Chapter 1
Thermodynamics and Its Concepts in Nonequilibrium

Thermodynamics deals with the behavior of macroscopic bodies (systems) when heat, work, and mass are exchanged. It is usually divided into two parts: *equilibrium (classical) thermodynamics* deals with equilibrium states while *nonequilibrium* (or *irreversible*) *thermodynamics* studies nonequilibrium processes. Each approach can either disregard the molecular structure, in which case we discuss the *phenomenological* thermodynamics, or, in the contrary, stress it in the *statistical* thermodynamics. Although statistical thermodynamics offers a deeper insight and useful results it cannot totally replace the phenomenological (i.e., nonmolecular) description because the results of statistical theory are often interpreted in (macroscopic) terms of phenomenological theory (regardless of the difficulties given by the complexity of molecular models).

We prefer here the phenomenological approach permitting broader applications but then some (macroscopic) empirical data of the studied system are necessary.

Besides immense applications, the foundations of phenomenological thermodynamics are attempted to be reformulated in nearly every textbook or monography on the subject, cf., e.g., [1–16],[1] see also thorough discussions in [17–23]. The main reason for this situation consists in the fact that thermodynamics gives in principle only an incomplete description because the macroscopic objects it deals with are too intricate and composed of an immense number of particles the detailed behavior of which is mostly not necessary to know (disregarding the practical impossibility of such description). Moreover in nonequilibrium situations time rates and gradients of properties play an important role and thus the memory and neighborhood influences on a state in a considered time and place become more important.

Therefore, we must deal with idealized thermodynamic models of real materials forming a system (body) studied, models which stress only those material properties which are important in the intended applications. Thermodynamic concepts (like

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[1] Footnotes (remarks) are numbered in Chapters starting with its number and subsequent equations in them are denoted (*a*), (*b*), . . .; reference to them is, e.g.,: Eq. (*a*) in Rem. 10, Chap. 3. Appendices at the end are denoted A1, A2, . . . , their equations and footnotes are denoted by letter A.

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heat, work, temperature, entropy, equilibrium, nonequilibrium process, etc.) may have different meanings depending on such models and this may explain the various paradoxes and misunderstandings.

An overview of main approaches to the thermodynamics of nonequilibrium can be found in Ref. [24] and we review the most important of them here in brief. Perhaps the oldest theory is the *classical* or *linear irreversible thermodynamics* which represents a straightforward extension of classical equilibrium theory to nonequilibrium processes. The core is formed by the *local equilibrium hypothesis* already mentioned in the Preface. This hypothesis states that the relations between thermodynamic quantities at given time and place in a system out of equilibrium are the same as known for a uniform system in equilibrium. The most important consequence of this hypothesis is that the Gibbs equation, i.e., the relation between entropy and relevant state variables, remains valid locally though the involved quantities change in time and space. In other words, the (specific) entropy is a function of (specific) internal energy, (specific) volume, and composition (expressed usually in terms of mass fractions) and the differential of this function is given by (equilibrium) Gibbs equation. The local equilibrium hypothesis avoids the problem of the existence of entropy in nonequilibrium just because of the supposed (local) equilibrium. The rate of entropy change is supposed to be composed from two parts—the rate of exchange with the surroundings and the rate of *internal entropy production*. This enables to write down the balance of entropy and supplement it with the (second law) statement of nonnegative entropy production inside the system. Combining the balances and the Gibbs equation the entropy production is expressed as a sum of products which are interpreted as products of *forces* and conjugated *fluxes*. Linear relationships between conjugated forces and fluxes are supposed and their coefficients are called the *phenomenological coefficients*. The Second Law (the nonnegativity of entropy production) is used to set the restrictions on the sign of these coefficients. Interested reader can learn more about this theory in a modern version and with applications especially in chemistry and chemical engineering in books [25, 26].

This classical, linear theory has been really extended in the *extended irreversible thermodynamics* [27] by relaxing the local equilibrium hypothesis. The basic conception is very similar to that of the classical irreversible theory and the main difference is in a set of relevant independent variables. The set of classical variables used in the classical theory (mass, energy, composition, and also momentum) is extended including the corresponding fluxes. The extending fluxes may include, e.g., the heat flux, stress-related variables like scalar bulk viscous pressure, or tensorial shear viscous pressure. The Gibbs equation is then generalized, i.e., extended with the differential terms containing the extending variables. The existence of a nonequilibrium entropy is usually taken to be granted and the entropy is required to be a concave function of the whole set of variables (i.e., including the extending variables) with locally positive rate of production and additivity property. The concavity means that the entropy as a function lies everywhere below its family of tangent lines (the meaning of the opposite notions of concavity and convexity is interchanged in some works). The extending variables are nonconserved and usually fast-changing and are typically used to describe the nonequilibrium phenomena in systems (materials) with non-negligible (though apparently short) relaxation times, e.g., ultrasound propagation in dilute gases, neutron scattering in liquids, flow of, or diffusion in suspensions or polymer solutions. Generalized Gibbs equation is used to derive the expression for the entropy production. To obtain practically applicable expressions this usually calls for introducing additional hypothesis, presumptions, or simplifications. The linearizations around the local equilibrium values or in the dependence of some coefficients on the extending fluxes were applied as well as specific properties of isotropic systems or functions (used also in our approach in Sects. 3.5, 3.7, or 4.5; see also Appendix A.2). Once the expression for the time derivative of (specific) entropy is obtained (on the basis of generalized Gibbs equation and its modifications) and the specific expression for the dependence of the entropy flux on independent variables is suggested they can be combined with the general form of balance equations and the expression for the entropy production is thus identified. The concavity requirement places additional restrictions on derived equations or their coefficients, i.e., on the model of a specific system or material behavior.

The youngest nonequilibrium thermodynamic theories are represented by the GENERIC formalism which stands for the abbreviation of the *General Equation for the Non-Equilibrium Reversible-Irreversible Coupling* [28]. Similarly, as rational thermodynamics, the approach used in this book, also the GENERIC is rooted in and closely related to mechanics. In contrast to rational thermodynamics, which has "unwound" of the continuum mechanics, GENERIC belongs to Hamiltonian formulations of mechanics and originally evolved from a generalization of the Poisson bracket formalism proposed in the classical (Hamiltonian) mechanics particularly to model the flow properties of complex fluids like polymer melts or solutions. Hamilton's reformulation of mechanics consists in the description of the time evolution of a (mechanical) system using the position and (generalized) momentum vectors as the principal set of variables. The time evolution is described by the Hamilton equations expressing the dependence of time derivatives of positions or momenta on total energy of the system (on its derivatives with respect to momenta or positions, more precisely). The Hamilton equations can be reformulated introducing the Poisson brackets [24]. The total energy, i.e., the sum of kinetic and potential energies, is also called the Hamiltonian of the system and referring to the Hamilton equations it can be viewed as a potential driving the time evolution of the system.

GENERIC tries to formulate a general time evolution equation by which the time evolution (derivative) of a state variable (which can be, e.g., mass density or fraction, momentum, energy) is determined by two potentials: the total energy of the system and a dissipation function. Just the latter one introduces the irreversibility (and, in this way, "the thermodynamics") into consideration and description of the system behavior. The dissipation function or potential is a function of derivatives (with respect to the state variables) of a quantity which should have the physical meaning of the entropy of the system and this latter function is minimum at zero state variables, is zero at zero entropy derivatives just mentioned and a concave function. The general evolution equation can be reformulated by means of Poisson brackets. To apply the GENERIC formalism first one has to select suitable state variables for the problem or system which is to be modeled. The next step is to formulate the appropriate set of evolution equations (this, in fact, involves also finding the Poisson brackets) which may not be an easy task. To establish a valuable expression for the dissipation potential it requires the information on parameters related to the nonequilibrium behavior like diffusion coefficients, viscosities, thermal conductivity, tensors describing hydrodynamic interactions, and others. More information on this general formalism capable of providing universal approach on every level of material description, being it macroscopic, mesoscopic, or microscopic, can be found in the book by Öttinger [28].

We also want to mention the contribution to modern thermodynamics made by Müller [10, 16, 29] which lies somewhere between the extended irreversible and rational approaches as indicated in the title of one of corresponding books, co-authored by Ruggeri [30]. Particularly, the reference [16] can be recommended even for the very beginners in modern approaches to fundaments of thermodynamics. Although the substantial part of this book deals with the equilibrium theory Müllers reintroduce time into consideration and thermodynamics equations and treat both the equilibrium and (and least some) nonequilibrium processes within a natural, common framework. Their book contains a lot of real application examples and explains and illustrates the common basis of probably all rigorous thermodynamic approaches—the equations of balance of mass, momentum, and energy and equations describing the specific behavior of different material bodies (systems) which were traditionally called the *equations of state* and in modern terms the *constitutive equations*.

The last theory we want to refer to in this brief overview is the *rational thermodynamics*. Because this is the core theory of our book it is explained in more detail in subsequent parts and here only some new achievements are mentioned which are relevant to our treatment and not included in it. The foundations and theoretical aspects of practical applications were further elaborated and precised by Rajagopal and his school (though now without the title "rational"). Sections 3.1 and 3.2 of our book stress the importance of the referential frame for the mathematical description and of the configurations of material bodies (systems) which should be recorded by this frame. A new concept of natural configuration was introduced [31] which enables more proper description of behavior of deformable bodies (therefore it seems to have no essential effect on linear fluids which are the subject of our book). Chapters 2 through 4 systematically use the traditional principles of rational thermodynamics to derive final versions of thermodynamic equations, i.e., mathematical models describing the behavior of the material system of interest. References [31–34] introduced another principle—the principle of maximum rate of dissipation—and showed how it can guide and simplify the process of finding thermodynamically consistent constitutive equations. Several works from Rajagopal's school are devoted to chemically reacting systems which are one of the principal subjects of this book. A general framework for such systems was presented in Ref. [35], however, for systems without diffusion only. This framework is based on Gibbs potential, which is also an important quantity in our book, particularly as a "source" of chemical potential (cf. especially Sects. 4.4 and 4.6), and on maximization of the rate of dissipation (maximization of entropy production, in other words). Finally, derived evolution equations for the concentrations of reacting species (kinetic or rate equations, in fact) contain chemical potentials as the quantities determining (among others) the evolution. This is similar to our results where chemical potentials are among possible sets of independent variables determining the reaction rates [Sect. 4.5, (4.79)]. However, in the example of rubber vulcanization the traditional kinetic mass action law was applied directly in its standard form (cf. our more general treatment in Sect. 4.9). Specific examples of similar treatment of reactive pulsatile or Hagen-Poiseuille flow can be found in Refs. [36, 37], respectively, and of synovial fluid in Ref. [38]. A simplified description of a two-component reaction-diffusion system was presented in paper [39].

As already stated in this book we follow neither the usual method of classical equilibrium thermodynamics [1, 2, 12, 21] nor the one of irreversible thermodynamics [3–6, 9, 40] even in their recent variants [11, 41] although we often discuss the same problems, cf. Rem. 2 in Chap. 2. We prefer the method of rational thermodynamics introduced in the following section. The main reason is very simple—it is the field we have been working in, we are familiar with. Furthermore, it seems to be the most elaborated approach in the principal area of our interest—the chemically reacting systems (see also [42]). Classical and extended reversible thermodynamics use the flux-force view on the Second Law—as a rule, the affinity is then identified as the force driving the “chemical flux”, i.e., the rates of chemical reactions which are usually expressed in terms of the extent of reaction. It is shown in Sect. 4.5 of this book that due to certain orthogonality other type of affinity is not seen in the Second Law and thus it is overlooked as a part of that “driving force” for chemical reactions. Further, it has been demonstrated that the extent of reaction cannot be used in chemically reacting mixtures with diffusion [17] (more precisely, when the diffusion is not “self-balanced”). GENERIC applications to the reactive systems are apparently still in their infancy [43, 44]. Rational methodology as presented in this book enables to rederive the whole classical chemical thermodynamics and to extend it to (at least some areas of) nonequilibrium. In other words, the rational thermodynamic theory of linear fluids puts the chemical classics onto a firm basis of nonequilibrium theory and supplies it with nonequilibrium capabilities. Of course, this book does not provide any “theory of everything” and it does not claim that all systems encountered in chemistry, chemical engineering, and related areas belong to the class of linear fluids. This book just presents a set of models which adequately correspond to lot of chemical experience and the application of which in a specific problem should and can be tested. The methodology is based on clearly defined principles and axioms the validity of which in a specific real situation can be verified or a priori estimated. The rational thermodynamics was also a subject of criticism, see e.g., [24, 45]. Whereas the critics can be relevant in some (perhaps very) specific systems (like plasma) in our case of linear fluids it can be neglected.

1.1 Introduction

Models and their developments in this book are based on the method of rational thermodynamics which has substantially contributed to the present-day understanding of the bases of thermodynamics.

Rational thermodynamics tries to construct systematically and with logical clarity mathematical models of thermomechanic phenomena in arbitrary situations on a nonmolecular level and therefore it is in fact modern phenomenological thermodynamics or the thermomechanics of continua. It was developed in the last decades mainly by Truesdell, Noll, Coleman, Gurtin, Bowen, Müller, Rajagopal, Šilhavý [10, 13, 17, 23, 46–50].[2] The basic procedure of rational thermodynamics (in principle the same as in the most elaborate physical theories such as mechanics or electromagnetism) may be outlined as follows: First, the *primitives*, i.e., a priori formulated (nondefined) concepts are introduced to describe the phenomena intended to study. Such concepts follow from the theoretical (even molecular) ideas as well as practical experience (immediate experience being the best) with (often special) thermomechanic phenomena and from the level of description intended. Primitives used in theories might be very different but some which are "nonmechanical" are necessary in phenomenological thermodynamics, cf. [17, Introit] (e.g., in this book these primitives are (macroscopic) motion, work, and "nonmechanical" heat, temperature). In terms of primitives the *defined concepts* are obtained (e.g., velocity from motion, entropy from heat and temperature).

Primitives and definitions are used to formulate *general postulates* (e.g., the First and Second Laws, balances of mass, momentum, etc.) valid for all (in fact for a broad class of) material models. Real materials are expressed through special mathematical models in the form of *constitutive equations* which describe "idealized materials" expressing features important in assumed applications. Moreover, the same real material may be described by more models with various *levels of description*. The levels are motivated by the *observer's time* and *space scales*—typically the time and space intervals chosen (by the observer) for description of a real material having its own

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[2] Rational thermodynamics develops from critical revision of continuum mechanics [21–23, 48, 50–52], thanks to pioneer work of Coleman and Noll [46] concerning the new interpretation of the entropy inequality (see also [53–61]).

For introduction to this theory there are useful books and results connected with the names of Truesdell [22, 52, 62, 63], Eringen [64–66], Rajagopal [50, 67], Müller [10, 68], Šilhavý [13], Astarita [69], Owen [70], Wilmanski [71], and others [47, 72, 73].

The physical content of the theory is discussed mainly in Truesdell's polemics with previous theories [17, 19, 20, 62].

For further developments see Truesdell and Noll [23], Eringen [65, 66, 74] and others [75–81], and most papers published in Archive for Rational Mechanics and Analysis and (mostly for applications) in International Journal of Engineering Science.

Concerning mixtures, which are of special interest in this book, the basic information may be found in the works of Bowen [49, 82], Müller [10, 68], Truesdell and Toupin [21], Williams [83, 84], Rajagopal and Tao [67], surveys of Atkin and Craine [85, 86], Hrma [87, 88] and Samohýl [89, 90], see also [91–93].

natural space and *time scales* (e.g., size of property inhomogeneities and typical time of their disappearance); see Sect. 2.3 for further details. In phenomenological theory all such scales are macroscopic (nonmolecular), cf. Sect. 1.2. The same real material may therefore have different constitutive equations from which we can choose the appropriate model for the intended application.

Constitutive equations have often been proposed empirically, intuitively, from molecular models, etc., and some of them have been well-known for a long time (state equations, transport laws of Fourier, Fick, etc.) but experience with their proposals may be generalized in plausible *constitutive principles*, see also Rem. 2 in Chap. 2. These principles are used in rational thermodynamics for generalized motivations, proposals, and further rearrangements of constitutive equations and, as a result, for finding the final form of constitutive equations, cf. further sections of this book, e.g., Sect. 2.1. Important and specific role in the process of deriving final constitutive equations is played by the Second Law or the entropy inequality. The subsequent logical step—introduction of constitutive equations into balances and the solution of resulting (usually differential) equations for given (boundary, initial) conditions is a traditional task of other disciplines like hydrodynamics, elasticity, heat conduction, chemical kinetics, etc.. But, sometimes, such a task is considered a part of thermodynamics, e.g., the issue of stability or formation of dissipative structures [4, 7, 11]; correspondingly, these problems will be discussed in this book only marginally.

At the end of the discussion of rational thermodynamics we stress that in this theory we in fact study mathematical models (in this sense this theory is a part of mathematics) and only after their application in a real situation and with real material we can decide about the limits of their practical validity.[3] Although practical application is out of scope of the theory developed here, it motivates the types of material models studied in this book and offered as various constitutive equations to be selected for particular application. Such applications motivate some concepts or procedures in the theory and also exclude some unusual properties of these models because the real materials are much more complicated: to avoid, e.g., instabilities (manifested, e.g., by phase changes), we exclude zero values of some transport coefficients or heat capacities. Such and similar *regularity* properties we add to constitutive equations and the resulting models we then denote as *regular* (see (3.232), (3.234), Rems. in Chap. 1, 2, 6, 8, and 9).

Thermodynamics is generally a very broad discipline, and to write an introductory book self-consistently we had to select only certain, typical part. Constitutive equations offer very different models of thermomechanical phenomena in many diverse materials for applications. In this book, intended for students of chemistry and chemical engineering and related fields, we choose only a narrow sector from these immense fields. Namely, we discuss the (mainly nonequilibrium) thermodynamics of fluids (i.e., gas or liquid; for difference see Sect. 4.8) and their reacting mixture with

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[3] E.g., in developing this theory we assume that some quantities may be arbitrary reals (cf. application of Lemma A.5.1 from Appendix A.5 in Sect. 2.2) though we know that all such possible values are far out of the limits of practical applicability of the mathematical model studied.

unique temperature, with (linear) transport properties (heat conduction, viscosity, diffusion) and (nonlinear) chemical reactions. We try to show that rational thermodynamics describes naturally the typical nonequilibrium situations (say in chemical engineering) of (chemically) reacting fluid mixtures where transport phenomena take place simultaneously: local state equations fulfill the classical thermodynamic relations and linear transport laws (Fourier, Newton, Fick) and also equations of (nonlinear) homogeneous chemical kinetics are valid.

The other important issues (often not sufficiently established in phenomenological nonequilibrium thermodynamics) like transport through the phase boundary, heterogeneous chemical kinetics, fluid–solid (heterogeneous) mixtures, etc., are noted here only marginally for simplicity, see Sects. 2.4, 2.5 and Rem. 1 in Chap. 3.

1.2 General Concepts and Framework, Thermodynamic Systems, Processes, and the Universe

Basic ideas of (phenomenological) thermodynamics need to use some "nonmechanical" concepts, like temperature, internal energy, or entropy.[4]

In this section we introduce these concepts in a very broad way, valid generally for "any thermodynamics" including nonequilibrium theories, to justify their application in our methodology. For this goal, only several primitives well-known from common life are sufficient. We use the Šilhavý's method [59, 60, 94–97], following mostly the papers of Kratochvíl and Šilhavý [98, 99] (see Sects. 1.3, 1.4), because it is appropriate for (at least some) nonequilibrium situations. Unfortunately, this procedure has been demonstrated for pure materials only (for discussion of mixtures see below).

The construction of entropy and absolute temperature (even in nonequilibrium) fulfilling entropy inequality is done by Šilhavý's method in terms of the primitives *work*, *heat* and *empirical temperature* (for the latter, see Appendix A.1; cf. Zemansky cited in [17, p. 53]). Moreover, the existence of energy satisfying the energy balance will be also proved.

These results are achieved by postulating the First and Second Laws of thermodynamics (in subsequent sections) as inequality assertions in terms of the primitives mentioned (and therefore directly experimentally verifiable). These basic

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[4] Such concepts as entropy or (absolute) temperature are usually constructed, or motivated in equilibrium. Their transfer to nonequilibrium situations is not so clear; therefore in nonequilibrium thermodynamics either the existence of these concepts was simply assumed [17, 19] or hypothesis on the local equilibrium was used [3–5, 9] (cf. also Appendix A.1).

Originally, rational thermodynamics assumed the existence of entropy and absolute temperature in nonequilibrium (cf. Lecture 1 of [17, 19]) but this assumption has been shown to be derivable by Šilhavý [59, 60, 94–97]. In simplified terms this was explained by Kratochvíl and Šilhavý [98, 99] and it will be used subsequently.

Similar results were obtained by Serrin [58] (he used the concept of "hotness"), Man [100] and Feinberg and Lavine [56, 57] (temperature was avoided completely from primitives).

Laws may be also presented as classical statements about the impossibility of the perpetual motion of the first and second kind.

The procedure is performed generally for all constitutive models (independently of the choice of independent variables of constitutive equations, cf. Rem. 6) and therefore the great generality of the results (mainly energy balance and entropy inequality) is guaranteed. Conversely, however, we deal with phenomenological models where the observer's time and space scales are macroscopic ("human", "terrestrial") and therefore giant against microscopic natural scales (molecular scales, like the relaxation times of energy exchange among motion modes of molecule or intramolecular distances). This great difference between these types of scales permits to distinguish clearly between heat and work, to formulate empirical temperature and to rely on the inviolability of macroscopic principles with statistical origin.[5]

These results are obtained and applied for pure materials and closed systems (which do not change their mass, cf. Chap. 2). They may be enlarged even at mass exchange systems using instruments like material volume or material (time) derivative, see Chap. 3. But, with the exception of some simple models, difficulties begin with mixtures, especially with those which are diffusing or exchanging mass and heat simultaneously. Here, because the similar Šilhavý procedure is not known for the mixture, some further primitives must be introduced (by analogy with pure materials), and the basic Laws must be reformulated, see Chap. 4, Sects. 4.1–4.4 and Rem. 14 in Chap. 2.

In (phenomenological) thermodynamics we study the (macroscopic) *thermodynamic system* (also called the *body*) and we assume that we know how its *state* can be described.[6] By *process* we understand realizable time sequence of states from the initial to the final state.

The manner of the description of the state plays no role in this chapter; the only thing which is important here is that we are able to say whether two states are the same or not. Therefore, the results are general and valid for all constitutive models or at least for those discussed in the following Chaps. 2 and 3. But we emphasize that phenomenological models expressed by constitutive equations, i.e., by a concrete choice of state, may be various and therefore, the concrete meaning of concepts discussed in this chapter (like work, definition of equilibrium, entropy values, etc.) may differ among such models, cf., e.g., [10, 17, 47, 101]. This will be demonstrated in constitutive models discussed in the following Chaps. 2, 3 (see Sects. 2.1–2.3, 3.6–3.8).

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[5] Like the Second Law. Difficulties may be expected if this giant difference between the observer's and the molecular scales breaks down as, e.g., in nanotechnologies, but we avoid these problems here.

[6] State is given by independent variables of constitutive equations modeling the properties of such system, e.g., density, temperature, their gradients and time derivatives, deformation rate, etc. Constitutive equations need not be only functions, but, e.g., functionals where state variables may also be functions of time (histories in materials with memory, cf. example in Rem. 3 in Chap. 2) or space (nonuniform or nonlocal systems). Sometimes (e.g., for energy) the state is determined also by velocity and other external influences, e.g., gravitation or radiation. cf. also Chap. 2.

We suppose that in any process we can determine the following three primitives *work*, *empirical temperature*, and *heat exchanged at each empirical temperature* during the process. The sum of such heats (through all empirical temperatures in process) gives *heat* in the whole process.[7] We assume that such determinations (measurements) are possible at least in principle.[8]

Work w may be measured in the usual way known from mechanics[9] and *heat exchanged at given empirical temperature* may be measured by a calorimeter (e.g., by "phase calorimeter" measuring heat by the mass of a new phase formed by suitable substance the phase change of which is just at considered temperature).

Empirical temperature ϑ is a number adjoined to every place and instant of process in the system and may be measured by *thermometer* (see Appendix A.1 for further details; note that a priori assumptions, like thermal equilibrium, Zeroth law, are necessary here). We use for ϑ the same units, namely Kelvins, and because we try to measure ϑ generally in nonequilibrium situations, we consider as a reliable that value of ϑ read from thermometer the dimension and relaxation time of which are both much smaller than observer's scales (cf. Rem. 8 and Sects. 1.1, 2.3, Appendix A.1). The right value of ϑ is assured if by repeating of identical measurement with other thermometers with smaller and smaller dimensions and relaxation times the same values (in Kelvins) are obtained.

In this book, we consider only the systems where empirical temperature just described has the sense and may be used even in nonequilibrium situations. There are, of course, also more complicated systems, e.g., mixtures with more temperatures (like plasma from electrons and ions) see, e.g., [10, 105, 106] and [107, Sect. 4], which will be not discussed here.

After discussion of basic primitive concepts we can proceed with the theory as follows: Adding together the heat exchanged at all instances of the process and in

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[7] We use the (newer) convention in which work done by the system is negative and done on the system is positive similarly as heat emitted from (absorbed by) the system is negative (positive), e.g., [11, 17, 19, 21, 102–104]. See also Rem. 20 in Chap. 3.

But the traditional reversed convention for work has been often used just in the Šilhavý's proof, see [13, 60, 90, 96, 98, 99].

[8] The dimension and the time constant (or "relaxation time"—time interval needed for right response) of measuring devices must be much smaller than the observer's scales of space and time; then it may be expected that the measured quantity has meaning even in the nonequilibrium processes where heat, work, and empirical temperature may be field quantities changing with finite rates (cf. also Appendix A.1).

[9] Caused, in macroscopic thermodynamic systems, by surface or volume forces, see Sect. 3.3. Often the *volume work* is used, which is defined by

$$w = -\int_{V_i}^{V_f} P \, \mathrm{d}V$$

where the volume V changes from the initial V_i to final V_f value under the external pressure P coming from the outside as boundary condition ($P > 0$ at compression, $P < 0$ at expansion). But in important models neglecting motion (classical thermodynamics, uniform models of Chap. 2), P is determined by constitutive equations of material inside the volume, cf. Rems. 1 and 37 in Chaps. 2, and 3, respectively.

all places of the system where empirical temperature achieves some fixed value ϑ_j and denoting this sum by Q_j we can obtain the *heat distribution* $\vec{Q}$ which gives an information how much heat was exchanged during the process at each empirical temperature. To avoid the exact and nontrivial mathematical definition of this quantity [59, 60, 98, 99] and to show here only the principles of Šilhavý's method with the use of simple mathematical means (namely finite dimensional vector space) we introduce the following "step" approximation: we assume that empirical temperature may be measured only by steps and the number N of all possible empirical temperatures ϑ_j ($j = 1, 2, \ldots, N$) is finite and fixed (to make this approximation realistic we assume high number of steps, say exactly $N = 10^9$, i.e., steps are small).[10]

Then the heat distribution $\vec{Q}$ in the given process and given system may be represented by an N-dimensional vector

$$\vec{Q} = (Q_1, Q_2, \ldots, Q_N) \tag{1.1}$$

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[10] If we are not satisfied with this "step" approximation giving results in the form of sums (1.20), (1.21) instead of usual integrals (1.41), (1.42) we can proceed as follows (according to [98, 99]):

Heat distribution $\vec{Q}$ (of given process in the given system) is now infinite dimensional vector with components $\mathrm{d}Q$ (i.e., Q_j in (1.1) with $N \to \infty$) having similar properties: $\mathrm{d}Q$ for each empirical temperature ϑ (generally different for different $\mathrm{d}Q$) is the sum of heat exchanged at all instances of the process and in all places of the system with this empirical temperature ϑ_j and $\mathrm{d}Q$ are defined as zero on these temperatures ϑ which do not occur in the process.

From a mathematical point of view the heat distribution is the function which to each set of empirical temperatures ϑ furnish the (real) number, i.e., it is the *measure* defined on the reals ϑ (cf. [59, 60, 98, 99]). Therefore, the heat q exchanged during the process (1.2) is now expressed by

$$q = \int \mathrm{d}Q = \int \eta(\vartheta)\mathrm{d}\vartheta \tag{a}$$

where we integrate through all possible empirical temperatures ϑ. For simplification we use here the second integral with (primitive) *density of heat distribution* $\eta = \eta(\vartheta)$ (function of ϑ) [98, 99] (more general procedure see [59, 60]). It gives $\mathrm{d}Q = \eta(\vartheta)\mathrm{d}\vartheta$ as the amount of heat exchanged between empirical temperatures ϑ and $\vartheta + \mathrm{d}\vartheta$ (of course in all (possible different) parts and instants in the process of the system with temperature ϑ). But, then we must admit that density of heat distribution $\eta(\vartheta)$ may be also a δ-function: If a process is isothermal exchanging heat Q_i at the unique empirical temperature ϑ_i, the density of heat distribution is

$$\eta(\vartheta) = Q_i \delta(\vartheta - \vartheta_i) \tag{b}$$

Indeed, these Eqs. (a), (b) then give for all exchanged heat q

$$q = Q_i \int \delta(\vartheta - \vartheta_i)\mathrm{d}\vartheta = Q_i \tag{c}$$

(we recall that by definition of δ-function $\delta(x)$ its value is nonzero only when $x = 0$, $\delta(0) \neq 0$ and $\delta(x) = 0$ for $x \neq 0$, but its integral through all x is equal one $\int \delta(x) = 1$).

For further developments of this "integral" procedure see Rems. 16, 21 in Sect. 1.4.

Its components Q_j have the signs according to the convention mentioned in Rem. 7 or they are zero; the values of Q_j at empirical temperatures which do not occur in the given process (usually great majority from N possible) are zero by definition.

In fact we need heat distribution only in the discussion of the Second Law in Sect. 1.4; for the First Law we need only the heat q exchanged during the whole process which is the sum of heats exchanged at each temperature

$$q = \sum_{j=1}^{N} Q_j \tag{1.2}$$

("step" approximation has no influence on the following postulates of theory [60, 98, 99]).

We postulate now (nearly obvious) properties for studied systems and their processes with ϑ, w, q, $\vec{Q}$ [or Q_j in (1.1)]:

S1. The work w and heat distribution $\vec{Q}$ may be determined in an arbitrary process [we assume w, q finite as well as components Q_j in (1.1)].

S2. *Composition of processes*: The work or the heat distribution of the process formed by two successive processes following each other is the sum of works or heat distributions of both processes (vectorial sum in the last case).

S3. It is possible to connect two arbitrary states by some process. From this also existence of *cyclic process* follows, i.e., cyclic process starts and ends at the same state.

S4. The system has *equilibrium state* defined as the state in which the system persists arbitrarily long time without exchange of work and heat with surroundings, i.e., with $w = 0$ and $\vec{Q} = \vec{0}$.[11]

The set of all systems (and their processes) with properties S1–S4 and all their (though conceivable) combinations is called a (thermodynamic) *universe*. We postulate that the universe has the following properties:

U1. *Closeness of the universe*: the composition of two arbitrary systems from the universe is again the system from this universe. Thus, if in both such individual systems there are processes with w_1, $\vec{Q}_1$ and w_2, $\vec{Q}_2$ both of which having the same duration, then these processes may be regarded as one process in the compound system with $w = w_1 + w_2$ and $\vec{Q} = \vec{Q}_1 + \vec{Q}_2$.

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[11] Concrete definition of equilibrium state must be performed for each constitutive model (characterized by the observer's scales of Sect. 1.1 and mainly Sect. 2.3) by time fixing of some quantities from those determining their states (see Rem. 6). Time persistency is usually difficult to achieve (because of molecular fluctuation) and therefore to describe real materials by such constitutive models we must add to constitutive equations (as their regularity) the conditions of *stability* by which the time permanence of equilibrium state S4 is assured. For details see Sects. 2.1–2.4, 3.8, 4.7 and Rems. 7, 9, 11 in Chap. 2. Although one equilibrium state would suffice, typically there are more equilibrium states often forming the *equilibrium process* as their time sequence, see Rem. 12.

Equilibrium states and equilibrium processes therefore depend on the choice of constitutive model.

To explain the remaining property of the universe we introduce two special types of processes.

A process with $w, \overrightarrow{Q}$ is called *reversible* if a *reverse* process with $-w, -\overrightarrow{Q}$ exists in the universe (usually in the same system) which passes the same states but in reverse order comparing to the original "straight" one with $w, \overrightarrow{Q}$.[12]

Process with $w, \overrightarrow{Q}$ is called *homogeneous* if a process with $\alpha w, \alpha\overrightarrow{Q}$ for each $\alpha > 0$ exists in the universe (e.g., in uniform systems, i.e., those without space gradient of properties, changing the mass α-times we change the work and heat distribution in $\alpha w, \alpha\overrightarrow{Q}$ because of extensivity of these quantities).

For further explanation we introduce the *set* A of $w, \overrightarrow{Q}$ of all *cyclic* processes in the universe and of all *ideal* cyclic processes $w, \overrightarrow{Q}$ which are some limits of preceding "real" cyclic processes (running cycle slower and slower as we approach the reversible one, cf. Rem. 12, cycles with real gas running at lower and lower pressure approach those with ideal gas, etc. These are experimental examples of possible limitations to ideal cyclic process; of practical importance is the Carnot cycle used below and discussed in Rem. 4 in Appendix A.1 in details).

Then we introduce the *set* B of $w, \overrightarrow{Q}$ of all real and ideal cyclic processes which start in equilibrium (therefore $B \subset A$).

Ultimately, we introduce the *set* C of $w, \overrightarrow{Q}$ of all cyclic processes starting in equilibrium with the following property: with each such process characterized by $w, \overrightarrow{Q}$, the set C contains the cyclic process starting in equilibrium, work, and heat distribution of which is $\alpha w, \alpha\overrightarrow{Q}$ respectively, where α is an arbitrary *real* number. Therefore C is the set of $w, \overrightarrow{Q}$ of the cyclic reversible and homogeneous processes starting in equilibrium (see definitions above with $\alpha = -1$ meaning reversibility and $\alpha > 0$ meaning homogeneity respectively).

Subset C is not empty (and therefore also B, A, because $C \subset B \subset A$) because for two different empirical temperatures the ideal cyclic reversible and homogeneous processes starting in equilibrium may be introduced, namely those with ideal gas—Carnot cycle of Appendix A.1 (cf., e.g., [1, 12, 110, 111]).

As the second property of universum we postulate:

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[12] Cf. [98, 99, 108, 109] and classical texts [1, 12]. The states passed in reversible process are not specified here but the results following from their existence in Sect. 1.4 [equalities in Clausius (1.20) or (1.41) and entropy (1.21) or (1.42) inequalities, (1.40)] show how to find reversible processes in each constitutive model of this book. Namely, such are equilibrium processes from Rem. 11 defined in each constitutive model (see Sects. 2.1, 2.2, 2.4, 3.8, 4.7) by zero *entropy production* [e.g. (2.11), (3.109), i.e., in fact by equalities in (1.21), (1.42)]. They form the time sequence of equilibrium states S4 and their reversibility may be shown explicitly in examples, see Sect. 2.2 (models A, B), Rem. 41 in Chap. 3. The stability of such equilibrium states (cf. Rem. 11) explains the experience that real processes approach those reversible if they are sufficiently slow, cf. [109], Rem. 48 in Chap. 3.

U2. *Completeness of the universe*: for every two empirical temperatures (from N possible in our "step" approximation) there is the process in the universe which is from C (cyclic, reversible, and homogeneous process starting in equilibrium) with nonzero heat and work ($q \neq 0$, $w \neq 0$), exchanging heat only at these two empirical temperatures. Specifically we can assume, that in C such are the *Carnot cycles* (defined in Appendix A.1) for each two temperatures.

Summary. Basic thermodynamic concepts were introduced in this section which form a very general framework to formulate two basic thermodynamic laws also at nonequilibrium conditions. Only three primitive notions of work, heat, and empirical temperature and several simple general properties of thermodynamic systems and universe were sufficient for this purpose. In the following two sections, we postulate the First and the Second Laws of thermodynamics and deduce the consequences. Because they are formulated in terms of heat, work, empirical temperatures, and cyclic processes (including those which are ideal) their direct experimental confirmation is possible.

1.3 The First Law of Thermodynamics

In this section we continue with the method of Šilhavý and Kratochvíl [13, 59, 60, 98, 99]; here we need only work and heat in the entire process (heat distribution is not necessary and therefore also an approximation by finite numbers of empirical temperatures is redundant) moreover we consider here often cyclic processes.

We postulate the *First Law of thermodynamics* as follows:

In any cyclic process (real and ideal from the set A, see end of Sect. 1.2) the system can perform work if and only if it absorbs heat, i.e.,

$$w < 0 \Leftrightarrow q > 0 \tag{1.3}$$

As we noted at the end of Sect. 1.2, direct experimental confirmation of this postulate is possible (even for ideal process).

Examples are cyclic working heat machines producing work from absorbed heat but (cyclic) perpetuum mobile (of the first kind) performing work $w < 0$ without absorbing heat or even producing it (by friction) $q \leq 0$ are excluded. Note that if a process is not cyclic, inequalities (1.3) not be valid, e.g., at adiabatic expansion.

From this First Law and postulates about the system and universe S1–S4, U1, U2 we can prove the following results:

1. Existence of the *mechanical equivalent of heat* J: there exists a positive, universal (i.e., the same in the whole universe) constant J such that for each *cyclic* process in the arbitrary system of the universe we have

$$w = -\mathrm{J}q \tag{1.4}$$

Therefore, the value of J is given by the choice of heat and work units (usually they are chosen the same and consequently J $= 1$; if different, e.g., formerly "Calorie" for heat, J $\neq 1$).

2. Existence of energy and balance of energy: for each system in the universe there exists a *state function*—the *energy* U (determined within an additive constant) such that the *balance of energy* holds

$$U_f - U_i = \mathrm{J}q + w \tag{1.5}$$

for an arbitrary process in the system. Here U_f and U_i denote values of U in the final and the initial state, respectively.

Values of a state function are determined only by quantities describing the state and U is the whole energy of the system if the state is described (besides the independent variables of constitutive model) also by the macroscopic velocity of the system and/or even by its position in external fields like the gravitation. But the influence of these last macroscopic parameters can be included [in balance (1.5)][13] into the work w of inertial forces in the form of (macroscopic) kinetic energy (or even potential energy of an external field), cf. [47, 112, 113]. Then U may be interpreted as *internal energy* depending on the independent variables of the constitutive model, cf. (1.12), Rem. 15, Sects 2.1, 3.4, e.g., (3.97).

Proof of these assertions (1.4), (1.5) may be sketched geometrically.[14] Values of q and w of each *cyclic* process in the universe (i.e., from the set A) may be represented by the point of the plane putting q and w on perpendicular axes, see Fig. 1.1 (cf. [103] and, with Rem. 7, [90, 98, 99]).

According to the First Law (1.3) these representing points $(w, q) \in$ A cannot fall in the first and in the third quadrants (here is $w > 0$ and $q > 0$ or $w < 0$ and $q < 0$). By the completeness of universe U2 there is a $(w_0, q_0) \in$ C (real or ideal cyclic process starting from (stable) equilibrium which is reversible and homogeneous, say the Carnot cycles). Therefore, also $(\alpha w_0, \alpha q_0) \in$ C exists (with arbitrary real α) and such processes are situated on the line going through the origin but not crossing the first and the third quadrant and not coinciding the axes (C $\subset$ A, $w_0 \neq 0$, $q_0 \neq 0$). Then however, all the cyclic (real and ideal) processes starting from equilibrium, i.e., from the set B, must have their representing points on the same line. Indeed, if it would not be true, i.e., if there would be a (cyclic) process (say (w_1, q_1) on Fig. 1.1) not situated on this line, we could find a (cyclic) process $(\alpha w_0, \alpha q_0) \in$ C (on this line) such that the sum of these two processes in the sense of the closeness of the universe U1 form a cyclic process, the representing point $(\alpha w_0 + w_1, \alpha q_0 + q_1)$ of which would fall into the forbidden (first or third) quadrant (waiting appropriately in initial equilibrium state we can achieve the same duration of both process), see Fig. 1.1.

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[13] Or even neglected as in classical thermodynamics and other models of Sects. 2.1, 2.2.

[14] Original proof in [59, 60, 98, 99] stresses more the difference between First and Second Laws, cf. Rem. 17. See also Rem. 7 concerning sign of work.

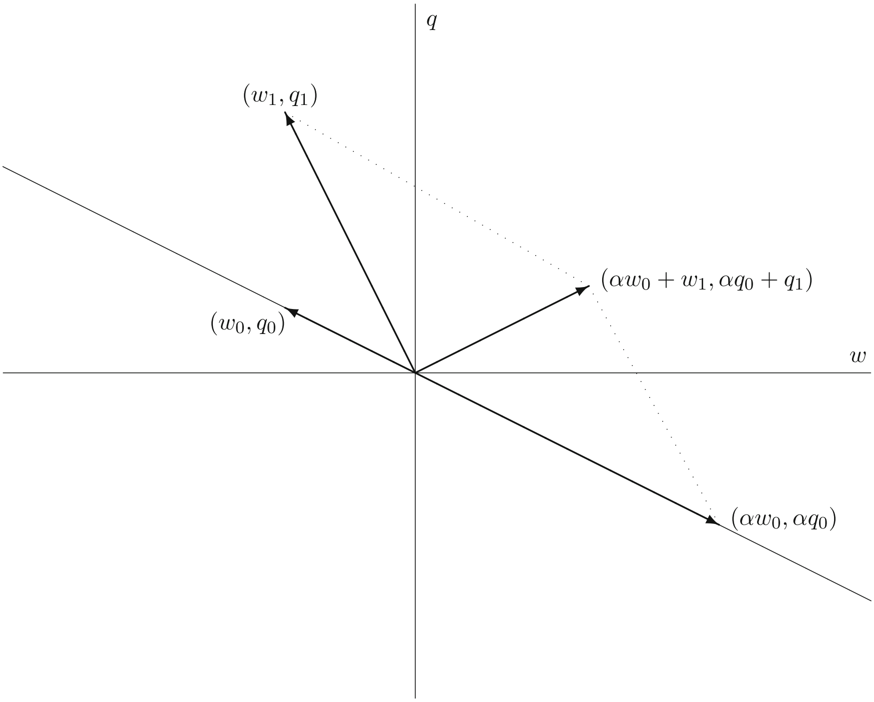

Fig. 1.1 Plane representing work and heat in cyclic processes. The First Law prohibits points (ω, q) to fall in the first or third quadrants

Thus Eq. (1.4) is proved for the set B (and C $\subset$ B) with positive constant J the same in the whole universe. Before extending this result to all cyclic processes (set A) we take some *equilibrium* state σ_0 (cf. postulate S4 in Sect. 1.2) as a reference state and define the energy U in an arbitrary state σ by

$$U = \mathrm{J}q + w \tag{1.6}$$

where w, q are the work and heat of some process p (cf. S3) from the (equilibrium) reference state σ_0 to σ.

The energy U just defined is independent of the process p from σ_0 to σ. Indeed, let us consider the fixed backward process p_0 from σ to σ_0 with w_0, q_0. Because p followed by p_0 is a cyclic process starting in equilibrium, by S2, (1.4) and (1.6) we obtain

$$(\mathrm{J}q_0 + w_0) + U = 0 \tag{1.7}$$

The same equation is valid for another process p' from σ_0 to σ with w', q'. Therefore

$$U = \mathrm{J}q + w = \mathrm{J}q' + w' = -(\mathrm{J}q_0 + w_0) \tag{1.8}$$

This means that U is a *state function*, i.e., depending on the state σ (and, of course, on the reference state σ_0) and not on the processes (like p, p').

Let us consider now two arbitrary states, the initial σ_i and the final σ_f and a process with w, q from σ_i to σ_f. If we choose some equilibrium state σ_0 as a reference state, then from the composition of the processes S2 (schematically: $\sigma_0 \to \sigma_i \to \sigma_f$) and (1.6) it follows that

$$U_f = U_i + \mathrm{J}q + w \tag{1.9}$$

where U_f and U_i are the energies in the final and initial states, respectively. This is the balance (1.5). If the initial and the final state coincide $\sigma_f = \sigma_i$ (cyclic process) then $U_f = U_i$ and we obtain from (1.9) the general validity of Eq. (1.4) for *any* cyclic process (i.e., from the set A). This also permits the definition of state function U based on any (and not only equilibrium) reference state σ_0 repeating with it the procedure from analogs of (1.6) to (1.9); therefore (1.9), i.e., (1.5), is valid also for energy defined in this general reference state.

Moreover, repeating the deduction of (1.9) for the same process from σ_i to σ_f with the same w, q but also with another (general) reference state σ_0' giving energies U_f' and U_f' in σ_f and σ_i respectively, we have

$$U_f' - U_i' = \mathrm{J}q + w = U_f - U_i \tag{1.10}$$

Taking $U = U_f$, $U' = U_f'$ and $\sigma_0' = \sigma_i$ (i.e., $U_i' = 0$) we find that the energy of an arbitrary state (σ_f in our case) relative to the new reference state U' and to the original reference state U respectively are in the relation

$$U = U' + \text{const.} \tag{1.11}$$

where "const." is the energy of the new reference state relative to the original. Consequently, energy (defined to general reference state) is determined within an arbitrary constant. Therefore proof of results 1 and 2. is complete. Q.E.D.

The classical special case of (1.5) (here and in the following we use mostly $\mathrm{J} = 1$) is arrived at when the volume work in Rem. 9 is the only work considered (the work of inertial and/or external forces is neglected); U is then internal energy.[15]

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[15] Experience (and also most constitutive models in this book, e.g., models A, B in Sects. 2.1, 2.2 and in Chap. 3) shows that the internal energy of (uniform) fluids (namely real gases) are functions only of V and ϑ (denoted later as T, see (1.30) below). For the special case of *ideal gas* (defined by i., ii. in Appendix A.1, cf. end of Sect. 3.7) the internal energy is a rising function of temperature ϑ only

$$U = U(\vartheta)$$

Therefore $\mathrm{d}U/\mathrm{d}\vartheta$ (heat capacity of ideal gas) is positive which is also a stability condition, cf. Rem. 7 in Chap. 2, (3.256).

$$U_f - U_i = q - \int_{V_i}^{V_f} P \, \mathrm{d}V \tag{1.12}$$

For a small change of internal energy $\mathrm{d}U$ by small quantities of heat $\mathrm{d}q$ and volume work $\mathrm{d}w = -P \, \mathrm{d}V$ we have the classical form

$$\mathrm{d}U = \mathrm{d}q - P \, \mathrm{d}V \tag{1.13}$$

Summary. The First Law was postulated as a simple general statement on performing work by a system exclusively upon the absorption of heat. Such a general statement was demonstrated to lead to the proof of equivalency between heat and work and to the proof of existence of the internal energy and its balance (with heat and work).

1.4 The Second Law of Thermodynamics

Using still the method of Šilhavý and Kratochvíl [13, 59, 60, 94–96, 98, 99] for the formulation of the Second Law we need more detailed information than for the First Law. It is necessary to know how much heat is exchanged at every empirical temperature. This is given by the heat distribution $\overrightarrow{Q}$ (cf. the discussion of this quantity in Sect. 1.2). Now we define the *heat absorbed* q^+ and the *heat emitted* q^- during the process as follows:

$$q^+ \equiv \sum_k Q_k \quad \text{if } Q_k > 0 \tag{1.14}$$

$$q^- \equiv -\sum_l Q_l \quad \text{if } \quad Q_l < 0 \tag{1.15}$$

where we sum through all empirical temperatures ϑ_j where the heat is absorbed $Q_k > 0$ or emitted $Q_l < 0$, respectively (cf. Rem. 7); if such Q_k or Q_l do not exist in the process, q^+ or q^- are zero (see 1.1). We note that both the heat absorbed and the heat emitted are nonnegative

$$q^+ \geq 0, \quad q^- \geq 0 \tag{1.16}$$

The net heat exchanged q (1.2) is then[16]

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[16] Using more general concepts from Rem. 10 we can analogously define heat absorbed q^+ and emitted q^- (both nonnegative) as (using also the concept of density of heat distribution $\eta(\vartheta)$ Eq. (a) in Rem. 10)

$$q^+ = \int \mathrm{d}Q^+ = \int \eta^+(\vartheta) \, \mathrm{d}\vartheta, \quad q^- = \int \mathrm{d}Q^- = \int \eta^-(\vartheta) \, \mathrm{d}\vartheta \tag{a}$$

where, integrating through all temperatures ϑ [cf. (1.22), (1.15)],

$$q = q^+ - q^-. \tag{1.17}$$

Now we are able to postulate the Second Law of thermodynamics as will be used in the following.[17]

The *Second Law of thermodynamics* is postulated as follows: In a *cyclic* process (from the set A of all real and ideal cyclic processes) a system can absorb heat ($q^+ > 0$) only if it also emits some heat ($q^- > 0$), i.e.,

$$q^+ > 0 \Rightarrow q^- > 0 \tag{1.18}$$

This is in fact the Carnot-Clausius formulation of the Second Law [94–96]; we stress here especially that the inverse implication of (1.18) is not valid (e.g., on–off cycle of electrical heating has $q^- > 0$ but $q^+ = 0$).

Formulation (1.18) is independent of the First Law and permits a comparison with the Second Law. Namely, the symmetry $\Leftrightarrow$ of the First Law and asymmetry $\Rightarrow$ of the Second Law may be stressed [59, 60, 98, 99], cf. Rem. 14.

Alternatively, however, accepting the First Law (i.e., nonexistence of perpetuum mobile of the first kind), the Second Law (1.18) may be reformulated as the nonexistence of perpetuum mobile of the second kind as follows:

In a cyclic process a system can perform the work w only if it absorbs heat q^+ and also emits some heat q^-

$$w < 0 \Rightarrow q^+ > 0 \quad \text{and} \quad q^- > 0 \tag{1.19}$$

This formulation excludes the perpetuum mobile of the second kind having in (1.19) $q^- = 0$.

Proof of (1.19) from (1.3), (1.18): if $w < 0$ then $q > 0$ by (1.3) and by (1.17) and (1.16) we obtain $q^+ > 0$. Then from (1.18) we obtain (1.19). Conversely from (1.3) and (1.19) relation (1.18) follows: if $w < 0$ then from (1.19) we obtain (1.18). For $w \geq 0$ we obtain from (1.4) [which is a consequence of (1.3)] $q \leq 0$, and by (1.17) $q^- \geq q^+$. Then (1.18) follows (if $q^+ > 0$ then $q^- > 0$). Q.E.D.

(Footnote 16 continued)

$$\begin{gathered}
\mathrm{d}Q^+ = \mathrm{d}Q, \quad \mathrm{d}Q^- = 0 \quad \text{for} \quad \mathrm{d}Q > 0 \\
(\text{or} \quad \eta^+(\vartheta) = \eta(\vartheta), \quad \eta^-(\vartheta) = 0 \quad \text{if} \quad \eta(\vartheta) > 0) \\
\mathrm{d}Q^- = -\mathrm{d}Q, \quad \mathrm{d}Q^+ = 0 \quad \text{for} \quad \mathrm{d}Q \leq 0 \\
(\text{or} \quad \eta^-(\vartheta) = -\eta(\vartheta), \quad \eta^+(\vartheta) = 0 \quad \text{if} \quad \eta(\vartheta) \leq 0)
\end{gathered} \tag{b}$$

Net heat (Eq. (a) from Rem. 10) may be expressed through (1.17) again. See also Rem. 21.

[17] We proceed according to [60, 98, 99] (cf. [90]) simplified [103] by using empirical temperature ϑ of the ideal gas thermometer and using as the set C (cf. property U2 in Sect. 1.2) the Carnot cycles from Appendix A.1 (these fulfill, e.g., the relation (4.6) of [90]).

For thorough discussion of all classical formulations of Second Laws see [94–96].

Going back we demonstrate that from the formulation of the Second Law (1.18) and properties of the system S1–S4 and the universe U1, U2, the following results may be obtained (for simplicity we use the "step" approximation by the finite number N of empirical temperatures ϑ_j but the known "integral" form (1.41) and (1.42) of results (1.20) and (1.21) may be understood, say by the simplified method of Rems. 16, 17, 21):

1. The existence of the *absolute temperature* T (applicable in all the universe) which may be identified with the empirical temperature of the ideal gas thermometer $\vartheta = T$ and is therefore positive (and increasing with physiological "hotness") and measurable in Kelvins.

For every system from the universe and every cyclic process (real and ideal, i.e., from the set A) the following *Clausius inequality* is valid

$$\sum_j Q_j/T_j \leq 0 \tag{1.20}$$

where the sum is taken over all possible (in our "step" approximation $j = 1, \ldots, N$) temperatures $T_j = \vartheta_j$ and Q_j are the components of the heat distribution $\vec{Q}$ (1.1) in the cyclic process considered.

2. Existence of *entropy* and the *entropy inequality*: for each system in the universe there exists a *state* function S, called *entropy*, such that for every process in the system the following *entropy inequality*, is valid

$$S_f - S_i \geq \sum_j Q_j/T_j \tag{1.21}$$

Here S_f and S_i are values of S corresponding to the final and initial state of the system in the process, respectively. The meaning of the sum in (1.21) is the same as in (1.20) (but the process is not cyclic) and in fact in both of them we sum only through the nonzero components of $\vec{Q}$ in the given process [cf. discussion of Eq. (1.1)]. Equalities in (1.20), (1.21) are valid for any reversible process (cyclic in the first case). Entropy S is the state function (its values are determined by the state σ) but it is not generally unique in the sense that more entropies satisfying (1.21) and differing by a function of the state may be constructed. But in special cases (important in applications) the entropy is unique within an additive constant (see (1.40) below).

Proof of these assertions will be outlined geometrically [the proof is possible also for the more general concept, see Rem. 21; note also that some limiting assumptions during this proof [e.g., special reference state in definition (1.31)] will be gradually removed]. The vector $\vec{Q}$ of heat distribution of any cyclic process in the universe (from the set A) may be situated in the N-dimensional Cartesian system, if we put components Q_j on each axis (accounting for each possible empirical temperature in our "step" approximation); see Fig. 1.2 for two dimensions: From the Second Law (1.18) we can see that any heat distribution $\vec{Q}$ of any process from A cannot be situated in the hyperquadrant given by positive values of $Q_j > 0$ [otherwise $q^+ > 0$ by (1.14) and $q^- = 0$ by (1.15) which contradicts (1.18)]. Let us consider two heat distributions $\vec{Q}_1$, $\vec{Q}_2$ from C (cyclic, reversible, and homogeneous processes starting in equilibrium state; by completeness U2 they exist as, e.g., Carnot cycles). Then (see closeness U1) for any real α_1, α_2 there is a cyclic process with $\alpha_1 \vec{Q}_1 + \alpha_2 \vec{Q}_2$ from C (because both processes with $\vec{Q}_1$, $\vec{Q}_2$ may have the same duration achievable due to the stability of equilibrium in S4) and also a process with $\alpha(\alpha_1 \vec{Q}_1 + \alpha_2 \vec{Q}_2)$ exists for any real α). Therefore all $\vec{Q} \in$ C form a subspace. But this subspace must have the dimension smaller than N because $\vec{Q}$ (from C $\subset$ A) cannot be present in the forbidden hyperquadrant mentioned above.

On the other hand, we are able to show that this subspace of all $\vec{Q} \in$ C has dimension $N - 1$: let us consider a cyclic process from the postulate U2, specifically the Carnot cycle from Appendix A.1, with two arbitrary empirical temperatures $\vartheta_b > \vartheta_a$, the heat distribution of which has only two nonzero components (of opposite sign) $Q_b = q^+ > 0$, $Q_a = -q^- < 0$ [cf. Appendix A.1 below, Formulae (A.5), (A.4), (A.7) respectively, see also below (A.9)].

Now we select and consider processes with indices $a = j$ and $b = j + 1$ where $j = 1, 2, \dots, N - 1$ is index of empirical temperatures in our "step" approximation. Then the heat distributions $\vec{Q}_j$ of such processes (with components $Q_a = Q_{jj}$, $Q_b = Q_{j,j+1}$) are

$$\vec{Q}_j = (0, \dots, Q_{jj}, Q_{j,j+1}, \dots, 0) \quad j = 1, 2, \dots, N - 1 \tag{1.22}$$

These $N - 1$ vectors (1.22) from C, both components of which being different from zero and of opposite sign (i.e., Carnot cycles between adjacent pairs of all possible temperatures according to our "step" approximations and completeness U2) are linearly independent. Therefore, the subspace of vectors $\vec{Q}$ from C has dimension $N - 1$ and forms a hyperplane coming through the origin in the N-dimensional Cartesian system, see Fig. 1.2 (according to our construction this $(N-1)$-dimensional hyperplane contains all possible Carnot cycles; but in fact it contains any reversible cyclic process, see below). Moreover, this hyperplane contains vectors with at least two nonzero components (1.22) [Carnot cycles fulfill the Second Law (1.18)] and therefore does not meet any hyperplane formed by the axes of the Cartesian system.

Then there exists an N-dimensional vector $\vec{f}$ which is perpendicular to this hyperplane and is directed into the forbidden hyperquadrant, i.e., all its components f_j are positive only

$$f_j > 0 \quad j = 1, 2, \dots, N \tag{1.23}$$

fulfilling for any $\vec{Q} \in$ C

$$\vec{Q} \cdot \vec{f} = 0 \tag{1.24}$$

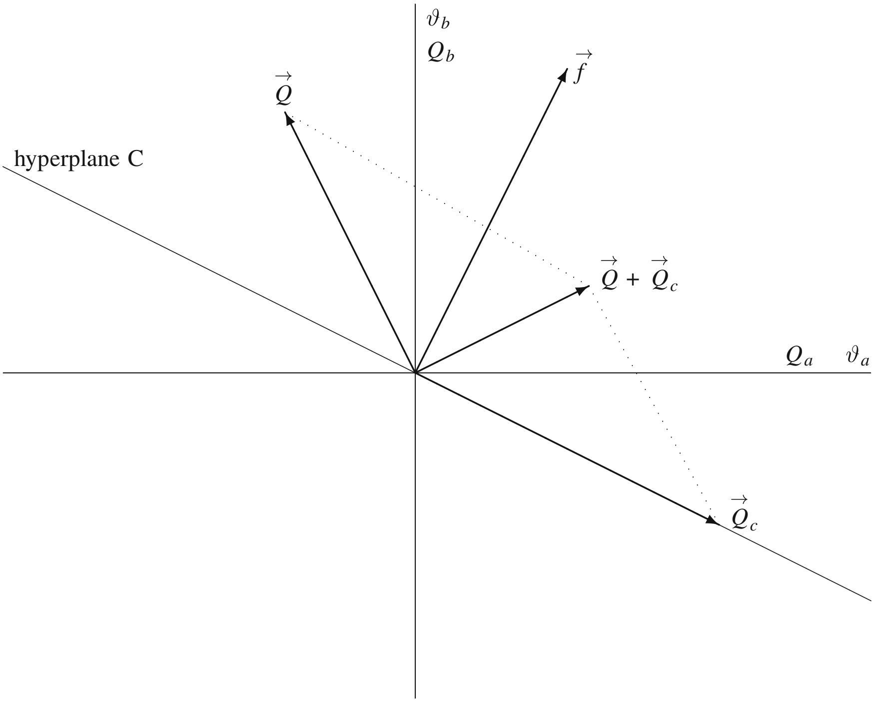

Fig. 1.2 Two dimensional example of the heat distribution vectors for cyclic processes

Now let us consider arbitrary vector $\vec{Q} \in \mathrm{B}$, i.e., the heat distribution of any cyclic process starting in equilibrium. We will now show that vector $\vec{Q} \in \mathrm{B}$ cannot form a sharp angle with vector $\vec{f}$, i.e., it must be

$$\vec{Q} \cdot \vec{f} \leq 0 \tag{1.25}$$

Indeed, because $\vec{Q} \in \mathrm{B} \subset \mathrm{A}$ it cannot be in the forbidden hyperquadrant or situated between the hyperplane C and the forbidden hyperquadrant. In the latter case specifically, we are able to find such vector $\vec{Q}_c \in \mathrm{C}$ (e.g., such Carnot cycle) which together with $\vec{Q}$ gives a compound process with $\vec{Q} + \vec{Q}_c$ (by U1 from Sect. 1.2; because both processes start in equilibrium, the same duration may be achieved) which is again in the forbidden hyperquadrant (cf. Fig. 1.2 for two dimensions). Therefore for arbitrary $\vec{Q} \in \mathrm{B}$ the relation (1.25) must be valid.

Now, we can define the values (permitted by our step approximation) of *absolute temperature* T_j by

$$T_j \equiv 1/f_j \quad j = 1, 2, \ldots, N \tag{1.26}$$

and therefore T_j are positive numbers [cf. (1.23)] unique for the whole universe within multiplicative positive constant (because the length of vector $\vec{f}$ is arbitrary). Each T_j corresponds to empirical temperature ϑ_j of the ideal gas thermometer (Appendix A.1) and therefore absolute temperature T is its function

$$T_j = T(\vartheta_j) \tag{1.27}$$

universal within a positive multiplicative constant. To know more about this function we use completeness U2 of the universe from Sect. 1.2, specifically in the form that between every two (empirical) temperatures (of the ideal gas thermometer), say $\vartheta_b > \vartheta_a$, some Carnot cycle exists, specifically those above (1.22) with $Q_b = q^+ > 0$, $Q_a = -q^- < 0$. Then

$$\vartheta_b/\vartheta_a = q^+/q^- = (Q_b/-Q_a) = T_b/T_a \tag{1.28}$$

The first equalities are the equalities (A.9) proved in Appendix A.1 and the last one follows from (1.24), (1.26)

$$(Q_a/T_a) + (Q_b/T_b) = 0 \tag{1.29}$$

because Carnot cycle is reversible from subset C (and its heat distribution have only two nonzero members, cf. Appendix A.1).

From results (1.28) we can see that absolute temperature [introduced, after all, within a positive constant, cf. (1.27)] is proportional to the empirical temperature of the ideal gas thermometer $T = c\vartheta$. Arbitrary universal constant c may be chosen; usually $c = 1$ and we can identify the absolute temperature with empirical temperature of ideal gas thermometer

$$T = \vartheta \tag{1.30}$$

Absolute temperature is therefore positive and measured in Kelvins.

Recapitulating hitherto existing results we can see that by (1.26) and (1.1), relation (1.25) is in fact the Clausius inequality (1.20) for arbitrary cyclic process from B (i.e., starting from equilibrium state) and, by (1.24), equality in (1.20) is valid for any Carnot cycle.

Now we are able to construct the *entropy* S of arbitrary (even instable or non-equilibrium) state σ of a given system in the following way. We choose an (stable) equilibrium state σ_0 (from S4, Sect. 1.2) as a reference state [it may be chosen even arbitrarily as we show below (1.40)]. As entropy S in the state σ we take the supremum[18] of the set of the sums $\sum_p Q_j/T_j$ corresponding to all processes p from σ_0 to σ

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[18] Supremum (least upper bound) of a given set A of real numbers (containing even infinite elements) is the least from all numbers which are greater than, or equal to the numbers of the set.

From this definition the following Lemma follows:

If for reals X we have $X \geq Y$ for all $Y \in A$, then $X \geq \sup A$.

$$S \equiv \sup \sum_{p} Q_j/T_j \tag{1.31}$$

(we write $\sum_j Q_j/T_j = \sum_p Q_j/T_j$; in fact only nonzero components of $\overrightarrow{Q}$ play role in the sum in the given process p).

From the definition (1.31) we can see that S is independent of the process p among the same states σ_0 and σ and therefore entropy S is a *state function* depending only on the state σ (and on chosen reference state σ_0).[19]

Now we consider an arbitrary process p passing arbitrary states between two such states—initial σ_i and final σ_f. Choosing the (stable equilibrium) reference state σ_0 and a process p_i from σ_0 to σ_i, we can regard the process p_i followed by process p as a combined process connecting σ_0 and σ_f. Therefore it follows from the definition (1.31) for S_f (entropy in the state σ_f with σ_0 as a reference state) and postulate S2 that

$$S_f \geq \sum_{p_i} Q_j/T_j + \sum_{p} Q_j/T_j \tag{1.32}$$

This inequality is valid for any process p_i (from σ_0 to σ_i) and therefore by Lemma in Rem. 18

$$S_f - \sum_{p} Q_j/T_j \geq S_i \equiv \sup \sum_{p_i} Q_j/T_j \tag{1.33}$$

Thus, we obtain entropy inequality (1.21) for entropies defined relative to the same (stable equilibrium) reference state σ_0.

Equality in (1.21) is valid in any reversible process (cf. its definition in Sect. 1.2) coming from σ_i to σ_f and vice versa for forward and reverse process through the same states respectively. Indeed, if (1.21) is valid for the forward process p with $\overrightarrow{Q}$ from σ_i to σ_f, then for the reverse process p' with $-\overrightarrow{Q}$ from σ_f to σ_i we have by (1.21)

$$S_i - S_f \geq \sum_{p'} -Q_j/T_j = -\sum_{p} Q_j/T_j \tag{1.34}$$

where the last equality follows from the reversibility (passed states are the same at p' and p with the heats of reverse sign). Comparing this inequality with (1.21) for the forward process p we have for the reversible process between σ_i and σ_f

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[19] Because the number of processes p may be infinite, the definition (1.31) has sense if $S < \infty$. But this is fulfilled: indeed, connecting the σ with σ_0 by some fixed process $\bar{p}$ we form the cyclic process (starting in equilibrium) where by (1.20) $\sum_p Q_j/T_j + \sum_{\bar{p}} Q_j/T_j \leq 0$ (process is from B), i.e.,

$$\sum_{p} Q_j/T_j \leq -\sum_{\bar{p}} Q_j/T_j < \infty$$

The expression in the middle is a finite number ($T_j > 0$, Q_j and sum are finite in chosen $\bar{p}$, see S1 from Sect. 1.2) (even for non "step" approximation, cf. end of Rem. 21). First inequality is valid for every process p and therefore, by Lemma in Rem. 18, S is finite.

$$S_f - S_i = \sum_p Q_j/T_j \tag{1.35}$$

Thus, the entropy inequality (1.21) was proved for any process p from state σ_i to σ_f with entropies S_i and S_f respectively, defined relative to the same (equilibrium stable) reference state σ_0 (states σ_i, σ_f and processes p between them may be arbitrary).

Now, if we choose (arbitrary) $\sigma_i = \sigma_f$ in (1.33) [our (1.21)], then p is some cyclic process from A and we have $S_i = S_f$ (supremum (1.31) is unique); inequality (1.20) thus follows. Analogously taking $\sigma_i = \sigma_f$ in (1.35) we can see that for any reversible cyclic process (the forward process and the reverse come through the same states) equality in (1.20) is valid. Therefore the Clausius inequality (1.20) is thus proved to be valid for any cyclic process A [and not only for B as (1.25)] and equality in (1.20) is valid in any reversible cyclic process [and not only for C or Carnot cycles as (1.24)]. Then $\vec{Q}$ for arbitrary cyclic process must be situated in N-dimensional Cartesian system below or on the hyperplane of Fig. 1.2 (containing all reversible cyclic processes).

We now demonstrate nonuniqueness of the entropy S (1.31) of the state σ which was defined relative to the reference (stable equilibrium) state σ_0. Choosing another (stable equilibrium) state, say σ_0', as the reference state, then the same state σ will have the (new) entropy S' by (1.31). Denoting by p_0 a process from σ_0 to σ_0' and by p' a process from σ_0' to σ, we have by definition (1.31) and by combination of the processes (S2 in Sect. 1.2)

$$S \geq \sum_{p_0} Q_j/T_j + \sum_{p'} Q_j/T_j \tag{1.36}$$

This is valid also for supremas of these quantities through all possible p_0 and p', cf. Lemma in Rem. 18. The supremum taken for the process p' is entropy S' and supremum for p_0 is entropy S_0 (the entropy of the new reference state σ_0' relative to the original reference state σ_0'). Therefore

$$S - S' \geq S_0 \geq \sum_{p_0} Q_j/T_j \tag{1.37}$$

We can see that the difference between entropies of the same state σ taken relative to different referential (equilibrium) states [the left hand side of (1.37)] is generally not smaller than the constant quantity on the right hand side, i.e., S' is distinguished from S by some state function of σ [note the different behaviour of energy U, cf. (1.11)].

Only in special cases is the difference between S and S' a constant, e.g., when among the processes p_0 from σ_0 to σ_0' a reversible process p_{01} (with Q_i) exists: then starting from σ_0' to σ_0 by reverse (to p_{01} process (with $-Q_i$) and continuing from σ_0 to σ by some process p we have for S' from (1.31)

$$S' \geq \sum_{p_{01}} -Q_i/T_i + \sum_{p} Q_j/T_j \tag{1.38}$$

Because (1.38) is valid also for supremum from processes p (see Lemma in Rem. 18) we have

$$S - S' \leq \sum_{p_{01}} Q_i/T_i \leq S_0 \tag{1.39}$$

where the last inequality follows from the definition of S_0. Comparing (1.37) and (1.39) we obtain

$$S - S' = S_0 \tag{1.40}$$

which proves our assertion (S_0 is the (constant) entropy of σ_0'; all entropies in (1.40) are relative to (stable equilibrium) reference state σ_0).

As has been shown above the Clausius inequality (1.20) is valid for any cyclic process (i.e., from A) and it remains to show that also the entropy inequality (1.21) [where, of course, the states of considered process p are arbitrary, cf. (1.33)] is valid for quite arbitrary reference state σ_0 in the definition of entropy (1.31). Indeed, using the general validity of (1.20), it is sufficient to repeat the arguments giving (1.33) (including inequality in Rem. 19 valid now for A). Moreover, we can repeat the arguments giving (1.35), (1.37), (1.40) and therefore equality in (1.21) is valid for any reversible processes with arbitrary entropies but now defined relative to general σ_0 [or in case (1.37), (1.40) also to another general σ_0'].[20] Thus the proof of our assertions 1, 2 [i.e., (1.20), (1.21) and below them] is accomplished. Q.E.D.

As we noted above all states σ (including those of reference σ_0) may be arbitrary, e.g. those which are instable or nonequilibrium [cf. above (1.31)]. Specification of such states depends on the chosen constitutive model and its formulation of equilibrium or reversible process (cf. Rems. 11, 12). In most constitutive models in this book, where the local equilibrium is typically valid, the states of such processes are equilibrium and even stable; entropies may be determined with precision of constant (1.40), see end of this Sects. 1.4, 2.1, 2.2, and 3.7.

We now remove our "step" approximation, i.e., the assumption that the empirical temperature could be measured by definite steps only with finite number N of "permitted" temperatures. This approximation was used only to obtain the results by simple mathematics. Namely, it may be expected that by allowing the steps of empirical temperature to approach zero (i.e., the number of temperatures N goes to infinity), in resulting formulae (1.20), (1.21) the sums change into integrals and components

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[20] The same form of entropy inequality (1.21) may be obtained also with another definition of entropy than (1.31). Such is, e.g. the entropy $\bar{S}$ defined by (with general σ_0) $\bar{S} \equiv -\sup \sum_{\bar{p}} Q_j/T_j$ [cf. (1.31)] giving again entropy inequality $\bar{S}_f - \bar{S}_i \geq \sum_p Q_j/T_j$. The difference between S and $\bar{S}$ in the same state σ (and with the same reference state σ_0) is generally a function of state σ (i.e., not constant), $S - \bar{S} \leq 0$. But the difference disappears, if reversible process from σ_0 to σ exists. See [60, 98, 99] for details.

of heat distributions at temperature T change to $\mathrm{d}Q$. So we obtain from (1.20) the Clausius inequality for any cyclic process

$$\int \frac{\mathrm{d}Q}{T} \leq 0 \tag{1.41}$$

and, from (1.21), the entropy inequality for an arbitrary process between arbitrary initial and final states with entropies S_i and S_f respectively.

$$S_f - S_i \geq \int \frac{\mathrm{d}Q}{T} \tag{1.42}$$

Here $\mathrm{d}Q$ is the heat exchanged in the process (may be their sum at different places and instants) where their absolute temperature has the same value T. We recall that T are identified with (positive) empirical temperature ϑ of the ideal gas thermometer (1.30).

Results (1.41), (1.42) are precisely proved by Šilhavý [59, 60, 96] with a more general empirical temperature (cf. Rems. 17) and without the "step" approximation.[21]

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[21] Following [98, 99] we sketch this procedure in simplified form used in Rems. 10, 16 (using existence of the density of heat distribution η). Similarly as in Rem. 10 we consider $N \to \infty$ in our "step" approximation; components of heat distribution are now $\mathrm{d}Q$ for each temperature ϑ of ideal gas thermometer. Proof in this Sect. 1.4 then needs the infinite dimensional space with such vectors of heat distribution. Using (nonnegative) heat absorbed q^+ and emitted q^- given now by Eq. (a) from Rem. 16, the Second law (1.18) forbids for (infinite dimensional vector of) heat distribution of cyclic processes (or its densities) the region with absorbed heat only ($q^+ > 0$, $q^- = 0$). Moreover, using closeness and completeness of universe U1, U2 with Carnot cycles, the heat distributions (or their densities) must fall into halfspace which does not meet the forbidden region (with corresponding boundary hyperplane of reversible cyclic processes). This may be similarly expressed through positive function $f(\vartheta) > 0$ of empirical temperature ϑ by

$$\int f \mathrm{d}Q = \int f(\vartheta)\eta(\vartheta)\mathrm{d}\vartheta \leq 0 \tag{a}$$

Defining absolute temperature as $T(\vartheta) = 1/f(\vartheta)$ we obtain Clausius inequality (1.41) for cyclic process

$$\int (\eta(\vartheta)/T(\vartheta))\mathrm{d}\vartheta = \int \frac{\mathrm{d}Q}{T} \leq 0 \tag{b}$$

Again absolute temperature may be identified with empirical temperature of ideal gas thermometer (1.30) admitting of course, that the Carnot cycle may be introduced for any two empirical temperatures ϑ.

Entropy S of state σ (relative to reference σ_0) may be now defined analogously [as (1.31)] as the supremum

$$S = \sup \int \frac{\mathrm{d}Q}{T} \tag{c}$$

of all processes p from σ_0 to σ. This is the state function fulfilling the entropy inequality (1.42) which may be proved quite analogously as before substituting finite sums $\sum_p Q_j/T_j$ by corresponding finite integrals $\int \mathrm{d}Q/T$ through the same corresponding process p. All other considerations are similarly valid in Sect. 1.4 above, e.g., sum in the center of inequality in Rem. 19 is substituted by corresponding finite integral.

In (1.41), (1.42) we integrate dQ [a component of infinite dimensional heat distribution (1.1)] through all temperatures of our process, but, because dQ are the sums of heat exchanged at all instants and places the temperature of which has a given value T, we may use in (1.41), (1.42) the integrals in time and space instead [in "step" approximation this is represented by summations according to postulates S2 and U1 respectively; cf. discussion of (1.1) and, e.g., (1.32)].

Such a form of entropy inequality (1.42) and likewise the energy balance (1.5) will be used (in fact by further simplifications) in Chap. 2 where uniform systems without space gradients are treated: The process is a time sequence of the states and we may expect the validity of (1.5), (1.42) for arbitrarily close time instants. Therefore we formulate these basic laws for the rate (time derivative) of the state functions (entropy, energy) with heatings (rate of heat exchange) and power, cf. (2.1), (2.2). Using these rate arguments in nonuniform systems (Chaps. 3, 4), an analogical assumption in the space leads to the densities of the quantities used in the formulation of these basic laws (see, e.g., Sect. 3.4).

Recapitulating, the results of this chapter look plausible, but there is a problem[22]: while the definition of energy (1.6) may be expected and useful, using the definition of entropy as a supremum (1.31) (or by (c) in Rem. 21) will be scarcely possible. Moreover, it is not clear how to find the reference (especially nonequilibrium) state and also the existence of more possible definitions (noted in Rem. 20) complicates the situation further.

Conversely the results that energy and entropy are the state functions permit us to formulate their constitutive equations in rational thermodynamics. These, together with balances (say of energy (1.5), (2.1), etc.) and entropy inequality (like (1.42), (2.2), etc.) with the constitutive principle of admissibility (see, e.g., Sect. 2.1), permit to calculate entropy within a constant in constitutive models describing equilibrium or near equilibrium situations; in this book we study models of this type almost exclusively. This follows from Gibbs equations (i.e., local equilibrium) proved in such constitutive models and seems to correspond to (1.40) and to the existence of a reversible process between states (which, although nonequilibrium states, permit to calculate entropy, cf., e.g. model B in Sect. 2.2). This is in accord with results of classical (equilibrium) thermodynamics [1, 12], and irreversible (nonequilibrium) thermodynamics [4, 5, 9] (its basic hypothesis—the principle of local equilibrium—may be therefore proved in rational thermodynamics).

In more general constitutive models the Gibbs equations (local equilibrium) are not valid and therefore explicit calculations of entropy are impossible. This seems to correspond to the nonuniqueness of entropy or to irreversibility of processes between nonequilibrium states [see below (1.37) and Rem. 20]. Such are some constitutive models in Sects. 2.1–2.3, but in particular models with long range memory [17, 23, 48]. Even the usefulness of entropy in situations far from equilibrium [11, 101, 114–120] seems questionable, the entropy inequality deduced and used in

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[22] Such problems, giving more or less only partial interpretation of entropy defined in this chapter in terms of entropies introduced in the remaining chapters, are similar, apparently not incidentally, to the interpretation of statistically defined entropy, cf., e.g., [12, Sect. 11.14].

rational thermodynamics [13, 17, 19, 59, 60, 94–96] gives interesting information about possible material behavior (moreover, in physics are also known further useful nonunique quantities, e.g., Lagrange function or electromagnetic potentials).

Summary. The Second Law was postulated as a simple general statement on heat exchange in cyclic processes. It was demonstrated that when this statement is combined with the properties of thermodynamic systems and universe introduced in Sect. 1.2 the existence of the absolute temperature and entropy follows, even out of equilibrium. The entropy should satisfy an inequality (1.21) which can be viewed as an alternative form of the Second Law and is called the entropy inequality. However, entropy need not be unique especially in complex (nonequilibrium) systems or processes and even the transferability of the proof of its existence at such conditions remains unclear. Even in such cases the supposed existence of entropy can give important information on possible behavior which can be subjected to experimental testing.

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