperature constant. Let us calculate the amount of heat supplied from the outside world to the condenser.

Consider an infinitesimal process. From Eq. (10.28) we have

$$
\begin{equation*}
\mathrm{d} S=V_{\text {cond }} \frac{\mathrm{d} \epsilon}{\mathrm{~d} T} E \mathrm{~d} E=\frac{\hat{d} Q}{T} \tag{10.63}
\end{equation*}
$$

Since $\epsilon$ depends only on temperature and density, if we neglect electrostriction we can integrate and obtain

$$
\begin{equation*}
Q_{0 \rightarrow E}=\frac{1}{2} V_{\text {cond }} T \frac{\mathrm{~d} \epsilon}{\mathrm{~d} T} E^{2} \tag{10.64}
\end{equation*}
$$

In general we have $\mathrm{d} \epsilon / \mathrm{dT}<0$ and hence $Q_{0 \rightarrow E}<0$ which means that, when the condenser is charged isothermally, it must expel heat to the external world. On the contrary it must be "warmed up" when it is discharged.

## Example 10.3 Electrostriction in dielectrics.

As regards the electrostriction, in order to highlight variations in volume as an effect of the intensity variation of the electric field, we will consider processes at
constant temperature and pressure. Hence we shall refer to Eq. (10.15) but in order to work with the intensity of the electric field as the independent state variable, it will be convenient to subtract to the differential of the Gibbs potential, the differential of the state function $V_{\text {cond }} \epsilon E^{2}$. We obtain the following exact differential:

$$
\begin{equation*}
\mathrm{d}\left(G-V_{\text {cond }} \epsilon E^{2}\right)=-S \mathrm{~d} T+V \mathrm{~d} p-V_{\text {cond }}(\epsilon E) \mathrm{d} E+\sum_{\gamma} \mu_{\gamma} \mathrm{d} n_{\gamma} \tag{10.65}
\end{equation*}
$$

We apply the Schwarz identity between the second and the third term of the second member:

$$
\begin{align*}
& \left(\frac{\partial V}{\partial E}\right)_{T, p, n_{\gamma}}=-V_{\mathrm{cond}}\left[\frac{\partial(\epsilon E)}{\partial p}\right]_{T, E, n_{\gamma}},  \tag{10.66}\\
& \left(\frac{\partial V}{\partial E}\right)_{T, p, n_{\gamma}}=-V_{\mathrm{cond}} E\left(\frac{\partial \epsilon}{\partial p}\right)_{T, n_{\gamma}} \tag{10.67}
\end{align*}
$$

If we consider only the dielectric inside the condenser, i.e., we put $V=V_{\text {cond }}$, we have:

$$
\begin{align*}
\left(\frac{d V}{V}\right)_{T, p, n_{\gamma}} & =-\left(\frac{\partial \epsilon}{\partial p}\right)_{T, n_{\gamma}} E \mathrm{~d} E  \tag{10.68}\\
\ln \left(\frac{V}{V_{0}}\right)_{T, p} & =-\frac{1}{2}\left(\frac{\partial \epsilon}{\partial p}\right)_{T, n_{\gamma}} E^{2} \tag{10.69}
\end{align*}
$$

## Chapter 11 <br> Magnetic Field


#### Abstract

Starting from the macroscopic Maxwell equations, the expressions for the electric work, magnetic work, and radiation of energy are derived. This is, in turn, the starting point for deriving the expressions of thermodynamic potentials. A brief outlook to the constitutive relations for diamagnetic, paramagnetic, and ferromagnetic materials is given and hence the expressions for the thermodynamical potentials in the presence of magnetostatic fields are given. A short reference to the adiabatic demagnetization closes this chapter.


Keywords Magnetic fields • Diamagnetism • Paramagnetism• Thermodynamic potentials $\cdot$ Linear media $\cdot$ Adiabatic demagnetization

### 11.1 Introduction

There are many similarities with the case electrostatic field but also some conceptual differences should be highlighted.

The first analogy is obvious because it is of general methodological nature: as we did in the case of the electrostatic field, we have to start considering the operations that the observer must take to create or to vary the magnetic field in the region occupied by the macroscopic system under observation and, in particular, we need to calculate the amount of work done.

As in the case of the electrostatic field, the operations that the observer performs in a controlled way always consist in the movement of free charges. These operations have two possible outcomes: the construction of different static configurations (for example, the charge of a capacitor) or the generation and the variation of free currents. To begin with the study of thermodynamics in a more general context, it is necessary to recall the macroscopic Maxwell equations [9].

The sources of the fields are the electric charges and the electric currents. For the charges, we have to distinguish between free charges and polarization charges: the former are the charges controlled by the observer, while the latter constitute the response of the medium to the presence of the free charges. Similarly, we have to
distinguish between free currents, operated by the observer, and the magnetization currents as the response of the medium.

Free charges $q_{\mathrm{fr}}$, whose density is denoted by $\rho_{\mathrm{fr}}$, are the sources of the electric displacement $\mathbf{D}$ while the free currents, denoted by the current density $\mathbf{j}$, are the sources of the vector $\mathbf{H}$ that we call magnetizing field. ${ }^{1}$ The roles of the free charges and of the free currents are well visible, respectively, in the first and in the fourth of the four macroscopic Maxwell equations that we report here:

$$
\begin{align*}
& \boldsymbol{\nabla} \cdot \mathbf{D}=\rho_{\mathrm{fr}}  \tag{11.1}\\
& \nabla \cdot \mathbf{B}=0  \tag{11.2}\\
& \nabla \times \mathbf{E}=-\frac{\partial \mathbf{B}}{\partial t},  \tag{11.3}\\
& \boldsymbol{\nabla} \times \mathbf{H}=\mathbf{j}+\frac{\partial \mathbf{D}}{\partial t} . \tag{11.4}
\end{align*}
$$

As the sources of the electric displacement $\mathbf{D}$ and of the magnetizing field $\mathbf{H}$ are the free sources, these two fields may be considered analogous. Similarly, we consider the fields $\mathbf{E}$ and $\mathbf{B}$ analogous to each other because each one is, in its domain, defined by the force that is exerted, respectively, on a test charge at rest and on an infinitesimal segment of wire, very thin, through which an electric (free) current flows.

Thinking in terms of the microscopic view, the two fields are defined by the so-called Lorentz force which is the force exerted on a point charge $q$ :

$$
\begin{equation*}
\mathbf{F}=q(\mathbf{E}+\mathbf{v} \times \mathbf{B}) . \tag{11.5}
\end{equation*}
$$

### 11.2 Electric Work, Magnetic Work, and Radiation

In order to construct a given magnetic configuration in space, the observer has to move electric charges and launch electric currents in suitable circuits and in a suitable way. To do this, he must operate on electric charges, and this implies doing a certain amount of work. The latter can be subdivided, in a sensible way, in a part that is expended to modify the electric field and another part that we associate to the change of the magnetic field. The latter contribution is called "magnetic work," and the former "electric work."

To give a rigorous quantitative evaluation we must, as always, proceed through infinitesimal changes. We consider the distribution of the electric and magnetic fields at a given time $t$ in the whole space, and then we operate to produce a small change in the fields and calculate the amount of work done in an infinitesimal time interval $\mathrm{d} t$.

Let $\mathbf{E}, \mathbf{B}$, and $\mathbf{j}$ be, respectively, the electric field, the magnetic field, and the free current density at time $t$ in a given infinitesimal volume $\mathrm{d} V$.

[^34]Consider the Maxwell equations and multiply Eq.(11.3) by $\mathbf{H}$ and Eq. (11.4) by E. After subtracting side by side and recalling the identity

$$
\begin{equation*}
\mathbf{H} \cdot \boldsymbol{\nabla} \times \mathbf{E}-\mathbf{E} \cdot \boldsymbol{\nabla} \times \mathbf{H}=\boldsymbol{\nabla} \cdot(\mathbf{E} \times \mathbf{H}) \tag{11.6}
\end{equation*}
$$

we obtain

$$
\begin{equation*}
\mathbf{E} \cdot \mathbf{j}+\boldsymbol{\nabla} \cdot(\mathbf{E} \times \mathbf{H})+\mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t}+\mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t}=0 \tag{11.7}
\end{equation*}
$$

These terms should be analyzed and interpreted one by one. To do this, we consider a volume $V$ bounded by a surface $\Omega$ and, after multiplying the above equation by $\mathrm{d} V \mathrm{~d} t$, we integrate over the volume. The integral of the first term in Eq. (11.7)

$$
\begin{equation*}
-\int_{V} \mathrm{~d} V(\mathbf{j} \cdot \mathbf{E}) \mathrm{d} t=\hat{d} W \tag{11.8}
\end{equation*}
$$

represents the total amount of work performed by the electromagnetic field in the considered volume $V$ and in the infinitesimal time interval $\mathrm{d} t$. The integral on the second term in Eq. (11.7)

$$
\int_{V} \mathrm{~d} V \nabla \cdot(\mathbf{E} \times \mathbf{H}) \mathrm{d} t
$$

may be written using the Gauss theorem in the form

$$
\begin{equation*}
\int_{\Omega}(\mathbf{E} \times \mathbf{H}) \cdot \mathrm{d} \boldsymbol{\Sigma} \mathrm{~d} t \tag{11.9}
\end{equation*}
$$

and it represents the amount of energy transferred in the time interval $\mathrm{d} t$ through the surface $\Omega$ that delimits the volume under observation.

The two remaining terms in Eq. (11.7) represent the part of the work that is spent to change the fields. Equation (11.7) can be rearranged putting in evidence the total work done on the charges:

$$
\begin{align*}
\hat{d} W=-\int \mathrm{d} V(\mathbf{E} \cdot \mathbf{j}) \mathrm{d} t= & \int(\mathbf{E} \times \mathbf{H}) \cdot \mathrm{d} \boldsymbol{\Sigma} \mathrm{~d} t+  \tag{11.10}\\
& +\int \mathrm{d} V(\mathbf{E} \cdot \mathrm{~d} \mathbf{D}) \mathrm{d} t+\int \mathrm{d} V(\mathbf{H} \cdot \mathrm{~d} \mathbf{B}) \mathrm{d} t
\end{align*}
$$

The last two terms are, as a whole, the amount of work that is used to change the values of the fields in the volume under consideration. We agree that the second term on the right represents the part of the total work devoted to vary the electric field in the considered time interval and denote this term with $\hat{d} W_{\mathrm{el}}$. This term is called "electric work":

$$
\begin{equation*}
\hat{d} W_{\mathrm{el}}=\int \mathrm{d} V(\mathbf{E} \cdot \mathrm{~d} \mathbf{D}) \mathrm{d} t \tag{11.11}
\end{equation*}
$$

and, similarly, we agree that the last term represents the amount of work devoted to vary the magnetic field. We denote this contribution with symbol $\hat{d} W_{\text {mag }}$ and call this term "magnetic work":

$$
\begin{equation*}
\hat{d} W_{\mathrm{mag}}=\int \mathrm{d} V(\mathbf{H} \cdot \mathrm{~d} \mathbf{B}) \mathrm{d} t \tag{11.12}
\end{equation*}
$$

### 11.3 Constitutive Relations

In order to write how the thermodynamic potentials change in connection with the introduction of electromagnetic fields, it is necessary to establish the relationships between the fields appearing in the four Maxwell's equations and more precisely between the magnetic field $\mathbf{B}$ and the magnetizing field $\mathbf{H}$ and between electric displacement $\mathbf{D}$ and the electric field $\mathbf{E}$. These two relations describe the response of the materials to the electromagnetic actions performed by the observer.

The functional relation between electric field and displacement field was already discussed in Chap. 10.

Having in mind to create a homogeneous magnetic field in a small volume, we consider a rectilinear solenoid with cross section $\Sigma$ and length $l$, with $l \gg \sqrt{\Sigma}$. Let $N$ be the total number of coils, uniformly distributed, and denote with $n=N / l$ the number of turns per unit length.

Consider first the case in which the solenoid is in a vacuum. The magnetic field and the magnetizing field in the inner parts of the solenoid are given by

$$
\begin{equation*}
B=\mu_{0} n I, \tag{11.13}
\end{equation*}
$$

where $\mu_{0}$ is a constant whose value depends on the units of measure and is called magnetic permeability in vacuum and

$$
\begin{equation*}
H=n I \tag{11.14}
\end{equation*}
$$

Moving to a vectorial formalism, Eqs. (11.13) and (11.14) may be written as follows:

$$
\begin{align*}
\frac{\mathbf{B}}{\mu_{0}} & =\frac{N I \mathbf{\Sigma}}{l \Sigma}=\frac{N \mathbf{m}}{V_{\mathrm{sol}}}  \tag{11.15}\\
\frac{\mathbf{B}}{\mu_{0}} & =\mathbf{H} \tag{11.16}
\end{align*}
$$

where $\mathbf{m}=I \boldsymbol{\Sigma}$ is the magnetic moment of one coil, $(N \mathbf{m})$ is the total magnetic moment of the solenoid, $V_{\text {sol }}=l \Sigma$ its volume, and $\Sigma$ is a vector with modulus $\Sigma$ (the area of the coil), normal to the coil, oriented according to the "right-hand-rule" convention.

Neglecting edge effects, that is, considering $\mathbf{B}$ uniform in the whole volume occupied by the solenoid, we see that we can interpret the quantity $\left(\mathbf{B} / \mu_{0}\right)$ as the magnetic
moment per unit volume. The reason to give such an evidence to an apparently trivial comment is the following: while in the case of the electrostatic field the source is the electric charge, in the case of the magnetic field, the primary source is the magnetic dipole; it follows that the field responsible for mechanical actions will be written, in the general case, as a superposition of the fields created by (elementary) dipoles. Hence, the convenience of describing the basic elementary situations in terms of dipole moments. Furthermore, it is necessary to point out the true meaning of the vector $\mathbf{H}$ : it represents the dipole moment per unit volume generated by the free currents (see Eq. (11.16)).

### 11.3.1 Uniform Medium

Let us consider, now, the effect of the presence of matter. We know that matter, in the presence of free currents, is magnetized and we describe this modification, in analogy with the electrostatic case, defining, point by point, the density of induced magnetic moment or magnetization vector which we denote by the symbol $\mathbf{M}$.

Unlike the electrostatic case in which the density of the induced electric dipole moment can be well modeled with appropriate modifications of the dislocation of atomic or molecular charges, in our case the distribution of the magnetization $\mathbf{M}$, not always, can be reduced to a suitable distribution and orientation of closed elementary currents, but in some cases, it can be attributed to the overall motions (Larmor rotations) or to effects of electronic and/or nuclear spin, which do not have the analogue in the electrostatic case. Therefore, the thermodynamic properties of a medium in a magnetic field are a more complex matter compared with the electrostatic case and needs to make a brief recapitulation of what has been learned in the study of electromagnetism.

Suppose we fill the solenoid with a homogeneous and isotropic material. This material will magnetize and, given the symmetry of the situation, it will do it uniformly. Therefore, the density of induced magnetic moment will be described by a uniform vector $\mathbf{M}$. If through the solenoid winding a current with intensity $I$ (free current) is flowing, the total magnetic moment per unit volume will be the sum of that generated by the free current (see (11.15)) and that generated by the magnetization of the material (magnetization currents):

$$
\begin{equation*}
\frac{\mathbf{B}}{\mu_{0}}=\frac{N I \mathbf{\Sigma}}{l \Sigma}+\mathbf{M}=\frac{N \mathbf{m}}{V_{\mathrm{sol}}}+\mathbf{M} \tag{11.17}
\end{equation*}
$$

The magnetic moment density generated by the free current is represented by the vector field $\mathbf{H}$ which, for this reason, is called magnetizing field and, in our simple example, is given by

$$
\begin{equation*}
\mathbf{H}=\frac{N \mathbf{m}}{V_{\mathrm{sol}}} . \tag{11.18}
\end{equation*}
$$

So we can write the relation of general validity:

$$
\begin{equation*}
\frac{\mathbf{B}}{\mu_{0}}=\mathbf{H}+\mathbf{M} \tag{11.19}
\end{equation*}
$$

This relation expresses well the fact that the overall effect exerted on a test charge in motion is given by the sum of the effect generated by the free currents, that is, those directly controlled by the observer, to which is added the effect produced by the currents of magnetization which describe the response of the medium to these actions.

The expression of Eq. (11.19) is the analogue of that already seen in electrostatics:

$$
\begin{equation*}
\varepsilon_{0} \mathbf{E}=\mathbf{D}-\mathbf{P} \tag{11.20}
\end{equation*}
$$

In the latter case, with rare exceptions if we know one of the three vectors in Eq. (11.20), we can derive the other two provided that we know enough about the properties of the material (substantially if we know the dielectric susceptibility which will be a function of density, temperature, and, in general, also of the field).

In the case of the magnetostatic field, this does not always happen as in the case of ferromagnetic materials and, more generally, in all cases in which the phenomenon of hysteresis is present. In these cases, the relationship between the magnetic field and the magnetizing field also depends on the procedures that have been followed in the past to achieve a given configuration. For this reason, they do not allow a simple thermodynamic treatment and are beyond the scope of this discussion. Then, we write

$$
\begin{equation*}
\frac{\mathbf{B}}{\mu}=\mathbf{H} . \tag{11.21}
\end{equation*}
$$

This relation defines the quantity $\mu$ which is called magnetic permeability of the material and, in general, depends on chemical composition, density, temperature, and the intensity of the magnetizing field. The ratio $\mu / \mu_{0}$ is called magnetic coefficient and, in the case that it does not depend on the intensity of the magnetic field, will be called magnetic constant.

From the point of view of their magnetic behavior, the materials can be grouped into three categories: diamagnetic, paramagnetic, and ferromagnetic materials.

To characterize the behavior of a material in a magnetic field, it will be more functional to refer to the behavior of the magnetic susceptibility.

So, the magnetic susceptibility tells us how the material is magnetized when immersed in a given magnetizing field. It may depend on the composition, the density, the temperature, and the intensity of the magnetizing field.

It is defined by the relation

$$
\begin{equation*}
\mathbf{M}=\chi_{m} \mathbf{H} \tag{11.22}
\end{equation*}
$$

from which we have the relation

$$
\begin{equation*}
\mu=\mu_{0}\left(1+\chi_{m}\right) . \tag{11.23}
\end{equation*}
$$

In the cases where the susceptibility can be considered independent of the intensity of the magnetizing field, the material will be said to be a linear material because, in these cases, the magnetization is proportional to the intensity of the magnetizing field (of course at constant values of the other state variables).

### 11.4 Diamagnetic Materials

The diamagnetic materials are characterized by a negative value of the susceptibility:

$$
\begin{equation*}
\chi_{m}<0 . \tag{11.24}
\end{equation*}
$$

In this case, the magnetization has opposite direction to the magnetizing field, and then the resulting magnetic field $\mathbf{B}$ has a value smaller than that in the case of the vacuum in correspondence to the same intensity of the magnetizing field. Its numerical value is always $\ll 1$ and it follows that $\mathbf{B}$ and $\mathbf{H}$ are always parallel.

Diamagnetic materials are glass, water, oil, carbon, mercury, gold and silver, copper and zinc, nitrogen, chlorine, and many organic compounds.

Diamagnetism is explained by the Langevin theory [17]. The introduction of an external magnetic field alters the motion of atomic or molecular electrons superimposing on their "normal motion" (i.e., in the absence of field), an overall precession (Larmor precession), with an angular velocity proportional to the intensity of the external magnetic field.

If the atoms or the molecules have zero magnetic dipole moment, this precession motion induces on them a magnetic moment proportional to the external field (i.e., to the angular velocity of the precession motion) and such as to generate a magnetic field with the opposite orientation (see Lenz law).

So we would expect that the magnetic susceptibility is independent of the intensity of the external field (linear medium).

Further, we expect that the angular velocity of precession is independent of the speed of translation or rotation of the molecules and therefore the susceptibility is independent of temperature. Experience confirms very well the Langevin theory.

### 11.5 Paramagnetic Materials

In paramagnetic materials, the elementary constituents (atoms or molecules) possess a non-zero magnetic moment and then behave as dipoles whose magnetic moment can be reasonably kept constant in absolute value. The treatment is similar to the case
already seen for polar dielectrics: for weak external field, the dipoles are partially oriented parallel to the field and the magnetization increases linearly with the field.

For intense fields, the orientation of the dipoles tends to saturation, and then the magnetization no longer increases. In this case, $\chi_{m} \propto B^{-1}$. For weak fields, $\mathbf{M} \propto \mathbf{B}$ and hence $\chi_{m}$ does not depend on the external field. In all cases, the magnetization is parallel and concordant with the external field then we will have

$$
\begin{equation*}
\chi_{m}>0 \tag{11.25}
\end{equation*}
$$

and consequently the magnetic field intensity increases. An increase in temperature causes a decrease in the degree of orientation of the dipoles and so decreases the magnetization.

For weak fields, i.e., in cases of a magnetization proportional to the field, the dependence of the magnetic susceptibility on temperature has been experimentally found by P. Curie in 1906, for some substances, and is of the type $\chi_{m}=A / T$. Of course, the precession (Larmor) of the motion of electrons that explains well the phenomenon of diamagnetism is present also in this case but the effect is, in absolute value, much smaller than the effect due to partial orientation of the magnetic dipoles and therefore results, in practice, negligible.

As we saw in the discussion of the Langevin's theory for the case of electrostatic fields, it is supposed that the orientation of each elementary dipole can be treated "individually", i.e., the different dipoles are not significantly related to each other. The calculations already performed in the electrostatic case for polar molecules can be repeated in the case of paramagnetic materials by substituting the electrostatic field with the magnetic field and the elementary dipole moment of the molecule with its elementary magnetic moment.

### 11.5.1 Long, Rectilinear, and Homogeneous Solenoid

Let us apply, now, the previous relations to the case of a rectilinear solenoid filled with an isotropic, homogeneous, and non-ferromagnetic material. In this case, we have

$$
\begin{equation*}
\mathbf{H}=n I \frac{\boldsymbol{\Sigma}}{\Sigma} \tag{11.26}
\end{equation*}
$$

and making use of Eq. (11.12) the amount of work we have to do in order to produce an infinitesimal change of the magnetic field intensity, will be

$$
\begin{equation*}
\hat{d} W_{\mathrm{mag}}=V_{\mathrm{sol}} n^{2} I \mathrm{~d}(\mu I) \tag{11.27}
\end{equation*}
$$

which may, also, be written as

$$
\begin{equation*}
\hat{d} W_{\mathrm{mag}}=\frac{\Sigma}{l} N^{2} I \mathrm{~d}(\mu I) . \tag{11.28}
\end{equation*}
$$

As it can be seen, the amount of work we have to spend to create a given current depends on the procedure used, and this is true not only because the magnetic permeability of the material may depend on all the state variables, but also because in the expression Eq. (11.10) the contribution relative to the flux of the vector $(\mathbf{E} \times \mathbf{H})$ may be non-negligible. In our treatment, we shall neglect this term.

### 11.6 Thermodynamic Potentials in the Presence of Magnetostatic Fields

Let us consider a material whose fundamental relation in the absence of magnetic field is known and let us denote all its thermodynamic potentials by the suffix ${ }^{0}$ like, for instance, $U^{0}, S^{0}, F^{0}, \mu^{0}$.

We now want to obtain their expression when the material is immersed in a magnetostatic field $\mathbf{B}$ (function of the coordinates). To do this, we will have to build a suitable distribution of free currents which will be increased from zero to their suitable final values needed to obtain the desired magnetic field configuration. The total amount of magnetic work done will be given by the integral given in Eq. (11.12). It will be

$$
\begin{equation*}
W_{\mathrm{mag}}=\int \mathrm{d} V \int_{0}^{\mathbf{B}} \mathbf{H} \cdot \mathrm{d} \mathbf{B} \tag{11.29}
\end{equation*}
$$

As it can be seen, in the process that leads the current from the initial zero value to the final value, this integral depends, in general, on the procedure followed in the process because, in general, the magnetic permeability depends on all the state variables and therefore cannot be considered as being constant during the onset of the free currents.

We will then need to focus on what we know of quite simple on the magnetic properties of the material in order to choose the appropriate mode of operation.

### 11.6.1 Expression of the Thermodynamic Potentials

We will limit ourselves to processes in which the density is considered as a constant (neglect thermal dilatation and/or magnetostriction). The relation between $\mathbf{H}$ and $\mathbf{B}$ will depend only on temperature. If we operate with isothermal processes, $W_{\text {mag }}$ will give the measure of the variation in the free energy:

$$
\begin{equation*}
F-F^{0}=\int \mathrm{d} V \int_{\text {isoth. }}^{\mathbf{B}} \mathbf{H} \cdot \mathrm{d} \mathbf{B} \tag{11.30}
\end{equation*}
$$

and, in the case of very long solenoid (in which we can neglect the edge effects and consider the fields homogeneous inside and zero outside), we define the variation of free energy density:

$$
\begin{equation*}
f=f^{0}+\int_{\text {isoth. }}^{\mathbf{B}}\left(\frac{1}{\mu}\right) \mathbf{B} \cdot \mathrm{d} \mathbf{B} \tag{11.31}
\end{equation*}
$$

From the general relation $S=-(\partial F / \partial T)_{V}$, we immediately obtain the following expressions for the entropy and energy densities, respectively,

$$
\begin{align*}
& s=s^{0}-\int_{\substack{\text { isoth. }}}^{\mathbf{B}} \frac{\partial(1 / \mu)}{\partial T} \mathbf{B} \cdot \mathrm{~d} \mathbf{B}  \tag{11.32}\\
& u=u^{0}+\int_{\substack{\text { isoth. }}}^{\mathbf{B}}\left\{\left[\frac{1}{\mu}-T \frac{\partial(1 / \mu)}{\partial T}\right]\right\} \mathbf{B} \cdot \mathrm{d} \mathbf{B} \tag{11.33}
\end{align*}
$$

### 11.6.2 Linear Media

For materials with no hysteresis and for weak fields (as it is very often in lab activities), we can consider $\mu$ independent of the field and therefore dependent, at most, only on temperature.

In this case, the relations that provide the thermodynamic potentials are simplified into

$$
\begin{align*}
& f=f^{0}+\frac{1}{\mu} \frac{1}{2} \mathbf{B}^{2}=f^{0}+\frac{1}{2} \mu \mathbf{H}^{2}  \tag{11.34}\\
& s=s^{0}+\frac{1}{2} \frac{1}{\mu^{2}} \frac{\mathrm{~d} \mu}{\mathrm{~d} T} \mathbf{B}^{2}=\frac{1}{2} \frac{\mathrm{~d} \mu}{\mathrm{~d} T} \mathbf{H}^{2}  \tag{11.35}\\
& u=u^{0}+\frac{1}{2}\left(\mu+T \frac{\mathrm{~d} \mu}{\mathrm{~d} T}\right) \mathbf{H}^{2} \tag{11.36}
\end{align*}
$$

### 11.7 Adiabatic Demagnetization

It is of particular interest to study the behavior of some paramagnetic substances in the conditions in which only the degrees of freedom related to paramagnetic behavior are relevant. For instance, in the case of ferric alum $\mathrm{NH}_{4} \mathrm{Fe}\left(\mathrm{SO}_{4}\right)_{2} 12 \mathrm{H}_{2} \mathrm{O}$
at temperatures about 2-3K, the vibrational, rotational, and translational degrees of freedom are substantially "frozen" in the sense that the molecules are all in their respective fundamental states. The only contribution to the entropy of the material is due to the paramagnetic response of the material to an external magnetic field $\mathbf{B}_{\text {ext }}$.

It is relatively simple to consider a spherical sample immersed in a uniform magnetic field and calculate the entropy of interaction between the sample and the external field. It can be shown that, in these conditions and for weak fields ( $N_{\mathrm{A}} \beta B \ll R T$ with $N_{\mathrm{A}}$ Avogadro's number and $\beta$ Bohr's magneton), the entropy depends on the total spin quantum number $s$ and on the ratio $\left(\beta B_{\text {ext }} / R T\right)^{2}$.

In an adiabatic transformation, that is, at constant entropy, the ratio ( $B_{\text {ext }} / T$ ) must be kept constant:

$$
\begin{equation*}
\frac{B_{\mathrm{ext}}}{T}=\text { constant } \tag{11.37}
\end{equation*}
$$

If we bring the material to a temperature sufficiently low that the above conditions are verified and we do it in the presence of a magnetic field $B_{\text {ext }}$, and thereafter we diminish the intensity of the magnetic field while maintaining the system adiabatically isolated, the temperature will decrease further and the decrease will be proportional to the decrease of the intensity of the magnetic field. The process is named adiabatic demagnetization.

By means of this technique, we can easily go to temperatures of the order of $T \sim 10^{-3} \mathrm{~K}$.

Fortunately (or unfortunately depending on your point of view), we cannot bring the system to zero temperature by letting the intensity of the magnetic field go to zero because at temperatures of the order of $10^{-2}-10^{-3} \mathrm{~K}$ the material ceases to be paramagnetic and becomes either diamagnetic or ferromagnetic.

### 11.8 Ferromagnetic Materials

Also, in this case the susceptibility is positive, and then the magnetization strengthens the external field, but in this case its value is several orders of magnitude greater than in the case of paramagnetism. This so striking difference is explained by admitting a strong correlation between neighboring dipoles within regions whose size depends on the material and are determined by quantum phenomena.

These regions are called "domains" and constitute, in their turn, a sort of "big elementary dipoles" with magnetic moment equal to the sum of the dipole moments of all the elementary constituents contained in the same domain (which defines the level of correlation).

At a very gross level, then, we could think of a treatment similar to that seen for paramagnetic materials but in which the elementary constituent has a dipole moment $N$ times more intense. The number $N$ corresponds to the order of magnitude of the magnetic susceptibility in relation to the one we have in the case of paramagnetic substances. However, the analogy cannot be sustained because, unlike the case of
paramagnetism, the dimensions of the Weiss domains also depend on the intensity of the magnetizing field. The latter increases the level of correlation (and therefore the size) of the domains oriented parallel to the field and reduces the dimension, and then the magnetic moment, of those oriented in the opposite direction.

The phenomenon of the magnetic hysteresis poses severe obstacles to the definition of thermodynamic equilibrium states and, as a consequence, of the thermodynamic potentials. In addition, the dependence of the magnetization intensity on the magnetizing field is very complex and will not be treated here.

## Chapter 12 <br> Thermodynamics of Radiation


#### Abstract

The problem of the thermodynamical properties of radiation in equilibrium with matter is studied. After defining the emissivity and the absorptivity of material surfaces, the Kirchhoff's law in the extended form is discussed together with some fundamental consequences. After deriving the relation between spectral energy density and spectral emissivity in a cavity, the Wien's law is derived from relativistic invariance requirements. The Wien's displacement law and the StefanBoltzman law are obtained as consequences of the Wien's law. Some examples concerning the solar constant and the temperature of the solar corona are given. The thermodynamic potentials of radiation in thermal equilibrium with matter are obtained, and some exercises are proposed. In the appendix to the chapter, the spectral energy density of black-body radiation is obtained, from experimental data and through thermodynamics, according to the original line of thought by Planck in 1900.


Keywords Absorptivity • Emissivity • Emittance • Black body • Kirchhoff's law • Radiation density • Wien's law • Thermodynamic potentials • Rayleigh-Jeans • Ultraviolet catastrophe $\cdot$ M. Planck solution • Adiabatic expansion of radiation

### 12.1 Introduction

All materials interact, with different modalities, with electromagnetic radiation, and this shows that they are all composed of different agglomerates of electric charges. For a detailed description of this mutual interaction, it is necessary to refer to a specific atomic-molecular model but much can be understood by the general principles of physics no matter what the detailed microscopic nature of matter is.

Recall that a very important part of the study of matter-radiation, formerly known as the "problem of the black body," has been a major moment of transition to the so-called "modern physics" but it was the deep knowledge of thermodynamics which allowed Planck to find that lucky interpolation ${ }^{1}$ which led him to the solution of the problem.

[^35]Let us see, briefly, some fundamental experimental observations that will allow us, on one side, to begin the study of these phenomena and, on the other, to understand why physicists at the end of the nineteenth century found themselves facing contradictions that were to prove insurmountable.

### 12.2 Kirchhoff's Law

Kirchhoff's law establishes some universal features of the matter-radiation interaction but it is necessary to define, first, some fundamental quantities.

### 12.2.1 Absorptivity of Material Bodies

If the surface of a body, call it $\mathbb{C}$, is hit by some electromagnetic radiation, the latter is partly absorbed and partly reflected. The quantitative study of this phenomenon shows that, in general, it depends on the nature of the body $\mathbb{C}$, on its temperature, on the wavelength of the incident radiation, on its state of polarization, and on the geometry (angle of incidence, etc.).

We define absorptivity (or absorptive power) $\mathscr{A}$ of a surface, the ratio of the amount of energy absorbed to the amount of incident energy in the same time interval.

As, in general, this ratio depends certainly on the temperature of the body and on the wavelength of the incident radiation, but also the angle of incidence of the radiation, we will speak of absorptivity of a body at a certain temperature and relative to radiation of a certain wavelength $\lambda$ (more precisely in the interval $(\lambda, \lambda+\mathrm{d} \lambda)$ ) as its integral value when it is hit by isotropically distributed radiation (we always refer, here, to isotropic bodies and in a state of thermodynamic equilibrium). The absorptivity is a pure number in the interval between 0 and 1 .

### 12.2.2 Emissivity of Material Bodies

Consider one surface element of a body $\mathbb{C}$ and let $\mathrm{d} \Sigma$ be its area and $\hat{\mathbf{n}}$ the normal unit vector oriented outward. At a distance $r$ from this surface element we place another body $\mathbb{R}$, that we might consider a receiver, by means of which we want to analyze the radiation emitted by the elementary surface of area $d \Sigma$ of body $\mathbb{C}$. Denote by $d \Sigma^{\prime}$ the area of a surface element of this body detector and by $\hat{\mathbf{n}}^{\prime}$ its normal unit vector oriented outward. We denote, respectively, by $\vartheta$ and $\vartheta^{\prime}$ the angles that the unit vectors $\mathbf{n}$ and $\hat{\mathbf{n}}^{\prime}$ form with the line joining the two elementary surfaces (see Fig. 12.1).

Suppose, for the moment, that there are no other sources of radiation in the vicinity so that we can assume that every surface element of the body $\mathbb{C}$ is not reflecting


Fig. 12.1 The geometrical quantities used throughout the chapter are defined: $\mathrm{d} \Sigma$ and $\mathrm{d} \Sigma^{\prime}$ are two surface elements of the two bodies $\mathbb{C}$ and $\mathbb{R}$, respectively. The unit vectors $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}^{\prime}$ directions are oriented outward the two bodies and the two angles $\vartheta$ and $\vartheta^{\prime}$ are formed by the two normals with the segment of length $r$ connecting the two surface elements
radiation emitted by other bodies. For the moment, we assume also that $\mathbb{R}$ is not emitting significantly.

The infinitesimal quantity of energy $\mathrm{d} \varepsilon$, emitted by $\mathrm{d} \Sigma$ and impinging on the infinitesimal part $\mathrm{d} \Sigma^{\prime}$ of the receiver is written in this way:

$$
\begin{equation*}
\mathrm{d} \varepsilon=\mathcal{B} \frac{\mathrm{d} \Sigma \cos \vartheta \mathrm{~d} \Sigma^{\prime} \cos \vartheta^{\prime}}{r^{2}} \mathrm{~d} t \tag{12.1}
\end{equation*}
$$

This relation defines the quantity $\mathcal{B}$, which has the dimension of a power per unit area, and is called the emissivity of the body $\mathbb{C}$ at the point considered.

As the emissivity has been defined by Eq. (12.1) in which the geometric factors have been put in evidence, it will happen in many cases, for example, for isotropic and homogeneous materials, that the coefficient $\mathcal{B}$ proves to be independent of the direction along which the surface $\mathrm{d} \Sigma$ is observed. In other words, this means that if we place the receiver at a distance $r$, we receive a power which is proportional, according to the coefficient $\mathcal{B}$, to the projection of the emitting surface $\mathrm{d} \Sigma$ perpendicular to the line of sight.

Suppose that the amount of energy received per unit time by the element surface $\mathrm{d} \Sigma^{\prime}$ of the detector $\mathbb{R}$ depends only on the projection of the surface $\mathrm{d} \Sigma^{\prime}$ perpendicular to the line of sight. If we denote by

$$
\begin{equation*}
\mathrm{d} \Omega=\frac{\mathrm{d} \Sigma^{\prime} \cos \vartheta^{\prime}}{r^{2}} \tag{12.2}
\end{equation*}
$$

the elementary solid angle subtended by the receiver $\mathrm{d} \Sigma^{\prime}$ when seen from $\mathrm{d} \Sigma$, Eq. (12.1) may also be written as

$$
\begin{equation*}
\mathrm{d} \varepsilon=\mathcal{B} \mathrm{d} \Sigma \cos \vartheta \mathrm{~d} \Omega \mathrm{~d} t \tag{12.3}
\end{equation*}
$$

The emissivity depends on the nature of the emitting material, on its temperature, and on the observed wavelength. In the case mentioned above and throughout the
following discussion, we will consider $\mathcal{B}$ independent of the direction of emission and the state of polarization.

Likewise, if the body $\mathbb{R}$ emits isotropically with emissivity $\mathcal{B}^{\prime}$, the energy radiated by the elementary surface $\mathrm{d} \Sigma^{\prime}$ on the elementary surface $\mathrm{d} \Sigma$ per unit time can be written as

$$
\begin{equation*}
\mathrm{d} \varepsilon^{\prime}=\mathcal{B}^{\prime} \mathrm{d} \Sigma^{\prime} \cos \vartheta^{\prime} \mathrm{d} \Omega^{\prime} \mathrm{d} t \tag{12.4}
\end{equation*}
$$

where

$$
\begin{equation*}
\mathrm{d} \Omega^{\prime}=\frac{\mathrm{d} \Sigma \cos \vartheta}{r^{2}} \tag{12.5}
\end{equation*}
$$

is the solid angle subtended by $\mathrm{d} \Sigma$ when seen from $\mathrm{d} \Sigma^{\prime}$. Like in the previous case, the effective surface is the projection of $\mathrm{d} \Sigma^{\prime}$ orthogonal to the direction $\vartheta^{\prime}$. In conclusion, definition Eq. (12.1) of the emissivity $\mathcal{B}$ allows to consider only the projections of the emitter or receiver surfaces perpendicular to the mutual line of sight, and the solid angle within which each one sees the other.

### 12.2.3 Black Body

In the definition of emissivity, we have assumed that the power radiated by the surface $\mathrm{d} \Sigma$ toward the detector was solely due to the electromagnetic processes occurring in the body $\mathbb{C}$. Even when we have considered the case in which also the body $\mathbb{R}$ was a normal emitter, we have neglected the possibility of a mutual reflection between the two elementary surfaces.

The radiation collected by a detector in a given direction and coming from a surface element of the body $\mathbb{C}$ will, in general, be given by the superposition of a component radiated from the material which constitutes the body (and this contribution is described by the emissivity) and a component that derives from reflection by the surface element (and according to specific laws) of the radiation emitted by all the other surrounding bodies.

We will call black body a body that has absorptivity $\mathscr{A}_{0}=1$ at all wavelengths. For a black body, therefore, the radiation emitted by one of its surface elements is entirely due to the component radiated by the material.

The black body, therefore, represents an asymptotic situation but the reasoning on this abstract system is of fundamental importance for understanding the behavior of real bodies. As is well known, we can visualize a black body in the following way:

Consider a cavity made in the interior of a material body kept at a constant temperature. This body has reached a state of thermodynamic equilibrium.

We practice a small hole in the wall of the cavity. ${ }^{2}$

[^36]

Fig. 12.2 Schematic representation of a black body with area $d \Sigma$. The surface of the hole in the material cavity, observed from outside has the property of absorbing completely all the radiation incident on it. The radiation emerging from inside is entirely due to the electromagnetic processes active inside the cavity. If the opening is small enough, the outgoing radiation observed from outside in any direction $\vartheta$ with the normal $\hat{\mathbf{n}}$ is a faithful sample of the radiation inside the cavity when it is closed

The external surface of this small hole has the following properties: (i) any ray coming from the outside of the cavity and which impinges on this surface of the hole enters the cavity, undergoes a number of interactions with the inner walls of the cavity, and is completely absorbed. (ii) The small size of the hole does not substantially disturb the distribution of the radiation that was determined within the cavity when it was closed and all had stabilized in an equilibrium configuration (see Fig. 12.2).

The radiation coming out of the small hole can thus be considered a fairly faithful sample of the equilibrium radiation inside the cavity before the opening of the hole. For this, it is also necessary that the thickness of the material in the vicinity of the hole is small compared to the size of the hole itself.

The surface of this small hole, seen from the outside, will thus show an absorptivity $\mathscr{A}_{0}=1$ for all wavelengths and is therefore a black body. The radiation that we observe from the outside is entirely due to the outflow of a small part of the radiation which is created inside the cavity by the radiative processes active within the material which constitutes the cavity.

With different geometries of the hole, we can study the intensity of radiation that propagates inside the cavity, in different directions and, with the use of filters, at different frequencies (or wavelengths). In this way, the equilibrium of radiation present in the cavity can be considered as the superposition of monochromatic rays (in geometrical optics sense) which propagate in different directions. The analysis shows that the flux density is isotropic whatever the shape of the cavity is.

### 12.2.4 Kirchhoff's Law for the Emissivity of a Black Body

Let us investigate the spectral distribution of the radiation emitted by a black body.
If we denote by $\mathcal{B}_{0}(\nu, T)$ the spectral emissivity of a black body at frequency $\nu$, or more exactly in the frequency interval ( $v, \nu+d \nu$ ), the infinitesimal amount of energy received by the observer (surface element of the receiver as in Fig. 12.1) in this frequency range and per unit time, can be written as

$$
\begin{equation*}
\mathrm{d} \varepsilon_{v}=\mathcal{B}_{0}(\nu, T) \frac{\mathrm{d} \Sigma \cos \vartheta \mathrm{~d} \Sigma^{\prime} \cos \vartheta^{\prime}}{r^{2}} \mathrm{~d} v \mathrm{~d} t \tag{12.6}
\end{equation*}
$$

If we compare this with Eq. (12.1), we see that the total emitted energy $\mathrm{d} \varepsilon$ will be

$$
\begin{equation*}
\mathrm{d} \varepsilon=\int_{0}^{\infty} \mathrm{d} \varepsilon_{\nu} \mathrm{d} \nu \tag{12.7}
\end{equation*}
$$

and, if we denote by $\mathcal{B}_{0}$ the emissivity of a black body, we have

$$
\begin{equation*}
\mathcal{B}_{0}(T)=\int_{0}^{\infty} \mathcal{B}_{0}(\nu, T) d \nu \tag{12.8}
\end{equation*}
$$

Kirchhoff has shown that the spectral intensity of the radiation emitted by a black body depends only on the temperature $T$ of the material and on the observed frequency $v$ but does not depend on the nature of the material used.

Kirchhoff, directed by some experimental observations, has proved this proposition by referring to the second principle of thermodynamics.

We build two cavities with different materials and keep them at the same temperature $T$. On each of them, we make a small hole and make sure that the outgoing radiation from each is oriented so as to enter into the other and, with the use of suitable filters, we do this for each frequency.

Let us denote with $\mathcal{B}_{0}^{a}(v, T)$ and with $\mathcal{B}_{0}^{b}(v, T)$ the spectral emissivity of each of the two black bodies, at the same frequency $v$ and temperature $T$. If one of them was greater than the other, we would get a net transfer of energy between the two bodies. This would mean that, without any external intervention, we could obtain a temperature difference between two bodies initially at the same temperature.

One important consequence of this result is that it allows to treat the radiation contained in a cavity at equilibrium as a thermodynamic system in its own right, that is, to which the thermodynamic potentials can be attributed regardless of the nature of the material wall with which it is in interaction. Indeed, if we refer to Eq. (12.34), we see that, for the Kirchhoff's law, also the energy density of the equilibrium radiation that is formed in the cavity will be independent of the material which has generated it , and then is a property of the radiation only.

### 12.2.5 One Fundamental Consequence of Kirchhoff's Law

Kirchhoff's law states, then, that the spectral emissivity of a black body $\mathcal{B}_{0}(\nu, T)$ is a universal function with exactly the same value of universality that we ascribe to the second principle of thermodynamics.

Let us see how the expression of a black-body emissivity can be derived, apart from a multiplicative constant, from arguments based solely on the dimensional analysis.

All laws of classical physics are built on five fundamental quantities: the three of mechanics (mass, length, and time), the electric charge $q$, and the temperature $T$. From Kirchhoff's Law ${ }^{3}$ we can assume that $\mathcal{B}_{0}(\nu, T)$ does not depend on the value of the electric charge which couples radiation with matter but depends only on the frequency $v$, on the temperature of the cavity $T$ and on the remaining fundamental constants with which the laws of physics are given.

In a classical context, that is pre-quantum, these fundamental constants are $c$ (speed of light in vacuum) and $k_{B}$ (Boltzmann's constant).

We build the product:

$$
\begin{equation*}
\mathcal{B}_{0}(\nu, T) v^{n} c^{p} T^{q} k_{B}^{r}=\Gamma, \tag{12.9}
\end{equation*}
$$

with $n, p, q, r$ constants to be determined on the sole condition that expression Eq. (12.9) is adimensional. This condition is also called scale invariance condition and let us denote with $\Gamma$ the value of the product Eq. (12.9). ${ }^{4}$ Imposing this condition is equivalent to Kirchhoff's law, i.e., to the universality of the law that regulates the emissivity of a black body at thermodynamic equilibrium.

For convenience we replace, among the fundamental quantities of mechanics, the mass $m$ with the unit of energy $e$. This means that with this new fundamental system of units, mass would have the dimension:

$$
\begin{equation*}
[\text { mass }]=[\text { energy }] \times[\text { length }]^{-2} \times[\text { time }]^{2} \tag{12.10}
\end{equation*}
$$

The dimensions of the five quantities involved in the product Eq. (12.9) are

$$
\begin{align*}
& \mathcal{B}_{0}(v, T)=[\text { energy }] \times[\text { length }]^{-2},  \tag{12.11}\\
& \nu=[\text { time }]^{-1},  \tag{12.12}\\
& c=[\text { length }] \times[\text { time }]^{-1},  \tag{12.13}\\
& T=[\text { temperature }]  \tag{12.14}\\
& k_{B}=[\text { energy }] \times[\text { temperature }]^{-1} \tag{12.15}
\end{align*}
$$

[^37]Substituting in Eq. (12.9), we obtain

$$
\begin{align*}
\Gamma= & {[\text { energy }] \times[\text { length }]^{-2} \times[\text { time }]^{-n} \times[\text { length }]^{p} \times }  \tag{12.16}\\
& \times[\text { time }]^{-p} \times[\text { temperature }]^{q} \times[\text { energy }]^{r} \times[\text { temperature }]^{-r} .
\end{align*}
$$

By performing algebraic simplifications, we obtain

$$
\begin{equation*}
\Gamma=[\text { energy }]^{(1+r)} \times[\text { length }]^{(-2+p)} \times[\text { time }]^{(-n-p)} \times[\text { temperature }]^{(q-r)} \tag{12.17}
\end{equation*}
$$

The requirement of scale invariance demands that the four following relations are verified:

$$
\begin{align*}
& (1+r)=0  \tag{12.18}\\
& (-2+p)=0,  \tag{12.19}\\
& (-n-p)=0,  \tag{12.20}\\
& (q-r)=0 \tag{12.21}
\end{align*}
$$

These relationships lead to a unique solution:

$$
\begin{equation*}
\mathcal{B}_{0}(v, T)=\Gamma \frac{v^{2}}{c^{2}} k_{B} T \tag{12.22}
\end{equation*}
$$

and, using Eq. (12.34) we get, for the spectral energy density ${ }^{5}$ :

$$
\begin{equation*}
u(v, T)=\Gamma 4 \pi \frac{v^{2}}{c^{3}} k_{B} T . \tag{12.23}
\end{equation*}
$$

Apart from the numerical value for the coefficient $\Gamma$, whose value cannot be determined by the Kirchhoff's law only, this is the expression for the energy spectral density provided by classical physics (pre-quantum) [7].

This expression leads to an irreconcilable contradiction that is called the ultraviolet catastrophe. This name derives from the fact that the expression for the energy density

$$
\begin{equation*}
u(T)=\int_{0}^{\infty} u(v, T) \mathrm{d} v \tag{12.24}
\end{equation*}
$$

diverges for any value of the temperature. It should be noted that we are forced to this result because we have assumed a theoretical framework based on two fundamental constants $k_{B}$ and $c$ only.

[^38]To overcome this difficulty, we must recognize that there must be at least another fundamental constant of physics on which this phenomenon depends.

It is very interesting to note that if we apply the same procedure (i.e., "scale invariance") assuming the post-1900 theoretical framework which is based on the three fundamental constants $k_{B}, c$, and $h$, we are led to the Wien's law and to the correct expression for the spectral energy density (always apart from a multiplicative constant). This result can be seen in [18].

### 12.2.6 Extended Form of the Kirchhoff's Law

Let us now consider a cavity constructed of a material that, at the frequency which we are concerned with, has a coefficient of absorption very close to unity. At that frequency (and at equilibrium), the emissivity of the wall of the cavity will be that of a black body $\mathcal{B}_{0}(\nu, T)$.

Let us introduce, inside the cavity, a small body built with any material (for simplicity homogeneous and isotropic) and the whole is in a thermodynamic equilibrium situation.

This implies that for every surface element of each body, the power emitted in any direction is equal to the power absorbed and transported by the radiation impinging on it in the same direction and this must happen for every frequency and polarization state. If this detailed balance were not fulfilled, we could violate the second principle with the same argument that led Kirchhoff to prove the universality of the black-body emissivity.

Let us denote with $\mathcal{B}(v, T)$ and $\mathscr{A}(\nu, T)$, respectively, the spectral emissivity and spectral absorptivity of the small body introduced in the cavity and let $\mathrm{d} \Sigma$ and $\mathrm{d} \Sigma^{\prime}$ be two surface elements belonging to the black cavity and to the small body, respectively. If we consider the elementary surface $\mathrm{d} \Sigma^{\prime}$ and make use of Eqs. (12.1) and (12.4), at equilibrium, we impose the balance between the absorbed power coming from $\mathrm{d} \Sigma$ and the power emitted toward the same elementary surface of the black cavity and obtain

$$
\begin{equation*}
\mathscr{A}(v, T) \mathcal{B}_{0}(\nu, T)=\mathcal{B}(\nu, T) . \tag{12.25}
\end{equation*}
$$

Exchanging parts, the surface $\mathrm{d} \Sigma$ entirely absorbs the power that comes from the small body and within the solid angle subtended by $\mathrm{d} \Sigma^{\prime}$, and it is the sum of that emitted by the small body, and then proportional according to the geometric factors to its emissivity $\mathcal{B}(v, T)$, plus the power reflected on $\mathrm{d} \Sigma$ by $\mathrm{d} \Sigma^{\prime}$ for being illuminated by the whole cavity. It is easy to realize that $\mathrm{d} \Sigma^{\prime}$ is seen by $\mathrm{d} \Sigma$ as having a "virtual emissivity" $\mathcal{B}+(1-\mathscr{A}) \mathcal{B}_{0}$. The balance condition then reads

$$
\begin{equation*}
\mathcal{B}_{0}(\nu, T)=\mathcal{B}(\nu, T)+(1-\mathscr{A}(v, T)) \mathcal{B}_{0}(v, T) . \tag{12.26}
\end{equation*}
$$

In both cases, we have

$$
\begin{equation*}
\frac{\mathcal{B}(v, T)}{\mathscr{A}(v, T)}=\mathcal{B}_{0}(v, T) \tag{12.27}
\end{equation*}
$$

This is the extended form of Kirchhoff's Law.
It states that the ratio of the emissivity and the absorptivity of any surface depends only on frequency and temperature but is independent of the nature of the material and, as a consequence, is equal to the emissivity of a black body. This is equivalent to say that the ratio $(\mathcal{B} / \mathscr{A})$ is a universal function as we have seen for the black body.

### 12.2.7 Emittance

Let us consider a material body and one point P of its surface. If $\mathcal{B}$ is the emissivity of the surface at point $P$, we want to calculate the total, i.e., integrated over all directions, energy emitted per second and per unit area by the body at point $P$. This quantity is called emittance of the body at point P and will be denoted by $\mathcal{W}$.

Let us consider a small area $\mathrm{d} \Sigma$ around P and consider the energy emitted in a certain direction $\mathrm{d} \Omega$ in the time interval dt as written in Eq. (12.3). If the emissivity does not depend on the direction, let us integrate over all the directions and, after dividing $\mathrm{d} \Sigma \mathrm{d} t$, we obtain the total power emitted per unit area by the body at point P. This quantity is related to the emissivity by

$$
\begin{equation*}
\mathcal{W}=\mathcal{B} \int_{0}^{2 \pi} \mathrm{~d} \varphi \int_{0}^{\frac{\pi}{2}} \cos \vartheta \sin \vartheta \mathrm{~d} \vartheta=\pi \mathcal{B} \tag{12.28}
\end{equation*}
$$

The same relation can be written for the spectral quantities. This relation is important because for a body at thermodynamical equilibrium, the emissivity is the same at every point of its surface and then it is relatively simpler to measure the total emitted energy per second by a surface and from this to calculate the emissivity. Remember that only for a black body we are sure that the power emitted toward the calorimeter is entirely due to its emissivity. If, as a first instance, we assume a star to be sphericalsymmetric body with radius $R_{\text {star }}$ whose surface is radiating with emissivity $\mathcal{B}(T)$, the quantity of energy emitted per second from the unit area of the surface of the star is proportional to the emissivity according to Eq. (12.28). The total energy emitted by the star per second is called luminosity of the star, denoted by $L$, and is given by

$$
\begin{equation*}
L=\left(4 \pi R_{\text {star }}^{2}\right) \pi \mathcal{B}(T) \tag{12.29}
\end{equation*}
$$

### 12.2.8 Radiation Energy Density and Emissivity

Let us consider a closed cavity made with a completely absorbing material (black cavity) maintained at temperature $T$ and suppose that a state of thermodynamical equilibrium has been achieved. All the points of the surface of the cavity will be at the same temperature and will have the same emissivity $\mathcal{B}_{0}$. As the radiation propagates at a finite speed, we can define the energy density, associated with radiation, at every point internal to the cavity. More precisely, we will call spectral energy density of radiation at the frequency $v$ in the point $\mathrm{P}(x, y, z)=\mathbf{r}$, the quantity $u(\nu, T, \mathbf{r})$ such that $u(\nu, T, \mathbf{r}) \mathrm{d} v$ is the energy density in the infinitesimal frequency interval $(\nu, v+\mathrm{d} v)$ at the point P of the cavity whose walls are at temperature $T$. We call energy density of radiation at point $P$ inside the cavity whose walls are at temperature $T$, the quantity $u(T, \mathbf{r})$ such that $u(T, \mathbf{r}) \mathrm{d} V$ is the total energy contained in the infinitesimal volume $\mathrm{d} V$ at point P . Clearly, we have

$$
\begin{equation*}
u(T, \mathbf{r})=\int_{0}^{\infty} u(\nu, T, \mathbf{r}) \mathrm{d} v \tag{12.30}
\end{equation*}
$$

Consider a closed cavity formed by a perfectly absorbing material. Every surface element $\mathrm{d} \Sigma$ of the wall of the cavity will send, within an infinitesimal solid angle oriented toward the point P , a certain amount of energy per second, and then generate, in the vicinity of the point P a certain energy density (both spectral and total).

The energy density and the spectral energy density at point $P$ will be the sum of all contributions for all the surface elements that form the wall of the cavity. Consider, then, an elementary surface $\mathrm{d} \Sigma$ of the wall and, correspondingly, consider an infinitesimal surface $\mathrm{d} \Sigma^{\prime}$ around the point P and oriented normal to the direction of emission (see Fig. 12.3).

The amount of energy emitted by the elementary surface $\mathrm{d} \Sigma$ in the time interval $\mathrm{d} t$, in the frequency interval $(\nu, \nu+\mathrm{d} \nu)$ and directed toward the surface $\mathrm{d} \Sigma^{\prime}$ will be given by the relation (see Eq. (12.6)):

$$
\begin{equation*}
\mathrm{d} \varepsilon=\mathcal{B}_{0}(\nu, T) \frac{\mathrm{d} \Sigma \cos \vartheta \mathrm{~d} \Sigma^{\prime}}{r^{2}} \mathrm{~d} v \mathrm{~d} t \tag{12.31}
\end{equation*}
$$

This amount of energy will flow through $\mathrm{d} \Sigma^{\prime}$ in the time interval $\mathrm{d} t$ and, therefore, will be distributed in the infinitesimal volume $\mathrm{d} V^{\prime}=\mathrm{d} \Sigma^{\prime} c \mathrm{~d} t$. The contribution of this infinitesimal energy flow to the spectral energy density at point P will be

$$
\begin{equation*}
d u(v, T, P) \mathrm{d} v=\mathcal{B}_{0}(v, T) \frac{\mathrm{d} \Sigma \cos \vartheta}{r^{2}} \frac{\mathrm{~d} v}{c} \tag{12.32}
\end{equation*}
$$

which can also be written in the following form:


Fig. 12.3 $P$ is a point inside a cavity which is in a state of thermodynamical equilibrium and, hence, at uniform temperature $T$. The point P "sees" a generic surface element $\mathrm{d} \Sigma$ of the surface of the cavity, within the solid angle $\mathrm{d} \Omega^{\prime}$. The surface element $\mathrm{d} \Sigma$ emits radiation, with some intensity, within the solid angle $\mathrm{d} \Omega$ toward point P . The surface element $\mathrm{d} \Sigma^{\prime}$ is taken perpendicular to the vector $\mathbf{r}$ from $\mathrm{d} \Sigma$ to the point P and the volume $\mathrm{d} V^{\prime}=\mathrm{d} \Sigma^{\prime} c \mathrm{~d} t$ is filled by the radiation emitted by $\mathrm{d} \Sigma$ in the time interval $\mathrm{d} t$

$$
\begin{equation*}
\mathrm{d} u(v, T, P)=\mathcal{B}_{0}(v, T) \mathrm{d} \Omega^{\prime} \frac{1}{c} \tag{12.33}
\end{equation*}
$$

where $\mathrm{d} \Omega^{\prime}=\mathrm{d} \Sigma \cos \vartheta / r^{2}$ is the infinitesimal solid angle subtended by $\mathrm{d} \Sigma$ when it is observed from the point P .

From this relation, we can integrate over the entire (closed) surface of the cavity to obtain

$$
\begin{equation*}
u(v, T)=\frac{4 \pi}{c} \mathcal{B}_{0}(v, T) \tag{12.34}
\end{equation*}
$$

This result shows that the value of the spectral energy density does not depend on the position of the point P , in other words, that it is homogeneously distributed inside the cavity. In addition, from the above relations, one can easily see that an observer introduced inside a "black" cavity (that is, the small surface $\mathrm{d} \Sigma^{\prime}$ is considered as the sensitive surface of an instrument) would see in all directions the same flow of energy per unit frequency interval and per unit of solid angle; this means that this observer could not distinguish objects (provided that they are at thermodynamical equilibrium) in the cavity but would be immersed in a "fog" with uniform brightness at each frequency.

By integrating over all frequencies, we define the energy density of the radiation and it will result

$$
\begin{equation*}
u(T)=\int_{0}^{\infty} u(v, T) \mathrm{d} v=\frac{4 \pi}{c} \mathcal{B}_{0}(T) \tag{12.35}
\end{equation*}
$$

Also, the (total) energy density is homogeneously distributed within the cavity and its value will depend only on the emissivity of the walls and then it will depend only on the temperature. It is immediate to prove that, in equilibrium conditions, among the energy density, the emissivity $\mathcal{B}_{0}$ and the emittance of the surface, the following relations hold:

$$
\begin{equation*}
u=\frac{4 \pi}{c} \mathcal{B}_{0}=\frac{4 \mathcal{W}_{0}}{c} \tag{12.36}
\end{equation*}
$$

These relations allow us to switch from the measurement of the emittance to the energy density. In this way, Stefan has found the law of proportionality of the energy density to the fourth power of the temperature.

### 12.3 Wien's Law

Sometimes, the denomination "Wien's law" is used to indicate the law more correctly named "Wien's displacement law" which is summarized by the relation

$$
\begin{equation*}
\lambda_{\max } T=\text { constant }=2.90 \times 10^{-3} \mathrm{~m} \mathrm{~K} . \tag{12.37}
\end{equation*}
$$

This relation provides the value of the wavelength $\lambda_{\text {max }}$ at which the spectral energy density, and then the spectral emissivity, of a black body, is maximum at a given temperature. We can say, with a short but efficacious expression used by astronomers, that it establishes the relationship between the color of a body in thermodynamic equilibrium and its temperature.

At ambient temperatures (say roughly in the interval 290-300 K), the wavelength of the emission peak is near $10 \mu \mathrm{~m}$ that is in the far infrared and then, to obtain the emission peak in the visible wavelengths, a body must be brought to a temperature of at least 3000 K .

At this temperature, the maximum of emission is at the beginning of the visible range. The photosphere of the Sun (i.e., the external part that we see "normally" with the eye) has a temperature of about 5500 K , and then the emission peak is at $\lambda \simeq 0.53 \mu \mathrm{~m}$.

Equation (12.37) is one of the main pillars on which the possibility of applying the theory of Stellar Evolution to astronomical observations rests and is, therefore, one of the fundamental blocks with which modern cosmology is built.

However, this relation, so important, represents only "one" functional aspect of a more fundamental law, correctly named Wien's law, whose complete formal expression is given at the end of Sect. 12.3.2 in Eq. (12.47).

The relevance of this finding is that it shows that the universal function $u(\nu, T)$ which appears to be a function of the two variables $v$ e $T$ is, in principle, a universal function of the single variable $\nu / T$. In particular, it follows that the frequency at which the specific emissivity is maximum is proportional to the temperature of the black body, which is the content of the Wien's displacement law.

### 12.3.1 Wien's Law According to Wien

The result, known as Wien's law, was obtained by W. Wien studying the change in the radiation frequency that would occur in a cavity with perfectly reflecting walls, in which the volume is made to vary for example with a movable piston.

During the expansion, the frequency of this radiation changes in the reflection process against the moving piston (it is a simple exercise on the Doppler effect of electromagnetic waves reflected from a moving mirror). Moreover, if we operate in order to ensure also the thermodynamic equilibrium (and this requires some attention), we achieve the desired result.

Other authors [19] have faced, with some variations, the same problem but the fundamental idea remains that of Wien.

Many authors, who are mainly interested in the displacement law, obtain Eq. (12.37) operating "a posteriori" simply by calculating the point in which the spectral energy density, as provided by quantum physics, is maximum. It is immediate to verify that this happens for a well-defined value of the ratio $v / T$ but the reader should be aware that Wien's displacement law is not a consequence of quantum physics.

We want, here, to refer to the demonstration given by von Laue in an article of 1943. In this article, von Laue highlights the fundamental fact that Wien's law is a consequence of the theory of relativity and does not need ad hoc assumptions.

### 12.3.2 Wien's Law and Relativity

Max von Laue [20] considers a surface element $\mathrm{d} \Sigma$ of a black body and the pencil of rays emitted at an angle $\vartheta$ with respect to the normal to the surface and within a solid angle $\mathrm{d} \Omega$, as shown in Fig. 12.4.

The energy, per unit frequency, contained in this pencil of rays in the time interval $\Delta t$ can be written recalling Eq. (12.3). If, as usual, we denote with $\mathcal{B}_{0}(\nu, T)$ the spectral emissivity of the surface element and take into account that the time interval is related to the length $l$ of the pencil by $l=c \Delta t$, we get


Fig. 12.4 The surface element $\mathrm{d} \Sigma$ of a black body is considered to be an emitter both of energy and of entropy. We consider the pencil emitted in a direction $\vartheta$ with respect to the normal to the surface, in a time interval $\Delta t$

$$
\begin{equation*}
\mathrm{d} \varepsilon_{\nu}=\frac{l}{c} \mathcal{B}_{0}(\nu, T) \mathrm{d} \nu \mathrm{~d} \Sigma \cos \vartheta \mathrm{~d} \Omega \tag{12.38}
\end{equation*}
$$

In a similar way, we consider the surface element as an entropy emitter. This point will be made clearer in Sect. 12.4 where entropy, together with the other relevant thermodynamic potentials for the radiation field will be defined.

In analogy of what we have made for the definition of the energy density $u(T)$ and of the spectral energy density $u(\nu, T)$ starting from the emissivity and the spectral emissivity of the surface elements, we shall consider the entropy density $s(T)$ and the spectral entropy density $s(v, T)$ as radiated by the surface elements of the black body, by developing the analogous formalism. Then, for the amount of entropy possessed by the pencil of radiation considered above and in the same frequency interval, we may write the following expression:

$$
\begin{equation*}
\mathrm{d} S_{v}=\frac{l}{c} \mathcal{S}_{0}(v, T) \mathrm{d} v \mathrm{~d} \Sigma \cos \vartheta \mathrm{~d} \Omega \tag{12.39}
\end{equation*}
$$

where $\mathcal{S}_{0}(\nu, T)$ is the spectral emissivity of entropy of the surface element $\mathrm{d} \Sigma$. Obviously, $\mathcal{B}_{0}(\nu, T)$ and $\mathcal{S}_{0}(\nu, T)$ are mutually dependent, and von Laue shows what kind of constraint is required by the theory of relativity to this mutual dependence.

This result can be achieved as follows. First, we observe that the two quantities $\left(\mathrm{d} \varepsilon_{v} / v\right)$ and $\mathrm{d} S_{v}$ are two relativistic invariants (see [20]). Besides this, also the quantity

$$
\begin{equation*}
\mathrm{d} \mathcal{Z}=\frac{\nu^{2}}{c^{2}} \frac{l}{c} \mathrm{~d} \nu \mathrm{~d} \sigma \cos \vartheta \mathrm{~d} \Omega \tag{12.40}
\end{equation*}
$$

is relativistically invariant. Since the ratio of two invariants is an invariant, it follows that both

$$
\begin{equation*}
\frac{\mathcal{B}_{0}(\nu, T)}{v^{3}}=\frac{\mathrm{d} \varepsilon_{v}}{c^{2} \mathrm{~d} \mathcal{Z} v}, \tag{12.41}
\end{equation*}
$$

and

$$
\begin{equation*}
\frac{\mathcal{S}_{0}(v, T)}{v^{2}}=\frac{\mathrm{d} S_{v}}{c^{2} \mathrm{~d} \mathcal{Z}} \tag{12.42}
\end{equation*}
$$

are two relativistic invariants. As a consequence, we may write

$$
\begin{equation*}
\frac{\mathcal{S}_{0}(\nu, T)}{v^{2}}=f\left(\frac{\mathcal{B}_{0}(v, T)}{v^{3}}\right) \tag{12.43}
\end{equation*}
$$

where $f(q)$ is a universal function to be determined. From the definition of temperature, we have

$$
\begin{equation*}
\frac{1}{T}=\frac{\partial \mathcal{S}_{0}}{\partial \mathcal{B}_{0}} \tag{12.44}
\end{equation*}
$$

and then, from Eq. (12.43) we obtain

$$
\begin{equation*}
\frac{1}{T}=\frac{1}{v} f^{\prime}\left(\frac{\mathcal{B}_{0}(v, T)}{v^{3}}\right) \tag{12.45}
\end{equation*}
$$

which is equivalent to write

$$
\begin{equation*}
\mathcal{B}_{0}(v, T)=v^{3} F\left(\frac{v}{T}\right), \tag{12.46}
\end{equation*}
$$

where $F$ is a universal function to be determined. From Eq. (12.34), we obtain the spectral energy density:

$$
\begin{equation*}
u(v, T)=\frac{4 \pi}{c} v^{3} F\left(\frac{v}{T}\right) \tag{12.47}
\end{equation*}
$$

### 12.3.3 Some Consequences of the Wien's Law

From Eq. (12.47), some important consequences can be derived.
The first one is the famous "Wien's displacement law" Eq. (12.37). Indeed, if we ask, given a temperature $T$, at which frequency the spectral emissivity, and hence the spectral energy density, is maximum we proceed as follows.

Let us write Eq. (12.47) in the form

$$
\begin{equation*}
u(v, T)=\frac{4 \pi}{c} T^{3} x^{3} F(x) \tag{12.48}
\end{equation*}
$$

having posed

$$
\begin{equation*}
x=\frac{v}{T} . \tag{12.49}
\end{equation*}
$$

For a fixed temperature, the required frequency $v_{\max }$ of maximum emission can be obtained from the value $x_{\max }$ which maximizes the function $x^{3} F(x)$. From this, we have

$$
\begin{equation*}
v_{\max }=x_{\max } T \tag{12.50}
\end{equation*}
$$

The proportionality of the frequency of maximum emissivity to temperature is independent of the shape of $F(x)$, while the numerical value of $x_{\max }$ depends on it.

From the Wien's Law in the form Eq. (12.47), we can obtain two other results of fundamental importance.

One is the dependence of the maximum emissivity on temperature. From Eq. (12.48), we see that the ratio of the spectral energy densities at $x_{\max }$ obeys the relation

$$
\begin{equation*}
\frac{u\left(v_{\max _{2}}, T_{2}\right)}{u\left(v_{\max _{1}}, T_{1}\right)}=\left(\frac{T_{2}}{T_{1}}\right)^{3} \tag{12.51}
\end{equation*}
$$

which means that the maximum emissivity increases with the cube of the temperature.

Another fundamental result, of general validity, we can obtain from Wien's law refers to the temperature dependence of the energy density of black-body radiation. From Eq. (12.48), we may write

$$
\begin{equation*}
u(T)=\int_{0}^{\infty} u(v, T) \mathrm{d} v=\frac{4 \pi}{c} T^{4} \int_{0}^{\infty} x^{3} F(x) \mathrm{d} x . \tag{12.52}
\end{equation*}
$$

If we denote with $a$ the quantity

$$
\begin{equation*}
a=\frac{4 \pi}{c} \int_{0}^{\infty} x^{3} F(x) \mathrm{d} x \tag{12.53}
\end{equation*}
$$

the energy density will be given by

$$
\begin{equation*}
u(T)=a T^{4} \tag{12.54}
\end{equation*}
$$

where $a$ is the fundamental constant known as the Stefan-Boltzmann constant whose value is $a=7.56 \times 10^{-16} \mathrm{~J} \mathrm{~m}^{-3} \mathrm{~K}^{-4}$.

If we recall Eq. (12.36), we may write the expression for the emittance of a black body at temperature $T$ :

$$
\begin{equation*}
\mathcal{W}_{0}=\frac{a c}{4} T^{4}=\sigma T^{4} \tag{12.55}
\end{equation*}
$$

with $\sigma=5.67 \mathrm{~J} \mathrm{~s}^{-1} \mathrm{~m}^{-2} \mathrm{~K}^{-4}$ called radiation constant. For instance, we may see that for a black body at $T \simeq 300 \mathrm{~K}$ the emittance is $W_{0}(300) \simeq 460 \mathrm{~W} \mathrm{~m}^{-2}$ and is the upper limit to the emittance of a real body at this temperature.

At this point, the only thing we can tell about the universal function $F(x)$ is that the integral

$$
\begin{equation*}
\int_{0}^{\infty} x^{3} F(x) \mathrm{d} x=\frac{a c}{4 \pi} \simeq 1.8 \times 10^{-8} \mathrm{~J} \mathrm{~m}^{-2} \mathrm{~s} \mathrm{~K}^{-4} \tag{12.56}
\end{equation*}
$$

but nothing more concerning the form of that function. The complete expression of the spectral energy density of the radiation in thermodynamic equilibrium $u(v, T)$ of the black body will be obtained by M. Planck in his master paper of late 1900. His result is

$$
\begin{equation*}
u(v, T)=\frac{8 \pi}{c^{3}} v^{2} \frac{h v}{\exp (h v / k T)-1} . \tag{12.57}
\end{equation*}
$$

The procedure adopted by Planck in order to obtain this result is briefly summarized in Sect. 12.6.

Example 12.1 The temperature of the Sun from the solar constant. Suppose that the Sun emits radiation as a spherical isotropic body having radius $R_{\odot} \simeq 7 \times 10^{8} \mathrm{~m}$ at a distance $R_{\mathrm{ES}} \simeq 15 \times 10^{10} \mathrm{~m}$ from the Earth. We measure, on the Earth, the total power collected by $1 \mathrm{~m}^{2}$ plane detector perpendicular to the direction toward the center of the Sun and we find $\mathscr{S}_{\odot} \simeq 1366 \mathrm{~W} / \mathrm{m}^{2}$. This is called the "solar constant."

If we assume that the "surface" of the Sun, the photosphere, emits as a black body, we may determine the value of its temperature $T$.

Our detector collects the total flux coming from the different portions of the Sun's surface. Let us assume, as a first approximation, that all these portions of the Sun's surface are at the same distance $R_{\mathrm{ES}}$ from the detector, and that they all "see" the detector under the same solid angle $\delta \Omega=1 / R_{\mathrm{ES}}^{2}$. After integrating over the whole surface of the Sun, we can state that the detector is traversed by the total energy emitted by the Sun in the solid angle:

$$
\begin{equation*}
\Omega \simeq \frac{\pi R_{\odot}^{2}}{R_{\mathrm{ES}}^{2}} \tag{12.58}
\end{equation*}
$$

Let us denote with $\mathcal{B}_{0}(T)$ the emissivity of the surface of the photosphere. The energy collected per second and per unit area by our detector will be what we call the "solar constant":

$$
\begin{equation*}
\mathscr{S}_{\odot}=\frac{\pi R_{\odot}^{2}}{R_{\mathrm{ES}}^{2}} \mathcal{B}_{0}(T) \tag{12.59}
\end{equation*}
$$

where

$$
\begin{equation*}
\mathcal{B}_{0}(T)=\frac{R_{\mathrm{ES}}^{2}}{\pi R_{\odot}^{2}} \mathscr{S}_{\odot} \simeq \frac{225 \times 10^{20}}{3.14 \times 49 \times 10^{16}} \times 1366 \simeq 2 \times 10^{7} \frac{\mathrm{~W}}{\mathrm{~m}^{2}} \tag{12.60}
\end{equation*}
$$

The dependance of the emissivity on temperature can be obtained from the StefanBoltzman law Eq. (12.54) and from the relation between emissivity and energy density in a black cavity in Eq. (12.35):

$$
\begin{equation*}
\mathcal{B}_{0}(T)=\frac{c a}{4 \pi} T^{4} \tag{12.61}
\end{equation*}
$$

By substituting Eq. (12.60) in Eq. (12.61), we obtain

$$
\begin{equation*}
T=\left(\frac{4 \times 3.14}{3 \times 10^{8} \times 7.56 \times 10^{-16}} \times 2 \times 10^{7}\right)^{\frac{1}{4}} \simeq\left(1.1 \times 10^{15}\right)^{\frac{1}{4}} \simeq 5760 \mathrm{~K} \tag{12.62}
\end{equation*}
$$

Example 12.2 The temperature of the Sun from spectroscopy. It is interesting to compare the result obtained in Eq. (12.62) with that obtained by using the Wien's displacement law.

According to this law, in a black body at equilibrium temperature $T$, the energy spectral density exhibits its maximum at the wavelength given by Eq. (12.37) and
hence the same holds for the spectral emissivity. From spectroscopic measurements, the peak of emission from the solar photosphere is at a wavelength very near (a little longer then) to

$$
\begin{equation*}
\lambda_{\max } \simeq 5 \times 10^{-7} \mathrm{~m} \tag{12.63}
\end{equation*}
$$

If, again, we assume that the emitting body is a black body, we get the following value for the temperature of the emitting surface:

$$
\begin{equation*}
T \simeq \frac{2.9 \times 10^{-3}}{5 \times 10^{-7}} \simeq 5800 \mathrm{~K} \tag{12.64}
\end{equation*}
$$

which is very close to the value previously found and based on a total energy argument.

Example 12.3 The luminosity of the Sun. Having derived the value of the emissivity we may apply Eq. (12.29) and obtain

$$
\begin{equation*}
L_{\odot} \simeq\left(4 \times 3.14 \times 49 \times 10^{16}\right) \times 3.14 \times 2 \times 10^{7} \simeq 3.86 \times 10^{26} \mathrm{~J} \mathrm{~s}^{-1} \tag{12.65}
\end{equation*}
$$

Notice that the emitted energy will be uniformly distributed on the surface of a sphere of radius $R_{\mathrm{ES}} \simeq 15 \times 10^{10} \mathrm{~m}$ and then the power collected by $1 \mathrm{~m}^{2}$ of this sphere will be

$$
\begin{equation*}
\mathscr{S}_{\odot} \simeq\left(\frac{3.86 \times 10^{26}}{4 \times 3.14 \times 2.25 \times 10^{22}}\right) \mathrm{W} \mathrm{~m}^{-2} \simeq 1.366 \times 10^{3} \mathrm{~W} \mathrm{~m}^{-2} \tag{12.66}
\end{equation*}
$$

We have derived an approximate value for the emissivity of the Sun's photosphere by two independent ways. One is based on the Wien's displacement law and can be applied to any star without having further information on its radius and distance.

The other one (see Eq. (12.59)) requires the knowledge of the solid angle subtended by the star and of the energy density flux on the observation point.

### 12.4 Thermodynamic Potentials for Radiation

Let us consider a cavity within a material body and let us write the expressions of the thermodynamical potentials for the radiation contained in the cavity provided that the whole system is in a state of thermodynamical equilibrium.

First, it is necessary to establish the relation between the radiation energy density and the pressure exerted by radiation on the walls of the cavity. We first refer to Eq. (B.18) obtained in Eq. (B.18) which shows the general result in the case of perfectly reflecting walls.

The same relation holds for "black walls," i.e., for walls with absorptivity $\mathscr{A}=$ 1 , provided that the walls are in thermodynamic equilibrium with the radiation.

Indeed, the wall absorbs completely the incident radiation but emits exactly the same power, in the reverse direction, with the same angular and energy distribution. The momentum transferred per unit time will be twice that calculated in Eq. (B.10) for totally absorbing walls.

Similarly, for a real surface, the result will be the same provided that it is in thermodynamical equilibrium with radiation. Indeed, we can subdivide the incident radiation, for every frequency and direction, into two components: one absorbed (according to the value of the absorptivity $\mathscr{A}$ ) and the other reflected. For the former, the condition of thermodynamic equilibrium requires that at the same frequency and in the reverse direction, the wall emits the same energy, and hence the reverse amount of momentum, per unit time. As regards the latter, Eq. (B.11) holds by definition. In conclusion, the two components realize the condition described in Eq. (B.18).

Notice that this is valid for every frequency interval for if we denote with $p_{\nu} \mathrm{d} \nu$ the contribution to the total pressure given by the radiation with frequency in the interval ( $v, v+\mathrm{d} \nu)$, we have

$$
\begin{equation*}
p_{v} \mathrm{~d} v=\frac{1}{3} u_{v} \mathrm{~d} v, \tag{12.67}
\end{equation*}
$$

where $u_{v}$ is the spectral energy density.
Consider the radiation contained in a cavity in thermodynamic equilibrium. Owing to homogeneity, as we proved in Sect. 12.2.8 the energy $U$ and the entropy $S$ must be written in the following form:

$$
\begin{align*}
& U(V, T)=u(T) V  \tag{12.68}\\
& S(V, T)=s(T) V \tag{12.69}
\end{align*}
$$

where $u(T)$ and $s(T)$ are, respectively, the energy and the entropy densities. For a generic quasi-static transformation, we have

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V, \tag{12.70}
\end{equation*}
$$

and differentiating Eq. (12.68), we obtain

$$
\begin{equation*}
\mathrm{d} U=\frac{\mathrm{d} u}{\mathrm{~d} T} V \mathrm{~d} T+u \mathrm{~d} V \tag{12.71}
\end{equation*}
$$

Finally, substituting Eq. (12.71) in Eq. (12.70) and remembering Eq. (B.18), we have

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \frac{\mathrm{~d} u}{\mathrm{~d} T} V \mathrm{~d} T+\frac{4}{3} \frac{u}{T} \mathrm{~d} V \tag{12.72}
\end{equation*}
$$

Since $\mathrm{d} S$ is an exact differential the cross-derivatives must be equal and this leads to

$$
\begin{equation*}
\frac{\mathrm{d} u}{\mathrm{~d} T}=4 \frac{u}{T} . \tag{12.73}
\end{equation*}
$$

If we integrate the above equation, we obtain the Stefan-Boltzmann law

$$
\begin{equation*}
u=a T^{4} \tag{12.74}
\end{equation*}
$$

where $a=7.56 \times 10^{-16} \mathrm{~J} \mathrm{~m}^{-3} \mathrm{~K}^{-4}$. For energy, we have ${ }^{6}$

$$
\begin{equation*}
U(V, T)=a T^{4} V \tag{12.75}
\end{equation*}
$$

From Eq. (12.72), we can write the expressions for entropy and density of entropy:

$$
\begin{equation*}
\mathrm{d} S=4 a\left[T^{2} V \mathrm{~d} T+\frac{1}{3} T^{3} \mathrm{~d} V\right]=\frac{4}{3} a \mathrm{~d}\left(V T^{3}\right) \tag{12.76}
\end{equation*}
$$

which leads to

$$
\begin{align*}
& S(T)=\frac{4}{3} a T^{3} V,  \tag{12.77}\\
& S(T)=\frac{4}{3} a T^{3} . \tag{12.78}
\end{align*}
$$

for the thermal dependency of the entropy and the entropy density, respectively. In parallel, for the Gibbs potential of the radiation, we have $G=U+p V-T S=0$. From the particle point of view, this implies that the chemical potential of the photon gas is zero.

### 12.5 Thermodynamical Processes for Radiation

In this section, we briefly consider the basic thermodynamical transformations for radiation in a state of thermodynamical equilibrium. Radiation possesses its own thermodynamical potentials as any thermodynamical system but we must keep in mind that, in general, radiation must be kept in constant interaction with matter if we want to achieve equilibrium states (remember that in the classical context electromagnetic waves do not interact with each other).

[^39]
### 12.5.1 Isothermal Processes

The isothermal transformations of a radiation gas are also isobaric transformations. The volume of the cavity is varied while keeping the walls at a constant temperature. The work that we do and the amount of heat that we must provide the walls correspond to the work and the amount of heat supplied to the black-body radiation which is generated inside in order to preserve the condition of thermodynamic equilibrium. It is supposed that the properties of the matter that constitutes the walls remain constant as, for example, in cases in which the change of volume is realized by moving a (frictionless) piston. If the volume varies from an initial value $V_{1}$ to the final value $V_{2}$, the variation of energy and the amount of work done by the radiation are, respectively,

$$
\begin{align*}
\Delta U & =u(T)\left[V_{2}-V_{1}\right]  \tag{12.79}\\
W^{r} & =\frac{1}{3} u(T)\left[V_{2}-V_{1}\right] \tag{12.80}
\end{align*}
$$

To do this, we must transfer to the walls the amount of heat

$$
Q=T \Delta S=\frac{4}{3} a T^{4}\left[V_{2}-V_{1}\right]
$$

This quantity of heat corresponds to the variation of energy of the radiation plus the work done by the latter in the expansion Eq. (12.80).

### 12.5.2 Adiabatic Processes

In this type of transformations, the cavity walls are thermally insulated. In this case, however, the thermal capacity of the walls plays a predominant role in the energy balance of the overall system. If we are interested only in the variations of the properties of the radiation, we have to consider the cavity with perfectly reflecting walls.

This, however, poses a problem: if the radiation is in an initial state of thermodynamic equilibrium, at the temperature $T$, within a cavity with perfectly reflecting walls and we do vary the volume in any way, we will get a new situation in which the radiation can no longer be considered in a state of thermodynamic equilibrium. The reason is evident in a classical context (pre-quantum) if one keeps in mind that electromagnetic waves do not interact with each other, and then the system cannot thermalize as would happen for example with a real gas. ${ }^{7}$

[^40]To realize a quasi-static adiabatic process is necessary therefore to ensure that the radiation can thermalize quickly. This can be obtained by entering into the cavity with reflecting walls a small sample of any material (preferably a conductor) such as a small piece of copper. Of course, this little bit of material will participate in the overall balance equations but if its mass is small enough the introduced perturbation of the equations that govern the energy balances of the radiation, it can be accounted for and possibly neglected. ${ }^{8}$

After these preliminary considerations, we can write the equations for the adiabatic transformation in the following form:

$$
\begin{equation*}
T^{3} V=\text { constant } \tag{12.81}
\end{equation*}
$$

Referring to Eq. (B.18) and to the Stefan-Boltzmann law Eq. (12.54), we have

$$
\begin{equation*}
p V^{\frac{4}{3}}=\text { constant } \tag{12.82}
\end{equation*}
$$

then the amount of work done by the radiation in an adiabatic quasi-static process from an initial state with initial volume $V_{1}$ and pressure $p_{1}$, to the final volume $V_{2}$ will be

$$
\begin{equation*}
W_{1,2}^{\mathrm{ad}}=p_{1} V_{1}^{\frac{4}{3}} \int_{V_{1}}^{V_{2}} V^{-\frac{4}{3}} \mathrm{~d} V \tag{12.83}
\end{equation*}
$$

and

$$
\begin{equation*}
W_{1,2}^{\mathrm{ad}}=3 p_{1} V_{1}\left[1-\left(\frac{V_{1}}{V_{2}}\right)^{\frac{1}{3}}\right] . \tag{12.84}
\end{equation*}
$$

### 12.5.3 Isochoric Transformations (Constant Volume)

For constant volume transformations $T \mathrm{~d} S=\mathrm{d} U$ and then the amount of heat supplied to the system in the transition from temperature $T_{1}$ to temperature $T_{2}$ will be

$$
\begin{align*}
& Q_{1,2}=a V\left[T_{2}^{4}-T_{1}^{4}\right],  \tag{12.85}\\
& Q_{1,2}=3 V\left(p_{2}-p_{1}\right) . \tag{12.86}
\end{align*}
$$

Following the general definition, the heat capacity at constant volume for the radiation will be given by

$$
\begin{equation*}
C_{V}=T\left(\frac{\partial S}{\partial T}\right)_{V}=4 a T^{3} V \tag{12.87}
\end{equation*}
$$

[^41]
### 12.5.4 Free Expansion

Suppose we have a black-body radiation field at temperature $T$ contained in a cavity with perfectly reflecting walls and volume $V$. This cavity can be placed in communication with another cavity with perfectly reflecting walls and having the same volume simply by removing a partition. In this second cavity, the existing radiation is at very low temperature so that its energy content can be neglected.

The dividing wall is removed. What can we say about the final state of the radiation contained in the total volume $V^{\prime}=2 V$ ?

We denote by the index 1 all the values of the quantities in the initial state in which the radiation occupies the volume $V$ and by the index 2 the values when the radiation occupies the volume $2 V$. Let us examine two situations.

## Absence of Matter in the Cavity

The energy of the radiation will be constant and therefore the energy density will be halved.

With reference to mechanical interpretation of pressure treated in Appendix B.1, we proved that the relation between pressure and energy density is not dependent on the establishment of thermodynamical equilibrium, the pressure exerted on the reflecting walls will (we assume that the radiation is kept in a condition of isotropy) be

$$
\begin{equation*}
p_{2}=\frac{1}{2} p_{1} \tag{12.88}
\end{equation*}
$$

As it regards the temperature, this is not definable because the radiation is not in a state of thermodynamic equilibrium.

## Presence of a Small Quantity of Matter in the Cavity

In this case, the radiation will settle in a new state of thermodynamic equilibrium. The total energy will always be constant and, for this reason (see Eq. (12.75)), the final temperature will be

$$
\begin{equation*}
T_{2}=\frac{1}{2^{1 / 4}} T_{1} \tag{12.89}
\end{equation*}
$$

As in the previous situation of the absence of matter, the new pressure will be $p_{2}=$ $1 / 2 p_{1}$. The entropy variation in this process will be

$$
\begin{equation*}
\Delta S=2 V \frac{4}{3} a T_{2}^{3}-V \frac{4}{3} a T_{1}^{3} \tag{12.90}
\end{equation*}
$$

therefore,

$$
\begin{align*}
\Delta S & =\frac{4}{3} a V T_{1}^{3}\left[2^{\frac{1}{4}}-1\right]  \tag{12.91}\\
S & \simeq 0.19 S_{1} \tag{12.92}
\end{align*}
$$

The entropy increase is $\simeq 19 \%$ of the initial value. As regards the final pressure the reader should remember that in the case of absence of matter in the cavity, the term "pressure" has been improperly used just to mean that the mechanical effect on the walls has a halved value. Only in the second case (thermodynamical equilibrium) the term pressure can be properly used.

### 12.6 Planck and the Problem of Black-Body Radiation

We have seen how relativity leads us to Wien's law Eq. (12.47) and to StefanBoltzmann law Eq. (12.54) but, of course, does not allow us to determine the form of the function $F(v / T)$ and, as a consequence, the form of the spectral emissivity and of the spectral energy density of black-body radiation. We say "of course" because such a determination must be the product of the general theoretical context and, indeed, we have seen that, in the classical (i.e., pre-quantum) context, the request of universality contained in Kirchhoff's law led to the "catastrophe" expressed by Eq. (12.23) and then, for the function $F$ in Eq. (12.47), to the form

$$
\begin{equation*}
F\left(\frac{v}{T}\right) \propto\left(\frac{T}{v}\right) \tag{12.93}
\end{equation*}
$$

This is the crisis situation that physicists had to face at the end of the nineteenth century. It was a profound, conceptual, crisis, because the onset of the energy divergence had conceptual roots and was not "adjustable" with appropriate models. It made it inevitable to abandon the current theoretical context.

It is very interesting to go through, very briefly, the starting point of the complex work by Planck in a treatise on thermodynamics because it was his deep knowledge of this discipline, applied to the available experimental data, that allowed him to get the determination of the function $F(\nu / T)$. After that, and thanks to the birth, in those years, of statistical mechanics founded by Boltzmann, he gave his fundamental contribution to the birth of quantum physics. In this last step, however, also the contribution of Einstein with his works of 1905 and later was decisive.

### 12.6.1 The Situation at the End of the Nineteenth Century and the Black-Body Radiation

At the end of the nineteenth century, the situation, with regard to the experimental study of $u(v, T)$, was the following:
(1) At high frequencies, ${ }^{9}$ various empirical formulae had been proposed but by 1900 most of physicists believed that Wien's proposal was definitely the best. It was summarized by the relation

$$
\begin{equation*}
u(v, T) \propto v^{3} \exp (-\beta v / T) \tag{12.94}
\end{equation*}
$$

where $\beta$ is a parameter whose value is derived from the "best-fit" with the experimental data.
(2) Later, when new techniques for measurements in the far infrared ${ }^{10}$ were developed, the situation appeared to be quite different. The spectral energy density, at low frequencies, was well described by the relation

$$
\begin{equation*}
u(v, T)=\frac{8 \pi}{c^{3}} v^{2} k_{B} T \tag{12.95}
\end{equation*}
$$

This relation not only described well the experimental data at low frequencies but was exactly what the theoretical context of the time foresaw. This part of the spectrum is currently named as "the Rayleigh-Jeans region" because Eq. (12.95) was previously obtained by Lord Rayleigh and then developed by J.H. Jeans. As we have seen in Sect. 12.2.5, the form of the Rayleigh-Jeans formula is a product of the requirement of universality contained in Kirchhoff's law and of the classical theoretical context.

Of course we have to consider that both the "Rayleigh-Jeans region" and the "Wien's region" constitute two branches of the same function, but while the former (low frequency) was "welcome", the latter (Wien's at high frequencies) represented a contradiction.

### 12.6.2 Planck and the Problem of Matter-Radiation Interaction

The radiation field within the cavity is created by the electric charges which constitute the walls of the cavity and is in constant interaction with them. The spectral density of the radiation must be correlated with the thermodynamic state of the walls and

[^42]then Planck worked out a model in order to find this correlation. The model was based on the following assumptions:
(1) Matter is constituted by an agglomeration of charged harmonic oscillators with proper pulsation $\omega_{0}$ as indicated by the atomic theory of matter at that time; the oscillators are put into forced oscillation by the radiation field of the cavity.
(2) The radiation field of the cavity is decomposed into plane waves mutually incoherent.
(3) If the electric fields are not too intense, the motion of the oscillators can be well described by the usual equation of forced elastic oscillations, with a weak damping due to the radiation of e.m. waves in the cavity.

Planck found a relationship between the oscillator's energy distribution and the spectral energy density of the electromagnetic field that is established at equilibrium. The relation found by Planck is

$$
\begin{equation*}
u(v, T)=\frac{8 \pi}{c^{3}} v^{2} \varepsilon \tag{12.96}
\end{equation*}
$$

where $\varepsilon$ is the oscillator's energy. In the model developed by Planck that led to Eq. (12.96), the following points should be highlighted: (i) the energy of a single oscillator is the sum of kinetic and potential energy, and these are proportional to the square of the amplitude of the harmonic motion; (ii) the frequency of the forced oscillation that is established is given by the frequency of the incident e.m. wave but the amplitude of the resulting motion is significant only for those oscillators that have a proper frequency close to the frequency of the incident wave.

After having established the relation between specific energy density and the energy of the corresponding material oscillators, Planck changes the point of view and he uses the observed spectral energy density of the radiation as revealing the distribution in energy of the material oscillators of the body in thermodynamic equilibrium at temperature $T$.

Then if we observe a specific density of radiation at the frequency $v$, the amount of energy of the oscillators associated to that frequency is given by

$$
\begin{equation*}
\varepsilon=\frac{1}{8 \pi} \frac{c^{3}}{v^{2}} u(v, T) \tag{12.97}
\end{equation*}
$$

From this point of view, the above relation gives us the energy distribution of the material oscillators of whatever body at thermodynamic equilibrium and then Kirchhoff's law, initially formulated for radiation, implies a sort of "reversed Kirchhoff's law" according to which the distribution in energy of the material oscillators of a body at thermodynamic equilibrium, does not depend on the nature of the material and is, therefore, given by a universal. function.

### 12.6.3 The Planck Solution (Through Thermodynamics)

How to find this universal function? At low frequencies, in the "Rayleigh-Jeans" branch, if we use Eq. (12.97) together with Eq. (12.95), we immediately find the relation

$$
\begin{equation*}
\varepsilon=k_{B} T \tag{12.98}
\end{equation*}
$$

while at high frequencies, if we make use of the "Wien's branch" experimentally determined, we find

$$
\begin{equation*}
\varepsilon \propto \frac{c^{3}}{8 \pi} \nu \exp (-\beta \nu / T) \tag{12.99}
\end{equation*}
$$

The point is the following: these two expressions for $\varepsilon$ are the two branches, at low frequencies and at high frequencies, of one single function that links the energy of the oscillators to the frequency of the radiation at a given temperature.

It is at this point that thermodynamics allowed Planck to take the decisive step. From the fundamental equations of thermodynamics, we know that for every system, entropy, and internal energy, at a given temperature, are related by the following equation:

$$
\begin{equation*}
\frac{1}{T}=\left(\frac{\partial S}{\partial \varepsilon}\right)_{V} \tag{12.100}
\end{equation*}
$$

which, if we take the second derivative, leads to

$$
\begin{equation*}
\left(\frac{\partial^{1} / T}{\partial \varepsilon}\right)_{V}=\left(\frac{\partial^{2} S}{\partial \varepsilon^{2}}\right)_{V} \tag{12.101}
\end{equation*}
$$

Planck considered the fundamental relation of the material body in the entropy representation, written in the form $S=S(\varepsilon, T)$. About this function, we have two partial information, in the zones at low and high frequencies. More precisely, we know the expression of the second derivatives $\left(\partial^{2} S / \partial \varepsilon^{2}\right)_{V}$ in these two parts. Planck aims at finding the form of the function $\left(\partial^{2} S / \partial \varepsilon^{2}\right)_{V}$ in the whole energy spectrum.

As regards the first part, that is, in the "Rayleigh-Jeans branch", he can obtain $1 / T$ from Eq. (12.98) and, deriving further, he gets

$$
\begin{equation*}
\left(\frac{\partial^{2} S}{\partial \varepsilon^{2}}\right)_{V}=-\frac{k_{B}}{\varepsilon^{2}} . \tag{12.102}
\end{equation*}
$$

As regards the relatively high-frequency zone, i.e., the "Wien's zone," he operates in a similar manner starting from Eq. (12.99) and he obtains

$$
\begin{equation*}
\left(\frac{\partial^{2} S}{\partial \varepsilon^{2}}\right)_{V}=-\frac{1}{\beta \nu \varepsilon} \tag{12.103}
\end{equation*}
$$

The problem, at this point, was to find one complete expression for the function $\left(\partial^{2} S / \partial \varepsilon^{2}\right)_{V}$ with the requirement that it must coincide with Eq. (12.102) and with Eq. (12.103) at low and high energies, respectively.

The simplest interpolation that Planck could try at this point was to write

$$
\begin{equation*}
\left(\frac{\partial^{2} S}{\partial \varepsilon^{2}}\right)_{V}=-\frac{k_{B}}{\varepsilon\left[\varepsilon+\left(\beta k_{B}\right) \nu\right]} \tag{12.104}
\end{equation*}
$$

By introducing

$$
\begin{equation*}
h=\beta k_{B} \tag{12.105}
\end{equation*}
$$

the tentative interpolated expression takes the following form:

$$
\begin{equation*}
\left(\frac{\partial^{2} S}{\partial \varepsilon^{2}}\right)_{V}=-\frac{k_{B}}{\varepsilon(\varepsilon+h \nu)} \tag{12.106}
\end{equation*}
$$

Indeed, Eq. (12.106) gives Eq. (12.102) when $h v \ll \varepsilon$, while it gives Eq. (12.103) in the region where $h v \gg \varepsilon$.

This is the famous "interpolation formula which resulted from a lucky guess" and is just the starting point for the development of a line of thought that would revolutionize, with the participation of other great physicists, the basic foundations of physics.

Having in mind to integrate the interpolated formula Eq. (12.106) once, it is convenient to write it in the following form:

$$
\begin{equation*}
\left(\frac{\partial^{2} S}{\partial \varepsilon^{2}}\right)_{V}=-\frac{k_{B}}{h \nu}\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon+h v}\right) . \tag{12.107}
\end{equation*}
$$

This equation can easily be integrated and obtain

$$
\begin{equation*}
\left(\frac{\partial S}{\partial \varepsilon}\right)_{V}=-\frac{k_{B}}{h v} \ln \left(\frac{\varepsilon}{\varepsilon+h v}\right) \tag{12.108}
\end{equation*}
$$

that is,

$$
\begin{equation*}
\frac{1}{T}=-\frac{k_{B}}{h v} \ln \left(\frac{\varepsilon}{\varepsilon+h v}\right) \tag{12.109}
\end{equation*}
$$

and the above expression can be put in the familiar form:

$$
\begin{equation*}
\varepsilon=\frac{h v}{\exp \left(h v / k_{B} T\right)-1} . \tag{12.110}
\end{equation*}
$$

Combining Eq. (12.110) with Eq. (12.96), we obtain the expression for the spectral density of the black-body radiation:

$$
\begin{equation*}
u(v, T)=\frac{8 \pi}{c^{3}} v^{2} \frac{h v}{\exp \left(h v / k_{B} T\right)-1} \tag{12.111}
\end{equation*}
$$

### 12.6.4 The Dawn of Quantum Physics

In his fundamental paper very briefly described in the previous sections, Planck adopts a model in which the charges responsible of the absorption/production of the radiation are electrons with well-defined charge $e$ and mass $m$, elastically bound to atoms.

The expression given in Eq. (12.96), which concisely summarizes his calculation, does not depend on the charge and the mass of electrons as well as on the proper frequency of the oscillator. It does not depend on $\epsilon_{0}$ (the vacuum dielectric permittivity) on which the equations of electromagnetic theory are based. ${ }^{11}$ This is a result of great importance because it gives the right interpretation of the demand for universality expressed by Kirchhoff's Law. As already pointed out in the previous section, also the distribution of energy of the oscillators (that is Eq. (12.110)) is a universal function and the fundamental equations of thermodynamics were applied to this system.

After obtaining the two fundamental Eqs. (12.110) and (12.111), the scientific contribution by L. Boltzmann emerges.

For reasons totally independent of the black-body problem, Boltzmann had founded the new branch of physics, named statistical mechanics, and, in particular, had established a fundamental principle which is summarized in the famous formula attributed to him (and carved on his grave):

$$
\begin{equation*}
S=k_{B} \ln W, \tag{12.112}
\end{equation*}
$$

where $W$ is the, so-called, thermodynamical probability of an equilibrium state whose entropy will be $S$.

With reference to this Planck had recognized that "if the energy of the oscillators, instead of assuming continuous values, could only take values multiple of a fundamental amount, then the average value of their energy would be compatible with Eq. (12.110)."

At the end of his fundamental article of 1900, however, he does not yet dare the conclusion that he had at hand.

[^43]

Fig. 12.5 The Carnot cycle for radiation is represented in a ( $T, V$ ) plane (a) and in a $(T, S)$ plane (b)

### 12.7 Exercises

12.1 A cavity with volume $V_{0}=20 \mathrm{~m}^{3}$ at temperature $T=10^{3} \mathrm{~K}$ is expanded isothermally and quasi-statically until its volume is doubled. Determine the quantity of heat supplied to the cavity.
12.2 Calculate the efficiency of a Carnot cycle performed with radiation as working fluid. The transformations are represented in Fig. 12.5.

## Chapter 13 <br> Third Law of Thermodynamics


#### Abstract

The third law of thermodynamics is discussed starting from the NernstPlanck formulation. Some observational consequences and experimental confirmations are summarized and the formulation concerning the unattainability of absolute zero is briefly commented.


Keywords Third law • Nernst-Planck formulation • Attainability of absolute zero

### 13.1 The Third Law of Thermodynamics

The first and second principles of thermodynamics lead, respectively, to the definition of energy and entropy with all the consequences.

We have seen that both the definitions of energy and entropy contain one arbitrary additive constant because for both potentials only the changes in a process are defined. This does not create any difficulty because, in practice, in applications we are always involved in using variations.

Things are not so simple for $F$ and $G$ potentials because in their definitions, they contain the term $(-T S)$. It is clear that the indetermination of entropy by the additive constant $S_{0}$, has, as a consequence, an indetermination of the free energy and of the Gibbs potential, of the type

$$
\begin{equation*}
-S(O) T+\text { constant } \tag{13.1}
\end{equation*}
$$

where $O$ is an arbitrarily selected reference state. Once again, if we are interested in isothermal transformations, this indetermination of the $F$ and $G$ potentials is irrelevant but for transformations between states at different temperatures the variations of free energy and of Gibbs potential are undetermined.

Therefore, the absolute determination of entropy is needed to make defined and "usable" all the thermodynamic potentials in any transformations (the energy indeterminacy has fundamental connections with other issues; however, we do not want to deal with here).

The third law of thermodynamics does not lead to the definition of any new thermodynamic potential but makes already defined potentials fully defined, except energy whose "zero-point" problem must find the solution in another context.

### 13.1.1 Formulation According to Nernst and Planck

The third law has found its first formulation by Nernst as part of his studies, together with Berthelot, of the electrochemical reactions.

By studying the properties of these processes at gradually decreasing temperatures, he compared the values of the "affinity $\mathcal{A}$ of the reaction," which corresponded in his language to the maximum work obtainable (what we call now free energy change), with the values of the variation of energy $\Delta U$ that, at constant volume, corresponded to the amount of heat developed in the reaction.

Nernst commented the general trend of experimental data in this way:
"... I observe here an asymptotic law as the difference between $\mathcal{A}$ and $\Delta U$ is very small. It seems that at absolute zero $\mathcal{A}$ and $\Delta U$ are not only equal but also asymptotically tangent to each other so as to have:

$$
\begin{equation*}
\lim _{T \rightarrow 0} \frac{\mathrm{~d} \mathcal{A}}{\mathrm{~d} T}=\lim _{T \rightarrow 0} \frac{\mathrm{~d} \Delta U}{\mathrm{~d} T}=0 \ldots " \tag{13.2}
\end{equation*}
$$

Taking into account that $\mathcal{A}=\Delta F=\Delta U-T \Delta S$ it followed that $\Delta S \rightarrow 0$ as $T \rightarrow 0$.

This proposition can be formulated as follows: let us consider an isothermal transformation between two equilibrium states $\mathrm{A}^{\prime}$ and $\mathrm{A}^{\prime \prime}$ (they are at the same temperature). The variation of entropy in this transformation tends to zero as the temperature goes to zero:

$$
\begin{equation*}
\lim _{T \rightarrow 0}\left[S\left(\mathrm{~A}^{\prime \prime}\right)-S\left(\mathrm{~A}^{\prime}\right)\right]=0 \tag{13.3}
\end{equation*}
$$

Planck has given the following formulation to the third law: "When the temperature of a physical system tends to zero, its entropy tends to a value $S_{0}$ which is independent of pressure, of the state of aggregation, of the presence of external fields and from any other state variable."

We can agree to put this constant equal to zero so the entropy for all systems is determined absolutely.

### 13.1.2 Some Observational Consequences

If the entropy tends to a value which is independent from all other state variables, as the temperature approaches to zero, we have

$$
\begin{align*}
& \lim _{T \rightarrow 0}\left(\frac{\partial S}{\partial p}\right)_{T}=0  \tag{13.4}\\
& \lim _{T \rightarrow 0}\left(\frac{\partial S}{\partial V}\right)_{T}=0 \tag{13.5}
\end{align*}
$$

## Thermal Expansion Coefficient

If we recall the general Maxwell's relation (5.15), we conclude that the coefficient of thermal expansion vanishes when approaching $T \simeq 0$ :

$$
\begin{equation*}
\alpha(T)=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p} \rightarrow 0 \quad \text { as } T \rightarrow 0 \tag{13.6}
\end{equation*}
$$

Indeed from Eq. (5.15), we see that this is equivalent to saying that as the temperature tends to zero the entropy of the system is independent of pressure.

## Tension Coefficient

We define tension coefficient $\mathscr{T}$ the quantity:

$$
\begin{equation*}
\mathscr{T} \equiv\left(\frac{\partial p}{\partial T}\right)_{V} \tag{13.7}
\end{equation*}
$$

From Eq. (5.12), it is immediate to see that even the tension coefficient tends to zero close 0 K :

$$
\begin{equation*}
\lim _{T \rightarrow 0}\left(\frac{\partial p}{\partial T}\right)_{V}=\lim _{T \rightarrow 0}\left(\frac{\partial S}{\partial V}\right)_{T}=0 \tag{13.8}
\end{equation*}
$$

## Specific Heats

In principle, we can calculate the entropy of a system in a generic state $(V, T)$ integrating $\mathrm{d} S$ in a transformation at constant volume from $T=0$ to the final temperature $T$. Since

$$
\begin{equation*}
\mathrm{d} S=\left(\frac{\partial S}{\partial T}\right)_{V} \mathrm{~d} T \tag{13.9}
\end{equation*}
$$

we may write

$$
\begin{equation*}
S(V, T)=\int_{0}^{T} \frac{C_{V}}{T} \mathrm{~d} T+S(V, 0) \tag{13.10}
\end{equation*}
$$

Similarly, if we describe the state in terms of pressure and temperature, we may write ${ }^{1}$

$$
\begin{equation*}
S(p, T)=\int_{0}^{T} \frac{C_{p}}{T} \mathrm{~d} T+S(p, 0) \tag{13.11}
\end{equation*}
$$

The two constant of integration $S(V, 0)$ e $S(p, 0)$ must have the same value and may be put equal to zero according to Planck's or Nernst's statements of the third law. We may then write

$$
\begin{align*}
& S(V, T)=\int_{0}^{T} \frac{C_{V}}{T} \mathrm{~d} T  \tag{13.12}\\
& S(p, T)=\int_{0}^{T} \frac{C_{p}}{T} \mathrm{~d} T \tag{13.13}
\end{align*}
$$

Both specific heats must tend to zero when the temperature tends to zero. If it were not so, the integrals would diverge.

## Solidification of Liquid Helium at Low Temperatures

This is the only known substance that remains liquid "at absolute zero" but can be made to solidify by increasing the pressure. If we consider, therefore, the solid-liquid equilibrium and denote by $p$ the melting pressure of solid helium, the Clapeyron's equation connects it to the entropy difference as is well known:

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{\Delta S}{\Delta V} \tag{13.14}
\end{equation*}
$$

Experimental evidence is shown in Fig. 13.1 and we can see that

$$
\begin{equation*}
\lim _{T \rightarrow 0} \frac{\mathrm{~d} p}{\mathrm{~d} T}=0 \tag{13.15}
\end{equation*}
$$

Since $\Delta V$ maintains a non-zero value, the evidence on the melting pressure shows that

$$
\begin{equation*}
\lim _{T \rightarrow 0}\left[S_{\mathrm{liq}}-S_{\mathrm{sol}}\right]=0 \tag{13.16}
\end{equation*}
$$

[^44]

Fig. 13.1 The solid-liquid equilibrium curve of Helium at very low temperatures. Experimental data show that the equilibrium pressure tends to a constant value as temperature decreases. Figure reproduced with permission from Guggenheim, Thermodynamics: An Advanced Treatment for Chemists and Physicists [3]

## Unattainability of Absolute Zero

Some authors propose a formulation of the third law based on a new principle named "the Principle of unattainability of absolute zero." More precisely, the formulation they give is as follows:

It is not possible, with a finite number of transformations, to reach the temperature $T=0$.

The issue of the attainability of the zero value of the temperature is a very delicate one because, as we can well imagine, the error with which we can measure the temperatures may make the question meaningless.

A correct formulation is the following: Starting from a state at $T>0$ it is not possible to realize a reversible adiabatic transformation which brings the system to $T=0$.

Let us briefly discuss how this proposition can be derived from the Nernst's or Planck's formulation of the third law. Let us go back to the proof given in Sect. 13.1.2 to justify the fact that the specific heats tend to zero as $T \rightarrow 0$.

The argument can be put in a more general form. We express the entropy in a generic state as follows:

$$
\begin{equation*}
S(\alpha, T)=\int_{0}^{T} \frac{C_{\alpha}}{T} \mathrm{~d} T+S(\alpha, 0) \tag{13.17}
\end{equation*}
$$

where the symbol $\alpha$ is a control parameter which represents the particular transformation along which we calculate the integral of the entropy (in the two previous examples $\alpha$ indicated a transformation either at constant volume or at constant pressure).

Another control parameter might be (and this is precisely the case when we want to reach the lowest temperatures) the intensity of an external magnetic field.

In this case, the transformation connecting the two temperatures is realized at constant field and, in this situation, the specific heat must be defined as

$$
\begin{equation*}
C_{B}=T\left(\frac{\partial S}{\partial T}\right)_{B} \tag{13.18}
\end{equation*}
$$

In Fig. 13.2, we describe, in a qualitative way, the entropy as a function of temperature for two different values of the field kept constant. The magnetic field is indicated by the value of the magnetizing field which is more easily controlled by the experimenter. The curve marked by the value $H=H_{1} \neq 0$ shows that entropy must be an increasing function of temperature owing to the ordering effect of the magnetic field: indeed as temperature increases the ordering effect becomes less and less effective. Furthermore, for any given temperature, the curve with $H=0$ is expected to be above the corresponding value with $H=H_{1}$ because of the partial ordering effect.

If the third law is valid, as temperature tends to zero the two curves must tend to the same value which can be assumed to be zero. If the third law is violated, the curve with $H=0$, extrapolated at $T=0$, must cross the vertical axis at an entropy $S_{0}>0$, as shown by the dashed line, because it cannot cross the $H=H_{1}$ curve at any $T>0$.

The argument concerning the unattainability of absolute zero is based on the fact that the most powerful technique we know for reaching low temperatures consists in the process of adiabatic demagnetization already described in Sect.11.7. Let $T_{1}$ be the lowest temperature available with any method but adiabatic demagnetization and consider the diagram ( $S, T$ ) shown in Fig. 13.2 for magnetized materials. Let us take our system to $T_{1}$ when it is magnetized by a magnetizing field $H_{1}$. If we operate reversibly and adiabatically and reduce the intensity of the magnetizing field from $H_{1}$ to $H=0$, we perform a transformation which can be represented by the horizontal line in Fig. 13.2 and then we reach a temperature $T_{2}$ lower than the initial temperature $T_{1}$.


Fig. 13.2 Qualitative behavior of the entropy as a function of temperature at constant magnetic field for a paramagnetic salt. The intensity of the magnetic field is labeled by the value of the magnetizing field $H=|\mathbf{H}|$ which is more easily controlled. Solid lines describe the situation according to the provisions of the third law. Dashed line shows a possible behavior in violation of the third law. The change of curvature at $H=0$ accounts for spontaneous magnetization typical of all paramagnetic material when approaching $T \simeq 0$

If the third law holds, the two solid lines converge at the same point as $T \rightarrow 0$ (and only in this limit) and hence it shall be $T_{2}>0$. It follows that the approaching to the "absolute zero" will be a process constituted by an infinite number of single steps of adiabatic demagnetization.

If the third law is not valid (dashed line case), there will be one initial temperature such that the absolute zero will be reached by means of just one adiabatic demagnetization process.

In this sense the third law, as formulated by Nernst and Planck, has the consequence that the absolute zero can be approached only asymptotically.

## The Third Law and Statistical Mechanics

The formulations of the third law given by Nernst and Planck originate from some experimental evidence and constitute an abstract statement capable of making various predictions. These predictions are well confirmed by experiments as we have seen in the preceding discussion; however, the formulation acquires a fundamental character in the light of its statistical interpretation, and thanks to the development of quantum mechanics.

The statistical interpretation of the concept of entropy was given by Boltzmann by means of the famous relation

$$
\begin{equation*}
S=k \ln w, \tag{13.19}
\end{equation*}
$$

in which the entropy $S$ for any equilibrium state is related to the number $w$ of microstates that "correspond" to the macroscopic state. In this context, to establish the value $S_{0}=0$ for the entropy of a system at the absolute zero is equivalent to establish $w=1$. This is equivalent to say that as the temperature decreases the number of microstates decreases as well and tends to the value $w=1$ as the temperature tends to zero. ${ }^{2}$

To what extent this may seem "intuitive" or not is a meaningless question but, instead, it becomes of paramount interest to ask ourselves if our theoretical framework is compatible with or, better, provides or does not provide for such a limit.

For this reason, the answer must be sought among the laws governing quantum physics.

A thorough discussion of this topic is far beyond the scope of this book but we still need to focus on the key point that lies in the process to move to the limit of zero temperature.

Consider a system at a very low temperature $T$ and subject to certain external constraints (such as volume, pressure, external field, etc.). Let us subtract energy, and by doing so we decrease the temperature. In the atomic-molecular description of the system, each elementary constituent will gradually be at lower and lower energy values and its quantum nature will manifest itself in a dominant way. This process of energy subtraction will lead the system toward a limit configuration in which all the elementary constituents will have minimal energy (which is not necessarily zero).

All models to which we are led according to the laws of quantum mechanics and of statistical mechanics, lead to configurations with $w=1$, but this is obtained by assuming that during the energy subtraction the macroscopic system always remains in a state of thermodynamic equilibrium.

This is a very delicate problem because as the average energy of each elementary constituent decreases, the relaxation time (i.e., the time required by the elementary constituents to redistribute their energy among them in order to create a thermodynamic equilibrium situation) increases very rapidly.

The result is that we can lead to states of minimum energy (in the sense that we can no longer extract) systems that are frozen in nonequilibrium configurations. We call, in general, these systems vitreous.

One common example is given precisely by the silicon glass $\left(\mathrm{SiO}_{2}\right)$. At very low temperatures, it does not have time to transform into a crystalline solid, maintains its glass configuration, and also maintains a large number of possible microscopic configurations with the same energy level.

[^45]
## Part III

## Irreversible Processes

## Chapter 14 <br> Irreversible Processes: Fundamentals


#### Abstract

Within the approximation of discontinuous systems, the entropy production is calculated in a variety of nonequilibrium situations in open/closed systems and for chemical and electrochemical reactions. The definition of generalized fluxes and forces is widely discussed. The dependence of fluxes on forces is explored and for near to equilibrium configurations this dependence is linearized. The linearization leads to the Onsager relations which give the quantitative characterization of the cross-interference of different irreversible processes. The non-unique determination of the fluxes and of the relative forces is widely discussed and the limits of validity for the linear relations between fluxes and forces are examined with particular reference to chemical reactions.


Keywords Irreversible processes • Discontinuous systems • Chemical reactions • Affinity • Reaction rate • Open systems • Electrochemical reactions • Generalized fluxes - Generalized forces - Onsager relations - Linearity • Equivalent systems Relaxation time

### 14.1 Introduction

Irreversible processes occur either within systems not in internal equilibrium or when systems, in internal equilibrium but not in mutual equilibrium, are allowed to interact. Chemical reactions are one example of the former type and will be extensively studied throughout the whole part. Just as equilibrium states are, in the first instance, defined by a set of extensive quantities, so interactions consist in the exchange of one or more extensive quantities between interacting systems; indeed in various fields of physics, specific natural processes take their name from the flows of appropriate extensive quantities like, for instance, mass, energy ${ }^{1}$ or electric charge. This part is devoted to the study of the dynamics of natural, or irreversible, processes, how they evolve over time and how they interfere with each other. The generalization of the formalism to continuous systems will be done in Chap. 16 but, before this,

[^46]many things can be understood in the present chapter and Chap. 15, in the context of the approximation of discontinuous systems, which is formally simpler and more intuitive. The approximation of discontinuous systems was already discussed in Sect. 3.6 for closed systems. Here, we recall the most important points and prepare the necessary generalizations to open systems with variable chemical composition.

Individual systems are supposed to be in internal equilibrium and, when they are put into interaction, the region where intensive properties vary in a continuous manner (transition region) is neglected. The time scales of the interaction processes are long with respect to the relaxation times of the individual systems so they can be assumed, in every instant, to be in internal equilibrium. Before proceeding with the development of the formalism, a general consideration should be made clear. Interactions consist in exchanges, between individual systems, of extensive quantities ${ }^{2}$ then it is necessary, for each of them, to split their variation, in an infinitesimal process, into the sum of two contributions:

$$
\begin{equation*}
\mathrm{d} \mathcal{E}=\hat{d}_{\mathrm{i}} \mathcal{E}+\hat{d}_{\mathrm{e}} \mathcal{E} \tag{14.1}
\end{equation*}
$$

where $\hat{d}_{\mathrm{e}} \mathcal{E}$ is the part due to the interaction with external world and $\hat{d}_{\mathrm{i}} \mathcal{E}$ is the part due to processes taking place within the system.

Here, $\mathcal{E}$ is any extensive quantity and is a thermodynamic potential (function of state) and its variation in an infinitesimal process is described as the exact differential of a function while both $\hat{d}_{\mathrm{i}} \mathcal{E}$ and $\hat{d}_{\mathrm{e}} \mathcal{E}$ describe infinitesimal quantities but are not exact differentials.

When we affirm that a certain quantity $\mathcal{E}$ is a conserved quantity, we mean that

$$
\begin{equation*}
\hat{d}_{\mathrm{i}} \mathcal{E}=0, \tag{14.2}
\end{equation*}
$$

for every infinitesimal process. This is equivalent to say that the value of the quantity $\mathcal{E}$ can vary only by interaction with the external world.

### 14.1.1 Rephrasing the First Principle

Since we are going to deal with processes in open systems, it is useful to rewrite the first principle in the following form:

$$
\begin{equation*}
\mathrm{d} U=\hat{d} \Phi-p \mathrm{~d} V, \tag{14.3}
\end{equation*}
$$

[^47]where $\hat{d} \Phi$ represents the variation of energy of the system in an infinitesimal process after removing the infinitesimal quantity of work $-p \mathrm{~d} V$ done on the system in the same time interval $\mathrm{d} t$. This is written in the case of a simple system but in the general case we have to subtract all the similar terms due to the other work parameters.

With this notation, the first principle states that the energy of a system varies in two ways: because work is done on the system ( $-p \mathrm{~d} V$ plus other work parameters) and because energy is transferred by other means and the latter contribution is represented by $\hat{d} \Phi$. The term $\hat{d} \Phi$ becomes $\hat{d} Q$ in the case of closed systems and takes the familiar name of quantity of heat transferred from the external world to the system.

It would be a nonsense, at this stage, to think that $\hat{d} \Phi$ contains a contribution due to the "transfer of heat" and a contribution due to the "transfer of matter." It is one term and the concept of "heat" or of "heat transfer" becomes meaningless but only the concept of "energy transfer" remains.

In the following, we shall consider various situations which will be treated in the discontinuous systems approximation and each situation may be described in different ways. The selected description will give the names to the various irreversible processes.

### 14.2 Heat Exchange

Let us refer to the example discussed in Sect. 3.6. On that occasion, it was used as a paradigmatic example with the purpose of showing the way in which the propositions that define the second principle are necessary and sufficient for the operational definition of entropy. Here, we want to go ahead and use the same configuration as a paradigmatic example of how the second principle constitutes the fundamental evolutionary criterion.

If we divide both sides of Eq. (3.14) by the infinitesimal time interval $\mathrm{d} t$, we may write

$$
\begin{equation*}
\mathcal{P}=\frac{\hat{d}_{\mathrm{i}} S}{\mathrm{~d} t}=\frac{\hat{d}^{\mathrm{II}} Q}{\mathrm{~d} t}\left(\frac{1}{T^{\mathrm{II}}}-\frac{1}{T^{\mathrm{I}}}\right)>0 . \tag{14.4}
\end{equation*}
$$

The first term $\hat{d}_{\mathrm{i}} S / \mathrm{d} t$ measures how much entropy is produced, per second, by the process taking place within the overall system. Let us underline that this term is not a sort of time derivative of a function but it is just the ratio of two infinitesimals. It is called entropy production (but, more precisely, the meaning is that of velocity of entropy production).

When the system is in an equilibrium configuration (and we have seen that this is the case when $T^{\mathrm{I}}=T^{\mathrm{II}}$ ), the entropy production is zero. If the two temperatures are different but close one another, the amount of entropy production will be small. If the two temperatures are very different from each other, we expect that the amount given by Eq. (14.4) will be relatively high. This leads us to think of $\mathcal{P}$ as an indicator of the "level of irreversibility" of a nonequilibrium configuration.

Obviously, we have to remember that the entropy production is an extensive quantity and, in general, it would be of no use to compare its amount between different systems but this problem will not arise when we will adopt the optics of continuous systems where the greater or lesser distance from equilibrium will be described by the entropy production per unit volume, and then point by point.

The term $\hat{d}{ }^{\mathrm{II}} Q / \mathrm{d} t$ has an evident physical meaning. It measures the amount of energy that is transferred, per second, between the two systems and more exactly $\hat{d}^{\mathrm{II}} Q / \mathrm{d} t$ measures the power passing from I to II. In many other previously encountered situations, we called this term "flow of energy" or, in particular contexts, "heat flow." The flux describes the dynamics of the irreversible process at stake: in our example, the speed with which the energy is transferred and in which direction (from I to II if the flux is positive in our choice). The quantity,

$$
\begin{equation*}
X=\left(\frac{1}{T^{\mathrm{II}}}-\frac{1}{T^{\mathrm{I}}}\right) \tag{14.5}
\end{equation*}
$$

depends on the configuration at that moment and "pilots" the development of the process: if its value is zero the flow is zero, if it has a positive value also the flow of energy will have a positive direction and, conversely, if it is negative, the flow of energy will be negative. It plays, therefore, a role similar to the one that the force has in mechanics: it determines both the direction and the intensity of the process. We shall call the quantity $X$, given by Eq. (14.5), a generalized force. The role of generalized force is assigned by the second principle because it is the latter that determines the direction of the process. The expression given by Eq. (14.4) may be written as

$$
\begin{equation*}
\mathcal{P}=J X>0, \tag{14.6}
\end{equation*}
$$

in which we may adopt any of the two signs in the definition of the flux and, consequently of the force, corresponding to the two possible directions of flow. We adopt the following:

$$
\begin{equation*}
J=-\frac{\hat{d}^{\mathrm{I}} Q}{\mathrm{~d} t}=\frac{\hat{d}^{\mathrm{II}} Q}{\mathrm{~d} t} \tag{14.7}
\end{equation*}
$$

which corresponds to consider as positive the energy flow from I to II and hence the correspondent generalized force, will be

$$
\begin{equation*}
X=-\left(\frac{1}{T^{\mathrm{I}}}-\frac{1}{T^{\mathrm{II}}}\right)=\Delta\left(\frac{1}{T}\right) . \tag{14.8}
\end{equation*}
$$

Consider now the case in which the overall system can exchange heat with thirdparty systems. In this case, $\hat{d} Q=\hat{d}^{\mathrm{I}} Q+\hat{d}^{\mathrm{II}} Q$ will no longer be zero. In order to proceed, we must increase the level of complexity, i.e., we must be able to distinguish, in each of the two component systems, the amount of heat that it receives from the other and the amount of heat that it receives from third-party systems. Let us distinguish the former and the latter with the subscripts $i$ and $e$, respectively,

$$
\begin{align*}
& \hat{d}^{\mathrm{I}} Q=\hat{d}_{\mathrm{i}}^{\mathrm{I}} Q+\hat{d}_{\mathrm{e}}^{\mathrm{I}} Q  \tag{14.9}\\
& \hat{d}^{\mathrm{II}} Q=\hat{d}_{\mathrm{i}}^{\mathrm{II}} Q+\hat{d}_{\mathrm{e}}^{\mathrm{II}} Q \tag{14.10}
\end{align*}
$$

with

$$
\begin{equation*}
\hat{d}_{\mathrm{i}}^{\mathrm{I}} Q=-\hat{d}_{\mathrm{i}}^{\mathrm{II}} Q . \tag{14.11}
\end{equation*}
$$

Then, for the overall system, we can write

$$
\begin{equation*}
\mathrm{d} S=\hat{d}_{\mathrm{i}} S+\hat{d}_{\mathrm{e}} S \tag{14.12}
\end{equation*}
$$

with

$$
\begin{equation*}
\hat{d}_{\mathrm{e}} S=\frac{1}{T^{\mathrm{I}}} \hat{d}_{\mathrm{e}}^{\mathrm{I}} Q+\frac{1}{T^{\mathrm{II}}} \hat{d}_{\mathrm{e}}^{\mathrm{II}} Q, \tag{14.13}
\end{equation*}
$$

and

$$
\begin{equation*}
\hat{d}_{\mathrm{i}} S=\left(\frac{1}{T^{\mathrm{I}}}-\frac{1}{T^{\mathrm{II}}}\right) \hat{d}_{\mathrm{i}}^{\mathrm{I}} Q \tag{14.14}
\end{equation*}
$$

and for the entropy production we will meet exactly Eq. (14.4). For the overall system, the entropy change per unit of time will be written as

$$
\begin{align*}
\frac{\mathrm{d} S}{\mathrm{~d} t} & =\frac{\hat{d}_{\mathrm{e}} S}{\mathrm{~d} t}+\frac{\hat{d}_{\mathrm{i}} S}{\mathrm{~d} t}  \tag{14.15}\\
& =\frac{1}{T^{\mathrm{I}}} \frac{\hat{d}_{\mathrm{e}}^{\mathrm{I}} Q}{\mathrm{~d} t}+\frac{1}{T^{\mathrm{II}}} \frac{\hat{d}_{\mathrm{e}}^{\mathrm{II}} Q}{\mathrm{~d} t}+J X . \tag{14.16}
\end{align*}
$$

### 14.3 Chemical Reactions

Let us now consider a class of irreversible processes in which the chemical composition varies with time. This can happen for two different reasons: either because some components $\gamma$ are exchanged with the outside world (that is, the system is open with respect to the component $\gamma$ ) or because the component $\gamma$ is involved in some internal processes that, if the system were closed, would change the chemical concentration.

In general, these two causes are present simultaneously and this will be covered in Sect.14.4. In order to provide the necessary descriptive tools let us deal, for the moment, with them separately. Let us start with closed systems.

The processes in question will be called "chemical reactions" meaning by this term, not only the chemical reactions in the traditional sense but also any process which can be treated with the same formalism by analogy.

### 14.3.1 The Rate of Reaction

As the name makes us understand, this physical quantity describes the speed with which each process develops over time.

## Case of One Reaction

Suppose, at the beginning, that in the system one single chemical reaction is taking place, and this means that the variations in time of the number of moles $n_{\gamma}$ of all the components can be correlated by one linear equation only. For example, consider the synthesis of ammonia:

$$
\begin{equation*}
\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightarrow 2 \mathrm{NH}_{3} . \tag{14.17}
\end{equation*}
$$

The observer will see that the abundances of the different components vary in time and that the variations are related by very precise quantitative ratios as described by Eq. (14.17). If we denote by $\mathrm{d} n_{\gamma}$ the variation of the number of moles of the various components in the infinitesimal time interval $\mathrm{d} t$, we will observe that

$$
\begin{equation*}
\frac{\mathrm{d} n_{\mathrm{N}_{2}}}{-1}=\frac{\mathrm{d} n_{\mathrm{H}_{2}}}{-3}=\frac{\mathrm{d} n_{\mathrm{NH}_{3}}}{2} \tag{14.18}
\end{equation*}
$$

Now consider a generic chemical reaction described by the stoichiometric equation:

$$
\begin{equation*}
v_{\mathrm{A}} \mathrm{~A}+v_{\mathrm{B}} \mathrm{~B}+\cdots \rightarrow v_{\mathrm{M}} \mathrm{M}+v_{\mathrm{N}} \mathrm{~N}+\cdots \tag{14.19}
\end{equation*}
$$

where $\mathrm{A}, \mathrm{B}, \mathrm{M}, \mathrm{N}, \ldots$ are the chemical components which take part to the reaction and $v_{\mathrm{A}}, \nu_{\mathrm{B}}, \nu_{\mathrm{M}}, v_{\mathrm{N}}, \ldots$ the relative stoichiometric coefficients. If we adopt the convention of giving the stoichiometric coefficients the negative sign for the components that are to the left of Eq. (14.19) and the positive sign to stoichiometric coefficients of the components that are on the right, we see that, for all components involved in the chemical reaction, the ratio $\mathrm{d} n_{\gamma} / v_{\gamma}$ has the same value. Hence, this ratio is no longer referred to a particular component but describes the evolution of the process as such. We may, then, define an adimensional parameter $\xi$, called degree of advancement of the chemical reaction so that its variation $\mathrm{d} \xi$, in the time interval $\mathrm{d} t$, is, for any $\gamma$ :

$$
\begin{equation*}
\frac{\mathrm{d} n_{\gamma}}{v_{\gamma}}=\mathrm{d} \xi \tag{14.20}
\end{equation*}
$$

It is a dimensionless parameter and since only the variations of it are defined, it will be undetermined by an arbitrary additive constant. As already mentioned, it describes the evolution of the process and its variation per unit of time:

$$
\begin{equation*}
\mathrm{v}=\frac{\mathrm{d} \xi}{\mathrm{~d} t} \tag{14.21}
\end{equation*}
$$

is called velocity of the reaction, or reaction rate. It is a dynamic variable and, as the flow of energy in the previous example, adequately expresses the speed with which the process proceeds and its direction. By analogy with the previous case, we will call it flux in a generalized sense.

## General Case with Many Chemical Reactions

Suppose that, in our closed system, are active $r$ chemical reactions. This means that to have a complete description of the variations in time of the abundances of all the components, it is necessary and sufficient to write $r$ independent stoichiometric equations.

We denote by the symbol $\nu_{\gamma}^{\rho}$ the stoichiometric coefficient with which the component $\gamma$ participates in $\rho$ th chemical reaction. Of course we maintain the agreement to assign the negative or the positive sign to the stoichiometric coefficient depending on whether the component is on the left or on the right of the arrow which denotes the assumed direction for the reaction. If the component $\gamma$ does not take part to reaction $\rho$, the corresponding $v_{\gamma}^{\rho}$ will be $v_{\gamma}^{\rho}=0$.

For each chemical reaction, the degree of advancement $\xi_{\rho}$ will be defined and for each component, we have

$$
\begin{equation*}
\mathrm{d} n_{\gamma}=\sum_{\rho=1}^{r} v_{\gamma}^{\rho} \mathrm{d} \xi_{\rho} \tag{14.22}
\end{equation*}
$$

then for each process (chemical reaction), we define the speed with which it develops by the quantity $\mathrm{v}_{\rho}$ :

$$
\begin{equation*}
\mathrm{v}_{\rho}=\frac{\mathrm{d} \xi_{\rho}}{\mathrm{d} t} \tag{14.23}
\end{equation*}
$$

$\mathrm{v}_{\rho}$ being called velocity of the reaction, or reaction rate, of the $\rho$ th reaction. With reference to Eq. (14.19), it is clear that the choice on the direction of the arrow that distinguishes the "reagents" from "products of the reaction" (and therefore that distinguishes the positive and negative stoichiometric numbers) can be made in an arbitrary manner and it is in no way binding for the correct description of the process. It will be the analysis of the thermodynamic process that will give us an indication of whether it is in equilibrium (and thus with zero rate) or if the chemical reaction is active and what will be its effective direction. We must then find the expression of the "generalized force" that is of the quantity that is responsible for equilibrium, or for the development of the considered process and its direction.

### 14.3.2 Entropy Production and the Chemical Affinity

As the state of being in equilibrium or the direction of development of natural processes are ensured by the second principle, we have to start from the fundamental equation for an infinitesimal process written in the entropy representation:

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V-\sum_{\gamma} \frac{\mu_{\gamma}}{T} \mathrm{~d} n_{\gamma} \tag{14.24}
\end{equation*}
$$

We start with the simple case where the description requires the presence of a single chemical reaction and we express the variation of the number of moles of each component using Eq. (14.20)

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V-\frac{1}{T}\left(\sum_{\gamma} \mu_{\gamma} v_{\gamma}\right) \mathrm{d} \xi \tag{14.25}
\end{equation*}
$$

We define the affinity of the chemical reaction and denote it with the symbol $\mathcal{A}$ the quantity:

$$
\begin{equation*}
\mathcal{A}=-\sum_{\gamma} v_{\gamma} \mu_{\gamma} \tag{14.26}
\end{equation*}
$$

and hence the infinitesimal entropy variation will be

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V+\frac{\mathcal{A}}{T} \mathrm{~d} \xi, \tag{14.27}
\end{equation*}
$$

with

$$
\begin{align*}
& \hat{d}_{\mathrm{e}} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V,  \tag{14.28}\\
& \hat{d}_{\mathrm{i}} S=\frac{\mathcal{A}}{T} \mathrm{~d} \xi>0 . \tag{14.29}
\end{align*}
$$

By dividing each side by the duration of the infinitesimal time interval, we obtain

$$
\begin{equation*}
\mathcal{P}=\frac{\mathcal{A}}{T} \mathrm{v}>0 . \tag{14.30}
\end{equation*}
$$

From Eq. (14.29), we see that the condition which ensures the equilibrium of the chemical reaction (that is that the infinitesimal process is quasi-static) is $\hat{d}_{\mathrm{i}} S=0$ and hence

$$
\begin{equation*}
\mathcal{A}=0 . \tag{14.31}
\end{equation*}
$$

If the affinity is non-zero, the chemical reaction proceeds and the direction is the one that makes Eq. (14.30) positive, that is,

$$
\begin{array}{ll}
\mathcal{A}>0 & \mathrm{v}>0 \\
\mathcal{A}<0 & \mathrm{v}<0 . \tag{14.33}
\end{array}
$$

In other words, the sign of the affinity determines the sign of the velocity. Here, we see why the arbitrariness of the choice on the direction when we write the formal
expression of a chemical reaction is irrelevant: if we make the opposite choice, the affinity will change sign but also the velocity changes sign and then the entropy production maintains the positive value.

In the simple case in which only one process (chemical reaction) is taking place, the relationship of cause and effect between the affinity and velocity emerges clearly in the sense of what we have already seen for the heat flow. The expression in Eq. (14.30) may be written as

$$
\begin{equation*}
\mathcal{P}=J X, \tag{14.34}
\end{equation*}
$$

with $J=\mathrm{v}$ physical quantity which describes the speed and the direction of the process and which, by analogy, will be called generalized flux, and

$$
\begin{equation*}
X=\frac{\mathcal{A}}{T}, \tag{14.35}
\end{equation*}
$$

will be called generalized force. Notice that the velocity of a chemical reaction is an extensive quantity (as in the previous example of the flow of energy) in fact it is proportional, through a stoichiometric coefficient, to the variation of the number of moles of a given component. Conversely, the force associated to the velocity, namely, the affinity divided by the temperature, is an intensive quantity because so are the chemical potentials.

## Generalization to Several Chemical Reactions: Interference

Consider now the case in which there are, simultaneously and in the same place, several chemical reactions. In order to calculate the entropy production, we have certainly to restart from Eq. (14.24) but, in this case, the terms $\mathrm{d} n_{\gamma}$ will be substituted by their expressions given in Eq. (14.22). Reversing the order of summations, we write

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V-\frac{1}{T} \sum_{\rho=1}^{r}\left(\sum_{\gamma} \nu_{\gamma}^{\rho} \mu_{\gamma}\right) \mathrm{d} \xi_{\rho}, \tag{14.36}
\end{equation*}
$$

and hence, after defining the affinity $\mathcal{A}_{\rho}$ of the $\rho$ th reaction as

$$
\begin{equation*}
\mathcal{A}_{\rho}=-\sum_{\gamma} v_{\gamma}^{\rho} \mu_{\gamma}, \tag{14.37}
\end{equation*}
$$

the entropy variation will be

$$
\begin{equation*}
\mathrm{d} S=\frac{1}{T} \mathrm{~d} U+\frac{p}{T} \mathrm{~d} V+\frac{1}{T} \sum_{\rho=1}^{r} \mathcal{A}_{\rho} \mathrm{d} \xi_{\rho} \tag{14.38}
\end{equation*}
$$

where the first two terms of the second member form the contribution to the change of entropy due to the interaction with the outside, while the contribution due to the internal processes will be given by

$$
\begin{equation*}
\hat{d}_{\mathrm{i}} S=\sum_{\rho=1}^{r} \frac{\mathcal{A}_{\rho}}{T} \mathrm{~d} \xi_{\rho} \tag{14.39}
\end{equation*}
$$

and for the entropy production:

$$
\begin{equation*}
\mathcal{P}=\sum_{\rho=1}^{r} \frac{\mathcal{A}_{\rho}}{T} \mathrm{v}_{\rho}>0 \tag{14.40}
\end{equation*}
$$

Indicating the generalized force for each chemical reaction with

$$
\begin{equation*}
X_{\rho}=\frac{\mathcal{A}_{\rho}}{T} \tag{14.41}
\end{equation*}
$$

we finally get

$$
\begin{equation*}
\mathcal{P}=\sum_{\rho=1}^{r} X_{\rho} \mathrm{v}_{\rho}>0 \tag{14.42}
\end{equation*}
$$

As we know, the second principle requires that

$$
\begin{equation*}
\mathcal{A}_{1} \mathrm{v}_{1}+\mathcal{A}_{2} \mathrm{v}_{2}+\cdots+A_{r} \mathrm{v}_{r}>0 \tag{14.43}
\end{equation*}
$$

but tells nothing about the sign of each product $\mathcal{A} v$. We could have, for example, for some chemical reactions:

$$
\begin{equation*}
\mathcal{A}_{\rho} \mathrm{v}_{\rho}<0 \tag{14.44}
\end{equation*}
$$

Then we say that the $\rho$ th reaction proceeds in the direction opposite to that intended by its own affinity.

This is permitted because the second principle requires only that the sum given by Eq. (14.43) over all the reactions, be positive.

If, for some reactions, Eq. (14.44) holds, we see in a striking way that there is interference among the various chemical reactions. In this case, we speak of "coupled reactions."

This does not mean that if we have $\mathcal{A}_{\rho} \mathrm{v}_{\rho}>0$ for every reaction, there is no interference. Normally, the numerical values of the speed of each individual reaction depend on the presence of the others, and then the interference between different reactions is present even though the sign of every single reaction is concordant with the sign of the respective affinities.

### 14.4 Open Systems

We return to the approximation of discontinuous systems and consider two phases, which we will denote by the indices I and II, each in a state of internal equilibrium but not in mutual equilibrium. We allow a weak interaction (in the sense already discussed in Sect. 14.2) but we now drop the constraint that they should be closed.

Also, we assume that each one can interact with third-party systems, but without exchanging matter, then the overall system is closed. We will consider, of course, an infinitesimal transformation and the infinitesimal variations of the extensive quantities will be separated, as already stated in Eq. (14.1) into one contribution due to internal processes and one due to the exchange with the external world. Further on, it will be necessary to subdivide the latter term into the contribution due to the interaction with the other system and what is left to the interaction with third-party systems. We write, first, the infinitesimal entropy change for system I, then simply changing the index, we will do the same for system II and we add up to find the entropy change of the overall system:

$$
\begin{equation*}
\mathrm{d} S^{\mathrm{I}}=\frac{1}{T^{\mathrm{I}}} \hat{d}^{\mathrm{I}} \Phi-\sum_{\gamma} \frac{\mu_{\gamma}^{\mathrm{I}}}{T^{\mathrm{I}}} \mathrm{~d} n_{\gamma}^{\mathrm{I}}, \tag{14.45}
\end{equation*}
$$

where $\hat{d}^{\mathrm{I}} \Phi$ stands for the total amount of energy that the system I receives from the outside world in the infinitesimal time interval $\mathrm{d} t$. Let us separate it in the following form:

$$
\begin{equation*}
\hat{d}^{\mathrm{I}} \Phi=\hat{d}_{\mathrm{e}}^{\mathrm{I}} Q+\hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi \tag{14.46}
\end{equation*}
$$

where the contribution coming from third-party systems has been written in the form of heat transfer because in this part of the interaction, no matter is exchanged while the remaining part, $\hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi$ is the energy coming from system II and has been denoted with the suffix i which stands for "internal to the overall system." As far as the $\mathrm{d} n_{\gamma}^{\mathrm{I}}$ term is concerned, it will be separated according to the general criterion Eq. (14.1):

$$
\begin{equation*}
\mathrm{d} n_{\gamma}^{\mathrm{I}}=\hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}+\hat{d}_{\mathrm{i}} n_{\gamma}^{\mathrm{I}}, \tag{14.47}
\end{equation*}
$$

but in this case the suffix i denotes the contribution due to chemical reactions in system I, while the suffix e denotes the transfer of matter with system II.

Now if we insert Eqs. (14.46) and (14.47) into Eq. (14.45), we shall obtain four terms. Let us analyze them one by one. The first will be written in the following form:

$$
\begin{equation*}
\hat{d}_{\mathrm{e}}^{\mathrm{I}} Q / T^{\mathrm{I}} \tag{14.48}
\end{equation*}
$$

and it simply describes the injection of entropy in I coming from third-party systems.
The second

$$
\begin{equation*}
\frac{\hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi}{T^{\mathrm{I}}} \tag{14.49}
\end{equation*}
$$

describes the injection of entropy in system I because of the energy that is provided by the system II. The third term

$$
\begin{equation*}
-\sum_{\gamma} \frac{\mu_{\gamma}^{\mathrm{I}}}{T^{\mathrm{I}}} \hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}} \tag{14.50}
\end{equation*}
$$

describes the amount of entropy supplied to system I by system II due to the transfer of matter, and finally the last term will be of the following type:

$$
\begin{equation*}
-\sum_{\gamma} \frac{\mu_{\gamma}^{\mathrm{I}}}{T^{\mathrm{I}}} \hat{d}_{\mathrm{i}} n_{\gamma}^{\mathrm{I}} \tag{14.51}
\end{equation*}
$$

describes the contribution of the chemical reactions that take place in system I.
Reworking the last terms in (14.51) as we have done in the previous section (see Eq. (14.40)), we may write

$$
\begin{equation*}
\sum_{\rho^{\prime}} \frac{A_{\rho^{\prime}}^{\mathrm{I}}}{T^{\mathrm{I}}} \mathrm{v}_{\rho^{\prime}}^{\mathrm{I}} . \tag{14.52}
\end{equation*}
$$

The total variation of entropy of system I will be

$$
\begin{equation*}
\mathrm{d} S^{\mathrm{I}}=\frac{\hat{d}_{\mathrm{e}}^{\mathrm{I}} Q}{T^{\mathrm{I}}}+\frac{\hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi}{T^{\mathrm{I}}}-\sum_{\gamma} \frac{\mu_{\gamma}^{\mathrm{I}}}{T^{\mathrm{I}}} \hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}+\sum_{\rho^{\prime}} \frac{A_{\rho^{\prime}}^{\mathrm{I}}}{T^{\mathrm{I}}} \mathrm{~d} \xi_{\rho^{\prime}}^{\mathrm{I}} \tag{14.53}
\end{equation*}
$$

We will repeat the same analysis also for system II getting the same above expression but with the index II replacing I, and finally it is necessary to note that, given the assumptions made at the beginning, we have the following relations:

$$
\begin{align*}
& \hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi=-\hat{d}_{\mathrm{i}}^{\mathrm{II}} \Phi  \tag{14.54}\\
& \hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}=-\hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{II}} \tag{14.55}
\end{align*}
$$

and hence for the overall system we shall write the entropy change in the following form:

$$
\begin{align*}
\mathrm{d} S=\frac{\hat{d}_{\mathrm{e}}^{\mathrm{I}} Q}{T^{\mathrm{I}}}+\frac{\hat{d}_{\mathrm{e}}^{\mathrm{II}} Q}{T^{\mathrm{II}}}+\left(\frac{1}{T^{\mathrm{I}}}-\frac{1}{T^{\mathrm{II}}}\right) \hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi & -\sum_{\gamma}\left(\frac{\mu_{\gamma}^{\mathrm{I}}}{T^{\mathrm{I}}}-\frac{\mu_{\gamma}^{\mathrm{II}}}{T^{\mathrm{II}}}\right) \hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}+ \\
& +\sum_{\rho^{\prime}} \frac{A_{\rho^{\prime}}^{\mathrm{I}}}{T^{\mathrm{I}}} \mathrm{~d} \xi_{\rho^{\prime}}^{\mathrm{I}}+\sum_{\rho^{\prime \prime}} \frac{A_{\rho^{\prime \prime}}^{\mathrm{II}}}{T^{\mathrm{II}}} \mathrm{~d} \xi_{\rho^{\prime \prime}}^{\mathrm{II}} \tag{14.56}
\end{align*}
$$

From this expression, it is immediate to separate the two contributions: that due to the interaction with the outside $\hat{d}_{\mathrm{e}} S$ and that due to internal processes $\hat{d}_{\mathrm{i}} S$ and obtain, respectively,

$$
\begin{align*}
& \hat{d}_{\mathrm{e}} S=\frac{\hat{d}_{\mathrm{e}}^{\mathrm{I}} Q}{T^{\mathrm{I}}}+\frac{\hat{d}_{\mathrm{e}}^{\mathrm{II}} Q}{T^{\mathrm{II}}},  \tag{14.57}\\
& \hat{d}_{\mathrm{i}} S=\left(\frac{1}{T^{\mathrm{I}}}-\frac{1}{T^{\mathrm{II}}}\right) \hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi-\sum_{\gamma}\left(\frac{\mu_{\gamma}^{\mathrm{I}}}{T^{\mathrm{I}}}-\frac{\mu_{\gamma}^{\mathrm{II}}}{T^{\mathrm{II}}}\right) \hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}+\sum_{\rho^{\prime}} \frac{A_{\rho^{\prime}}^{\mathrm{I}}}{T^{\mathrm{I}}} \mathrm{~d} \xi_{\rho^{\prime}}^{\mathrm{I}}+\sum_{\rho^{\prime \prime}} \frac{A_{\rho^{\prime \prime}}^{\mathrm{II}}}{T^{\mathrm{II}}} \mathrm{~d} \xi \rho_{\rho^{\prime \prime}}^{\mathrm{II}}, \tag{14.58}
\end{align*}
$$

and, finally, dividing by the infinitesimal time interval $\mathrm{d} t$ we obtain the expression for the entropy production:

$$
\begin{align*}
\mathcal{P}=\left(\frac{1}{T^{\mathrm{I}}}-\frac{1}{T^{\mathrm{II}}}\right) \frac{\hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi}{\mathrm{~d} t} & -\sum_{\gamma}\left(\frac{\mu_{\gamma}^{\mathrm{I}}}{T^{\mathrm{I}}}-\frac{\mu_{\gamma}^{\mathrm{II}}}{T^{\mathrm{II}}}\right) \frac{\hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}}{\mathrm{~d} t}+  \tag{14.59}\\
& +\sum_{\rho^{\prime}} \frac{A_{\rho^{\prime}}^{\mathrm{I}}}{T^{\mathrm{I}}} \mathrm{v}_{\rho^{\prime}}^{\mathrm{I}}+\sum_{\rho^{\prime \prime}} \frac{A_{\rho^{\prime \prime}}^{\mathrm{II}}}{T^{\mathrm{II}}} \mathrm{v}_{\rho^{\prime \prime}}^{\mathrm{II}}
\end{align*}
$$

This expression for the entropy production is formed by the sum of several terms. The latter two describe the sets of chemical reactions that are active in system I and in system II. We must remember that the coupling as shown in Eq. (14.44) or even a mere interference among different reactions can occur within each system separately but not between reactions that take place in distinct regions. More generally, the second principle must be satisfied point by point and not only for the overall system. The other two terms that form the second member should be analyzed carefully and separately.

They are all formed by the product of a term that describes the speed and the direction of an irreversible process times a function of the state. The latter certifies a situation of nonequilibrium, between the two internal parts of the overall system, with respect to the transfer of some extensive quantities, while the former expresses precisely the amount of extensive quantity transferred per second.

In the first term, the dynamic variable represents the transfer of energy and if we choose to consider as positive the fluxes of energy from I to II, we shall define the flux as

$$
\begin{equation*}
J_{U}=-\frac{\hat{d}_{\mathrm{i}}^{\mathrm{I}} \Phi}{\mathrm{~d} t} \tag{14.60}
\end{equation*}
$$

It follows that in order to reproduce the term which appears in Eq. (14.59) we have to define the associated force as

$$
\begin{equation*}
X_{U}=\Delta\left(\frac{1}{T}\right) \tag{14.61}
\end{equation*}
$$

Similarly, regarding the second term, it is formed by the sum, for each component, of products of terms of type $\hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}} / \mathrm{d} t$, times a function of the state given by the difference, between the two phases, of the ratios of the chemical potential over
temperature. If we choose as positive the fluxes going from system I to system II, we define as $f l u x$ for each component $\gamma$ the quantity:

$$
\begin{equation*}
J_{\gamma}=-\frac{\hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}}{\mathrm{~d} t} \tag{14.62}
\end{equation*}
$$

and the significance of these fluxes is obvious: each of them describes the amount (measured in number of moles) of component $\gamma$ transferred per second from zone I to zone II. We shall call them flows of matter. Each of them, in the expression of $\mathcal{P}$, is multiplied by the corresponding intensive term (generalized force):

$$
\begin{equation*}
X_{\gamma}=-\Delta\left(\frac{\mu_{\gamma}}{T}\right) \tag{14.63}
\end{equation*}
$$

Let us note that, in the case in which there is only one flow of matter (say relative to the component $\gamma$ ) all the other fluxes being null, the state variables must be combined in such a way that

$$
\begin{align*}
& T^{\mathrm{I}}=T^{\mathrm{II}}  \tag{14.64}\\
& \mathcal{A}_{\rho^{\prime}, \rho^{\prime \prime}}^{\mathrm{I}, \mathrm{II}}=0 \tag{14.65}
\end{align*}
$$

Then, the entropy production reduces to

$$
\begin{equation*}
\mathcal{P}=-\frac{1}{T} \Delta \mu_{\gamma} J_{\gamma} \tag{14.66}
\end{equation*}
$$

Therefore, the flux of $\gamma$ is multiplied by a term which depends essentially on the difference of the chemical potentials. As we have seen in Chap. 7, this is exactly the quantity which governs the phase transition of component $\gamma$, hence $-1 / T \Delta\left(\mu_{\gamma}\right)$ deserves the name of generalized force. The role of force emerges clearly when we deal with one single process, while in the case of several concurrent processes mutual interference makes the cause-effect relationship less evident.

In conclusion, let us rewrite the entropy production in the following form:

$$
\begin{equation*}
\mathcal{P}=J_{U} X_{U}+\sum_{\gamma} J_{\gamma} X_{\gamma}+\mathrm{v}^{\mathrm{I}} X_{\mathrm{ch}}^{\mathrm{I}}+\mathrm{v}^{\mathrm{II}} X_{\mathrm{ch}}^{\mathrm{II}}>0 . \tag{14.67}
\end{equation*}
$$

In this expression, the suffix "ch" denotes the forces relative to the chemical reactions which have been summarized, for brevity, with two compact expressions that refer briefly to the processes which take place separately in phases I and II. The flux $J_{U}$ denotes the flux of energy between the two systems and $X_{U}$ the associated force.

### 14.5 Electrochemical Reactions

We can generalize the relations obtained in the previous section to processes which take place in the presence of external fields.

We consider the case of an electrolytic cell formed by two containers, each at uniform temperature, homogeneous, and maintained at uniform electrostatic potential $\psi^{\mathrm{I}}$ and $\psi^{\mathrm{II}}$. Each of the two cells is an open system with respect to the other but the set of the two (the overall system) is closed.

For simplicity, we assume that the temperatures have the same value in the two parts. In each part, or phase owing to their homogeneity, there are various components, some electrically neutral some bearing positive or negative charges as, for instance, in the case of ionic solutions, and let us denote with $z_{\gamma}$ the electrovalency of component $\gamma$. The electrovalency of a component is an integer number which may be positive, negative, or null and represents its the degree of ionization. For instance, in a solution containing sulfuric acid, we shall have hydrogen ions having electrovalency $z_{\mathrm{H}^{+}}=+1$, ( $\mathrm{SO}_{4}$ ) ions with electrovalency $z_{\mathrm{SO}_{4}}=-2$ and $(\mathrm{OH})$ ions with electrovalency $z_{\mathrm{OH}}=-1$ together with other possible components with $z=0$.

We can describe the processes with the same formalism of phase transitions or that of chemical reactions. If in the solution there are $r$ components, we can treat them as $r$ chemical reactions of the following type:

$$
\begin{equation*}
\gamma^{\mathrm{I}} \rightarrow \gamma^{\mathrm{II}} \tag{14.68}
\end{equation*}
$$

The dynamics of each of these processes will be described by the respective degree of advancement $\xi_{\gamma}$ :

$$
\begin{equation*}
-\mathrm{d} n_{\gamma}^{\mathrm{I}}=\mathrm{d} n_{\gamma}^{\mathrm{II}}=\mathrm{d} \xi_{\gamma} \tag{14.69}
\end{equation*}
$$

and hence by the respective rates:

$$
\begin{equation*}
\mathrm{v}_{\gamma}=\frac{\mathrm{d} \xi_{\gamma}}{\mathrm{d} t} \tag{14.70}
\end{equation*}
$$

Suppose that the two phases are separated by a membrane so as to allow the maintenance of different pressures and assume that for each phase we can write the fundamental equation in the form Eq. (14.24) to which is sufficient to add the term relative to the electrostatic work that the observer has to do, in an infinitesimal process, to keep the two phases at constant potentials $\psi^{\text {I }}$ and $\psi^{\text {II }}$, respectively. This is equivalent to assume that the entropy does not depend explicitly on the value of the electrostatic field and then neglect the effects due to electrostatic polarization of the material (see Sect. 10.4.1). If we write directly the fundamental equation for the overall system, we obtain

$$
\begin{equation*}
\mathrm{d} S=\frac{\hat{d}^{\mathrm{I}} Q+\hat{d}^{\mathrm{I}} Q}{T}+\frac{1}{T}\left(\psi^{\mathrm{I}}-\psi^{\mathrm{II}}\right) I \mathrm{~d} t-\sum_{\gamma}\left(\frac{\mu_{\gamma}^{\mathrm{I}}}{T} \mathrm{~d} n_{\gamma}^{\mathrm{I}}+\frac{\mu_{\gamma}^{\mathrm{II}}}{T} \mathrm{~d} n_{\gamma}^{\mathrm{II}}\right), \tag{14.71}
\end{equation*}
$$

where $I$ is the intensity of the electric current observed at the instant $t$ and this is related to the rates defined in Eq. (14.70), by the relation,

$$
\begin{equation*}
I=\sum_{\gamma} z_{\gamma} \mathfrak{F} \mathrm{v}_{\gamma}, \tag{14.72}
\end{equation*}
$$

$\mathfrak{F}$ being the Faraday, i.e., the electric charge of one mole of ions bearing a unit electrovalency. If we denote with $e$ the charge of the proton $e=1.6 \times 10^{-19}$ coulomb and with $N_{\mathrm{A}}=6.023 \times 10^{23}$ the Avogadro's number, we have

$$
\begin{equation*}
\mathfrak{F}=e N_{\mathrm{A}} \simeq 0.96549 \times 10^{5} \text { coulomb } \tag{14.73}
\end{equation*}
$$

After separating in Eq. (14.71) the terms that describe the interaction with the outside from those that are due to internal processes, we get

$$
\begin{equation*}
\hat{d}_{\mathrm{i}} S=\frac{1}{T} \sum_{\gamma}\left(\psi^{\mathrm{I}}-\psi^{\mathrm{II}}\right) z_{\gamma} \mathfrak{F} \mathrm{d} \xi_{\gamma}+\sum_{\gamma}\left(\frac{\mu_{\gamma}^{\mathrm{I}}}{T}-\frac{\mu_{\gamma}^{\mathrm{II}}}{T}\right) \mathrm{d} \xi_{\gamma}, \tag{14.74}
\end{equation*}
$$

where we used Eq. (14.69). For the entropy production, we have

$$
\begin{equation*}
\mathcal{P}=\frac{1}{T}\left[\sum_{\gamma}\left(\psi^{\mathrm{I}}-\psi^{\mathrm{II}}\right) z_{\gamma} \mathfrak{F}+\sum_{\gamma}\left(\mu_{\gamma}^{\mathrm{I}}-\mu_{\gamma}^{\mathrm{II}}\right)\right] \mathrm{v}_{\gamma} . \tag{14.75}
\end{equation*}
$$

This relation can be written in the following form:

$$
\begin{equation*}
\mathcal{P}=\sum_{\gamma} \frac{\tilde{\mathcal{A}}_{\gamma}}{T} \mathbf{v}_{\gamma}, \tag{14.76}
\end{equation*}
$$

in which we set

$$
\begin{align*}
\tilde{\mathcal{A}}_{\gamma} & =\left(\mu_{\gamma}^{\mathrm{I}}+z_{\gamma} \mathfrak{F} \psi^{\mathrm{I}}\right)-\left(\mu_{\gamma}^{\mathrm{II}}+z_{\gamma} \mathfrak{F} \psi^{\mathrm{II}}\right)  \tag{14.77}\\
& =\tilde{\mu_{\gamma}^{\mathrm{I}}}-\tilde{\mu_{\gamma}^{\mathrm{II}}}, \tag{14.78}
\end{align*}
$$

with

$$
\begin{equation*}
\tilde{\mu_{\gamma}}=\mu_{\gamma}+z_{\gamma} \mathfrak{F} \psi . \tag{14.79}
\end{equation*}
$$

We point out that the expression Eq. (14.79) shows the modification to the expression of the chemical potential due to the presence of the external electrostatic field and Eq. (14.77) represents the generalization, in our case, of the definition of affinity.

They are called, respectively, electrochemical potential and electrochemical affinities. The equilibrium condition becomes

$$
\begin{equation*}
\tilde{\mathcal{A}}_{\nu}=0, \tag{14.80}
\end{equation*}
$$

which becomes

$$
\begin{equation*}
\mu_{\gamma}^{\mathrm{I}}-\mu_{\gamma}^{\mathrm{II}}=-z_{\gamma} \mathfrak{F}\left(\psi^{\mathrm{I}}-\psi^{\mathrm{II}}\right) \tag{14.81}
\end{equation*}
$$

### 14.6 Generalized Fluxes and Forces

In the previous subsections, we have computed the entropy production in different situations but always in the context of the approximation of discontinuous systems. We have seen that, in all generality, the entropy production appears to be given by the sum of $n$ terms:

$$
\begin{equation*}
\mathcal{P}=J_{1} X_{1}+J_{2} X_{2}+\cdots+J_{n} X_{n} \tag{14.82}
\end{equation*}
$$

each of which is constituted by the product of a term that we called generalized flow or generalized flux, $J_{\rho}$, times the associated generalized force $X_{\rho}$. The fluxes describe the rate at which extensive quantities are exchanged, while the generalized forces determine, all together, the onset of the irreversible processes described by the generalized fluxes. The cause-effect relationship between these two classes of physical quantities requires a more in-depth analysis of their functional dependence.

### 14.6.1 Determination of Generalized Fluxes and Forces

A very important question in order to understand more deeply the nature of generalized flows and in view of some concrete applications is the following: given a certain configuration of nonequilibrium thermodynamics, are the fluxes uniquely determined or is there a substantial indetermination that leaves a large discretion in the identification of the processes? And in the latter case, what is the physical quantity objectively determined by the given physical situation?

The examination of two paradigmatic examples will make us understand how things are.

## The Case of Chemical Reactions

Let us consider, as the first example, the case of a closed system in which two chemical reactions are active. For instance, let us consider the combustion of carbon in which both carbon monoxide and carbon dioxide are produced while carbon and oxygen are consumed. The processes can be described by the two chemical reactions:

$$
\begin{align*}
& 2 \mathrm{C}+\mathrm{O}_{2} \rightarrow 2 \mathrm{CO}  \tag{14.83}\\
& \mathrm{C}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2} \tag{14.84}
\end{align*}
$$

In order to write the expression of the entropy production, we need to determine the two reaction rates and the two affinities. If denote by $v_{1}$ and $v_{2}$ the rates of reaction Eqs. (14.83) and (14.84), respectively, and by $\mathcal{A}_{1}$ and $\mathcal{A}_{2}$ their affinities, we have

$$
\begin{align*}
& \frac{\mathrm{d} n_{\mathrm{C}}}{\mathrm{~d} t}=-2 \mathrm{v}_{1}-\mathrm{v}_{2},  \tag{14.85}\\
& \frac{\mathrm{~d} n_{\mathrm{O}_{2}}}{\mathrm{~d} t}=-\mathrm{v}_{1}-\mathrm{v}_{2},  \tag{14.86}\\
& \frac{\mathrm{~d} n_{\mathrm{CO}}}{\mathrm{~d} t}=2 \mathrm{v}_{1},  \tag{14.87}\\
& \frac{\mathrm{~d} n_{\mathrm{CO}_{2}}}{\mathrm{~d} t}=\mathrm{v}_{2}  \tag{14.88}\\
& \mathcal{A}_{1}=2 \mu_{\mathrm{C}}+\mu_{\mathrm{O}_{2}}-2 \mu_{\mathrm{CO}},  \tag{14.89}\\
& \mathcal{A}_{2}=\mu_{\mathrm{C}}+\mu_{\mathrm{O}_{2}}-\mu_{\mathrm{CO}_{2}}, \tag{14.90}
\end{align*}
$$

and the entropy production is

$$
\begin{equation*}
T \mathcal{P}=\mathcal{A}_{1} \mathrm{v}_{1}+\mathcal{A}_{2} \mathrm{v}_{2} \tag{14.91}
\end{equation*}
$$

It is important to recall that the thermodynamic point of view has to provide a full description of the evolution of the macroscopic state of the system and this, in our example, means to give a correct description of the evolution of the macroscopic state variables $n_{\mathrm{C}}, n_{\mathrm{O}_{2}}, n_{\mathrm{CO}}$ and $n_{\mathrm{CO}_{2}}$.

For this purpose, we could adopt a different pair of chemical reactions like, for example,

$$
\begin{align*}
& 2 \mathrm{C}+\mathrm{O}_{2} \rightarrow 2 \mathrm{CO}  \tag{14.92}\\
& 2 \mathrm{CO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{CO}_{2} \tag{14.93}
\end{align*}
$$

With this new description, we shall have new rates, new affinities, and a new entropy production. If we denote with $\mathcal{A}_{1^{\prime}}^{\prime}$ and $\mathcal{A}_{2}^{\prime}$ the affinities of reactions Eqs. (14.92) and (14.93), respectively, it is easy to demonstrate that they are related to the affinities $\mathcal{A}_{1}$ and $\mathcal{A}_{2}$ relative to the first description by

$$
\begin{align*}
& \mathcal{A}_{1}^{\prime}=\mathcal{A}_{1}  \tag{14.94}\\
& \mathcal{A}_{2}^{\prime}=2 \mathcal{A}_{2}-\mathcal{A}_{1} \tag{14.95}
\end{align*}
$$

As far the new rates are concerned, their relations with the previous rates can be easily found requiring that the new ones give the same time derivatives of the mole
numbers $\mathrm{d} n_{\gamma} / \mathrm{d} t$. The latter quantities are the observables of the problem and are, therefore, objective, then it is easy to show that the new rates can be expressed as functions of the old rates by

$$
\begin{align*}
\mathrm{v}_{1}^{\prime} & =\mathrm{v}_{1}+\frac{1}{2} \mathrm{v}_{2}  \tag{14.96}\\
\mathrm{v}_{2}^{\prime} & =\frac{1}{2} \mathrm{v}_{2} \tag{14.97}
\end{align*}
$$

As for the entropy production $\mathcal{P}^{\prime}$, in the new description, its formal expression is

$$
\begin{equation*}
T \mathcal{P}^{\prime}=\mathcal{A}_{1}^{\prime} \mathrm{v}_{1}^{\prime}+\mathcal{A}_{2}^{\prime} \mathrm{v}_{2}^{\prime} \tag{14.98}
\end{equation*}
$$

If we use Eqs. (14.94)-(14.97), we obtain

$$
\begin{equation*}
\mathcal{P}^{\prime}=\mathcal{P} \tag{14.99}
\end{equation*}
$$

The essential point in this discussion is the following: the "objective" facts, that is what the observer really observes, is the changes in the composition in the time interval $\mathrm{d} t$ that is $\mathrm{d} n_{\mathrm{C}}, \mathrm{d} n_{\mathrm{O}_{2}}, \mathrm{~d} n_{\mathrm{CO}}$ and $\mathrm{d} n_{\mathrm{CO}_{2}}$, but he does not observe which specific chemical reactions are taking place. The latter are just a descriptive instrument adopted by the observer in order to account for the observations. The two sets of chemical reactions adopted in the example constitute two different descriptions of the same physical situation and are called, therefore, equivalent systems. In conclusion, the observer has a certain arbitrariness in assuming which processes (in our example which chemical reactions) are taking place as long as the different descriptions are equivalent which means that they provide the same description of the variations of the state variables. The latter requirement provides Eqs. (14.96) and (14.97), i.e., the relations between the generalized fluxes in the two descriptions. As a consequence we proved in Eq. (14.99) that the entropy production is invariant with respect to the change of the adopted description. In this sense, we may affirm that entropy production is "objective."

In the second example, we will make a different choice of flows and will use the required invariance of the entropy production to find, quickly, the expression of the new forces as a function of the forces of the first choice.

## The Case of Open Systems

Let us return to consider the situation which led to the calculation of the entropy production Eq. (14.59) and, for simplicity of writing we put to zero the terms related to chemical reactions. One possible choice of flows and forces is illustrated by Eq. (14.60) with the related Eq. (14.61) as the relative force and the fluxes shown in Eq. (14.62) with their relative forces Eq. (14.63). The value of the latter depends on both the temperature difference between the two phases and the difference of the
chemical potential for each component. It may happen, however, that it is preferable to think in terms of temperature and pressure differences separately which might be the state variables that the experimenter easily controls. If we assume that between the two phases the temperature difference is small $\Delta T \ll T^{\mathrm{I}}, T^{\mathrm{II}}$ and similarly for the pressures $\Delta p \ll p^{\mathrm{I}}$, $p^{\mathrm{II}}$, we can approximate Eq. (14.63) to the linear terms:

$$
\begin{align*}
X_{\gamma} & =-\Delta\left(\frac{\mu_{\gamma}}{T}\right)  \tag{14.100}\\
& \simeq \frac{1}{T^{2}} \mu_{\gamma} \Delta T-\frac{1}{T}\left(\frac{\partial \mu_{\gamma}}{\partial T}\right)_{p} \Delta T-\frac{1}{T}\left(\frac{\partial \mu_{\gamma}}{\partial p}\right)_{T} \Delta p  \tag{14.101}\\
& =\frac{1}{T^{2}}\left(\mu_{\gamma}+T S_{\mathrm{m}_{\gamma}}\right) \Delta T-\frac{1}{T}\left(\frac{\partial \mu_{\gamma}}{\partial p}\right)_{T} \Delta p  \tag{14.102}\\
& =\frac{1}{T^{2}} H_{\mathrm{m}_{\gamma}} \Delta T-\frac{1}{T} V_{\mathrm{m}_{\gamma}} \Delta p \tag{14.103}
\end{align*}
$$

in which we used the relation $H_{\mathrm{m}_{\gamma}}=\mu_{\gamma}+T S_{\mathrm{m}_{\gamma}}$ for the molar enthalpy of the $\gamma$ component with $S_{\mathrm{m}_{\nu}}$ and $V_{\mathrm{m}_{\nu}}$ being its molar entropy and the molar volume, respectively. While the force Eq. (14.61) depends only on the temperature difference, the one relative to the flow of matter depends on both $\Delta T$ and the pressure difference. Let us look for a different description, in terms of a different choice of flows and related forces, so that the forces depend only either on $\Delta T$ or on $\Delta p$ so that their effects are clearly disentangled.

Consider the following choice of generalized flows:

$$
\begin{align*}
& J_{\mathrm{th}}^{\prime}=J_{U}-\sum_{\gamma} H_{\mathrm{m}_{\gamma}} J_{\gamma}  \tag{14.104}\\
& J_{\gamma}^{\prime}=J_{\gamma} \tag{14.105}
\end{align*}
$$

We now want to find the expression of the related generalized forces. To do this, we impose that the equality

$$
\begin{equation*}
J_{U} X_{U}+\sum_{\gamma} J_{\gamma} X_{\gamma}=J_{\mathrm{th}}^{\prime} X_{\mathrm{th}}^{\prime}+\sum_{\gamma} J_{\gamma}^{\prime} X_{\gamma}^{\prime} \tag{14.106}
\end{equation*}
$$

is an identity, that is, it must be verified for any value of the flows.
If we consider the case in which all fluxes $J_{\gamma}$ are zero, from Eq. (14.104), we obtain $J_{\text {th }}^{\prime}=J_{U}$ and from Eq. (14.106), we get

$$
\begin{equation*}
X_{\mathrm{th}}^{\prime}=X_{U} \tag{14.107}
\end{equation*}
$$

Similarly if we put to zero all the fluxes but one $J_{\gamma}$ we obtain $J_{\mathrm{th}}^{\prime}=-H_{\mathrm{m}_{\gamma}} J_{\gamma}$ and, in these cases, Eq. (14.106), will give

$$
\begin{equation*}
J_{\gamma} X_{\gamma}=-H_{\mathrm{m}_{\gamma}} J_{\gamma} X_{\mathrm{th}}+J_{\gamma} X_{\gamma}^{\prime} \tag{14.108}
\end{equation*}
$$

and hence

$$
\begin{equation*}
X_{\gamma}^{\prime}=X_{\gamma}+H_{\mathrm{m}_{\gamma}} X_{U} \tag{14.109}
\end{equation*}
$$

In conclusion, by dropping the prime from Eqs. (14.104) to (14.109), the new fluxes and the corresponding associated forces are written as

$$
\begin{align*}
& J_{\mathrm{th}}=J_{U}-\sum_{\gamma} H_{m_{\gamma}} J_{\gamma}  \tag{14.110}\\
& X_{\mathrm{th}}=\Delta\left(\frac{1}{T}\right) \simeq-\frac{\Delta T}{T^{2}}  \tag{14.111}\\
& J_{\gamma}=-\frac{\hat{d}_{\mathrm{e}} n_{\gamma}^{\mathrm{I}}}{\mathrm{~d} t}  \tag{14.112}\\
& \quad X_{\gamma} \simeq-\frac{1}{T} V_{m_{\gamma}} \Delta p \tag{14.113}
\end{align*}
$$

In this way, we reached the goal of separating the effects of temperature and pressure differences but it is useful to observe that the meaning of the new flow $J_{\text {th }}$ while maintaining the dimension of a flow of energy, it no longer represents the energy transferred per unit time. We will resume this issue later when we shall deal with the quantities of transport.

In conclusion, we have seen that the choice of flows and their respective forces is not unique but depends on what the observer believes more convenient and this , in turn, depends on the specific problem and on the quantities we want to measure. Of course also the names of the irreversible processes taking place in a given nonequilibrium situation are not objective but the result of a particular choice.

### 14.7 Onsager Relations

We have seen that, in all generality, the entropy production in a nonequilibrium system is given by the sum of the products of the flows times the relative generalized forces:

$$
\begin{equation*}
\mathcal{P}=\sum_{\rho} J_{\rho} X_{\rho} \tag{14.114}
\end{equation*}
$$

The generalized forces depend on the difference of the state parameters between the two phases and the equilibrium situation is guaranteed by the condition that for all the forces we have

$$
\begin{equation*}
X_{\rho}=0 \tag{14.115}
\end{equation*}
$$

In such a case for all the fluxes, it will be

$$
\begin{equation*}
J_{\rho}=0 \tag{14.116}
\end{equation*}
$$

We shall assume that the values of the flows in a given nonequilibrium configuration depend on the values, in that instant, of all the generalized forces in that instant ${ }^{3}$ and let $n$ be the number of fluxes and forces, then we write

$$
\begin{equation*}
J_{\rho}=J_{\rho}\left(X_{1}, X_{2}, \ldots, X_{n}\right) \tag{14.117}
\end{equation*}
$$

and we have $J_{\rho}(0,0, \ldots, 0)=0$ for every $\rho$. Hence, for small values of $X_{\rho}$, we can linearize the previous relation:

$$
\begin{equation*}
J_{\rho}\left(X_{1}, X_{2}, \ldots, X_{n}\right)=J_{\rho}(0,0, \ldots, 0)+\sum_{\rho^{\prime}=1}^{n}\left(\frac{\partial J_{\rho}}{\partial X_{\rho^{\prime}}}\right)_{\mathrm{eq}} X_{\rho^{\prime}} \tag{14.118}
\end{equation*}
$$

with

$$
\begin{equation*}
J_{\rho}=\sum_{\rho^{\prime}=1}^{n} L_{\rho \rho^{\prime}} X_{\rho^{\prime}} \tag{14.119}
\end{equation*}
$$

The coefficients $L_{\rho \rho^{\prime}}$ are called linear phenomenological coefficients and, as it is clear from their definition, their value depends on the equilibrium state close to which we have altered the equilibrium conditions.

The coefficients $L_{\rho \rho^{\prime}}$ form a matrix $n \times n$ called linear phenomenological matrix in which the diagonal elements describe the proportionality of a generalized flux to its own generalized force, while the nondiagonal elements describe the possible interference between different irreversible processes. Consider, as an example, two chemical reactions simultaneously present:

$$
\begin{equation*}
\mathcal{P}=\left(\frac{\mathcal{A}_{1}}{T}\right) \mathrm{v}_{1}+\left(\frac{\mathcal{A}_{2}}{T}\right) \mathrm{v}_{2} . \tag{14.120}
\end{equation*}
$$

Let us write the linear relation between flows and forces near equilibrium:

$$
\begin{align*}
& \mathrm{v}_{1}=L_{11}\left(\frac{\mathcal{A}_{1}}{T}\right)+L_{12}\left(\frac{\mathcal{A}_{2}}{T}\right),  \tag{14.121}\\
& \mathrm{v}_{2}=L_{21}\left(\frac{\mathcal{A}_{1}}{T}\right)+L_{22}\left(\frac{\mathcal{A}_{2}}{T}\right) \tag{14.122}
\end{align*}
$$

The diagonal terms $L_{11}$ and $L_{22}$ describe how strongly each chemical reaction is driven by their own affinity, while the terms $L_{12}$ and $L_{21}$ describe, quantitatively, the effect of each of the two forces on the evolution of the other reaction. These nondiagonal terms describe the interference between the two reactions.

[^48]In general, if we have two irreversible processes (i.e., the production of entropy is given by the sum of two terms), we will have

$$
\begin{equation*}
\mathcal{P}=J_{1} X_{1}+J_{2} X_{2} . \tag{14.123}
\end{equation*}
$$

The linear relations between fluxes and forces are

$$
\begin{align*}
& J_{1}=L_{11} X_{1}+L_{12} X_{2}  \tag{14.124}\\
& J_{2}=L_{21} X_{1}+L_{22} X_{2} \tag{14.125}
\end{align*}
$$

and the entropy production becomes

$$
\begin{equation*}
\mathcal{P}=L_{11} X_{1}^{2}+\left(L_{12}+L_{21}\right) X_{1} X_{2}+L_{22} X_{2}^{2}>0 \tag{14.126}
\end{equation*}
$$

The second principle requires this quadratic form to be positive definite. This implies that the diagonal coefficients are positive and also

$$
\begin{equation*}
\left(L_{12}+L_{21}\right)^{2}<4 L_{11} L_{22} . \tag{14.127}
\end{equation*}
$$

The phenomenological matrix is the matrix of a positive definite quadratic form and this imposes some conditions on the minors of the matrix. The most obvious is that it must be $L_{\rho \rho}>0$ for every $\rho$.

The next step, the most important step, is to formulate the phenomenological symmetry properties of the matrix. This is expressed by the condition

$$
\begin{equation*}
L_{\rho \rho^{\prime}}=L_{\rho^{\prime} \rho} \tag{14.128}
\end{equation*}
$$

This condition, named also as reciprocity condition, states, in practice, that if the phenomenon (i.e., the flow) $J_{\rho}$ is influenced by the presence of the force $X_{\rho^{\prime}}$ relative to phenomenon $J_{\rho^{\prime}}$, also the $\rho^{\prime}$-th phenomenon is influenced by the force $X_{\rho}$ relative to the $\rho$-th phenomenon and the coefficient which measures the strength of this mutual interference takes the same value.

These symmetry relations provided by Eq. (14.128) are also called Onsager reciprocity (symmetry) relations in honor of Lars Onsager Nobel Prize in Chemistry in 1968.

Some authors refer to them as to the Onsager theorem (see for instance [21]) because of the considerable theoretical work which, primarily due to the contribution of L. Onsager, has been developed to demonstrate these symmetry relations in the study on the decay of fluctuations of a system at equilibrium. The fact that the same reciprocal relations are applied among the irreversible processes in thermodynamic nonequilibrium configurations represents a generalization of Onsager theorem and constitutes a sort of fourth postulate.

It is just the application of these conditions of reciprocity that the thermodynamic study of irreversible processes, in the linear region, provides qualitative and quantitative results of fundamental importance not achievable otherwise.

### 14.7.1 The Curie Symmetry Principle

In general, if the entropy production is formed by $n$ terms, and then if we have $n$ irreversible processes, the Onsager theory requires to consider each flow coupled through the phenomenological coefficients $L_{\rho \rho^{\prime}}$ to all the $n$ generalized forces.

Let us examine a particular example in which the entropy production is formed by only two terms, one that describes the dynamics of a chemical reaction $(\mathcal{A} / T) \mathrm{v}$ and another describing a flow of heat in the presence of a temperature gradient. As we will see in detail in the chapter devoted to the study of thermodynamics in continuous systems (see Chap. 16), the contribution of the latter process to the entropy production can be described by a "vectorial" flux in the sense that for a complete determination of the flux we have to specify also the direction along which heat flows. Obviously, also its generalized force will be of "vectorial" nature, in the same sense, and, as we shall demonstrate in Eqs. (16.67) and (16.68), it will depend on the gradient of $1 / T$. As far as the chemical reaction is concerned, let us remember that the rate $v$ is an extensive quantity and then, for small volumes it will be written as $\mathrm{v} \simeq j_{\mathrm{ch}} \delta V$ (this will be shown more clearly in Chap. 16). This relation defines $j_{\mathrm{ch}}$, which is the rate per unit volume of the chemical reaction, point by point. Suppose that at a certain point the temperature gradient is parallel to the $x$-axis, then for an isotropic material the production of entropy per unit volume, will be

$$
\begin{equation*}
\pi=\frac{\mathcal{A}}{T} j_{\mathrm{ch}}+J_{x} \frac{\partial}{\partial x}\left(\frac{1}{T}\right) . \tag{14.129}
\end{equation*}
$$

The corresponding linear relationship between fluxes and forces will be of the type [21]:

$$
\begin{align*}
j_{\mathrm{ch}} & =L_{11} \frac{\mathcal{A}}{T}+L_{12} \frac{\partial}{\partial x}\left(\frac{1}{T}\right)  \tag{14.130}\\
J_{x} & =L_{21} \frac{\mathcal{A}}{T}+L_{22} \frac{\partial}{\partial x}\left(\frac{1}{T}\right) \tag{14.131}
\end{align*}
$$

If we consider the particular case of a system at uniform temperature, the heat flux becomes

$$
\begin{equation*}
J_{x}=L_{21} \frac{\mathcal{A}}{T} \tag{14.132}
\end{equation*}
$$

This result forces us to require that

$$
\begin{equation*}
L_{21}=0 \tag{14.133}
\end{equation*}
$$

because there is no reason that a "scalar cause" as the affinity of a chemical reaction produces a vector effect as the heat flow in a particular direction ( $x$-axis in our example).

This particular result can be generalized by requiring that the nondiagonal coefficients, which describe the coupling between different irreversible phenomena, may be non-zero only when they couple phenomena with the same degree of symmetry, that is, scalar forces with scalar flows, vector forces with vector flows, and tensorial forces with tensorial flows. This is the so-called Curie symmetry principle.

As a consequence, in the case of the entropy production shown by Eq. (14.67) discussed in Sect. 14.4, we shall, in complete generality, write the linear relationships between flows and forces by coupling only the flows of energy and matter, while the chemical reactions will only be coupled to each other (and in this example separately in each phase).

### 14.8 The Approximation of Linearity

Here, we want to discuss, briefly, the condition of linearity between fluxes and forces, which is the basis of the reciprocity relations. The question of how small a force should be in order to be allowed to linearize the flux-force dependance cannot be answered in general but must be examined case by case.

We will examine here the case of chemical reactions: we will see that, in the very frequent cases where it is possible to have a suitable approximation for the chemical potentials of the components, we can easily calculate the affinity on one side, the velocity on the other, express the latter as a function of the affinity and then see under what assumptions this relationship can be linearized.

### 14.8.1 Chemical Affinity

Consider as an example the general chemical reaction:

$$
\begin{equation*}
\left|v_{M}\right| M+\left|v_{N}\right| N \rightarrow v_{R} R+v_{S} S, \tag{14.134}
\end{equation*}
$$

where $\mathrm{M}, \mathrm{N}, \mathrm{R}$, and S are chemical components and the relative stoichiometric coefficients are written with the convention on the signs already adopted in Sect. 14.3. Let us suppose that the chemical potentials $\mu_{\gamma}$ may be written, with good approximation, in the form already adopted for ideal gases or for ideal solutions in Eq. (6.52), and in which their dependence on molar concentration $C_{\gamma}$ is evidenced:

$$
\begin{equation*}
\mu_{\gamma}=\eta_{\gamma}(p, T)+R T \ln C_{\gamma} . \tag{14.135}
\end{equation*}
$$

The expression for the affinity $\mathcal{A}=-\sum_{\gamma} \nu_{\gamma} \mu_{\gamma}$ can be written in the form

$$
\begin{equation*}
\mathcal{A}=-\sum_{\gamma} v_{\gamma} \eta_{\gamma}(p, T)-R T \sum_{\gamma} v_{\gamma} \ln C_{\gamma} . \tag{14.136}
\end{equation*}
$$

Let us define the function $K=K(p, T)$ so that

$$
\begin{equation*}
R T \ln K(p, T)=-\sum_{\gamma} v_{\gamma} \eta_{\gamma}(p, T) . \tag{14.137}
\end{equation*}
$$

The quantity $K(p, T)$ is called equilibrium constant of the chemical reaction at given pressure and temperature (the justification will be given in Eq. (14.139)) and the affinity will be written in the useful form:

$$
\begin{equation*}
\mathcal{A}=R T \ln \frac{K(p, T)}{\Pi_{\gamma} C_{\gamma}^{v_{\gamma}}} . \tag{14.138}
\end{equation*}
$$

From this expression, it appears that at given pressure and temperature the chemical reaction will be in a state of equilibrium if (and only if) the concentrations of the components satisfy the relation

$$
\begin{equation*}
\Pi_{\gamma} C_{\gamma}^{v_{\gamma}}=K(p, T) \tag{14.139}
\end{equation*}
$$

and this relation justifies the name for $K(p, T)$. It is a constant with respect to different choices of the concentrations but its value depends on $p, T$. The expression in Eq. (14.139) is sometimes called law of mass action.

### 14.8.2 Reaction Rate

Let us refer to the molecular theory of matter. From the microscopic point of view, we may consider the elementary events taking place when two, or more, molecules interact. We are interested in those events in which the outcome of the interaction consists in the formation of those new bound states as described in the reaction formula. The probability of this outcome will depend primarily on the energy of the reacting molecules and on the geometry of the collision. If we integrate over geometrical factors and over the energies, we obtain a sort of average probability for each final outcome, whose value will depend on pressure and on temperature.

It will be useful to define two partial rates the "forward rate" denoted by $\mathrm{v}^{+}$and the "backward rate" denoted by $\mathrm{v}^{-}$. They express, respectively, the number of forward events and of backward events taking place in the whole system per second. It is clear that their value will be proportional to the concentrations in the form

$$
\begin{align*}
& \mathrm{v}^{+} \propto C_{\mathrm{M}}^{\left|\nu_{\mathrm{M}}\right|} C_{\mathrm{N}}^{\left|\nu_{\mathrm{N}}\right|},  \tag{14.140}\\
& \mathrm{v}^{-} \propto C_{\mathrm{R}}^{v_{\mathrm{R}}} C_{\mathrm{S}}^{v_{\mathrm{S}}}, \tag{14.141}
\end{align*}
$$

while the proportionality factors depend on a sort of average cross section for forward/backward events and will depend on temperature and pressure. These factors are called forward and backward kinetic constants and are denoted, respectively, with $k^{+}(p, T)$ and $k^{-}(p, T)$. Then we may write

$$
\begin{align*}
& \mathrm{v}^{+}=C_{\mathrm{M}}^{\left|v_{\mathrm{M}}\right|} C_{\mathrm{N}}^{\left|v_{\mathrm{N}}\right|} k^{+}(p, T),  \tag{14.142}\\
& \mathrm{v}^{-}=C_{\mathrm{R}}^{v_{\mathrm{R}}} C_{\mathrm{S}}^{\mathrm{v}_{\mathrm{S}}} k^{-}(p, T) \tag{14.143}
\end{align*}
$$

The reaction rate, by definition, will be

$$
\begin{equation*}
\mathrm{v}=\mathrm{v}^{+}-\mathrm{v}^{-} . \tag{14.144}
\end{equation*}
$$

Hence, by substituting Eqs. (14.142) and (14.143) in Eq. (14.144), we have ${ }^{4}$

$$
\begin{equation*}
\mathrm{v}=C_{\mathrm{M}}^{\left|\nu_{\mathrm{M}}\right|} C_{\mathrm{N}}^{\left|\nu_{\mathrm{N}}\right|} k^{+}(p, T)-C_{\mathrm{R}}^{\nu_{\mathrm{R}}} C_{\mathrm{S}}^{\nu_{\mathrm{S}}} k^{-}(p, T) \tag{14.145}
\end{equation*}
$$

and factorizing $\mathrm{v}^{+}$we obtain

$$
\begin{align*}
\mathrm{v} & =\mathrm{v}^{+}\left(1-\frac{C_{\mathrm{R}}^{\nu_{\mathrm{R}}} C_{\mathrm{S}}^{\nu_{\mathrm{S}}}}{C_{\mathrm{M}}^{\left|\nu_{\mathrm{M}}\right|} C_{\mathrm{N}}^{\left|\nu_{\mathrm{N}}\right|}} \frac{k^{-}}{k^{+}}\right) \\
& =\mathrm{v}^{+}\left(1-\Pi_{\gamma} C_{\gamma}^{\nu_{\gamma}} \frac{k^{-}}{k^{+}}\right) \tag{14.146}
\end{align*}
$$

In order to obtain the desired relation between the reaction rate and the affinity, it is necessary to express the ratio $k^{-} / k^{+}$as a function of the macroscopic parameters. Let us consider one possible set of concentrations that we denote by $C_{\gamma}^{*}$, which give an equilibrium configuration for the chemical reaction (see the law of mass action). By inserting this set of concentrations into the expressions of the affinity and in that of the rate, we obtain two relations: one which expresses that the affinity is zero and the other expressing that the rate is zero. By considering Eq. (14.138), the former condition leads to

$$
\begin{equation*}
\Pi_{\gamma}\left(C_{\gamma}^{*}\right)^{v_{\gamma}}=K(p, T) \tag{14.147}
\end{equation*}
$$

while the condition of zero rate leads to (see Eq. (14.146))

$$
\begin{equation*}
\Pi_{\gamma}\left(C_{\gamma}^{*}\right)^{v_{\nu}} \frac{k^{-}}{k^{+}}=1 \tag{14.148}
\end{equation*}
$$

[^49]From these two relations, we easily obtain the following general result:

$$
\begin{equation*}
\frac{k^{-}}{k^{+}}=\frac{1}{K(p, T)} . \tag{14.149}
\end{equation*}
$$

Finally, from Eqs. (14.149) and (14.138), we obtain the desired relation between rate and affinity:

$$
\begin{equation*}
\mathrm{v}=\mathrm{v}^{+}\left[1-\exp \left(-\frac{\mathcal{A}}{R T}\right)\right] . \tag{14.150}
\end{equation*}
$$

### 14.8.3 Linear Relations Between Rates and Affinities

We can now, with some awareness, tell under what conditions we can speak of linear relationship between flow (rate) and force (affinity/temperature).

With reference to Eq. (14.150), we can approximate the function

$$
[1-\exp (-x)] \simeq x
$$

for small $x$ which means

$$
\begin{equation*}
\frac{\mathcal{A}}{R T} \ll 1 . \tag{14.151}
\end{equation*}
$$

The linear relation becomes

$$
\begin{equation*}
\mathrm{v}=\frac{\mathrm{v}^{+}}{R} \frac{\mathcal{A}}{T} \tag{14.152}
\end{equation*}
$$

and the phenomenological coefficient $L_{\mathrm{ch}}$ for the chemical reaction is

$$
\begin{equation*}
L_{\mathrm{ch}}=\frac{\mathrm{v}^{+}}{R} . \tag{14.153}
\end{equation*}
$$

In the opposite situation, namely, for

$$
\begin{equation*}
\frac{\mathcal{A}}{R T} \gg 1, \tag{14.154}
\end{equation*}
$$

we have $\mathrm{v} \approx \mathrm{v}^{+}$, i.e., the reaction rate is independent of the affinity and is equal to the "forward rate." If we go back to Eq. (14.138), we see that at a given temperature, that is for a given value of the equilibrium constant, the affinity assumes very large values (with respect to $R T$ ), when

$$
\begin{equation*}
\Pi_{\gamma} C_{\gamma}^{v_{\gamma}} \rightarrow 0 \tag{14.155}
\end{equation*}
$$

and this happens if the concentration of at least one component with positive stoichiometric number (and then to the right of the chemical reaction) tends to zero. This means that the reaction is at the "beginning" meaning by this that all or some of the reaction products are absent. In this case, the number of "backward events" per second is practically zero.

## Chain of Reactions

It is interesting, at this point, to consider the case of consecutive chemical reactions meaning, with this expression, a situation that can, schematically, be described by a sequence of reactions of the following type:

$$
\begin{align*}
& \mathrm{B} \rightarrow \mathrm{C}  \tag{14.156}\\
& \mathrm{C} \rightarrow \mathrm{D}  \tag{14.157}\\
& \cdots \cdots  \tag{14.158}\\
& \mathrm{M} \rightarrow \mathrm{~N} .
\end{align*}
$$

In general, the entropy production is written as

$$
\begin{equation*}
T \mathcal{P}=\mathcal{A}_{1} \mathrm{v}_{1}+\mathcal{A}_{2} \mathrm{v}_{2}+\cdots+\mathcal{A}_{n} \mathrm{v}_{n} . \tag{14.160}
\end{equation*}
$$

In some cases of considerable importance, we might have to deal with situations in which the concentrations of the "intermediate" components can quickly become constant in time. Then,

$$
\begin{equation*}
\mathrm{v}_{1}=\mathrm{v}_{2}=\cdots=\mathrm{v}_{n}=\mathrm{v} \tag{14.161}
\end{equation*}
$$

In parallel, the entropy production becomes

$$
\begin{equation*}
T \mathcal{P}=\left(\mathcal{A}_{1}+\mathcal{A}_{2}+\cdots+\mathcal{A}_{n}\right) \mathrm{v} \tag{14.162}
\end{equation*}
$$

To some extent, it is as if we had only one global reaction:

$$
\begin{equation*}
\mathrm{B} \rightarrow \mathrm{~N}, \tag{14.163}
\end{equation*}
$$

whose affinity is

$$
\begin{equation*}
\mathcal{A}=\mathcal{A}_{1}+\mathcal{A}_{2}+\cdots+\mathcal{A}_{n} \tag{14.164}
\end{equation*}
$$

whose rate is v and with entropy production:

$$
\begin{equation*}
T \mathcal{P}=\mathcal{A} \mathrm{v} \tag{14.165}
\end{equation*}
$$

It is easy to conceive that we may violate the linearity condition for the global reaction Eq. (14.163), i.e.,

$$
\begin{equation*}
\frac{\mathcal{A}}{R T}>1 \tag{14.166}
\end{equation*}
$$

and, at the same time, for each "partial" reaction, the linearity condition can be saved:

$$
\begin{equation*}
\frac{\mathcal{A}_{i}}{R T} \ll 1, \tag{14.167}
\end{equation*}
$$

where $\mathcal{A}_{i}$ is the affinity of the $i$ th reaction. So it may happen that even for reactions that, overall, cannot be linearized we can still make use of relations in the linear regime if the overall process can be thought of as the cumulative effect of various partial processes each of which proceeds in a near equilibrium condition.

### 14.8.4 Relaxation Time for a Chemical Reaction

After having examined more closely the linearity condition in a chemical reaction, it is interesting to consider in more detail the dynamics of an irreversible process near equilibrium.

In general, the linearity condition can be written in the form

$$
\begin{equation*}
\frac{\mathrm{d} \xi}{\mathrm{~d} t}=\frac{L}{T} \mathcal{A} \tag{14.168}
\end{equation*}
$$

and, in turn, the affinity will be a function of the state of the system, and hence of the degree of advancement $\xi$. This function must be zero at equilibrium and then we can write in all generality:

$$
\begin{equation*}
\mathcal{A}=\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{\mathrm{eq}}\left(\xi-\xi_{\mathrm{eq}}\right)+\cdots \tag{14.169}
\end{equation*}
$$

and then the dynamics will be described by the differential equation:

$$
\begin{equation*}
\frac{\mathrm{d} \xi}{\mathrm{~d} t}=\frac{L}{T}\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{\mathrm{eq}}\left(\xi-\xi_{\mathrm{eq}}\right) \tag{14.170}
\end{equation*}
$$

whose solution is

$$
\begin{equation*}
\xi-\xi_{\mathrm{eq}}=\left(\xi-\xi_{\mathrm{eq}}\right)_{t=0} \exp \left(-\frac{t}{\tau}\right) \tag{14.171}
\end{equation*}
$$

where $\tau$, called relaxation time of the process, is given by

$$
\begin{equation*}
\tau=-\frac{T}{L\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{\mathrm{eq}}} \tag{14.172}
\end{equation*}
$$

It can be proved (see discussion in Sect. 15.3.1 and Eq. (15.153)) that the derivative $(\partial \mathcal{A} / \partial \xi)_{\text {eq }}$ is negative.

The development of the dynamical theory of a system with several, mutually interfering, chemical reactions goes beyond the scope of this book and will not be treated here.

## Chapter 15 <br> Irreversible Processes: Applications


#### Abstract

The Onsager symmetry relations are applied to the study of electrokinetic effects and of thermomechanical effects. In the latter case the relation between thermomolecular pressure difference and the heat of transfer is calculated, for comparison, also for Knudsen gases in a classical kinetic model. The characterization of stationary states as states of minimum entropy production are studied. The determination of stationary states, their stability and the principles of Le Chatelier and of Le Chatelier-Braun, find their correct explanation within the context of the thermodynamical theory of stationary states. The model by Prigogine and Waime is presented as an example. Within the theory of fluctuations in an isolated thermodynamical system, the decay of fluctuations are treated with the formalism of linear irreversible processes and the symmetry properties of the linear phenomenological matrix is derived from the postulate of time reversal symmetry for microscopic physics.


Keywords Thermomechanical effects • Thermomolecular pressure difference Heat of transfer • Knudsen gases • Electrokinetic effects • Stationary states • Minimum entropy production - Le Chatelier • Le Chatelier-Braun • Fluctuations • Mean values • Correlations - Decay of fluctuations • Microscopic reversibility • Onsager's relations

### 15.1 Introduction

In order to understand the importance of the methods of thermodynamics and their predictive power it is necessary to show some examples. In this chapter in which we adopted the perspective of discontinuous systems, we will see, as examples, the thermomechanical effects and the electrokinetic effects.

### 15.1.1 Thermomechanical Effects

Let's go back to Sect. 14.4 and adopt the description in terms of the fluxes and forces given by Eqs. (14.110)-(14.113) because, as we have seen, with this choice,
in the expressions of the forces, the effects of the pressure difference and of the temperature difference are disentangled. For simplicity, we put to zero the chemical reactions (whose dynamics would, in any case, be decoupled at the level of Onsager relations) and suppose that there is only one component so that the various fluxes of matter reduce to one that we denote with the symbol $J_{\mathrm{m}}$ (and similarly for the notation of the associated generalized force).

With these simplifications, the entropy production becomes

$$
\begin{equation*}
\mathcal{P}=J_{\mathrm{th}} X_{\mathrm{th}}+J_{\mathrm{m}} X_{\mathrm{m}} \tag{15.1}
\end{equation*}
$$

and the linear relations will be written as

$$
\begin{align*}
& J_{\mathrm{th}}=-L_{11} \frac{\Delta T}{T^{2}}-L_{12} \frac{V_{\mathrm{m}} \Delta p}{T}  \tag{15.2}\\
& J_{\mathrm{m}}=-L_{21} \frac{\Delta T}{T^{2}}-L_{22} \frac{V_{\mathrm{m}} \Delta p}{T} \tag{15.3}
\end{align*}
$$

If we act on the pressure and temperature differences we obtain various configurations. Two situations are of particular interest.

## Thermomolecular Pressure Difference

If we set the temperature difference between the two containers at a constant value there is a particular value of the pressure difference which brings to zero the value of the flow of matter. In the linear approximation, this difference in pressure is proportional to the temperature difference. The pressure difference which compensates for a unit difference of temperature is called thermomolecular pressure difference and its value, in terms of phenomenological coefficients turns out to be

$$
\begin{equation*}
\left(\frac{\Delta p}{\Delta T}\right)_{J_{\mathrm{m}}=0}=-\frac{L_{21}}{L_{22}} \frac{1}{V_{\mathrm{m}} T} \tag{15.4}
\end{equation*}
$$

As we shall discuss in the following, this configuration is a stationary state configuration and it will constitute the starting point for a general discussion of the theory of stationary states.

## Heat of Transfer

The other relevant quantity which characterizes transport phenomena with this choice of fluxes and forces, is the so-called heat of transfer. Let us set the two containers to have the same constant temperature. The pressure difference will cause a flux of matter and, owing to interference phenomena, also a flux of energy. Since the force relative to $J_{\text {th }}$ is zero we can say that its non-zero value can be entirely ascribed to
the flow of matter in other words it is transported by the flux of matter. We call it heat of transfer and it shall be denoted by the symbol $\tilde{Q}$, the value of the flux $J_{\text {th }}$ transported by the unit flux of matter $J_{\mathrm{m}}$ when $\Delta T=0$.

From linear relations written in Eqs. (15.2) and (15.3) we obtain

$$
\begin{equation*}
\tilde{Q}=\left(\frac{J_{\mathrm{th}}}{J_{\mathrm{m}}}\right)_{\Delta T=0}=\frac{L_{12}}{L_{22}} . \tag{15.5}
\end{equation*}
$$

From the Onsager reciprocity relations $L_{21}=L_{12}$ we obtain the general relation

$$
\begin{equation*}
\left(\frac{\Delta p}{\Delta T}\right)_{J_{\mathrm{m}}=0}=-\frac{\tilde{Q}}{V_{\mathrm{m}} T} \tag{15.6}
\end{equation*}
$$

The linear relations written in Eqs. (15.2) and (15.3) show very clearly how interference between different irreversible phenomena works.

The pressure difference, which we consider the force responsible for the flow of matter, also affects the value of the energy flow whose associated force is related to the temperature difference and the same can be said for the influence of the temperature difference on the flow of matter. The fact that the two processes mutually interfere is certainly qualitatively predictable having in mind the atomic-molecular model of matter but in order to have a quantitative estimate we must go to a specific modeling as we will see in the next section. In that occasion, we shall appeal to a specific statistics and to a specific modeling of the septum that allows the passage of matter from one container to the other.

The result given in Eq. (15.6) is of general validity because it does not depend on the adopted assumptions except for the linearity between fluxes and forces.

It is useful to obtain Eq. (15.6) also in the particular case of perfect gases using classical Maxwellian statistical mechanics together with the hypothesis of molecular flow.

### 15.1.2 Knudsen Gases

Consider the same situation discussed in the previous subsection but suppose, now, that in both tanks is present an ideal gas. Suppose, for the moment, that we are dealing with a monoatomic gas but, as we shall see in the end, this assumption will easily be abandoned.

The two tanks (for example, two cylinders that communicate through a tube of small cross section) the gas will be maintained at a temperature and pressure, respectively, $T^{\mathrm{I}}, T^{\mathrm{II}}, p^{\mathrm{I}}, p^{\mathrm{II}}$ and in each part we assume the gas to obey the MaxwellBoltzmann statistics. Let us denote by $F(\mathbf{v})$ the velocity distribution function which is defined by the relation

$$
\begin{equation*}
\mathrm{d} N=F(\mathbf{v}) \mathrm{d} \mathbf{v} \tag{15.7}
\end{equation*}
$$

where $\mathrm{d} N$ represents the number of particles per unit volume with velocity within the infinitesimal interval $(\mathbf{v}, \mathbf{v}+\mathrm{d} \mathbf{v})$. As is well known, the distribution function is proportional to

$$
\begin{equation*}
F(\mathbf{v})=\Gamma \exp \left(-\frac{\varepsilon}{k_{B} T}\right) \tag{15.8}
\end{equation*}
$$

$\varepsilon$ being the energy of a single particle which, in our case, for a monoatomic molecule, is

$$
\begin{equation*}
\varepsilon=\frac{1}{2} m\left(v_{x}^{2}+v_{y}^{2}+v_{z}^{2}\right) \tag{15.9}
\end{equation*}
$$

and the normalization constant $\Gamma$ will be determined by the requirement that the integral of Eq. (15.7) over the entire set of allowed velocities (in our case over the interval $(-\infty,+\infty)$ for each component of the velocity) gives the following result:

$$
\begin{equation*}
\Gamma \int_{-\infty}^{+\infty} \int_{-\infty} \exp \left(-\frac{\varepsilon}{k_{B} T}\right) \mathrm{d} v_{x} \mathrm{~d} v_{y} \mathrm{~d} v_{z}=\frac{n}{V} N_{\mathrm{A}} \tag{15.10}
\end{equation*}
$$

where $N_{\mathrm{A}}=6.022 \times 10^{23}$ is the Avogadro's number, $n$ the total number of moles contained in the container at a given instant and $V$ is the volume.

Let us calculate separately the integral in Eq. (15.10). It can be written as a product of three independent integrals in the form

$$
\begin{align*}
& \iiint_{-\infty}^{+\infty} \exp \left(-\frac{\varepsilon}{k_{B} T}\right) \mathrm{d} v_{x} \mathrm{~d} v_{y} \mathrm{~d} v_{z}= \\
& =\int_{-\infty}^{+\infty} \exp \left(-\frac{m v_{x}^{2}}{2 k_{B} T}\right) \mathrm{d} v_{x} \int_{-\infty}^{+\infty} \exp \left(-\frac{m v_{y}^{2}}{2 k_{B} T}\right) \mathrm{d} v_{y} \int_{-\infty}^{+\infty} \exp \left(-\frac{m v_{z}^{2}}{2 k_{B} T}\right) \mathrm{d} v_{z} \tag{15.11}
\end{align*}
$$

If we put

$$
\begin{equation*}
\zeta=\frac{m}{2 k_{B} T} \tag{15.12}
\end{equation*}
$$

it is easy to show that

$$
\begin{equation*}
\int_{-\infty}^{+\infty} \exp \left(-\zeta x^{2}\right) \mathrm{d} x=\left(\frac{\pi}{\zeta}\right)^{\frac{1}{2}} \tag{15.13}
\end{equation*}
$$

and condition of normalization Eq. (15.10) leads to

$$
\begin{equation*}
\Gamma=\left(\frac{\zeta}{\pi}\right)^{\frac{3}{2}} \frac{n}{V} N_{\mathrm{A}} \tag{15.14}
\end{equation*}
$$

$$
\begin{equation*}
F(\mathbf{v})=\left(\frac{\zeta}{\pi}\right)^{\frac{3}{2}} \frac{n}{V} N_{\mathrm{A}} \exp \left(-\frac{v}{k_{B} T} .\right) \tag{15.15}
\end{equation*}
$$

Now we can proceed to calculate the flux of matter and then that of energy.
Suppose that the communication between the two containers occurs via a small tube of constant cross-sectional area $\Sigma$ with $\sqrt{\Sigma} \ll \lambda$ where $\lambda$ is the mean free path of a molecule in the gas.

Furthermore, we must assume that in the transfer of a molecule from one container to the other every molecule does not undergo collisions with other molecules in transit as well, with significant probability. Moreover, the collisions with the boundaries of the pipe connecting the two tanks are supposed to be elastic. The reason for this assumption will be made clear when we shall calculate the energy transferred.

The whole of these conditions produces a transfer mode of the gas that is called molecular flow. This condition is necessary in order to be able to consider that if a molecule enters the opening that allows communication between the two tanks, with a certain velocity, it can be considered acquired on the other container and with the same kinetic energy.

## Flux of Matter

Consider the tank I and let's calculate the number of molecules with velocity in the interval $(\mathbf{v}, \mathbf{v}+\mathrm{d} \mathbf{v})$ impinging the surface of area $\Sigma$ per second, as shown in Fig. 15.1. Let us take as reference system a Cartesian tern with the $x$ axis normal to $\Sigma$ and going from vessel I to vessel II, we consider a cylindroid with base $\Sigma$, height $v_{x}$ and parallel to the direction of $\mathbf{v}$. The volume of this cylindroid is $\left(\Sigma v_{x}\right)$ and the molecules with velocity in the given interval which are contained in this cylindroid will be the only ones which enter the pipe in one second. Their number is

$$
\begin{equation*}
\mathrm{d} N=F(\mathbf{v}) \Sigma v_{x} \mathrm{~d} v_{x} \mathrm{~d} v_{y} \mathrm{~d} v_{z} \tag{15.16}
\end{equation*}
$$

Let us indicate with $J^{+}$the flux of matter passing from I to II defined as the number of moles which leave tank I and pass to tank II in one second.

Since we assume that all the molecules impinging the surface $\Sigma$ in one second may be considered transferred to the other tank in the same time interval, the flux $J^{+}$may be obtained by integration of Eq. (15.16) over all the possible values of the molecular velocity allowing it to enter the area $\Sigma$, i.e., with positive $v_{x}$ component. The domains of integration will be

After dividing Eq. (15.15) by the Avogadro's number $N_{\mathrm{A}}$ we obtain

Fig. 15.1 $\Sigma$ is the area of the opening between two vessels. The dashed lines depict a cylindroid with volume ( $\Sigma v_{x}$ ). Among the molecules with velocity whithin $(\mathbf{v}, \mathbf{v}+\mathrm{d} \mathbf{v})$ the only ones that will enter the aperture in one second are those inside the cylindroid


$$
\begin{equation*}
J^{+}=\left(\frac{\zeta}{\pi}\right)^{\frac{3}{2}} \frac{n}{V} \Sigma \int_{-\infty}^{+\infty} \exp \left(-\zeta v_{y}^{2}\right) \mathrm{d} v_{y} \int_{-\infty}^{+\infty} \exp \left(-\zeta v_{z}^{2}\right) \mathrm{d} v_{z} \int_{0}^{+\infty} v_{x} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x} \tag{15.18}
\end{equation*}
$$

As far as the first and the second integrals are concerned, we obtain the same result as given in Eq. (15.13), while for the third integral, the one over the variable $v_{x}$, the result is quite different:

$$
\begin{align*}
\int_{0}^{+\infty} v_{x} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x} & =\frac{1}{2 \zeta} \int_{0}^{+\infty} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d}\left(\zeta v_{x}^{2}\right)  \tag{15.19}\\
& =\frac{1}{2 \zeta} \tag{15.20}
\end{align*}
$$

Summarizing the calculation for $J^{+}$and making use of the equation of state for the ideal gas in the tank I, we get

$$
\begin{align*}
J^{+} & =\left(\frac{\zeta^{\mathrm{I}}}{\pi}\right)^{\frac{1}{2}} \frac{n^{\mathrm{I}}}{V^{\mathrm{I}}} \Sigma \frac{1}{2 \zeta^{\mathrm{I}}}  \tag{15.21}\\
J^{+} & =\frac{1}{R}\left(\frac{k_{B}}{2 \pi m}\right)^{\frac{1}{2}} \Sigma \frac{p^{\mathrm{I}}}{\sqrt{T^{\mathrm{I}}}} \tag{15.22}
\end{align*}
$$

In a similar way, and recalling that the tube is cylindrical so that the area of the inlet section will be $\Sigma$ on both sides, we obtain for the flow of matter in the opposite direction (and which we will obviously indicate with $J^{-}$):

$$
\begin{equation*}
J^{-}=\frac{1}{R}\left(\frac{k_{B}}{2 \pi m}\right)^{\frac{1}{2}} \Sigma \frac{p^{\mathrm{II}}}{\sqrt{T^{\mathrm{II}}}} . \tag{15.23}
\end{equation*}
$$

The flux of matter $J_{\mathrm{m}}$, defined in the thermodynamical treatment in Eq. (15.1) (which in turn derives from the definition in Eq. (14.112) for the case of one single component), represents the time variation of the total amount of matter contained in vessel I and this depends on the fluxes $J^{+}$and $J^{-}$just calculated according to the obvious relation:

$$
\begin{equation*}
J_{\mathrm{m}}=J^{+}-J^{-}, \tag{15.24}
\end{equation*}
$$

and then it is given by

$$
\begin{equation*}
J_{\mathrm{m}}=\frac{1}{R}\left(\frac{k_{B}}{2 \pi m}\right)^{\frac{1}{2}} \Sigma\left(\frac{p^{\mathrm{I}}}{\sqrt{T^{\mathrm{I}}}}-\frac{p^{\mathrm{II}}}{\sqrt{T^{\mathrm{II}}}}\right) . \tag{15.25}
\end{equation*}
$$

## Thermomolecular Pressure Difference in a Knudsen Gas

From Eq. (15.25) we have the value of the flow of matter in a perfect gas in the conditions considered before. In particular we can obtain the relationship between the difference of pressure and the temperature difference in the case of flow of matter being zero. We find

$$
\begin{align*}
& J_{\mathrm{m}}=0  \tag{15.26}\\
& \frac{p^{\mathrm{II}}}{p^{\mathrm{I}}}=\sqrt{\frac{T^{\mathrm{II}}}{T^{\mathrm{I}}}} \tag{15.27}
\end{align*}
$$

and for small pressure and temperature differences we obtain

$$
\begin{equation*}
\left(\frac{\Delta p}{\Delta T}\right)_{J_{\mathrm{m}}=0} \simeq \frac{1}{2} \frac{p}{T} \tag{15.28}
\end{equation*}
$$

where we made use of the linear term approximation in the Taylor expansion of a small number $\delta$ :

$$
\begin{equation*}
\sqrt{1+\delta} \simeq 1+\frac{1}{2} \delta \tag{15.29}
\end{equation*}
$$

## Average Energy Transported in a Molecular Flux

In order to calculate the energy carried by the flow of matter we must proceed in the following way: when a molecule, belonging to the vessel I enters the opening of area $\Sigma$, the energy content of this vessel will decrease by the amount $\delta U$ equal to the energy possessed by the same molecule and the energy contained in the vessel

II will increase by the same amount (given the hypothesis on the molecular flow). Of course, for each molecule passing from vessel II to vessel I the same argument will apply but it will represent the reverse energy flow. The total flow of energy, the macroscopic flow, will be the difference between these two molecular flows.

Initially, we suppose that the energy possessed and hence transferred by each molecule is $\frac{1}{2} m\left(v_{x}^{2}+v_{y}^{2}+v_{z}^{2}\right)$ (monoatomic case). If we consider, once again, the molecules with velocity within the small interval $(\mathbf{v}, \mathbf{v}+\mathrm{d} \mathbf{v})$ they will transfer to vessel II, in unit time, the infinitesimal amount of energy:

$$
\begin{equation*}
\mathrm{d} J_{U}^{+}=\frac{1}{2} m\left(v_{x}^{2}+v_{y}^{2}+v_{z}^{2}\right) F(\mathbf{v}) \Sigma v_{x} \mathrm{~d} v_{x} \mathrm{~d} v_{y} \mathrm{~d} v_{z} \tag{15.30}
\end{equation*}
$$

and, after integrating over the three components of the velocity (with limits of integration given by Eq. (15.17)) we shall obtain the partial energy flux toward vessel II. Then, after changing index I into II we shall obtain the reverse partial flux. As before the macroscopic energy flux shall be given by the difference of the two. We need to compute the sum of three integrals each of them representing the contribution to the flow of energy by each of the three degrees of freedom. ${ }^{1}$

$$
\begin{equation*}
\frac{1}{2} m v_{x}^{2}, \quad \frac{1}{2} m v_{y}^{2}, \quad \frac{1}{2} m v_{z}^{2} \tag{15.31}
\end{equation*}
$$

The three integrals, coming from Eq. (15.30) are

$$
\begin{align*}
& \frac{1}{2} m\left(\frac{\zeta}{\pi}\right)^{\frac{3}{2}} \frac{n}{V} N_{\mathrm{A}} \Sigma \int_{0}^{+\infty} v_{x}^{3} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x} \int_{-\infty}^{+\infty} \exp \left(-\zeta v_{y}^{2}\right) \mathrm{d} v_{y} \int_{-\infty}^{+\infty} \exp \left(-\zeta v_{z}^{2}\right) \mathrm{d} v_{z} \\
& \frac{1}{2} m\left(\frac{\zeta}{\pi}\right)^{\frac{3}{2}} \frac{n}{V} N_{\mathrm{A}} \Sigma \int_{0}^{+\infty} v_{x} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x} \int_{-\infty}^{+\infty} v_{y}^{2} \exp \left(-\zeta v_{y}^{2}\right) \mathrm{d} v_{y} \int_{-\infty}^{+\infty} \exp \left(-\zeta v_{z}^{2}\right) \mathrm{d} v_{z}  \tag{15.33}\\
& \frac{1}{2} m\left(\frac{\zeta}{\pi}\right)^{\frac{3}{2}} \frac{n}{V} N_{\mathrm{A}} \Sigma \int_{0}^{+\infty} v_{x} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x} \int_{-\infty}^{+\infty} \exp \left(-\zeta v_{y}^{2}\right) \mathrm{d} v_{y} \int_{-\infty}^{+\infty} v_{z}^{2} \exp \left(-\zeta v_{z}^{2}\right) \mathrm{d} v_{z} \tag{15.34}
\end{align*}
$$

they have to be calculated separately then sum the results. Some integrals appearing in Eqs. (15.32)-(15.34) have already been calculated before while some other appear for the first time. Let us now calculate them and we start from the second integral Eq. (15.33):

[^50]\[

$$
\begin{align*}
\int_{-\infty}^{+\infty} v_{y}^{2} \exp \left(-\zeta v_{y}^{2}\right) \mathrm{d} v_{y} & =-\int_{-\infty}^{+\infty} \frac{\mathrm{d}}{\mathrm{~d} \zeta}\left[\exp \left(-\zeta v_{y}^{2}\right)\right] \mathrm{d} v_{y}  \tag{15.35}\\
& =-\frac{\mathrm{d}}{\mathrm{~d} \zeta} \int_{-\infty}^{+\infty} \exp \left(-\zeta v_{y}^{2}\right) \mathrm{d} v_{y} \tag{15.36}
\end{align*}
$$
\]

and then we obtain

$$
\begin{equation*}
\int_{-\infty}^{+\infty} v_{y}^{2} \exp \left(-\zeta v_{y}^{2}\right) \mathrm{d} v_{y}=\left(\frac{\pi}{\zeta}\right)^{\frac{1}{2}} \frac{1}{2 \zeta} \tag{15.37}
\end{equation*}
$$

The same result for the third term in Eq. (15.34) for the $v_{z}$ component. With regard to the first term in Eq. (15.32) we have:

$$
\begin{align*}
\int_{0}^{+\infty} v_{x}^{3} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x} & =\frac{1}{2} \int_{0}^{+\infty} v_{x}^{2} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x}^{2}  \tag{15.38}\\
& =\frac{1}{2} \int_{0}^{+\infty} \eta \exp (-\zeta \eta) d \eta  \tag{15.39}\\
& =-\frac{1}{2} \frac{\mathrm{~d}}{\mathrm{~d} \zeta} \int_{0}^{+\infty} \exp (-\zeta \eta) d \eta \tag{15.40}
\end{align*}
$$

and finally we obtain

$$
\begin{equation*}
\int_{0}^{+\infty} v_{x}^{3} \exp \left(-\zeta v_{x}^{2}\right) \mathrm{d} v_{x}=\frac{1}{2 \zeta^{2}} \tag{15.41}
\end{equation*}
$$

Remembering that (see Eq. (15.13))

$$
\begin{equation*}
\int_{-\infty}^{+\infty} \exp \left(-\zeta v_{z}^{2}\right) \mathrm{d} v_{z}=\left(\frac{\pi}{\zeta}\right)^{\frac{1}{2}} \tag{15.42}
\end{equation*}
$$

we may write the partial energy fluxes I $\rightarrow$ II for each of the three degrees of freedom. If we denote them by $J_{U_{x}}^{+}, J_{U_{y}}^{+}$and $J_{U_{z}}^{+}$we obtain

$$
\begin{equation*}
J_{U_{x}}^{+}=\frac{1}{2} m \frac{n}{V} N_{\mathrm{A}} \Sigma\left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} \frac{1}{2 \zeta^{2}} \tag{15.43}
\end{equation*}
$$

$$
\begin{align*}
& J_{U_{y}}^{+}=\frac{1}{2} m \frac{n}{V} N_{\mathrm{A}} \Sigma\left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} \frac{1}{4 \zeta^{2}}, \text { and }  \tag{15.44}\\
& J_{U_{z}}^{+}=\frac{1}{2} m \frac{n}{V} N_{\mathrm{A}} \Sigma\left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} \frac{1}{4 \zeta^{2}} . \tag{15.45}
\end{align*}
$$

After summing up the contributions relative to the three degrees of freedom we write the expression of the partial (forward) energy flux I $\rightarrow$ II in the form

$$
\begin{align*}
J_{U}^{+} & =\frac{1}{2} m \frac{n}{V} N_{\mathrm{A}} \Sigma\left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}}\left(\frac{1}{2 \zeta^{2}}+\frac{1}{4 \zeta^{2}}+\frac{1}{4 \zeta^{2}}\right)=  \tag{15.46}\\
& =\frac{1}{2} m \frac{n}{V} N_{\mathrm{A}} \Sigma\left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} \frac{1}{\zeta^{2}} \tag{15.47}
\end{align*}
$$

From Eqs. (15.43)-(15.45) we see that the contribution to the energy transfer associated to the $v_{x}$ component of the kinetic energy, is twice that relative to the other two components $v_{y}$ and $v_{z}$.Then it is interesting to calculate the mean value of the energy by the positive ( $J^{+}$) flux of molecules. To do this we will have to consider the three partial energy flows Eqs. (15.43)-(15.45), and divide each one by the number of molecules passing in one second. The latter is easily obtained by multiplying the partial flow given by Eq. (15.21) by the Avogadro's number $N_{\mathrm{A}}$. Let us drop, for the moment, the index that refers to the specific vessel and let us denote the three mean values of the energy along the $x, y$ and $z$ directions with the $\langle\varepsilon\rangle$ symbol. We get:

$$
\begin{align*}
\left\langle\varepsilon_{x}\right\rangle & =k_{B} T  \tag{15.48}\\
\left\langle\varepsilon_{y}\right\rangle & =\frac{1}{2} k_{B} T  \tag{15.49}\\
\left\langle\varepsilon_{z}\right\rangle & =\frac{1}{2} k_{B} T \tag{15.50}
\end{align*}
$$

and, for the mean value of the total transported energy we have

$$
\begin{equation*}
\langle\varepsilon\rangle=2 k_{B} T \tag{15.51}
\end{equation*}
$$

while the equipartition value $\langle\varepsilon\rangle_{\text {eqp }}$ of the energy in the gas, is

$$
\begin{equation*}
\langle\varepsilon\rangle_{\mathrm{eqp}}=\frac{3}{2} k_{B} T \tag{15.52}
\end{equation*}
$$

It is worth noticing that the average energy delivered by the flux of matter and associated to the $y$ and $z$ components of the velocity, is equal to their equipartition value while the average value of energy transported and associated to the $x$ component is twice the equipartition value.

That the latter term should be larger than the average values of the energy associated with the $y$ and $z$ components it is easy to envisage. Indeed the probability that a molecule having a particular velocity $\mathbf{v}$ passes through the hole per unit time, is not simply proportional to the number density of such molecules in the gas (e.g., see Eq. (15.7)), but also it depends on the value of the x component of the velocity. This dependance is such that the molecules having larger value of $v_{x}$ are favored with respect to those having low $v_{x}$. One might say that the hole acts as a speed selector "preferring" the molecules with larger $v_{x}$ while the probability of crossing the hole per unit time is independent of the values of $y$ or $z$ component of the velocity.

Summarizing, we can say that the probability that a molecule passes through the hole in the unit time is not dependent on the value of its energy in the $y$ or $z$ components while depends on the value of its energy component in the $x$ direction and this probability is larger for those who have larger value of $\varepsilon_{x}$. From this it follows that the average value of energy transported in the $y$ and $z$ components depend only on the concentration of the molecules and then $\left\langle\varepsilon_{y}\right\rangle$ and $\left\langle\varepsilon_{z}\right\rangle$ will be equal to the equipartition value, while the average value of energy transported in the $x$ component is larger.

Of course, we have to repeat the same calculations also for molecules that migrate from container II to container I in order to find the macroscopic flow of energy. Notice that each of the two partial energy flows would cause a decrease in the temperature of the respective vessel because, in this process, each one is expelling its most energetic particles. A consequence of this is that if the two vessels are maintained at the same temperature, the one that loses matter will absorb heat from the thermostat, and, vice versa, the reservoir which gradually fills must be cooled.

## Energy of Transfer and Heat of Transfer in a Knudsen Gas

Let us now calculate, in the context of this modeling, the macroscopic flux of energy $J_{U}$. We refer to Eq. (15.47), and we express the energy flux $J_{U}^{+}$after substituting the values for pressure and temperature relative to container I. In order to obtain the reverse flux $J_{U}^{-}$of the energy transported per second by the molecules moving from II to I we have just to replace, in the same relation, the values for pressure and temperature relative to container II.

The macroscopic flow of energy; as that defined in Eq. (14.60), will be

$$
\begin{equation*}
J_{U}=J_{U}^{+}-J_{U}^{-} \tag{15.53}
\end{equation*}
$$

We will not take care of the general structure of this flow of energy but we shall only consider its expression in the particular case in which the two containers are maintained at the same constant temperature $(\Delta T=0)$ in order to find, in this particular case, the relationship between the thermomolecular pressure difference and the heat of transfer Eq. (15.6). With this limitation, we can write the expression for the flow of energy:

$$
\begin{equation*}
J_{U}(\Delta T=0)=\frac{1}{2} m \frac{N_{\mathrm{A}}}{R T} \Sigma\left(\frac{\zeta}{\pi}\right)^{\frac{1}{2}} \frac{1}{\zeta^{2}}\left(p^{\mathrm{I}}-p^{\mathrm{II}}\right) \tag{15.54}
\end{equation*}
$$

In the same condition $\Delta T=0$ let's write the expression for the flow of matter:

$$
\begin{equation*}
J_{\mathrm{m}}(\Delta T=0)=\frac{1}{R}\left(\frac{k_{B}}{2 \pi m}\right)^{\frac{1}{2}} \Sigma \frac{1}{\sqrt{T}}\left(p^{\mathrm{I}}-p^{\mathrm{II}}\right) . \tag{15.55}
\end{equation*}
$$

We can now calculate the energy transported by a unit flux of matter (one mole per second). Let us call it energy of transfer and denote this quantity by the symbol $\tilde{U}$ :

$$
\begin{equation*}
\tilde{U}=\frac{J_{U}(\Delta T=0)}{J_{\mathrm{m}}(\Delta T=0)}=2 R T \tag{15.56}
\end{equation*}
$$

In order to calculate the heat of transfer we must make the appropriate change of flows, already examined, which led to Eq. (14.111) (for simplicity the sum over the index $\gamma$ extends to one component only).

From the definition Eq. (15.5) of heat of transfer we easily obtain its relation to the energy of transfer:

$$
\begin{equation*}
\tilde{Q}=\tilde{U}-H_{m} \tag{15.57}
\end{equation*}
$$

where $H_{m}$ is the molar enthalpy. The latter, by definition, is

$$
\begin{equation*}
H_{m}=U_{m}+p V_{\mathrm{m}}, \tag{15.58}
\end{equation*}
$$

where $U_{m}$ and $V_{\mathrm{m}}$ are, respectively, the molar energy and volume. Within the ideal gas approximation we shall write, for monoatomic molecules

$$
\begin{align*}
& U_{m}=\frac{3}{2} R T  \tag{15.59}\\
& p V_{\mathrm{m}}=R T \tag{15.60}
\end{align*}
$$

and from these relations:

$$
\begin{equation*}
\tilde{Q}=2 R T-\frac{5}{2} R T=-\frac{1}{2} R T \tag{15.61}
\end{equation*}
$$

and combining this result with the thermomolecular pressure difference given by Eq. (15.28) we get

$$
\begin{equation*}
\left(\frac{\Delta p}{\Delta T}\right)_{J_{\mathrm{m}}=0} \simeq-\frac{\tilde{Q}}{V_{\mathrm{m}} T} \tag{15.62}
\end{equation*}
$$

The detailed examination of this example (in the ideal gases approximation) clearly shows the power of thermodynamics.

As a final comment, we want to mention the general case of a polyatomic gas. In this case, the energy of a single molecule will be given by the summation of several terms discussed in Eq. (6.58):

$$
\begin{equation*}
\varepsilon=\frac{1}{2} m\left(v_{x}^{2}+v_{y}^{2}+v_{z}^{2}\right)+\varepsilon_{\mathrm{rot}}+\varepsilon_{\mathrm{vib}}+\cdots \tag{15.63}
\end{equation*}
$$

where $\mathbf{v}=\left(v_{x}, v_{y}, v_{z}\right)$ is the velocity of the center of mass of the molecule and the two terms $\varepsilon_{\text {rot }}$ and $\varepsilon_{\text {vib }}$ are the contributions to the energy of the molecule due to the rotational and to the vibrational degrees of freedom, respectively. As the selective effect of the hole only affects the contribution relative to the $\varepsilon_{x}$ component of the energy, all other terms will contribute to the energy transported by the flux of molecules, with their equipartition values. Then if we assume that all the degrees of freedom are harmonic, the energy of transfer will be

$$
\begin{equation*}
\tilde{U}=\frac{1}{2} R T+f \frac{1}{2} R T \tag{15.64}
\end{equation*}
$$

where $f$ is the number of degrees of freedom of the molecule. Likewise also the molar enthalpy becomes

$$
\begin{equation*}
H_{m}=f \frac{1}{2} R T+R T \tag{15.65}
\end{equation*}
$$

and then the value of the heat of transfer will remain unchanged.

### 15.1.3 Electrokinetic Effects

We return to the case examined in Sect. 14.5 and to the expression of entropy production:

$$
\begin{equation*}
\mathcal{P}=\sum_{\gamma} \frac{\tilde{\mathcal{A}}_{\gamma}}{T} \mathrm{v}_{\gamma} . \tag{15.66}
\end{equation*}
$$

Going back to Eqs. 14.75), (14.70) and (14.69), for the the definition of the rates $\mathrm{v}_{\gamma}$, we obtain

$$
\begin{equation*}
\mathcal{P}=-\frac{1}{T} \sum_{\gamma}\left(\psi^{\mathrm{I}}-\psi^{\mathrm{II}}\right) z_{\gamma} \mathfrak{F} \frac{\mathrm{d} n_{\gamma}^{\mathrm{I}}}{\mathrm{~d} t}-\sum_{\gamma}\left(\mu_{\gamma}^{\mathrm{I}}-\mu_{\gamma}^{\mathrm{II}}\right) \frac{\mathrm{d} n_{\gamma}^{\mathrm{I}}}{\mathrm{~d} t} . \tag{15.67}
\end{equation*}
$$

Let us limit ourselves to the case in which the entire system, consisting (as described in Sect. 14.5) by two phases which communicate through a capillary or a porous septum, is maintained at a uniform and constant temperature.

There remain then the two "free parameters" that we can vary independently of each other, namely the potential difference and the pressure difference. The former
determines the value of the generalized force that we associate with the observed electric current while the pressure difference governs the value of the force associated to the flow of matter. Our purpose is to study the interference between these two processes but in order to do this we need to define the flows (which give the name to the processes) properly and their related forces. It is then necessary to start with the production of entropy Eq. (15.67). Let us agree to choose as positive the fluxes from system I to system II.

One flux is precisely the electric current intensity that we shall denote by $I$ and is written in the form

$$
\begin{equation*}
I=-\sum_{\gamma} z_{\gamma} \mathfrak{F} \frac{\mathrm{d} n_{\gamma}^{\mathrm{I}}}{\mathrm{~d} t}, \tag{15.68}
\end{equation*}
$$

and hence the associated generalized force will be

$$
\begin{equation*}
X_{I}=-\frac{\Delta \psi}{T} . \tag{15.69}
\end{equation*}
$$

where the symbol $\Delta$ indicates the variation of any quantity as its value in system II minus its value in system I. In a similar way we define the "flux of matter" that we shall indicate with the symbol $J_{\mathrm{m}}$. In the second term of Eq. (15.67) we write the variation of the chemical potentials up to the linear term in $\Delta p$ (the two phases are at the same temperature):

$$
\begin{equation*}
\mu_{\gamma}^{\mathrm{II}} \simeq \mu_{\gamma}^{\mathrm{I}}+V_{m_{\gamma}} \Delta p . \tag{15.70}
\end{equation*}
$$

Then we choose as flux of matter the quantity:

$$
\begin{equation*}
J_{\mathrm{m}}=-\sum_{\gamma} V_{m_{\gamma}} \frac{\mathrm{d} n_{\gamma}^{\mathrm{I}}}{\mathrm{~d} t}, \tag{15.71}
\end{equation*}
$$

and as the corresponding force, the expression:

$$
\begin{equation*}
X_{\mathrm{m}}=-\frac{\Delta p}{T} . \tag{15.72}
\end{equation*}
$$

With these determinations, the entropy production becomes

$$
\begin{equation*}
\mathcal{P}=-I X_{I}-J_{\mathrm{m}} X_{\mathrm{m}}>0 . \tag{15.73}
\end{equation*}
$$

It should be noted, at this point, that the flow Eq. (15.71), that we somehow improperly called "flow of matter", should be more properly referred to as "flow of volume", in fact, it corresponds exactly to the decrease of volume of phase I per unit time (this shows that the two fluxes so defined are physically independent of each other). We now want to study how the two fluxes interfere, i.e., in which way the two forces, depending separately on the pressure difference and on the potential difference, combine to determine the overall effects. These results will be of general validity, that
is regardless the specific assumptions on the capillary or on the statistical mechanics which regulates the microscopic behavior.

The linear relations between fluxes and forces are

$$
\begin{align*}
& I=-L_{11} \frac{\Delta \psi}{T}-L_{12} \frac{\Delta p}{T}  \tag{15.74}\\
& J_{\mathrm{m}}=-L_{21} \frac{\Delta \psi}{T}-L_{22} \frac{\Delta p}{T} \tag{15.75}
\end{align*}
$$

Let us define some relevant coefficients that characterize the electrokinetic processes.
Two of these concern transport phenomena. More precisely, given one flux we measure the intensity of the other flux in the condition in which its own force is zero. In this sense, we speak of a flux "transported" by the former.

The other two effects which give a quantitative idea of the strength of the interference between different processes, concern the measure of the "mutual neutralization" between the two forces $\Delta p$ and $\Delta \psi$ in the following sense: given one of the two forces, there may exist an appropriate value of the other which brings to zero its own associated flux. In this sense, we say that the former force "neutralizes" the effect of the latter.

Starting with the first two effects we have two typical situations. The first effect called streaming current is defined by the measurement of the intensity of electrical current dragged by the flow of matter in the condition $\Delta \psi=0$ that is, in the condition in which the force related to the electrical current is zero. For this effect, given the linear relations written in Eqs. (15.74) and (15.75), we obtain

$$
\begin{equation*}
\left(\frac{I}{J_{\mathrm{m}}}\right)_{\Delta \psi=0}=\frac{L_{12}}{L_{22}} \tag{15.76}
\end{equation*}
$$

Symmetrically we define as "electro-osmotic coefficient" the measure of the flow of matter (volume) dragged by a unit electric current in the condition in which its force $\Delta p=0$.

$$
\begin{equation*}
\left(\frac{J_{\mathrm{m}}}{I}\right)_{\Delta p=0}=\frac{L_{21}}{L_{11}} \tag{15.77}
\end{equation*}
$$

As regards the other two effects, if we fix a certain pressure difference $\Delta p$ between the two phases, we shall observe, for different values of the potential difference, different values of the electric current. We define the streaming potential as the potential difference that must be established between the two phases, per unit of pressure difference, in order to turn the electric current to zero:

$$
\begin{equation*}
\left(\frac{\Delta \psi}{\Delta p}\right)_{I=0}=-\frac{L_{12}}{L_{11}} \tag{15.78}
\end{equation*}
$$

Finally we fix the value of the potential difference and determine for what value of the pressure difference the flow of matter will be zero. This value, per unit potential
difference, will be called electro-osmotic pressure:

$$
\begin{equation*}
\left(\frac{\Delta p}{\Delta \psi}\right)_{J_{\mathrm{m}}=0}=-\frac{L_{21}}{L_{22}} \tag{15.79}
\end{equation*}
$$

The Onsager reciprocity relation:

$$
\begin{equation*}
L_{12}=L_{21} \tag{15.80}
\end{equation*}
$$

allows us to determine, in all generality, the following two relationships between these effects:

$$
\begin{align*}
\left(\frac{\Delta p}{\Delta \psi}\right)_{J_{\mathrm{m}}=0} & =-\left(\frac{I}{J_{\mathrm{m}}}\right)_{\Delta \psi=0}  \tag{15.81}\\
\left(\frac{\Delta \psi}{\Delta p}\right)_{I=0} & =-\left(\frac{J_{\mathrm{m}}}{I}\right)_{\Delta p=0} \tag{15.82}
\end{align*}
$$

This relationship is known as Saxen relation and was first obtained by Saxen with mechanical-statistical calculations in a way similar as to the one we have seen in the example of the thermomechanical effects and also in this case it is necessary to make restrictive assumptions about the nature of the porous separator. Now we proved that these relationships are quite general. It's true that thermodynamics does not allow us to find the values of these coefficients (and we have to get back to statistical models), but it allows us to "...find connections between effects that, at first glance, seem to be completely independent..." [22].

### 15.2 Stationary States

In this section we will study, briefly, the properties of the stationary states: their characterization and, within certain limits, their stability properties.

We say that a physical system is in a stationary state when the values of all its state parameters are constant in time.

The concept of state of equilibrium was introduced, at the beginning, from an empirical point of view as the thermodynamic configuration, constant in time, that each isolated system spontaneously reaches. The state of equilibrium, then, is an example of a stationary state but, as we see in ordinary life, the most frequent situation is that of thermodynamic nonequilibrium configurations that are constant in time.

A trivial example is that of a resistor (old electric heater) to which a constant potential difference is applied. Initially it dilates, its color changes and its temperature increases. After a while, it is in a stationary state: its color does not change anymore as well as its temperature, its volume is maintained constant, the potential is constant point by point and so on. It is in a stationary state but it is not in a state of equilibrium.

Also, all living organisms appear, in a short time scale, in a stationary state but are certainly not in an equilibrium state.

The most evident property of nonequilibrium stationary states is that they cannot exist in isolated systems but they can be maintained only if the system is in constant interaction with the external world.

In fact, like all other state variables, also entropy must have a constant value, then its variation in a time interval $\mathrm{d} t$ must be $\mathrm{d} S=0$. Therefore

$$
\begin{equation*}
\mathrm{d} S=\hat{d}_{\mathrm{i}} S+\hat{d}_{\mathrm{e}} S=0 \tag{15.83}
\end{equation*}
$$

If the thermodynamical configuration is a nonequilibrium configuration then it shall be $\hat{d}_{\mathrm{i}} S>0$ and hence

$$
\begin{equation*}
\hat{d}_{\mathrm{e}} S=-\hat{d}_{\mathrm{i}} S<0 \tag{15.84}
\end{equation*}
$$

that is, the system must absorb a negative amount of entropy or in other words, must eject outwards the entropy that it produces in the time interval $\mathrm{d} t$ because of its internal processes.

In isolated systems it would always be $\hat{d}_{\mathrm{e}} S=0$, and then, for stationarity, $\hat{d}_{\mathrm{i}} S=0$, and this is equivalent to say that the state is an equilibrium state. Therefore the difference between a stationary state of equilibrium and one of nonequilibrium, lies in having, in the former case a null value and in the latter case a positive value for the entropy production:

$$
\begin{equation*}
\mathcal{P}>0 \tag{15.85}
\end{equation*}
$$

One significant example of nonequilibrium stationary state has been examined in some detail when, dealing with the thermomechanical effects, we defined the thermomolecular pressure difference.

In that example, the two vessels can exchange matter between them through a capillary or a porous septum, and are kept at constant temperatures $T^{\mathrm{I}}$ and $T^{\mathrm{II}}$. With this constraint the stationary state is reached when the flow of matter is zero. The flow of energy can be non-zero because the requirement that the energy should be constant is satisfied thanks to the intervention of the thermostats which supply and take away, in the form of heat, the amount of energy that is transferred, per unit time, between the two vessels. ${ }^{2}$ As we have seen this occurs when the pressure difference is adjusted to the value Eq. (15.6). Let us write the expression of the entropy production in the case, for simplicity, in which only one component is present.

$$
\begin{equation*}
\mathcal{P}=J_{\mathrm{th}} X_{\mathrm{th}}+J_{\mathrm{m}} X_{\mathrm{m}} . \tag{15.86}
\end{equation*}
$$

If we limit ourselves to the case of linear relationships between fluxes and forces and recall the Onsager symmetry relations, the entropy production is expressed by a bilinear positive-semidefinite quadratic form

[^51]\[

$$
\begin{equation*}
\mathcal{P}=L_{11} X_{\mathrm{th}}^{2}+2 L_{12} X_{\mathrm{th}} X_{\mathrm{m}}+L_{22} X_{\mathrm{m}}^{2} \geq 0 \tag{15.87}
\end{equation*}
$$

\]

Suppose that process 1 is the transport of energy and the process 2 the transport of matter. We set the value of the two temperatures and this means having fixed the value of the $X_{\mathrm{th}}$, then the entropy production will be a function of the $X_{\mathrm{m}}$ variable only.

It is easy to recognize that such a function (second-order polynomial) has a minimum in correspondence to the steady-state configuration. In fact if we look for the extrema of this polynomial, we get

$$
\begin{equation*}
\frac{\partial \mathcal{P}}{\partial X_{\mathrm{m}}}=2\left(L_{12} X_{\mathrm{th}}+L_{22} X_{\mathrm{m}}\right)=0 \tag{15.88}
\end{equation*}
$$

which is equivalent to

$$
\begin{equation*}
J_{\mathrm{m}}=0 \tag{15.89}
\end{equation*}
$$

which is the stationary state condition. Moreover

$$
\begin{equation*}
\frac{\partial^{2} \mathcal{P}}{\partial^{2} X_{\mathrm{m}}}=L_{22}>0 \tag{15.90}
\end{equation*}
$$

and this establishes that the extremum point is a point of minimum.
The conclusion, if it could be generalized, would be very important: fixed the value of one force (in our case $X_{\text {th }}$ ), the stationary state is realized when the other flux (in our case $J_{\mathrm{m}}$ ) is zero, and this is equivalent to the condition that the entropy production has a minimum in the steady-state configuration.

### 15.2.1 Configurations of Minimal Entropy Production

The example discussed above introduces us to an important general theorem due to de Groot and Mazur [23] concerning stationary states. The idea to characterize the stationary states as thermodynamic configurations corresponding to a minimum value for the entropy production consistent with externally fixed constraints, which was suggested by the study of thermomechanical effects is confirmed, ${ }^{3}$ in the general case for stationary nonequilibrium configurations.

Consider a discontinuous system composed by two homogeneous subsystems (phases) I and II. Suppose that each phase has $n$ degrees of freedom ${ }^{4}$ and denote by $\mathcal{E}_{\rho}^{\mathrm{I}}$ and $\mathcal{E}_{\rho}^{\mathrm{II}}$ with $\rho$ varying in the interval $1 \leq \rho \leq n$, the values, in some time

[^52]instant $t$, of the $n$ extensive quantities we chose to define the states in phases I and II, respectively.

The entropy production will be written, as always, in the form

$$
\begin{equation*}
\mathcal{P}=\sum_{\rho=1}^{n} J_{\rho} X_{\rho} \tag{15.91}
\end{equation*}
$$

For every extensive quantity, in each phase, we can express its variation per unit of time as

$$
\begin{equation*}
\frac{\mathrm{d} \mathcal{E}_{\rho}^{\mathrm{I}, \mathrm{II}}}{\mathrm{~d} t}=\frac{\hat{d}_{\mathrm{e}} \mathcal{E}_{\rho}^{\mathrm{I}, \mathrm{II}}}{\mathrm{~d} t}+\frac{\hat{d}_{\mathrm{i}} \mathcal{E}_{\rho}^{\mathrm{I}, \mathrm{II}}}{\mathrm{~d} t} \tag{15.92}
\end{equation*}
$$

where $\hat{d}_{\mathrm{e}} / \mathrm{d} t$ and $\hat{d}_{\mathrm{i}} / \mathrm{d} t$ have, respectively, the meaning of variation per unit time due to the interaction with the external world (third-party systems) and due to the exchanges within the two phases overall system. ${ }^{5}$ In this perspective, the generalized flows are defined by ${ }^{6}$

$$
\begin{equation*}
J_{\rho}=-\frac{\hat{d}_{\mathrm{i}} \mathcal{E}_{\rho}^{\mathrm{I}}}{\mathrm{~d} t}=\frac{\hat{d}_{\mathrm{i}} \mathcal{E}_{\rho}^{\mathrm{II}}}{\mathrm{~d} t} \tag{15.93}
\end{equation*}
$$

To each of the $n$ fluxes $J \rho$ is associated the corresponding force $X_{\rho}$ which, as we have seen in all the previous examples, is given by the difference, between the two phases, of a suitable intensive quantity that we shall denote by $x_{\rho}$ :

$$
\begin{equation*}
X_{\rho}=-\left(x_{\rho}^{\mathrm{II}}-x_{\rho}^{\mathrm{I}}\right) . \tag{15.94}
\end{equation*}
$$

As we have seen previously, the values of the flows, at a certain instant, can be considered as functions of the values of the forces in that instant: $J_{\rho}=J_{\rho}\left(X_{1}, X_{2}, \ldots, X_{n}\right)$ and, at this point, we make two assumptions:

1. $k$ out of the $n$ forces (with $k<n$ ) are constrained, by external interaction, to maintain constant values (for instance, by keeping the temperatures of the two systems at constant values, we fix the value of $\Delta(1 / T))$. Suppose, for convenience, that this happens for $\rho$ between $1 \leq \rho \leq k$.
2. as far as the other $(n-k)$ degrees of freedom are concerned, we suppose that the overall system is closed with respect to these $\mathcal{E}_{\rho}$. This is equivalent to impose that for $(k+1) \leq \rho \leq n$ the following condition holds:

$$
\begin{equation*}
\left(\frac{\hat{d}_{\mathrm{e}} \mathcal{E}_{\rho}}{\mathrm{d} t}\right)=0 \quad \text { for } \quad(k+1) \leq \rho \leq n \tag{15.95}
\end{equation*}
$$

[^53]The theorem proves that if:

1. We may write linear relations between fluxes and forces;
2. The phenomenological coefficients are constant in time;
3. The Onsager reciprocity relations $L_{i j}=L_{j i}$ apply,
then, at the stationary state the amount of entropy production is at a relative minimum.
Suppose that the system has evolved into a steady state. This means

$$
\begin{equation*}
\frac{\mathrm{d} \mathcal{E}_{\rho}^{\mathrm{I}, \mathrm{II}}}{\mathrm{~d} t}=0 \tag{15.96}
\end{equation*}
$$

for every $\rho$. We then we have

$$
\begin{array}{ll}
J_{\rho}=\frac{\hat{d}_{\mathrm{e}} \mathcal{E}_{\rho}^{\mathrm{I}}}{\mathrm{~d} t}=-\frac{\hat{d}_{\mathrm{e}} \mathcal{E}_{\rho}^{\mathrm{II}}}{\mathrm{~d} t} & \text { for } 1 \leq \rho \leq k \\
J_{\rho}=0 & \text { for } \quad(k+1) \leq \rho \leq n \tag{15.98}
\end{array}
$$

In other words, the intensities of the fluxes associated with constrained forces are fully determined by the interaction of the overall system with the external world. ${ }^{7}$ On the other hand the fluxes associated with the free forces (i.e., the unconstrained forces) have to be zero because the overall system is closed with respect to the respective state variables $\mathcal{E}_{\rho} \operatorname{con}(k+1) \leq \rho \leq n$.

We write, now, the linear relations between fluxes and forces and express, consequently, the production of entropy as a bilinear form in the forces:

$$
\begin{align*}
& J_{\rho}=\sum_{\rho^{\prime}=1}^{n} L_{\rho \rho^{\prime}} X_{\rho^{\prime}} \quad \text { for } \quad 1 \leq \rho \leq n  \tag{15.99}\\
& \mathcal{P}=\sum_{\rho, \rho^{\prime}=1}^{n} L_{\rho \rho^{\prime}} X_{\rho} X_{\rho^{\prime}} . \tag{15.100}
\end{align*}
$$

If we calculate the first derivatives with respect to the free forces and we make use of the symmetry properties of the phenomenological coefficients, we obtain

$$
\begin{equation*}
\frac{\partial \mathcal{P}}{\partial X_{\rho}}=\sum_{\rho^{\prime}=1}^{n}\left(L_{\rho \rho^{\prime}}+L_{\rho^{\prime} \rho}\right) X_{\rho^{\prime}}=2 J_{\rho} \quad(k+1) \leq \rho \leq n \tag{15.101}
\end{equation*}
$$

If the system is in a stationary state the fluxes relative to the "free forces" must be zero, then we have

$$
\begin{equation*}
\frac{\partial \mathcal{P}}{\partial X_{\rho}}=0 \quad \text { for } \quad(k+1) \leq \rho \leq n \tag{15.102}
\end{equation*}
$$

[^54]So, the stationary state constitutes a configuration in which the entropy production exhibits an extremum. Since the bilinear form is positive semidefinite, at the configuration of stationary state the entropy production possesses a minimum value. It is, obviously, a conditioned minimum since we imposed $k$ constraints to the first $k$ forces to the function $\mathcal{P}$.

### 15.2.2 Determination of the Stationary State

In the $n$ linear relations given by Eq. (15.99) we have, for a general configuration, $n^{2}$ phenomenological coefficients out of which only $n(n+1) / 2$ are independent if the reciprocity relations hold.

If we start from a generic initial configuration in which the first $k$ forces are fixed at their constrained values and the remaining $(n-k)$ (with $(k+1) \leq \rho \leq n)$ free forces have arbitrary initial values (but small enough to ensure the linearization of fluxes), we will see that the values of unconstrained forces will evolve in time until a steady-state configuration is reached. ${ }^{8}$

If we could calculate the values of the unconstrained forces at the stationary state, we would completely determine the final, stationary state, because the set of the $n$ forces would be completely defined.

This is possible if we can assume that the values of the phenomenological coefficients remain constant during the evolution from the state initially prepared and the steady state that will be reached.

We have already seen that at the stationary state the $(n-k)$ fluxes relative to the unconstrained force have to be zero.

If we take into account the $(n-k)$ equations in Eq. (15.99) with $(k+1) \leq \rho \leq n$, and require that the fluxes be zero, we obtain a linear system of $(n-k)$ equations in the $(n-k)$ unknowns $X_{\rho}$ with $(k+1) \leq \rho \leq n$.

The solution of this system gives us the $(n-k)$ "free forces" as a function of the $k$ constrained forces $X_{\rho}$ with $1 \leq \rho \leq k$ and of all (in general) the coefficients $L_{\rho \rho^{\prime}}$.

Thus the stationary configuration is uniquely determined (but remember that this is true if all the assumptions about linear coefficients are verified).

### 15.2.3 Stability of Stationary States and the Principles of Le Chatelier and of Le Chatelier-Braun

Consider the situation examined in the previous subsections, i.e., that of a discontinuous system in a stationary state. As we have already proved this is a configuration of minimum entropy production consistent with the imposed constraints that is, in our case, the values of the first $k$ forces.

[^55]Let us denote with $J_{\rho}^{0}$ and $X_{\rho}^{0}$ the values of the fluxes and of the forces in this configuration.

As we have seen in Sect. 15.2.2 the remaining $(n-k)$ forces can be calculated while, as regards the fluxes, the first $k$ are determined by the interactions with the external world the remaining $(n-k)$ being null.

Suppose that, due to some internal fluctuation or to some perturbation produced either by some external noise or intentionally by the observer, a small change in the value of one of the non-constrained forces takes place.

Denote by $\delta X_{\eta}$ this small change in the value of the force $X_{\eta} \eta$ being a particular value in the interval $(k+1) \leq \eta \leq n$. The new set of forces will be

$$
\begin{align*}
& X_{\rho}=X_{\rho}^{0} \quad \text { for } \quad \rho \neq \eta  \tag{15.103}\\
& X_{\eta}=X_{\eta}^{0}+\delta X_{\eta} \tag{15.104}
\end{align*}
$$

Also the fluxes will suffer alterations and, in particular, for the flux $J_{\eta}$, the use of Eq. (15.99) will provide the value

$$
\begin{align*}
J_{\eta} & =J_{\eta}^{0}+L_{\eta \eta} \delta X_{\eta}  \tag{15.105}\\
J_{\eta} & =L_{\eta \eta} \delta X_{\eta} \tag{15.106}
\end{align*}
$$

Since we know that $L_{\eta \eta}>0$, Eq. (15.106) shows that value of the perturbation of the force and the flux that this perturbation generates have always the same sign:

$$
\begin{equation*}
J_{\eta} \delta X_{\eta}>0 \tag{15.107}
\end{equation*}
$$

This means that the flux which is activated and which is directly connected to the perturbation, always works in the direction to decrease the intensity of the disturbance. For instance, if the perturbation results in a temperature difference, the heat flow that is triggered is in the direction of decreasing the temperature difference itself as we can se if we remember that the force is equal to

$$
\begin{equation*}
\Delta\left(\frac{1}{T}\right) \simeq-\frac{\Delta T}{T^{2}} \tag{15.108}
\end{equation*}
$$

Similarly, the fluxes of matter are in the direction of decreasing the concentration gradients of chemical potential.

The expression in 15.107 provides an important indication: it seems that stationary states are stable configurations as the deviations that may arise in the value of one free force seem to be reabsorbed by internal processes.

## Le Chatelier Principle (1884)

The Le Chatelier's principle has been formulated in relation to equilibrium states. It states that in a system in a state of equilibrium, if for any reason an inhomogeneity in a uniform extensive quantity is produced, internal processes are excited that tend to reabsorb the inhomogeneities and to bring the system back to the original equilibrium configuration.

This inhomogeneity may be, for instance, in the density, concentration, energy density, and so on.

The principle of Le Chatelier was formulated on an empirical basis but now it finds an explanation within the theory of Thermodynamics as it has evolved to the present day. Two points should be emphasized. The first is that Le Chatelier principle is substantially equivalent to the stability criteria of equilibrium states already examined in Sect. 4.3.6 and which lead to the positivity of the specific heat, of the coefficient of isothermal and adiabatic compressibility.

The second point is that Le Chaelier principle, which was conceived for equilibrium states, appears to be just a particular case of a more general law regarding stationary states, i.e., thermodynamical configurations possessing a (local) minimum for the entropy production. As it will be proved in Sect. 15.2.3 the internal processes will steer the system toward states with lower entropy production (under certain conditions). If we start from a configuration of minimum entropy production the perturbation will be reabsorbed and the initial configuration shall be restored.

In conclusion, we see that the development of thermodynamics gives a satisfactory explanation to an old empirical law.

## Le Chatelier-Braun Principle

Le Chatelier's principle finds its justification in the theory of irreversible processes as we saw obtaining Eq. (15.107) but this constitutes only a "partial result". Although within the limits of validity that we have recalled, it refers only to the case of a system with a single degree of freedom $(n=1)$ because only, in this case, it can ensure that the disturbance is reabsorbed by the flux that was excited.

In the general case, more degrees of freedom are present and the problem is more complicated. The fact remains that the effect produced by the perturbation $\delta X_{\eta}$ on the flux linked to it is governed by Eq. (15.107) but this does not guarantee that the disturbance is reabsorbed. For a full explanation of the principle of Le Chatelier we should also look at the changes that the same disturbance $\delta X_{\eta}$ produces on the other fluxes.

In this more general view, Le Chatelier's principle is modified into Le ChatelierBraun principle which generalizes the former to the fluxes which are not directly coupled to the occurring perturbation but that can be excited as a side effects.

In the most rigorous language of thermodynamics, we will refer to the flows that are coupled to the force $\delta X_{\eta}$ through non-diagonal coefficients of the phenomenological matrix. For example a variation in the pressure difference may produce a
"volume flow" (flow directly connected to the pressure variation) it can also produce a variation in the temperature and the latter can excite a flow of heat. According to the principle of Le Chatelier-Braun, in systems with several degrees of freedom all the fluxes excited by one perturbation, cooperate to reabsorb it.

A useful discussion of Le Chatelier-Braun principle can be found in [4]. Here, we want to take the opportunity to introduce an important theorem which provides an important evolutionary criterion. It is within the latter that both the principle of Le Chatelier and of Le Chatelier-Braun finds their full explanation.

## Time Derivative of Entropy Production

We have seen that, given a discontinuous system described by $n$ degrees of freedom (the values of $n$ forces mutually independent), if we constrain $k$ out of these $n$ forces and for the remaining $(n-k)$ the system is closed toward the outside, then the steady state which is realized is characterized by a minimum of entropy production.

It can be shown that if, after the constraints on the first $k$ forces have been fixed and the system is initially prepared in a generic configuration, it will evolve in such a way that

$$
\begin{equation*}
\frac{\mathrm{d} \mathcal{P}}{\mathrm{~d} t}<0 . \tag{15.109}
\end{equation*}
$$

This implies the generalization of the stability properties that we have discussed in Sect. 15.2.3 limited to the case in which the perturbation, for a system already in a stationary state, concerns the value of one free force.

This theorem establishes an overall evolutionary criterion, that is without going into details of what happens to individual fluxes when they are modified by some changes in the individual forces.

For this reason, it is appropriate to state that Eq. (15.109) includes the principle of Le Chatelier-Braun in a wider perspective.

The validity of this theorem is based on the same assumptions that we have seen previously, namely:

1. Linear relations between fluxes and forces;
2. Symmetry of he phenomenological coefficients;
3. The coefficients $L_{\rho \rho^{\prime}}$ are constant in time.

The proof is based on the properties of the matrix which defines the bilinear form that expresses the entropy production and that will be examined in Sect. 15.3.1. For a detailed discussion of Eq. (15.109) see de Groot-Mazur [23] or de Groot [24]. The result of their demonstration is as follows: under the assumptions of linearity, symmetry and constancy in time of the phenomenological coefficients it can be shown that

$$
\begin{equation*}
\frac{\mathrm{d} \mathcal{P}}{\mathrm{~d} t}=-\sum_{\rho, \rho^{\prime}=k+1}^{n} g_{\rho \rho^{\prime}}^{-1} \frac{\mathrm{~d} x_{\rho}}{\mathrm{d} t} \frac{\mathrm{~d} x_{\rho^{\prime}}}{\mathrm{d} t} \tag{15.110}
\end{equation*}
$$

in which the matrix $g_{\rho \rho^{\prime}}^{-1}$ is the matrix of a positive-definite quadratic form and is defined by Eq. (15.153). The expression in Eq. (15.110) expresses the time derivative of the entropy production as a quadratic form in the variables $\dot{X}_{\rho}$ and $\dot{X}_{\rho^{\prime}}$ and no matter how they vary in time, the entropy production always decreases until it reaches its minimum value. In this sense, the principle of Le Chatelier-Braun is immersed in a more general formulation.

It is clear that the theorem Eq. (15.109) has as a consequence that stationary states are stable configurations. Indeed if some perturbations occur (obviously consistent with the imposed constraints) the triggered internal processes (all together) tend to bring the configuration toward the one with minimum entropy production.

## One Simple Example: The Prigogine and Wiame Model

Prigogine and Wiame [25] have developed a simplified thermodynamic model of a biological system.

The model, briefly sketched in Fig. 15.2, considers an open system that absorbs from outside a substance M , which is processed through a series of consecutive chemical reactions to produce a final substance $F$ which is returned outside. The external environment is considered at a constant temperature and such as to keep at constant values the concentrations of all the substances present.

Let us denote with the superscript I and II respectively the values of the properties in the system and in the external world and suppose that, within the system, we have $k$ consecutive chemical reactions that we indicate with an index $\rho$ with $1 \leq \rho \leq k$.

All together we have $k+2$ processes taking take place and more precisely $k$ chemical reactions and 2 transport phenomena. We describe the processes with the following formalism:


Fig. 15.2 An open system, denoted by the superscript I, absorbs from the outside world (denoted by the superscript II) a substance indicated by M. This substance is "metabolized" within system I through a sequence of consecutive chemical reactions until the final product $F$ is produced. Then the substance $F$ is transferred to the external world. In the external world pressure, temperature and the concentrations are kept as constant

$$
\begin{gather*}
\mathrm{M}^{\mathrm{II}} \rightarrow \mathrm{M}^{\mathrm{I}},  \tag{15.111}\\
\mathrm{M}^{\mathrm{I}} \rightarrow \mathrm{~N}^{\mathrm{I}},  \tag{15.112}\\
\mathrm{~N}^{\mathrm{I}} \rightarrow \mathrm{O}^{\mathrm{I}},  \tag{15.113}\\
\ldots \rightarrow \ldots,  \tag{15.114}\\
\mathrm{R}^{\mathrm{I}} \rightarrow \mathrm{~F}^{\mathrm{I}},  \tag{15.115}\\
\mathrm{~F}^{\mathrm{I}} \rightarrow \mathrm{~F}^{\mathrm{II}} . \tag{15.116}
\end{gather*}
$$

For each of these $k+2$ processes, which are expressed here with the formalism used for "chemical reactions", we define the degree of advancement whose time derivative defines the rate (the generalized flux) of the process. Let us denote with $\mathrm{v}_{\rho}$ the rates of the $k$ chemical reactions, with $J_{\mathrm{M}}$ the flux of the transfer process $\mathrm{M}^{\mathrm{II}} \rightarrow \mathrm{M}^{\mathrm{I}}$ and with $J_{\mathrm{F}}$ the flux of the other transfer process $\mathrm{F}^{\mathrm{I}} \rightarrow \mathrm{F}^{\mathrm{II}}$. The flux $J_{\mathrm{M}}$ is defined as positive when component $M$ is transferred from outside to the system while the flux $J_{\mathrm{F}}$ is set as positive when component F is transported from inside the system to the external world. The state variables $n_{\gamma}$ are the numbers of moles of each component $\gamma$ within the system. The production of entropy will be written as

$$
\begin{equation*}
T \mathcal{P}=A_{\mathrm{M}} J_{\mathrm{M}}+\sum_{\rho=1}^{k} A_{\rho} \mathrm{v}_{\rho}+A_{\mathrm{F}} J_{\mathrm{F}} \tag{15.117}
\end{equation*}
$$

where $A_{M}$ and $A_{\mathrm{F}}$ are the affinities of the transport phenomena and $A_{\rho}$ the affinities of the $k$ chemical reactions. The variations per unit time of the state variables can be written as a function of the rates of the different processes:

$$
\begin{align*}
& \frac{\mathrm{d} n_{\mathrm{M}}}{\mathrm{~d} t}=J_{\mathrm{M}}-\mathrm{v}_{1},  \tag{15.118}\\
& \frac{\mathrm{~d} n_{\mathrm{N}}}{\mathrm{~d} t}=\mathrm{v}_{2}-\mathrm{v}_{1},  \tag{15.119}\\
& \cdots \cdots  \tag{15.120}\\
& \frac{\mathrm{~d} n_{\mathrm{F}}}{\mathrm{~d} t}=\mathrm{v}_{k}-J_{\mathrm{F}} .
\end{align*}
$$

At the stationary state, i.e., for $\mathrm{d} n_{\gamma} / \mathrm{d} t=0$ we will have

$$
\begin{equation*}
J_{\mathrm{M}}=\mathrm{v}_{1}=\mathrm{v}_{2}=\ldots=\mathrm{v}_{k}=J_{\mathrm{F}} \tag{15.122}
\end{equation*}
$$

If we denote with $v$ the common value of the rates Eq. (15.122), the entropy production becomes

$$
\begin{equation*}
T \mathcal{P}=\left(A_{\mathrm{M}}+\sum_{\rho=1}^{k} A_{\rho}+A_{\mathrm{F}}\right) \mathrm{v}>0 \tag{15.123}
\end{equation*}
$$

The situation that is determined at the steady state is the following: the state of system I does not change (stationary state) and the $k+2$ processes are equivalent to one irreversible process operating within the external world and it can be treated, formally, as one "chemical reaction":

$$
\begin{equation*}
\mathrm{M}^{\mathrm{II}} \rightarrow \mathrm{~F}^{\mathrm{II}} \tag{15.124}
\end{equation*}
$$

while entropy production is

$$
\begin{equation*}
T \mathcal{P}=A v \tag{15.125}
\end{equation*}
$$

and comparing the last two expressions, we see that the affinity of the overall process Eq. (15.124) will prove to be the sum of the affinities of the $k+2$ processes:

$$
\begin{equation*}
A=\left(A_{\mathrm{m}}+\sum_{\rho=1}^{k} A_{\rho}+A_{\mathrm{F}}\right) \tag{15.126}
\end{equation*}
$$

The affinity of the overall process Eq. (15.124) may be written as

$$
\begin{equation*}
A=\mu_{\mathrm{M}^{\mathrm{I}}}-\mu_{\mathrm{F}}{ }^{\mathrm{II}} \tag{15.127}
\end{equation*}
$$

and in many instances, the chemical potential can be expressed in a form that explicits the concentration dependence:

$$
\begin{equation*}
\mu=\eta+R T \ln C \tag{15.128}
\end{equation*}
$$

so that the affinity of the overall process may be written in the form

$$
\begin{equation*}
A=R T \ln \left[\frac{K(T)}{\left(C_{\mathrm{M}}^{\mathrm{II}}\right)^{-1} C_{\mathrm{F}}^{\mathrm{II}}}\right] \tag{15.129}
\end{equation*}
$$

From this expression, it is clear that the condition of having constant temperature and concentrations in the external world has the consequence that the generalized force of the overall process is fixed.

Let us now reverse the perspective and write the expression of the entropy production for a generic configuration provided that we are allowed to use linear relations between fluxes and forces. We shall obtain a quadratic form in the forces $A / T$ :

$$
\begin{equation*}
\mathcal{P}=\sum_{\rho, \rho^{\prime}=1}^{k+2} L_{\rho \rho^{\prime}}\left(\frac{A_{\rho}}{T}\right)\left(\frac{A_{\rho^{\prime}}}{T}\right) . \tag{15.130}
\end{equation*}
$$

The problem we want to solve can be formulated in this way: we impose the constraint that the sum of the affinities of the $(k+2)$ processes (see Eq. (15.126)) has a fixed value and ask for which thermodynamical configurations the entropy production given in Eq. (15.130) has an extremum value consistent with the imposed constraint. We can solve the problem by using the method of Lagrange multipliers, and this is equivalent to finding the extremes of unconditional expression

$$
\begin{equation*}
\mathcal{P}=\sum_{\rho, \rho^{\prime}=1}^{k+2} L_{\rho \rho^{\prime}}\left(\frac{A_{\rho}}{T}\right)\left(\frac{A_{\rho^{\prime}}}{T}\right)-2 \lambda \sum_{\rho=1}^{k+2}\left(\frac{A_{\rho}}{T}\right) \tag{15.131}
\end{equation*}
$$

in other words we require that, for the above expression:

$$
\begin{equation*}
\frac{\partial \mathscr{P}}{\partial\left(\frac{A_{\rho}}{T}\right)}=0 \tag{15.132}
\end{equation*}
$$

Making use of the Onsager reciprocity Eq. (14.128), we are led to

$$
\begin{equation*}
\frac{\partial \mathcal{P}}{\partial\left(\frac{A_{\rho}}{T}\right)}=2 \sum_{\rho^{\prime}=1}^{k+2} L_{\rho \rho^{\prime}}\left(\frac{A_{\rho^{\prime}}}{T}\right)-2 \lambda=0 \tag{15.133}
\end{equation*}
$$

Then we find, for each one of the $k+2$ processes the rate has one common value $\lambda$ :

$$
\begin{equation*}
\mathrm{v}_{\rho}=\lambda \quad \rho=1,2, \ldots(k+2) \tag{15.134}
\end{equation*}
$$

and this is the condition of the stationary configuration.

### 15.3 Fluctuations

In 1826, the botanist Robert Brown described, officially for the first time, a very curious phenomenon to which he attended regularly when he observed under the microscope, small colloidal particles, pollen or simply dust particles suspended in liquids or gases. He observed movements in a zig-zag, completely at random and with short duration, and their origin remained, for many decades, a mystery. Indeed he could not understand why in a state of stable equilibrium, i.e., in a perfectly homogenous configuration in which the liquid or the gas were expected to be, so rapid and disorderly interactions with pollen particle could be developed. The clarification of the phenomenon was given by A. Einstein in one of the four articles he published in the memorable year 1905 and is based on the recognition that perfectly homogeneous configurations that characterize the states of stable equilibrium, are "average configurations" that appear uniform and static to an observer (which we called "macroscopic observer") when he is observing with relatively low spatial and
temporal resolution instruments. However, when the observation relies on instruments with higher spatial and temporal resolution, then the static and homogeneous configurations expected in an equilibrium state turn out to be rapidly changing both spatially and temporally in a "small-scale".

The reader must not be tempted to automatically connect this type of observations to the atomic-molecular structure of matter. We are still dealing with macroscopic observations, rather we could say that two types of macroscopic observer emerge and that these differ because of the high or low spatial and temporal resolution of their instruments of observation. Nevertheless the discovery of such new phenomena, on a small macroscopic scale, forces us to substantially revise the fundamental concepts of thermodynamics starting from the concept of equilibrium state.

The equilibrium state that we represent in the space of thermodynamical configurations will no longer correspond to the observations performed by an Accurate Macroscopic Observer (AMO) but it represents the average point around which a large number of observations by AMO will condensate with a certain probability distribution. The whole thermodynamics of equilibrium states will keep unchanged its validity but with the caveat that we are referring to average states from the point of view of an accurate observer or to just "the state" from the point of view of a low-accuracy macroscopic observer (LMO). ${ }^{9}$

Another comment concerns the Second Principle. As we have seen it classifies as natural or unnatural processes, changes of state occurring between equilibrium states in the sense of an LMO, that is between average states in the sense of an AMO and when we speak of infinitesimal transformations we refer to extrapolations to zero of transformations between equilibrium states gradually getting closer and closer.

This should not be confused with the changes of state, which will also be considered infinitesimal, by an AMO on the scale that is proper to him.

It should be understood, however, that this double figure of Macroscopic Observer contains a potential conflict between LMO and AMO as regards the meaning of the Second Principle and, therefore, the very foundation of Thermodynamics. If we think of the latter in its original meaning of "impossibility of achieving perpetual motion", we see that the theory developed by the macroscopic observer (in the version of LMO) and based on the definition of entropy, does not protect us from the risk of using observations on a "small scale" as a possible way of getting perpetual motion. This paradox known as the problem of the "Maxwell Demon" is the essential example of how AMO may take advantage from his accurate observations.

This conflict has been solved with the formulation of the "Landauer's principle" within the theory of the information and which will be discussed in Chap. 17.

[^56]It is clear that the first observations, reported in 1826 and universally known as "Brownian motions" reveal the existence of an inhomogeneous and rapidly variable structure under a static and homogeneous appearance but all this happens well within that world which, in the first chapter, we have called "macroscopic world". It is within classical physics that the theory of fluctuations was set by Einstein in 1905 when the bridge with quantum physics (i.e., with the atomic-molecular theory of matter) had yet to be started.

With this premise, it is also natural that a hinge between the macroscopic and microscopic observations find a suitable tool in the development Statistical Mechanics and, in particular, in that part of the theory that seeks to explain the macroscopic observations as average results of microscopic phenomena. This is beyond the scope of this discussion and in accordance with the views stated in the introduction of this book, we will discuss the issue from a purely macroscopic point of view that is, without regard to any hypothesis about the discrete structure of matter. ${ }^{10}$

The explanation of Brownian motions as due to collisions symmetrical on a large scale but strongly asymmetrical on a small scale, leads us to consider all the state parameters as parameters subject to such rapid random changes, on a small scale, that will be called random fluctuations.

If we start considering the existence of fluctuations in the distribution of matter it is natural to expect that all of the extensive quantities, which represent the state from the thermodynamic point of view, are subject to rapid variations (fluctuations) in a manner which depends on the nature of the constraints. Consequently, even intensive variables such as density, pressure, and temperature will be subject to fluctuations.

For example, if we consider a system in thermal contact with a thermostat (say the external environment) we can see, with accurate observations, that also the energy contained in the system is subject to rapid changes around the equilibrium value. Similarly, if the system is constituted by a cylinder confined by a piston free to move against a constant pressure (for example of the environment), we will notice that its position is subject to small variations and hence also the volume of the system fluctuates around a mean value.

If, then, the piston is diathermic, then we will see fluctuations both in the volume and in energy. These fluctuations may be correlated or unrelated with each other. Similarly, we can imagine that a chemical reaction at equilibrium is such on average only but that, a detailed observation would show fluctuations in the degree of advancement around the equilibrium value that is, rapid and small variations of the concentrations of the components around the respective equilibrium values.

We will say that "the state of the system fluctuates around a reference equilibrium state" meaning with this expression the fact that the state parameters, both intensive and extensive, are subject to rapid and random variations around their equilibrium values and these rapid variations are called fluctuations.

Returning to the description of the thermodynamic state by determining the extensive parameters (therefore considering intensive variables as derived quantities), if we denote with $\xi$ a generic extensive state parameter and with $\xi^{\mathrm{e}}$ its value corre-

[^57]sponding to the equilibrium state, we will define fluctuation of the state parameter $\xi$ at the instant $t$, the quantity:
\[

$$
\begin{equation*}
\alpha(t)=\xi(t)-\xi^{\mathrm{e}} . \tag{15.135}
\end{equation*}
$$

\]

More generally, if we assume that the system under consideration is defined by $n$ independent state parameters $\xi_{\rho}$ with $1 \leq \rho \leq n$ we consider the fluctuation of each state parameter at time $t$ :

$$
\begin{equation*}
\alpha_{\rho}(t)=\xi_{\rho}(t)-\xi_{\rho}^{\mathrm{e}}, \tag{15.136}
\end{equation*}
$$

where the functions $\alpha_{\rho}(t)$ are rapidly varying functions of time with zero mean value. By rapidly varying we mean that changes take place in a timescale which is short if compared to the timescale characterizing the macroscopic observer in its LMO version but still very long compared to the timescale of the microscopic phenomena.

Given a state of equilibrium, the mean value of any state variable of the system will be denoted with the symbol between brackets. For instance the mean value of the fluctuation of the $\rho$ th fluctuation will be

$$
\begin{equation*}
\left\langle\alpha_{\rho}(t)\right\rangle=0 . \tag{15.137}
\end{equation*}
$$

The mean value is zero by definition of equilibrium state, but we shall have also

$$
\begin{equation*}
\left\langle\alpha_{\rho}^{2}\right\rangle \geq 0 \tag{15.138}
\end{equation*}
$$

The mean value of any function of the time, say $g(t)$ is defined by the relation:

$$
\begin{equation*}
\langle g\rangle=\lim _{T \rightarrow \infty} \frac{1}{2 T} \int_{-T}^{T} g(t) \mathrm{d} t \tag{15.139}
\end{equation*}
$$

### 15.3.1 Theory of Fluctuations in a Isolated System

If we denote by $S_{0}$ the value of the entropy of the system in the equilibrium state, and with $S(\alpha)$ the value of the entropy in the time instant in which a fluctuation $\alpha_{\rho}$ of the state parameters $\xi_{\rho}(1 \leq \rho \leq n)$ occurs, we may write the series expansion:

$$
\begin{equation*}
S(\alpha)=S_{0}+\sum_{\rho=1}^{n}\left(\frac{\partial S}{\partial \xi_{\rho}}\right)_{\mathrm{eq}} \alpha_{\rho}+\frac{1}{2} \sum_{\rho, \rho^{\prime}=1}^{n}\left(\frac{\partial^{2} S}{\partial \xi_{\rho} \partial \xi_{\rho^{\prime}}}\right)_{\mathrm{eq}} \alpha_{\rho} \alpha_{\rho^{\prime}}+\cdots \tag{15.140}
\end{equation*}
$$

Since we are dealing with fluctuations around an equilibrium state it will be

$$
\begin{equation*}
\left(\frac{\partial S}{\partial \xi_{\rho}}\right)_{\mathrm{eq}}=0 \tag{15.141}
\end{equation*}
$$

and hence:

$$
\begin{equation*}
S(\alpha)=S_{0}+\frac{1}{2} \sum_{\rho, \rho^{\prime}=1}^{n}\left(\frac{\partial^{2} S}{\partial \xi_{\rho} \partial \xi_{\rho^{\prime}}}\right)_{\mathrm{eq}} \alpha_{\rho} \alpha_{\rho^{\prime}}+\ldots \tag{15.142}
\end{equation*}
$$

Let us define the matrix:

$$
\begin{equation*}
g_{\rho \rho^{\prime}}=-\left(\frac{\partial^{2} S}{\partial \xi_{\rho} \partial \xi_{\rho^{\prime}}}\right)_{\mathrm{eq}} \tag{15.143}
\end{equation*}
$$

then Eq. (15.142) may be written as

$$
\begin{equation*}
S(\alpha)=S_{0}-\frac{1}{2} \sum_{\rho, \rho^{\prime}=1}^{n} g_{\rho \rho^{\prime}} \alpha_{\rho} \alpha_{\rho^{\prime}} \tag{15.144}
\end{equation*}
$$

where $g_{\rho \rho^{\prime}}$ is the matrix of a positive-definite quadratic form. ${ }^{11}$ Notice, also, that $g_{\rho \rho^{\prime}}$ is a symmetric matrix:

$$
\begin{equation*}
g_{\rho \rho^{\prime}}=g_{\rho^{\prime} \rho} \tag{15.145}
\end{equation*}
$$

We now introduce, explicitly, an additional hypothesis: we treat the temporal evolution of the fluctuations with the same formalism with which we describe, in a macroscopic viewpoint, irreversible processes. With this in mind, the interactions between parts in internal equilibrium (those interactions which we describe as irreversible processes), produce entropy at the rate (recall Sect. 14.7) $\mathcal{P}=\sum_{\rho} J_{\rho} X_{\rho}$. From the latter relation we find that the entropy variation in the time interval $\mathrm{d} t$ will be

$$
\begin{equation*}
\hat{d}_{\mathrm{i}} S=\sum_{\rho=1}^{n} X_{\rho} \mathrm{d} \xi_{\rho} \tag{15.146}
\end{equation*}
$$

We assume, therefore, that the same description can be adopted when we consider the change (infinitesimal transformation) from a configuration in which the system exhibits a fluctuation from the configuration

$$
\left\{\alpha_{1}, \alpha_{2}, \ldots, \alpha_{n}\right\}
$$

to the nearby configuration

$$
\left\{\left(\alpha_{1}+\mathrm{d} \alpha_{1}\right),\left(\alpha_{2}+\mathrm{d} \alpha_{2}\right), \ldots,\left(\alpha_{n}+\mathrm{d} \alpha_{n}\right)\right\}
$$

In addition we consider small fluctuations around the equilibrium state so that also the forces $X_{\rho}$ can be expressed, with sufficient accuracy, as linear functions of the fluctuations:

[^58]\[

$$
\begin{equation*}
X_{\rho}\left(\alpha_{1}, \alpha_{2}, \ldots, \alpha_{n}\right)=X_{\rho}(0,0, \ldots \ldots, 0)+\sum_{\rho^{\prime}=1}^{n}\left(\frac{\partial X_{\rho}}{\partial \alpha_{\rho^{\prime}}}\right)_{\mathrm{eq}} \alpha_{\rho^{\prime}} \tag{15.147}
\end{equation*}
$$

\]

with $X_{\rho}(0,0, \ldots, 0)=0$ for every $\rho$ because configuration $\{0,0, \ldots, 0\}$ corresponds to the equilibrium state. Since we are considering a thermally isolated systems $\hat{d}_{\mathrm{e}} S=0$, and $\mathrm{d} \xi_{\rho}=\mathrm{d} \alpha_{\rho}$, it results that Eq. (15.146) may be written in the form

$$
\begin{equation*}
\mathrm{d} S=\sum_{\rho, \rho^{\prime}=1}^{n}\left(\frac{\partial X_{\rho}}{\partial \alpha_{\rho^{\prime}}}\right)_{\mathrm{eq}} \alpha_{\rho^{\prime}} \mathrm{d} \alpha_{\rho} . \tag{15.148}
\end{equation*}
$$

Since the $n$ variables are mutually independent the differential form Eq. (15.148) can be easily integrated from $\{0,0, \ldots, 0\}$ to $\left\{\alpha_{1}, \alpha_{2}, \ldots, \alpha_{n}\right\}$ and we obtain

$$
\begin{equation*}
S\left(\alpha_{1}, \alpha_{2}, \ldots, \alpha_{n}\right)=S(0,0, \ldots, 0)+\frac{1}{2} \sum_{\rho, \rho^{\prime}=1}^{n}\left(\frac{\partial X_{\rho}}{\partial \alpha_{\rho^{\prime}}}\right)_{\mathrm{eq}} \alpha_{\rho} \alpha_{\rho^{\prime}} \tag{15.149}
\end{equation*}
$$

and, if we compare the latter with Eq. (15.142) we obtain the identity

$$
\begin{equation*}
\left(\frac{\partial X_{\rho}}{\partial \alpha_{\rho^{\prime}}}\right)_{\mathrm{eq}}=\left(\frac{\partial^{2} S}{\partial \xi_{\rho} \partial \xi_{\rho^{\prime}}}\right)_{\mathrm{eq}} \tag{15.150}
\end{equation*}
$$

for every $\rho$ and $\rho^{\prime}$, and then we have

$$
\begin{equation*}
X_{\rho}=\left(\frac{\partial S}{\partial \xi_{\rho}}\right) . \tag{15.151}
\end{equation*}
$$

From this relation we may write the expression for the force and for the amplitude of the fluctuations as a function of the fluctuation matrix Eq. (15.143). If we take the derivative of Eq. (15.144), we obtain

$$
\begin{equation*}
X_{\rho}=\left(\frac{\partial S}{\partial \xi_{\rho}}\right)=-\sum_{\rho^{\prime}=1}^{n} g_{\rho \rho^{\prime}} \alpha_{\rho^{\prime}} . \tag{15.152}
\end{equation*}
$$

This relation can be reversed to give

$$
\begin{equation*}
\alpha_{\rho}=-\sum_{\rho^{\prime}=1}^{n} g_{\rho \rho^{\prime}}^{-1} X_{\rho^{\prime}} \tag{15.153}
\end{equation*}
$$

where $g_{\rho \rho^{\prime}}^{-1}$ in the inverse matrix of $g_{\rho \rho^{\prime}}$.

### 15.3.2 Fluctuations Distribution Function

Remaining in the case of thermally insulated systems, we can draw the distribution function for the fluctuations which is defined in this way: the infinitesimal probability $\mathrm{d} P$ that, in a system at equilibrium, the fluctuations of the state parameters is within the infinitesimal interval $\left(\alpha_{\rho} ; \alpha_{\rho}+\mathrm{d} \alpha_{\rho}\right)$ with $1 \leq \rho \leq n$, is

$$
\begin{equation*}
\mathrm{d} P=P\left(\alpha_{1}, \alpha_{2}, \ldots, \alpha_{n}\right) \mathrm{d} \alpha_{1} \mathrm{~d} \alpha_{2} \ldots \mathrm{~d} \alpha_{n} . \tag{15.154}
\end{equation*}
$$

According to Einstein's theory of fluctuations the fluctuation distribution function is related to the entropy as follows:

$$
\begin{equation*}
\mathrm{d} P \propto \exp \left(\frac{\Delta_{i} S}{k_{B}}\right) \mathrm{d} \alpha_{1} \mathrm{~d} \alpha_{2} \ldots \mathrm{~d} \alpha_{n} \tag{15.155}
\end{equation*}
$$

hence, the distribution function is

$$
\begin{equation*}
P=\frac{\exp \left(\Delta_{i} S / k_{B}\right)}{\int \cdots \int_{-\infty}^{+\infty} \exp \left(\Delta_{i} S / k_{B}\right) \mathrm{d} \alpha_{1} \mathrm{~d} \alpha_{2} \ldots \mathrm{~d} \alpha_{n}} \tag{15.156}
\end{equation*}
$$

because of the normalization condition. Here $\Delta_{i} S$ is

$$
\begin{equation*}
\Delta_{i} S=S\left(\alpha_{1}, \alpha_{2}, \ldots, \alpha_{n}\right)-S(0,0, \ldots, 0) \tag{15.157}
\end{equation*}
$$

As we have previously discussed $\Delta_{i} S<0$ and the exponential dependence justifies the approximation to consider only small fluctuations.

### 15.3.3 Mean Values and Correlations

Now that we have established the form of the distribution function of the fluctuations, we can calculate the mean values of all the macroscopic quantities of interest. In particular, it will be interesting to calculate the mean value of a fluctuation, the mean value of the decrease in entropy due to fluctuations and the correlation between a fluctuation and a generalized force. Let us start with the latter term and, as will be shown below, all the other mean values will be obtained from it using Eqs. (15.152) and (15.153):

$$
\begin{equation*}
\left\langle\alpha_{\rho} X_{\rho^{\prime}}\right\rangle=\int \cdots \int \alpha_{\rho} X_{\rho^{\prime}} P \mathrm{~d} \alpha_{1} \mathrm{~d} \alpha_{2} \ldots \mathrm{~d} \alpha_{n} . \tag{15.158}
\end{equation*}
$$

From Eqs. (15.156) and (15.151) we have immediately

$$
\begin{equation*}
X_{\rho^{\prime}}=k_{B} \frac{1}{P}\left(\frac{\partial P}{\partial \alpha_{\rho^{\prime}}}\right) \tag{15.159}
\end{equation*}
$$

and then the required mean value is

$$
\begin{equation*}
\left\langle\alpha_{\rho} X_{\rho^{\prime}}\right\rangle=k_{B} \int \ldots \int \alpha_{\rho}\left(\frac{\partial P}{\partial \alpha_{\rho^{\prime}}}\right) \mathrm{d} \alpha_{1} \mathrm{~d} \alpha_{2} \ldots \mathrm{~d} \alpha_{n} . \tag{15.160}
\end{equation*}
$$

This integral may be calculated by parts starting with the integration on the variable $\alpha_{\rho^{\prime}}$ :

$$
\begin{align*}
& \int \cdots \int \alpha_{\rho}\left(\frac{\partial P}{\partial \alpha_{\rho^{\prime}}}\right) \mathrm{d} \alpha_{1} \mathrm{~d} \alpha_{2} \ldots \mathrm{~d} \alpha_{n}=  \tag{15.161}\\
& =\int \ldots \int \mathrm{d} \alpha_{1} \ldots \mathrm{~d} \alpha_{\rho^{\prime}-1} \mathrm{~d} \alpha_{\rho^{\prime}+1} \ldots \mathrm{~d} \alpha_{n} \int_{-\infty}^{+\infty} \alpha_{\rho}\left(\frac{\partial P}{\partial \alpha_{\rho^{\prime}}}\right) \mathrm{d} \alpha_{\rho^{\prime}}, \tag{15.162}
\end{align*}
$$

where

$$
\begin{equation*}
\int_{-\infty}^{+\infty} \alpha_{\rho}\left(\frac{\partial P}{\partial \alpha_{\rho^{\prime}}}\right) \mathrm{d} \alpha_{\rho^{\prime}}=\left[\alpha_{\rho} P\right]_{-\infty}^{+\infty}-\int_{-\infty}^{+\infty} P\left(\frac{\partial \alpha_{\rho}}{\partial \alpha_{\rho^{\prime}}}\right) \mathrm{d} \alpha_{\rho^{\prime}} \tag{15.163}
\end{equation*}
$$

The first term in the right side is zero for $P$ goes rapidly to zero for high values of the fluctuations and for the second term we have

$$
\begin{equation*}
\left(\frac{\partial \alpha_{\rho}}{\partial \alpha_{\rho^{\prime}}}\right)=\delta_{\rho \rho^{\prime}} \tag{15.164}
\end{equation*}
$$

$\delta_{\rho \rho^{\prime}}$ being the Kronecker delta symbol, due to the mutual independence of the two variables and to the normalization of the distribution function. Then we have:

$$
\begin{equation*}
\left\langle\alpha_{\rho} X_{\rho^{\prime}}\right\rangle=-k_{B} \delta_{\rho \rho^{\prime}} . \tag{15.165}
\end{equation*}
$$

## Second Moments

From Eq. (15.165) we can calculate other mean values. Using Eq. (15.153) we can obtain the correlation between two fluctuations:

$$
\begin{align*}
\left\langle\alpha_{\rho} \alpha_{\rho^{\prime}}\right\rangle=\left\langle\alpha_{\rho} \sum_{\rho^{\prime \prime}=1}^{n} g_{\rho^{\prime} \rho^{\prime \prime}}^{-1} X_{\rho^{\prime \prime}}\right\rangle & =  \tag{15.166}\\
& =-\sum_{\rho^{\prime \prime}=1}^{n} g_{\rho^{\prime} \rho^{\prime \prime}}^{-1}\left\langle\alpha_{\rho} X_{\rho^{\prime \prime}}\right\rangle \tag{15.167}
\end{align*}
$$

$$
\begin{align*}
& =k_{B} \sum_{\rho^{\prime \prime}=1}^{n} g_{\rho^{\prime} \rho^{\prime \prime}}^{-1} \delta_{\rho \rho^{\prime \prime}}  \tag{15.168}\\
& =k_{B} g_{\rho^{\prime} \rho}^{-1} . \tag{15.169}
\end{align*}
$$

In particular the mean quadratic value is

$$
\begin{equation*}
\left\langle\alpha_{\rho}^{2}\right\rangle=k_{B} g_{\rho \rho}^{-1}, \tag{15.170}
\end{equation*}
$$

with

$$
\begin{equation*}
g_{\rho \rho}^{-1}=\left(\frac{\partial^{2} S}{\partial \xi_{\rho}^{2}}\right)^{-1} \tag{15.171}
\end{equation*}
$$

## Average Entropy Decrease

We have denoted with $S_{0}=S(0,0, \ldots, 0)$ the value of the entropy in the equilibrium state. If we imagine to make an accurate observation with a short time scale, we would not find the system in the equilibrium state $(0,0, \ldots, 0)$ but in a state more or less close to it (fluctuation) to which a lower value of the entropy will correspond. Let us calculate the mean value of the deficit of entropy caused by the fluctuations of the state variables. If we go back to Eq. (15.144) and to Eq. (15.169) we find the result:

$$
\begin{equation*}
\left\langle S-S_{0}\right\rangle=-\frac{1}{2} k_{B} n . \tag{15.172}
\end{equation*}
$$

This can be interpreted as a kind of equipartition theorem of the decrease in entropy: all degrees of freedom (mutually independent) contribute to the average decrease in entropy due to fluctuations with the same amount $k_{B} / 2$.

### 15.3.4 Onsager Relations and the Decay of Fluctuations in Isolated Systems

In this subsection we want to study, in some detail, the dynamics of the fluctuations decay. Consider a system in a state of equilibrium in a thermally isolated system and remember that the equilibrium state is characterized by a point with maximum entropy.

## Fluctuations and Microscopic Reversibility

The term "microscopic reversibility" refers to the property of the laws of microscopic physics to be invariant under inversion of the time axis. More precisely, we want to
allude to the fact that the laws of motion, at the microscopic level, are invariant under the transformation $t \rightarrow-t$.

This means, in a problem of point mechanics, that if, in some instant of time, we operate the change of variable $t \rightarrow-t$ in the equations of motion, the velocity of the point in that instant changes sign $(\mathbf{v} \rightarrow-\mathbf{v})$ and we will see the point retrace the same trajectory that it had traveled so far and with the same temporal law but in the "reversed" direction, i.e., backwards.

This requires that the interaction forces between the point and the rest of the universe, do not depend on the velocity of the particles and thus remain unchanged. We know a situation in which this property of the forces seems not to be true: it is the case of the Lorentz force for the part that concerns the interaction with the magnetic field $\mathbf{B}$. The invariance of the force under the inversion of the velocity is resumed if, at the same time, we also reverse the direction of magnetic field.

This must not be understood as a mere expedient invented to save a symmetry law but, on the contrary, it is intrinsic to the time reversal symmetry in a theoretical context that does not provide for the existence of magnetic monopoles. The magnetic field is not generated by charges but only by currents and so if all the velocities are reversed also the magnetic field changes sign.

The particular evolution of the fluctuations in a system at equilibrium, in a classical (non-quantum) context, is determined by the initial conditions and by the laws of interaction between the microsystems. Two distinct macroscopic systems but in the same macroscopic state of equilibrium, will show two sequences of fluctuations certainly different from each other but with two fundamental properties in common: (a) the mean value of the fluctuations of each state parameter will be zero; (b) the distribution function of the fluctuations will be precisely the same and will be given by Eq. (15.156).

A succession of fluctuations which has these two characteristics is called a "normal sequence of fluctuations". An infinite number of "equal" systems from the macroscopic point of view, will all have different successions of fluctuations but each one will be a normal succession of fluctuations and then all mean values will have the same result.

The principle of symmetry under time reversal of the laws of microscopic physics, applied to the thermodynamic context, means:
"If we consider a thermodynamic system in a state of equilibrium, the succession of fluctuations that we would observe if at a certain instant we would reverse the values of the velocities of all the particles, would still be a normal sequence of fluctuations". Therefore, any mean value calculated along the development of the observed fluctuations, would have the same result of the one calculated on the succession of fluctuations that we would observe after applying the time reversal operation $t \rightarrow-t$.

For our purposes, this conclusion implies the following result: consider the time evolutions of the fluctuations of two degrees of freedom say $\alpha_{\rho}(t)$ e $\alpha_{\rho^{\prime}}(t)$. We want to calculate the correlation between the fluctuation of the parameter $\rho$ with the parameter $\rho^{\prime}$ not at the same instant but taken with a constant delay say $\tau$ with $\tau>0$. Formally we want to calculate:

$$
\begin{equation*}
\left\langle\alpha_{\rho}(t) \alpha_{\rho^{\prime}}(t+\tau)\right\rangle=\lim _{T \rightarrow \infty} \frac{1}{2 T} \int_{-T}^{T} \alpha_{\rho}(t) \alpha_{\rho^{\prime}}(t+\tau) \mathrm{d} t \tag{15.173}
\end{equation*}
$$

As a consequence of the ergodic hypothesis, any mean value, defined in the form of time average in a very long $(\infty)$ time interval, may be equivalently calculated by averaging the measurements of the quantity of interest observed in a large number $(\infty)$ of "equal" systems and in the same instant. This implies that, in order to calculate the above mean value, we observe, in many equal systems, the value of the $\rho$ parameter at the same instant $t$ and the value of the $\rho^{\prime}$ parameter $\tau$ seconds later.

Subsequently, with the same observation conditions, we measure the product of the value of the $\alpha_{\rho^{\prime}}$ taken at the instant $t$ and the value of the $\alpha_{\rho}$ taken $\tau$ seconds later.

In its expression as a time integral, the two mean values differ from each other only for the temporal order of the observations of the two fluctuations. In other words, the second mean value is obtained from the time integral which defines the first mean value where we operated the change of variable $t^{\prime}=-t$.

In conclusion owing to the principle of symmetry under time reversal formulated for a thermodynamical system, the two time averages must be equal:

$$
\begin{equation*}
\left\langle\alpha_{\rho}(t) \alpha_{\rho^{\prime}}(t+\tau)\right\rangle=\left\langle\alpha_{\rho^{\prime}}(t) \alpha_{\rho}(t+\tau)\right\rangle \tag{15.174}
\end{equation*}
$$

If we subtract from both members, the mean value of the product of the two fluctuations taken at the same instant, if we take into account that the difference of two average values is equal to the average value of the difference and divide both sides by $\tau$ we obtain

$$
\begin{gather*}
\frac{1}{\tau}\left\langle\alpha_{\rho}(t) \alpha_{\rho^{\prime}}(t+\tau)-\alpha_{\rho}(t) \alpha_{\rho^{\prime}}(t)\right\rangle=\frac{1}{\tau}\left\langle\alpha_{\rho^{\prime}}(t) \alpha_{\rho}(t+\tau)-\alpha_{\rho}(t) \alpha_{\rho^{\prime}}(t)\right\rangle \\
\left\langle\alpha_{\rho}(t) \frac{\alpha_{\rho^{\prime}}(t+\tau)-\alpha_{\rho^{\prime}}(t)}{\tau}\right\rangle=\left\langle\alpha_{\rho^{\prime}}(t) \frac{\alpha_{\rho}(t+\tau)-\alpha_{\rho}(t)}{\tau}\right\rangle \tag{15.175}
\end{gather*}
$$

and passing to the limit for increasingly smaller values of $\tau$ we get

$$
\begin{equation*}
\left\langle\alpha_{\rho}(t) \dot{\alpha}_{\rho^{\prime}}(t)\right\rangle=\left\langle\alpha_{\rho^{\prime}}(t) \dot{\alpha}_{\rho}(t)\right\rangle \tag{15.177}
\end{equation*}
$$

## Fluctuation Decay in the Irreversible Processes Formalism

Let us now apply the Onsager theorization for the treatment of irreversible processes to the study of the time evolution of fluctuations. We identify the time derivative of a state variable with a generalized flux:

$$
\begin{equation*}
J_{\rho}=\dot{\xi}_{\rho}=\dot{\alpha}_{\rho} \tag{15.178}
\end{equation*}
$$

and suppose that the deviations from equilibrium are small enough to be able to express the fluxes as linear functions of $n$ forces at play, namely:

$$
\begin{equation*}
J_{\rho}=\sum_{\rho^{\prime}=1}^{n} L_{\rho \rho^{\prime}} X_{\rho^{\prime}} \tag{15.179}
\end{equation*}
$$

Then if we use Eq. (15.177) and take into account the fact that the mean value of a sum is the sum of the mean values and that the mean value of a quantity multiplied by a constant is equal to the product of the constant times the mean value of the quantity, we can write

$$
\begin{equation*}
\sum_{\rho^{\prime \prime}=1}^{n} L_{\rho^{\prime} \rho^{\prime \prime}}\left\langle\alpha_{\rho} X_{\rho^{\prime \prime}}\right\rangle=\sum_{\rho^{\prime \prime}=1}^{n} L_{\rho \rho^{\prime \prime}}\left\langle\alpha_{\rho^{\prime}} X_{\rho^{\prime \prime}}\right\rangle \tag{15.180}
\end{equation*}
$$

and with reference to Eq. (15.165) we shall obtain

$$
\begin{align*}
\sum_{\rho^{\prime \prime}=1}^{n} L_{\rho^{\prime} \rho^{\prime \prime}} \delta_{\rho \rho^{\prime \prime}} & =\sum_{\rho^{\prime \prime}=1}^{n} L_{\rho \rho^{\prime \prime}} \delta_{\rho^{\prime} \rho^{\prime \prime}}  \tag{15.181}\\
L_{\rho^{\prime} \rho} & =L_{\rho \rho^{\prime}} \tag{15.182}
\end{align*}
$$

Making use of Einstein's theory of fluctuations and of the invariance of the laws of microscopic physics under time reversal, Onsager showed the symmetry properties for linear phenomenological coefficients in the case of the decay of fluctuations in the case of systems in a state of equilibrium.

The validity of this theorem is assumed also for systems that are maintained in nonequilibrium configurations as we have seen in the examples that we have examined up to this point. This symmetry property is not demonstrated, but constitutes, to a certain extent, a sort of "fourth postulate" of Thermodynamics and the experimental observations will show whether there are contradictions or not.

In the case where we consider irreversible processes in the presence of magnetic fields, it is possible that the linear phenomenological coefficients (or some of them) depend on the value of the present magnetic field. In this case, the symmetry condition must be applied in the form

$$
\begin{equation*}
L_{\rho \rho^{\prime}}(\mathbf{B})=L_{\rho^{\prime} \rho}(-\mathbf{B}) \tag{15.183}
\end{equation*}
$$

This is to be expected as was seen from the discussion on microscopic reversibility but the formal proof is more complicated and will not be pursued here.

# Chapter 16 <br> Thermodynamics of Continua 


#### Abstract

The extension of the fundamental equations of Thermodynamics to a description of macroscopic systems in terms of continuous state variables is developed. All the basic relations as mass conservation in the presence of chemical reactions, the equation of motion and the equations for energy and that for entropy which express, in the new formalism, the First and the Second Principles, respectively, must be reformulated. The correct expression for the entropy production and the consequent expressions for the fluxes and the corresponding generalized forces are obtained. In the linear regime, the general relation between the mobility of ionic species and the coefficient of diffusion (Einstein relation) is demonstrated. The thermoelectric phenomena (Seebeck, Peltier, and Thomson effects) are discussed together with the thermodiffusion processes. An appendix concerning the GibbsDuhem relation closes the Chapter.


Keywords Continuous systems • Entropy balance • Entropy production • Mechanical equilibrium • Mobility • Diffusion coefficient • Einstein relation • Thermoelectric phenomena • Seebeck effect • Thermoelectric power • Peltier coefficient • Thomson effect • Galvanomagnetic and thermomagnetic effects • Thermodiffusion processes • Dufour effects • Gibbs-Duhem relation

### 16.1 Introduction

We have seen how, in many practical situations, it is useful to treat nonequilibrium systems as a collection of two or more portions, each in a state of internal equilibrium but not in equilibrium with each other and assuming that the contribution attributable to the zones of transition between the various portions can be neglected, in the economy of the variations of extensive variables.

We called this way of describing the processes "discontinuous systems approximation" and the utility is in the fact of being able to treat a variety of irreversible processes with the same formalism developed for systems in equilibrium and applying the additivity property of extensive thermodynamic potentials cutting away the contribution of transition zones (boundaries).

Not always this cut-off is allowed and so it is necessary to rewrite the basic equations of thermodynamics to adapt the theory to the need to describe the systems with the "perspective of continua".

We will call "continuous systems" the systems in which we will consider all intensive state parameters defined point by point $\mathbf{r}$ in a certain instant $t$, and described by continuous and differentiable functions:

$$
\begin{equation*}
x=x(\mathbf{r}, t) . \tag{16.1}
\end{equation*}
$$

For instance

$$
\begin{align*}
& \varrho(\mathbf{r}, t)=\frac{\mathrm{d} m}{\mathrm{~d} V}  \tag{16.2}\\
& \varrho_{\gamma}=\varrho_{\gamma}(\mathbf{r}, t)=\frac{\mathrm{d} m_{\gamma}}{\mathrm{d} V}  \tag{16.3}\\
& c_{\gamma}(\mathbf{r}, t)=\frac{\varrho_{\gamma}}{\varrho} \tag{16.4}
\end{align*}
$$

are, respectively, the density, the density of component $\gamma$ and the mass concentration of component $\gamma .{ }^{1}$

### 16.2 Definition of System

As we have seen in the study of irreversible processes in the discontinuous approximation, all the processes consist of the transfer of extensive quantities between interacting systems.

Consider a volume $V$ delimited by a closed surface $\Sigma$. This volume and this surface define the system and its extensive properties are

$$
\begin{equation*}
\mathcal{E}(t)=\int_{V} e(\mathbf{r}, t) \mathrm{d} V \tag{16.5}
\end{equation*}
$$

where

$$
\begin{equation*}
e=\frac{\mathrm{d} \mathcal{E}}{\mathrm{~d} V} \tag{16.6}
\end{equation*}
$$

is the density of $\mathcal{E}$ and, in general, it will depend on the coordinates and time. Likewise we can define:

$$
\begin{equation*}
\mathcal{E}(t)=\int_{V} \varrho(\mathbf{r}, t) \mathcal{E}^{*}(\mathbf{r}, t) \mathrm{d} V \tag{16.7}
\end{equation*}
$$

[^59]where $\mathcal{E}^{*}(\mathbf{r}, t)$ is the specific $\mathcal{E}$, i.e., the amount of $\mathcal{E}$ per unit mass. Obviously between the specific amount and its density, the relation is
\[

$$
\begin{equation*}
e=\mathcal{E}^{*} \varrho \tag{16.8}
\end{equation*}
$$

\]

The time variation of $\mathcal{E}$ will be written as

$$
\begin{equation*}
\frac{\mathrm{d} \mathcal{E}}{\mathrm{~d} t}=\int_{V} \frac{\partial e}{\partial t} \mathrm{~d} V \tag{16.9}
\end{equation*}
$$

This expression will always be brought to the following form in which it is expressed as the sum of a volume integral plus a surface integral:

$$
\begin{equation*}
\frac{\mathrm{d} \mathcal{E}}{\mathrm{~d} t}=\int_{V} \pi[\mathcal{E}] \mathrm{d} V-\int_{\Sigma} \mathbf{J}[\mathcal{E}] \cdot \mathrm{d} \boldsymbol{\Sigma} \tag{16.10}
\end{equation*}
$$

with $\mathrm{d} \boldsymbol{\Sigma}=\mathrm{d} \boldsymbol{\Sigma} \hat{\mathbf{n}}$ where $\mathrm{d} \boldsymbol{\Sigma}$ is the area of the surface element and $\hat{\mathbf{n}}$ is the unit vector perpendicular to the surface at that point and oriented outwards. Writing the integral in this general form, the term $\pi[\mathcal{E}]$ will have the meaning of density of production of the quantity $\mathcal{E}$, i.e., it denotes the amount of $\mathcal{E}$ produced per unit volume and per unit time at the point $(\mathbf{r}, t)$ by processes occurring within the volume $V$. The vector $\mathbf{J}[\mathcal{E}]$ is the flux density of the quantity $\mathcal{E}$ through the surface $\Sigma$. It represents the amount of $\mathcal{E}$ entering the volume which defines the system, per unit area, and per unit time. This is the term which correctly describes the interaction, as regards the exchange of $\mathcal{E}$, between the system and the external world. In this way we have formalized, in this new context, the expression $\mathrm{d} \mathcal{E}=\hat{d}_{\mathrm{i}} \mathcal{E}+\hat{d}_{\mathrm{e}} \mathcal{E}$ that we have postulated from the beginning, for the change of any extensive quantity. Making use of the Gauss theorem:

$$
\begin{equation*}
\int_{V} \frac{\partial e}{\partial t} \mathrm{~d} V=\int_{V} \pi[\mathcal{E}] \mathrm{d} V-\int_{V} \nabla \cdot \mathbf{J}[\mathcal{E}] \mathrm{d} V \tag{16.11}
\end{equation*}
$$

and hence:

$$
\begin{equation*}
\frac{\partial e}{\partial t}=\pi[\mathcal{E}]-\nabla \cdot \mathbf{J}[\mathcal{E}] \tag{16.12}
\end{equation*}
$$

We define conserved quantities those extensive quantities for which

$$
\begin{equation*}
\pi[\mathcal{E}]=0 \tag{16.13}
\end{equation*}
$$

### 16.3 Mass Conservation

The mass of the system is written as

$$
\begin{equation*}
m=\int_{V} \varrho \mathrm{~d} V \tag{16.14}
\end{equation*}
$$

and the conservation of mass is expressed by the condition:

$$
\begin{equation*}
\pi[m]=0 \tag{16.15}
\end{equation*}
$$

and hence:

$$
\begin{align*}
& \frac{\partial \varrho}{\partial t}=-\nabla \cdot \mathbf{J}[m]  \tag{16.16}\\
& \frac{\partial \varrho}{\partial t}=-\nabla \cdot(\varrho \mathbf{v}) \tag{16.17}
\end{align*}
$$

$\varrho \mathbf{v}$ being the flux density of mass if we consider, for the moment, the presence of only one component.

If there are various components which may have different velocities and take part in chemical reactions, the conservation of mass is no longer valid for each component. Let us suppose that $n$ chemical components are present and are denoted by the index $\gamma$. Let us denote by $\delta m_{\gamma}$ the small amount of mass of component $\gamma$ in the small volume element $\delta V$ at a certain instant. If $\gamma$ takes part to one chemical reaction within the volume element, the change of mass per unit time, due to this internal process is

$$
\begin{equation*}
\frac{\hat{d}_{\mathrm{i}}}{\mathrm{~d} t} \delta m_{\gamma}=v_{\gamma}^{\prime} \mathrm{v} \tag{16.18}
\end{equation*}
$$

where $v_{\gamma}^{\prime}=v_{\gamma} M_{\gamma}, v_{\gamma}$ being the stoichiometric number (with sign) with which the component $\gamma$ takes part to the chemical reaction, $M_{\gamma}$ its molecular weight and $\mathrm{v}=$ $\mathrm{v}(\mathbf{r}, t)$ is the rate of the chemical reaction in the region occupied by the small volume under consideration (remember that the rate of a chemical reaction is an extensive quantity).

The term $\pi[\gamma]$, describing the production of component $\gamma$ per unit volume, can be written as

$$
\begin{equation*}
\frac{\hat{d}_{\mathrm{i}} \varrho_{\gamma}}{\mathrm{d} t}=\pi[\gamma]=v_{\gamma}^{\prime} j_{\mathrm{ch}} \tag{16.19}
\end{equation*}
$$

where $j_{\text {ch }}$ is the rate per unit volume of the chemical reaction. The continuity equation for the component $\gamma$ becomes

$$
\begin{equation*}
\frac{\partial \varrho_{\gamma}}{\partial t}=-\nabla \cdot\left(\varrho_{\gamma} \mathbf{v}_{\gamma}\right)+v_{\gamma}^{\prime} j_{\mathrm{ch}} \tag{16.20}
\end{equation*}
$$

where $\mathbf{v}_{\gamma}$ is the velocity (macroscopic) of the component $\gamma$ at that point, and in that instant.

The center of mass velocity $\mathbf{v}$ of the fluid in that point, is linked to the velocities of the individual components by the well known relation:

$$
\begin{equation*}
\varrho \mathbf{v}=\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{v}_{\gamma} \tag{16.21}
\end{equation*}
$$

with $\varrho=\sum_{\gamma=1}^{n} \varrho_{\gamma}$. The conservation of mass for each chemical reaction is written as

$$
\begin{equation*}
\sum_{\gamma=1}^{n} v_{\gamma} M_{\gamma}=0 \quad \text { or } \quad \sum_{\gamma=1}^{n} v_{\gamma}^{\prime}=0 \tag{16.22}
\end{equation*}
$$

and if we sum Eq. (16.20) over all components we obtain Eq. (16.17).
In many applications, for example, for nonviscous fluids, the entropy production is not dependent on the velocity of the whole fluid (i.e., the center of mass velocity), but rather on the velocities of each component relative to the other.

It is, therefore, appropriate to define the fluxes of each individual component relative to the motion of the center of mass:

$$
\begin{align*}
& \mathbf{J}_{\gamma}=\varrho_{\gamma}\left(\mathbf{v}_{\gamma}-\mathbf{v}\right),  \tag{16.23}\\
& \varrho_{\gamma} \mathbf{v}_{\gamma}=\mathbf{J}_{\gamma}+\varrho_{\gamma} \mathbf{v} \tag{16.24}
\end{align*}
$$

Substituting in Eq. (16.20) we get

$$
\begin{equation*}
\frac{\partial \varrho_{\gamma}}{\partial t}+\mathbf{v} \cdot \nabla \varrho_{\gamma}=-\nabla \cdot \mathbf{J}_{\gamma}-\varrho_{\gamma} \nabla \cdot \mathbf{v}+v_{\gamma}^{\prime} j_{\mathrm{ch}} . \tag{16.25}
\end{equation*}
$$

## The Lagrangian or Substantial Derivative

Let us introduce the Lagrangian or substantial derivative operator:

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{~d} t}=\frac{\partial}{\partial t}+\mathbf{v} \cdot \nabla . \tag{16.26}
\end{equation*}
$$

This operator, applied to any function of the space and time coordinates, expresses the variation per unit time of that quantity as would be measured by an observer who moves with barycentric velocity along a flow line of the fluid.

It is necessary to highlight one important point: the equations which will be discussed in the following sections in order to formulate the fundamental equation of thermodynamics for continuous systems, will all be written as seen by such an observer (let us call him Lagrangian, or substantial, observer). Then the equation of motion in Sect. 16.4, the equation for the energy balance in Sect. 16.5 and that for entropy in Sect. 16.6 must be written in terms of Lagrangian derivatives.

For this (Lagrangian) observer, the continuity equation is written as

$$
\begin{equation*}
\frac{\mathrm{d} \varrho_{\gamma}}{\mathrm{d} t}=-\nabla \cdot \mathbf{J}_{\gamma}-\varrho_{\gamma} \nabla \cdot \mathbf{v}+v_{\gamma}^{\prime} j_{\mathrm{ch}} \tag{16.27}
\end{equation*}
$$

Summing Eq. (16.27) over all the components and remembering that $\varrho=\Sigma_{\gamma} \varrho_{\gamma}$ and therefore $\sum_{\gamma} \mathbf{J}_{\gamma}=0$, we obtain

$$
\begin{equation*}
\frac{\mathrm{d} \varrho}{\mathrm{~d} t}=-\varrho \nabla \cdot \mathbf{v} \tag{16.28}
\end{equation*}
$$

which is a form entirely equivalent to the mass conservation law expressed in the form of Eq. (16.17) for a Eulerian observer.

Using the definition of substantial derivative it is useful to derive a relation of general validity for the substantial derivative of the densities and of the specific values of extensive quantities, which will be used further on.

Consider any extensive quantity $\mathcal{E}$ and denote by $e$ and by $\mathcal{E}^{*}$ its density and its specific value, respectively. Recalling Eqs. (16.8) and (16.28) we may write

$$
\begin{equation*}
\frac{\mathrm{d}\left(\varrho \mathcal{E}^{*}\right)}{\mathrm{d} t}=\varrho \frac{\mathrm{d} \mathcal{E}^{*}}{\mathrm{~d} t}+\mathcal{E}^{*} \frac{\mathrm{~d} \varrho}{\mathrm{~d} t}=\varrho \frac{\mathrm{d} \mathcal{E}^{*}}{\mathrm{~d} t}-\left(\mathcal{E}^{*} \varrho\right) \nabla \cdot \mathbf{v} \tag{16.29}
\end{equation*}
$$

but considering the definition of substantial derivative we have

$$
\begin{equation*}
\frac{\mathrm{d}\left(\varrho \mathcal{E}^{*}\right)}{\mathrm{d} t}=\frac{\partial\left(\varrho \mathcal{E}^{*}\right)}{\partial t}+\mathbf{v} \cdot \nabla\left(\varrho \mathcal{E}^{*}\right) \tag{16.30}
\end{equation*}
$$

therefore equating the two expressions we obtain

$$
\begin{equation*}
\varrho \frac{\mathrm{d} \mathcal{E}^{*}}{\mathrm{~d} t}=\frac{\partial\left(\varrho \mathcal{E}^{*}\right)}{\partial t}+\nabla \cdot\left(\varrho \mathcal{E}^{*} \mathbf{v}\right) \tag{16.31}
\end{equation*}
$$

The relevance of this equation is in the physical meaning of the last term, in which the divergence of the vector describing the convective transport of the quantity $\mathcal{E}$ appears. We will meet this term when the convective energy and entropy transport will have to be computed.

### 16.4 Equation of Motion

As we aim to reformulate the equations of thermodynamics for continuous systems it is necessary to recall some fundamental notions in fluid mechanics, in order to characterize the terms representing the work done on the portions of fluid that we will consider.

Let us consider a small mass $\delta m$ located in the point $\mathbf{r}$ at the time $t$, and having the volume $\delta V=\delta m / \varrho$. This small mass will be subject to various kinds of forces.

First, let's consider the forces on the surface of the small mass $\delta m$, that is, the forces acting on the surface of the little volume $\delta V$. If the material is isotropic, nonviscous (and if we can assume the condition of local thermodynamic equilibrium to hold) these forces can be completely described by the pressure from the surrounding environment. In this case they will have as a resultant:

$$
\begin{equation*}
\delta \mathbf{F}_{p}=(-\nabla p) \delta V \tag{16.32}
\end{equation*}
$$

In addition to pressure forces, we assume that there are also forces distributed through the volume of the small mass. These forces are due to the interactions of the various components present in $\delta m$ with external fields. The resultant will be

$$
\begin{equation*}
\delta \mathbf{F}_{\mathrm{vol}}=\sum_{\gamma=1}^{n} \varrho_{\gamma} \delta V \mathbf{F}_{\gamma} \tag{16.33}
\end{equation*}
$$

$\mathbf{F}_{\gamma}$ being the force per unit mass acting on component $\gamma$ in the point $(\mathbf{r}, t)$. Remembering that $\delta m=\varrho \delta V$ and denoting by $\mathbf{v}$ the velocity of the center of mass of $\delta m$ at time $t$ in the point $\mathbf{r}$, the Newtonian equation of motion may be written as

$$
\begin{equation*}
\varrho \frac{\mathrm{d} \mathbf{v}}{\mathrm{~d} t}=-\nabla p+\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{F}_{\gamma} \tag{16.34}
\end{equation*}
$$

### 16.5 The Equation for Energy

Consider a volume $V$ bounded by a closed surface $\Sigma$. We write the total energy contained in the volume $V$ at time $t$ (that is, the total energy of the system at time $t$ ) in the form

$$
\begin{equation*}
U=\int_{V}\left(\varrho U^{*}\right) \mathrm{d} V \tag{16.35}
\end{equation*}
$$

where $U^{*}$ is the specific energy.
The work done per unit time on the system at the instant $t$ :

$$
\begin{equation*}
\frac{\hat{d} W}{\mathrm{~d} t}=\int_{V} \sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{v}_{\gamma} \cdot \mathbf{F}_{\gamma} \mathrm{d} V-\int_{\Sigma} p \mathbf{v} \cdot \mathrm{~d} \boldsymbol{\Sigma} \tag{16.36}
\end{equation*}
$$

The volume integral represents the work per unit time done by the volume forces on the various components; the second term, the integral over the surface, represents the work done by the pressure forces on the boundary of the system.

In addition to the work done by external forces, in order to determine the change in the energy of the system, we must take into account also of the amount of energy transferred, per unit of time, from the outside through the boundary. This contribution had already been defined in Sect. 14.1.1 by Eq. (14.3). If we divide the infinitesimal amount of transferred energy $\hat{d} \Phi$ by the infinitesimal time interval $\mathrm{d} t$ we define the total energy flux density vector $\mathbf{J}_{u}$ by the relation:

$$
\begin{equation*}
\frac{\hat{d} \Phi}{\mathrm{~d} t}=-\int_{\Sigma} \mathbf{J}_{u} \cdot \mathrm{~d} \boldsymbol{\Sigma} \tag{16.37}
\end{equation*}
$$

The vector $\mathbf{J}_{u}$ is defined point by point at the surface $\Sigma$ of the volume $V$ which defines the system. The First Principle of Thermodynamics will, therefore, be written as

$$
\begin{equation*}
\frac{\mathrm{d} U}{\mathrm{~d} t}=\frac{\hat{d} W}{\mathrm{~d} t}+\frac{\hat{d} \Phi}{\mathrm{~d} t} \tag{16.38}
\end{equation*}
$$

which becomes

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{~d} t} \int_{V}\left(\varrho U^{*}\right) \mathrm{d} V=\int_{V} \sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{v}_{\gamma} \cdot \mathbf{F}_{\gamma} \mathrm{d} V-\int_{\Sigma} p \mathbf{v} \cdot \mathrm{~d} \boldsymbol{\Sigma}-\int_{\Sigma} \mathbf{J}_{u} \cdot \mathrm{~d} \boldsymbol{\Sigma} \tag{16.39}
\end{equation*}
$$

By making use of the Gauss' theorem to transform the surface integrals into volume integrals, we obtain

$$
\begin{equation*}
\frac{\partial\left(\varrho U^{*}\right)}{\partial t}=\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{v}_{\gamma} \cdot \mathbf{F}_{\gamma}-\nabla \cdot(p \mathbf{v})-\nabla \cdot \mathbf{J}_{u} \tag{16.40}
\end{equation*}
$$

and making use of Eq.(16.31) in which the specific quantity is the specific energy $U^{*}$, we have

$$
\begin{equation*}
\varrho \frac{\mathrm{d} U^{*}}{\mathrm{~d} t}=\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{v}_{\gamma} \cdot \mathbf{F}_{\gamma}-\nabla \cdot(p \mathbf{v})-\nabla \cdot \mathbf{J}_{u}+\nabla \cdot\left(\varrho U^{*} \mathbf{v}\right) \tag{16.41}
\end{equation*}
$$

Recalling the definition Eq. (16.23) for the diffusion flows $\varrho_{\gamma} \mathbf{v}_{\gamma}=\mathbf{J}_{\gamma}+\varrho_{\gamma} \mathbf{v}$, the above relation becomes

$$
\begin{equation*}
\varrho \frac{\mathrm{d} U^{*}}{\mathrm{~d} t}=\left(\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{F}_{\gamma}\right) \cdot \mathbf{v}+\sum_{\gamma=1}^{n}\left(\mathbf{J}_{\gamma} \cdot \mathbf{F}_{\gamma}\right)-\nabla \cdot(p \mathbf{v})-\nabla \cdot\left(\mathbf{J}_{u}-\varrho U^{*} \mathbf{v}\right) \tag{16.42}
\end{equation*}
$$

From the equation of motion Eq. (16.34) we have

$$
\begin{equation*}
\left(\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{F}_{\gamma}\right) \cdot \mathbf{v}=\varrho \mathbf{v} \cdot \frac{\mathrm{d} \mathbf{v}}{\mathrm{~d} t}+\mathbf{v} \cdot \nabla p \tag{16.43}
\end{equation*}
$$

and then after substitution and a little algebra, we obtain

$$
\begin{equation*}
\varrho \frac{\mathrm{d} U^{*}}{\mathrm{~d} t}=\varrho \frac{\mathrm{d}}{\mathrm{~d} t}\left(\frac{1}{2} \mathbf{v}^{2}\right)+\sum_{\gamma=1}^{n}\left(\mathbf{J}_{\gamma} \cdot \mathbf{F}_{\gamma}\right)-p \nabla \cdot \mathbf{v}-\nabla \cdot\left(\mathbf{J}_{u}-\varrho U^{*} \mathbf{v}\right) \tag{16.44}
\end{equation*}
$$

Equation (16.44) gives the lagrangian time derivative of the specific energy and it is important to highlight two points.

One is the following: the first term on the second member, $\mathbf{v}^{2} / 2$, is the specific kinetic energy due to the overall, i.e., of the center of mass, motion. Since the entropy does not depend on the system being at rest or being in motion, it will be necessary to define the specific internal energy as the total specific energy minus the specific, center of mass, kinetic energy. The necessity of this new definition comes from the requirement that in the Fundamental Relation per unit mass Eq. (16.55) the center of mass kinetic energy does not influence the value of the entropy hence only the internal energy must be relevant. Then Eq. (16.44) may be written in the form

$$
\begin{equation*}
\varrho \frac{\mathrm{d}\left(U^{*}-\mathbf{v}^{2} / 2\right)}{\mathrm{d} t}=\sum_{\gamma=1}^{n}\left(\mathbf{J}_{\gamma} \cdot \mathbf{F}_{\gamma}\right)-p \nabla \cdot \mathbf{v}-\nabla \cdot\left(\mathbf{J}_{u}-\varrho U^{*} \mathbf{v}\right) . \tag{16.45}
\end{equation*}
$$

It is necessary to comment on the last term in Eq. (16.44). It expresses the divergence of a new vector resulting from the difference between the total energy flux and the convective energy flux. This new vectorial quantity will be denoted by $\mathbf{J}_{q}$ and will be called, by convention, the heat flux density in a generalized sense. It is defined as

$$
\begin{equation*}
\mathbf{J}_{q}=\mathbf{J}_{u}-\varrho U^{*} \mathbf{v} \tag{16.46}
\end{equation*}
$$

This designation is justified if we consider the meaning of the vector

$$
\begin{equation*}
\mathbf{J}_{u, \text { conv }}=\varrho U^{*} \mathbf{v} \tag{16.47}
\end{equation*}
$$

It is the energy carried by the convective motion of matter that crosses the border. As it is evident, for closed systems in which the transport of matter is inhibited, $\mathbf{J}_{q}$ coincides with the already well-known flux density of heat.

Furthermore Eq. (16.45) needs another comment. It expresses the total time derivative of the specific energy to which the term describing the kinetic energy of the bulk motion is subtracted. This is what defines the internal specific energy. This is precisely the term which enters in the equation for the entropy variations (as will be commented in the following section) then from now on the notation $U^{*}$ will refer to the internal specific energy, Taking this warning in mind, the new expression for the relation which summarizes the First Principle for the specific internal energy is

$$
\begin{equation*}
\varrho \frac{\mathrm{d} U^{*}}{\mathrm{~d} t}=\sum_{\gamma=1}^{n}\left(\mathbf{J}_{\gamma} \cdot \mathbf{F}_{\gamma}\right)-p \boldsymbol{\nabla} \cdot \mathbf{v}-\boldsymbol{\nabla} \cdot \mathbf{J}_{q} . \tag{16.48}
\end{equation*}
$$

### 16.6 The Equation for Entropy

Consider a phase of volume $V$ in a state of internal equilibrium. All intensive properties like density, pressure, and temperature are uniform throughout the system and if some instantaneous perturbation destroys this configuration, internal processes are activated in order to reestablish a new homogeneous state. The time interval required to reabsorb the perturbation is of the order of:

$$
\begin{equation*}
\tau_{\mathrm{r}} \simeq V^{1 / 3} / \mathrm{v}_{\text {sound }}, \tag{16.49}
\end{equation*}
$$

where $\mathrm{v}_{\text {sound }}$ is the speed of sound and $\tau_{\mathrm{r}}$ is called relaxation time of the system. If we consider a system of volume $V$ as composed by a large number of still macroscopic subsystems of much smaller volume, we expect that, normally, each subsystem achieves a state of local equilibrium in a much shorter time lapse then the system as a whole. In other words, in its way toward equilibrium the large system can be well described by a collection of small parts instantaneously in local equilibrium. When this condition is achieved we will talk about Local Thermodynamic Equilibrium (LTE) and, in this case, it will be possible to consider every intensive parameter as described by continuous functions of the space-time coordinates. Therefore, in order to proceed, we must bear in mind the following points:

1. All state variables are defined locally;
2. The entropy depends on the other state variables in the same way as in a state of equilibrium, that is, at every point the same fundamental equation that we have observed at equilibrium, holds;
3. In particular, as a consequence of the preceding statement, in every point the same equation of state that we have found for equilibrium states, applies.

To formalize the preceding requirements consider a small mass $\delta m$ located in the position $\mathbf{r}$ at the time $t$. Equation (4.23) can be rewritten in the form

$$
\begin{equation*}
T \mathrm{~d} S=\mathrm{d} U+p \mathrm{~d} V-\sum_{\gamma=1}^{n} \mu_{\gamma} \mathrm{d} n_{\gamma} \tag{16.50}
\end{equation*}
$$

must be applied to the small mass for which all extensive quantities are written in the general form

$$
\begin{equation*}
\delta \mathcal{E}=\mathcal{E}^{*} \delta m \tag{16.51}
\end{equation*}
$$

where $\mathcal{E}^{*}(\mathbf{r}, t)$ is the specific value of the state parameter $\mathcal{E}$ in the point $(\mathbf{r}, t)$.
For our purpose let us define, respectively, the specific entropy, the specific energy, the specific volume:

$$
\begin{equation*}
S^{*}=\frac{\delta S}{\delta m}, \quad U^{*}=\frac{\delta U}{\delta m}, \quad V^{*}=\frac{\delta V}{\delta m} \tag{16.52}
\end{equation*}
$$

Further let $c_{\gamma}$ be the mass concentration of component $\gamma\left(c_{\gamma}=\delta m_{\gamma} / \delta m\right)$ and define the symbol $\mu_{\gamma}^{*}$, called specific chemical potential of component $\gamma$, by the relation:

$$
\begin{equation*}
\mu_{\gamma}^{*}=\frac{\mu_{\gamma}}{M_{\gamma}} \tag{16.53}
\end{equation*}
$$

then the fundamental equation becomes

$$
\begin{equation*}
T \mathrm{~d} S^{*}=\mathrm{d} U^{*}+p \mathrm{~d} V^{*}-\sum_{\gamma=1}^{n} \mu_{\gamma}^{*} \mathrm{~d} c_{\gamma} \tag{16.54}
\end{equation*}
$$

The Fundamental Relation given in Eq. (16.54) that appears in the above differential form will be written, in finite terms:

$$
\begin{equation*}
S^{*}=S^{*}\left(U^{*}, V^{*}, c_{\gamma}\right) \tag{16.55}
\end{equation*}
$$

### 16.6.1 Entropy Balance in Continuous Systems

Consider the fundamental equation applied to the unit mass (Eq. (16.54)) and consider the rate at which the changes occur

$$
\begin{equation*}
T \frac{\mathrm{~d} S^{*}}{\mathrm{~d} t}=\frac{\mathrm{d} U^{*}}{\mathrm{~d} t}+p \frac{\mathrm{~d} V^{*}}{\mathrm{~d} t}-\sum_{\gamma=1}^{n} \mu_{\gamma}^{*} \frac{\mathrm{~d} c_{\gamma}}{\mathrm{d} t} \tag{16.56}
\end{equation*}
$$

Inserting Eq. (16.48) we obtain

$$
\begin{equation*}
T \frac{\mathrm{~d} S^{*}}{\mathrm{~d} t}=\frac{1}{\varrho} \sum_{\gamma=1}^{n} \mathbf{J}_{\gamma} \mathbf{F}_{\gamma}-\frac{p}{\varrho} \nabla \cdot \mathbf{v}-\frac{1}{\varrho} \nabla \cdot \mathbf{J}_{q}+p \frac{\mathrm{~d} V^{*}}{\mathrm{~d} t}-\sum_{\gamma=1}^{n} \mu_{\gamma}^{*} \frac{\mathrm{~d} c_{\gamma}}{\mathrm{d} t} \tag{16.57}
\end{equation*}
$$

Recalling the definition of specific volume $V^{*}=1 / \varrho$ and the continuity equation in the form Eq. (16.28), it is straightforward to show that

$$
\begin{equation*}
p \frac{\mathrm{~d} V^{*}}{\mathrm{~d} t}=\frac{p}{\varrho} \nabla \cdot \mathbf{v} \tag{16.58}
\end{equation*}
$$

and then the entropy equation simplifies to

$$
\begin{equation*}
T \frac{\mathrm{~d} S^{*}}{\mathrm{~d} t}=\frac{1}{\varrho} \sum_{\gamma=1}^{n} \mathbf{J}_{\gamma} \cdot \mathbf{F}_{\gamma}-\frac{1}{\varrho} \nabla \cdot \mathbf{J}_{q}-\sum_{\gamma=1}^{n} \mu_{\gamma}^{*} \frac{\mathrm{~d} c_{\gamma}}{\mathrm{d} t} \tag{16.59}
\end{equation*}
$$

A further step is to transform the last term of the second member in a form in which it appears explicitly the contribution of chemical reactions. For this purpose we use Eq. (16.31) where $\mathcal{E}=m_{\gamma}$ and therefore the associated specific quantity is the mass concentration $c_{\gamma}$, so that

$$
\begin{equation*}
\varrho \frac{\mathrm{d} c_{\gamma}}{\mathrm{d} t}=\frac{\partial \varrho_{\gamma}}{\partial t}+\nabla \cdot\left(\varrho_{\gamma} \mathbf{v}\right) \tag{16.60}
\end{equation*}
$$

With regard to the first term of the second member we use Eq. (16.20) and recalling the definition of the diffusion fluxes Eq. (16.23) we obtain

$$
\begin{equation*}
\varrho \frac{\mathrm{d} c_{\gamma}}{\mathrm{d} t}=-\nabla \cdot \mathbf{J}_{\gamma}+v_{\gamma}^{\prime} j_{\mathrm{ch}} \tag{16.61}
\end{equation*}
$$

Equation (16.59) for the entropy can now be written in the form

$$
\begin{equation*}
\varrho \frac{\mathrm{d} S^{*}}{\mathrm{~d} t}=\frac{1}{T} \sum_{\gamma=1}^{n} \mathbf{J}_{\gamma} \cdot \mathbf{F}_{\gamma}-\frac{1}{T} \nabla \cdot \mathbf{J}_{q}+\frac{1}{T} \sum_{\gamma=1}^{n} \mu_{\gamma}^{*} \boldsymbol{\nabla} \cdot \mathbf{J}_{\gamma}-\frac{1}{T} j_{\mathrm{ch}} \sum_{\gamma=1}^{n} v_{\gamma}^{\prime} \mu_{\gamma}^{*} . \tag{16.62}
\end{equation*}
$$

The last term of the second member can be recognized immediately as the affinity of the reaction:

$$
\begin{equation*}
-\sum_{\gamma=1}^{n} v_{\gamma}^{\prime} \mu_{\gamma}^{*}=-\sum_{\gamma=1}^{n} v_{\gamma} \mu_{\gamma}=\mathcal{A} \tag{16.63}
\end{equation*}
$$

As regards the other terms that appear in the form $f \nabla \cdot \mathbf{b}$ where $f$ is a scalar and $\mathbf{b}$ is a generic vector, they must be reported to the form

$$
\begin{equation*}
f \nabla \cdot \mathbf{b}=\nabla \cdot(f \mathbf{b})-\mathbf{b} \cdot \nabla f \tag{16.64}
\end{equation*}
$$

Working in this way we get to formula:

$$
\begin{equation*}
\varrho \frac{\mathrm{d} S^{*}}{\mathrm{~d} t}=-\nabla \cdot \mathbf{J}_{s}^{\prime}+\pi \tag{16.65}
\end{equation*}
$$

where

$$
\begin{equation*}
\mathbf{J}_{s}^{\prime}=\frac{\mathbf{J}_{q}-\sum_{\gamma=1}^{n} \mu_{\gamma}^{*} \mathbf{J}_{\gamma}}{T} \tag{16.66}
\end{equation*}
$$

and

$$
\begin{equation*}
\pi=\mathbf{J}_{q} \cdot \mathbf{X}_{q}+\sum_{\gamma=1}^{n} \mathbf{J}_{\gamma} \cdot \mathbf{X}_{\gamma}+j_{\mathrm{ch}} X_{\mathrm{ch}} \tag{16.67}
\end{equation*}
$$

In this equation it is useful to report the expressions for individual generalized forces explicitly:

$$
\begin{align*}
& \mathbf{X}_{q}=\nabla\left(\frac{1}{T}\right),  \tag{16.68}\\
& \mathbf{X}_{\gamma}=\frac{1}{T}\left[\mathbf{F}_{\gamma}-T \cdot \nabla\left(\frac{\mu_{\gamma}^{*}}{T}\right)\right],  \tag{16.69}\\
& X_{\mathrm{ch}}=\frac{\mathcal{A}}{T} \tag{16.70}
\end{align*}
$$

The vector defined in Eq. (16.66) undoubtedly has the meaning of entropy flux that is of entropy transmitted per unit time through the border $\Sigma$ of the system but, as we shall see now, it does not represent the whole entropy which flows through the border but just one part of it. To understand this very important point we need to go back to the definition of entropy of the system:

$$
\begin{equation*}
S=\int_{V}\left(\varrho S^{*}\right) \mathrm{d} V \tag{16.71}
\end{equation*}
$$

and calculate the variation per unit time

$$
\begin{equation*}
\frac{\mathrm{d} S}{\mathrm{~d} t}=\int_{V} \frac{\partial\left(\varrho S^{*}\right)}{\partial t} \mathrm{~d} V=\frac{\hat{d}_{\mathrm{i}} S}{\mathrm{~d} t}+\frac{\hat{d}_{\mathrm{e}} S}{\mathrm{~d} t} \tag{16.72}
\end{equation*}
$$

If, once again, we make use of Eq. (16.31):

$$
\begin{equation*}
\frac{\partial\left(\varrho S^{*}\right)}{\partial t}=\varrho \frac{\mathrm{d} S^{*}}{\mathrm{~d} t}-\nabla \cdot\left(\varrho S^{*} \mathbf{v}\right) \tag{16.73}
\end{equation*}
$$

we obtain

$$
\begin{align*}
\frac{\mathrm{d} S}{\mathrm{~d} t} & =-\int_{V} \nabla \cdot \mathbf{J}_{s}^{\prime}+\int_{V} \pi \mathrm{~d} V-\int_{V} \nabla \cdot\left(\varrho S^{*} \mathbf{v}\right) \mathrm{d} V  \tag{16.74}\\
& =-\int_{V} \mathbf{J}_{s, \text { tot }} \cdot \mathrm{d} \boldsymbol{\Sigma}+\int_{V} \pi \mathrm{~d} V  \tag{16.75}\\
& =\frac{\hat{d}_{\mathrm{e}} S}{\mathrm{~d} t}+\frac{\hat{d}_{\mathrm{i}} S}{\mathrm{~d} t} \tag{16.76}
\end{align*}
$$

From this we get

$$
\begin{align*}
& \frac{\hat{d}_{\mathrm{i}} S}{\mathrm{~d} t}=\int_{V} \pi \mathrm{~d} V  \tag{16.77}\\
& \frac{\hat{d}_{\mathrm{e}} S}{\mathrm{~d} t}=-\int_{V} \mathbf{J}_{S, \text { tot }} \cdot \mathrm{d} \boldsymbol{\Sigma} \tag{16.78}
\end{align*}
$$

and

$$
\begin{equation*}
\mathbf{J}_{s, \text { tot }}=\frac{\mathbf{J}_{q}-\sum_{\gamma=1}^{n} \mu_{\gamma}^{*} \mathbf{J}_{\gamma}}{T}+\varrho S^{*} \mathbf{v} \tag{16.79}
\end{equation*}
$$

As we see, in order to obtain the total flux of entropy we had, in addition, to take into account the convective transport term $\varrho S^{*} \mathbf{v}$.

### 16.6.2 The Entropy Production

From the previous relations it is clear that the quantity $\pi$ defined in Eq. (16.67) together with Eqs. (16.68)-(16.70) has exactly the meaning of entropy production per unit volume. This means that $\pi \delta V$ is the production of entropy in the system defined by the small volume $\delta V$.

The production of entropy is still given by the sum of various terms each of which is the product of a generalized flux, which gives the name to the irreversible process, times an associated generalized force.

The term that comes closest to its counterpart already studied in the discontinuous systems approximation, is the term related to the chemical reaction: $j_{\mathrm{ch}} \delta V$ is exactly the rate of the chemical reaction within the volume considered and $X_{\text {ch }}$ is exactly the relative generalized force already seen.

The first term in the second member of Eq. (16.67) describes a heat flow, in the generalized sense, and the corresponding force is virtually identical to the corresponding term $\Delta(1 / T)$ already seen previously.

The second term in Eq.(16.67) describes the diffusion motions of the individual components with respect to the velocity of the center of mass (bulk motion of the fluid). The corresponding fluxes are

$$
\begin{equation*}
\mathbf{J}_{\gamma}=\varrho_{\gamma}\left(\mathbf{v}_{\gamma}-\mathbf{v}\right) \tag{16.80}
\end{equation*}
$$

and the corresponding generalized forces are given in Eq.(16.69). Various causes contribute to determining the force related to the diffusion of each component: external volume forces that act directly on the component itself, a possible temperature gradient and possible gradients of concentrations (the latter is contained in the gradients of chemical potentials), but it is necessary to note that these causes concur, in a well-determined way, to compose a unique force.

This result allows us to study the correlations between the effects of each partial cause in absolute generality that is, regardless of the modeling. A very clear and interesting example is provided by the relationship between the diffusion coefficient in a two-component system and the mobility coefficient under an external volume force. This relationship is known as Einstein relation.

Before addressing this problem we need to study some general properties that arise in the condition known as mechanical equilibrium.

### 16.6.3 Mechanical Equilibrium

The expression "mechanical equilibrium" denotes a situation in which the motion of the fluid is point-by-point stationary:

$$
\begin{equation*}
\frac{\mathrm{d} \mathbf{v}(\mathbf{r})}{\mathrm{d} t}=0 \tag{16.81}
\end{equation*}
$$

For example, if we have an ionic solution and, at a given instant, we apply a constant electric field, after a short initial phase a configuration in which the various components will flow with constant speed will be established. This is the situation named condition of mechanical equilibrium.

The same thing happens when we apply a potential difference in a conductor: Ohm's law refers, in fact, to a configuration of "mechanical equilibrium". This approximation is justified by the fact that the timescale for the mechanical equilibrium to be reached is very short compared with the timescales of the thermodynamic processes we are studying and, accordingly, represents the typical situation in which the thermodynamical relations will be applied.

Prigogine (1947) showed that in this condition and in the absence of temperature gradients, the following relation applies [25]:

$$
\begin{equation*}
\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{X}_{\gamma}=0 \tag{16.82}
\end{equation*}
$$

This relation is important because, in the expression of the entropy production Eq. (16.67), it allows us to replace the fluxes $\mathbf{J}_{\gamma}$, which describe the diffusion with respect to the center of mass motion, with fluxes describing the motion of the different components with respect to any other reference velocity. The utility of this will be shown in Sect. 16.6.4.

In order to prove Eq. (16.82) let us refer to the form given in Eq. (16.90), for the forces and obtain the following expression:

$$
\begin{equation*}
\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{X}_{\gamma}=\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{F}_{\gamma}-\sum_{\gamma=1}^{n} \varrho_{\gamma} \nabla \mu_{\gamma}^{*} \tag{16.83}
\end{equation*}
$$

In general we can write the chemical potentials as functions of temperature, pressure and concentrations, that is $\mu_{\gamma}^{*}=\mu_{\gamma}^{*}\left(T, p, c_{1}, c_{2}, \ldots, c_{n}\right)$ and then the last term of the above equation can be rewritten as

$$
\begin{equation*}
\sum_{\gamma=1}^{n} \varrho_{\gamma} \nabla \mu_{\gamma}^{*}=\varrho \sum_{\gamma, \gamma^{\prime}=1}^{n} c_{\gamma}\left(\frac{\partial \mu_{\gamma}^{*}}{\partial c_{\gamma^{\prime}}}\right) \nabla c_{\gamma^{\prime}}+\varrho \sum_{\gamma=1}^{n} c_{\gamma}\left(\frac{\partial \mu_{\gamma}^{*}}{\partial p}\right) \nabla p \tag{16.84}
\end{equation*}
$$

The first term of the second member is zero for the Gibbs-Duhem relation and this shall be proved in Sect. 16.9. As regards the third term recall that

$$
\begin{equation*}
\left(\frac{\partial \mu_{\gamma}^{*}}{\partial p}\right)=V_{\gamma}^{*} \tag{16.85}
\end{equation*}
$$

$V_{\gamma}^{*}$ being the partial specific volume of component $\gamma$, then we obtain

$$
\begin{equation*}
\varrho \sum_{\gamma=1}^{n} c_{\gamma}\left(\frac{\partial \mu_{\gamma}^{*}}{\partial p}\right)=\varrho \sum_{\gamma=1}^{n} c_{\gamma} V_{\gamma}^{*}=\varrho V^{*}=1 \tag{16.86}
\end{equation*}
$$

$V^{*}$ being the specific volume of the fluid, hence we have

$$
\begin{equation*}
\sum_{\gamma=1}^{n} \varrho_{\gamma} \nabla \mu_{\gamma}^{*}=\nabla p \tag{16.87}
\end{equation*}
$$

From the equation of motion Eq. (16.34) and requiring the condition of mechanical equilibrium, we obtain

$$
\begin{equation*}
-\nabla p+\sum_{\gamma} \varrho_{\gamma} \mathbf{F}_{\gamma}=0 \tag{16.88}
\end{equation*}
$$

In conclusion we find

$$
\begin{equation*}
\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{X}_{\gamma}=\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{F}_{\gamma}-\sum_{\gamma=1}^{n} \varrho_{\gamma} \nabla \mu_{\gamma}^{*}=0 \tag{16.89}
\end{equation*}
$$

In this demonstration, we have assumed that the temperature is uniform; it may be extended to a more general situation but the issue will not be further pursued.

### 16.6.4 The Einstein Relation Between Mobility and Diffusion Coefficient

Let us go back to the entropy production density expressed by Eq. (16.67) and restrict ourselves to the case of uniform temperature and with no chemical reactions. Then the entropy produnction density reduces to $\pi=\sum_{\gamma=1}^{n} \mathbf{J}_{\gamma} \cdot \mathbf{X}_{\gamma}$ and the forces $\mathbf{X}_{\gamma}$ will have the form

$$
\begin{equation*}
\mathbf{X}_{\gamma}=\frac{1}{T}\left(\mathbf{F}_{\gamma}-\nabla \mu_{\gamma}^{*}\right) \tag{16.90}
\end{equation*}
$$

It is important to underline that the form Eq. (16.90) shows clearly how volume forces and concentration gradients combine to give one resultant force.

The two particular situations in which one of these two causes is absent, leads us to consider on the one hand the differential motion of one component relative to
the others due to the presence of an external force but with uniform concentration and, on the other, the diffusion flow of one component relative to the others in the absence of an external force but in the presence of a concentration gradient. The phenomenological study of these two situations leads us to define two phenomenological coefficients: the mobility coefficient in the former case and the diffusion coefficient in the latter.

Owing to Eq. (16.82) the density of entropy production gets the form

$$
\begin{equation*}
\pi=\sum_{\gamma=1}^{n} \varrho_{\gamma}\left(\mathbf{v}_{\gamma}-\mathbf{v}\right) \cdot \mathbf{X}_{\gamma}=\sum_{\gamma=1}^{n} \varrho_{\gamma} \mathbf{v}_{\gamma} \cdot \mathbf{X}_{\gamma} \tag{16.91}
\end{equation*}
$$

If we select an arbitrary reference velocity $\mathbf{a}$ and we define new fluxes with respect to it as

$$
\begin{equation*}
\mathbf{J}_{\gamma}^{(a)}=\varrho_{\gamma}\left(\mathbf{v}_{\gamma}-\mathbf{a}\right), \tag{16.92}
\end{equation*}
$$

we see that, owing to Eq. (16.82), the entropy production density, in the condition of mechanical equilibrium, may be expressed as a function of these new fluxes:

$$
\begin{equation*}
\pi=\sum_{\gamma=1}^{n} \mathbf{J}_{\gamma}^{(a)} \cdot \mathbf{X}_{\gamma} \tag{16.93}
\end{equation*}
$$

Consider now, for simplicity, a fluid composed of two components only and let's write the entropy production density. According to Eq. (16.91):

$$
\begin{equation*}
\pi=\varrho_{1} \mathbf{v}_{1} \cdot \mathbf{X}_{1}+\varrho_{2} \mathbf{v}_{2} \cdot \mathbf{X}_{2} \tag{16.94}
\end{equation*}
$$

We choose now as the reference velocity, the value $\mathbf{a}=\mathbf{v}_{2}$. The entropy production density becomes

$$
\begin{equation*}
\pi=\varrho_{1}\left(\mathbf{v}_{1}-\mathbf{v}_{2}\right) \cdot \mathbf{X}_{1} . \tag{16.95}
\end{equation*}
$$

Here the flux $\mathbf{J}_{1}=\varrho_{1}\left(\mathbf{v}_{1}-\mathbf{v}_{2}\right)$ now describes the diffusion motion of the component 1 relative to component 2 . The corresponding force will be written as

$$
\begin{equation*}
\mathbf{X}_{1}=\frac{1}{T}\left(\mathbf{F}_{1}-\nabla \mu_{1}^{*}\right)=\frac{1}{T} \frac{1}{M_{1}}\left(M_{1} \mathbf{F}_{1}-\nabla \mu_{1}\right) . \tag{16.96}
\end{equation*}
$$

If we now denote by $C_{1}$ the molar concentration of component 1 (mole/volume and therefore $\varrho_{1}=M_{1} C_{1}$ ) and denote by $\mathbf{F}_{\mathrm{m}, 1}=M_{1} \mathbf{F}_{1}$ the molar force i.e., the force acting on one mole of component 1 , the linear relation between flux and force will be written as

$$
\begin{equation*}
C_{1}\left(\mathbf{v}_{1}-\mathbf{v}_{2}\right)=\frac{L}{T}\left(\mathbf{F}_{\mathrm{m}, 1}-\nabla \mu_{1}\right) . \tag{16.97}
\end{equation*}
$$

In order to go further, let us resort to the expression for the chemical potential already seen for ideal solutions, in which the concentration dependence is put in evidence:

$$
\begin{equation*}
\mu(p, T)=\eta(p, T)+R T \ln C \tag{16.98}
\end{equation*}
$$

In this approximation the linear relationship between flux and force becomes

$$
\begin{equation*}
C_{1}\left(\mathbf{v}_{1}-\mathbf{v}_{2}\right)=-\frac{L}{T} \frac{R T}{C_{1}}\left(\nabla C_{1}-\frac{C_{1}}{R T} \mathbf{F}_{\mathrm{m}, 1}\right) \tag{16.99}
\end{equation*}
$$

In the following, we consider two particular situations.

## Mobility

System at uniform concentration (as well as at uniform $T$ and $p$ ) then Eq.(16.99) becomes

$$
\begin{equation*}
\mathbf{v}_{1}-\mathbf{v}_{2}=\frac{L}{T C_{1}} \mathbf{F}_{\mathrm{m}, 1} \tag{16.100}
\end{equation*}
$$

Experimentally it is seen that, for fields not too intense, a constant rate of migration of a component relative to the other settles quickly and that the relative velocity is proportional to the intensity of the specific volume force. We define mobility or mobility coefficient of component 1 relative to component 2 , the parameter $\mu_{\mathrm{d}}$ defined by the equation:

$$
\begin{equation*}
\mathbf{v}_{1}-\mathbf{v}_{2}=\mu_{\mathrm{d}} \mathbf{F}_{\mathrm{m}, 1} \tag{16.101}
\end{equation*}
$$

## Diffusion Coefficient

Consider now the other particular situation, the one in which there is a nonuniform concentration $(\nabla C \neq 0)$ of component 1 but the external volume forces are absent $\left(\mathbf{F}_{\mathrm{m}, 1}=0\right)$. The diffusion coefficient describes how quickly an inhomogeneous concentration tends to be reabsorbed into a uniform configuration. Fick's law defines the diffusion coefficient $\mathcal{D}$, with the relation:

$$
\begin{equation*}
C_{1}\left(\mathbf{v}_{1}-\mathbf{v}_{2}\right)=-\mathcal{D} \nabla C_{1} \tag{16.102}
\end{equation*}
$$

in which the diffusion velocity is related to the concentration gradient.
Now we can express each of these two coefficients as a function of the same phenomenological coefficient $L$ that appears in Eq.(16.99). This demonstrates the power of the thermodynamic approach: two phenomena which are generally treated as independent, appear to be two particular cases of one phenomenon in which the force has a well determined overall expression.

As regards the mobility coefficient, from the comparison we have

$$
\begin{equation*}
\mu_{\mathrm{d}}=\frac{L}{T C_{1}}, \tag{16.103}
\end{equation*}
$$

while by analogy, for the diffusion coefficient we get

$$
\begin{equation*}
\mathcal{D}=\frac{L R}{C_{1}} . \tag{16.104}
\end{equation*}
$$

## Einstein Relation

Comparing the Eqs.(16.103) and (16.104) we find a very general relationship between the mobility coefficient and the diffusion coefficient:

$$
\begin{equation*}
\mathcal{D}=R T \mu_{\mathrm{d}} . \tag{16.105}
\end{equation*}
$$

This relation was first established by Einstein.

### 16.7 Thermoelectric Phenomena

This section is devoted to the study of thermoelectric phenomena and to the fundamental role played by the Onsager theory of irreversible processes. We know that a temperature gradient in a material gives rise to a heat flux. More precisely, if only a temperature gradient is present the heat flux density is locally described by the Fourier theory of heat conduction according to which

$$
\begin{equation*}
\mathbf{J}_{q}=-\lambda \nabla T . \tag{16.106}
\end{equation*}
$$

This relation defines the heat conductivity $\lambda$ of the material. It must be remembered that the heat conductivity is defined in the condition when no other effect is present and in particular, as regards the matters dealt within this section, in the absence of electric currents.

Likewise, the electric conductivity $\sigma_{\mathrm{el}}$ of a material is defined by the relation:

$$
\begin{equation*}
\mathbf{j}=\sigma_{\mathrm{el}} \mathbf{E} \tag{16.107}
\end{equation*}
$$

for isotropic materials and for an isothermal configuration. The same relation for stationary or slowly varying fields can be written as

$$
\begin{equation*}
\mathbf{j}=-\sigma_{\mathrm{el}} \nabla \psi \tag{16.108}
\end{equation*}
$$

Fig. 16.1 A thermocouple is a circuit formed by two wires $A$ and $B$ made of different metals. They are welded in the two junctions $G_{1}$ and $G_{2}$. Wire A is continuous from $G_{1}$ to $G_{2}$ while the wire B is made by two sections coming out of the junctions $G_{1}$ and $G_{2}$ and ending in points P and Q , respectively

$\psi$ being the electrostatic potential. When temperature gradients and electric fields are simultaneously present, interference effects become dominant, the single-process theories no longer apply and we have to refer to the Onsager theory of irreversible processes developed in this and in the previous chapters for a deep, model independent, understanding.

Before entering into the study of the dynamic equations that govern the thermoelectric effects it is appropriate to define the parameters that describe the behavior of the different conductors when particular conditions are realized. In order to measure the relevant quantities we want to deal with, we refer to a thermocouple as described in Fig. 16.1. The two junctions $G_{1}$ and $G_{2}$ are in thermal contact with two heat reservoirs at temperatures $T$ and $T+\Delta T$, respectively. They may ensure either a temperature gradient or an isothermal condition in wire A while the two free ends P and Q of wire B are at the same temperature $T_{0}$ or they may be used either to measure the potential difference between them or to inject the desired electric current in the circuit.

### 16.7.1 Seebeck Effect—Thermoelectric Power

When the temperature in a conductor is nonuniform an electric field appears. This effect is to be expected since the chemical potential of the electrons depends both on their number density and on the temperature, so to compensate for a nonuniformity in the latter it is necessary to realize nonuniformity in the distribution of the charges. We define absolute thermoelectric power of the conductor A the quantity $\omega_{A}$ defined by

$$
\begin{equation*}
E=-\omega_{A} \frac{\partial T}{\partial x} . \tag{16.109}
\end{equation*}
$$

where, for simplicity, we have adopted a one-dimensional formalism.
A potential difference between point $P$ and $Q$ of the thermocouple is expected and can be evaluated in terms of the absolute thermoelectric powers of the two metals and as a function of the temperature difference of the thermocouple $\Delta T$.

Suppose that P and Q are at the same temperature (for instance $T_{0}$ ). In order to calculate the potential difference we shall integrate the electric field Eq. (16.109) along the path $\mathrm{P}-G_{1}-G_{2}-\mathrm{Q}$ as seen in Fig. 16.1.

The path integral is changed into an integral in the temperature variation along the circuit, then we have

$$
\begin{align*}
& V_{P}-V_{Q}=-\left[\int_{T_{o}}^{T} \omega_{B} \mathrm{~d} T+\int_{T}^{T+\Delta T} \omega_{A} \mathrm{~d} T+\int_{T+\Delta T}^{T_{0}} \omega_{B} \mathrm{~d} T\right]  \tag{16.110}\\
& V_{P Q}=V_{P}-V_{Q}=\int_{T}^{T+\Delta T}\left(\omega_{B}-\omega_{A}\right) \mathrm{d} T=\int_{T}^{T+\Delta T} \omega_{A B} \mathrm{~d} T \tag{16.111}
\end{align*}
$$

with

$$
\begin{equation*}
\omega_{A B}=\omega_{B}-\omega_{A} \tag{16.112}
\end{equation*}
$$

is called thermoelectric power of the thermocouple. It is important to emphasize that the potential difference $V_{P Q}$, sometimes called thermoelectric emf, of the thermocouple, does not depend on the temperature $T_{0}$ and, therefore, Eq. (16.111) gives the following operational definition of the thermoelectric power of the thermocouple:

$$
\begin{equation*}
\omega_{A B}=\frac{\mathrm{d} V_{P Q}}{\mathrm{~d} T} . \tag{16.113}
\end{equation*}
$$

This effect was first studied by Seebeck in 1821. If we construct a thermocouple combining wire A with a superconductor as wire B, Eq.(16.113) gives us the way to measure the absolute thermoelectric power of metal A. This is because the absolute thermoelectric power of a superconductor (below the Curie temperature) is substantially zero.

### 16.7.2 Peltier Coefficient—Phenomenology

Consider the thermocouple in Fig. 16.1 and let us keep it at uniform temperature $(\Delta T=0)$. If we apply at points P and Q an emf and we circulate an electric current $I$, we observe that in one of the two heat reservoirs at the two junctions, heat must be supplied (the junction tends to cool) while at the other we have to take away the same amount of heat per second (the junction tends to warm). For current intensities not too high the power exchanged by each junction is proportional to $I$. If we invert the direction of the electric current the effects change sign, i.e., the junction that previously cooled will tend to warm and vice versa.

Consider the junction traversed by the current when it flows from metal A to metal B. The amount of heat absorbed by this junction is written in the form

$$
\begin{equation*}
\frac{\hat{d} Q}{\mathrm{~d} t}=\Pi_{A B} I, \tag{16.114}
\end{equation*}
$$

where $\Pi_{A B}$ is named the Peltier coefficient of the thermocouple and depends on the temperature of the junction.

### 16.7.3 Thomson Effect—Phenomenology

Let us consider the case in which electric currents and temperature gradients occur simultaneously. For simplicity let us refer to the same thermocouple depicted in Fig. 16.1 where the two junctions are maintained at different temperatures as in Sect. 16.7.1. Along wire A a temperature gradient will be established and will be maintained by means of a suitable series of heat reservoirs at the same local temperature point by point. Let us, now, inject an electric current in the circuit. We observe that, in order to maintain unaltered the temperature distribution, the heat reservoirs must exchange heat with each portion of the wire. The amount of heat exchanged is proportional to the length $\mathrm{d} x$ of the wire element but is not proportional to $I^{2}$ (electric current intensity squared) as expected from Ohm's law. It results composed of two terms: one as expected from Ohm's law and proportional to $I^{2}$, and another proportional to the intensity of the flowing electric current. The latter term changes sign under inversion of the direction of the current so that the total amount of heat delivered to the reservoir may be larger or less than the Joule term. The experimental study of this component shows that the amount of heat delivered by the small segment of wire to the local reservoir is proportional to $\mathrm{d} x$ and to the temperature gradient $\nabla T$ :

$$
\begin{equation*}
\frac{\hat{d} Q}{\mathrm{~d} t}=\tau_{A}^{\mathrm{Th}} I \mathrm{~d} T \tag{16.115}
\end{equation*}
$$

where $\mathrm{d} T$ is the temperature variation along the wire segment $\mathrm{d} x, \tau_{A}^{\mathrm{Th}}$ is called the Thompson coefficient of metal A and depends on temperature.

In order to study the interference between heat flux and electric current we shall refer to Eq. (16.67) for the entropy production density and Eqs. (16.68) and (16.69) for the forces. In the case of a metallic wire we consider the presence of just two components: the ionic structure which will be considered at rest (diffusion velocity $\mathbf{v}_{\text {ion }}=0$ ) and the electronic component which diffuses with respect to ions with drift velocity $\mathbf{v}_{\mathrm{el}}$.

Let us, for convenience, rewrite these relations with the following assumptions: chemical reactions are absent and only one diffusion flux $\mathbf{J}_{\gamma}$ is present describing the motion of the electronic component and for this reason all quantities referring to it will be denoted by the index "el". We have

$$
\begin{align*}
& \pi=\mathbf{J}_{q} \cdot \mathbf{X}_{q}+\mathbf{J}_{\mathrm{el}} \cdot \mathbf{X}_{\mathrm{el}},  \tag{16.116}\\
& \mathbf{X}_{\mathrm{el}}=\frac{1}{T}\left[\mathbf{F}_{\mathrm{el}}-T \cdot \nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{T}\right)\right], \tag{16.117}
\end{align*}
$$

the expression for $\mathbf{F}_{\mathrm{el}}$ which refers to the mass unit, and in the absence of magnetic fields, shall be written as

$$
\begin{equation*}
\mathbf{F}_{\mathrm{el}}=q_{\mathrm{el}}^{*} \mathbf{E} \tag{16.118}
\end{equation*}
$$

where $q_{\mathrm{el}}^{*}=-e / m_{\mathrm{el}}$ is the charge per unit mass of the electronic component, being $e$ the absolute value of the electron charge and $m_{\mathrm{el}}$ the electron mass. The diffusion density flux $\mathbf{J}_{\mathrm{el}}$ of the electrons represents, in a particular form, the current density in the wire and in order to make this more explicit let us rewrite its expression as follows:

$$
\begin{equation*}
\mathbf{J}_{\mathrm{el}}=\varrho_{\mathrm{el}} \mathbf{v}_{\mathrm{el}}=N_{\mathrm{el}} m_{\mathrm{el}} \mathbf{v}_{\mathrm{el}}=\frac{\mathbf{j}}{q_{\mathrm{el}}^{*}} \tag{16.119}
\end{equation*}
$$

where $N_{\mathrm{el}}$ is the number density of electrons and $\mathbf{j}$ the free current density. The contribution of the electric current to the entropy production density is, then, made explicit in the form

$$
\begin{equation*}
\pi=\mathbf{J}_{q} \cdot \nabla\left(\frac{1}{T}\right)+\mathbf{j} \cdot \frac{1}{T}\left[\mathbf{E}-T \nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*} T}\right)\right] . \tag{16.120}
\end{equation*}
$$

In Eq. (16.120) the two fluxes have clear meanings: one describes the energy flux minus a very small correction due to the center of mass motion. The other one has the clear meaning of current density. On the other hand the two conjugated forces depend, respectively, the former on the temperature gradient only while the latter depends on all the state variables. It is convenient to proceed adopting, as basic forces, temperature gradients and electrochemical potential gradients separately, as will be shown below in Eq. (16.128). This can be easily obtained by operating a change in the definition of the fluxes similarly to what was shown in Sect.14.6.1. In that case, the aim was to separate the effects of temperature differences from those of pressure differences, here we separate the role of temperature gradient from that of chemical potential gradient.

This can be easily obtained by splitting the term $\nabla\left(\mu_{\mathrm{el}}^{*} / T q_{\mathrm{el}}^{*}\right)$ in the following way:

$$
\begin{equation*}
\nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{T q_{\mathrm{el}}^{*}}\right)=\frac{1}{T} \nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*}}\right)+\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*}} \nabla\left(\frac{1}{T}\right) \tag{16.121}
\end{equation*}
$$

and then we substitute this expression into Eq. (16.120), the entropy production density becomes

$$
\begin{equation*}
\pi=\mathbf{J}_{q} \cdot \nabla\left(\frac{1}{T}\right)+\mathbf{j} \cdot \frac{1}{T}\left[\mathbf{E}-\nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*}}\right)\right]-\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*}} \mathbf{j} \cdot \nabla\left(\frac{1}{T}\right) . \tag{16.122}
\end{equation*}
$$

The last term on the right gives a contribution equal to $-\mu_{\mathrm{el}}^{*} \mathbf{J}_{\mathrm{el}} \cdot \nabla(1 / T)$ which is put together with $\mathbf{J}_{q} \cdot \nabla(1 / T)$ and the two terms give the expression of the new flux and, consequently, of the new forces.

The heat flux $\mathbf{J}_{q}$ will be changed into

$$
\begin{equation*}
\mathbf{J}_{q} \rightarrow \mathbf{J}_{q}-\mu_{\mathrm{el}}^{*} \mathbf{J}_{\mathrm{el}} . \tag{16.123}
\end{equation*}
$$

It is useful to interpret the new flux remembering the definition of entropy flux density $\mathbf{J}_{s}$ as given in Eq. (16.66) (here the notation for the flux has been changed dropping the prime). The new flux Eq. (16.123). still maintaining the dimension of flux density of energy, is more closely related to the density flux of entropy as is clear by the relation:

$$
\begin{equation*}
\mathbf{J}_{q}-\mu_{\mathrm{el}}^{*} \mathbf{J}_{\mathrm{el}}=\left(T \mathbf{J}_{s}\right) . \tag{16.124}
\end{equation*}
$$

The flux $\mathbf{J}_{\mathrm{el}}$ will remain unchanged and consequently its new force, say $\mathbf{X}_{\mathrm{el}}$, will become

$$
\begin{equation*}
\mathbf{X}_{\mathrm{el}}=\frac{1}{T}\left[\mathbf{E}-T \nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*} T}\right)\right]+\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*}} \nabla\left(\frac{1}{T}\right)=\frac{1}{T}\left[\mathbf{E}-\nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*}}\right)\right] \tag{16.125}
\end{equation*}
$$

and then the entropy production density, in the new representation, becomes:

$$
\begin{equation*}
\pi=\left(\mathbf{J}_{q}-\mu_{\mathrm{el}}^{*} \mathbf{J}_{\mathrm{el}}\right) \cdot \nabla\left(\frac{1}{T}\right)+\mathbf{j} \cdot \frac{1}{T}\left[\mathbf{E}-\nabla\left(\frac{\mu_{\mathrm{el}}^{*}}{q_{\mathrm{el}}^{*}}\right)\right] . \tag{16.126}
\end{equation*}
$$

For static or slowly varying fields we may substitute $\mathbf{E}=-\nabla \psi$ where $\psi$ is the electrostatic potential and the density of entropy production may be written in the form

$$
\begin{align*}
\pi & =\left(T \mathbf{J}_{s}\right) \cdot \nabla\left(\frac{1}{T}\right)-\mathbf{J}_{\mathrm{el}} \cdot \frac{1}{T} \nabla\left(\mu_{\mathrm{el}}^{*}+q_{\mathrm{el}}^{*} \psi\right),  \tag{16.127}\\
\pi & =\left(T \mathbf{J}_{s}\right) \cdot \nabla\left(\frac{1}{T}\right)-\mathbf{J}_{\mathrm{el}} \cdot \frac{1}{T} \nabla \tilde{\mu}_{\mathrm{el}}^{*} . \tag{16.128}
\end{align*}
$$

In Eq. (16.128), a new thermodynamic potential appears, called specific electrochemical potential. Its definition is

$$
\begin{equation*}
\tilde{\mu}_{\mathrm{el}}^{*}=\mu_{\mathrm{el}}^{*}+q_{\mathrm{el}}^{*} \psi . \tag{16.129}
\end{equation*}
$$

We see clearly how the chemical potential, which is a function of temperature and particle density, combines with the electrostatic potential in order to constitute one force associated directly with the electric current in perfect analogy with the example studied in Sect. 16.6.4.

$$
\begin{align*}
\left(T \mathbf{J}_{s}\right) & =L_{11} \nabla\left(\frac{1}{T}\right)-L_{12} \frac{1}{T} \nabla \tilde{\mu}_{\mathrm{el}}^{*}  \tag{16.130}\\
\mathbf{J}_{\mathrm{el}} & =L_{21} \nabla\left(\frac{1}{T}\right)-L_{22} \frac{1}{T} \nabla \tilde{\mu}_{\mathrm{el}}^{*} \tag{16.131}
\end{align*}
$$

with the condition:

$$
\begin{equation*}
L_{12}=L_{21} \tag{16.132}
\end{equation*}
$$

The diagonal phenomenological coefficients $L_{11}$ and $L_{22}$ describe the proportionality of a flux with its own force and, therefore are connected, respectively, with the thermal and electrical conductivities. First, let us consider the case of isothermal metals. In Eq. (16.131) the chemical potential $\mu_{\mathrm{el}}^{*}$ is also uniform $\left(\nabla \mu_{\mathrm{el}}^{*}=0\right)$ because we consider homogeneous, isotropic metals. Then, the Eq. (16.131) becomes

$$
\begin{align*}
& \mathbf{J}_{\mathrm{el}}=-L_{22} \frac{1}{T} \nabla\left(q_{\mathrm{el}}^{*} \psi\right)=L_{22} \frac{1}{T} q_{\mathrm{el}}^{*} \mathbf{E},  \tag{16.133}\\
& \mathbf{j}=L_{22} \frac{q_{\mathrm{el}}^{* 2}}{T} \mathbf{E}=\sigma_{\mathrm{el}} \mathbf{E}, \tag{16.134}
\end{align*}
$$

then the electrical conductivity gives the value of the $L_{22}$ coefficient according to the following relation:

$$
\begin{equation*}
L_{22}=\frac{\sigma_{\mathrm{el}} T}{q_{\mathrm{el}}^{* 2}} . \tag{16.135}
\end{equation*}
$$

Recalling Eq. (16.106), where the thermal conductivity of a medium is defined by the proportionality relation between the flux of heat and the temperature gradient in a medium with no electrical current, if we set $\mathbf{J}_{\mathrm{el}}=0$ we get

$$
\begin{equation*}
\frac{1}{T} \nabla \tilde{\mu}_{\mathrm{el}}^{*}=\frac{L_{21}}{L_{22}} \nabla\left(\frac{1}{T}\right) \tag{16.136}
\end{equation*}
$$

and then:

$$
\begin{equation*}
\left(T \mathbf{J}_{s}\right)=\left[L_{11}-L_{12} \frac{L_{21}}{L_{22}}\right] \nabla\left(\frac{1}{T}\right), \tag{16.137}
\end{equation*}
$$

and since $\left(T \mathbf{J}_{s}\right)=\mathbf{J}_{q}-\mu_{\mathrm{el}}^{*} \mathbf{J}_{\mathrm{el}}=\mathbf{J}_{q}$ we obtain

$$
\begin{equation*}
\mathbf{J}_{q}=-\frac{1}{T^{2}} \frac{L_{11} L_{22}-L_{12}^{2}}{L_{22}} \nabla T \tag{16.138}
\end{equation*}
$$

We see that the thermal conductivity, defined in Eq.(16.106), is bound to the phenomenological coefficients $L_{i j}$ by the relation:

$$
\begin{equation*}
\lambda=\frac{1}{T^{2}} \frac{L_{11} L_{22}-L_{12}^{2}}{L_{22}} \tag{16.139}
\end{equation*}
$$

The expressions (16.135) and (16.139) connect experimentally measured parameters to the phenomenological coefficients. If we can connect another important physical parameter to the phenomenological equations (16.130) and (16.131), remembering the symmetry condition (16.132), we can completely determine the dynamical equations (16.130) and (16.131) and then describe all thermoelectric effects as a function of three of them.

Let us consider a thermocouple as the one treated in Sect. 16.7.1 and let us describe the Seebeck effect in the language of the dynamical equations (16.130) and (16.131). Since the circuit is open, Eq. $(16.136)$ holds and may be written conveniently in the form

$$
\begin{equation*}
\nabla \tilde{\mu}_{\mathrm{el}}^{*}=-\frac{L_{21}}{L_{22}} \frac{1}{T} \nabla T \tag{16.140}
\end{equation*}
$$

Let us restrict ourselves to a one-dimensional formalism and integrate Eq. (16.140) along the path P- $G_{1}, G_{1}-G_{2}, G_{2}-\mathrm{Q}$ (as in Sect. 16.7.1) we obtain the following relations:

$$
\begin{align*}
& \left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{G_{1}}-\left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{P}=-\int_{P}^{G_{1}}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{B}} \frac{1}{T} \mathrm{~d} T  \tag{16.141}\\
& \left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{G_{2}}-\left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{G_{1}}=-\int_{G_{1}}^{G_{2}}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{A}} \frac{1}{T} \mathrm{~d} T  \tag{16.142}\\
& \left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{Q}-\left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{G_{2}}=-\int_{G_{2}}^{Q}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{B}} \frac{1}{T} \mathrm{~d} T \tag{16.143}
\end{align*}
$$

If we sum the left hand terms of Eqs.(16.141)-(16.143) we obtain the difference of the electrochemical potential between points Q and P . These two points are at the same temperature and are made with the same metal then the chemical potential of the electrons has the same value. It follows that

$$
\begin{equation*}
\left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{Q}-\left(\tilde{\mu}_{\mathrm{el}}^{*}\right)_{P}=q_{\mathrm{el}}^{*}\left(\psi_{Q}-\psi_{P}\right) \tag{16.144}
\end{equation*}
$$

As for the right-hand side integrals we have

$$
\begin{equation*}
\int_{P}^{G_{1}}\left(\frac{L_{21}}{L_{22}}\right)_{\text {в }} \frac{1}{T} \mathrm{~d} T+\int_{G_{1}}^{G_{2}}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{B}} \frac{1}{T} \mathrm{~d} T+\int_{G_{2}}^{Q}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{B}} \frac{1}{T} \mathrm{~d} T=0 \tag{16.145}
\end{equation*}
$$

Finally, summing up Eqs. (16.141)-(16.143) we obtain

$$
\begin{equation*}
\left(\psi_{Q}-\psi_{P}\right)=-\int_{G_{1}}^{G_{2}}\left[\frac{1}{q_{\mathrm{el}}^{*}}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{A}}-\frac{1}{q_{\mathrm{el}}^{*}}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{B}}\right] \frac{1}{T} \mathrm{~d} T . \tag{16.146}
\end{equation*}
$$

Let us denote by $T$ the temperature at junction $G_{1}$ and by $T+\Delta T$ that at junction $G_{2}$. For small values of $\Delta T$ Eq. (16.146) can be written as follows:

$$
\begin{equation*}
\left(\psi_{Q}-\psi_{P}\right)=-\left[\frac{1}{q_{\mathrm{el}}^{*}}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{A}}-\frac{1}{q_{\mathrm{el}}^{*}}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{B}}\right] \frac{1}{T} \Delta T . \tag{16.147}
\end{equation*}
$$

If we put $\left(\psi_{Q}-\psi_{P}\right)=\Delta \psi$, then Eq. (16.147) shows that if we increase by an infinitesimal amount the temperature of the hot junction ( $G_{2}$ if $\Delta T>0$ ) the increment in $\Delta \psi$ is given by

$$
\begin{equation*}
\frac{\mathrm{d} \Delta \psi}{\mathrm{~d} T}=\left[\frac{1}{q_{\mathrm{el}}^{*}} \frac{1}{T}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{B}}-\frac{1}{q_{\mathrm{el}}^{*}} \frac{1}{T}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{A}}\right]=\omega_{A B}, \tag{16.148}
\end{equation*}
$$

where $\omega_{A B}$ is called thermoelectric power of the thermocouple. If we put

$$
\begin{equation*}
\omega_{A}=\frac{1}{q_{\mathrm{el}}^{*}} \frac{1}{T}\left(\frac{L_{21}}{L_{22}}\right)_{\mathrm{A}}, \tag{16.149}
\end{equation*}
$$

we refer to $\omega_{A}$ as the absolute thermoelectric power of metal A (and the same for metal B) we may write the thermoelectric power of the thermocouple as the difference of the absolute thermoelectric powers of the two metals:

$$
\begin{equation*}
\omega_{A B}=\omega_{B}-\omega_{A} . \tag{16.150}
\end{equation*}
$$

From Eqs. (16.132), (16.135), (16.139) and (16.149) we can determine the four phenomenological coefficients as a function of the electrical conductivity $\sigma_{\mathrm{el}}$, the thermal conductivity $\lambda$ and the absolute thermoelectric power $\omega$ of a conductor. We find

$$
\begin{align*}
& L_{11}=\lambda T^{2}+\sigma_{\mathrm{el}} \omega^{2} T^{3},  \tag{16.151}\\
& L_{22}=\sigma_{\mathrm{el}} T q_{\mathrm{el}}^{*-2},  \tag{16.152}\\
& L_{12}=L_{21}=\omega \sigma_{\mathrm{el}} T^{2} q_{\mathrm{el}}^{*-1} \tag{16.153}
\end{align*}
$$

and then we may obtain the dynamical equations as follows:

$$
\begin{align*}
\left(T \mathbf{J}_{S}\right) & =\left[\lambda T^{2}+\sigma_{\mathrm{el}} \omega^{2} T^{3}\right] \nabla\left(\frac{1}{T}\right)-\frac{\sigma_{\mathrm{el}} \omega T}{q_{\mathrm{el}}^{*}} \nabla \tilde{\mu}_{\mathrm{el}}^{*}  \tag{16.154}\\
\mathbf{J}_{\mathrm{el}} & =\frac{\sigma_{\mathrm{el}} \omega T^{2}}{q_{\mathrm{el}}^{*}} \nabla\left(\frac{1}{T}\right)-\frac{\sigma_{\mathrm{el}}}{q_{\mathrm{el}}^{* 2}} \nabla \tilde{\mu}_{\mathrm{el}}^{*} \tag{16.155}
\end{align*}
$$

From Eqs. (16.154) and (16.155) any other thermoelectric effect can be quantitatively explained as a function of the three selected basic properties of the conductor.

### 16.7.4 Peltier Effect—Explanation

Consider two wires A and B made with different metals and welded in the junction G. They are kept at the same, uniform temperature $T$ and for simplicity, we suppose that their cross-sectional area is the same.

From Eqs. (16.154) and (16.155) we can write the following relation between the entropy density flux and the current density for each metal:

$$
\begin{equation*}
\left(T \mathbf{J}_{s}\right)=\omega T\left(q_{\mathrm{el}}^{*} \mathbf{J}_{\mathrm{el}}\right)=\omega T \mathbf{j} \tag{16.156}
\end{equation*}
$$

Since the current density is the same in the two conductors we see that the heat flux density has different values. Their difference is

$$
\begin{equation*}
\left(T \mathbf{J}_{s}\right)_{\mathrm{wireB}}-\left(T \mathbf{J}_{s}\right)_{\mathrm{wireA}}=\left(\omega_{B}-\omega_{A}\right) T \mathbf{j} \tag{16.157}
\end{equation*}
$$

Since also the electrochemical potential is continuous when traversing the junction, the change in $\left(T \mathbf{J}_{s}\right)$ corresponds to a variation in the heat flux density $\mathbf{J}_{q}$ and this variation amounts to

$$
\begin{equation*}
\left(\mathbf{J}_{q}\right)_{\text {wireB }}-\left(\mathbf{J}_{q}\right)_{\text {wireA }}=\left(\omega_{B}-\omega_{A}\right) T \mathbf{j} \tag{16.158}
\end{equation*}
$$

This difference corresponds to the amount of heat absorbed or given off at the junction per second. More precisely, if we integrate Eq. (16.158) over the cross section of the wires, the amount of heat exchanged, per second, with the outside per unit current intensity is

$$
\begin{equation*}
\Pi_{A B}=\left(\omega_{B}-\omega_{A}\right) T \tag{16.159}
\end{equation*}
$$

From Eq. (16.158) we see, for instance, that if $\omega_{B}>\omega_{A}$ and the current is flowing from A to $B$, the junction will tend to cool and then heat must be supplied to the wire in order to keep it at constant temperature $T$. If the current flows from B into A the junction must be cooled by an external thermostat because the junction will tend to become hotter.

Let us consider, as an example, a thermocouple formed by Bi and Sb traversed by an electric current with intensity $I=20 \mathrm{~A}$. The Peltier coefficient of this couple is $\Pi_{\mathrm{BiSb}} \simeq 40 \mathrm{mV}$ and we can use the junction which tends to cool in order to produce refrigeration effects. If we consider, for example, 20 wires of Antimony and 20 of Bismuth welded in an alternate configuration and we put together the junctions which absorb heat, the power subtracted to the ambient is

$$
\begin{equation*}
\frac{\hat{d} Q}{\mathrm{~d} t} \simeq 20 \times 4 \times 10^{-2} \times 20 \simeq 16 \mathrm{~W} \tag{16.160}
\end{equation*}
$$

### 16.7.5 Thomson Effect

In order to discuss the interference between temperature gradients and electrochemical potential gradients ${ }^{2}$ in metals, it is necessary to refer to the dynamical Eqs. (16.154) and (16.155). If we consider a small segment of wire of length $\mathrm{d} x$ the increment of heat flux along $\mathrm{d} x$ must be compensated by the equivalent amount of heat absorbed from the external world per second. Then the effect we want to discuss is directly linked to the divergence of $\mathbf{J}_{q}$ and this can be easily calculated from the dynamical equations taking care to connect the heat flux density $\mathbf{J}_{q}$ to the electric current density $\mathbf{j}$ and to the temperature gradient. Let us write the expression of $\nabla \tilde{\mu}_{\mathrm{el}}^{*}$ from Eq. (16.155) and substitute in Eq. (16.154) and, after some calculations, obtain:

$$
\begin{equation*}
\left(T \mathbf{J}_{s}\right)=\lambda T^{2} \nabla\left(\frac{1}{T}\right)+q_{\mathrm{el}}^{*} \omega T \mathbf{J}_{\mathrm{el}} \tag{16.161}
\end{equation*}
$$

and remembering Eq. (16.124) we have

$$
\begin{equation*}
\mathbf{J}_{q}=\lambda T^{2} \nabla\left(\frac{1}{T}\right)+q_{\mathrm{el}}^{*} \omega T \mathbf{J}_{\mathrm{el}}+\left(\tilde{\mu}_{\mathrm{el}}^{*}\right) \mathbf{J}_{\mathrm{el}} \tag{16.162}
\end{equation*}
$$

The calculation of the divergence of the heat density flux gives rise to several terms which must be analized one by one. Recalling that $J_{\mathrm{el}}=q_{\mathrm{el}}^{*-1} \mathbf{j}$ is a divergenceless (solenoidal) vector because of charge conservation, we obtain

$$
\begin{equation*}
\nabla \cdot \mathbf{J}_{q}=\nabla \cdot\left[\lambda T^{2} \nabla\left(\frac{1}{T}\right)\right]+q_{\mathrm{el}}^{*} T \nabla \omega \cdot \mathbf{J}_{\mathrm{el}}+q_{\mathrm{el}}^{*} \omega \nabla T \cdot \mathbf{J}_{\mathrm{el}}+\nabla \tilde{\mu}_{\mathrm{el}}^{*} \cdot \mathbf{J}_{\mathrm{el}} \cdot \tag{16.163}
\end{equation*}
$$

From Eq. (16.155) we obtain the expression for $\nabla \tilde{\mu}_{\mathrm{el}}^{*}$ :

$$
\begin{equation*}
\nabla \tilde{\mu}_{\mathrm{el}}^{*}=-\frac{q_{\mathrm{el}}^{* 2}}{\sigma_{\mathrm{el}}} \mathbf{J}_{\mathrm{el}}+q_{\mathrm{el}}^{*} \omega T^{2} \nabla\left(\frac{1}{T}\right) \tag{16.164}
\end{equation*}
$$

and substituting in Eq. (16.163) we have

$$
\begin{equation*}
\nabla \cdot \mathbf{J}_{q}=\nabla \cdot\left[\lambda T^{2} \nabla\left(\frac{1}{T}\right)\right]+q_{\mathrm{el}}^{*} T \nabla \omega \cdot \mathbf{J}_{\mathrm{el}}-\frac{q_{\mathrm{el}}^{* 2}}{\sigma_{\mathrm{el}}} \mathbf{J}_{\mathrm{el}}^{2} . \tag{16.165}
\end{equation*}
$$

As far as the first term on the right is concerned we have to remember that the temperature distribution we are dealing with, is the one that was determined in condition of zero electric current and in that case we have $\nabla \cdot \mathbf{J}_{q}=0$. From Eq. (16.165) this implies that

[^60]$$
\nabla \cdot\left[\lambda T^{2} \nabla\left(\frac{1}{T}\right)\right]=0
$$

We know that the absolute thermoelectric power $\omega$ depends only on temperature then its gradient may be expressed in the form

$$
\begin{equation*}
\nabla \omega=\frac{\mathrm{d} \omega}{\mathrm{~d} T} \nabla T \tag{16.166}
\end{equation*}
$$

and, finally, Eq. (16.165) may be written as

$$
\begin{equation*}
\nabla \cdot \mathbf{J}_{q}=T \frac{\mathrm{~d} \omega}{\mathrm{~d} T} \nabla T \cdot \mathbf{j}-\frac{1}{\sigma_{\mathrm{el}}} \mathbf{j}^{2} . \tag{16.167}
\end{equation*}
$$

The divergence of the heat flux density gives the amount of heat exchanged with the external reservoirs in order to maintain the given temperature distribution. We see that it is composed by two terms. The second on the right is proportional to the current density squared and the electrical resistivity $\sigma_{\text {el }}^{-1}$ and, clearly, describes the heat given off by Joule effect.

The first term on the right depends on the scalar product between the current density and the temperature gradient. This term describes the Thomson effect and the Thomson coefficient $\tau^{\mathrm{Th}}$ is linked to the absolute thermoelectric power of the metal, by the relation:

$$
\begin{equation*}
\tau^{\mathrm{Th}}=T \frac{\mathrm{~d} \omega}{\mathrm{~d} T} \tag{16.168}
\end{equation*}
$$

Notice that, given one temperature distribution, the scalar product changes sign if the electric current is inverted and then the Thomson heat may be absorbed or expelled by the wire accordingly.

If we consider two metals A and B joined at the junction $G$ we may relate the Peltier coefficient of the junction to the Thomson coefficients of the two metals. The Peltier coefficient defined in Eq. (16.159) depends only on the temperature (and of the nature of the two metals of course) and hence, taking the temperature derivative of the Peltier coefficient $\Pi_{A B}$, we obtain

$$
\begin{equation*}
\frac{\mathrm{d} \Pi_{A B}}{\mathrm{~d} T}=\left(\omega_{B}-\omega_{A}\right)+\left(\tau_{B}^{\mathrm{Th}}-\tau_{A}^{\mathrm{Th}}\right) \tag{16.169}
\end{equation*}
$$

This relation was first obtained by Lord Kelvin and is called "the first Kelvin relation".

### 16.7.6 Galvanomagnetic and Thermomagnetic Effects

This brief discussion of the thermomechanical effects clearly shows the power of Thermodynamics in establishing general connections between different phenomena.

It should be stressed that everything derives from the expression of the entropy production and from the form of the generalized force connected to the diffusion flows (in this latter case, the electric current) of the various components. In this expression the role of the chemical potential and that of the volume forces are appropriately combined to form "one force" and an example of what the consequences of this are, had already been seen in the derivation of Einstein's relation between the diffusion coefficient and mobility.

Many other effects can be studied by modifying the expression of the volume force acting on the various components such as, for example, adding magnetic or centrifugal fields. In the former case, the volume force per unit of mass changes to

$$
\begin{equation*}
\mathbf{F}_{\mathrm{el}}=q_{\mathrm{el}}^{*}\left[\mathbf{E}+\mathbf{v}_{\mathrm{el}} \times \mathbf{B}\right] . \tag{16.170}
\end{equation*}
$$

In this case the phenomenological coefficients $L_{i j}$ depend, in general, on the magnetic field intensity and direction therefore the Onsager symmetry relations defined in Eq. (16.132) must be changed into

$$
\begin{equation*}
L_{i j}(\mathbf{B})=L_{j i}(-\mathbf{B}) \tag{16.171}
\end{equation*}
$$

as was discussed in Sect. 15.3.4. It is clear that many effects arise from the simultaneous presence of temperature gradients, electric fields and megnetic fields and their different mutual orientations.

The Nernst effects take place in a metal in which a heat flux is flowing along one direction (say $x$ axis) and a magnetic field is applied, for instance, perpendicular (for simplicity) to the heat flux. In this cases a potential difference will appear in the direction perpendicular to the previous two. The Ettingshausen effects consist in the appearance of a temperature gradients along, for instance, the $z$-axis when an electric current flowing along the $x$-direction and a magnetic field are imposed along $y$-axis. When a magnetic field is applied normal to the current density in a conductor a potential difference appears in the direction normal to both the current and field directions; this effect is well known as Hall effect. All these phenomena are deeply entangled with each other and can be explained if we start from the principle of the impossibility of perpetual motion as it was made for thermoelectric phenomena. We shall not go further into the dicussion of this subject.

### 16.8 Thermodiffusion Processes

In this subsection, we discuss briefly the interference between temperature gradients and concentration gradients. It is experimentally observed that in a mixture initially at uniform temperature, the presence of a concentration gradient will cause the diffusion of a substance relative to the others and this gives rise to the establishment of a temperature gradient. Conversely if a temperature gradient is created in an initially homogeneous system, this will give rise to a concentration gradient. The former is
called Dufour effect and the latter is called Thermodiffusion or, in condensed phases, Soret effect. The Onsager theory of irreversible processes establishes a deep (model independent) correlation between these two phenomena and for this reason, they are said to be "reciprocal effects" as we shall see below.

Let us refer to the general Eq. (16.67) for the entropy production density and to Eqs. (16.68), (16.69) for the generalized forces. We consider the case in which chemical reactions and external volume forces are absent. Then the entropy production density becomes

$$
\begin{equation*}
\pi=\mathbf{J}_{q} \cdot \mathbf{X}_{q}+\sum_{\gamma=1}^{n} \mathbf{J}_{\gamma} \cdot \mathbf{X}_{\gamma} \tag{16.172}
\end{equation*}
$$

where the forces conjugated to the diffusion fluxes, $\mathbf{J}_{\gamma}$, are

$$
\begin{equation*}
\mathbf{X}_{\gamma}=-\nabla\left(\frac{\mu_{\gamma}^{*}}{T}\right) \tag{16.173}
\end{equation*}
$$

Since we want to study the interference between flows originating from temperature and concentration gradients, it is convenient that in the expression for the density of production of entropy, the forces depend separately on these two gradients. For this reason we shall consider the chemical potentials as functions of temperature, pressure and of the concentrations in the form

$$
\begin{equation*}
\mu_{\gamma}^{*}=\mu_{\gamma}^{*}\left(T, p, c_{1}, c_{2}, \ldots, c_{n}\right) \tag{16.174}
\end{equation*}
$$

where it must be remembered that

$$
\begin{equation*}
\sum_{\gamma=1}^{n} c_{\gamma}=1 \tag{16.175}
\end{equation*}
$$

Moreover the pressure in the fluid will be considered uniform because we shall consider only situations in which mechanical equilibrium holds as already considered in Sect. 16.6.4 It is , then, convenient to arrange the gradient in Eq. (16.173) in the following way:

$$
\begin{equation*}
\nabla\left(\frac{\mu_{\gamma}^{*}}{T}\right)=-\frac{H_{\gamma}^{*}}{T^{2}} \nabla(T)+\frac{1}{T} \nabla_{T}\left(\mu_{\gamma}^{*}\right), \tag{16.176}
\end{equation*}
$$

where $H_{\gamma}^{*}$ is the enthalpy per unit mass and the operator $\nabla_{T}$ denotes the gradient of a quantity keeping the temperature constant. With this modification of the form of the forces. the entropy production density in Eq. (16.172) may be conveniently be written as

$$
\begin{equation*}
\pi=\mathbf{J}_{q}^{\prime \prime} \cdot \mathbf{X}_{q}-\frac{1}{T} \sum_{\gamma=1}^{n} \mathbf{J}_{\gamma} \cdot \nabla_{T}\left(\mu_{\gamma}^{*}\right) \tag{16.177}
\end{equation*}
$$

and the new flux $\mathbf{J}_{q}^{\prime \prime}$, which still has the dimension of a "heat flux density", is defined as ${ }^{3}$

$$
\begin{equation*}
\mathbf{J}_{q}^{\prime \prime}=\mathbf{J}_{q}-\sum_{\gamma=1}^{n} H_{\gamma}^{*} \mathbf{J}_{\gamma} \tag{16.178}
\end{equation*}
$$

Before proceeding to examine, briefly, an application to the phenomena of thermodiffusion, it is appropriate to carry out some considerations on the formal structure of Eq. (16.177) that provides the density of production of entropy.

One comes from the definition Eq. (16.23) of barycentric fluxes which leads to the condition:

$$
\begin{equation*}
\sum_{\gamma=1}^{n} \mathbf{J}_{\gamma}=0 \tag{16.179}
\end{equation*}
$$

As a consequence of Eq. (16.179) one flux, for instance $\mathbf{J}_{n}$ may be eliminated from Eqs. (16.177) and (16.178) because only $n-1$ fluxes are independent. Then the density of entropy production may be written as

$$
\begin{equation*}
\pi=\mathbf{J}_{q}^{\prime \prime} \cdot \mathbf{X}_{q}-\frac{1}{T} \sum_{\gamma=1}^{n-1} \mathbf{J}_{\gamma} \cdot\left[\nabla_{T}\left(\mu_{\gamma}^{*}\right)-\nabla_{T}\left(\mu_{n}^{*}\right)\right] \tag{16.180}
\end{equation*}
$$

Similarly, for the $n$ forces appearing in the equation of the density of entropy production Eq. (16.177) we may prove that only $n-1$ of them are independent. This is obtained from the application of the Gibbs-Duhem equation, which will be discussed in Sect. 16.9 and summarized in Eq. (16.220). Here it will be rearranged in order to be written in terms of the the specific chemical potentials and, as a consequence, mass concentrations. It results in the form

$$
\begin{equation*}
\sum_{\gamma=1}^{n} c_{\gamma} \nabla_{T}\left(\mu_{\gamma}^{*}\right)=0 \tag{16.181}
\end{equation*}
$$

Equation(16.181) allows to eliminate one force, for instance $\nabla_{T}\left(\mu_{n}^{*}\right)$, so that Eq. (16.180) may be easily written as a function of the new heat flux plus $n-1$ diffusion fluxes and $n-1$ relative forces which result as linear combinations of the ones appearing in Eq. (16.177). More precisely

$$
\begin{equation*}
\pi=\mathbf{J}_{q}^{\prime \prime} \cdot \mathbf{X}_{q}-\frac{1}{T} \sum_{\gamma, \gamma^{\prime}=1}^{n-1} \mathbf{J}_{\gamma} \cdot \nabla_{T}\left(\mu_{\gamma^{\prime}}^{*}\right)\left[\delta_{\gamma, \gamma^{\prime}}+\frac{c_{\gamma^{\prime}}}{c_{n}}\right] \tag{16.182}
\end{equation*}
$$

The new form of the expression of the density of entropy production Eq. (16.182) is necessary in order to give an exhaustive discussion of diffusion phenomena in

[^61]multicomponent systems. Here we shall limit ourselves to binary systems but for a complete treatment the reader is addressed to [23, 26].

Since the diffusion phenomena and the relative coefficients are described with reference to concentration gradients, it is appropriate to change further the form of the forces in Eq. (16.177) in order to make the role of concentrations explicit.

Let us define the symbol:

$$
\begin{equation*}
\mu_{\gamma^{\prime}, \gamma^{\prime \prime}}^{*}=\left(\frac{\partial \mu_{\gamma^{\prime}}^{*}}{\partial c_{\gamma^{\prime \prime}}}\right)_{T, p, c_{\gamma^{\prime \prime} \neq \gamma^{\prime}}} \tag{16.183}
\end{equation*}
$$

so the gradients of the specific chemical potentials become

$$
\begin{equation*}
\nabla\left(\mu_{\gamma^{\prime}}^{*}\right)=\sum_{\gamma^{\prime \prime}=1}^{n-1} \mu_{\gamma^{\prime}, \gamma^{\prime \prime}}^{*} \nabla\left(c_{\gamma^{\prime \prime}}\right) \tag{16.184}
\end{equation*}
$$

We can, now, write a suitable expression for the density of entropy production in such a way that one force depends on the temperature gradient and the others on the concentration gradients only. If we insert Eq. (16.184) into Eq. (16.172) after some simple algebra we obtain

$$
\begin{equation*}
\pi=\mathbf{J}_{q}^{\prime \prime} \cdot \mathbf{X}_{q}-\frac{1}{T} \sum_{\gamma, \gamma^{\prime}, \gamma^{\prime \prime}=1}^{n-1} \mathbf{J}_{\gamma} \cdot\left[\delta_{\gamma, \gamma^{\prime}}+\frac{c_{\gamma^{\prime}}}{c_{n}}\right] \mu_{\gamma^{\prime}, \gamma^{\prime \prime}}^{*} \nabla\left(c_{\gamma^{\prime \prime}}\right) . \tag{16.185}
\end{equation*}
$$

### 16.8.1 Binary Systems

Let us consider, for simplicity, the case of a binary system, i.e., the case in which only two components are present $(n=2)$ as we did in Sect. 16.6.4.

Let us go back to Eq. (16.185) and make it explicit for the case of a two-component system. The expression for the density of entropy production becomes

$$
\begin{equation*}
\pi=\mathbf{J}_{q}^{\prime \prime} \cdot \mathbf{X}_{q}-\frac{1}{T} \frac{\mu_{1,1}^{*}}{c_{2}} \mathbf{J}_{1} \cdot \nabla\left(c_{1}\right) \tag{16.186}
\end{equation*}
$$

With reference to Eq. (16.186) for the density of entropy production, let us write the linear relations between fluxes and forces:

$$
\begin{equation*}
\mathbf{J}_{q}^{\prime \prime}=-L_{11} \frac{1}{T^{2}} \nabla(T)-L_{12} \frac{1}{T} \frac{\mu_{1,1}^{*}}{c_{2}} \nabla\left(c_{1}\right) \tag{16.187}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathbf{J}_{1}=-L_{21} \frac{1}{T^{2}} \nabla(T)-L_{22} \frac{1}{T} \frac{\mu_{1,1}^{*}}{c_{2}} \nabla\left(c_{1}\right) \tag{16.188}
\end{equation*}
$$

with the symmetry condition:

$$
\begin{equation*}
L_{12}=L_{21} \tag{16.189}
\end{equation*}
$$

The four phenomenological coefficients are simply related to the various coefficients measured experimentally when different situations are realized.

First, we may consider the case of homogeneous systems in which only heat conduction is active. If we write the expression of the heat flux obtained from Eq. (16.187) in this particular configuration and compare it with the Fourier's law of heat conduction (see Eq. (16.106)) we obtain

$$
\begin{equation*}
\mathbf{J}_{q}^{\prime \prime}=\mathbf{J}_{q}=-L_{11} \frac{1}{T^{2}} \nabla(T)=-\lambda \nabla T \tag{16.190}
\end{equation*}
$$

and then the phenomenological coefficient $L_{11}$ is related to the heat conductivity by

$$
\begin{equation*}
L_{11}=\lambda T^{2} \tag{16.191}
\end{equation*}
$$

The symmetrical situation occurs when we consider the presence of diffusion flows in a system maintained at a uniform temperature. In this case the diffusion coefficients with respect to a generic reference velocity a are defined by a general relation of the type:

$$
x_{1}\left(\mathbf{v}_{1}-\mathbf{a}\right)=-\mathcal{D} \nabla\left(x_{1}\right)
$$

where $\mathbf{a}$ is the reference velocity (in the case we are considering here $\mathbf{a}=\mathbf{v}$ is the c.m. velocity) and $x_{1}$ the diffusion property like, for instance $\varrho_{1}, C_{1}$ or $c_{1}$. In the case we are discussing we observe the diffusion of the mass concentration $c_{1}$ with respect to the c.m. motion and then Eq. (16.188), for isothermal systems, gives

$$
\begin{equation*}
\varrho c_{1}\left(\mathbf{v}_{1}-\mathbf{v}\right)=-L_{22} \frac{1}{T} \frac{\mu_{1,1}^{*}}{c_{2}} \nabla\left(c_{1}\right)=-\varrho \mathcal{D} \nabla\left(c_{1}\right) . \tag{16.192}
\end{equation*}
$$

The phenomenological coefficient $L_{22}$ is related to the diffusion coefficient by

$$
\begin{equation*}
L_{22}=\frac{\varrho c_{2} T}{\mu_{1,1}^{*}} \mathcal{D} \tag{16.193}
\end{equation*}
$$

The other two phenomenological coefficient describe the cross effects originating by temperature gradients and concentration gradients.

### 16.8.2 Thermodiffusion

One consists of the onset of a diffusion flow generated by a temperature gradient in the absence of a concentration gradient and is called Thermodiffusion.

The phenomenon of thermodiffusion was discovered by Ludwig in 1856 [27] but was studied in a systematic way by the Swiss scientist Charles Soret in 1879 (see [28]) when he observed that in a tube containing a saline solution, initially homogeneous, a different concentration was established, in the stationary state, when the two ends were kept at different temperatures (in particular the cold end was the one in which the concentration was higher).

Today the effect is generally referred to as the Soret effect. Starting from a homogeneous configuration, Eq. (16.188) shows that a temperature gradient gives rise to a diffusion flux proportional to the temperature gradient:

$$
\begin{equation*}
\mathbf{J}_{1}=c_{1} \varrho\left(\mathbf{v}_{1}-\mathbf{v}\right)=-L_{21} \frac{1}{T^{2}} \nabla(T) . \tag{16.194}
\end{equation*}
$$

The Soret coefficient, or thermodiffusion coefficient, describes the proportionality between the diffusion flux of component 1 due to the temperature gradient as expressed in Eq. (16.194). It is denoted by $\mathcal{D}_{\mathrm{T}}$ and is defined by the relation:

$$
\begin{equation*}
\mathbf{J}_{1}=-\varrho c_{1} c_{2} \mathcal{D}_{\mathrm{T}} \boldsymbol{\nabla}(T) . \tag{16.195}
\end{equation*}
$$

The reason for this definition in which the product of the two concentrations are put into evidence is the following: it is experimentally observed that the thermodiffusion phenomena occur only in mixtures and are absent in system composed by one component. It is expected that the thermodiffusion coefficient depends on temperature and also on concentrations and the latter must give a null value both for either $c_{1}=0$ or $c_{2}=0$. Definition Eq. (16.195) satisfies this requirement but this does not mean that $\mathcal{D}_{\mathrm{T}}$ does not depend on the concentration of one of the two components. Of course $\mathcal{D}_{\mathrm{T}}$ depends also on temperature. If we compare Eqs. (16.194) and (16.195) we find that the phenomenological coefficient $L_{21}$ is related to the thermodiffusion coefficient by

$$
\begin{equation*}
L_{21}=\varrho c_{1} c_{2} T^{2} \mathcal{D}_{\mathrm{T}} \tag{16.196}
\end{equation*}
$$

In general, when both concenration and temperature gradients are present, the flux of matter results:

$$
\begin{equation*}
\mathbf{J}_{1}=-\varrho c_{1} c_{2} \mathcal{D}_{\mathrm{T}} \boldsymbol{\nabla}(T)-\varrho \mathcal{D} \nabla\left(c_{1}\right) \tag{16.197}
\end{equation*}
$$

hence in the stationary state ${ }^{4}$, that is $\mathbf{J}_{1}=0$, the ratio between the variation in the concentration and in temperature is

$$
\begin{equation*}
\frac{\Delta c}{\Delta T}=-c_{1} c_{2} \frac{\mathcal{D}_{\mathrm{T}}}{\mathcal{D}}=-c_{1} c_{2} \mathrm{~S}_{\mathrm{T}} \tag{16.198}
\end{equation*}
$$

[^62]where $\mathrm{S}_{\mathrm{T}}$ is called Soret coefficient. It describes quantitatively the relative importance between the thermal diffusion and the diffusion due to concentration gradients in determining the resulting flux of matter. For organic mixtures or aqueous solutions it is of the order of $10^{-2}-10^{-3} \mathrm{~K}^{-1}$.

### 16.8.3 Dufour Effect

The symmetrical effect to Thermodiffusion is the onset of a heat flow caused by a gradient of concentration in a isothermal system and is called Dufour effect. If we consider Eq. (16.187) and set $\nabla(T)=0$, we obtain: :

$$
\begin{equation*}
\mathbf{J}_{q}^{\prime \prime}=-L_{12} \frac{1}{T} \frac{\mu_{1,1}^{*}}{c_{2}} \nabla\left(c_{1}\right) \tag{16.199}
\end{equation*}
$$

The Dufour coefficient $\mathcal{D}_{\mathrm{F}}$ is defined by the relation:

$$
\begin{equation*}
\mathbf{J}_{q}^{\prime \prime}=-\varrho_{1} \mu_{1,1}^{*} T \mathcal{D}_{\mathrm{F}} \boldsymbol{\nabla}\left(c_{1}\right) \tag{16.200}
\end{equation*}
$$

and hence, the phenomenological coefficient $L_{12}$ is related to the Dufour coefficient by

$$
\begin{equation*}
L_{12}=\varrho c_{1} c_{2} T^{2} \mathcal{D}_{\mathrm{F}} \tag{16.201}
\end{equation*}
$$

Remembering that $c_{1} \varrho=\varrho_{1}$, we may, now, write the dynamical equations for thermodiffusion phenomena as a function of three coefficient taken as independent:

$$
\begin{gather*}
\mathbf{J}_{q}^{\prime \prime}=-\lambda \nabla(T)-\varrho_{1} \mu_{1,1}^{*} T \mathcal{D}_{\mathrm{F}} \boldsymbol{\nabla}\left(c_{1}\right),  \tag{16.202}\\
\mathbf{J}_{1}=-\varrho c_{1} c_{2} \mathcal{D}_{\mathrm{T}} \boldsymbol{\nabla}(T)-\varrho \mathcal{D} \nabla\left(c_{1}\right),  \tag{16.203}\\
\mathcal{D}_{\mathrm{T}}=\mathcal{D}_{\mathrm{F}}=\mathcal{D}^{\prime} \tag{16.204}
\end{gather*}
$$

where Eq.(16.204) comes from the comparison of Eq. (16.196) with Eq. (16.201) and the application of the Onsager symmetry requirement for the phenomenological coefficients.

Finally let us go back to the phenomenological Eqs. (16.187) and (16.188). The Second Principle requires that the entropy production be positive, then if fluxes are written as linear that the phenomenological coefficient satisfy the following conditions:

$$
\begin{align*}
& L_{11}>0,  \tag{16.205}\\
& L_{22}>0,  \tag{16.206}\\
& \left(L_{11} L_{22}-L_{12} L_{21}\right)>0 . \tag{16.207}
\end{align*}
$$

These conditions come from Eq. (14.127), when the symmetry property of the phenomenological coefficients is applied. Requirements of Eq. (16.207) have important consequences on the various coefficients defined in this section. Following the order of presentation we have

$$
\begin{align*}
& L_{11}>0 \Longrightarrow \lambda>0  \tag{16.208}\\
& L_{22}>0 \Longrightarrow \mu_{1,1}^{*}>0,  \tag{16.209}\\
& \mathcal{D}_{\mathrm{T}} \mathcal{D}_{\mathrm{F}}=\left(\mathcal{D}^{\prime}\right)^{2}<\frac{\lambda}{\varrho T c_{1}^{2} c_{2} \mu_{1,1}^{*}} \mathcal{D} . \tag{16.210}
\end{align*}
$$

Conditions given in Eqs. (16.204), (16.208) (16.209), and (16.210) are of general validity, i.e., model independent. They follow from the impossibility of perpetual motion.

### 16.9 Appendix-The Gibbs-Duhem Relation

Let us consider a phase in which, for simplicity, one work parameter only is present (say the volume) and let it be composed by $n$ independent chemical components. Recalling the discussion in Sect.4.3.1 the Fundamental Relation in the Entropy representation will be written as

$$
\begin{equation*}
S=S\left(U, V, n_{\gamma}\right), \quad \gamma=1,2, \ldots, n \tag{16.211}
\end{equation*}
$$

and we see that the number of degrees of freedom is $n+2$. It is clear, however, that if we leave aside the amount of matter, the number of independent state parameters will be $n+1$. If we write Eq. (16.211) for one mole, and we denote by $\mathrm{c}_{\gamma}=n_{\gamma} / n_{\text {tot }}$ the molar fraction of component $\gamma$ we obtain:

$$
\begin{equation*}
S_{m}=S\left(U_{m}, V_{m}, \mathrm{c}_{\gamma}\right), \quad \gamma=1,2, \ldots, n \tag{16.212}
\end{equation*}
$$

where $n_{\text {tot }}$ is the total number of moles and the $n$ mole fractions $n_{\gamma} / n_{t o t}$, satisfy the obvious relation:

$$
\begin{equation*}
\sum_{\gamma=1}^{n} \mathrm{c}_{\gamma}=1 \tag{16.213}
\end{equation*}
$$

It follows that if we decide to describe the system as a function of $T$ and $p$ plus the $k$ mole fractions (that is, we don't take into account the size of the system), the number of degrees of freedom is $n+1$. This means that among the $n+2$ quantities $T, p$ and $n_{\gamma}$ there must be one mutual dependence. This relation is called the Gibbs-Duhem Relation. Let us write it explicitly.

It is convenient to refer to the Fundamental Equation in the Gibbs representation Eq. (4.32) and to remember expression Eq. (4.78) of the Gibbs potential integrated at constant temperature and pressure. If we differentiate the latter we have:

$$
\begin{equation*}
\mathrm{d} G=\sum_{\gamma=1}^{n} \mu_{\gamma} \mathrm{d} n_{\gamma}+\sum_{\gamma=1}^{n} n_{\gamma} \mathrm{d} \mu_{\gamma} \tag{16.214}
\end{equation*}
$$

and if we substitute Eq. (4.32) we obtain:

$$
\begin{equation*}
\sum_{\gamma=1}^{n} n_{\gamma} \mathrm{d} \mu_{\gamma}=-S \mathrm{~d} T+V \mathrm{~d} p \tag{16.215}
\end{equation*}
$$

This is the Gibbs-Duhem relation. In particular, for processes at constant $T$ and p, Eq. (16.215) becomes:

$$
\begin{equation*}
\sum_{\gamma=1}^{n} n_{\gamma} \mathrm{d} \mu_{\gamma}=0 \tag{16.216}
\end{equation*}
$$

Let us go back to Eq. (16.84) and in particular let us consider the first term of the second member. The first step is to recognize that the summation over the mass concentration gradients are equivalent to the gradients of the specific chemical potentials as shown in the following relation:

$$
\begin{equation*}
\sum_{\gamma^{\prime}=1}^{n}\left(\frac{\partial \mu_{\gamma}^{*}}{\partial c_{\gamma^{\prime}}}\right) \nabla c_{\gamma^{\prime}}=\nabla \mu_{\gamma}^{*} \tag{16.217}
\end{equation*}
$$

Hence we may write

$$
\begin{equation*}
\varrho \sum_{\gamma=1}^{n} c_{\gamma} \sum_{\gamma^{\prime}=1}^{n}\left(\frac{\partial \mu_{\gamma}^{*}}{\partial c_{\gamma^{\prime}}}\right) \nabla c_{\gamma^{\prime}}=\varrho \sum_{\gamma=1}^{k} c_{\gamma} \nabla \mu_{\gamma}^{*} \tag{16.218}
\end{equation*}
$$

and since $\mu_{\gamma}^{*}=\left(1 / M_{\gamma}\right) \mu_{\gamma}$ and $c_{\gamma}=m_{\gamma} / m$, we may replace $\left(\varrho c_{\gamma} / M_{\gamma}\right)$ with $n_{\gamma} / V$ and, finally, Eq. (16.218) can be written as

$$
\begin{equation*}
\varrho \sum_{\gamma=1}^{n} c_{\gamma} \nabla \mu_{\gamma}^{*}=\frac{1}{V} \sum_{\gamma=1}^{n} n_{\gamma} \nabla \mu_{\gamma} \tag{16.219}
\end{equation*}
$$

and

$$
\begin{equation*}
\sum_{\gamma=1}^{n} n_{\gamma} \nabla \mu_{\gamma}=0 \tag{16.220}
\end{equation*}
$$

by the Gibbs-Duhem relation for isothermal and isobaric processes as shown in Eq. (16.216).

## Part IV Thermodynamics and Information

# Chapter 17 <br> Introduction to the Role of Information in Physics 

One must not think slightingly of the paradoxical...for the paradox is the source of the thinker's passion, and the thinker without a paradox is like a lover without feeling: a paltry mediocrity.

Soren Kierkegaard


#### Abstract

The paradox first proposed by Maxwell and well known under the name of "The Maxwell's Demon paradox" is discussed starting from the contribution to the issue given by L. Szilard in 1929. The accurate analysis of the paradox shows that, in order to violate the Second Principle, Maxwell's Devil must perform observations and adapt his own strategy accordingly. Performing observations involves creating information. To save the Second Principle, it is required that the created information should be deleted. The latter operation requires dissipation in the form of heat and the Landauer Principle fixes the minimum amount of heat dissipated by erasing one bit of information. The nonseparability of the observer from the observed constitutes a new epistemological paradigm in which the theory of information, both classical and quantum, ceases to be a purely technical discipline to become a fundamental constituent of the theories of Physics. In this chapter, some elements of classical and quantum information theory are briefly dealt with. Zurek's theory, which explores the possibility that thermodynamic potentials of thermodynamic systems should contain additive contributions due to the description of the configuration by the observer (algorithmic complexity), is reported as an example.


Keywords Information • Maxwell's paradox •L. Szilard • Landauer principle Classical information • Shannon's and Weaver entropy • Entropy of information • Algorithmic complexity

### 17.1 The Maxwell's Paradox

Maxwell considered a gas contained in a vessel divided into two parts by an adiabatic septum, bearing a small opening provided with a very light cover which could be easily opened or closed. Maxwell imagined the existence of a small being with
particular visual acuity and great rapidity of movement, located near the opening, and that could open and close the lid quickly whenever a very fast molecule was directed toward the opening on the side which he was. In this way, this being, which for its extraordinary faculties was indicated as a devil (demon), would act selectively in order to favor the passage of the faster molecules and thus obtain a temperature difference from an isothermal situation.

This temperature difference could operate a thermal engine allowing to produce work outside. The vessel is immersed in an environment at constant temperature and in the overall process, the work produced by the engine would be compensated by an equivalent quantity of heat supplied by the environment to the gas. By this way we could get a perpetual motion (of the second kind), that is, the violation of the Second Principle of Thermodynamics.

Various attempts were made to build some automatic mechanism, that is, that would not require the presence of an imp (demon), to achieve this result: light doors that can be opened in one direction only under the thrust of a suitable fluctuation and close again very quickly before an opposite fluctuation nullify or even reverses the sign of the phenomenon, but with no success.

It is not forbidden that a favorable fluctuation gives us an occasional advantage: it would show, the probabilistic nature of the Second Principle. What it prohibits is that this can be done in a repetitive and predetermined manner.

The paradox remained unsolved because these attempts did not grasp the essential point of the paradox itself. This step was taken in an article by Leo Szilard in 1929 [29]. This was a first step, necessary, but certainly not conclusive.

### 17.2 The Leo Szilard's Article in 1929

L. Szilard, pointed out a key fact: physics could not solve the paradox because it was not able to deal with the fundamental point that the devil, in addition to having exceptional physical gifts, had to be an intelligent being [29]. The essence of Maxwell's paradox was schematized by L. Szilard in the following way. A gas consisting of only one molecule is contained in a cylindrical container fitted at each base with a piston.

Each piston can, if necessary, be moved in either direction without appreciable dissipation. In correspondence to the cylinder centerline may be introduced, where appropriate, a septum which would divide the volume of the entire cylinder into two halves; also this operation can, ideally, be accomplished without an appreciable energy dissipation by the observer. The cylinder is constructed with a material which is a good heat conductor and is held in a thermal bath (environment).

The observer (a more modern version of Maxwell's demon) can get perpetual motion by making the gas to perform a cyclic transformation determined by the following four equilibrium states:

1. At the starting state the molecule occupies the entire volume of the cylinder and is at ambient temperature.
2. The partition is introduced: the molecule will occupy a volume equal to half of the initial volume, but the observer does not know in which part the molecule is; this operation can be accomplished with an expenditure of energy which can be made arbitrarily small.
3. The observer performs an observation to know in which side the molecule is, then he moves the piston corresponding to the empty portion so as to bring it into contact with the partition; subsequently, the latter is removed.
4. The piston that was brought in contact with the partition is slowly (reversibly) moved to the initial position. In doing this the gas undergoes an isothermal expansion and produces work by absorbing an equivalent amount of energy from the environment in the form of heat flow.

The various steps are resumed in Fig. 17.1. So we produced mechanical work with a $100 \%$ efficiency (dissipations relative to the movement of mechanical parts are considered negligible). There are other ways we can produce work with a yield equal to $100 \%$. One way is to expand isothermally and reversibly a gas, in conditions


Fig. 17.1 In (a) the initial state is represented: the molecule occupies the entire volume $2 V$ and is at ambient temperature $T$. In (b) a partition is introduced in the central part. In (c) the piston corresponding to the empty part is moved to the center. In (d) the partition is removed and in (e) the piston expands reversibly to the initial position. Finally, in (f) the molecule is again in the initial state
close to those of ideal gas. Since the internal energy of the gas remains constant the work done by the gas is compensated by an equivalent amount of heat absorbed from the surrounding environment. Also in this case the complete conversion of environmental heat energy into mechanical energy is achieved but this is not the only result. In fact, the gas is in a state different from the initial state because it occupies a larger volume and therefore, this procedure can not be repeated indefinitely. In order to bring the thermal machine (the gas) back to the initial situation (in order to be able to indefinitely repeat the operation) it becomes necessary to employ part of the stored mechanical work during the expansion to bring the gas to the initial volume.

In the thought experiment by Szilard, instead, the gas at the end of the operations is exactly in the same initial state (that is, it occupies the entire volume of the cylinder always at room temperature), and then this transformation of the gas can be repeated endlessly. As regards the gas this is a cyclic transformation and the work was produced by taking the corresponding amount of heat from the surrounding environment, and then with a $100 \%$ yield. So the Second Principle seems to be violated.

It is necessary, at this point, to quantify the amount of work obtained and the amount of heat supplied from the outside, i.e. from the thermostat at temperature $T$.

The energy of the molecule, limited to the terms describing to the motion of the center of mass, is

$$
\begin{equation*}
\varepsilon=\frac{3}{2} k_{B} T \tag{17.1}
\end{equation*}
$$

and then the energy contained in the expanding volume will have the same value that will remain constant during the operation.

We know that, for a classical gas with perfectly reflecting walls, the pressure is related to the energy density by the relationship (see Appendix B.1, (B.13)):

$$
\begin{equation*}
p=\frac{2}{3} u=\frac{2}{3} \frac{U}{V}=\frac{k_{B} T}{V} \tag{17.2}
\end{equation*}
$$

and then the amount of work we will obtain after the isothermal expansion is

$$
\begin{equation*}
W=\int_{V}^{2 V} p \mathrm{~d} V=k_{B} T \ln 2 \tag{17.3}
\end{equation*}
$$

Consequently, as the expanding gas energy content is constant, the environment will provide the cylinder the corresponding amount of heat:

$$
\begin{equation*}
Q=k_{B} T \ln 2 . \tag{17.4}
\end{equation*}
$$

### 17.3 The Observer Creates Information

The key point in this "gedanken experiment" is the following: the operator must know in which sector of the cylinder the molecule is in order to know which piston corresponds to the empty part and, subsequently, start the operations as described before. For this, we need an intelligent being. Intelligent in the sense that he has to make an observation and then adjust his action according to the outcome. ${ }^{1}$ What Szilard called "intelligent being" is, in a nutshell, what we call observer.

It will be a more careful consideration of the role that the observer plays in this thought experiment and of its real nature, that will allow us to solve the paradox and save the Second Principle. On the one hand this will cause us to lay the foundations for a definition of the concept of information as a physical quantity and on the other we will be led to a generalization of the concept of entropy.

It is assumed that the observer, in order to determine the location of the molecule (it is to the right or to the left), has designed, built and used an appropriate detection apparatus: for example he could illuminate the two rooms with a light beam of low frequency waiting to see a diffused photon. In principle only the diffuse photon energy would represent a cost for the observation and this could be selected so as to possess a very small fraction of the kinetic energy of the molecule (the lower the frequency the lower the energy of the photon "dissipated" by the observation). In Physics we call resolving power of an optical instrument, the minimum distance $d$ at which two point sources are declared as "distinct". We know the resolving power of an optical instrument which uses a radiation with wavelength $\lambda$ is of order $\lambda$.

Since the observer is interested to discover whether the molecule is on the right or on the left, he may (in principle) use of a radiation that has a wavelength of the order of the size of the two containers. Therefore the energy cost associated with the operation of the apparatus of observation decreases with the increase of the size of the cylinder and hence this energy cost cannot "save" the Second Principle because the work produced is independent of the size of the machine (see Eq. (17.3)) [30, 31]. There is an additional step to consider. If we associate the idea of intelligent being to the figure of the observer intended as a human being, we have to take into account the fact that, after having observed the diffused photon, his mental state suffered a modification. He has reached an awareness he had not before making the observation: we can state that his mind, considered as a physical system, has undergone a change of state.

Now he knows that the molecule is to the right (for instance). A process took place, analogous to the collapse of the wave function which occurs in quantum mechanics whenever you make an observation: in our case, at the beginning the state of the

[^63]molecule was represented by a linear combination with coefficients $1 / \sqrt{2}$ of the states right and left. After the observation, the state collapses to one of the two. How can we bring in the analysis of the phenomenon, the change of state that occurs in the mind of the observer? Certainly, the observer must have stored the observation datum in order to perform, as a consequence, the right procedure.

We suppose that the participation of the observer's mind in this process can be reduced to the setting of the datum in a memory, as is the case for example for the memory of a computer.

We do not attribute to the original formulation of Szilard, about the necessity of the presence of an intelligent being, any reference to the human mind.

We can, for the moment, limit ourselves to consider automaton which: first observes the position; then it stores the datum in a memory and then, instructed with a suitable program, it performs the right procedure, depending on the result of the observation.

This should be considered an intelligent being, in the sense of Artificial Intelligence.

It should be noted that our emphasis on identifying the position of the molecule before starting the operations, must not be overestimated.

Let us modify the apparatus in this way: the two pistons at the ends of the cylinder are replaced by two end-walls that can be removed if desired. The central septum is constructed in such a way as to be able to move without friction in either direction once it has been introduced into the central position of the cylinder. In this way, once introduced, it will move in the right direction depending on the position of the molecule and the isothermal expansion will be realized.

To repeat the operation it will be necessary to remove the end-wall where the expansion terminated and use it as the central partition in the new cycle.

It is at this point that the operator will have to perform a binary observation in order to establish which of the two end-walls is to be removed, and hence the observer has to create one bit of information in order to proceed correctly (this procedure could also be considered a way to "observe" the position of the molecule even if someone could, mistakenly in our opinion, call it "an indirect observation"). In conclusion, sooner or later, a bit of information will be created and this is the fundamental point.

### 17.4 The Solution of Maxwell-Szilard Paradox

The need to store the result of an observation, suggested to Bennett [30] a possible solution to the paradox "of Maxwell's demon".

As already noted, it is true that gas has made a cyclic transformation, but the observer will now be, in a state different from his initial state.

The acquisition of the information about the position of the molecule has changed the state of the memory used by the observer (for instance an automaton). In order to store the datum, the observer had to change, or create, a physical system and, in so doing, created information (in our example one bit). Therefore, the procedure used
by the observer may continue until all the entire available memory will have been used.

This situation is analogous to the example mentioned at the beginning in which a gas, in ideal conditions, was made to expand at a constant temperature.

In the latter case the yield was maximum but, as we have noted, this result could be obtained up to a certain amount of produced work, limited by the fact that the expansion of the gas could not continue indefinitely. Similarly, in this case, we can produce work with $100 \%$ efficiency until we have exhausted all available memories.

In conclusion in both cases, we produced work with the maximum efficiency but some change has been produced in the universe. In the isothermal expansion case the change is in the engine "strictly speaking" and therefore easily recognizable. In the case of the Szilard engine, the change is in the memory of the observer.

The possibility of creating perpetual motion requires that the operation can be repeated indefinitely, i.e., the engine "in the broadest sense" must perform a cyclic transformation. The analogy between the two situations shows that it is necessary to consider the memory of the observer, or better the observer as a whole, as a part of the engine.

In conclusion, if we want to perform a cyclic transformation we have to erase the information that we had to store during the operation.

### 17.5 Landauer Principle

The solution came from an intuition of Rolf Landauer in 1961 [32] (see also [31, 33]) in a paper devoted to the study of the constraints imposed by Physics to the phase of information processing (by this we mean the realization of an observation, the setting a result in memory and the processing of the data).

While the process of copying information (classical) can be done reversibly and without any cost, the process of erasing information requires a minimum, non-zero, production of entropy: for 1 bit of information this entropic cost $S_{\text {bit }}$ is set to be

$$
\begin{equation*}
S_{\mathrm{bit}}=k_{B} \ln 2 . \tag{17.5}
\end{equation*}
$$

In the case of Szilard machine the entropic cost for the cancelation of the memory results in an energy cost equal to (at least):

$$
\begin{equation*}
Q=T \Delta S=k_{B} T \ln 2 \tag{17.6}
\end{equation*}
$$

So to perform a completely cyclical process we should use, at least, all the work that the gas has produced.

### 17.6 On the Separation Observer-Observed

The preceding discussion has forced us to consider the overall system [gas + observer] as the overall "isolated" system to which the requirement to perform a cyclic transformation applies and, in this new perspective, we have verified the need of taking into account the changes of state of the observer.

The conclusion we reach is, at first glance, rather surprising: the saving of the Second Principle of Thermodynamics is based on the impossibility of separating the observer from the observed. Staying within the optics of a "macroscopic" observer that describes the system with the usual macroscopic variables volume, pressure and temperature, the two possible states (molecule to the right molecule to the left) constitute, before the acquisition of the information, one ensemble of states described by the same macroscopic state variables. In exactly the same sense, by adopting the statistical mechanical description, we consider the macroscopic state as an ensemble of a (large) number $W$, of equivalent microscopic states.

From the macroscopic system, we cannot get any work. We have seen, however, that this becomes possible if the observer can distinguish between the two "microscopic" states.

Generalizing this result we can say that if the observer increases the degree of complexity of observation, which in this case means to distinguish between some microscopic states of the ensemble, new results become possible.

With the words used at the beginning of this section, we will say that "some processes that are unnatural to a certain level of complexity, can become natural at a higher level of complexity."

This conceptual change in the observer-observed relationship opens the way to new developments, in the direction of broader generalizations of Thermodynamics and Statistical Mechanics.

As the central point in this new conceptual development, is the need to fix a given datum (that is, the result of an observation) in a memory, it is natural that the great development of information theory, initially motivated by technological and economic reasons connected with the transmission of messages, in fact, constitutes a fundamental domain of knowledge.

### 17.6.1 Information as a Physical Quantity Which Acquires a Physical Reality

This link between observer and observed is determined by the definition of a new physical quantity called briefly information or more precisely amount of information. In the above discussion, we have highlighted a crucial point: if we want that the observation could lead to the production of work it is necessary that the datum becomes an information and this implies

1. It must be fixed in a physical medium (memory);
2. It must be able to be transmitted to another observer; the latter can reconstruct the observation and eventually proceed accordingly.

The observer's ability to create and process information is determined, and then it is also limited, by the laws of mechanics, electromagnetism, quantum mechanics, more in general by the laws of Physics. ${ }^{2}$ This means that the theory of information is not a purely mathematical theory but is a physical theory and the information is physical quantity (physical information) [34].

We will call information processing the set of two operations: (i) the deposit or fixation of the information in some physical medium (the memory); (ii) the data transmission.

It is important to emphasize the role of the data transmission process in the definition of information processing because, as we can easily understand, this part will inevitably introduce some corruption of the encoded information due, for instance, to what is called "noise" present in all channels of data transmission. For example to encode 1 bit we can use a system with two states (a relais with on/off positions, spin up/down, an atom with two energy levels, etc.) but during the "transport" (transmission of the information) this system can interact with the environment in which it is immersed and undergo a change of state. In this case, the information which will arrive might be the opposite one. In the cases in which the observer is not able to control the phenomenon that generates the error we call this, uncontrolled interaction, interaction with a "thermal noisy environment" (recall the definition of amount of heat as a descriptor of the interactions "not controlled"). In other cases, the observer recognizes a precise cause of error but is not able to remedy them due to external constraints that can be either of technical or economic nature (such as in some phenomena of crosstalk between transmission lines or between electronic components). In all cases, the observer will have to measure or at least to estimate the probability that the stored information "flips" that is, changes the state during transmission. The observer will, then, be able to put into play suitable defence strategies against these errors and, in principle, he will be able to make the error probability as small as he wants. To do this, however, he will have to pay a price: he will send more "binary words" to transmit only one bit of information.

For example if he has to transmit the "datum" $|1\rangle$ and he knows that during the transmission it can switch, due to the external noise, to $|0\rangle$ with probability $p$, the observer will be able to transmit a message composed by three binary words $|a\rangle|b\rangle|c\rangle$ and agree with the recipient that it should be considered as $|1\rangle$ the message formed by $|1\rangle|1\rangle|1\rangle$ and that it should be considered as $|0\rangle$ the message which arrives in the form $|0\rangle|0\rangle|0\rangle$. With this agreement, the recipient will receive two types of messages with certain identification (that is, those with three identical symbols) and six types of message with uncertain identification (i.e. those in which only two symbols are equal). Attributing to each of these last six "mixed" events the meaning relative to the datum that appears twice he misses only in the cases in which, during transmission,

[^64]two words have suffered an inversion but this event occurs with a probability that is of order $p^{2}$.

For example, if the probability of error on the single word is $10^{-3}$, the recipient will be in error once in a thousand (probabilistically speaking) if the transmission is made with "one symbol message" but if the message is made by three binary words the receiver will be in error about once in a million.

Therefore, the error can be made smaller then a predetermined amount but at the price of transmitting less data given the same message length.

This brief account is intended to show that the two "constitutive" parts of the concept of information processing, i.e., the storage and the transmission, are separated only for practical convenience of discussion, but the two parts should be considered complementary to each other in the definition of the concept of information. The study of the noisiness of the transmission channels is therefore a fundamental part in information theory. For a detailed discussion see, for example, [35-37].

## Measure of the Quantity of Information (Classical)

From the above discussion we have seen that the "datum" that the observer defines as the simplest one, that is what can be described in the most economical way, is a binary choice: the molecule is to the right or to the left and, in this case, the datum to be fixed expresses a choice between two equally likely possibilities. The system is located in one of two equally probable situations and we will consider this one as the elementary situation. We will say that the information possessed by such a simple system is the unit information and we will call this unit of information bit abbreviation that stands for the English term binary digit. If the system we are observing can be found in $n$ different and equally likely states, our uncertainty will be larger and therefore an observation that chooses one possibility among many, will provide "a more valuable information". We say that it will provide more information and we have to define, quantitatively, how much the contained information is.

This is, by definition, equal to the amount of information contained in the message sent to a receiver to enable him to reconstruct the observation. The amount of information contained in a message is defined in the Theory of Information (see for instance the seminal book [35]).

The transmission of a "given observation" which requires the minimum amount of information is then the one for a binary situation (right-left, open-closed, up-down, etc.), i.e., we are transmitting one bit. When the observation selects one outcome out of a larger number of possibilities it will require a longer message, that will be composed by a higher number of bits. In this sense we will say that the system which can be in a higher number of possibilities "contains" a larger "quantity" of information. What we can say about the codification of observational data can be extended, in the theory of communication, to the definition of the amount of information contained in a message .

The elementary message is composed of one symbol selected from two possibilities: this is a message composed of one bit and contains a unitary information. If
the message is one choice among $N$ equiprobable possibilities then we will say, by definition, that the message contains an amount of information $\mathbb{I}$ given by

$$
\begin{equation*}
\mathbb{I}=\log _{2} N \text { bits of information. } \tag{17.7}
\end{equation*}
$$

In general consider a message consisting of $n$ symbols belonging to an alphabet consisting of $N$ different symbols (including spaces and punctuation).

If all the symbols were equiprobable in the composition of a message, then a given message composed of $n$ symbols would constitute one possibility out of $N^{n}$ and therefore the amount of information $\mathbb{I}$ contained in such a message would be equal to:

$$
\begin{equation*}
\mathbb{I}=\log _{2} N^{n}=n \log _{2} N \text { bits of information. } \tag{17.8}
\end{equation*}
$$

As we may have to compose messages of different length, it is useful to observe that, in this simple case, we can define the information per symbol which is equal to $\log _{2} N$. The information contained in a message composed of $n$ symbols is $n$ times the average information per symbol. This apparently trivial step is useful in view of the generalization to the case of non-equiprobable symbols which is based on the concept of average information per symbol.

Example 17.1 Still remaining in the case of equiprobable symbols we consider a very simple example. In the case in which the "elementary choice" is between two equally probable states, i.e., $N=2$. the amount of information contained in a message composed by $n$ symbols can be calculated with Eq. (17.8) and we find, as the result, the value of $n$ bits. The average information per symbol is, obviously, 1 bit $\left(\log _{2} 2=1\right)$.

If the system can be found in 8 equally probable states, that is if the "elementary choice" is one among eight possibilities, using the same expression Eq. (17.8) we see that a message composed by $n$ symbols contains $3 n$ bits of information and that the information per symbol is 3 bits $\left(\log _{2} 8=3\right)$. In fact, it is easy to see that with three binary memories we can describe the eight possible states. In the case of a number of 5 decimal digits each symbol contains 3.32 bits of information then a 5 -digit number contains 16.6 bits.

As we know, however, in the different languages that are used in communications, the various symbols with which we construct the messages are not equally probable as can be seen by a statistical analysis of the frequency with which each symbol appears in a very long written text. Furthermore, the probability that a given symbol occurs also depends on the occurrence of other symbols before it.

We are thus led to consider situations in which the probability of occurrence of the various symbols in the message are different from one another. If we denote with $p_{i}$ the probability with which a given symbol may occur, we define the amount of information possessed by a message of $n$ symbols, by the quantity:

$$
\begin{equation*}
\mathbb{H}=-n \sum_{i=1}^{N} p_{i} \log _{2} p_{i} \tag{17.9}
\end{equation*}
$$

Here, we see that the average amount of information per symbol is

$$
\begin{equation*}
\langle\mathbb{I}\rangle=-\sum_{i=1}^{N} p_{i} \log _{2} p_{i} \tag{17.10}
\end{equation*}
$$

Therefore, the amount of information in a message composed of $n$ symbols is $n$ times the average information per symbol. This is a generalized expression for the measure of the amount of information contained in a message but, as we see, the notation to indicate this amount has also been changed $(\mathbb{I} \rightarrow \mathbb{H})$. The reason lies in the fact that the expression for the amount of information coincides with the expression for the entropy of a physical system when this is described in the mechanical-statistical perspective as we shall see in the following subsection.

## Entropy of Information (Alias "Shannon Entropy")

In the formulation of the First Principle we have seen how the effect of all unknown interactions is summed up in the so-called amount of heat $Q$. This step is sufficient for the energy balance but cannot, by itself, constitute a measure of our degree of ignorance with respect to a knowledge of the configuration that we consider "complete". The physical quantity to which we must attribute this function is entropy.

To understand why this represents the right choice, we need to define what we mean by a complete knowledge and what we mean by saying that the level of knowledge that we have about a configuration, will increase or decrease as a result of a change of state.

This step is made clear (within the atomic-molecular theory of matter) by the basic relation due to L. Boltzmann in which entropy is linked to the number $w$ of microscopic configurations that are compatible with a given macroscopic state:

$$
\begin{equation*}
S=k_{B} \ln w, \tag{17.11}
\end{equation*}
$$

where $k_{B}=1.38 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ is the well known Boltzmann constant. Our macroscopic observation defines the macroscopic state with a small number of parameters (the macroscopic properties) but we know that, from the microscopic point of view, this macroscopic state corresponds to a large number, $w$, of microscopic configurations. It makes sense to establish that if after a change in the macroscopic state, the number of the corresponding microscopic states increases, our level of knowledge of the system has decreased.

Further, it makes sense to say that we will have the complete knowledge if the number of possible configurations is equal to 1 . As we know this happens in the asymptotic situation to which the system is brought when its temperature is made to tend to zero.

Thus the thermodynamic entropy is the suitable quantity to measure our "level of ignorance" of the system with respect to its microscopic description.

In the elementary mechanical-statistical perspective, all the $w$ microstates that correspond to a given macroscopic state are considered equally probable. We may wonder what would be the correct generalization of Eq. (17.11) in the case of microscopic states with arbitrary probability $p_{i}$. It is found that the correct expression is

$$
\begin{equation*}
S=-k_{B} \sum_{i=1}^{w} p_{i} \ln p_{i} \tag{17.12}
\end{equation*}
$$

We see that in the case in which all microstates are equally probable, i.e., all microstates occur with probability $p_{i}=1 / w$, then the relation given by Eq. (17.12) gives

$$
\begin{equation*}
S=-k_{B} \ln \left(\frac{1}{w}\right)=k_{B} \ln w \tag{17.13}
\end{equation*}
$$

The analogy between Eqs. (17.9) and (17.12) is evident and so is evident the analogy of the meanings. First we rewrite the information per symbol contained in Eq. (17.9) so that it is expressed as a function of the natural logarithm:

$$
\begin{equation*}
\frac{\mathbb{H}_{\mathrm{st}}}{n}=-K \sum_{i=1}^{N} p_{i} \ln p_{i} \tag{17.14}
\end{equation*}
$$

where we posed

$$
\begin{equation*}
K=\log _{2} e=\frac{1}{\ln 2} \tag{17.15}
\end{equation*}
$$

In this way both the amount of information Eq. (17.9) and the generalized Entropy Eq. (17.12) are expressed in terms of natural logarithms and the different multiplicative constants, in these two expressions, assume the meaning of a different choice of the units of measure, being the bit for the amount of information and the joule/degree for the thermodynamic entropy.

The quantity introduced by Eq. (17.14) was proved by Shannon to be the right expression for the measurement of the amount of information in a message. The same quantity is also the proper expression for the entropy measure of a macroscopic system when the latter is measured in bits.

The microscopic point of view, then, justifies the analogy between entropy and amount of information possessed by a system. When we say that the observer performs the measurements and "increases his knowledge" on the system, we say that as a result of the measurements some microscopic states that were possible and equally probable before are now excluded or become accessible but with decreased probability.

We can verify that this corresponds to a decrease in the amount of information possessed by the system, or to an increase in the knowledge of the system by the observer.

Even L. Boltzmann proposed entropy as a measure of our remoteness from a complete knowledge or, to use his expression, he had highlighted the relationship between entropy and the missing information. He noted that an increase in entropy corresponded to an increase in "missing information".

## The Qbit

The concept of information discussed so far, originated and was developed in the context of classical physics (non quantum). For this reason sometimes, we refer to it as classical information when we want to distinguish it from the information theory that is developed in the context of quantum physics.

The substantial difference between the classical and the quantum cases lies in the concept of superposition of states and in the consequences which derive from it.

Remaining in the elementary case of the binary choice, or bit, the fundamental property that characterizes the classical information is that the "object" we choose to represent, and subsequently transmit, the information, can be prepared in one of its two possible states that we denote with $|\uparrow\rangle$ or $|\downarrow\rangle$ (they could represent, for instance, the states of spin up and spin down of an electron).

In the quantum context, the system can be prepared in any of the infinite number of states expressed, in general, by the relation:

$$
\begin{equation*}
|\psi\rangle=\alpha|\uparrow\rangle+\beta|\downarrow\rangle, \tag{17.16}
\end{equation*}
$$

where $\alpha$ and $\beta$ are two arbitrary complex numbers subject only to the condition that $|\alpha|^{2}+|\beta|^{2}=1$.

In the classical case, the information is encoded in one of two alternative states while in the quantum case the information is encoded in a state which can be, in some sense, in both the alternative states.

Since in the quantum description $|\alpha|^{2}$ and $|\beta|^{2}$ give the probability that a system which is in the state $|\psi\rangle$, if observed, appears in the state $|\uparrow\rangle$ and in the state $|\downarrow\rangle$ respectively, we might think that the quantum theory of information constitutes just a probabilistic generalization, we might say, of the classical theory. In other words, it would be reasonable to think that the use of the state $|\psi\rangle$ to encode information, allows us to encode information inherently probabilistic: for instance, in our case it would encode the information that the observation would show the state $|\uparrow\rangle$ with probability $p=|\alpha|^{2}$ and the state $|\downarrow\rangle$ with probability $(1-p)$.

This would certainly be a useful generalization compared to our starting point where, we recall, the observer encodes the result of his observation in a binary system and in a deterministic way.

The point is that the $\alpha$ and $\beta$ are complex numbers, and then possess an absolute value (or module) and a phase. If we limit ourselves to states describing one particle, only the relative phase between $\alpha$ and $\beta$, that is the difference of the two phases, is relevant. Then for every value of $|\alpha|^{2}=p$ and of $|\beta|^{2}=1-p$ (i.e. for given
probabilities) we have an infinite number of possible values for the relative phase, which is any real number in the interval $(0,2 \pi)$.

We can say that while the classical information can be represented with an object whose state is described by a unit vector which can point either upwards or downwards, the system that contains the elementary quantum information is described as a complex vector in a two-dimensional Hilbert space. It can be visualized as well by a unit vector in a three-dimensional space (Bloch's sphere). In the same Bloch's sphere the bit is represented by a unit vector that can have only one direction and the two possible opposite orientations.

Either in the classical or in the quantum case the physical system chosen to encode the minimum amount of information is a system of two states such as, for example, an object of $\operatorname{spin} 1 / 2$.

If this system is treated classically, it will constitute the classic representation of the unit of information, the bit. If this system is treated according to the theoretical framework of quantum mechanics it constitutes, by definition, the basic unit of quantum information that, by analogy to the classical case, will be called Qbit.

However, we must emphasize that this infinitely greater capacity to store information by one Qbit is strongly reduced by the information-processing operations.

After preparing the Qbit, Alice must send it and the recipient (Bob) must receive and decode it, that is to say he has to reconstruct the original state (the transmitted Qbit). Even if transmission occurred without loss of information, that is without corruption during the transmission, Bob will not be able to completely rebuild the original Qbit. In fact the only measurement that Bob can do is to choose an orientation for its detector and determine if the received Qbit (for example we speak of a particle of spin $1 / 2$ ), will have positive or negative projection with respect to the direction of the detector. In other words, when we want to extract information from one Qbit we extract a classical bit. So, much of the information contained in the Qbit can be elaborated but remains inaccessible.

The major difference between the quantum and classical information appears completely when we use and send $n$ Qbits.

Suppose that we want to transmit an object composed of $n$ particles (for example $n$ particles of spin 1/2). In the classical context the complete knowledge of a system composed of $n$ particles is obtained if we know the state of each particle. Since each particle is described by a vector in a two-dimensional space, the state of $n$ particles will be represented in a $2 n$-dimensional space.

In the quantum description, the perspective changes radically. The state that will be prepared, transmitted, and measured (namely, the information) will be a vector in a Hilbert space with $2^{n}$ dimensions. For instance, in a three particles state the quantum description requires a vector in an eightfold space: the state of a three particles system is described by a vector of the type $|\alpha, \beta, \gamma\rangle$, where $\alpha, \beta, \gamma$ can have a binary value. We see that we can construct a basis of 8 mutually orthogonal unit vectors which generate a eightfold Hilbert space while in the classical description the dimensionality is 6 .

Another fundamental difference with respect to the classical case regards the phase of transmission of the information through a quantum channel that is a channel that
interacts with the "environment" according to interactions governed by quantum physics. For instance, if the original message is encoded in "pure states" (mutually orthogonal and analogous, in some sense, to the classical bits) these pure states can be transformed in non-pure states: this limits the amount of information that can be transmitted with one quantum state (Holevo bound) but we shall not enter in this field.

A thorough treatment of basic quantum information theory would require to go through the foundations of Quantum Mechanics and this goes beyond the purpose of this book, nevertheless it is worth pointing out the connection between Thermodynamics and some of the most important development of the fundamental Physics in these years.

### 17.6.2 New Perspectives: The Physical Entropy According to Zurek

Maxwell-Szilard's paradox solution has called into question the theory of information, or better, in essence, the concept of information. This concept and the theory that has been developed around it, gives a new and fundamental representation of the role that our knowledge and its transmission among observers, have in the study of natural phenomena.

This path opens the way to further expansion of already established concepts and, then, to the formulation of new paradigms. In this subsection we want to quote, as an example, the new paradigm proposed by W.H. Zurek [38]. This new point of view proposes, as a starting point, a new definition of entropy and, consequently, of other thermodynamic potentials. This new paradigm has important consequences in the way of opening up new horizons for statistical mechanics and suggests a contribution to the solution to the secular problem of the "arrow of time". As we have very briefly seen, at a higher level of complexity (microscopic vision), Statistical Mechanics defines Entropy according to the number of microscopic states in the two basic formulations:

$$
\begin{equation*}
\mathbb{H}_{\mathrm{st}}=\ln w \tag{17.17}
\end{equation*}
$$

for the Gibbs-Boltzmann case and:

$$
\begin{equation*}
\mathbb{H}_{\mathrm{st}}=-\operatorname{Tr}(\tilde{\rho}, \ln \tilde{\rho}) \tag{17.18}
\end{equation*}
$$

for the quantum case where $\tilde{\rho}$ is the density matrix and $\operatorname{Tr}$ is the trace operator (see [39, 40]).

This probabilistic description of reality certainly captures a profound aspect and thus represents a real increase in the level of complexity but poses an apparently irresolvable problem. If a system evolves over time according to Hamiltonian dynamics, the number of microstates (phase space volume) remains constant over time, and so
the so-called entropy increase law is not justified. In other words, we can say that the hope of reconciling reversibility by inversion of the temporal axis of microscopic laws of motion with the irreversible "thermodynamic arrow of time", fails.

Already von Neumann had seen, in his discussion about the measurement in quantum mechanics, the relevance of entropy and information theory. The analogy first between the thermodynamic entropy and that of Gibbs-Boltzmann and later, between these two and the theory of communication developed by Shannon and Weaver [35], laid the foundation for further generalizations and a possible solution to the problem.

Maxwell, first, and Boltzmann, later, suggested that entropy was linked to a kind of measure of our ignorance: the concepts of "order" and "disorder" are linked, starting from the use we make of these terms in common language, to our ability to describe our observations more or less fully. Important contributions come from Jaynes [41, 42] and Brillouin [43].

The increase in Entropy, measures the increase in the amount of information contained in the system and this allows us to say that "the disorder has increased" but does not measure the amount of order. This is related to the ability of the observer to describe, with the desired accuracy, the observation. More precisely, a messy system is a system that requires a very long description to be reproduced with the desired accuracy. The length depends on the minimum number of bits a message must contain so that the receiver can understand the description. The message will be considered as understood when the receiver will be able to reproduce the configuration at the required level of detail.

For example, the description of a microstate will be understood by the receiver if he is able to print a two-dimensional plot or a graph with the desired accuracy, with the aid of a normal computer that uses the data contained in the message.

The minimum length of the message required by a universal computer (the receiver) to reproduce the observed state is called algorithmic information content, algorithmic randomness, algorithmic entropy, or, sometimes, algorithmic complexity [30, 44-48].

This quantity, named algorithmic randomness or algorithmic entropy, measures the level of randomness and the evolution of a state toward configurations that we call more disordered might be described by the increase in this term. This constitutes a possibility, therefore, that the thermodynamic arrow of time, which can not be explained by the probabilistic entropy for Hamiltonian systems, might then be attributed to the increase of algorithmic entropy.

In typical (traditional) macroscopic treatment, the relevant properties are determined by a few macroscopic parameters such as pressure, volume, temperature. From these data relating to the above parameters, we can calculate the entropy and from this, the maximum amount of extractable work. More detailed knowledge of microscopic states is absolutely useless because the machine was designed to ignore microstate information (we say that the observer has chosen this level of complexity of observation). We may think that a different design could benefit from a variable strategy based on the information obtained from the observations. The question then becomes: what physical quantity should an intelligent entity use to maneuver the
machine so that it can also benefit from opportunities that may arise (such as, for instance, fluctuations)?

Zurek proposes a quantity that he calls "physical entropy" which is defined as the sum of:

1. Statistical Entropy, $\mathbb{H}_{\mathrm{st}}$. The term, which in the macroscopic description coincides with thermodynamic entropy and measures our ignorance of the system;
2. Algorithmic Entropy, $\mathbb{K}$ for the representation of known data; This term is the measure of the minimum length of the string describing the data (the measure of what we know).

This formulation of the entropy concept provides a proposition to formulate the Principles of Thermodynamics from the point of view of an "information gathering and using system" (IGUS) that is, an entity-observer that can make measurements, process the acquired information and use the results to take the right actions to increase the performance of the machine that he controls [38].

$$
\begin{equation*}
S=\mathbb{H}_{\mathrm{st}}+\mathbb{K} \tag{17.19}
\end{equation*}
$$

In this way, the degree of knowledge on the system by the observer helps to define the thermodynamic potentials of the system. This might seem to be a weird artifact because we are fond of the idea that the properties of an object are, in fact, objective. How can the same "thing" be described by different properties depending on whether the observer knows more or less? Are these "different things"?

They are, indeed, different things in fact we can obtain different amounts of work without violating the Second Principle.

In the paradigmatic case (Maxwell-Szilard engine and Bennett's solution) discussed above the situation seems well described: the violation of the Second Principle and its restoration depend on the observer-observed interaction and the observer's participation in the overall accounting.

In the Zurek's proposal, the role of the observer in determining the properties of the observed system becomes explicit. Algorithmic complexity helps to determine the potentials of the observed system, and these become fully defined according to the observer's presence, the theoretical context achieved and the level of complexity adopted for his observations. However, it must be emphasized that the presence of the observer manifests itself from the "established results" and nothing is said in this context about the observation process.

## Appendix A Math Tools

We recall here some useful mathematical relations widely used in the discussions contained in this volume. They are simple relations of general validity between the partial derivatives of functions of several variables.

## A. 1 Relation 1

Consider a real variable $z$ expressed as a function of two other real variables $x$ and $y$ in the following form:

$$
\begin{equation*}
z=z(x, y) . \tag{A.1}
\end{equation*}
$$

Let us write the differential of $z$ :

$$
\begin{equation*}
\mathrm{d} z=\left(\frac{\partial z}{\partial x}\right)_{y} \mathrm{~d} x+\left(\frac{\partial z}{\partial y}\right)_{x} \mathrm{~d} y . \tag{A.2}
\end{equation*}
$$

Let us suppose that the function can be inverted in the form $y=y(x, z)$ or $x=$ $x(y, z)$. The differential $\mathrm{d} y$ is written as

$$
\begin{equation*}
\mathrm{d} y=\left(\frac{\partial y}{\partial x}\right)_{z} \mathrm{~d} x+\left(\frac{\partial y}{\partial z}\right)_{x} \mathrm{~d} z \tag{A.3}
\end{equation*}
$$

By substituting Eq.(A.3) in Eq. (A.2), we get

$$
\begin{equation*}
\mathrm{d} z=\left(\frac{\partial z}{\partial x}\right)_{y} \mathrm{~d} x+\left(\frac{\partial z}{\partial y}\right)_{x}\left[\left(\frac{\partial y}{\partial x}\right)_{z} \mathrm{~d} x+\left(\frac{\partial y}{\partial z}\right)_{x} \mathrm{~d} z\right], \tag{A.4}
\end{equation*}
$$

and putting together the terms in $\mathrm{d} x$ and $\mathrm{d} z$ in Eq. (A.4) we obtain

$$
\begin{equation*}
\mathrm{d} z=\left[\left(\frac{\partial z}{\partial x}\right)_{y}+\left(\frac{\partial z}{\partial y}\right)_{x}\left(\frac{\partial y}{\partial x}\right)_{z}\right] \mathrm{d} x+\left(\frac{\partial z}{\partial y}\right)_{x}\left(\frac{\partial y}{\partial z}\right)_{x} \mathrm{~d} z \tag{A.5}
\end{equation*}
$$

Since Eq. (A.5) is an identity, the two following equations must hold:

$$
\begin{equation*}
\left(\frac{\partial z}{\partial x}\right)_{y}+\left(\frac{\partial z}{\partial y}\right)_{x} \cdot\left(\frac{\partial y}{\partial x}\right)_{z}=0 \tag{A.6}
\end{equation*}
$$

and

$$
\begin{equation*}
\left(\frac{\partial z}{\partial y}\right)_{x} \cdot\left(\frac{\partial y}{\partial z}\right)_{x}=1 \tag{A.7}
\end{equation*}
$$

Equation A. 6 leads to the following very useful identity involving the three partial derivatives:

$$
\begin{equation*}
\left(\frac{\partial z}{\partial x}\right)_{y}\left(\frac{\partial x}{\partial y}\right)_{z}\left(\frac{\partial y}{\partial z}\right)_{x}=-1 \tag{A.8}
\end{equation*}
$$

## A. 2 Relation 2

Let us consider a variable $w$ which is a function of two other variables $x, y$ :

$$
\begin{equation*}
w=w(x, y) . \tag{A.9}
\end{equation*}
$$

Let us suppose as well that $x$ and $y$ may be expressed in the form $x=x(y, z)$ or $y=y(x, z)$. The differential of $w$ is

$$
\begin{equation*}
\mathrm{d} w=\left(\frac{\partial w}{\partial x}\right)_{y} \mathrm{~d} x+\left(\frac{\partial w}{\partial y}\right)_{x} \mathrm{~d} y \tag{A.10}
\end{equation*}
$$

If we put the differential $\mathrm{d} y$ of the function $y=y(x, z)$, in Eq. (A.10) we obtain

$$
\begin{equation*}
\mathrm{d} w=\left(\frac{\partial w}{\partial x}\right)_{y} \mathrm{~d} x+\left(\frac{\partial w}{\partial y}\right)_{x}\left[\left(\frac{\partial y}{\partial x}\right)_{z} \mathrm{~d} x+\left(\frac{\partial y}{\partial z}\right)_{x} \mathrm{~d} z\right] . \tag{A.11}
\end{equation*}
$$

Putting together the terms in $\mathrm{d} x$ and $\mathrm{d} z$ in Eq. (A.11) we get

$$
\begin{equation*}
\mathrm{d} w=\left[\left(\frac{\partial w}{\partial x}\right)_{y}+\left(\frac{\partial w}{\partial y}\right)_{x}\left(\frac{\partial y}{\partial x}\right)_{z}\right] \mathrm{d} x+\left(\frac{\partial w}{\partial y}\right)_{x}\left(\frac{\partial y}{\partial z}\right)_{x} \mathrm{~d} z \tag{A.12}
\end{equation*}
$$

Considering that $w=w(x, y)=w(x, y(x, z))=w(x, z)$ and differentiating we get

$$
\begin{equation*}
\mathrm{d} w=\left(\frac{\partial w}{\partial x}\right)_{z} \mathrm{~d} x+\left(\frac{\partial w}{\partial z}\right)_{x} \mathrm{~d} z \tag{A.13}
\end{equation*}
$$

Comparing Eqs. (A.12) and (A.13), we obtain the two identities:

$$
\begin{align*}
& \left(\frac{\partial w}{\partial z}\right)_{x}=\left(\frac{\partial w}{\partial y}\right)_{x}\left(\frac{\partial y}{\partial z}\right)_{x}  \tag{A.14}\\
& \left(\frac{\partial w}{\partial x}\right)_{z}=\left(\frac{\partial w}{\partial x}\right)_{y}+\left(\frac{\partial w}{\partial y}\right)_{x}\left(\frac{\partial y}{\partial x}\right)_{z} \tag{A.15}
\end{align*}
$$

The expression given in Eq. (A.14) is an obvious expression of the theorem on the derivates of a composite function, while Eq. (A.15) is very useful since it establishes the relation between the partial derivatives of the variable $w$ with respect to the same variable $x$, keeping constant either $z$ or $y$.

## A. 3 Euler Theorem for Homogeneous Functions

Let us consider, for simplicity, a function of two variables in the following form:

$$
\begin{equation*}
z=f(x, y) \tag{A.16}
\end{equation*}
$$

This function is said to be a homogeneous function of degree $n$ if the following property holds:

$$
\begin{equation*}
f(t x, t y)=t^{n} f(x, y) \tag{A.17}
\end{equation*}
$$

where $t$ is an arbitrary parameter. At every point ( $x, y$ ), we differentiate (A.17) with respect to $t$. If we pose $x^{\prime}=t x$ and $y^{\prime}=t y$ we may write

$$
\begin{equation*}
\mathrm{d} f=\left[\left(\frac{\partial f}{\partial x^{\prime}}\right)\left(\frac{\partial x^{\prime}}{\partial t}\right)+\left(\frac{\partial f}{\partial y^{\prime}}\right)\left(\frac{\partial y^{\prime}}{\partial t}\right)\right] \mathrm{d} t=n t^{n-1} f(x, y) \mathrm{d} t \tag{A.18}
\end{equation*}
$$

and this leads to the identity

$$
\begin{equation*}
\left[\left(\frac{\partial f}{\partial x^{\prime}}\right)\left(\frac{\partial x^{\prime}}{\partial t}\right)+\left(\frac{\partial f}{\partial y^{\prime}}\right)\left(\frac{\partial y^{\prime}}{\partial t}\right)\right]=n t^{n-1} f(x, y) \tag{A.19}
\end{equation*}
$$

Taking into account that $\left(\partial x^{\prime} / \partial t\right)=x$ and that $\left(\partial y^{\prime} / \partial t\right)=y$, Eq. (A.19) becomes

$$
\begin{equation*}
x\left(\frac{\partial f}{\partial t x}\right)+y\left(\frac{\partial f}{\partial t y}\right)=n t^{n-1} f(x, y) \tag{A.20}
\end{equation*}
$$

and for the value $t=1$ of the parameter we finally obtain

$$
\begin{equation*}
x\left(\frac{\partial f}{\partial x}\right)+y\left(\frac{\partial f}{\partial y}\right)=n f(x, y) . \tag{A.21}
\end{equation*}
$$

Obviously, in the case of homogeneous functions of an arbitrary number of variables $x_{i}$ with $1 \leq i \leq k$, Eq. (A.21) is immediately generalized to

$$
\begin{equation*}
\sum_{i=1}^{k} x_{i}\left(\frac{\partial f}{\partial x_{i}}\right)=n f\left(x_{i}\right) \tag{A.22}
\end{equation*}
$$

In particular for homogeneous functions of the first degree, we obtain the following fundamental relation:

$$
\begin{equation*}
f\left(x_{i}\right)=\sum_{i=1}^{k} x_{i}\left(\frac{\partial f}{\partial x_{i}}\right) . \tag{A.23}
\end{equation*}
$$

## A. 4 Schwarz's Theorem

Schwarz's Theorem establishes a condition of symmetry between the partial derivatives of functions of $n$ variables.

It can be stated as follows: we are given a real function $f$ of $n$ real variables ( $x_{1}, x_{2}, \ldots, x_{n}$ ), differentiable and suppose that all partial derivatives are themselves differentiable. Under this condition it can be proved that

$$
\begin{equation*}
\frac{\partial}{\partial x_{j}}\left(\frac{\partial f}{\partial x_{i}}\right)=\frac{\partial}{\partial x_{i}}\left(\frac{\partial f}{\partial x_{j}}\right) . \tag{A.24}
\end{equation*}
$$

This result shows that if we take the cross derivative of the function $f$ with respect to any two variables $x_{j}$ and $x_{i}$, the order in which the two partial derivatives are performed, is irrelevant. In the literature, the cross differentiation is also denoted by the symbol $\partial^{2} / \partial x_{j} \partial x_{i}$ and then the Schwarz Theorem may be expressed by

$$
\begin{equation*}
\frac{\partial^{2} f}{\partial x_{j} \partial x_{i}}=\frac{\partial^{2} f}{\partial x_{i} \partial x_{j}} . \tag{A.25}
\end{equation*}
$$

It is rather common to find the symbol $\partial_{i}$ for denoting the partial derivative of the function $f$ with respect to the variable $x_{i}$. With this notation the Schwarz Theorem can be written in the following form:

$$
\begin{equation*}
\partial_{j i} f=\partial_{i j} f \tag{A.26}
\end{equation*}
$$

## A. 5 Differentials, Infinitesimals, Finite Differences

Throughout the treatise, we use different symbols to denote finite or infinitesimal variations of physical quantities. Let us introduce the symbols we used and their meaning.

## A.5.1 Finite Differences

In general, when we want to denote the variation of a property, i.e., a function of the state, either between two equilibrium states or between two system, we use the symbol $\Delta$. To be more precise, if we consider a change of state from an initial state A to a final state $B$, we denote by the symbol $\Delta$ the difference between the value of the property in the final state $B$ minus its value in the initial state A. Likewise, if we are considering two systems which can be designated with the symbols I and II (arbitrarily chosen) the symbol $\Delta$ will designate the value of a quantity in system II minus its value in system I . For instance $\Delta U, \Delta S, \Delta T$ denote the variations of energy, entropy and temperature respectively either in a process between two equilibrium states or the difference of the property between two different systems according to the convention:

$$
\begin{align*}
& \Delta U=U(B)-U(A)  \tag{A.27}\\
& \Delta S=S(B)-S(A)  \tag{A.28}\\
& \Delta T=T_{B}-T_{A} \tag{A.29}
\end{align*}
$$

## A.5.2 Finite Differences Small Compared to Characteristic Scales

The use of the symbol $\delta$ denotes small quantities and this situation occurs in two cases:

- Small variations of state functions;
- Small amounts of physical quantities, for instance work or heat, in equations describing small transformations.

By small transformations, we mean finite transformations in which the variations of the state functions are approximated by series expansions up to the linear terms. In the equations which describe small transformations, quantities like the amount of work done or the amount of heat exchanged which are not variations of a property, are also considered small (at the same order of magnitude) and are denoted by the same symbol $\delta$. The same applies to denote small variations of properties between two different systems.

For instance, if $\Delta T=\left(T_{B}-T_{A}\right) \ll T_{A}, T_{B}$ in Eq. (A.29), then, the temperature difference will be replaced by the expression $\delta T$. Similarly, for any other (small yet finite) variation like $\delta p, \delta U, \delta S$, etc.

## A.5.3 Differentials and Infinitesimals

In small transformations, in which small quantities are involved, we may imagine to consider smaller and smaller quantities and pass to the limit for variations tending to zero. One says that the quantities we are considering are infinitesimal. There are two kinds of infinitesimal quantities:

- The ones which are variations of some state functions $f$ and, therefore, are exact differentials of a state function and are denoted with $\mathrm{d} f$.
- The ones which are just infinitesimal but are not the differential of a state function, and are denoted as $\hat{d}$.


## A.5.4 Mutual Exchanges Between Two Systems

To complete the list of the symbols which particularly deserve to be brought to the reader's attention let us refer to the case where two systems (e.g., labeled as I and II) are considered. In writing the equations for energy and entropy variations either in small or infinitesimal processes, we have to distinguish between quantities referring to system I from quantities referring to system II. The notation we adopt is the following:

1. If we deal with small or infinitesimal variations of properties (like for instance energy, entropy, volume, mole numbers, and so on) the two alternatives are highlighted by the suffix placed on the state variable considered. For example $\mathrm{d} U^{\mathrm{I}}$, $\mathrm{d} S^{\mathrm{I}}$, or $\mathrm{d} V^{\mathrm{I}}$, etc.
2. If we deal with small or infinitesimal quantities which are not variations of state variables the distinction between quantities referring to one of the two systems is made by putting the symbol I or II as a suffix on the symbol $\delta$ or $\hat{d}$. For example, $\hat{d}^{\mathrm{I}} Q, \delta^{\mathrm{I}} \Phi$, etc.

## Appendix B <br> Pressure Exerted by a Particle Gas

## B. 1 Mechanical Interpretation of the Pressure Exerted by a Particle Gas

Consider a closed system consisting of a gas formed by a large number of elementary constituents (atoms, molecules, photons, etc.). The mechanical effect of the interaction of the elementary constituents with the walls of the vessel containing the gas, is, in general, a rather complicated problem but, in favorable conditions (for instance, when viscosity does not produce any effect) is recorded by a macroscopic observer under the name of "pressure". The pressure, which is defined in the maximum generality as a function of the thermodynamic potentials in Eqs. (4.21) and (4.25), in this particular context is measured as the force per unit of area, exerted by the gas, perpendicularly, on the walls of the container. Its value depends on the momentum distribution of the elementary constituents that form the gas, as well as on their modality of interaction with the walls. It is interesting to highlight to what extent the hypothesis of homogeneity and of isotropy of the gas contribute in determining the expression of the pressure no matter what the energy distribution of the particles is.

In this modeling, the pressure has a purely mechanical interpretation and must be traced back to the amount of total momentum exchanged by the elementary constituents per unit time and per unit area of the walls. Let us denote with d $\Sigma$ the area of a wall surface element that delimits the volume $V$ within which the gas is confined.

We will make the following assumptions:

1. The particles are distributed uniformly, for each range of energy, and do not interact with each other;
2. The particles are distributed isotropically;
3. The particles have no internal degrees of freedom, that is their energy is given by the kinetic energy associated with the motion of the center of mass. This hypothesis can immediately be abandoned if in the expression of the energy of a single particle, the term describing the motion of the c.m. can be additively
separated from the others. In this case, the contribution to the total energy of the particle due to the c.m. motion will be indicated by $\varepsilon$.

With this specification, we denote with $N(\varepsilon)$ the spectral energy number density. This means that the number of particles per unit volume with energy in the interval $(\varepsilon, \varepsilon+\mathrm{d} \varepsilon)$ is given by $N(\varepsilon) \mathrm{d} \varepsilon$. Isotropy means that the number of particles with energy in the interval ( $\varepsilon, \varepsilon+\mathrm{d} \varepsilon$ ) and moving within the solid angle $\mathrm{d} \Omega$, is given by

$$
\begin{equation*}
\mathrm{d} N=N(\varepsilon) \mathrm{d} \varepsilon \frac{\mathrm{~d} \Omega}{4 \pi} \tag{B.1}
\end{equation*}
$$

Let's assume the $z$-axis normal to the elementary surface $\mathrm{d} \Sigma$, oriented outside the volume. Consider the particles with energy in the interval $(\varepsilon, \varepsilon+\mathrm{d} \varepsilon)$ and be $v$ the module of their velocity, with $v=v(\varepsilon)$.

The number of particles in the latter energy interval, moving within the solid angle $\mathrm{d} \Omega$ and impinging the surface $\mathrm{d} \Sigma$ in the time interval $\mathrm{d} t$ will be given by

$$
\begin{gather*}
\mathrm{d} \mathcal{N}(\varepsilon, v, \vartheta, \varphi)=\mathrm{d} t \mathrm{~d} \Sigma v \cos \vartheta \mathrm{~d} N  \tag{B.2}\\
\mathrm{~d} \mathcal{N}(\varepsilon, v, \vartheta, \varphi)=\frac{1}{4 \pi} \mathrm{~d} t \mathrm{~d} \Sigma v \cos \vartheta \mathrm{~d}(\cos \vartheta) \mathrm{d} \varphi N(\varepsilon) \mathrm{d} \varepsilon . \tag{B.3}
\end{gather*}
$$

Further let's denote with $\mathbf{P}$ the momentum of one particle. Given the hypothesis of homogeneity and isotropy, the module of the momentum will depend on the particle energy only. We call dispersion relation the following:

$$
\begin{equation*}
\varepsilon=\varepsilon(P) . \tag{B.4}
\end{equation*}
$$

For instance, for nonrelativistic particles with mass $m$, we have

$$
\begin{equation*}
\varepsilon=\frac{P^{2}}{2 m} . \tag{B.5}
\end{equation*}
$$

For relativistic particle, the dispersion relation reads

$$
\begin{equation*}
\varepsilon=\sqrt{P^{2} c^{2}+m^{2} c^{4}} . \tag{B.6}
\end{equation*}
$$

and for photons (or, approximately, for ultrarelativistic particles that is with energy $\left.\varepsilon \gg m c^{2}\right)$ :

$$
\begin{equation*}
\varepsilon=P c . \tag{B.7}
\end{equation*}
$$

We then make two extreme hypotheses: that the individual particles are completely absorbed by the surface or that they are elastically reflected.

## B.1.1 Particles Completely Absorbed by the Wall

In this case, relevant only for the absorption of radiation, each (non-massive) particle impinging $\mathrm{d} \Sigma$ in the time interval $\mathrm{d} t$, will transfer its momentum to the wall element. Let us assume as $z$-axis of a local reference frame, the axis normal to the wall in $\mathrm{d} \Sigma$ and oriented outside. For symmetry reasons, we are interested only in the $z$ component of the transferred momentum, while the other components will balance. If we multiply Eq. (B.3) by $P_{z}=P \cos \vartheta$, and we integrate over all directions with $\vartheta$ in the interval $(0, \pi / 2)$, we find, for the $z$-component of the momentum transferred to $\mathrm{d} \Sigma$ in the time interval $\mathrm{d} t$ by the particles with energy in the interval $(\varepsilon, \varepsilon+\mathrm{d} \varepsilon)$, the expression:

$$
\begin{gather*}
\mathrm{d} P_{z}(\varepsilon)=\frac{1}{4 \pi} \mathrm{~d} t \mathrm{~d} \Sigma(P v) N(\varepsilon) \mathrm{d} \varepsilon \int_{0}^{1} \cos ^{2} \vartheta \mathrm{~d}(\cos \vartheta) \int_{0}^{2 \pi} \mathrm{~d} \varphi  \tag{B.8}\\
\mathrm{~d} P_{z}(\varepsilon)=\frac{1}{6} \mathrm{~d} t \mathrm{~d} \Sigma(P v) N(\varepsilon) \mathrm{d} \varepsilon \tag{B.9}
\end{gather*}
$$

The total amount of momentum transferred to the wall per unit area and per unit time will be given by

$$
\begin{equation*}
p=\frac{1}{6} \int_{0}^{\infty}(P v) N(\varepsilon) \mathrm{d} \varepsilon \tag{B.10}
\end{equation*}
$$

In the mechanical-statistical model of gases, this is the expression of the force per unit area, i.e., the pressure, if the particles are completely absorbed by the surface of the wall.

## B.1.2 Particles Elastically Reflected by the Wall

In this case, the calculation proceeds as in the previous case with the only difference that the value of the $z$-component of the momentum transferred by each particle in the impact with the wall will have the value $P_{z}=2 P \cos \vartheta$ that is twice the value transferred in the case in which the particle is completely absorbed. Then we have

$$
\begin{equation*}
p=\frac{1}{3} \int_{0}^{\infty}(P v) N(\varepsilon) \mathrm{d} \varepsilon \tag{B.11}
\end{equation*}
$$

Both in the case of completely absorbed and perfectly reflected particles, no hypothesis is made concerning the distribution function but that of isotropy and homogeneity. In particular, no hypothesis concerning thermodynamical equilibrium is necessary.

In both cases, the crucial point is the term $(P v)$ in the integrand and then the dependence of the momentum on the energy of the elementary constituent must be
known (in Eq. (B.11) the dependence of the velocity on energy is also given). We consider the two extreme cases of the Newtonian and that of the ultra-relativistic elementary constituent.

## B.1.3 Nonrelativistic Case

Let us consider, as a first example, the case of classical non relativistic particles for which the dispersion relation is $\varepsilon=P^{2} / 2 m$. In this case, we have

$$
\begin{equation*}
P v=m v^{2}=2 \varepsilon \tag{B.12}
\end{equation*}
$$

and hence Eq. (B.11) will give, for the exerted pressure, the value

$$
\begin{equation*}
p=\frac{2}{3} \int_{0}^{\infty} \varepsilon N(\varepsilon) \mathrm{d} \varepsilon=\frac{2}{3} u \tag{B.13}
\end{equation*}
$$

where

$$
\begin{equation*}
u=\frac{U}{V} \tag{B.14}
\end{equation*}
$$

is the energy density of the particle gas. In the case we are considering, if we denote with $N_{0}$ the total number of particles contained in the volume $V$ :

$$
\begin{equation*}
U=\sum_{i=1}^{N_{0}} \varepsilon_{i}=N_{0}\langle\varepsilon\rangle \tag{B.15}
\end{equation*}
$$

where $\langle\varepsilon\rangle$ is the mean value of the particle's energy (defined as $U / N_{0}$ ). If the gas is in a state of thermodynamical equilibrium we have

$$
\begin{equation*}
\langle\varepsilon\rangle=\frac{3}{2} k_{B} T \tag{B.16}
\end{equation*}
$$

and then Eq.(B.13) will give the well known:

$$
\begin{equation*}
p V=\frac{N_{0}}{N_{\mathrm{A}}} R T \tag{B.17}
\end{equation*}
$$

where $N_{\mathrm{A}}=6.022 \times 10^{23}$ is the Avogadro's number. It is useful to highlight that even far from thermodynamical equilibrium the pressure will obey to Eq.(B.13) provided the conditions of homogeneity and isotropy postulated at the beginning, are preserved.

## B.1.4 The Case of Radiation

In this case, the "particles" are photons for which the dispersion relation is given by Eq. (B.7) with $v=c$ for all particles. In this case Eq. (B.11) becomes

$$
\begin{equation*}
p=\frac{1}{3} \int_{0}^{\infty} \varepsilon N(\varepsilon) \mathrm{d} \varepsilon=\frac{1}{3} u . \tag{B.18}
\end{equation*}
$$

It is necessary to highlight that Eq.(B.18) between the pressure of the radiation and its energy density does not depend on choosing a particle model for radiation as we did in the preceding subsection. If we adopt the point of view of classical macroscopic electrodynamics, the only necessary condition for the validity of Eq. (B.18) is that the relationship between the momentum density (let's denote it with $\mathbf{g}$ ) and the density of energy flux (let's denote it with $\mathbf{S}$ ) of the electromagnetic field is

$$
\begin{equation*}
\mathbf{g}=\frac{1}{c^{2}} \mathbf{S} \tag{B.19}
\end{equation*}
$$

This is predicted by Maxwell's theory and for a clear discussion on the argument see [49]. The adopted particle model allows us to simplify the calculations and make the analogy between different cases clear.

## Solutions to the Problems

## Solutions to the Problems of Chap. 3

3.1 The Coefficient of Performance of the refrigerating cycle is defined by the ratio $\xi=Q_{1} / W_{1}$ of the heat extracted from the cell (the required effect) per hour to the work performed by the compressor on the refrigerating fluid in the same time interval. In our example $Q_{1}=4.2 \times 10^{7} \mathrm{~J}$ and hence

$$
\begin{equation*}
W_{1}=\frac{Q_{1}}{\xi} \simeq 1.4 \times 10^{7} \mathrm{~J} \tag{C.1}
\end{equation*}
$$

This useful work done on the fluid corresponds to the average performed power $P_{1} \simeq 3.9 \times 10^{3} \mathrm{~J} \mathrm{~s}^{-1}$. Then the power consumed from electricity will be

$$
\begin{equation*}
P \simeq \frac{3.9 \times 0^{3}}{0.9} \simeq 4.3 \times 10^{3} \mathrm{~W} \tag{C.2}
\end{equation*}
$$

After an integer number of cycles, the variation of energy of the fluid will be zero and the quantity of heat transferred to the environment will be qual to the quantity of work performed on the fluid plus the heat dissipated by the compressor plus the amount of heat extracted from the cell. In one hour, the latter will amount to $Q_{1}$ while the contribution of the compressor will be about $1.55 \times 10^{7} \mathrm{~J}$. The total quantity of heat transferred to the environment by the refrigerator, per hour, will be

$$
\begin{equation*}
Q_{\mathrm{tot}} \simeq 5.75 \times 10^{7} \mathrm{~J} \tag{C.3}
\end{equation*}
$$

The entropy variations per hour of the cell and the environment will be

$$
\begin{align*}
& \Delta S_{\mathrm{cell}} \simeq 0  \tag{C.4}\\
& \Delta S_{\mathrm{env}} \simeq 5.2 \times 10^{4} \mathrm{~J} \mathrm{~K} \tag{C.5}
\end{align*}
$$

The first result is due to the fact that the cell gives off to the engine the same amount of heat it gains from the environment and consequently, the environment gains, every hour, all the energy consumed by the engine. If the refrigerator worked as a reversible engine the COP would be

$$
\begin{equation*}
\mathrm{COP}_{\mathrm{rev}}=5 \tag{C.6}
\end{equation*}
$$

hence, the work required to the compressor, per hour, would be $W_{\text {rev }}=Q_{1} / \xi_{\text {rev }} \simeq$ $0.84 \times 10^{7} \mathrm{~J}$. The power of the compressor would be $P \simeq 2.6 \times 10^{3} \mathrm{~W}$.
3.2 In our case the so called "Universe" is formed by the engine and the two heat sources. The total entropy variation in every cycle is given by ( $\Delta S_{\mathrm{eng}}=0$ )

$$
\begin{equation*}
\Delta S_{\text {univ }}=-\frac{Q_{1}}{T_{1}}+\frac{Q_{2}}{T_{2}} \tag{C.7}
\end{equation*}
$$

where $Q_{1}$ is the quantity of heat given to the engine by source at $T_{1}$. Moreover, the First Principle for the engine gives $(\Delta U=0)$

$$
\begin{equation*}
W=Q_{1}-Q_{2}, \tag{C.8}
\end{equation*}
$$

where $W$ is the quantity of work produced by the engine per cycle. From Eqs. (C.7) and (C.8) we obtain $Q_{1} \simeq 247.5 \mathrm{cal}$ and

$$
\begin{equation*}
W \simeq 47.5 \mathrm{cal} \simeq 198.5 \mathrm{~J} \tag{C.9}
\end{equation*}
$$

and the efficiency of the engine is

$$
\begin{equation*}
\eta \simeq \frac{47.5}{247.5} \simeq 0.19 \tag{C.10}
\end{equation*}
$$

3.3 (a) The efficiency in the reversible initial conditions is

$$
\begin{equation*}
\eta_{\mathrm{rev}}=\frac{Q_{1}-Q_{2}}{Q_{1}}=0.25 \tag{C.11}
\end{equation*}
$$

(b) From the Second Principle, we know that the entropy of state C is equal to the entropy of the state B while the entropy variation in the irreversible adiabatic transformation $\mathrm{BC}^{\prime}$ will be positive and hence $S_{\mathrm{C}^{\prime}}>S_{\mathrm{C}}=S_{\mathrm{B}}$. This implies that in the transformation from $\mathrm{C}^{\prime}$ to C along the isotherm the entropy must decrease, i.e., a certain quantity of heat, say $Q_{\mathrm{C}^{\prime} \mathrm{C}}$ must be released by the engine to the thermostat $T_{2}$. As a consequence the total quantity of heat given off to the source $T_{2}$ will be

$$
\begin{equation*}
Q_{2}^{\prime}=Q_{\mathrm{C}^{\prime} \mathrm{C}}+Q_{2} . \tag{C.12}
\end{equation*}
$$

The value for the efficiency is

$$
\begin{align*}
\eta^{\prime} & =\frac{Q_{1}-Q_{2}-Q_{\mathrm{C}^{\prime} \mathrm{C}}}{Q_{1}}  \tag{C.13}\\
& =\eta_{\mathrm{rev}}-\frac{Q_{\mathrm{C}^{\prime} \mathrm{C}}}{Q_{1}} \tag{C.14}
\end{align*}
$$

In particular,

$$
\begin{equation*}
\eta^{\prime}=0.25-\frac{40}{400}=0.15 \tag{C.15}
\end{equation*}
$$

3.4 Let's denote with $Q_{1}, Q_{2}$, and $Q_{3}$ the absolute values of the heat quantities exchanged with the three sources, respectively. In every cycle, the entropy variation of the overall system (engine plus the three heat sources ) must satisfy the inequality $\Delta S_{\text {overall }}>0$ which implies

$$
\begin{align*}
& -\frac{Q_{1}}{T_{1}}-\frac{Q_{2}}{T_{2}}+\frac{Q_{3}}{T_{3}} \geq 0  \tag{C.16}\\
& Q_{3} \geq Q_{1} \frac{T_{3}}{T_{1}}+Q_{2} \frac{T_{3}}{T_{2}} \tag{C.17}
\end{align*}
$$

For the amount of work produced we have

$$
\begin{equation*}
W=Q_{1}+Q_{2}-Q_{3} \leq Q_{1}\left(1-\frac{T_{3}}{T_{1}}\right)+Q_{2}\left(1-\frac{T_{3}}{T_{2}}\right) \tag{C.18}
\end{equation*}
$$

The efficiency depends (for instance) on the ratio $\xi=Q_{2} / Q_{1}$ and must recover the Carnot values in the limiting cases $\xi=0$ and $\xi \rightarrow \infty$ and for reversible cycles. We may write

$$
\begin{equation*}
\eta=\frac{W}{Q_{1}+Q_{2}} \leq \frac{\left(1-\frac{T_{3}}{T_{1}}\right)+\xi\left(1-\frac{T_{3}}{T_{2}}\right)}{(1+\xi)} \tag{C.19}
\end{equation*}
$$

3.5 For the composite system, the entropy variation per cycle is

$$
\begin{align*}
& -\frac{Q_{1}}{T_{1}}+\frac{Q_{2}}{T_{2}}-\frac{Q_{3}}{T_{3}} \geq 0  \tag{C.20}\\
& Q_{2} \geq Q_{1} \frac{T_{2}}{T_{1}}+Q_{3} \frac{T_{2}}{T_{3}} \tag{C.21}
\end{align*}
$$

Taking into account that $W=Q_{1}-Q_{2}+Q_{3}$, we obtain

$$
\begin{equation*}
W \leq Q_{1}\left(1-\frac{T_{2}}{T_{1}}\right)+Q_{3}\left(1-\frac{T_{2}}{T_{3}}\right) . \tag{C.22}
\end{equation*}
$$

For a reversible engine

$$
\begin{equation*}
W=Q_{1}\left(1-\frac{T_{2}}{T_{1}}\right)+Q_{3}\left(1-\frac{T_{2}}{T_{3}}\right) \tag{C.23}
\end{equation*}
$$

and if we define the parameter $\xi=Q_{3} / Q_{1}$ then the work produced is zero for the particular value $\xi_{0}$ such that

$$
\begin{equation*}
\xi_{0}=\frac{\left(T_{1}-T_{2}\right) T_{3}}{\left(T_{2}-T_{3}\right) T_{1}} \tag{C.24}
\end{equation*}
$$

while for $0 \leq \xi \leq \xi_{0}$ the engine produces positive work and for $\xi \geq \xi_{0}$ the engine must absorb work from the outside.
3.6 From the Second Principle applied to the composite system,

$$
\begin{align*}
& \frac{Q_{1}}{T_{1}}-\frac{Q_{2}}{T_{2}}-\frac{Q_{3}}{T_{3}} \geq 0  \tag{C.25}\\
& Q_{1} \geq Q_{2} \frac{T_{1}}{T_{2}}+Q_{3} \frac{T_{1}}{T_{3}} \tag{C.26}
\end{align*}
$$

and for the work

$$
\begin{align*}
W & =Q_{2}+Q_{3}-Q_{1}  \tag{C.27}\\
& \leq Q_{2}\left(1-\frac{T_{1}}{T_{2}}\right)+Q_{3}\left(1-\frac{T_{1}}{T_{3}}\right)<0 \tag{C.28}
\end{align*}
$$

for any $Q_{2}$ and $Q_{3}$. If we use the engine as a heat pump it is convenient to consider the absolute value of $W$, which represents the amount of energy consumed by the heat pump per cycle and write the expression for the COP:

$$
\begin{equation*}
\mathrm{COP}=\frac{Q_{1}}{|W|}=\frac{Q_{2} \frac{T_{1}}{T_{2}}+Q_{3} \frac{T_{1}}{T_{3}}}{Q_{2}\left(\frac{T_{1}}{T_{2}}-1\right)+Q_{3}\left(\frac{T_{1}}{T_{3}}-1\right)} \tag{C.29}
\end{equation*}
$$

In the limit in which either $Q_{2}$ or $Q_{3}$ tends to zero the COP reduces to Eq. (3.70).
3.7 Clearly, we can extract some work only if the two bodies have different temperatures. If we denote by $T_{\mathrm{f}}$ the final common temperature we may write the amount of work from the First Principle:

$$
\begin{equation*}
W=\left[C_{1} T_{1}+C_{2} T_{2}-\left(C_{1}+C_{2}\right) T_{\mathrm{f}}\right] . \tag{C.30}
\end{equation*}
$$

It is clear that the maximum amount of work will be obtained with the procedure that leads to the minimum final temperature. The entropy variation of the universe is

$$
\begin{align*}
& \Delta S_{\text {univ }}=C_{1} \ln \frac{T_{\mathrm{f}}}{T_{1}}+C_{2} \ln \frac{T_{\mathrm{f}}}{T_{2}}  \tag{C.31}\\
& \Delta S=\ln \left[\frac{T_{\mathrm{f}}^{\left(C_{1}+C_{2}\right)}}{T_{1}^{C_{1}} T_{2}^{C_{2}}}\right] \tag{C.32}
\end{align*}
$$

and here we see that the minimum value for $T_{\mathrm{f}}$ will be obtained for $\Delta S=0$, that is,

$$
\begin{equation*}
T_{\mathrm{f}}=\left[T_{1}^{C_{1}} T_{2}^{C_{2}}\right]^{\frac{1}{\left(C_{1}+C_{2}\right)}} \tag{C.33}
\end{equation*}
$$

If the two bodies have the same heat capacity, we have

$$
\begin{equation*}
T_{\mathrm{f}}=\sqrt{T_{1} T_{2}} \tag{C.34}
\end{equation*}
$$

and, in this case, the amount of work is

$$
\begin{equation*}
W=C\left[T_{1}+T_{2}-2 \sqrt{T_{1} T_{2}}\right]=C\left(\sqrt{T_{1}}-\sqrt{T_{2}}\right)^{2} \tag{C.35}
\end{equation*}
$$

## 3.8

1. From the First Principle it results that $Q_{2}=400 \mathrm{~kJ}$, while from the Second Principle $\Delta S_{\text {tot }}=0$. Given that $\Delta S_{\text {eng }}=0$ (cyclic transformation), we find $\Delta S_{\text {source }}=0$ from which

$$
\begin{equation*}
T_{2}=T_{1} \frac{Q_{2}}{Q_{1}}=500 \times \frac{400}{1000}=200 \mathrm{~K} \tag{C.36}
\end{equation*}
$$

2. Answer: $T_{2}=100 \mathrm{~K}$.
3.9 By using the First Principle

$$
\begin{equation*}
Q_{2}=400 \mathrm{~kJ} \tag{C.37}
\end{equation*}
$$

As for the second question, we must impose two conditions:

$$
\begin{align*}
& -\frac{10^{6}}{500}+C \ln \frac{T_{\mathrm{f}}}{T_{\mathrm{i}}}=0  \tag{C.38}\\
& 4 \times 10^{5}=10^{4}\left(T_{\mathrm{f}}-T_{\mathrm{i}}\right), \tag{C.39}
\end{align*}
$$

where the first relation is due to reversibility ( $\Delta S_{\text {tot }}=0$ ) and the second one expresses the temperature variation of the body. The solution is $T_{\mathrm{i}} \simeq 182 \mathrm{~K}$ and $T_{\mathrm{f}} \simeq 222 \mathrm{~K}$.
3.10 The availability coincides with the energy variation since we neglect the volume variations. The change in the energy transformation from initial state to the dead state will be

$$
\begin{equation*}
\Delta U=-C \times 60, \tag{C.40}
\end{equation*}
$$

where $C$ is the heat capacity of water. Its variation of entropy in the same transformation will be

$$
\begin{align*}
\Delta S & =\int_{353}^{293} \frac{C \mathrm{~d} T}{T}=C \ln \frac{293}{353}  \tag{C.41}\\
& =4.18 \times 10^{6} \times \ln (0.83)  \tag{C.42}\\
& =-0.778 \times 10^{6} \mathrm{~J} \mathrm{~K}^{-1} \tag{C.43}
\end{align*}
$$

The availability coincides with the available energy because the volume is assumed to be constant and it will amount to

$$
\begin{align*}
\Phi_{\Lambda} & =-\Delta U+T_{0} \Delta S  \tag{C.44}\\
& =25.08 \times 10^{7}-22.82 \times 10^{7}  \tag{C.45}\\
& =2.26 \times 10^{7} \mathrm{~J} \tag{C.46}
\end{align*}
$$

This result could be found also imagining using a series of infinitesimal Carnot engines working between the generic temperature $T$ of the water and the room temperature $T_{0}$. The infinitesimal amount of work produced by one Carnot engine will be

$$
\begin{align*}
\delta W & =\eta\left(T, T_{0}\right) \delta Q  \tag{C.47}\\
& =-\left(1-\frac{T_{0}}{T}\right) C \mathrm{~d} T \tag{C.48}
\end{align*}
$$

In our case $\delta Q=-C \mathrm{~d} T$ and hence the maximum amount of work we will be able to obtain will be

$$
\begin{align*}
W & =C \times 60+C T_{0} \ln \frac{293}{353}  \tag{C.49}\\
& =4.18 \times 10^{6} \times(60-54.58)  \tag{C.50}\\
& =22.65 \times 10^{6} \mathrm{~J} \tag{C.51}
\end{align*}
$$

### 3.11

$$
\begin{equation*}
\Delta S_{\mathrm{univ}}=\frac{W}{\sqrt{T_{1} T_{2}}} \tag{C.52}
\end{equation*}
$$

3.12 We have to determine the quantity of work absorbed by the machine and this will be given by the following relation:

$$
\begin{equation*}
C\left(T_{0}-T_{\mathrm{cold}}\right)+W=C\left(T_{\mathrm{hot}}-T_{0}\right) \tag{C.53}
\end{equation*}
$$

where $C \simeq 41.8 \mathrm{~kJ} \mathrm{~K}^{-1}$ is the heat capacity of each vessel, $T_{0} \simeq 293 \mathrm{~K}$ is their initial temperature and $T_{\text {cold }} \simeq 281 \mathrm{~K}$ is the temperature of the cold body after 10 min . For
the temperature of the hot vessel, let's apply Eq. (C.34) in the reverse operation:

$$
\begin{equation*}
T_{\mathrm{cold}} \times T_{\mathrm{hot}}=T_{0}^{2} \tag{C.54}
\end{equation*}
$$

which gives $T_{\text {hot }} \simeq 305.5 \mathrm{~K}$. From the previous relation, we have

$$
\begin{equation*}
W=C\left(T_{\mathrm{cold}}+T_{\mathrm{hot}}-2 T_{0}\right) \tag{C.55}
\end{equation*}
$$

which can be written as

$$
\begin{equation*}
W=C \frac{\left(T_{\mathrm{hot}}-T_{0}\right)^{2}}{T_{\mathrm{hot}}}=C \frac{\left(T_{\mathrm{cold}}-T_{0}\right)^{2}}{T_{\mathrm{cold}}}=21.4 \mathrm{~kJ} \tag{C.56}
\end{equation*}
$$

The power consumed by the refrigerator is roughly

$$
\begin{equation*}
P \simeq 21.4 \times \frac{1000}{600} \simeq 35.6 \mathrm{~W} \tag{C.57}
\end{equation*}
$$

3.13 Let's call $Q_{2}$ and $Q_{3}$ the quantities of heat absorbed respectively from sources at $T_{2}$ and $T_{3}$. From the balance of energy we have

$$
\begin{equation*}
Q_{1}+Q_{2}+Q_{3}=600 \mathrm{~J} \tag{C.58}
\end{equation*}
$$

and from reversibility the total variation of entropy, in every cycle, must be zero. The entropy variation of the engine is zero (cyclic transformation) and we are left with the total entropy variation of the three reservoirs. This can be written as

$$
\begin{equation*}
-\frac{Q_{1}}{T_{1}}-\frac{Q_{2}}{T_{2}}-\frac{Q_{3}}{T_{3}}=0 \tag{C.59}
\end{equation*}
$$

We have two equations in the two unknowns $Q_{2}$ and $Q_{3}$ and we find $Q_{2}=-333.3 \mathrm{~J}$ and $Q_{3}=-66.6 \mathrm{~J}$. This means that the engine gives back heat both to reservoir 2 and to reservoir 3 .
3.14 In the second transformation, we have $Q_{\text {II }}=0$ and $W_{\text {II }}=-100 \mathrm{~J}$ therefore $U_{A}-U_{B}=-100 \mathrm{~J}$. For the first transformation we find $\Delta U=100 \mathrm{~J}, W_{\mathrm{I}}=212 \mathrm{~J}$ and hence $Q_{\mathrm{I}}=-112 \mathrm{~J}$. The change in entropy is

$$
\begin{equation*}
S_{\mathrm{B}}-S_{\mathrm{A}}=-0.265 \mathrm{~J} \mathrm{~K}^{-1} \tag{C.60}
\end{equation*}
$$

The second transformation cannot be quasi-static because we have an increase of the entropy.
3.15 The amount of heat given by the engine in order to melt the ice and to raise the temperature of the water by $20^{\circ} \mathrm{C}$ is, respectively,

$$
\begin{align*}
Q_{\text {melting }} & =m_{\text {ice }} \lambda=30 \times 334  \tag{C.61}\\
& \simeq 10^{4} \mathrm{~J}  \tag{C.62}\\
Q_{\mathrm{w}, \mathrm{tot}} & =\left(m_{\mathrm{w}}+m_{\mathrm{ice}}\right) \times 20 \times 4.18  \tag{C.63}\\
\simeq & 2 \times 10^{4} \mathrm{~J} \tag{C.64}
\end{align*}
$$

The amount of heat withdrawn from the hot source $Q_{\text {hot }}$, can be obtained from the condition that the engine is reversible. The latter condition is guaranteed by the equation $\Delta S_{\text {tot }}=0$ :

$$
\begin{equation*}
\frac{Q_{\mathrm{hot}}}{T_{1}}=\frac{m_{\text {ice }} \lambda}{273.16}+\left(m_{\mathrm{w}}+m_{\text {ice }}\right) \times 4.18 \times \ln \frac{293}{273} \tag{C.65}
\end{equation*}
$$

The work obtained in this transformation will be given by

$$
\begin{equation*}
W=Q_{\mathrm{hot}}-\left(Q_{\mathrm{melting}}+Q_{\mathrm{w}, \mathrm{tot}}\right) \tag{C.66}
\end{equation*}
$$

## Solutions to the Problems of Chap. 5

$5.1 \Delta H \simeq 1.6 \times 10^{4} \mathrm{~J}$.
$\Delta S \simeq 22.7 \mathrm{~J} \mathrm{~K}^{-1}$.
5.2 Let us refer to Eqs. (5.44) and to (5.45). In the first instance, we can consider the coefficient of compressibility constant in this range of pressures and express the volume as a linear function of the pressure variation.

$$
\begin{equation*}
V(p)=V\left(p_{\mathrm{i}}\right)\left[1-\chi_{T}\left(p-p_{\mathrm{i}}\right)\right] . \tag{C.67}
\end{equation*}
$$

At the lowest order in the change of volume we get

$$
\begin{equation*}
Q=-\langle\alpha\rangle T V\left(p_{\mathrm{i}}\right)\left[p_{\mathrm{f}}-p_{\mathrm{i}}\right] \tag{C.68}
\end{equation*}
$$

This is equivalent to keep the volume constant in Eq. (5.44); the successive correction, in the integral, would be

$$
\begin{equation*}
V\left(p_{\mathrm{i}}\right) \chi_{T} \frac{(\Delta p)^{2}}{2} \tag{C.69}
\end{equation*}
$$

The ratio with the first term is of order $\chi_{T} \Delta p$ which, in our example, is $\sim 10^{-3}$. Similarly, for the calculation of the amount of work, we refer to Eq.(5.45) and we calculate the integral to the lowest order getting

$$
\begin{equation*}
\int_{p_{\mathrm{i}}}^{p_{\mathrm{f}}}(p V) \mathrm{d} p=V\left(p_{\mathrm{i}}\right) \Delta\left(\frac{p^{2}}{2}\right) \tag{C.70}
\end{equation*}
$$

For the amount of work, we shall get the expression

$$
\begin{equation*}
W=\left\langle\chi_{T}\right\rangle V\left(p_{\mathrm{i}}\right) \frac{p_{\mathrm{f}}^{2}-p_{\mathrm{i}}^{2}}{2} \tag{C.71}
\end{equation*}
$$

Let's replace the numerical values. Regarding the volume of water at 40 atm we refer to Eq. (C.67) and evaluate the orders of magnitude. We obtain

$$
\begin{equation*}
Q=-0.2 \times 10^{-3} \times 293 \times 10^{-4} \times 39 \times 10^{5} \simeq 22.8 \mathrm{~J} \tag{C.72}
\end{equation*}
$$

Similarly, for the calculation of the amount of work we have

$$
\begin{equation*}
W=0.48 \times 10^{-9} \times 10^{-4} \times \frac{1600-1}{2} \times 10^{10}=-0.384 \mathrm{~J} \tag{C.73}
\end{equation*}
$$

For the variation of energy, we simply have

$$
\begin{equation*}
\Delta U=-22.8+0.384 \simeq 22.4 \mathrm{~J} \tag{C.74}
\end{equation*}
$$

In other words, we have to supply the water of 22.8 J under the form of heat transfer and we get, from the water 0.384 J under the form of mechanical work which is due to its expansion. We used the conversion factor $1 \mathrm{~atm}=10^{5} \mathrm{~N} \mathrm{~m}^{-2}$ for simplicity.
5.3 The amount of heat delivered to the water in this isothermal compression (using the same formulas contained in the above example), is about

$$
\begin{equation*}
Q \simeq 7.3 \mathrm{~J} \tag{C.75}
\end{equation*}
$$

and, as we can see, its value is positive as in the case of the isothermal expansion at $20^{\circ} \mathrm{C}$. This is due to the anomalous behavior of water: its coefficient of thermal expansion is $\alpha \simeq 0$ at the temperature $\vartheta \simeq 4^{\circ} \mathrm{C}$ and becomes negative for temperatures between 0 and $4^{\circ} \mathrm{C}$.

This implies that if we could make a Carnot cycle between the temperatures $\vartheta \simeq 20^{\circ} \mathrm{C}$ (as in Problem 5.2) and $\vartheta \simeq 0.2^{\circ} \mathrm{C}$ we could obtain perpetual motion because in both isotherm we transfer positive quantities of heat to the system. This raises the question whether it is possible to connect the two isotherms with two adiabatic processes In order to look for an answer consider Sect. 5.5.4 and remember that $\alpha$ changes sign when traversing the temperature $\vartheta \simeq 4{ }^{\circ} \mathrm{C}$.

## 5.4

$$
\begin{gather*}
W=-\int p d V=-m a \int_{p_{0}}^{p_{\mathrm{f}}} p d p \simeq-\frac{1}{2} m a\left(p_{\mathrm{f}}\right)^{2} \simeq 52 \mathrm{~J}  \tag{C.76}\\
\Delta U=m \Delta U^{*}=-m b T\left(p_{\mathrm{f}}-p_{0}\right) \simeq-89.3 \mathrm{~J} \tag{C.77}
\end{gather*}
$$

$$
\begin{equation*}
Q=\Delta U-W \simeq-141.3 \mathrm{~J} \tag{C.78}
\end{equation*}
$$

which means that the heat must be released to the environment.

## 5.5

(a)

$$
W=\Delta U=m c\left(T_{\mathrm{f}}-T_{0}\right)-m b\left(p_{\mathrm{f}} T_{\mathrm{f}}-p_{0} T_{0}\right) \simeq 1734 \mathrm{~J}
$$

(b)

$$
C_{V}=\left(\frac{\partial U^{*}}{\partial T}\right)_{V}=c-b p-b T\left(\frac{\partial p}{\partial T}\right)_{V}
$$

and from the equation of state we get

$$
\left(\frac{\partial p}{\partial T}\right)_{V}=\frac{b}{a}
$$

Then

$$
\begin{gathered}
C_{V}=c-b p-\frac{b^{2}}{a} \\
C_{p}=\left(\frac{\partial H^{*}}{\partial T}\right)_{p}=\left(\frac{\partial U^{*}}{\partial T}\right)_{p}+p\left(\frac{\partial V^{*}}{\partial T}\right)_{p}=c-b p+b p=c
\end{gathered}
$$

(c) We must choose one quasi static transformation connecting the initial state ( $p_{0}, T_{0}$ ) to the final state ( $p_{\mathrm{f}}, T_{\mathrm{f}}$ ). For instance, we may go from the initial state to the intermediate state ( $p_{0}, T_{\mathrm{f}}$ ) with an isobaric reversible transformation and later from the intermediate state to the final state with an isothermal reversible process. We have

$$
\begin{gathered}
\Delta S_{\text {isob }}=m C_{p} \int_{T_{0}}^{T_{\mathrm{f}}} \frac{d T}{T}=m c \ln \left(\frac{T_{\mathrm{f}}}{T_{0}}\right) \simeq 11 \mathrm{~J} \mathrm{~K}^{-1}, \\
\Delta S_{\mathrm{isoth}}=\frac{Q_{\mathrm{isoth}}}{T_{\mathrm{f}}},
\end{gathered}
$$

where $Q_{\text {isoth }}$ is the amount of heat given to the solid in the isothermal transformation at $T=300 \mathrm{~K}$.
Following the solution of the preceding exercise we find

$$
Q_{\text {isoth }}=(\Delta U)_{\text {isoth }}-W_{\text {isoth }}=-m b T_{\mathrm{f}}\left(p_{\mathrm{f}}-p_{0}\right)-\frac{1}{2} m a\left(p_{\mathrm{f}}\right)^{2} \simeq-316.1 \mathrm{~J}
$$

and

$$
\Delta S_{\mathrm{isoth}} \simeq-1.05 \mathrm{~J} \mathrm{~K}^{-1}
$$

Finally, $\Delta S \simeq 9.9 \mathrm{~J} \mathrm{~K}^{-1}$.
5.6 The amount of work is given by

$$
W=-\int_{p_{1}}^{p_{2}} p \mathrm{~d} V
$$

and the volume variation in an isothermal transformation is

$$
\mathrm{d} V=-\chi_{T} V \mathrm{~d} p
$$

Then we have

$$
W=\int_{p_{1}}^{p_{2}} \chi_{T} V p \mathrm{~d} p
$$

where the volume on the coefficient $\chi_{T}$ can be assumed to remain constant. Hence, the integral becomes

$$
W=\chi_{T} V\left(\frac{p_{2}^{2}}{2}-\frac{p_{1}^{2}}{2}\right)=8.6 \times 10^{-12} \times 3 \times 1.14 \times 10^{-4} \times 0.510^{16}=14.7 \mathrm{~J}
$$

In order to find the amount of heat given to the copper it is necessary to determine first, the entropy variation. This can be accomplished by using the Maxwell relation in Eq. (5.15) and the consequent Eq. (5.44):

$$
Q=-\alpha T V \Delta p \simeq-5.0 \times 10^{-5} \times 300 \times 3 \times 1.14 \times 10^{-4} \times 10^{8} \simeq 513 \mathrm{~J}
$$

The free energy variation in an isothermal transformation is given by the amount of word done on the system:

$$
\Delta F \simeq 14.7 \mathrm{~J}
$$

and for the variation of energy we may write $\Delta U=\Delta F+T \Delta S=\Delta F+Q$ :

$$
\Delta U \simeq 14.7+513=527.7 \mathrm{~J}
$$

## Solutions to the Problems of Chap. 7

7.1 The energy balance is satisfied if we calculate the amount of work that is done on the system from the outside in the infinitesimal transformation in which one mole of saturated vapor, treated as a perfect gas, is brought to the temperature $\mathrm{T}+\mathrm{dT}$ keeping in saturation condition. The energy increase will be $\mathrm{d} U=C_{V} \mathrm{~d} T$ while for the amount of work, we have

$$
\begin{equation*}
\hat{d} W=-p \mathrm{~d} V_{\mathrm{m}}=-R \mathrm{~d} T+V_{\mathrm{m}} \frac{\mathrm{~d} p}{\mathrm{~d} T} \mathrm{~d} T=-R \mathrm{~d} T+\frac{\Delta H_{\mathrm{m}}}{T} \mathrm{~d} T \tag{C.79}
\end{equation*}
$$

where we have made use of the identity

$$
\begin{equation*}
p \mathrm{~d} V_{\mathrm{m}}+V_{\mathrm{m}} \mathrm{~d} p=R \mathrm{~d} T \tag{C.80}
\end{equation*}
$$

From the First Principle $\hat{d} Q=\mathrm{d} U-\hat{d} W$, and therefore:

$$
\begin{equation*}
\hat{d} Q=\left(C_{V}+R\right) \mathrm{d} T-\frac{\Delta H_{\mathrm{m}}}{T} \mathrm{~d} T . \tag{C.81}
\end{equation*}
$$

Finally,

$$
\begin{equation*}
C_{\mathrm{sat}}^{\mathrm{vap}}=C_{p}-\frac{\Delta H_{m}}{T} \tag{C.82}
\end{equation*}
$$

7.2 The triple point is determined by the intersection of the two equilibrium lines. For the triple point, we have

$$
\begin{equation*}
19.49-\frac{3063}{T_{\mathrm{tr}}}=23.03-\frac{3754}{T_{\mathrm{tr}}} \quad T_{\mathrm{tr}} \simeq 195.3 \mathrm{~K} \quad p_{\mathrm{tr}} \simeq 45.1 \mathrm{torr}=5993.8 \mathrm{~Pa} \tag{C.83}
\end{equation*}
$$

For the latent heat of vaporization and sublimation, let us refer to Eq.(7.11). From the data, we have

$$
\begin{align*}
& \Delta H_{\mathrm{m}, \text { vap }} \simeq R \times 3063 \simeq 25.4 \mathrm{~kJ} \mathrm{~mole}^{-1}  \tag{C.84}\\
& \Delta H_{\mathrm{m}, \mathrm{sub}} \simeq R \times 3754 \simeq 31.2 \mathrm{~kJ} \mathrm{~mole}^{-1} \tag{C.85}
\end{align*}
$$

Imagine three close transformations, near the triple point, from solid to vapor, from vapor to liquid and from liquid to solid. With obvious meaning of notations we may write

$$
\begin{equation*}
\Delta H_{\mathrm{s} \rightarrow \mathrm{v}}+\Delta H_{\mathrm{v} \rightarrow \mathrm{l}}+\Delta H_{\mathrm{l} \rightarrow \mathrm{~s}}=0 \tag{C.86}
\end{equation*}
$$

then

$$
\begin{gather*}
\Delta H_{\mathrm{fus}}=\Delta H_{\mathrm{sub}}-\Delta H_{\mathrm{vap}}  \tag{C.87}\\
\Delta H_{\mathrm{m}, \mathrm{fus}} \simeq 31.2-25.4 \simeq 5.8 \mathrm{~kJ} \mathrm{~mole}^{-1} . \tag{C.88}
\end{gather*}
$$

7.3 From Eq. (7.13), given one pair of temperatures $T_{a}$ and $T_{b}$, the mean molar latent heat of evaporation in the interval of the two temperatures is given by

$$
\begin{equation*}
\Delta H_{\mathrm{m}}=R \ln \left(\frac{p_{a}}{p_{b}}\right)\left(\frac{T_{a} T_{b}}{T_{a}-T_{b}}\right) . \tag{C.89}
\end{equation*}
$$

For the interval $\left(\vartheta_{1}, \vartheta_{2}\right)$ Eq. (C.89) gives

$$
\begin{equation*}
\left(\Delta H_{\mathrm{m}}\right)_{(1,2)}=R \ln \left(\frac{1.01}{0.701}\right)\left(\frac{373.16 \times 363.16}{10}\right)=8.31 \times 0.365 \times 13551.7=41.1 \mathrm{~kJ} . \tag{C.90}
\end{equation*}
$$

For the interval $\left(\vartheta_{2}, \vartheta_{3}\right)$ we obtain

$$
\begin{equation*}
\left(\Delta H_{\mathrm{m}}\right)_{(2,3)}=R \ln \left(\frac{0.701}{0.474}\right)\left(\frac{363.16 \times 353.16}{10}\right)=8.31 \times 0.391 \times 12825.3=41.6 \mathrm{~kJ} . \tag{C.91}
\end{equation*}
$$

Let us calculate the same result in the temperature interval $\left(\vartheta_{1}, \vartheta_{3}\right)$ :

$$
\begin{equation*}
\left(\Delta H_{\mathrm{m}}\right)_{(1,3)}=R \ln \left(\frac{1.01}{0.474}\right)\left(\frac{373.16 \times 353.16}{20}\right)=8.31 \times 0.756 \times 6589.3=41.4 \mathrm{~kJ} \tag{C.92}
\end{equation*}
$$

These results show that the latent heat is fairly constant in the interval $\left(80^{\circ} \mathrm{C} 100^{\circ} \mathrm{C}\right)$.

## Solutions to the Problems of Chap. 8

8.1 In the free and adiabatic expansion the energy of the final state remains constant. If we treat the small expansion as an infinitesimal transformation we may refer to Eq. (8.31)and pose $\mathrm{d} U=0$. Then

$$
\left(\frac{\partial T}{\partial V}\right)_{U}=-\frac{1}{n C_{V}} \frac{a n^{2}}{V^{2}}
$$

The above relation allows, for a small re-expansion, to write

$$
\Delta T \simeq-\frac{1}{n C_{V}} \frac{a n^{2}}{V^{2}} \Delta V \simeq \frac{363.96 \times 10^{-3} \times 10^{2}}{10 \times 28.85 \times 4 \times 10^{-4}} \times 2 \times 10^{-3} \simeq 0.63 \mathrm{~K}
$$

8.2 Let us adopt the simplified expression Eq. (8.39) for the Joule-Thomson coefficient:

$$
C_{H}=\frac{V_{\mathrm{m}} T}{C_{p}} \frac{\left(\frac{2 a}{R T}-b\right)}{V_{\mathrm{m}} T}=\frac{1}{C_{p}}\left(\frac{2 a}{R T}-b\right)
$$

We have

$$
C_{H}=\frac{0.324 \times 10^{-3}-0.0427 \times 10^{-3}}{40.225} \simeq 7 \times 10^{-6} \mathrm{~K} \mathrm{~Pa}^{-1}
$$

The temperature drop is

$$
\Delta T \simeq 7 \times 10^{-6} \times 19 \times 10^{5}=13.3 \mathrm{~K}
$$

8.3 If we denote by $V_{1}$ and $V_{2}$ the volumes in the initial and final states, respectively, from definition Eq. (8.58) we get

$$
V_{1}=\frac{n Z_{1} R T}{p_{1}} V_{2}=\frac{n Z_{2} R T}{p_{2}}
$$

The condition

$$
\frac{V_{2}}{V_{1}} \simeq \frac{p_{1}}{p_{2}}
$$

simply means that $Z_{2} \simeq Z_{1}$ but this does not imply that $Z_{2} \simeq Z_{1} \simeq 1$. Indeed, we have to refer to the compressibility chart and calculate the reduced pressures and temperature for the two states. We have, respectively,

$$
\tilde{p}_{1} \simeq \frac{67.9}{33.95} \simeq 2 \quad \tilde{p}_{2} \simeq \frac{144.3}{33.95} \simeq 4.25
$$

and the reduced temperature is $\tilde{t} \simeq 164 / 126.2 \simeq 1.3$. From the compressibility chart, we find

$$
Z_{1}\left(\tilde{p}_{1}, \tilde{t}\right) \simeq 0.7 \times Z_{2}\left(\tilde{p_{2}}, \tilde{t}\right) \simeq 0.7
$$

and this shows that the gas cannot be treated as an ideal gas. The two volumes are respectively $V_{1}=n Z_{1} R T / p_{1} \simeq 151$ and $V_{2}=n Z_{2} R T / p_{2} \simeq 7.081$, the number of moles being $n \simeq 3000 / 28 \simeq 107.1$.
8.4 Let us write the volume of the fluid as a function of the compressibility factor $V=n R T Z / p$ and differentiate at constant temperature. We arrive to the following relation:

$$
\mathrm{d} V=-V\left[\frac{1}{p}-\frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_{T}\right] \mathrm{d} p
$$

From the general stability condition (4.116), we must have

$$
\left[\frac{1}{p}-\frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_{T}\right]>0
$$

and hence

$$
\frac{\mathrm{d} Z}{\mathrm{~d} p}<\frac{Z}{p}
$$

where the total derivative is calculated along an isothermal transformation. Integrating the above relation leads to the required result.
8.5 To calculate the coefficient of thermal expansion, let us differentiate the volume along an isobaric process:

$$
\mathrm{d} V=V\left[\frac{1}{T}+\frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_{p}\right] \mathrm{d} T
$$

and we obtain the result

$$
\alpha-\frac{1}{T}=\left(\frac{\partial \ln Z}{\partial T}\right)_{p}
$$

8.6 The experimental curve Eq. (8.89) can be written as

$$
\log \left(\frac{p}{p_{\mathrm{cr}}} p_{\mathrm{cr}}\right)=8.75-0.0437\left(\frac{T}{T_{\mathrm{cr}}} T_{\mathrm{cr}}\right)-\frac{127}{\left(\frac{T}{T_{\mathrm{cr}}} T_{\mathrm{cr}}\right)} .
$$

The critical pressure for Neon may be expressed in torr:

$$
p_{\mathrm{cr}}^{\mathrm{Ne}}=27 \times 760=2.05 \times 10^{4} \text { torr },
$$

and hence Eq. (8.89) may be written, in reduced variables, as follows:

$$
\log \tilde{p}=4.438-1.923-\frac{2.89}{\tilde{t}}
$$

The temperature $T=135 \mathrm{~K}$ corresponds to a reduced temperature $\tilde{t}=0.89$ and then the vapor pressure, for Argon, may be calculated from the relation $\log \tilde{p}=-0.52$ from which we obtain $\tilde{p} \simeq 0.3$ and $p_{\mathrm{Ar}} \simeq 14.4 \mathrm{~atm}$.
8.7 Before making use of the equation of state of ideal gases we verify, by means of the law of the corresponding states, if the compressibility factor is near to unity. The reduced variables, in the state we are considering, are

$$
\tilde{t}=\frac{395.46}{304.20}=1.3 \quad \tilde{p}=\frac{4.8}{7.39}=0.65
$$

If we refer to the compressibility chart in Fig. 8.6 we see that, with the above coordinates, the compressibility factor results in

$$
Z(0.65,1.3)=0.69
$$

Now we may calculate the volume making use of Eq. (8.58):

$$
V_{\mathrm{m}}=Z \frac{R T}{p}=0.69 \times \frac{8.31 \times 395.46}{4.8 \times 10^{6}}=472.4 \times 10^{-6} \mathrm{~m}^{3},
$$

and finally the requested volume is

$$
V \simeq 10^{3} \times 472.4 \times 10^{-6}=472.41
$$

8.8 We refer to the expression of the energy as a function of temperature and volume Eq. (8.27). Since in this process energy remains constant we have
$n C_{V}\left(T-T_{0}\right)=n^{2} a\left(\frac{1}{V}-\frac{1}{V_{0}}\right)$,
$T-T_{0}=n \frac{a}{C_{V}}\left(\frac{1}{V}-\frac{1}{V_{0}}\right) \simeq 10^{3} \times \frac{363.96 \times 10^{-3}}{28.85}\left(\frac{1}{1.2}-\frac{1}{0.47}\right) \simeq-16.4 \mathrm{~K}$, $T \simeq 583.6 \mathrm{~K}$.

## Solutions to the Problems of Chap. 12

12.1 The energy content of the cavity is doubled. The initial value is

$$
U_{0}=a T^{4} V_{0}=1.5 \times 10^{-2} \mathrm{~J}
$$

As regards the radiation pressure the value (constant during the expansion) is

$$
p=\frac{1}{3} a T^{4} \simeq 2.52 \times 10^{-4} \mathrm{~Pa}
$$

The energy variation is

$$
\Delta U \simeq 1.5 \times 10^{-2} \mathrm{~J}
$$

and the work done on the radiation field amounts to

$$
W=-p \Delta V \simeq-0.5 \times 10^{-2} \mathrm{~J}
$$

The quantity of heat supplied to the cavity is

$$
Q=\Delta U-W \simeq 2 \times 10^{-2} \mathrm{~J}
$$

The same result can be obtained calculating first the variation of entropy of the cavity:

$$
\Delta S=s \Delta V=\frac{4}{3} a T^{3} \Delta V \simeq 2.0 \times 10^{-5} \mathrm{~J} \mathrm{~K}^{-1}
$$

and the amount of heat can be obtained from the relation $Q=T \Delta S \simeq 2.0 \times 10^{-2} \mathrm{~J}$.
12.2 Denote with $T_{1}$ and $T_{2}<T_{1}$ the temperatures of the two isotherms and with $V_{1}$ and $V_{2}>V_{1}$ the volumes which define the expansion at isotherm $T_{1}$. As regards the volumes $V_{3}$ and $V_{4}$, we find

$$
\begin{aligned}
& V_{3}=V_{2}\left(\frac{T_{1}}{T_{2}}\right)^{3}, \\
& V_{4}=V_{1}\left(\frac{T_{1}}{T_{2}}\right)^{3}
\end{aligned}
$$

and then the amount of work done by the gas in the adiabatic processes will be, respectively,

$$
\begin{aligned}
& W_{2 \rightarrow 3}=3 p_{2} V_{2}\left[1-\left(\frac{T_{2}}{T_{1}}\right)\right], \\
& W_{3 \rightarrow 4}=3 p_{4} V_{4}\left[1-\left(\frac{T_{1}}{T_{2}}\right)\right] .
\end{aligned}
$$

We number the four transformations as shown in Fig. 12.5 with indexes from 1 to 4 . Let us denote with $W_{1}, W_{2}, W_{3}, W_{4}$ the amount of work done by the radiation to the outside world in the four transformations and with $Q_{1}, Q_{2}, Q_{3}, Q_{4}$ the analogues amounts of heat supplied from the outside world to the radiation. We will have, respectively,

$$
\begin{aligned}
W_{1} & =\frac{1}{3} a T_{1}^{4}\left(V_{2}-V_{1}\right), \\
W_{2} & =a\left(T_{1}-T_{2}\right) T_{1}^{3} V_{2}, \\
W_{3} & =-\frac{1}{3} a T_{2} T_{1}^{3}\left(V_{2}-V_{1}\right), \\
W_{4} & =-a\left(T_{1}-T_{2}\right) T_{1}^{3} V_{1},
\end{aligned}
$$

and for the quantities of heat:

$$
\begin{aligned}
& Q_{1}=T_{1}(\Delta S)_{1}=\frac{4}{3} a T_{1}^{4}\left(V_{2}-V_{1}\right) \\
& Q_{2}=0 \\
& Q_{3}=T_{2}(\Delta S)_{3}=\frac{4}{3} a T_{2}^{4}\left(V_{4}-V_{3}\right)=-\frac{4}{3} a T_{2} T_{1}^{3}\left(V_{2}-V_{1}\right) \\
& Q_{4}=0
\end{aligned}
$$

Adding up, for the total value of work done by the radiation we get

$$
W_{\mathrm{tot}}=\frac{4}{3} a T_{1}^{3}\left(T_{1}-T_{2}\right)\left(V_{2}-V_{1}\right) .
$$

For the efficiency of the engine, $\eta=W_{\mathrm{tot}} / Q_{1}$, we find the value

$$
\eta=1-\frac{T_{2}}{T_{1}} .
$$

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[^1]:    ${ }^{1}$ Temperature (absolute) should be correctly defined together with entropy, i.e., within the Second Principle.

[^2]:    ${ }^{1} \mathrm{~A}$ similar situation, will be encountered when the Einstein relation between the coefficient of diffusion and the coefficient of mobility in a ionic solution will be demonstrated in Sect. 16.6.4.
    ${ }^{2}$ The problem of the degrees of freedom for a macroscopic system will be extensively detailed in Sect.4.3.

[^3]:    ${ }^{3}$ For a discussion on the concept of causality see [1].

[^4]:    ${ }^{4}$ In order that any instrument can be considered a thermometer, it is necessary that the object observed has a much greater mass than the instrument itself.

[^5]:    ${ }^{5}$ These expressions in speech marks are true heresies from a scientific point of view but they can sometimes be found in regular language and in some (rare) texts.

[^6]:    ${ }^{1}$ The particular form of the Lorentz factor derives from the postulate on the invariance of the speed of light. This postulate affirms that a light signal is seen to propagate (in vacuum) with the same speed when observed from any inertial frame of reference. This postulate, together with the adoption of the Principle of Relativity, leads to a well-defined form of the laws of coordinate transformations between two different frames of reference called Lorentz transformations. Two popular consequences of these transformations are known as the length contraction and the time dilatation. Both these effects scale with the Lorentz factor.

[^7]:    ${ }^{1}$ See, for example, the article by A. Einstein quoted in the Introduction to the present book.

[^8]:    ${ }^{2}$ The necessity of distinguishing between these two contributions is due to the fact that the quantity we are going to define through the Second Principle is a non-conserved quantity. Conserved quantities can vary only because of interactions with the external world.

[^9]:    ${ }^{3}$ By thermodynamic phase we mean an homogeneous system, i.e., with uniform density.
    ${ }^{4}$ This definition ties the property of extensiveness to the metric being used in view of the generalization of the theory to a relativistic context.
    ${ }^{5}$ Other authors, especially when writing on Engineering, use mass as a reference quantity and therefore instead of "density" of $\mathcal{E}$, "specific" quantities are used, that is the amount of $\mathcal{E}$ transported by the unit of mass of the material.

[^10]:    ${ }^{6}$ For the positioning of indexes "I" and "II", see Appendix A.5.4.

[^11]:    ${ }^{7}$ The relaxation time for expansion or compression is of the order of the size of the container divided by the speed of sound; designing appropriate forms of the cylinders this time can be further reduced.

[^12]:    ${ }^{1}$ With the term "equivalent pressure", we mean to cover those situations in which, in addition to the external pressure in the strict sense (for example, exerted by the atmosphere on a movable piston) other forces applied to the mobile piston act such as a weight determined on a horizontal piston of the given area.

[^13]:    ${ }^{2}$ For a wider discussion on this topic, see [6].

[^14]:    ${ }^{3}$ This denomination is due to Gibbs and, as we shall see, it is absolutely appropriate.

[^15]:    ${ }^{4}$ In many texts designed for applications in engineering, however, it is useful to take the mass as a state variable.

[^16]:    ${ }^{5}$ And to do this the observer should ensure an efficient flow of extensive quantities such as energy or volume.

[^17]:    ${ }^{6}$ The rule of the "entropy increase" is an expression often used in a very rough manner. It can be considered correct strictly for isolated systems. In general, for systems in interaction with the external world this rule takes different expressions as we remarked in Sect.4.3.2 all resulting from the requirement $\hat{d}_{\mathrm{i}} S>0$, which is the only fundamental condition.

[^18]:    ${ }^{1}$ Also these three coefficients are, after all, three partial derivatives.

[^19]:    ${ }^{1}$ Low pressure means, in this case, pressure below the saturation pressure at that temperature (see Sect. 7.2.1).

[^20]:    ${ }^{1}$ Alternatively, we can consider phases consisting of ideal solutions, i.e., phases composed by a mixture of different noninteracting components. We can assume that the equation of state of each component does not depend on the presence of the other components. Moreover, as we have seen, with few formal changes we can consider phases at different pressures.

[^21]:    ${ }^{2}$ For simplicity, we refer only to three phases, namely, solid, liquid, and vapor. In nature, things are a bit more complicated because there may be multiple solid phases depending on different crystalline forms of aggregation. In principle, the treatment does not conceptually change even if it is necessary to provide a more detailed structure.

[^22]:    ${ }^{1}$ It is important to remember that we are referring to interactions between pairs of molecules. This assumption is justified when the density is low enough which is equivalent to say that the range of the interactions is small enough that the probability of finding three or more molecules at a distance below the range of the interaction potential $\mathcal{U}$ becomes negligible.

[^23]:    ${ }^{2}$ A detailed discussion is of major importance and for those interested in technical applications can be found in [10].

[^24]:    ${ }^{3}$ Not to be confused with the coefficient of compressibility $\chi=-V^{-1}(\partial V / \partial p)$.

[^25]:    ${ }^{4}$ This is a statement according to the Law of Corresponding States. It can be formulated by observing that, for $\tilde{t} \lesssim 0.65, Z$ is sufficiently near to 1 .

[^26]:    ${ }^{1}$ The internal zone is defined by the property that the distance of the molecule from the surface of separation between the two phases is larger than the radius of action of the molecule.
    ${ }^{2}$ The amount of work depends certainly on the number densities of the two phases and the latters, at phase equilibrium, depend only on temperature.

[^27]:    ${ }^{3}$ Indeed, in mechanics textbooks, it is common to introduce the surface tension by a force in specific frame supporting liquid membranes (e.g., soap films).

[^28]:    ${ }^{4}$ In view of the specific topic discussed in this section, the vapor pressure given by Eq. (7.9) is often quoted as $p_{\infty}$ that is for flat separation surface between the two phases.

[^29]:    ${ }^{5}$ See Eq. (4.84).

[^30]:    ${ }^{6}$ We point out that Cassie-Baxter's model can be applied as well to planar, yet chemically heterogeneous, surfaces like a sequence of regions 1,2 occupying fractions $f_{1}, f_{2}$ of the total surface with contact angles $\vartheta_{1}, \vartheta_{2}$ respectively, so that $\cos \vartheta_{\text {ap }}=f_{1} \cos \vartheta_{1}+f_{2} \cos \vartheta_{2}$ with $f_{1}+f_{2}=1$. In addition, the Wenzel's model of Eq. 9.101 can be also used with hydrophilic surfaces having a roughness index $r$. In this case, the effect is that of reinforcing its hydrophilic property [50].

[^31]:    ${ }^{1}$ This means that if we denote by $h$ the distance between the plates and by $\Sigma$ their area (we assume that the two dimensions are comparable) it must be $h \ll \sqrt{\Sigma}$ thus the portion of the capacitor, in which we commit a significant error in treating the fields and the charge distribution as perfectly homogeneous, will have a very small volume compared to the volume in which our description will be accurate enough.
    ${ }^{2}$ Let us avoid to refer to the "pressure" of the fluid inside the condenser. In this region the fluid is not, in general, isotropic and the formalism to be used might be quite complicated.

[^32]:    ${ }^{3}$ The density and the surface density of polarization charges is given, respectively, by $-\nabla \cdot \mathbf{P}$ and $P_{\mathrm{n}}$.

[^33]:    ${ }^{4}$ The denomination does not mean that the electric permittivity is a constant in the sense that it does not depend on the state variables, but means that it does not depend on the electric field.

[^34]:    ${ }^{1}$ There is not a universal agreement in the denomination of the vector field $\mathbf{H}$. Some authors use the denomination of magnetic field, while the vector $\mathbf{B}$ is called magnetic induction.

[^35]:    ${ }^{1}$ This was the expression used by M. Planck in his speech to the ceremony of the Nobel Prize in 1920. See Sect. 12.6.3.

[^36]:    ${ }^{2}$ The transverse dimension of the hole is very small compared to the transverse dimension of the cavity. Also, the thickness of the wall in which the hole is practiced must be small.

[^37]:    ${ }^{3}$ As we shall prove in Sect. 12.6 of this chapter, in the treatment by M. Planck of the coupling between matter and radiation, the result will appear to be independent of the magnitude of the electric charge. This can be seen as a consequence of the Kirchhoff's law.
    ${ }^{4}$ The value of $\Gamma$ can not be determined by the scale invariance arguments.

[^38]:    ${ }^{5}$ The expression of the spectral energy density Eq. (12.23) was first calculated in 1900 by Lord Rayleigh with an argument based on classical statistics. For the fundamental product $\Gamma$, he found the result $\Gamma=2$.

[^39]:    ${ }^{6}$ The dependence of the emittance of a black body (i.e., the emittance of the surface of the small hole practiced on a material cavity in thermodynamic equilibrium at temperature $T$ ) from the fourth power of the temperature had been found experimentally by Stefan. The derivation of the expression for the radiation energy density Eq. (12.54) of a black body was obtained from the principles of thermodynamics by L. Boltzmann.

[^40]:    ${ }^{7}$ In theory, this would be possible in a quantum-relativistic context but with enormous relaxation times at temperatures below $10^{9}-10^{10} \mathrm{~K}$ where the production of charged pairs becomes significant.

[^41]:    ${ }^{8}$ We may say that the little piece of copper has the function of a catalyst. It makes a process possible but does not enter in the balance equations.

[^42]:    ${ }^{9}$ In this context when we use the term high frequency or low frequency, reference must be made to the fact that at ordinary temperatures the maximum emissivity of the black body is about $10 \mu \mathrm{~m}$, that is, at a frequency of about $3 \times 10^{13} \mathrm{~Hz}$.
    ${ }^{10}$ In this context, far infrared means wavelengths of order $\lambda \sim 30-40 \mu \mathrm{~m}$.

[^43]:    ${ }^{11}$ We recall that thermodynamical equilibrium between matter and radiation is assumed.

[^44]:    ${ }^{1}$ Remember the definition Eqs. (5.18) and (5.19) for the heat capacities.

[^45]:    ${ }^{2}$ Hastily, for brevity, someone says that at "absolute zero" there is only one possible microscopic state.

[^46]:    ${ }^{1}$ The very common denomination "heat flux" seems to contradict this rule because "heat" is not an extensive property of a system. The point has been already discussed in Sect. 4.3.

[^47]:    ${ }^{2}$ This statement should not be understood as being limited to the thermodynamic context but must be considered to be of general validity. For example, in mechanics, the interaction consists of a transfer of extensive quantities possessed by the interacting systems, such as, for example, momentum, angular momentum, or energy. See also [1].

[^48]:    ${ }^{3}$ Let us assume that the values of the fluxes do not depend of the preceding history of the system as it happens in those situations in which hysteresis is important.

[^49]:    ${ }^{4}$ If a chemical reaction is in equilibrium, this does not mean that "nothing happens" but it means that the number of forward events per second and the number of backward events per second are equal.

[^50]:    ${ }^{1}$ The "degrees of freedom" are the terms that make up the expression total energy of the system. In the case of polyatomic molecules we should add more degrees of freedom that give account of the rotational and vibrational motions.

[^51]:    ${ }^{2}$ Energy can be transferred between the two vessels even if the flow of matter is zero.

[^52]:    ${ }^{3}$ For isolated systems the property is obviously verified: at equilibrium (stationary state), the entropy production is zero (minimum).
    ${ }^{4}$ See Sect. 4.3.1.

[^53]:    ${ }^{5}$ Chemical reactions are excluded and, more in general, let's treat the $n$ extensive quantities $E_{\rho}$ as a kind of "conserved quantities". If not, the expression for the entropy production would contain additional terms not coupled with the terms that describe the exchanges between the two phases. The changes due to interactions with the outside world are due to interactions with "third systems". ${ }^{6}$ For the fluxes we choose as positive the direction I $\rightarrow$ II.

[^54]:    ${ }^{7}$ We see that, in the stationary case, the flows represent the transfer, between the two external constraining systems, of a specific physical quantity the meaning of which depends, of course, on the choice of the state variables $\mathcal{E}_{\rho}^{\mathrm{I}, \mathrm{II}}$.

[^55]:    ${ }^{8}$ This statement will be proved in Sect. 15.2.3.

[^56]:    ${ }^{9}$ The reader should avoid the mistake of attributing the classification "accurate" and "less accurate" any hierarchy of merit. It is not true that to be more accurate (in this scientific context) is "better" than being less accurate. These are two different perspectives that, of course, must be integrated but which lead to different representations. By analogy, we can observe the details of the single stones (fossils and minerals) but if we did not consider the shape, altitude and the distribution of the mountain ranges, we would not have conceived the theory of continental collision and then of plate tectonics.

[^57]:    ${ }^{10}$ Indeed the presence of fluctuations can be conceived equally well in a continuum.

[^58]:    ${ }^{11} \mathrm{We}$ are dealing with deviations of the state around a state of equilibrium in an isolated system. In this case the entropy is maximum in the equilibrium configuration.

[^59]:    ${ }^{1}$ In general intensive quantities such as, for example, pressure, temperature, the chemical potential have been defined for systems in thermodynamic equilibrium then the condition of Local Thermodynamic Equilibrium (LTE) must be verified point by point, see Sect. 16.6.

[^60]:    ${ }^{2}$ Electrochemical potential gradients reduce to electrostatic potential gradients (i.e., electric fields) in homogeneous, isothermal conductors as we have seen in the preceding examples. In more general contexts it is the variation of electrochemical potential that acts as the emf in metals.

[^61]:    ${ }^{3}$ This flux of energy is analogous to the flux defined in Eq. (14.110) for the case of discontinuous systems and which leads to the definition of heat of transfer

[^62]:    ${ }^{4}$ For the use of the term "stationary state" remember, by analogy, the case of the thermomolecular pressure difference in Eq. (15.6) and its role in Sect. 15.2.

[^63]:    ${ }^{1}$ Suppose we want to avoid the need of an intelligent being in the sense said before i.e. we operate the engine always in the same manner: for instance, first, we always compress the piston on the right reducing its volume to one half. Then we remove the septum and expand. If the molecule was on the left we gain positive work but in the case, the molecule was on the right we have to do work for compression and the balance is negative. In one case out of two we gain, in the other we lose. It is easy to see that on the whole we lose.

[^64]:    ${ }^{2}$ May be, in the next future by other scientific domains like neuroscience if, for instance, a reasonable modeling of the operation of the human mind can be put into play.

