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Preface

During the last 50 years our understanding of thermodynamics has achieved considerable progress, particularly in relation to irreversible or non-equilibrium phenomena. The principal approaches were reviewed in the book by [1] and are briefly summarized at the beginning of Chap. 1. An important role has been played by phenomenological thermodynamics (or nonlinear thermomechanics) called *rational thermodynamics*, as developed by Truesdell and others. It has been shown that similarly as in other classical disciplines (e.g. mechanics or electromagnetism), the thermodynamics may be described through general postulates valid in all disciplines (e.g. First Law of thermodynamics (balance of energy), balance of mass, etc., or Second law of thermodynamics). Then special models of materials can be studied which are formulated by *constitutive equations* (e.g. uniform classical thermodynamics, mixtures with transport phenomena). As a result it has been not necessary to be confined to equilibrium phenomena only, and it has been possible also to describe the non-equilibrium phenomena, at least in principle.

This book aims at providing consistent and integrated thermodynamic description of chemically reacting systems which are often encountered in practice based on methodology developed within the framework of continuum, rational thermodynamics. Because of the extent and understanding of such a broad goal we limit the discussion to one phase, mostly fluid (gas or liquid) systems, pure substance or (even chemically reacting) fluid mixtures, which seem to cover the most important cases of applications. Although such modern thermodynamics is a mathematical theory established mainly by mathematicians, this book is focused on non-mathematicians—physicists, chemists and engineers. They are usually and typically studying systems where thermodynamic and transport phenomena and chemical reactions are running together (e.g. processes in industrial chemical reactors) using properties of these phenomena obtained from their separate and independent research. In other words, their approach is driven by (mostly tacit) assumption, that these separate knowledges are often also valid in such complex systems. For example, the oldest theory of non-equilibrium thermodynamics is based on a hypothesis called the "local equilibrium", i.e. the validity of classical thermodynamic relations in systems with (space) gradients is assumed even though they were obtained in a uniform equilibrium system without such gradients.

In this book we discuss models of traditional and industrially important situations in chemically reacting mixtures, which confirm (in accordance with experience), the validity of such a hypothesis, together with its limits. All the methodology has clearly and explicitly given all starting axioms, all applied assumptions and simplifications; therefore the range of its validity as well as of derived models can be easily estimated and tested. Specifically, we show that rational thermodynamics applied to a model of “chemically reacting mixture of fluids with linear transport properties” (the linear fluids in brief) fulfils these “separated” properties, even in complex systems, where all these processes take place together—thermodynamic relations are the same as in classical equilibrium thermodynamics (i.e. the “local equilibrium” is *proved* to be valid)—classical linear transport laws are valid (e.g. Fick or Fourier laws)—classical chemical kinetics is valid (typically, the reaction rate depends (nonlinearly) on concentrations and temperature only), i.e. the mass action kinetics is proved as well.

Thus, from the point of view of modern phenomenological thermodynamics, the current outputs of classical equilibrium thermodynamics (e.g. the description of thermochemistry of mixtures) and the tasks of irreversible thermodynamics, like the description of linear transport phenomena and nonlinear chemical kinetics, are valid much more generally, e.g. even when all these processes run simultaneously. As we noted above, these properties are not expected to be valid in any material models: in some models the local equilibrium may not be valid, reaction rates may depend not only on concentrations and temperature, etc.

We believe that the physical content and inner structure of this theory is not less interesting than its mathematical formalism and therefore in this book we stress the physical meaning omitting mathematical technicalities wherever possible and try to be consistent and self-contained. Nevertheless, familiarity with calculus, vectors and tensors at introductory level, at least, is supposed; as suitable and concise study references the books by [2] or [3] can be recommended.

The book is divided into four chapters containing 27 sections in total. The text starts with general concepts and develops and simplifies them progressively to the model of mixture of linear fluids for which explicit formulations can be derived and which is the model closest to common experience in chemistry and related fields. Chapter 1 states the general framework—besides others, it introduces general variables, explains the conception of primitive variables and states the two basic thermodynamic laws in a very general form as the relationships between heat and work. In this chapter, we demonstrate that general formulation enables a construction (or the proof of existence) of quantities which are specific and basic for thermodynamics—internal energy, entropy (even non-equilibrium) and absolute temperature. Although in this generality the laws, variables or quantities are not directly used in the subsequent development Chap. 1 justifies their existence and applicability also in non-equilibrium states.

Chapters 2 through 4 develop modern continuum (rational) thermodynamics in its standard and most elaborated form. The most simple example or model—uniform systems (without space gradients of properties)—is discussed in Chap. 2 which also serves as a basic and relatively simple introduction to the methodology (Sects. 2.1 and 2.2 in this chapter) which is not complicated by the description of spatial distribution. Four examples—models of uniform materials with increasing complexity are used to explain various aspects of the methodology and to stress the significance of *constitutive equations* and application of the Second Law in this approach. Section 2.3 gives basic information about the limitations of the validity of material models (constitutive equations). Section 2.4 shows how chemical reactions and their kinetics enter into the methodology and constitutive equations, whereas Sect. 2.5 illustrates the description of equilibrium between phases by our approach. Chapter 2 thus gives an explanation of principles of how the non-equilibrium is treated, without complicating it by spatial description, and demonstrates how equilibrium is naturally incorporated as a final state of non-equilibrium development.

Chapter 3 adds also the description of spatial distribution (gradients). Only single fluid is considered for the sake of simplicity and preparation of the basics for the subsequent treatment of mixtures. Mathematics necessary for the spatial description is introduced in Sect. 3.1. Section 3.2 in the same chapter stresses the importance of the referential frame (coordinate system) and its change in the mathematical description. Sections 3.3–3.6 shows the development of final material model (of a fluid) within our thermodynamic framework, consistent with general laws (balances) as well as with thermodynamic principles (the First and Second Laws and the principles of rational thermodynamics). The results of this development are simplified in Sect. 3.7 to the model of (single) fluid with linear transport properties. Sections 3.6 and 3.7 also show that the local equilibrium hypothesis is proved for fluid models. The linear fluid model is used in Sect. 3.8 to demonstrate how the stability of equilibrium is analysed in our approach.

The exposition culminates in Chap. 4 dealing with the mixture of fluids with linear transport properties and representing thus the most important part of this book. Section 4.1 explains the difference between the description of single-component and multi-component systems (mixtures). In Sects. 4.2–4.4 the basic principles and laws, presented in preceding chapters in the single-component version, are appropriately modified to mixtures and prepared to be used for the derivation of thermodynamically consistent models of a mixture. The properties of mixtures are described using *partial quantities* systematically. Special attention is paid to the accessibility of partial quantities from experiments—Sect. 4.4 also presents the special property related to this aspect, the *mixture invariance*. The derivation of consistent mixture model is exemplified in Sect. 4.5 in the mixture of chemically reacting fluids with linear transport properties. In Sect. 4.6 the whole classical chemical thermodynamics is derived on the basis of this model and the validity of its equations also in the linear fluid mixture out of equilibrium is demonstrated. Of course, the local equilibrium is completely proved in this mixture model, again. Section 4.7 analyses the equilibrium in the mixture of linear fluids in detail including its stability. In Sect. 4.8 the linear fluid model is modified to several yet simpler material models which reflect the systems analysed traditionally in classical chemical thermodynamics. Among others, this enables to analyse the applicability of traditional instruments of chemical thermodynamics like activity or fugacity under non-equilibrium conditions. The consequences of the presented thermodynamic method on the rates of chemical reactions, i.e. on chemical kinetics, are given in Sect. 4.9. Particularly, we show how the kinetic mass action law naturally emerges from thermodynamic considerations and how it can be generalised to non-ideal fluid mixtures. The last section, Sect. 4.10, elaborates on the transport properties (viscosity effects, diffusion, heat conduction and corresponding cross effects) and transforms the transport equations derived in Sect. 4.5 to more practical forms. Several traditional models or phenomena then follow as natural consequences of presented thermodynamic methodology—e.g. Fick or Fourier laws, Sorret and Dufour effects, as well as various phenomenological coefficients which are in classical irreversible thermodynamics introduced *a priori*.

Almost every section closes with a brief summary giving an outline of the most important information or equations and of what should be learned in the section. The summaries should serve as the study aids and can be read also before studying the corresponding section. Some additional thermodynamic and particularly mathematical instruments are collected in Appendices 1–5.

We want to express our gratitude to Prof. K. R. Rajagopal for the initiative to write this book and for stimulating discussions. Our thanks go to Drs. Miroslav Šilhavý, Willy Pabst and Pavel Hrma. We thank also the representatives of the publisher for the patience and care devoted to this manuscript. The authors will be grateful for any criticism concerning this book.

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Contents

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* $\overrightarrow{Q}$ 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 $\overrightarrow{Q}$ in the given process and given system may be represented by an N-dimensional vector

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

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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 $\overrightarrow{Q}$ (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 $w, \vec{Q}$ is called *reversible* if a *reverse* process with $-w, -\vec{Q}$ 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 $w, \vec{Q}$.[12]

Process with $w, \vec{Q}$ is called *homogeneous* if a process with $\alpha w, \alpha\vec{Q}$ 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 $\alpha w, \alpha\vec{Q}$ because of extensivity of these quantities).

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

Ultimately, we introduce the *set* C of $w, \vec{Q}$ of all cyclic processes starting in equilibrium with the following property: with each such process characterized by $w, \vec{Q}$, the set C contains the cyclic process starting in equilibrium, work, and heat distribution of which is $\alpha w, \alpha\vec{Q}$ respectively, where α is an arbitrary *real* number. Therefore C is the set of $w, \vec{Q}$ 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.

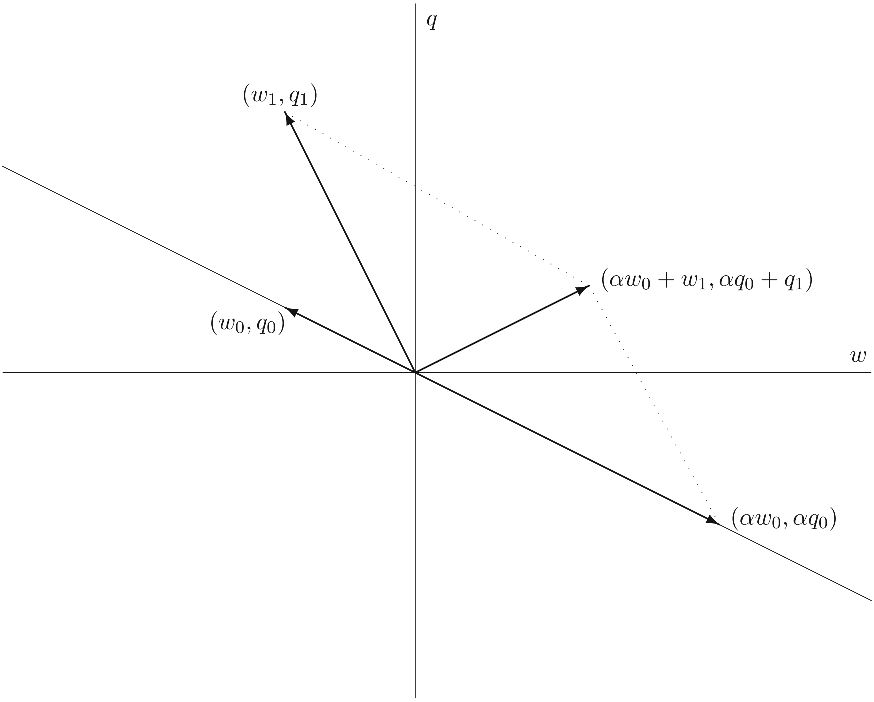

Fig. 1.1 Plane representing work and heat in cyclic processes. The First Law prohibits points (ω, q) to fall in the first or third quadrants

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 $\vec{Q}$ (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 $j = 1, 2, \ldots, N - 1$ 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

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

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

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

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

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

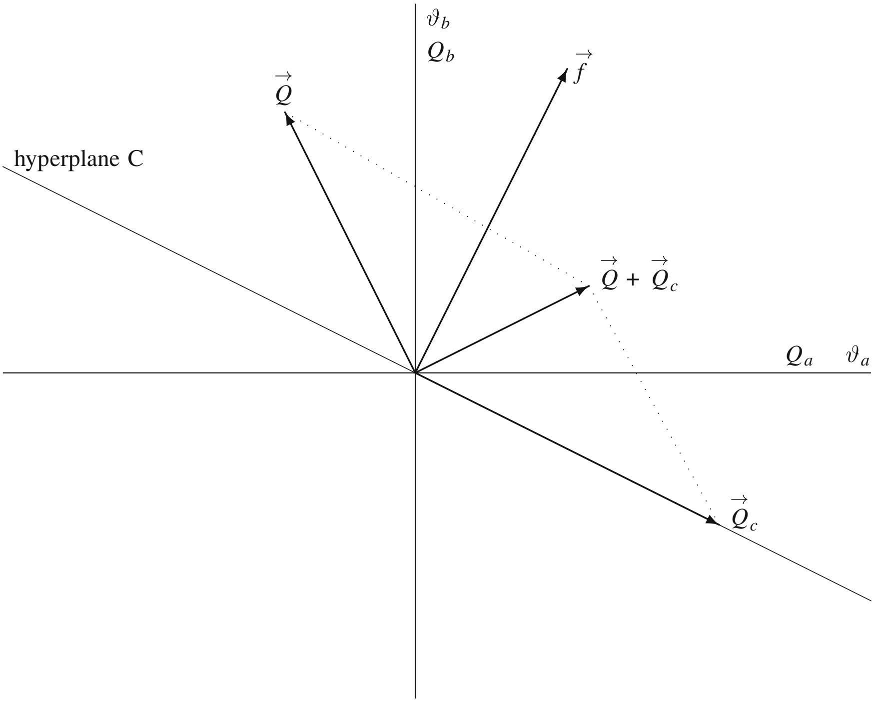

Fig. 1.2 Two dimensional example of the heat distribution vectors for cyclic processes

Now let us consider arbitrary vector $\vec{Q} \in$ B, i.e., the heat distribution of any cyclic process starting in equilibrium. We will now show that vector $\vec{Q} \in$ 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 $\vec{Q}_c \in$ 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 $\vec{Q} \in$ 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 $\vec{Q}$ 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 $\vec{Q}$ from σ_i to σ_f, then for the reverse process p' with $-\vec{Q}$ 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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Chapter 2
Thermodynamics of Uniform Systems

In this chapter we discuss *uniform* systems, the properties of which change only in time. Similarly as in [1–8] our main aim here is to demonstrate the method of rational thermodynamics and application of its principles in simple material models. In other words, the main aim is pedagogical—to begin with simple issues, demonstrations, and examples. Nevertheless, even this chapter contains practical results which can be applied on many simple real systems. Among others the principal results of classical equilibrium thermodynamics will be obtained and this will be shown also for reacting mixtures and heterogeneous (multiphase) uniform systems.

2.1 Energy Balance, Entropy Inequality and Constitutive Principles, and Equations in Uniform Systems

A uniform thermodynamic system—(uniform) *body*—may be visualized as a block of single (i.e., pure or one-constituent) material, the mass of which is fixed (closed system) with properties depending only on time (and not on space). Therefore, the state and state functions change only in time. Results (1.5) and (1.42) (where it is possible to use time integration) may be expressed in the rate form as it was explained at the end of Sect. 1.4. Consequently, such forms of energy balance and entropy inequality in uniform systems are [1, 3, 4]

$$\dot{U} = Q - P\dot{V} \tag{2.1}$$

$$\dot{S} \geq Q/T \tag{2.2}$$

Here the dot denotes the time derivative of state functions: the internal energy U, the entropy S, and the volume V of the body. Q is the *heating*, i.e., the heat exchanged in the time unit (we use J = 1; see (3.3)) in the considered instant when the absolute temperature is T. For the sake of simplicity we limit the material of the body to fluid (i.e., gas or liquid) only and neglect the motion (kinetic energy, inertial forces) and

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external volume forces (like gravitation). Therefore, we restrict the power only to "volume" working (see Rems. 9, 13 in Chap. 1) caused by the *pressure P*—force on the surface unit from its surroundings.[1]

Our thermodynamic system—the *uniform fluid body*—is therefore characterized by following 6 functions of time t (which may be looked upon as primitives in this chapter)

$$Q(t) \tag{2.3}$$

$$U(t), S(t), P(t) \tag{2.4}$$

$$V(t), T(t) \tag{2.5}$$

giving the values of these quantities in any instant of the process.

The ultimate aim of the application of thermodynamics is the finding of some of these functions (e.g., $P(t)$ at prescribed (2.3), (2.5)). But the balance (2.1) (and of course (2.2)) is not sufficient for a great class of all uniform fluids (we do not need the other balances here, e.g., for momentum and its moment and for mass, because of neglecting the inertial and volume forces and conserving the mass, see Chap. 3). We must introduce additional relations among quantities (2.3)–(2.5) which characterize the differences among different materials (of the given class of uniform fluids in this case)—*constitutive equations* [1, 3]. As we noted in previous Chap. 1, such equations are mathematical models of real materials ("ideal material", "material model") which stress those of its features which are important in assumed applications; the same real material may have different constitutive equations depending on the circumstances where the assumed model will be used (this depends on the relations between the natural and observer's time and space scales, cf. Sects. 1.1, 1.2, 2.3).

Rational thermodynamics proposes the construction of such equations by the use of *constitutive principles* [1, 3] which generalize long experience accumulated during the past with proposals of special constitutive equations (cf. Sect. 1.1). Some of these constitutive principles more resemble rules or recommendations (e.g., principles of determinism or equipresence below) serving rather as a guidance. On the other hand, some constitutive principles (of admissibility below and objectivity in Sect. 3.5) seem to be sufficiently general and therefore in turn all constitutive equations should be in accord with them.[2]

Going back to proposing constitutive equations in our simple systems we call the functions (2.3)–(2.5) fulfilling the balance (2.1) a *thermodynamic process*.

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[1] By neglecting the above noted, the momentum balance reduces per the action-reaction law. Closely around (part of) the surface this provides that the external pressure P is equal to those from the interior and therefore depends on the material inside (i.e., it is given by constitutive equations like (2.6), (2.7) below), cf. Rems. 9 in Chap. 1, 36 in Chap. 3, and e.g., [9, p.108].

[2] Other types of such principles were also proposed: "phenomenological relations" between "flows" and "forces" in classical irreversible thermodynamics [10–19], the use of pressure (flow of momentum) as independent variables in equilibrium thermodynamics and more generally the use of flows as independent variables in extended irreversible thermodynamics [20–23]. Cf. also "internal variables" in Sect. 2.3.

We regard the balance (2.1) as fulfilled in any process because the heating Q may be in principle adjusted from the surroundings of the studied body (and therefore we do not propose constitutive equation for Q).

We call the values of (2.4) *responses* and functions (2.5) a *thermokinetic process*; constitutive equations must be therefore relations among them (even if the pressure P comes from the surroundings (similarly as Q), it is included into responses because here it depends on material inside the body, as explained in Rem. 1).

According to the constitutive principle of *determinism* the response (in the actual instant) is given by deformation and temperature in the present and the past of the body (cf. also Sects. 3.5, 4.5, and Rem. 26 in Chap. 3). This means that constitutive equations give the responses (2.4) in the actual instant as functional-independent variables of which there are *histories*—thermokinetic processes (2.5) in the past and present (in fluids, by definition, the deformations which influence the response are expressible only through volume in mass conserving system; cf. Rems. 3, 4 in this chapter, 30 in Chap. 3).

Constitutive principles of *memory* give more detailed description of the influence of the past on the response. Section 2.3 describes the role of time scales (cf. Sect. 1.1) for this description and the expression of the influence of the past (or history) through *internal variables*. The influence of the past frequently expected from the experience is contained in the constitutive principle of *fading memory*: the more the past is remote, the less influence it has on the response. Mathematical formulation of this principle need not be unique [24–29] (for introduction see [2, 4, 6, 30]). In limit of equilibrium there is some time interval (natural time scale or relaxation time, cf. Rem. 11 in Chap. 1 Sects. 2.4, 3.8, 4.7) after which the (practical) influence of the past is negligible.

Here we confine ourselves to the short range memory expressed by the constitutive principle of *differential memory*: constitutive equations are functions of values and time derivatives of the thermokinetic process (2.5) taken in the present instant. Such constitutive equations may be expected in the material with fading memory where the history (2.5) is developed in the Taylor series about the present instant with restriction to the slow processes (2.5) when higher time derivatives are negligible, cf. [31].[3]

Further the constitutive principle of *equipresence* demands that independent variables have to be the same in all constitutive equations for responses (2.4). This principle prevents the nonjustified preference of some constitutive equations against

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[3] Let the response f be given by the function $g(.)$ through the following example of functional with fading memory $\mathcal{F}$

$$f = \mathcal{F}(g(.)) \equiv \int_0^\infty g(s)(\exp(-3s))\mathrm{d}s \qquad (a)$$

by which the number f is adjoined to functions $g(.)$, e.g., as in the following table

function $g(s)$	1	s	s^2	....
response f	1/3	1/9	2/27	....

Understanding s as an interval passed from present time t into the past (i.e., $s \equiv t - \tau$, where τ is time elapsed $\tau \in (-\infty, t]$). Therefore, $g(s)$ is the "history" of quantity g; the exponential in the others in general formulation of the material model (in special cases it need not be used, of course).

Guided by these three constitutive principles, we propose the following four material models of a uniform fluid body generally nonlinear in independent variables [1–4, 8]:

A. Fluid without memory

$$U = \hat{U}(V, T), \qquad S = \hat{S}(V, T), \qquad P = \hat{P}(V, T) \tag{2.6}$$

B. Fluid with memory to the volume

$$U = \hat{U}(V, \dot{V}, T), \qquad S = \hat{S}(V, \dot{V}, T), \qquad P = \hat{P}(V, \dot{V}, T) \tag{2.7}$$

C. Fluid with a higher order memory in volume

$$U = \hat{U}(V, \dot{V}, \ddot{V}, T), \qquad S = \hat{S}(V, \dot{V}, \ddot{V}, T), \qquad P = \hat{P}(V, \dot{V}, \ddot{V}, T) \tag{2.8}$$

D. Fluid with memory in volume and temperature

$$U = \hat{U}(V, \dot{V}, T, \dot{T}), \qquad S = \hat{S}(V, \dot{V}, T, \dot{T}), \qquad P = \hat{P}(V, \dot{V}, T, \dot{T}) \tag{2.9}$$

Here V, T are only positive and $\dot{V}, \ddot{V}, \dot{T}$ are arbitrary real numbers.

At this point we recall again the difference between the constitutive model and reality (cf. Rem. 3 in Chap. 1 and Sect. 2.3): here we study mathematical models and therefore (unless said otherwise) we assume that T, V are positive in these models and that $\dot{T}, \dot{V}, \ddot{V}$ are any real numbers (e.g., in study of model we apply Lemma A. 5.1 from Appendix A. 5 based on such assumptions). However, in practical choice of a model (say from A, B, C, D above, motivated, e.g., by the relation between the observer's and the natural scales, see Sect. 2.3) we consider only part of these possible values (i.e., these are considered in the application of a model and not in the model

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(Footnote 3 continued)
the functional (a) assures fading of memory in the past: the influence of great s (remote past) is suppressed. Developing $g(s)$ into a series around the present instant $s = 0$ we have

$$g(s) = g(0) + \dot{g}(0)s + (1/2)\ddot{g}(0)s^2 + \cdots \qquad (b)$$

which by inserting into functional (a) gives

$$f = (1/3)g(0) + (1/9)\dot{g}(0) + (1/27)\ddot{g}(0) + \cdots \qquad (c)$$

Neglecting the remaining members (which neglect the influence of the past by the fading exponential in (a) we obtain response f as a function of value $g(0)$ and its time derivatives $\dot{g}(0)$, $\ddot{g}(0)$ in the present instant t (i.e., $s = 0$):

$$f = f(g(0), \dot{g}(0), \ddot{g}(0)) \qquad (d)$$

For the general procedure of such an approximation of fading memory to a differential one (eliminating exceptional fading exponential $\exp(-3s)$) see [31].

itself as studied in theory presented as a mathematical object). For example, if we try to apply these models to real fluids with very high $\dot{V}$ we wish to prefer model B rather than model A. Similarly, some models, especially C, D, are not very realistic, because uniformity (as well as neglecting motion) is difficult to keep and we must apply some more realistic nonuniform models of Chap. 3 (of which the uniform models A, B are special cases), cf. Sect. 3.8. This consideration has been valid "unless said otherwise" (see above), i.e., mathematical constitutive models may also be studied with some a priori added *regularity* conditions (like conditions of stability, cf. Rem. 6 in this chapter below). This procedure will be used in Sects. 2.2, 2.3, 3.8, 4.7.

To find the final forms of constitutive equations (2.6)–(2.9) we will ultimately use[4] the constitutive principle of *admissibility* (called also the dissipation or entropy principle [3, 8, 34, 35]). This principle was proposed by Coleman and Noll [36] and it opens a way to building up rational thermodynamics. To formulate this principle we define the *admissible* thermodynamic process as any thermodynamic process (2.3)–(2.5) fulfilling (2.1) which is consistent with (admissible by) the proposed constitutive equations (some model from (2.6)–(2.9); such a process is a sequence of states in the sense of Sect. 1.2).

The constitutive principle of *admissibility* demands that the entropy inequality (2.2) must be valid in all admissible thermodynamic processes. This principle then restricts the form of constitutive equations.[5]

This principle will be used similarly also in other models of this book, see Sects. 3.5, 4.5. In more complicated cases it is not easy to find an admissible process and for these cases the admissibility principle may be achieved by I-Shih Liu method of Lagrange multipliers [35, 41, 42]; this will be explained in Appendix 5.

Now, in our uniform systems, an arbitrary thermokinetic process (2.5) gives some admissible thermodynamic process. Indeed, if any smooth functions (2.5) are taken we can calculate necessary values at the present time and introducing them into constitutive equations (2.6)–(2.9) we calculate the response. Heating Q is then adjusted so that the balance of energy (2.1) is satisfied (therefore this balance gives no restriction on constitutive equations; for a slightly different point of view see [35, 42–46], cf. also Rem. 14 in Chap. 4). Therefore, an admissible thermodynamic process is obtained and thus the constitutive admissibility principle may be

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[4] In more complicated material models we modify or use further constitutive principles: determinism is enlarged for densities (mass concentrations) in mixtures (cf. Sects. 2.4, 3.5, 4.5), and the definition of fluid used in this principle is in fact the result of constitutive principle of symmetry (see Rem. 30 in Chap. 3). Another constitutive principle is the objectivity (frame indifference) principle. Here it is trivially satisfied because motion is neglected and all quantities are objective (see Sects. 3.2, 3.5). In nonuniform systems the influence of neighborhood is described in the principle of local action (cf. Sect. 3.5). In mixtures, the property of mixture invariance [32] may also be used as a constitutive principle [33].

[5] This differs from classical interpretation which looks at the entropy inequality (i.e., at the Second Law) as the restriction on the process leaving the form of constitutive equations unchanged.

This admissibility is criticized by Rajagopal and his school; using instead the assumption of maximum of entropy production rate, their further restrictions may be obtained, see, e.g., [37–39]. However, there are also reservations to the principle of maximum entropy production [40].

formulated in our systems in the following way: entropy inequality (2.2) must be valid in any thermokinetic process (2.5).

For the majority of applications it is sufficient to assume that the thermokinetic process as well as the constitutive equations (2.6)–(2.9) are differentiable (for a more general case see [2, 3]).

Before going further we introduce some definitions: *Production of entropy* Σ is defined by

$$\Sigma \equiv \dot{S} - Q/T \tag{2.10}$$

Therefore, entropy inequality (2.2) may be expressed by

$$\Sigma \geq 0 \quad \text{or} \quad T\Sigma \geq 0 \tag{2.11}$$

Entropy production multiplied by (absolute) temperature, here $T\Sigma$, is called *dissipation*.

Another important concept in constitutive models is *equilibrium* introduced for each constitutive model with typical observer's scales (cf. Sects. 1.1, 1.2, 2.3). We define the *equilibrium process* as that with zero production of entropy. Namely, in uniform systems of this Chap. 2 the equilibrium process is given by $\Sigma = 0$ in any state (instant) of its sequence.

The special equilibrium process is the *equilibrium state* when the system is permanently in the one state (cf. Rems. 11, 12 in Chap. 1). Its entropy does not change in time (permanence) and there is no heat exchange in it, i.e., $\dot{S} = 0$ and heating is zero $Q = 0$ separately in (2.10); therefore $\Sigma = 0$.

But there are also equilibrium processes where $\Sigma = 0$ is achieved by compensating the two nonzero members in the right-hand side of (2.10). They may be constructed as *reversible* (see Sect. 1.2 below property U1) by zero values of quantities causing nonequilibrium and achievable by adequate slowing of corresponding nonequilibrium processes (see Rem. 48 in Chap. 3), cf. examples of Sect. 2.2.[6]

Others examples are given in Sects. 2.4, 2.5 and the concept of equilibrium reversible process may be enlarged also to nonuniform systems in the next Chapters, see Sects. 3.6, 3.8, 4.7, Rem. 41 in Chap. 3.

Free energy F of the body is defined by

$$F \equiv U - TS \tag{2.12}$$

Therefore, F is a state function for which a constitutive equation may be constructed if we insert those for U and S in (2.12) (e.g., for model B (2.7) is $F = \hat{F}(V, \dot{V}, T)$). It is convenient to use the free energy F instead of U which may be calculated back from (2.12) if necessary. Finally we eliminate heating from (2.1), (2.2) and we use (2.11), (2.12) to obtain the *reduced inequality*

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[6] As we noted in Rem. 11 in Chap. 1 we must add the stability conditions of the equilibrium state (as the part of regularity conditions of the constitutive model), see Rems. 7, 9, 11 in this chapter.

$$-T\Sigma = \dot{F} + P\dot{V} + S\dot{T} \leq 0 \tag{2.13}$$

Therefore, the principle of admissibility may now be reformulated in the following way now: reduced inequality (2.13) must be valid for any thermokinetic process (2.5).

In the following Sect. 2.2 we demonstrate how this requirement restricts the constitutive equations (2.6)–(2.9).

Summary. In this Section, the principles used in rational thermodynamics to derive constitutive equations modeling the behavior of specific (material) bodies (systems) were described. Four simple general models of behavior of fluids were proposed, (2.6)–(2.9), taking into account most of these principles. The entropy inequality was formulated for uniform systems and modified introducing the free energy, (2.12), to the final—reduced—form (2.13). The basic exposition of rational methodology is thus prepared for the application of the very thermodynamic principle in the following Section.

2.2 Constitutive Equations of Uniform Fluids

In this Section, we obtain the ultimate form of constitutive equations for model A, B, C, D (2.6)–(2.9) using the constitutive principle of admissibility in the form mentioned at the end of preceding Sect. 2.1 [1, 2, 4–8].

A. *Fluid without memory* has constitutive equations (2.6) and therefore (see (2.12)) the constitutive equation for the free energy is

$$F = \hat{F}(V, T) \tag{2.14}$$

Introducing (2.14) into reduced inequality (2.13) we have

$$-T\Sigma = \big(\frac{\partial\hat{F}}{\partial V}(V,T) + \hat{P}(V,T)\big)\dot{V} + \big(\frac{\partial\hat{F}}{\partial T}(V,T) + \hat{S}(V,T)\big)\dot{T} \leq 0 \tag{2.15}$$

According to the admissibility principle (in the form quoted at the end of the preceding Sect. 2.1) this inequality (2.15) must be valid in any thermokinetic process and therefore also in such a one where $T > 0$, $V > 0$, $\dot{V}$ are arbitrary constants and $\dot{T}$ may be an arbitrary real number. Then coefficient standing next to $\dot{T}$ in (2.15) must be zero; otherwise it is possible to find such a real $\dot{T}$ that inequality (2.15) is not valid. Here (and often in the following) the Lemma A. 5.1 of Appendix A. 5 is used (with $X = \dot{T}$). Therefore,

$$\partial\hat{F}/\partial T = -S \tag{2.16}$$

and (because V, T was fixed arbitrarily) this is valid identically (i.e., for any V, T). Similarly, choosing V, T, $\dot{T}$ constants and $\dot{V}$ arbitrarily, we prove an identity (again by Lemma A. 5.1 for any choice of $V, T, \dot{T}$)

$$\partial\hat{F}/\partial V = -P \tag{2.17}$$

Relationships (2.16), (2.17) are not only necessary but (inserting (2.16), (2.17) into (2.15)) also sufficient for validity of (2.15).

Therefore, the free energy is a potential for entropy and pressure, i.e., Gibbs equations are valid

$$\dot{F} = -S\dot{T} - P\dot{V} \tag{2.18}$$

$$\dot{U} = T\dot{S} - P\dot{V} \tag{2.19}$$

where the last equation follows from (2.12). Comparing (2.18) with (2.13) (or (2.19) with (2.12)) it follows that in (2.13) (or (2.2)) only the equality is valid, i.e., $\Sigma = 0$ identically. Thus, all processes possible in this fluid without memory A are the *equilibrium processes* (see definition under (2.11)).

Model A is in fact the main material model studied in the classical equilibrium thermodynamics. Each state in this model A may be an *equilibrium state* from postulate S4 in Sect. 1.2 by fixing not only V, T, but also $\dot{V} = 0$, $\dot{T} = 0$; then not only power but, by (2.1), $(2.6)_1$, also heating should be zero $Q = 0$. Its persistence is assured (cf. Rems. 6 in this chapter, 11 in Chap. 1) by stability conditions.[7]

All processes in model A may be considered also as those with *reversible* equilibrium because for each process passing a sequence of states with state variables V, T and with (nonzero) $\dot{V}, \dot{T}$ and therefore with (generally nonzero) $\dot{U}$, $\dot{S}$, heating Q, or power $P\dot{V}$ and $\Sigma = 0$, obviously there exists a reverse process passing a sequence of the same states in reverse order with V, T and $-\dot{V}$, $-\dot{T}$, $\Sigma = 0$ in which by (2.1), (2.19) we have $-\dot{U}$, $-\dot{S}$, and opposite power $-P\dot{V}$ and heating $-Q$. In such processes, which are equilibrium and reversible, we have $\Sigma = 0$ where both (nonzero) members on r.h.s. of (2.10) compensate. An equilibrium reversible process may be regarded as a sequence of such stable equilibrium states. An apparent contradiction ($\dot{V}, \dot{T}$ in the equilibrium process are nonzero, while in the equilibrium state are zeros, cf. their definitions under (2.11)) consists in the choice of the observer's time scale in practical applications of model A: this time scale is chosen to be sufficiently great and therefore (all) processes in A are slow and the equilibrium of each passed state is attained (by its stability from Rem. 7) instantaneously in this large time scale (i.e., $\dot{V}, \dot{T}$ are nonzero in the observer's time scale, but because of its choice, they are in fact very small and nearly zero). Cf. also analogous discussion of model B below and [47], Rem. 17.9, Sect. 2.3.

If we should shorten the observer's time scale, we cannot use this model A and (in the same material) we must use a more complicated model, e.g., B (or even C, D, etc.) discussed in the following.

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[7] Which in uniform models A (2.6) are $\partial\hat{U}/\partial T > 0$, $\partial\hat{P}/\partial V < 0$. They follow from the fact that model A may be deduced as a special case of nonuniform model in equilibrium (cf. below (3.239) in Sect. 3.8) stability conditions of which are (3.256), (3.257) (cf., e.g., (3.199)). Cf. Rem. 9 in this chapter, see Sects. 2.3, 3.8 Rem. 48 in Chap. 3 for further details.

B. *Fluid with memory in volume* has constitutive equations (2.7) and therefore by (2.12) we have

$$F = \hat{F}(V, \dot{V}, T) \tag{2.20}$$

Introducing it in (2.13) we obtain

$$-T\Sigma = (\partial\hat{F}/\partial V) + P)\dot{V} + (\partial\hat{F}/\partial T) + S)\dot{T} + (\partial\hat{F}/\partial\dot{V})\ddot{V} \leq 0 \tag{2.21}$$

By the principle of admissibility (see end of Sect. 2.1) this inequality (2.21) must be valid at all $T > 0$, $V > 0$, and all real $\dot{V}$, $\ddot{V}$, $\dot{T}$. Choosing some T, V, $\dot{V}$, $\dot{T}$ fixed, and $\ddot{V}$ arbitrary (Lemma A. 5.1 is used for any choice of T, V, $\dot{V}$, $\dot{T}$), we obtain the identity

$$\partial\hat{F}/\partial\dot{V} \equiv 0 \tag{2.22}$$

which means that instead of (2.20) we have

$$F = \hat{F}(V, T) \tag{2.23}$$

Introducing (2.22) to (2.21), choosing T, V, $\dot{V}$ fixed and $\dot{T}$ arbitrary (Lemma A. 5.1 is used for any choice of T, V, $\dot{V}$), we obtain identically

$$\partial\hat{F}/\partial T = -S \tag{2.24}$$

and by (2.23) we have also

$$S = \hat{S}(V, T) \tag{2.25}$$

$$U = \hat{U}(V, T) \tag{2.26}$$

instead of (2.7) (Eq. (2.26) followed by (2.12)). Therefore, from inequality (2.21) it remains

$$\Sigma = -(1/T)\left(\frac{\partial\hat{F}}{\partial V}(V, T) + \hat{P}(V, \dot{V}, T)\right)\dot{V} \geq 0 \tag{2.27}$$

Because of nonlinearity (in $\dot{V}$) the preceding arguments based on Lemma A. 5.1 are not usable.

Achievement of the same results is also demonstrated by application of the I-Shih Liu method on model B in Appendix 5.

Further results follow the *equilibrium process* in model B defined as a thermodynamic process with

$$\dot{V} = 0 \tag{2.28}$$

motivated by $\Sigma = 0$ in (2.27) (with compensation of both even nonzero members on r.h.s. of (2.10), cf. below (2.11)), see Rem. 9 in this chapter below.

As a consequence, the production of entropy $\Sigma = \hat{\Sigma}(V, \dot{V}, T)$ is not only zero in equilibrium but it also has (for given V, T) minimum here. Therefore, for fixed T, V, $\dot{V}$ and real parameter λ we have

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{\Sigma}(V, \lambda\dot{V}, T)\ |_{\lambda=0} = 0 \tag{2.29}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\lambda^2}\hat{\Sigma}(V, \lambda\dot{V}, T)\ |_{\lambda=0} \geq 0 \tag{2.30}$$

Introducing (2.27) into (2.29) we obtain

$$\left(\frac{\partial\hat{F}}{\partial V}(V, T) + \hat{P}(V, 0, T)\right)\dot{V} = 0 \tag{2.31}$$

and because l.h.s. of (2.31) depends linearly on $\dot{V}$ (which may be arbitrary) we have for any choice of V, T

$$\partial\hat{F}/\partial V = -P^o \tag{2.32}$$

i.e., identically for any V, T. Here the *equilibrium pressure* P^o

$$P^o = \hat{P}^o(V, T) \equiv \hat{P}(V, 0, T) \tag{2.33}$$

was defined (we shall denote the equilibrium values by superscript ^{o}). As *nonequilibrium pressure* P_N we denote

$$P_N = \hat{P}_N(V, \dot{V}, T) \equiv \hat{P}(V, \dot{V}, T) - \hat{P}^o(V, T) \tag{2.34}$$

which is at equilibrium zero

$$P_N^o \equiv \hat{P}_N(V, 0, T) = 0 \tag{2.35}$$

For production of entropy we thus obtain

$$-T\Sigma = P_N\dot{V} \leq 0 \tag{2.36}$$

Again we can see that the validity of (2.22), (2.24), (2.32), (2.36) is not only necessary but also sufficient for fulfilling (2.21).

From the second condition (2.30) we obtain

$$\frac{\partial \hat{P}_N}{\partial \dot{V}}(V, 0, T) \leq 0 \tag{2.37}$$

by (2.27) and (2.34).[8]

Summing the results for model B—fluid with memory to volume—we can see that thermodynamic responses U, S, F depend only on T, V and free energy F is a potential for entropy S but only for equilibrium pressure P^o. Gibbs equations are

$$\dot{F} = -S\dot{T} - P^o\dot{V}, \qquad \dot{U} = T\dot{S} - P^o\dot{V} \tag{2.38}$$

which are valid in all processes.

At the end we note (cf. below (2.11) and model A) that an *equilibrium state* in this model B is achieved by fixing not only $V, T, \dot{V} = 0$ but also $\dot{T} = 0$; then not only power but, by (2.1), (2.26), also heating should be zero $Q = 0$. Its permanence is given by stability, see below and Rem. 9 in this chapter.

The *equilibrium process*, defined by (2.28) in model B, is reversible: for any forward equilibrium process passing the states with $V, T, \dot{V} = 0$, and $\dot{T}, \dot{U}, Q$, zero power $P\dot{V}$, there seems to exist a reverse process passing these states in the reverse order, the same states with $V, T, \dot{V} = 0$ and $-\dot{T}, -\dot{U}, -Q$ and zero power (see (2.27), (2.26), (2.1), Rems. 12 in Chap. 1 and examples in Rem. 48 in Chap. 3). Zero entropy production is achieved but generally heat exchange Q may be nonzero, giving entropy change: both (nonzero) members on r.h.s. of (2.10) compensate in this case. The equilibrium process in this model B is a sequence of equilibrium states S4 of Sect. 1.2. The observer's time scale for volume V is much shorter than in model A, while temperature T has the observer's time scale similar to that in model A, i.e., greater and do not contribute to entropy production (2.36). By the difference in time scales for V and T, the equilibrium process in this model B has $\dot{V}$ nearly zero (similar to A model $\dot{T}$ is nearly zero), giving zero entropy production (2.36) (in the other, nonequilibrium processes, $\dot{V}$ may be great). Cf. analogous discussion of model A and Sect. 2.3, Rem. 48 in Chap. 3.

Important is that equilibrium states passed during such reversible processes are stable. Such a reversible process must be slow because the time scale (for volume) in the usual (irreversible) processes is much less than the relaxation time—practically finite time of achieving an equilibrium state during a change of V from the old (perturbed) value to the new equilibrium value during the process in B . These results

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[8] In the Sect. 3.7 a (nonuniform) fluid model is discussed which as a special case leads to uniform fluid of type B but with linear dependence on $\dot{V}$; namely, for nonequilibrium stress the relation (3.211) may be written as a special case of (2.34), (2.35)

$$P_N = -(\zeta/V)\dot{V}$$

Here the proportionality coefficient (possible function of V, T) is written with the help of *volume viscosity* coefficient $\zeta = \hat{\zeta}(V, T)$ used in nonuniform models of Sect. 3.7. From (2.37) it follows that $\zeta \geq 0$ which is of course in accord with (3.197). Moreover, usually as regular condition, we demand only positive ζ , see Rem. 9 in this chapter.

will be explicitly demonstrated in examples of reversible isothermal and adiabatic processes discussed in Rem. 48 in Chap. 3 in linear fluid of Sects. 3.7, 3.8 (uniform case of which may be considered as model B).[9]

Equations (2.38) (which are in fact the Gibbs equation with equilibrium pressure P^o, cf. (2.18), (2.19) of model A) are valid also in nonequilibrium processes and prove (in this uniform system B) an analog of the local equilibrium hypothesis of irreversible thermodynamics [12, 16].

Again, not all results for model B are valid if we come to more complicated models C and D.

C. *Fluid with a higher order memory in volume* [4] has constitutive equations (2.8) and therefore by (2.12)

$$F = \hat{F}(V, \dot{V}, \ddot{V}, T) \tag{2.39}$$

Inserting it in the reduced inequality (2.13) we obtain

$$-T\Sigma = ((\partial\hat{F}/\partial V)+P)\dot{V}+((\partial\hat{F}/\partial T)+S)\dot{T}+(\partial\hat{F}/\partial\dot{V})\ddot{V}+(\partial\hat{F}/\partial\ddot{V})\ \dddot{V}\leq 0 \tag{2.40}$$

which by principle of admissibility (cf. end of Sect. 2.1) must be valid in any thermokinetic process. Because of linearity in $\dddot{V}$ and $\dot{T}$ we obtain (by Lemma A. 5.1 analogously as above) the identities

$$\partial\hat{F}/\partial\ddot{V} \equiv 0 \tag{2.41}$$

$$\partial\hat{F}/\partial T = -S \tag{2.42}$$

Therefore, (instead of (2.8)) we have

$$F = \hat{F}(V, \dot{V}, T), S = \hat{S}(V, \dot{V}, T), U = \hat{U}(V, \dot{V}, T), P = \hat{P}(V, \dot{V}, \ddot{V}, T) \tag{2.43}$$

and inequality (2.40) then gives (note nonlinearity of $\hat{P}$ in $\ddot{V}$)

$$-T\Sigma = ((\partial\hat{F}/\partial V) + P)\dot{V} + (\partial\hat{F}/\partial\dot{V})\ddot{V} \leq 0 \tag{2.44}$$

Motivated analogously as in (2.28) we define the *equilibrium process* in model C by

$$\dot{V} = 0, \quad \ddot{V} = 0 \tag{2.45}$$

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[9] As we noted in Rems. 12 in Chap. 1, 6, 11 in this chapter, the stability conditions of equilibria must be added which in model B means that for equilibrium pressure (2.33) and (2.26) we have $\partial\hat{P}^o/\partial V < 0$, $\partial\hat{U}/\partial T > 0$. This follows from the fact that equilibrium in model B is, similarly as in model A (see Rem. 7 in this chapter), a special case of equilibrium in a model of nonuniform fluid from Sect. 3.8, cf. (3.256), (3.257). Stability forms a part of regular conditions (see end of Sect. 1.1, Rem. 6 in this chapter). To exclude rather pathological cases in applications we add to regular conditions that $P_N = 0$ only if $\dot{V} = 0$ (entropy production $\hat{\Sigma}(V, \dot{V}, T)$ has a sharp minimum at $\dot{V} = 0$, i.e., equalities in (2.30), (2.37) are excluded). In linearized model B from Rem. 8 such regularity means that volume viscosity coefficient is only positive $\zeta > 0$, cf. (3.232).

Production of entropy is now a function $\Sigma = \hat{\Sigma}(V, \dot{V}, \ddot{V}, T)$ (cf. (2.44)) and has a minimum in equilibrium (2.45). Thus

$$\frac{\mathrm{d}}{\mathrm{d}\lambda} \hat{\Sigma}(V, \lambda\dot{V}, \lambda\ddot{V}, T) \mid_{\lambda=0} = 0 \tag{2.46}$$

for arbitrarily chosen $V, \dot{V}, \ddot{V}, T$ where λ is a real parameter (sufficient inequality of minima (analogical to (2.30)) will not be discussed for simplicity).

We use the following definitions in model C for all V, T :
equilibrium pressure P^o

$$P^o = \hat{P}^o(V, T) \equiv \hat{P}(V, 0, 0, T) \tag{2.47}$$

nonequilibrium pressure P_N

$$P_N = \hat{P}_N(V, \dot{V}, \ddot{V}, T) \equiv \hat{P}(V, \dot{V}, \ddot{V}, T) - \hat{P}^o(V, T) \tag{2.48}$$

equilibrium free energy F^o

$$F^o = \hat{F}^o(V, T) \equiv \hat{F}(V, 0, T) \tag{2.49}$$

nonequilibrium free energy F_N

$$F_N = \hat{F}_N(V, \dot{V}, T) \equiv \hat{F}(V, \dot{V}, T) - \hat{F}^o(V, T) \tag{2.50}$$

Therefore, these definitions have in equilibrium (2.45) the following properties

$$\hat{F}_N(V, 0, T) = 0, \quad \frac{\partial \hat{F}_N}{\partial V}(V, 0, T) = 0, \quad \hat{P}_N(V, 0, 0, T) = 0 \tag{2.51}$$

Inserting (2.44) to (2.46) and using (2.47)–(2.51), we obtain equality linear in (arbitrarily and independently chosen) $\dot{V}$ and $\ddot{V}$ and therefore coefficients standing in this equality by $\dot{V}$ and $\ddot{V}$ must be identically zero; this means

$$\partial \hat{F}^o / \partial V = -P^o \tag{2.52}$$

$$\frac{\partial \hat{F}_N}{\partial \dot{V}}(V, 0, T) = 0 \tag{2.53}$$

The ultimate form of entropy production is (by (2.47)–(2.52) in (2.44))

$$-T\Sigma = \frac{\partial \hat{F}_N}{\partial V}\dot{V} + \frac{\partial \hat{F}_N}{\partial \dot{V}}\ddot{V} + P_N\dot{V} \leq 0 \tag{2.54}$$

Again, results (2.41), (2.42), (2.52), (2.54) are not only necessary but also sufficient for fulfilling (2.40). But in this material model with higher order memory the thermodynamic quantities F, S, U are functions not only T, V but also $\dot{V}$, free energy is potential for S (2.42), but only equilibrium part F^o is a potential for equilibrium pressure P^o (2.52). By (2.42), (2.43), (2.50), (2.52), (2.53)

$$\dot{F} = -S\dot{T} - P^o\dot{V} + \frac{\partial \hat{F}_N}{\partial V}\dot{V} + \frac{\partial \hat{F}_N}{\partial \dot{V}}\ddot{V} \tag{2.55}$$

This result gives the classical Gibbs equation only in equilibrium process (2.45), i.e., analog of "local equilibrium" hypothesis is not valid in this material model C. Two last members in (2.55) contribute to the entropy production.

Using appropriate regular condition (analogously as in Rems. 7, 9 in this chapter) we can achieve that in model C the equilibrium process is identical with the reversible or zero production processes, but we omit this for simplicity.

Again, other results follow in the last model D.

D. *Fluid with memory in volume and temperature* (2.9). Then, by (2.12), the constitutive equation for free energy is

$$F = \hat{F}(V, \dot{V}, T, \dot{T}) \tag{2.56}$$

Inserting it in (2.11) we have

$$-T\Sigma = ((\partial\hat{F}/\partial V) + P)\dot{V} + ((\partial\hat{F}/\partial T) + S)\dot{T} + (\partial\hat{F}/\partial\dot{V})\ddot{V} + (\partial\hat{F}/\partial\dot{T})\ddot{T} \leq 0 \tag{2.57}$$

According to the admissibility principle (quoted under (2.13)) and because of linearity of (2.57) in $\ddot{V}$ and $\ddot{T}$ we obtain (by Lemma A. 5.1 analogously as before) the identities

$$(\partial\hat{F}/\partial\dot{V}) \equiv 0, \quad (\partial\hat{F}/\partial\dot{T}) \equiv 0 \tag{2.58}$$

Therefore, in material model D

$$F = \hat{F}(V, T) \tag{2.59}$$

and from (2.57) it remains (nonlinear in $\dot{V}$, $\dot{T}$ by $(2.9)_{2,3}$))

$$-T\Sigma = ((\partial\hat{F}/\partial V) + P)\dot{V} + ((\partial\hat{F}/\partial T) + S)\dot{T} \leq 0 \tag{2.60}$$

In further results we obtain *equilibrium process* in model D defined as follow

$$\dot{T} = 0, \quad \dot{V} = 0 \tag{2.61}$$

motivated again by zero entropy production (cf. under (2.11)). At equilibrium, the entropy production is minimal and therefore

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{\Sigma}(V, \lambda\dot{V}, T, \lambda\dot{T}) \mid_{\lambda=0} = 0 \tag{2.62}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\lambda^2}\hat{\Sigma}(V, \lambda\dot{V}, T, \lambda\dot{T}) \mid_{\lambda=0} \geq 0 \tag{2.63}$$

valid for any $V, \dot{V}, T, \dot{T}$; λ is a real parameter. Inserting (2.60) into (2.62) we obtain an equality linear in arbitrary values of $\dot{V}, \dot{T}$ and therefore by standing coefficients must be zero (using again Lemma A. 5.1). This gives identities

$$\partial\hat{F}/\partial V = -P^o \tag{2.64}$$

$$\partial\hat{F}/\partial T = -S^o \tag{2.65}$$

where we use the following definitions in model D:
equilibrium pressure P^o

$$P^o = \hat{P}^o(V, T) \equiv \hat{P}(V, 0, T, 0) \tag{2.66}$$

equilibrium entropy S^o

$$S^o = \hat{S}^o(V, T) \equiv \hat{S}(V, 0, T, 0) \tag{2.67}$$

Therefore, the Gibbs equation is valid in the form

$$\dot{F} = -S^o\dot{T} - P^o\dot{V} \tag{2.68}$$

i.e., free energy is a potential for both equilibrium values of entropy and pressure.

Defining in model D the *nonequilibrium pressure* P_N

$$P_N = \hat{P}_N(V, \dot{V}, T, \dot{T}) \equiv \hat{P}(V, \dot{V}, T, \dot{T}) - \hat{P}^o(V, T) \tag{2.69}$$

and the *nonequilibrium entropy* S_N by

$$S_N = \hat{S}_N(V, \dot{V}, T, \dot{T}) \equiv \hat{S}(V, \dot{V}, T, \dot{T}) - \hat{S}^o(V, T) \tag{2.70}$$

we obtain the entropy production (2.60) in the final form

$$-T\Sigma = P_N\dot{V} + S_N\dot{T} \leq 0 \tag{2.71}$$

It may be seen that results (2.58), (2.64), (2.65), (2.71) are not only necessary but also sufficient for fulfilling (2.57).

Inserting (2.60) into (2.63) we obtain negative semidefinite quadratic form in $\dot{V}, \dot{T}$ with coefficients in equilibrium (2.61) and therefore, e.g.,

$$\frac{\partial \hat{P}_N}{\partial \dot{V}}(V, 0, T, 0) \leq 0, \qquad \frac{\partial \hat{S}_N}{\partial \dot{T}}(V, 0, T, 0) \leq 0$$

For simplicity we omit further results as well as the discussion of regularity conditions permitting equivalence of equilibrium process with the reversible and zero entropy production processes in model D (which are similar as in Rems. 7, 9 in this chapter).

We can see that in principle the same physical system may be described by various models with various constitutive equations with various entropies (cf., e.g. (2.25), (2.70)) and with various equilibrium processes (cf. (2.28), (2.45), (2.61)); see also the Sect. 2.3.

In "equilibrium thermodynamics" model A and in model B "not far from equilibrium" (and with no memory to temperature) the entropy may be calculated up to a constant. Namely, in both cases $S = \hat{S}(V, T)$ (2.6)$_2$, (2.25) and we can use the equilibrium processes (2.28) in B or arbitrary processes in A for classical calculation of entropy change: by integration of $\partial\hat{S}/\partial T$ or $\partial\hat{S}/\partial V$ expressible by Gibbs equations (2.18), (2.19), (2.38) through measurable heat capacity $\partial\hat{U}/\partial T$ or state Eqs. (2.6)$_3$, (2.33) (with equilibrium pressure P^o in model B).[10] This seems to accord with such a property as in (1.11), (1.40) in Sects. 1.3, 1.4. As we noted above, here the Gibbs equations used were proved to be valid not only in classical equilibrium thermodynamics (2.18), (2.19) but also in the nonequilibrium model B (2.38) and this expresses the "local equilibrium hypothesis" in model B (it will be proved also in nonuniform models in Chaps.3 (Sect. 3.6), 4, while in classical theories of irreversible processes [12, 16] it must be taken as a postulate).

On the other hand, in material models C, D with longer range memory or also with memory in temperature, the entropy cannot be calculated: because of (2.43)$_2$, (2.9)$_2$, we have no possibility to express, e.g., $\partial\hat{S}/\partial\dot{V}$, through measurable quantities because of more complicated (2.55) (as distinct from the finding of $\partial\hat{S}/\partial V$ from Gibbs equation (2.38) above). In model D, the Gibbs equation in the form (2.68) is valid, but it permits to calculate only the equilibrium (part of) entropy. This seems to correspond with property (1.37) in these models C, D.

Models A, B, C, D illustrate the general behaviour noted at the end of Sect. 1.4 and will be discussed further in the following Sect. 2.3.

Summary. This Section illustrates the application of a typical and genuine thermodynamic requirement—the admissibility principle or the conformity with the entropic inequality (the Second Law)—on the fluid models introduced in preceding Section. The principle simplifies the constitutive equations, cf. e.g., (2.20), (2.22), and (2.23), as well as the entropy inequalities, cf. e.g. (2.21) and (2.27); reveals the relationships between (thermodynamic) variables, e.g., (2.16), (2.24);

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[10] Internal energy may be calculated with Gibbs equations (2.19), (2.38) again with precision of constant, cf. Sect. 1.3. Calculation of free energy (2.14), (2.23) needs the constant with which the entropy is known (if temperature changes) which may be obtained on the basis of the "Third Law" of thermodynamics [48, 49] (zero entropy value of pure solids at 0 K). This is a rather constitutive assertion (as distinct from general First and Second Laws) appropriate, e.g., for calculating of equilibrium in reacting mixture, cf. Sect. 2.4.

confirms the validity of Gibbs equations, e.g., (2.18), (2.19); and "shows sources" of irreversibility (typically nonequilibrium variables), see (2.48), (2.50), or (2.69), (2.70), and inequalities below the latter.

2.3 Level of Description and Internal Variables

As we noted in Sect. 1.1 to describe different materials thermodynamically, general postulates (balances, Second Law) must be supplemented by *constitutive equations*. These are not only the mathematical models (or "ideal materials") of different classes of materials (like gases, liquids, solids, etc.) but, because it is superfluous and practically impossible to describe the behaviour of a body in all details, they represent a *level of description* stressing typical properties important in intended applications [17, 50, 51]. Besides others (e.g., mixture may be regarded as a single (pure, one constituent) body if diffusion and chemical reactions may be neglected) the important features of the level of description are *time* and *space scales of the observer*—typical time and length intervals in which a change of observed properties in the studied phenomenon plays a role. Intervals much smaller or greater than these scales are regarded by observer as infinitesimal (instants or points) or infinite respectively. On the other hand, each property of real material has its own *natural time* or *space scales* as, e.g., relaxation times (cf. memory and stability in Sects. 2.1, 3.8) or lengths on which the properties' changes influence the responses (cf. nonlocality in Sect. 3.5). Of course, all scales in our phenomenological (macroscopic) approach are still much greater than natural scales of molecular phenomena (cf. Sect. 1.1, Rem. 5 in Chap. 1).[11]

The choice of constitutive equations means in fact the choice of such properties the natural scales of which are comparable with the observer's scales. Quantities the natural scales of which are much greater than the observer's scale play a role of constant parameters in constitutive equations (they are in "frozen equilibrium" or uniform); on the other hand, quantities with a much shorter natural scale than the observer's may be regarded as in ("relaxed") equilibrium or having localized influence through their gradients.

We discuss the level of description on uniform fluid models from Chap. 2. Here the space gradients have no influence (observer's space scales are much less than the natural space scales) and therefore we discuss only the time scales.[12] Different constitutive models may be applied on the same physical system, say models A, B, C, D in Sect. 2.2 on a uniform, closed fluid body. This corresponds to the use of various observer's scales relative to the same natural time scales which are in this

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[11] Stability of states, i.e., the return (by some relaxation time) after some perturbation is not self-evident. For equilibrium states this is discussed in Sects. 3.8, 4.7, cf. Sects. 1.1, 1.2, Rems. 11 in Chap. 1, 7, 9 in this chapter; for stability of other states (steady states, dissipative structures) see [11, 16, 52–55].

[12] The following results are obviously valid locally in nonuniform systems of Chaps. 3, 4. Moreover, space scales may be discussed analogously, cf. similarity of differential memory with local action in Sect. 3.5.

example the relaxation times for T and V (which may be very different). Relative to them the observer's scales for T, V are very great for model A, for model B, C is the observer's scale for V comparable (with further shortening in model C) while the observer's scale for T remains very great; finally in model D the observer's scale is also comparable to T.

Processes in model A (which are all the equilibrium processes here, cf. Sect. 2.2) may be regarded as the time sequence of equilibrium states (in the sense of S4 in Sect. 1.2) because the "infinitesimal" instant (in fact the time interval between adjoining states) in A is greater than the natural scale (relaxation time) of quantities V, T which are in (relaxed) equilibrium, see also Rem. 48 in Chap. 3.

Only a part of processes in model B is the equilibrium process (2.28) because only T (but not V) is in relaxed equilibrium, (see Rem. 9). Such a limitation is more severe for models C, D where neither T nor V are relaxed in corresponding equilibrium processes.

Correspondingly, as we explained at the end of Sect. 2.2, the entropy in A may be calculated with precision of a constant using "classical" Gibbs equation. Entropy in B may be calculated (with precision of constant) through Gibbs equation but only with equilibrium pressure (2.33) (principally measurable in equilibrium) and, ultimately, entropy cannot be calculated in the remaining models C, D. It may be even expected [17] that the difference between entropies of the two constitutive models with different observer's scales, say C and A, is such that entropy in model A is greater than in model C because in some instant entropy grows in model C (nonnegative entropy production) while in model A has still an equilibrium (greater) value. It is because that "instant", i.e., "infinitesimal" time interval is, by the choice of observer's scale, much greater in model A than C. This dependence of entropy on the chosen model (constitutive equation even in the same material body) causes nonmeasureability of entropy and nonexistence of entropometers.

In this connection we recall the difference between the real material and its mathematical model, cf. Sect. 1.1 and below (2.9). In the model, i.e., in its constitutive equations, the rates may be arbitrary (e.g., $\dot{T}$, $\dot{V}$ in model A, cf. Rem. 3 in Chap. 1)—study of such mathematical models is in fact a part of pure mathematics. But in applications of the model these rates cannot be arbitrary but must be in accord with chosen observer's scale, e.g., in using model A, the maximum rate $\dot{V}$ must be such that observer's scale $V/\dot{V}$ (where V is some typical value) is much greater than the relaxation (natural scale) time for V. The model is thus tested on real materials and further simplifications or limitations on its parameters may then result.

An often used method describing the influence of the (long) past and expressing the natural scales more explicitly is the method of *internal variables* [17, 56–64]. Constitutive equations (for simplicity we discuss the uniform fluid body) even with long range memory are functions of *external* (i.e., from outside controlled) variables like V, T and of (even several) *internal variables* β_i. Each β_i is controlled by *evolution equation* for its rate $\dot{\beta}_i$

$$\dot{\beta}_i = f_i(V, T, \beta_j) \quad i, j = 1, 2, \ldots \tag{2.72}$$

given by constitutive function f_i of (generally all) external and internal variables.[13] Solving this system of differential Eq. (2.72) from the present time (as initial condition) to the past and inserting solutions for the present β_j into constitutive equations we obtain such equations for responses (2.4) as functionals in thermokinetic process (2.5) from the past to the present instant.

The problem is rather in the physical identification of these "hidden" β_j but if they are known the use of internal variables with evolution Eq. (2.72) is another way to describe materials with (long range) memory. Solutions of (2.72) is facilitated in the case of fading memory (where always $\dot{\beta}_j < 0$ [61]), but also more intricate cases may be described as phase changes [65], plasticity and generally any hysteresis [66], cf. also Rem. 31 in Chap. 3; important are applications in chemically reacting mixtures (where β_j may be, e.g., "extent of reaction") which will be discussed here in Sect. 2.4 and in Chap. 4.

Another simplification in solving (2.72) follows from the fact that from the generally immense number of internal variables only those play a role whose relaxation time (characterized by $\beta_i/\dot{\beta}_i$ for some typical values of β_i, $\dot{\beta}_i$ is comparable with the observer's time scale). Internal variables with sufficient shorter or greater relaxation times are in frozen or relaxed equilibrium respectively. In both these situations $\dot{\beta}_i = 0$. In the first case β_i are constant, in the second case, for example, the equilibrium values may be expressed from (2.72) as functions of T, V. Inserting these values in constitutive equations (for β_j contained in them in such internal variables' description) we obtain model A (for these relaxed internal variables).

In the next Sect. 2.4 we show a simple example of an internal variable.

2.4 Uniform Reacting Mixture in Closed System

Balance of energy (2.1) and entropy inequality (2.2) may be applied also for more complicated models [59, 67], namely mixtures and multiphase systems.[14] Similarly classical thermodynamics balances (2.1), (2.2) have given the equilibrium result (namely model A of Sect. 2.2) and we can then obtain classical results for chemical and phase equilibria; we show them on simple examples in Sects. 2.4, 2.5.

In this Sect. 2.4 we discuss the uniform fluid (i.e., gas or liquid) mixture composed of two constituents (components of mixture) 1, 2 which (possibly) chemically react by a simple chemical reaction

$$1 = 2 \tag{2.73}$$

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[13] The name internal (or hidden) variables (or parameters) are connected with the fact that they are present in expression for entropy production but not in the expression for power (where typically external variables occur, like V). Internal variables therefore cannot be controlled during the process with the exception of initial values.

[14] However, these models are closed (not exchanging mass with surroundings). In their opposite-open systems (the whole mass of which is not constant)-it is not clear how to formulate heat when mass passes through the boundary simultaneously [12, 43]. Plausible formulation seems to be known in continua, cf. Sects. 3.1, 4.4 and Rems. 23 in Chap. 3, 11 in Chap. 4.

The whole mass m of the system is constant and this closed system, exchanging only heat and volume work with its surroundings, is supposed to be described again by fields (time function) (2.3) and (2.4) added with fields of (positive) masses $m_1(t)$, $m_2(t)$ of both constituents 1, 2 respectively. For closed systems (cf. Sects. 1.2, 2.1) the balance of energy (2.1) and entropy inequality (2.2) are valid but now together with the *balance of mass*

$$m_1 + m_2 = m \tag{2.74}$$

where the whole (positive) mass of the system m is a known constant. This mass balance may be also written for time derivatives

$$\dot{m}_1 + \dot{m}_2 = 0 \tag{2.75}$$

Using free energy (2.12), we can also use the reduced inequality (2.13) joining energy balance and entropy inequality.

For the most simple model (in fact extended model A of Sects. 2.1, 2.2) of the *fluid mixture without memory*, motivated by principles of determinism (with enlarged thermokinetic process by masses m_1, m_2) and equipresence, the following are postulated for responses (2.4)

$$U = \tilde{U}(T, V, m_1, m_2) = \bar{U}(T, V, m_2) \tag{2.76}$$

$$S = \tilde{S}(T, V, m_1, m_2) = \bar{S}(T, V, m_2) \tag{2.77}$$

$$P = \tilde{P}(T, V, m_1, m_2) = \bar{P}(T, V, m_2) \tag{2.78}$$

$$F = \tilde{F}(T, V, m_1, m_2) = \bar{F}(T, V, m_2) \tag{2.79}$$

((2.79) follows from definition (2.12)).

Memory is removed completely assuming that values of responses in the present instant are given by values of thermokinetic process T, V, m_1, m_2 at the same present instant. The second functions, i.e., the functions $(2.76)_2$–$(2.79)_2$, follow for our closed system excluding m_1 by (2.74), because the whole mass m is the known constant.

Before discussing the physical sense of this model, we deduce the consequences of the admissibility principle: entropy inequality (2.2) must be valid at any admissible thermodynamic process. The last one is (by definition) the set of any functions (2.3), (2.4), $m_1(t)$, and thermokinetic process

$$T(t), \quad V(t), \quad m_2(t) \tag{2.80}$$

consistent with proposed constitutive equations (2.76)–(2.79) and fulfilling the balance of energy (2.1) and mass (2.74), cf. Sect. 2.1 (differentiability needed is assumed). Again, any thermokinetic process (2.80) gives some admissible thermodynamic process: it gives present values of independent variables in (2.76)–(2.79), balance of energy (2.1) is fulfilled by appropriate Q (2.3), and mass balance (2.74) is fulfilled by appropriate m_1 (m is constant). Therefore, the constitutive principle of admissibility demands the fulfilling of inequality (cf. Sects. 2.1, 2.2)

$$-T\Sigma = ((\partial\bar{F}/\partial T) + S)\dot{T} + ((\partial\bar{F}/\partial V) + P)\dot{V} + (\partial\bar{F}/\partial m_2)\dot{m}_2 \leq 0 \tag{2.81}$$

(arisen by inserting constitutive equation (2.79) into reduced inequality (2.13)) at any thermokinetic process (2.80), i.e. also at any mutually independent values of $T, V, m_2, \dot{T}, \dot{V}, \dot{m}_2$.

Thus from (2.81) we obtain (using Lemma A. 5.1) for fluid mixture without memory the following identities (valid at any T, V, m_2)

$$\partial\bar{F}/\partial T = -S \tag{2.82}$$

$$\partial\bar{F}/\partial V = -P \tag{2.83}$$

$$\partial\bar{F}/\partial m_2 = 0 \tag{2.84}$$

Therefore, instead of (2.76)–(2.79) we have (see (2.12))

$$U = \bar{U}(T, V), \quad S = \bar{S}(T, V), \quad P = \bar{P}(T, V), \quad F = \bar{F}(T, V) \tag{2.85}$$

As follows then from (2.81) this fluid mixture without memory has zero entropy production $\Sigma = 0$ in every process and also Gibbs equations (2.18), (2.19) are valid here. In fact, this model of fluid mixture without memory is the same as model A of Sects. 2.1, 2.2 (the form of functions (2.85) depends on the whole mass m chosen).

A trivial example of this model is the *nonreacting fluid mixture* where m_1, m_2 (and therefore m) are constant parameters on which, for example, the form of $\bar{F}(T, V)$ depends and (2.84) is valid trivially, see also the next model with memory. A more interesting example of such a fluid mixture without memory is a reacting fluid mixture (with reaction (2.73)) in chemical equilibrium given by result (2.84), namely zero chemical affinity (see below and Rem. 15). At usual (regular) conditions we can calculate m_2 from (2.73) (and from known m also m_1 by (2.74)) as the function of T, V which then provide results (2.85) from constitutive functions (2.76)–(2.79). All processes here are sequences of chemical equilibria (shifted with T, V). A more detailed physical insight into this model will be discussed below in the terms of the following model of reacting mixture with memory of which this model is a special "equilibrium" case.

The model of uniform *chemically reacting fluid mixture with memory* follows naturally because it describes chemical kinetics in uniform fluid mixture as an irreversible (nonequilibrium) process with (for simplicity) reaction (2.73) in instantaneous volume V and temperature T. Inside such a reacting mixture the masses m_1, m_2 of constituents transform to each other during the reaction and this reacting mixture exchanges only the volume work and heat(ing), but not masses of constituents, with its surroundings; therefore the mass of mixture m, given by (2.74), is (a known) constant. The forms of balance of energy (2.1) and entropy inequality (2.2) remain valid as well as that of mass balance (2.74). Constitutive equations (2.76)–(2.79) remain the same here (present values of thermokinetic process give present values of responses) but, as follows from experience of chemical kinetics, the rate of chemical reaction (which may be expressed here by $\dot{m}_2$ and depending on concentrations (densities—mass per unit volume) and temperature) is given by evolution equation

$$\dot{m}_2 = \bar{f}(T, V, m_2) \tag{2.86}$$

Taking this (2.86) (with present values of $\dot{m}_2$, T, V, m_2) as an additional constitutive equation to the original set of constitutive equations (2.76)–(2.79) (note that it is in accord with the principle of equipresence), we obtain an example of material with a long range memory expressed through the evolution equation (of the type (2.72)) with the internal variable m_2. Such a material model [59] (which for simple reaction (2.73) may be interpreted also as a fading memory model [61]) may be investigated with the use of the constitutive principle of admissibility: entropy inequality and therefore reduced inequality (2.13) must be valid in any admissible thermodynamic process (defined in the same way as in the preceding case around (2.80) but adding (2.86) to constitutive equations). Now, an admissible process may be obtained in this closed system with known mass m if we choose arbitrary functions $V(t)$, $T(t)$ from past to present (therefore we can choose arbitrarily and independently V, $\dot{V}$, T, $\dot{T}$ at the present time) and arbitrary value m_2 at present time. Indeed, the solution of (2.86) with this value m_2 as the initial one (from the present moment to past; we assume its existence with $0 < m_2 < m$) gives the function $m_2(t)$ and from such obtained (2.80) we get responses (2.4) (and $F(t)$ by (2.12)) through constitutive equations (2.76)–(2.79). With appropriate time functions $Q(t)$ and $m_1(t)$, the fulfilling of the balances (2.1) and (2.74) is achieved.

Inserting constitutive equation (2.79) into reduced inequality (2.13) we obtain again inequality (2.81) and this, by the admissibility principle, must be valid at any values of V, $\dot{V}$, T, $\dot{T}$, m_2 at the present instant. By usual arguments (based on the Lemma A. 5.1 from Appendix A.5) we obtain identities

$$\partial\bar{F}/\partial T = -S \tag{2.87}$$

$$\partial\bar{F}/\partial V = -P \tag{2.88}$$

But the last member in (2.81) remains in this reacting fluid mixture with memory, because $\dot{m}_2$ is not arbitrary but given by the evolution Eq. (2.86):

$$-T\Sigma = (\partial\bar{F}/\partial m_2)\dot{m}_2 \le 0 \tag{2.89}$$

Namely, the last member in (2.81) describes the irreversible process of chemical kinetics in the reacting system. Note that the final constitutive equations remain in the form (2.76)–(2.79) fulfilling (2.87), (2.88) (Eq. (2.89) expresses the typical influence of an internal variable on entropy production).

We denote $-\partial\bar{F}/\partial m_2$ (the negative derivative of function (2.79)$_2$ of reacting fluid mixture with memory) as the *chemical affinity* (cf. also (2.94). Because of the simple reaction (2.73) we use mass units here; for complicated stoichiometry we prefer molar units, see (4.176)).[15]

Motivated by zero entropy production in (2.89) we define the *equilibrium process* in the reacting fluid mixture with memory by zero reaction rate

$$\dot{m}_2 = 0 \tag{2.90}$$

at any T, V. Correspondingly, we denote as equilibrium value m_2^o of m_2 which is given by solution of

$$\bar{f}(V, T, m_2^o) = 0 \tag{2.91}$$

Uniqueness and $0 < m_2^o < m$ is assumed and to such *regularity* we add the condition that when $\dot{m}_2 \neq 0$ then also affinity $-\partial\bar{F}/\partial m_2 \neq 0$ and moreover we assume that affinity is continuous in m_2 (i.e., the equilibrium process is identical to those of zero entropy production and those which are reversible, cf. Sect. 2.2 models A, B). Then also (chemical) affinity in equilibrium must be zero

$$-(\partial\bar{F}/\partial m_2)(T, V, m_2^o) = 0 \tag{2.92}$$

because if $\dot{m}_2 > 0$ or $\dot{m}_2 < 0$ then $(\partial\bar{F}/\partial m_2) < 0$ or $(\partial\bar{F}/\partial m_2) > 0$ respectively as it follows from (2.89). Therefore, in equilibrium both members of product (2.89) must vanish simultaneously (thus the form of functions $\bar{f}$ and affinity are not independent, cf. Sect. 4.9).

In such a regular model the equilibrium may be also defined by zero chemical affinity (2.92) with result (2.90) (further discussion see Sect. 4.7).

The previous model of fluid mixture without memory (2.82)–(2.85) may be understood as the present model with memory in equilibrium process (as relaxed model from Sect. 2.3). It may be looked upon as the limiting case of a short natural time scale (caused by a great chemical reaction rate (2.86)) in comparison with the observer's scale. Equilibrium is achieved instantaneously in the observer's scale of this previous model and therefore affinity is persistently zero (2.84) (cf. (2.92)); m_2 in (2.76)–(2.79) (for m fixed) then follows from (2.91) in fact as m_2^o, (2.85) indeed. Arbitrariness and independency of m_2 and $\dot{m}_2$ used in deduction of (2.84) of previous model follows, because in the great observer's scale, they are in fact the initial value m_2 and its time change selected arbitrarily in present model with memory. On the other hand, a nonreacting mixture is another extreme ("frozen" equilibrium in Sect. 2.3) at which the rate (2.86) is practically zero (the natural scale is much greater than the observer's scale).

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[15] Using negative sign in this definition of chemical affinity we follow the tradition [12, 13, 15, 19, 68] and it even seems more natural to use such a reverse sign, cf. (2.94), (4.174), (4.176). Affinity with reverse sign was used, e.g., in [8, 33, 34, 69, 70].

At the end of this Section we discuss the starting forms of constitutive equations (2.76)$_1$–(2.79)$_1$ (their obtaining will be discussed below) which were used (with m as parameter) in a reacting mixture (where evolution equation (2.86) is given), in an equilibrium “relaxed” mixture (with (2.85)) and in a nonreacting mixture (all results of model A in Sect. 2.2 may be used with m_2, m_1 as parameters). We call the derivatives of (more general) function $\tilde{F}$ with respect to masses the (specific) *chemical potentials* g_1, g_2

$$g_1 = \partial\tilde{F}/\partial m_1, \quad g_2 = \partial\tilde{F}/\partial m_2 \tag{2.93}$$

of both constituents (they are in fact the classical definitions in mass units; cf. (2.100)). Using (2.79) and (2.74) we can see that chemical affinity is (see Rem. 15)

$$-\,\partial\bar{F}/\partial m_2 = g_1 - g_2 \tag{2.94}$$

Therefore, the condition of zero affinity (cf. (2.92) or (2.84)) gives equality of chemical potentials for reaction (2.73). Because of (2.87), (2.88) (or (2.82), (2.83)) we can see that

$$\partial\tilde{F}/\partial T = -S, \quad \partial\tilde{F}/\partial V = -P \tag{2.95}$$

and therefore we have the *Gibbs equation*

$$\dot{F} = -S\dot{T} - P\dot{V} + g_1\dot{m}_1 + g_2\dot{m}_2 \tag{2.96}$$

Defining the *free enthalpy (Gibbs energy)* G as

$$G = F + PV \tag{2.97}$$

we obtain with (2.96) the Gibbs equation in the form

$$\dot{G} = -S\dot{T} + V\dot{P} + g_1\dot{m}_1 + g_2\dot{m}_2 \tag{2.98}$$

From the assumption of invertibility of (2.78) for V we can use T, P, m_1, m_2 as classical independent variables. For instance,

$$G = \check{G}(T, P, m_1, m_2) \tag{2.99}$$

and (2.98) gives the classical forms for chemical potentials [67]

$$g_1 = \partial\check{G}/\partial m_1, \quad g_2 = \partial\check{G}/\partial m_2 \tag{2.100}$$

In uniform systems we have the extensivity of V, U, S (and therefore also F, G). This means that, e.g., F is a homogeneous function of first order in m_1, m_2, i.e., for any real α it is valid that

$$\tilde{F}(T, \alpha V, \alpha m_1, \alpha m_2) = \alpha \tilde{F}(T, V, m_1, m_2) \tag{2.101}$$

This property follows from additivity of these quantities, cf. Rem. 7 in Chap. 3 (for S and U this may be expected from their definitions and from the extensivity of heat and work in homogeneous processes, see Sect. 1.2); other fields, like T, P, g_1, g_2, are intensive ones .

By Euler theorem for homogeneous functions

$$V(\partial \tilde{F}/\partial V) + m_1(\partial \tilde{F}/\partial m_1) + m_2(\partial \tilde{F}/\partial m_2) = \tilde{F}(T, V, m_1, m_2) \tag{2.102}$$

from which, by (2.95), (2.93) and (2.97)

$$G = g_1 m_1 + g_2 m_2 \tag{2.103}$$

From (2.103) and the Gibbs Eq. (2.98) follows the *Gibbs-Duhem equation*

$$S\dot{T} - V\dot{P} + \dot{g}_1 m_1 + \dot{g}_2 m_2 = 0 \tag{2.104}$$

Thus the classical relations of equilibrium thermodynamics have been obtained.

Finally, we discuss how to obtain (in principle) the constitutive equations (2.76)–(2.79)$_1$. This is possible for the model of nonreacting mixture using the calculation of S, U as in model A described at the end of Sect. 2.2 for fixed but arbitrary parameters m_1, m_2 (this may be obtainable also for chemical reacting mixture by shortening of the observer's scale sufficiently to obtain chemical reaction rates of nearly zero). Integration constants also depend on such parameters. They may be obtained in the gas phase from U and S of pure constituents provided the pressure of the initial state is sufficiently low to use the change of U and S in mixing for ideal gases (such change in U is zero; cf. ideal gas from Appendix A. 1, Sect. 4.8). For liquid or solid phase we choose the initial state in phase equilibria with a gas phase (cf. conditions of phase equilibria (2.116), (2.129)) values of which may be calculated as before. By (2.103) and the composition of such a phase we know the initial value of G and from (2.98) every (2.76)$_1$–(2.79)$_1$ follows. Constitutive evolution equation for reaction rate (2.86) then remains as a postulate, the explicit form of which can be found from "external" theories, i.e., chemical kinetics. This is quite a common approach in thermodynamics of chemically reacting mixtures. A different approach is shown here in Sect. 26.

Summary. Section 2.4 illustrates the extension of rational thermodynamics methodology on mixtures with chemical reaction(s) using a very simple model of two-component uniform mixture. The composition variable(s) enters the constitutive equations, cf. (2.76)–(2.79). In a uniform mixture, the classical chemical thermodynamics was obtained, i.e., its validity also in nonequilibrium covered by this model was demonstrated, cf. e.g., (2.82), (2.83), (2.85), (2.87), (2.88). Traditional quantities known from the equilibrium chemical thermodynamics may be thus introduced and used out of equilibrium—affinity by (2.89), chemical potential by (2.93) or (2.100), or Gibbs energy by (2.97). Gibbs and Gibbs-Duhem equations also remain valid, cf. (2.96) and (2.104), respectively. The necessity of "external information" from chemical kinetics is indicated by (2.86); this requirement will be relaxed by more general thermodynamic treatment in Sect. 4.9.

2.5 Phase Equilibria

Another model for which (2.1), (2.2) may be applied is the *two-phase fluid system without memory* which models two-phase equilibria in pure fluid. It has one constituent in two phases which are uniform bodies where the masses and volumes of which are denoted by $m^{(1)}$, $m^{(2)}$ and $V^{(1)}$, $V^{(2)}$, respectively. For the whole volume V and mass m we have

$$V = V^{(1)} + V^{(2)} \tag{2.105}$$

$$m = m^{(1)} + m^{(2)} \tag{2.106}$$

where m is a known constant. Basic laws (2.1), (2.2) may be applied to this whole two-phase system because it exchanges with its surroundings only heat and volume work but not a mass (exchange of heat, volume work, and mass between its phases is possible).

Constitutive equations for a two-phase system are postulated as

$$U = \tilde{U}^{(1)}(T, V^{(1)}, m^{(1)}) + \tilde{U}^{(2)}(T, V^{(2)}, m^{(2)}) \tag{2.107}$$

$$S = \tilde{S}^{(1)}(T, V^{(1)}, m^{(1)}) + \tilde{S}^{(2)}(T, V^{(2)}, m^{(2)}) \tag{2.108}$$

$$P = \tilde{P}(T, V^{(1)}, V^{(2)}, m^{(1)}, m^{(2)}) \tag{2.109}$$

Therefore, we assume that energy and entropy are additive—each of them sums corresponding quantities of both phases taken as pure uniform bodies (i.e., we neglect surface energy or entropy on the phase contact). Memory is excluded because independent and dependent variables are taken in the same present instant. On the other hand, the pressure (2.109) and also temperature T (intensive quantities) are assumed to be the same in both phases (cf. discussion at the end of this Sect. 2.5). Using the definitions of free energies F for the whole system (2.12) and for both phases $F^{(1)}$, $F^{(2)}$

$$F^{(\alpha)} = U^{(\alpha)} - TS^{(\alpha)} \qquad \alpha = 1, 2 \tag{2.110}$$

we have the constitutive equation for free energy (by (2.106))

$$F = \tilde{F}^{(1)}(T, V^{(1)}, m^{(1)}) + \tilde{F}^{(2)}(T, V^{(2)}, m^{(2)}) \equiv \bar{F}(T, V^{(1)}, V^{(2)}, m^{(2)}) \tag{2.111}$$

Because also the reduced inequality (2.13) for the two-phase system is valid, introducing here (2.111) we obtain with (2.105), (2.106):

$$0 \geq ((\partial\tilde{F}^{(1)}/\partial T) + (\partial\tilde{F}^{(2)}/\partial T) + S)\dot{T} + ((\partial\tilde{F}^{(1)}/\partial V^{(1)}) + P)\dot{V}^{(1)} + ((\partial\tilde{F}^{(2)}/\partial V^{(2)}) + P)\dot{V}^{(2)} + (g^{(2)} - g^{(1)})\dot{m}^{(2)} \tag{2.112}$$

where chemical potentials of both phases are defined as (cf. (2.93))

$$g^{(1)} \equiv \partial\tilde{F}^{(1)}/\partial m^{(1)}, \quad g^{(2)} \equiv \partial\tilde{F}^{(2)}/\partial m^{(2)} \tag{2.113}$$

According to admissibility principle, the entropy inequality must be valid at any admissible thermodynamic process. The last one is again defined as time functions for V, $V^{(\alpha)}$, $m^{(\alpha)}$, m, T ($\alpha = 1, 2$), and (2.107)–(2.111), which fulfill the balances (2.1), (2.105), (2.106). Again, arbitrary time functions $T(t)$, $V^{(1)}(t)$, $V^{(2)}(t)$, $m^{(2)}(t)$ (thermokinetic process) suffice to obtain some admissible thermodynamic process, namely, (2.107)–(2.109) may be found and balances (2.1), (2.105), (2.106) may be satisfied by appropriate Q, V, $m^{(1)}$ (at given m). Then the inequality (2.112) (following from entropy inequality (2.2), balances (2.1), (2.105), (2.106), and constitutive equation (2.111)) must be satisfied at any mutually independent values in the present instant T, $V^{(1)}$, $V^{(2)}$, $m^{(2)}$, $\dot{T}$, $\dot{V}^{(1)}$, $\dot{V}^{(2)}$, $\dot{m}^{(2)}$ (because from them may be constructed a certain thermokinetic process).

In a standard way (with Lemma A. 5.1) we obtain from (2.112) identities

$$-S = (\partial\tilde{F}^{(1)}/\partial T) + (\partial\tilde{F}^{(2)}/\partial T) = \partial\bar{F}/\partial T \tag{2.114}$$

$$\partial\tilde{F}^{(1)}/\partial V^{(1)} = \partial\tilde{F}^{(2)}/\partial V^{(2)} = -P \tag{2.115}$$

$$g^{(1)} = g^{(2)} \tag{2.116}$$

The last Eq. (2.116) expresses the equality of chemical potentials in both phases. As a result only the equality is valid in (2.112) and therefore all processes in this model of a two-phase system may be considered those of zero entropy production and equilibrium (and those reversible). Namely, it is an analogical result as for model A in Sect. 2.2 because we confine to the model without memory: assuming the independence of $\dot{m}^{(2)}$ and $m^{(2)}$ we confine to the system the equilibrium of which (between the phases) is attained much more quickly than observer's time scale.

In a similar way we can discuss the more complicated system: a *two-phase and two-constituent fluid system without memory* which models (two-)phase equilibrium in fluid mixture. The model is composed of two phases (upper indices (2.105), (2.106)) each representing the (chemically) nonreacting fluid mixture containing two mutually nonreacting constituents (in the sense of Sect. 2.4; constituents are denoted by lower indices 1, 2). We have therefore two constituents distributed in two phases with the masses

$$m_1^{(1)}, \quad m_2^{(1)}, \quad m_1^{(2)}, \quad m_2^{(2)} \tag{2.117}$$

Mass balances are

$$m_1^{(1)} + m_1^{(2)} = m_1 \tag{2.118}$$

$$m_2^{(1)} + m_2^{(2)} = m_2 \tag{2.119}$$

where m_1, m_2 are known constants because the system (without chemical reactions) is closed exchanging heat(ing) and volume work (but not mass) with the surroundings. The balance of volume (2.105) and energy (2.1) as well as entropy inequality (2.2) are again valid for the whole system.

Constitutive equations of this two-phase and two-constituent fluid system without memory are assumed in the form

$$U = \tilde{U}^{(1)}(T, V^{(1)}, m_1^{(1)}, m_2^{(1)}) + \tilde{U}^{(2)}(T, V^{(2)}, m_1^{(2)}, m_2^{(2)}) \tag{2.120}$$

$$S = \tilde{S}^{(1)}(T, V^{(1)}, m_1^{(1)}, m_2^{(1)}) + \tilde{S}^{(2)}(T, V^{(2)}, m_1^{(2)}, m_2^{(2)}) \tag{2.121}$$

$$P = \tilde{P}(T, V^{(1)}, V^{(2)}, m_1^{(1)}, m_1^{(2)}, m_2^{(1)}, m_2^{(2)}) \tag{2.122}$$

($U^{(\alpha)}$ and $S^{(\alpha)}$ are the internal energy and entropy of each phase $\alpha = 1, 2$, respectively). Pressure P, similar to temperature T, is assumed to be equal in both phases. Defining the free energies of both phases again by (2.110) we have the constitutive equation for free energy (2.12) of the system

$$F = \tilde{F}^{(1)}(T, V^{(1)}, m_1^{(1)}, m_2^{(1)}) + \tilde{F}^{(2)}(T, V^{(2)}, m_1^{(2)}, m_2^{(2)}) \tag{2.123}$$

Now we insert (2.123) into reduced inequality (2.13) (which is valid by (2.1), (2.2) for the whole system). Because from masses in (2.118), (2.119) only $m_1^{(1)}, m_2^{(1)}$ are independent, we obtain

$$\begin{aligned} 0 \geq\ & ((\partial\tilde{F}^{(1)}/\partial T) + (\partial\tilde{F}^{(2)}/\partial T) + S)\dot{T} + ((\partial\tilde{F}^{(1)}/\partial V^{(1)}) \\ & + P)\dot{V}^{(1)} + ((\partial\tilde{F}^{(2)}/\partial V^{(2)}) + P)\dot{V}^{(2)} \\ & + (g_1^{(1)} - g_1^{(2)})\dot{m}_1^{(1)} + (g_2^{(1)} - g_2^{(2)})\dot{m}_2^{(1)} \end{aligned} \tag{2.124}$$

where chemical potentials of constituents 1, 2 in both phases (2.105), (2.106) are defined by

$$g_1^{(1)} \equiv \partial\tilde{F}^{(1)}/\partial m_1^{(1)}, \quad g_1^{(2)} \equiv \partial\tilde{F}^{(2)}/\partial m_1^{(2)} \tag{2.125}$$

$$g_2^{(1)} \equiv \partial\tilde{F}^{(1)}/\partial m_2^{(1)}, \quad g_2^{(2)} \equiv \partial\tilde{F}^{(2)}/\partial m_2^{(2)} \tag{2.126}$$

Again the time functions (thermokinetic process) for $T, V^{(1)}, V^{(2)}, m_1^{(1)}, m_2^{(1)}$ give some admissible process (Eqs. (2.120)–(2.123) fulfilling (2.1), (2.118), (2.119) by some $Q, m_1^{(2)}, m_2^{(2)}$; m_1, m_2 are known constants), for which (2.2) and therefore also reduced inequality (2.13) must be valid by the dissipation principle. Therefore, inequality (2.124) must be valid at any values of independent variables $T, V^{(1)}, V^{(2)}, m_1^{(1)}, m_2^{(1)}, \dot{T}, \dot{V}^{(1)}, \dot{V}^{(2)}, \dot{m}_1^{(1)}, \dot{m}_2^{(1)}$ (because some thermokinetic process may be constructed from them; absence of memory means that time for attaining the phase equilibrium is much smaller than the time scale of the observer, i.e., $m_1^{(1)}$, $m_2^{(1)}$, $\dot{m}_1^{(1)}$, $\dot{m}_2^{(1)}$ may be mutually independent). Thus, by usual arguments (Lemma A. 5.1), we obtain from (2.124) the identities

$$(\partial \tilde{F}^{(1)}/\partial T) + (\partial \tilde{F}^{(2)}/\partial T) = -S \tag{2.127}$$

$$\partial \tilde{F}^{(1)}/\partial V^{(1)} = \partial \tilde{F}^{(2)}/\partial V^{(2)} = -P \tag{2.128}$$

$$g_1^{(1)} = g_1^{(2)}, \quad g_2^{(1)} = g_2^{(2)} \tag{2.129}$$

where the last Eqs. (2.129) are known conditions for phase equilibria: equality of chemical potentials of both constituents in both phases.

In this and preceding Sects. 2.5, 2.4 (and also in Sect. 2.2 in model A) we showed how to obtain some classical results of equilibrium thermodynamics without stability arguments (which use extremes of thermodynamic functions, cf. Sects. 3.8, 4.7) as it is usually done in classical theory. Its modern version [65, 71, 72] give not only these results but also stability of equilibrium phases (through conditions like (3.256), (3.257)); moreover, the Gibbs phase rule may be properly founded as valid for stable phases [73, 74]. It would be desirable to enlarge these results by some models with memory and mass exchange (e.g., between the phases and by obtaining the equality of their temperatures and pressures in equilibrium). But (a sufficiently general) evolution equation (like (2.86)) is not known and moreover the main problem is how to formulate (or interpret) the entropy inequality for an open system, i.e., when heat and mass are simultaneously exchanged (cf. Rems. 14 in this chapter, 11 in Chap. 4).

Summary. The last Section illustrating the basics of rational thermodynamics shows how phase equilibria can be treated by this methodology. Constitutive equations should be modified to describe the effects of different phases, see (2.107)–(2.109). Traditional condition of phase equilibrium in terms of chemical potentials was derived, (2.116) or (2.129).

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Chapter 3
Continuum Thermodynamics of Single Fluid

In this chapter, we advance our exposition of rational thermodynamics further. The uniformity is abandoned and the description of space effects enters the scene. To keep the explanation simple, we deal with the rational thermodynamics of a single (pure) substance only (i.e., a substance composed of only one constituent as opposed to many constituent substances—mixtures—discussed in the following Chap. 4) and confine our discussion to fluids. We thus study properties changing not only in time but also in the space, but in such a way that the discrete structure of matter may be ignored. That is, we use the methods of continuum (thermo)mechanics by reducing properly the space scale (in comparison with uniform bodies of Chap. 2). On the other hand, the timescale will be similar to that in Chap. 2, i.e., we confine ourselves only to materials with differential memory. Finally, we discuss the linearized case, which is the most important model in applications, in the subsequent chapters of this book.[1]

3.1 Kinematics of Continua

First, we review some basic concepts from deformation theory; although they are not needed in most applications for fluids they are necessary to develop and understand the general theory [6–13].

We study the *body* (composed of a single substance) and its *parts* which we perceive through their *configurations* (connected region in three-dimensional Euclidean space), which this body (or its parts) occupies or may occupy in the space.

---

[1] For simplicity we do not discuss bodies in which there exist surfaces of discontinuity even though such models are very important in chemical engineering, e.g., they model phase boundaries, surface chemical reactions, or shock waves. But even in such simplified models (ignoring specific surface phenomena like surface tension) [1, 2], we obtain the important results of phase equilibria (like equality of chemical potentials in bulk phases, cf. Sect. 2.5, which may be generalized to Eshelby tensors of chemical potentials, cf. Rem. 38, [2, 3]). Further generalization with surface phenomena uses *configurational forces* (in fluids these are chemical potentials related to unit volume) see [4, 5].

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We select one arbitrary configuration as a *reference configuration* (we denote it simply as a “reference”) and radius vectors of points in such reference, **X**, we call the *particles* of the body (identified with their positions).[2]

The motion of the body is described mathematically as the time succession of the *actual* configurations in real space. Namely, vector **x** (relative to *frame* discussed in Sect. 3.2) gives the position of particle, **X**, in the instant t through the vector function $\underline{\chi}$ called the *motion* or *deformation function* as

$$\mathbf{x} = \underline{\chi}(\mathbf{X}, t)\ , \quad x^i = \chi^i(X^J, t) \quad i, J = 1, 2, 3 \tag{3.1}$$

The second expression is given in the component form (which is a concise form of $x^i = \chi^i(X^1, X^2, X^3, t)$). For simplicity, we use for the reference and actual configurations Cartesian coordinates only which need not coincide; therefore, we denote referential or actual (spatial) components by great or small upper Latin indices respectively. Motion (3.1) therefore assigns to every particle **X** its place **x** in the actual configuration in the instant t. A given body or its part contains in all its actual configurations the same particles (as in reference). For a given particle, the **X** gives (3.1) its trajectory. A simple example of (3.1) is the rigid motion in Rem. 5, others (shear, volume expansion, etc.) may be easily written [9, 12, 14]. For simplicity, we assume that function (3.1) is smooth (continuous and differentiable in both variables) and invertible for **X**

$$\mathbf{X} = \underline{\chi}^{-1}(\mathbf{x}, t) \tag{3.2}$$

Therefore, two particles cannot be present at the same place and conversely; we exclude from description such phenomena as a tearing or a penetrating of the bodies, destruction and origin of new particles and trajectories, crossing trajectories, etc. A typical quantity ψ we are interested in (which may be scalar, vector, or tensor) is a field, i.e.,

$$\psi = \psi(\mathbf{x}, t) \tag{3.3}$$

$$\psi = \psi(\mathbf{X}, t) \tag{3.4}$$

which are connected through (3.1) and (3.2). Using (3.3) we speak about *space* or *actual* (or *Euler*) description and using (3.4) we speak about *material* or *referential*,

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[2] From a molecular point of view such a “macroscopic” particle **X** contains a great number of molecules.

We fix this reference once and for all, but in the general theory the change in this reference may be used to describe the symmetry inherent to the material of the body; in the special case it may be used for the definition of fluid (cf. Sect. 3.5 and Rem. 30).

In some continuum theories of more complicated models (e.g., micromorphic or microcontinuous) **X** may have some inner structure (cf. Rem. 26).

(or *Lagrange*) description of the field for quantity ψ. The time or space derivative in space description (3.3) we denote $\partial\psi/\partial t$ or gradψ (in components $\partial\psi/\partial x^i$), respectively, the time derivative in referential description (3.4) we denote by a dot

$$\dot{\psi} = \frac{\partial\psi(\mathbf{X}, t)}{\partial t} \tag{3.5}$$

and call it the *material* or *substantial* (time) derivative. This quantity expresses the change of ψ in time along the trajectory of the chosen particle. Gradient in the referential description we denote as Grad:

$$\mathrm{Grad}\psi = \frac{\partial\psi(\mathbf{X}, t)}{\partial\mathbf{X}} \tag{3.6}$$

We define the *velocity* **v** of a particle as the time (material) derivative of the motion (3.1)

$$\mathbf{v} \equiv \partial\underline{\chi}/\partial\mathbf{t} = \dot{\underline{\chi}} \tag{3.7}$$

From (3.1), (3.3), (3.5), and (3.7), it follows for material derivative

$$\dot{\psi} = \frac{\partial\psi}{\partial t} + v^i\frac{\partial\psi}{\partial x^i} = \frac{\partial\psi}{\partial t} + \mathbf{v}.\mathrm{grad}\psi \tag{3.8}$$

where the second expression is valid for scalar ψ (dot in r.h.s. denotes the scalar product); for vector ψ^j

$$\dot{\psi}^j = \frac{\partial\psi^j}{\partial t} + v^i\frac{\partial\psi^j}{\partial x^i} \tag{3.9}$$

Here we use the *summation rule*: we sum through the repeating indexes, e.g.,

$$v^i\frac{\partial\psi^j}{\partial x^i} = \sum_{i=1}^{3} v^i\frac{\partial\psi^j}{\partial x^i}$$

Deformation gradient **F** is a derivative of a motion $\underline{\chi}$ with respect to **X**

$$\mathbf{F} = \frac{\partial\underline{\chi}}{\partial\mathbf{X}}, \quad F^{iJ} = \frac{\partial\chi^i}{\partial X^J} \tag{3.10}$$

It is a tensor of the second order[3] which describes changes in the mutual position of two close particles during the change of configuration from reference to actual one as it is seen from

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[3] Defined in the following Rem. 4 generalized here in a (generally) different Cartesian system (here, a space and referential one). Then, e.g., the matrix of $\mathbf{F} = \mathbf{1}$ need not be the unit one (Kronecker delta), but a so-called shifter; cf. e.g. [9, 15]. Here, for simplicity, both Cartesian systems are mostly chosen as the same.

$$\mathrm{d}\mathbf{x} = \mathbf{F}\,\mathrm{d}\mathbf{X} \tag{3.11}$$

Because of the invertibility of motion

$$J \equiv \mid \mathrm{det}\mathbf{F} \mid > 0 \tag{3.12}$$

and inverse of $\mathbf{F}$, denoted by $\mathbf{F^{-1}}$ (in components $\overset{-1}{F}{}^{Ji}$ is a gradient of χ^{-1} (3.2)). We note that

$$\mathrm{Grad}\psi = (\mathrm{grad}\psi)\mathbf{F} \tag{3.13}$$

Velocity gradient $\mathbf{L}$ is defined by

$$\mathbf{L} = \mathrm{grad}\mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1} \tag{3.14}$$

where the second relation follows from (3.6), (3.4) and (3.2). Symmetric or skew-symmetric parts of velocity gradient

$$\mathbf{D} \equiv \frac{1}{2}(\mathbf{L} + \mathbf{L}^T), \quad \mathbf{W} \equiv \frac{1}{2}(\mathbf{L} - \mathbf{L}^T), \quad \mathbf{L} = \mathbf{D} + \mathbf{W} \tag{3.15}$$

(where superscript T means transposition) we call *stretching* (or *rate of deformation*) $\mathbf{D}$ or *spin* $\mathbf{W}$ respectively. We note that (div and tr are divergence and trace, respectively)

$$\mathrm{div}\mathbf{v} = \mathrm{tr}\mathbf{L} = \mathrm{tr}\mathbf{D} \tag{3.16}$$

Euler's relation is

$$\dot{J} = J\mathrm{div}\mathbf{v} \tag{3.17}$$

which follows from (3.11), (3.12), (3.16) and from the properties of second order tensor function. [4]

---

[4] Tensors of 2nd order $\mathbf{A}$ are linear transformations (matrix 3 × 3) of vector $\mathbf{a}$ to vector $\mathbf{b}$

$$\mathbf{b} = \mathbf{A}\mathbf{a}$$
$$b^i = A^{ij}a^j \qquad (a)$$

where the second expression is in Cartesian components (with summation rule of course).

But vectors and tensors are more than matrices 3×1 and 3×3: changing (Cartesian) coordinates by orthogonal matrix Q^{kl} (cf. Rem. 8) the components b^i of vector $\mathbf{b}$ transforms into new (starred) components $\overset{*}{b}{}^{j}$ of the same vector $\mathbf{b}$ by

$$\overset{*}{b}{}^{j} = Q^{ji}b^i \qquad (b)$$

That is, $\mathbf{b}$ is the same "arrow" looked at from these different (starred and original) coordinates. Transformation (b) is valid for the usual *polar* vectors (less usual *axial* vectors, e.g., those obtainable by vector product [16], are discussed in Rem. 10). Similarly, the components A^{ij}

A motion is said to be *rigid* if the distances between the particles do not change in time.[5] *Killing's theorem* asserts that motion of the body is rigid if and only if stretching is zero in all its particles

$$\mathbf{D} = \mathbf{0} \tag{3.18}$$

This follows from the definition of rigid motion (3.11)–(3.13) and from the very definition of material derivative (quadratic form with skew-symmetric tensor $\mathbf{W}$ is zero):

$$0 = \dot{\overline{\mid \mathrm{d}\mathbf{x} \mid^2}} = \dot{\overline{\mathrm{d}\mathbf{x}.\mathrm{d}\mathbf{x}}} = 2\dot{\overline{\mathrm{d}\mathbf{x}}}.\mathrm{d}\mathbf{x} = 2\dot{\mathbf{F}}\mathrm{d}\mathbf{X}.\mathrm{d}\mathbf{x} = 2\mathbf{L}\mathrm{d}\mathbf{x}.\mathrm{d}\mathbf{x} = 2\mathbf{D}\mathrm{d}\mathbf{x}.\mathrm{d}\mathbf{x}$$

As a *material volume* we denote such volume which contains the same particles during the motion. Therefore, configurations of a given body or its parts occupy material volumes. Similarly, material surface and material line are defined. It follows from properties of (3.1) that material volume, surface, or line are those in any

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(Footnote 4 continued)

of tensor $\mathbf{A}$ transform into starred components $\overset{*}{A}{}^{kl}$ of the same $\mathbf{A}$ by

$$\overset{*}{A}{}^{kl} = Q^{ki} A^{ij} Q^{lj} \qquad (c)$$

(namely, transformation (c) guarantees linear transformation (a) with both vectors transformed by (b)).

Relations (b), (c) inspire in Sect. 3.2 the more general notion of changes of frame and frame indifference, cf. (3.31), (3.32).

Generalizations of tensors for nonCartesian coordinates see, e.g., [7, 16, 17] and Appendix A.4. Similar to matrices (3×3), tensors may be symmetric, skew-symmetric, etc., about vector and outer products. See Rems. 6, 16.

If $\mathbf{A} = \mathbf{A}(t)$ is a *tensor* function of the scalar t then $\det\mathbf{A}$ is the scalar function of t. Its derivative is

$$\frac{\mathrm{d}\det\mathbf{A}}{\mathrm{d}t} = \frac{\partial\det\mathbf{A}}{\partial A^{ij}}\frac{\mathrm{d}A^{ij}}{\mathrm{d}t} = (\det\mathbf{A})\frac{\mathrm{d}A^{ij}}{\mathrm{d}t}\overset{-1}{A}{}^{ji} \qquad (d)$$

where we use the following derivative of $\det\mathbf{A}$ with respect to its components (using its development according to line)

$$\frac{\partial\det\mathbf{A}}{\partial A^{ij}} = (\det\mathbf{A})\overset{-1}{A}{}^{ji} \qquad (e)$$

[5] Rigid motion (3.1) has the general form

$$\mathbf{x} = \underline{\Theta}\mathbf{X} + \underline{\gamma}$$

where $\underline{\Theta}(t)$ and $\underline{\gamma}(t)$ are some orthogonal (Rem. 8) and vector functions of time t respectively. This follows from the preservation of distances of any two particles in reference $\mathbf{X}, \mathbf{X}_0$ and in actual configurations (positions $\mathbf{x}, \mathbf{x}_0$) in rigid motion, i.e.,

$$\mathbf{x} - \mathbf{x}_0 = \underline{\Theta}(\mathbf{X} - \mathbf{X}_0)$$

where orthogonal $\underline{\Theta}$ and $\mathbf{x}_0$ are arbitrary time function, cf. analogous deduction of (3.25).

configuration even if their magnitude or shape changes. An element of material volume $\mathrm{d}V$ in reference configuration transforms into an element of material volume $\mathrm{d}v$ in actual configuration by

$$\mathrm{d}v = J\,\mathrm{d}V \tag{3.19}$$

Indeed, if we express such elements as parallepides with $\mathrm{d}\mathbf{X}_a$ or $\mathrm{d}\mathbf{x}_a$ $(a = 1, 2, 3)$ in reference or actual configurations, respectively, their volumes are given by triple products

$$\mathrm{d}v = \mid \varepsilon^{ijk}\mathrm{d}x_1^i \mathrm{d}x_2^j \mathrm{d}x_3^k \mid , \quad \mathrm{d}V = \mid \varepsilon^{JKL}\mathrm{d}X_1^J \mathrm{d}X_2^K \mathrm{d}X_3^L \mid \tag{3.20}$$

where ε^{ijk} (or ε^{JKL}) is the *permutation* or *Levi-Civita symbol*.[6]

Inserting (3.11) into (3.20)$_1$ (both elementary volumes contain the same particles) and using the property of det**A** from the end of Remark 6, Eq. (3.19) follows.

If $\psi(\mathbf{x}, t)$ has a meaning of the density of some quantity Ψ, then (at given instant)

$$\Psi = \int_{\mathcal{V}} \psi(\mathbf{x}, t)\,\mathrm{d}v = \int_{\mathcal{V}_0} \psi(\mathbf{X}, t)\,J\,\mathrm{d}V = \Psi(t) \tag{3.21}$$

where $\mathcal{V}_0$ is a material volume in reference configuration which in an actual one takes the material volume $\mathcal{V}$. The relation (3.21)$_2$ expresses the change of integral variables from actual to reference configuration.[7]

Now we can use the material derivative on the material volume: it is a time derivative of quantity (3.21) when the number of particles is constant

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[6] (In fact a cubic matrix) defined by

$$\varepsilon^{123} = \varepsilon^{231} = \varepsilon^{312} = 1$$

$$\varepsilon^{132} = \varepsilon^{213} = \varepsilon^{321} = -1$$

(the remaining elements of this 3 × 3 × 3 matrix are zero)

From this definition, it follows (by direct calculation) the following properties of the permutation symbol (and its relation to Kronecker delta δ^{ij})

$$\varepsilon^{ijk} = \varepsilon^{jki} = \varepsilon^{kij} = -\varepsilon^{kji} = -\varepsilon^{jik} = -\varepsilon^{ikj}$$

(such “cyclic” permutation does not change its value)

$$\varepsilon^{ijk}\varepsilon^{ilm} = \delta^{jl}\delta^{km} - \delta^{jm}\delta^{kl} \ , \quad \varepsilon^{ijk}\varepsilon^{jkn} = 2\delta^{in} \ , \quad \varepsilon^{ijk}\varepsilon^{ijk} = 6$$

With this symbol we can express the *vector* and *triple products* as ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are vectors)

$$(\mathbf{a} \times \mathbf{b})^i = \varepsilon^{ijk}a^j b^k \ , \quad \mathbf{c}.(\mathbf{a} \times \mathbf{b}) = \varepsilon^{ijk}c^i a^j b^k$$

and for the determinant of matrix **A** it is valid that

$$\varepsilon^{ijk}A^{im}A^{jn}A^{kp} = \varepsilon^{mnp}\det\mathbf{A}$$

See also Rems. 4, 10, 16.

[7] The density ψ may be deduced assuming Ψ as primitive and continuous with volume, i.e., when $\mathcal{V} \to 0$ also $\Psi \to 0$ [7, 10, 18–20].

$$
\begin{aligned}
\overline{\int_{\mathcal{V}} \psi \,\mathrm{d}v}^{\boldsymbol{\cdot}} &= \overline{\int_{\mathcal{V}_0} \psi J \,\mathrm{d}V}^{\boldsymbol{\cdot}} = \int_{\mathcal{V}_0} \dot{\overline{\psi J}} \,\mathrm{d}V = \int_{\mathcal{V}_0} (\dot{\psi} J + \dot{J} \psi) \,\mathrm{d}V \\
&= \int_{\mathcal{V}_0} (\dot{\psi} + \psi \mathrm{div}\mathbf{v}) J \,\mathrm{d}V = \int_{\mathcal{V}} (\dot{\psi} + \psi \mathrm{div}\mathbf{v}) \,\mathrm{d}v = \int_{\mathcal{V}} \frac{\partial \psi}{\partial t} \,\mathrm{d}v \\
&\quad + \int_{\mathcal{V}} (\mathrm{div}\, \psi \mathbf{v}) \,\mathrm{d}v
\end{aligned} \tag{3.22}
$$

Here (3.19), (3.21), the independence of the reference configuration on time, (3.17), (3.8) were used.

Using Gauss' theorem

$$
\int_{\mathcal{V}} (\mathrm{div}\, \psi \mathbf{v}) \,\mathrm{d}v = \int_{\partial \mathcal{V}} \psi \mathbf{v}.\mathbf{n} \,\mathrm{d}a \tag{3.23}
$$

(where $\mathbf{n}$ is an outside normal and $\mathrm{d}a$ is an element of the material surface $\partial \mathcal{V}$ of material volume $\mathcal{V}$ in actual configuration) we obtain from (3.22) the *Reynolds theorem*

$$
\overline{\int_{\mathcal{V}} \psi \,\mathrm{d}v}^{\boldsymbol{\cdot}} = \int_{\mathcal{V}} \frac{\partial \psi}{\partial t} \,\mathrm{d}v + \int_{\partial \mathcal{V}} \psi \mathbf{v}.\mathbf{n} \,\mathrm{d}a = \frac{\mathrm{d}}{\mathrm{d}t} \int_{V} \psi \,\mathrm{d}v + \int_{\partial V} \psi \mathbf{v}.\mathbf{n} \,\mathrm{d}a \tag{3.24}
$$

where the last expression follows for the fixed volume V with fixed surface ∂V (i.e., this geometrical object is not changed in time) which at a given instant coincides with material volume $\mathcal{V}$.

Therefore, the Reynolds theorem asserts that the rate of change of quantity ψ in a material volume $\mathcal{V}$ in a given instant is equal to the rate of its change in a fixed volume V (coincided with $\mathcal{V}$ in that instant) and the flow of such a quantity through its fixed surface ∂V. Consequently, it expresses the natural change from closed to open system in continuum theory where ψ is sufficiently smooth and $\mathcal{V}$ is a volume of any part inside the body (cf. solidification principle in Sect. 3.3 and Rems. 14 in Chap. 2, 23 in this chapter, 11 in Chap. 4). The Reynolds theorem may be generalized on a surface moving with arbitrary fictive velocity [13].

Summary. Mathematical basis for the description of space changes or effects is presented. They are based on calculus with vectors and tensors (usually of the second order) and their functions. The most important concepts or quantities are the two derivatives—time and space, cf. (3.5) and the notation above it, and (3.8)—the velocity gradient (3.14) and its decomposition (3.15), and the density of some physical quantity (3.21). It is also essential to realize the difference between the

---

(Footnote 7 continued)
The additivity of Ψ in volume (Ψ for volume consisting of two separate volumes is the sum of Ψ of each separate volume) follows from (3.21). Such quantities Ψ are usual in continuum thermomechanics, cf. mass, energy, entropy, etc.; using mass and mass density we can introduce specific quantities instead of densities (cf. (3.66) and Sects. 3.4, 4.6) and extensivity instead of additivity (cf. Sects. 1.2, 2.4). Similarly, [19, 20] there are quantities continuous in surface with surface densities (cf. (3.58), (3.99) and Rems. 14, 18).

actual and the material volume (see the paragraph above (3.19) and to understand related derivatives of volume integrals in (3.22) and (3.24)).

3.2 Change of Frame

It was assumed so far that the frame in which we observe our thermodynamic system in actual configuration is fixed. *Frame* is a set of objects the mutual distances of which do not change (like the walls of a laboratory, arms of the rotor of a centrifuge, distant stars, or any body in rigid motion) and which are combined with some clock. An observed *event* in the actual configuration is characterized by a place (position vector) $\mathbf{x}$ and an instant t and the same event may be described in a different "starred" frame by place $\mathbf{x}^*$ and instant t^*. Some frames—those which are inertial—play a special role (see below and Sect. 3.3), but more important is the change of frame in actual configurations (reference configuration is not influenced by it) [7, 10, 12, 21–24] (for generalization, see end of Sect. 3.4).

Change of frame from the original frame to a new "starred" one is given by

$$\mathbf{x}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{x} \ , \quad \overset{*}{x}{}^{j} = c^j(t) + Q^{ji}(t)x^i \tag{3.25}$$

$$t^* = t + b \tag{3.26}$$

Here, the function $\mathbf{c}(t)$ or $\mathbf{Q}(t)$ of time t (cf. under (3.119)) give vectors or orthogonal tensors,[8] respectively, and b is a scalar constant. In actual reference, the x^i or $\overset{*}{x}{}^{j}$ are Cartesian components of the same event in a Cartesian coordinate system fixed with an old (original) or new (starred) frame, respectively: in the Cartesian system of a new frame at given instant t, c^j and $Q^{ji}x^i$ are the positions of origin and of event (seen in the Cartesian system of the old frame), respectively, cf. Fig. 3.1.

Transformations (3.25) and (3.26) follow from the expected properties of the change of frame in classical physics: the distance between two simultaneous events

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[8] Orthogonal tensor $\mathbf{Q}$ transforms any vector $\mathbf{a}$ into vector $\mathbf{Qa}$ of the same length $\mathbf{a}.\mathbf{a} = \mathbf{Qa}.\mathbf{Qa}$. Then the basic properties of orthogonal tensor $\mathbf{Q}$ follow:

$$\mathbf{Q}^T\mathbf{Q} = \mathbf{Q}\mathbf{Q}^T = \mathbf{1} \ , \quad \text{in components} \quad Q^{ki}Q^{kj} = Q^{ik}Q^{jk} = \delta^{ij}$$

$$\mathbf{Q}^{-1} = \mathbf{Q}^T \ , \quad (\det\mathbf{Q})^2 = 1$$

An example of the orthogonal tensor is (3.29).

Orthogonal transformations $\mathbf{Q}$ form a group: generally (cf. [9, 15, 16]) a set of elements with a defined "product" giving another element from this set (here a matrix product of two orthogonal tensors giving again an orthogonal tensor) with inverse and unit elements (here $\mathbf{Q}^T$ and $\mathbf{1}$ respectively). This group is called a *full orthogonal group* with det $\mathbf{Q} = \pm 1$ which expresses rotation or/and reflection. A *proper orthogonal group* forms its subgroup with det $\mathbf{Q} = +1$ (a subgroup is a subset with group properties again).

The corresponding orthogonal matrix Q^{ij} may be also used for rotation (and/or inversion) of Cartesian coordinates, cf. (b), (c) in Rem. 4 and Rem. 10.

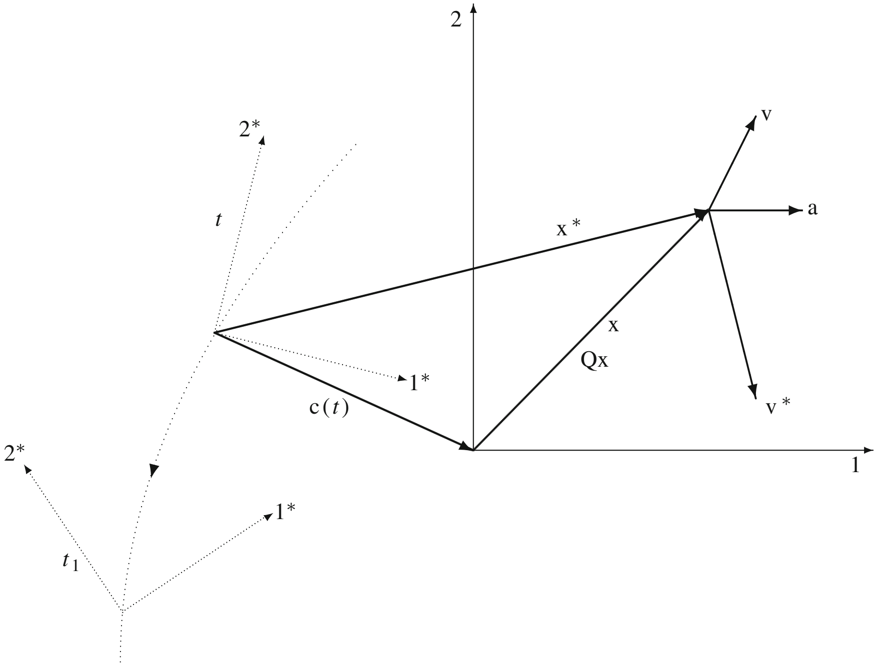

Fig. 3.1 On relationships between two frames

is preserved and the time interval between two events and the time order of events is left unchanged. Indeed [12, 14, 22], let us consider two simultaneous events taking place $\mathbf{x}$ and $\mathbf{x}_0$ in the original frame and $\mathbf{x}^*$ and $\mathbf{x}_0^*$ in the new, "starred" frame. Because their distance must be preserved $| \mathbf{x} - \mathbf{x}_0 | = | \mathbf{x}^* - \mathbf{x}_0^* |$, vectors in this equation must be connected by orthogonal transformation $\mathbf{Q}$ (see Rem. 8), i.e., $\mathbf{x}^* - \mathbf{x}_0^* = \mathbf{Q}(\mathbf{x} - \mathbf{x}_0)$. Taking $\mathbf{c} \equiv \mathbf{x}_0^* - \mathbf{Q}\mathbf{x}_0$ we obtain (3.25) because both frames are moving each to the other generally not steadily and therefore, $\mathbf{c}$ and $\mathbf{Q}$ are functions of time (see Fig. 3.1) (this deduction is analogous to the deduction of rigid motion in Rem. 5, where distances are also preserved, see also discussion of (3.223) and Rem. 40). Further, let us consider two arbitrary events, the earlier and latter having their instants t_0 and t or t_0^* and t^* in the original or "starred" frame, respectively. From the preservation of the time interval, we have $| t - t_0 | = | t^* - t_0^* |$ and from the preservation of the time order we have $t^* > t_0^*$ because of $t > t_0$. Then preceding equality gives $t^* - t_0^* = t - t_0$, i.e., (3.26) if we choose $b \equiv t_0^* - t_0$.

It is evident from (3.25) and (3.26) that b is the time shift in the origin of the time axes, $\mathbf{c}$ is the shift in the origins of the Cartesian systems and $\mathbf{Q}$ (from full orthogonal group, cf. Rem. 8) expresses the rotation ($\det\mathbf{Q} = 1$) or reflection ($\det\mathbf{Q} = -1$) of the starred frame relative to the original one.[9] We also note the inversions of change

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[9] Use of a full or proper orthogonal group puts the additional property of preservation of right- or left handedness on the change of frame; some authors [12, 23–26] (motivated usually

of frame (3.25), (3.26)

$$\mathbf{x} = \mathbf{Q}^T(t)(\mathbf{x}^* - \mathbf{c}(t)) \tag{3.27}$$

$$t = t^* - b \tag{3.28}$$

The change of frames (3.25), (3.26) and its consequences below is also demonstrated in the following example of centrifuge: We take as an original frame the walls of the laboratory and as a new "starred" frame the rotor of centrifuge, having a constant number $\omega/2\pi$ of revolutions in the time unit (ω is the angular velocity) and rotating from the first to the second axis around the third axis of original frame. Here, (3.25) is

$$\overset{*}{x}{}^{j} = Q^{ji}(t)x^i \ , \qquad \| \, Q^{ij}(t) \, \| = \begin{pmatrix} \cos\omega t & \sin\omega t & 0 \\ -\sin\omega t & \cos\omega t & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{3.29}$$

with corresponding orthogonal time function. There is also no shift in space and time origins: $c^j(t) \equiv 0$ and $b = 0$ in (3.25) and (3.26) respectively. Other results concerning centrifuge are noted below (3.41) and below (3.46).

The special case of (3.25) is the *Galileo transformation* where function $\mathbf{c}(t)$ is linear and $\mathbf{Q}$ is a constant, i.e., frames are moving each to the other with constant velocity and differ by a constant angle (or also by inversion). A special set of frames must be noted—*inertial frames* which contain the frame formed by distant stars and those obtained from it by Galileo transformation (cf. Sects. 3.3, 4.3; in many applications the frame fixed with earth surface may be taken as an approximately inertial one). Their typical property is zero inertial acceleration (3.48).

A more special case with $\mathbf{c} = \mathbf{o}$ and $\mathbf{Q}$ constant is physically trivial because it expresses the change of coordinate system only. Therefore, a change of coordinates (in Rem. 4) is not the same as the much more general change of frame (where time and its transformation (3.26) and shifts in origins are moreover considered).

Many quantities used in the following considerations are called *objective* or *frame-indifferent*, if they are "invariant" in the change of frame (3.25), (3.26) as follows (because this change contains rotations and/or inversions of corresponding Cartesian systems as a very special case (cf. Fig. 3.1), the following definition is motivated by (*b*), (*c*) of Rem. 4):

Objective or frame-indifferent scalar a, vector $\mathbf{a}$ and (second order) tensor $\mathbf{A}$ transform by the change of frame on scalar a^*, vector $\mathbf{a}^*$ and tensor $\mathbf{A}^*$ as follows:

$$a^* = a \tag{3.30}$$

$$\mathbf{a}^* = \mathbf{Q}\mathbf{a} \tag{3.31}$$

(Footnote 9 continued)
by nonmechanical arguments) confine (3.25) only to the rotations. This problem seems not to have been settled. Because it has no influence on the linear models preferred here, we use in the following the full orthogonal group, see Appendix A.2.

$$\mathbf{A}^* = \mathbf{Q}\mathbf{A}\mathbf{Q}^T \tag{3.32}$$

This is because an objective scalar a does not change its value, objective vector $\mathbf{a}$ is the same "arrow" looked at from different frames and, ultimately, an objective tensor $\mathbf{A}$ transforms an objective vector (say $\mathbf{a}_1$) to an objective vector (say $\mathbf{a}_2$) in all frames: indeed if in the original frame $\mathbf{a}_2 = \mathbf{A}\mathbf{a}_1$ and in the "starred" frame $\mathbf{a}_2^* = \mathbf{A}^*\,\mathbf{a}_1^*$ then by (3.31) we obtain (3.32).

But there are also quantities which are nonobjective, i.e., they do not transform by (3.30)–(3.32) when the frame is changed. Generally, we can find the transformation of any quantity at the transformation of $t, \mathbf{x}$ to $t^*, \mathbf{x}^*$ and vice versa according to (3.25), (3.26), (3.27), (3.28), i.e., to decide about objectivity or nonobjectivity (frame indifference or not) according to the following nearly obvious precepts:

- The reference configuration and its properties (like particles and bodies in reference) are not influenced by changing of frame (this affects actual references only).
- For primitives we must decide about their objectivity (frame indifference) a priori (e.g., it may be expected that primitives of this Chap. 3 connected with the body, like density, temperature, internal energy, entropy, etc., are objective).
- For the other defined quantities, we decide from their definitions assuming that the definition itself is not influenced by change of frame (i.e., definitions are the same in any frame). Not only those, but in fact all relations between quantities (e.g., those from Sect. 3.1) are valid also for new (starred) frame, i.e., for new starred quantities if we use $t^*, \mathbf{x}^*$ (3.25), (3.26) simultaneously. This is evident from the fact that the frame used for actual reference (say in Sect. 3.1) was chosen quite arbitrarily. Cf. also end of this section.

Applying the change of frame (3.25), (3.26) to the above definitions of Sect. 3.1 and, using these precepts, we can decide about objectivity or nonobjectivity (frame indifference or not) of the following quantities (more detailed proofs of some of them are written in the footnote-sized script below); the remainder from the next sections may be proved analogously.

It follows from (3.25), (3.26) that time t and place $\mathbf{x}$ are not objective because these scalar and vector do not transform as prescribed by (3.30), (3.31) (but time and space intervals are objective).

Motion (3.1) transforms as

$$\underline{\chi}^*(\mathbf{X}, \mathbf{t}^*) = \mathbf{c}(\mathbf{t}) + \mathbf{Q}(\mathbf{t})\,\underline{\chi}(\mathbf{X}, \mathbf{t}) \tag{3.33}$$

and therefore it is not an objective vector (cf. objective (3.31), (3.56))

Proof Motion (3.1) in the starred frame is by (3.25), (3.28)

$$\overset{*}{\chi}{}^{j}(\mathbf{X}, t^*) = \overset{*}{x}{}^{j} = c^j(t^* - b) + Q^{ji}(t^* - b)\,\chi^i(\mathbf{X}, t^* - b) \tag{3.34}$$

(particle $\mathbf{X}$ is not influenced) which is nonobjective (3.33). Q.E.D.

Velocity $\mathbf{v}$ is transformed as

$$\mathbf{v}^* = \mathbf{Q}\mathbf{v} + \dot{\mathbf{c}} + \dot{\mathbf{Q}}\mathbf{x} \tag{3.35}$$

and therefore it is not an objective vector.

Proof Velocity (3.7) in the new starred frame is (using (3.34))

$$\begin{aligned}
\overset{*}{v}{}^j &\equiv \frac{\partial \overset{*}{\chi}{}^j(X^J, t^*)}{\partial t^*} = \frac{\partial (c^j(t^* - b) + Q^{ji}(t^* - b)\chi^i(X^J, t^* - b))}{\partial t^*} \\
&= \frac{\mathrm{d}c^j(t)}{\mathrm{d}t}\frac{\mathrm{d}(t^* - b)}{\mathrm{d}t^*} + \frac{\mathrm{d}Q^{ji}(t)}{\mathrm{d}t}\frac{\mathrm{d}(t^* - b)}{\mathrm{d}t^*}\chi^i(X^J, t) + Q^{ji}(t)\frac{\partial \chi^i(X^J, t)}{\partial t}\frac{\mathrm{d}(t^* - b)}{\mathrm{d}t^*} \\
&= Q^{ji}(t)v^i(X^J, t) + \dot{c}^j(t) + \dot{Q}^{ji}(t)\chi^i(X^J, t)
\end{aligned} \tag{3.36}$$

which is (3.35) by (3.1); here

$$\dot{c}^j = \frac{\mathrm{d}c^j(t)}{\mathrm{d}t}, \quad \dot{Q}^{ji} = \frac{\mathrm{d}Q^{ji}(t)}{\mathrm{d}t}, \quad \frac{\mathrm{d}(t^* - b)}{\mathrm{d}t^*} = 1 \tag{3.37}$$

have been used. Q.E.D.

This (3.35) may be written by (3.27)

$$\mathbf{v}^* = \mathbf{Q}\mathbf{v} + \dot{\mathbf{c}} + \underline{\boldsymbol{\Omega}}(\mathbf{x}^* - \mathbf{c}) \tag{3.38}$$

where (tensor of) angular velocity $\underline{\Omega}$ (of original frame relative to the new one) is defined as

$$\underline{\Omega} \equiv \dot{\mathbf{Q}}\mathbf{Q}^T \tag{3.39}$$

and this tensor is skew-symmetric (this follows from time derivative of $\mathbf{Q}\mathbf{Q}^T = 1$, namely $\dot{\mathbf{Q}}\mathbf{Q}^T + \mathbf{Q}\dot{\mathbf{Q}}^T = \dot{\mathbf{Q}}\mathbf{Q}^T + (\dot{\mathbf{Q}}\mathbf{Q}^T)^T = \mathbf{0}$ which is zero tensor).

By inversion of (3.38) and by (3.39), (3.25), Rem. 8

$$\mathbf{v} = \mathbf{Q}^{\mathbf{T}}\mathbf{v}^* - \mathbf{Q}^{\mathbf{T}}\dot{\mathbf{c}} + \overset{*}{\underline{\boldsymbol{\Omega}}}\,\mathbf{x} \tag{3.40}$$

where we define the (tensor of) angular velocity $\overset{*}{\underline{\Omega}}$ (of the new frame relative to the original one) by

$$\overset{*}{\underline{\Omega}} = -\mathbf{Q}^T\underline{\Omega}\mathbf{Q} \tag{3.41}$$

The origin of the name "angular velocity" for (3.39), (3.41) may be seen in the example of centrifuge (3.29): Calculation of tensors of angular velocities (3.39), (3.41) gives for this example $\Omega^{12} = \overset{*}{\Omega}{}^{21} = \omega = -\overset{*}{\Omega}{}^{12} = -\Omega^{21}$ (their other components are zero). Define the vector of angular velocity $\underline{\omega}$ as axial one[10] corresponding to skew-symmetric tensor $\underline{\overset{*}{\Omega}}$ according to (b) in Rem. 10 as $\omega^i = (1/2)\varepsilon^{ijk}\overset{*}{\Omega}{}^{kj}$. This axial vector (changing parity it changes the sign) has only one nonzero component $\omega^3 = \omega$. From (3.40) for the point fixed on the rotor $\mathbf{v}^* = \mathbf{o}$ (we consider $\mathbf{x}$ perpendicular to the rotation axis, $\mathbf{c}(\mathbf{t}) \equiv \mathbf{o}$) we obtain

$$\mathbf{v} = \underline{\overset{*}{\Omega}}\,\mathbf{x}\,, \quad \mathbf{v} = \underline{\omega}\times\mathbf{x} \tag{3.42}$$

where the equivalent second relation (using the vector product) follows from (c) in Rem. 10 and the vector product noted in Rem. 6. This is in accord with the name of $\underline{\overset{*}{\Omega}}$ because $\underline{\omega}$ is the vector of angular velocity of new frame (centrifuge) relative to the old one (laboratory).

Similarly, for point fixed in laboratory ($\mathbf{v} = \mathbf{0}$) we have by (3.38)

$$\mathbf{v}^* = \underline{\Omega}\,\mathbf{x}^* \qquad \text{or} \qquad \mathbf{v}^* = -\underline{\omega}\times\mathbf{x}^* \tag{3.43}$$

($-\underline{\omega}$ is an axial vector equivalent to $\underline{\Omega}$: $\Omega^{jk} = -\overset{*}{\Omega}{}^{jk} = -\omega^i\varepsilon^{ikj}$). Acceleration $\dot{\mathbf{v}}$ is also not objective. Namely, by (3.38)

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[10] As distinct from usual polar vectors which by coordinate changes (characterized by orthogonal matrix Q^{ji}, see Rem. 8) transform by (b) of Rem. 4, the *axial vector* $\mathbf{w}$ is defined by transformation

$$\overset{*}{w}{}^{j} = (\det\mathbf{Q})Q^{ji}w^i \qquad (a)$$

and therefore changes the sign at parity (right-handedness or left-handedness) changes ($\det\mathbf{Q} = -1$, cf. Rem. 8)

Lemma (equivalency of skew-symmetric tensors with axial vectors): For every skew-symmetric tensor (of second order) $\mathbf{W}$ it is possible to define an axial vector $\mathbf{w}$ (both contain three (independent) components) and vice versa by

$$w^i = (1/2)\varepsilon^{ijk}W^{kj} \qquad (b)\,, \quad W^{jk} = w^i\varepsilon^{ikj} \qquad (c)$$

Indeed, the usual coordinate transformation of tensor $\mathbf{W}$ (i.e., of the type (c) in Rem. 4) leads to axiality transformation (a). Namely, (b) must be valid also for the new (starred) coordinate system

$$\overset{*}{w}{}^{i} = (1/2)\varepsilon^{ijk}\overset{*}{W}{}^{kj} = (1/2)\varepsilon^{ijk}Q^{kl}W^{lm}Q^{jm} = (1/2)\varepsilon^{ijk}Q^{kl}w^p\varepsilon^{pml}Q^{jm}$$

which multiplying by Q^{ir} gives

$$\overset{*}{w}{}^{i}Q^{ir} = (1/2)w^p\varepsilon^{pml}\varepsilon^{ijk}Q^{ir}Q^{jm}Q^{kl} = (1/2)w^p\varepsilon^{pml}\varepsilon^{rml}(\det\mathbf{Q}) = (\det\mathbf{Q})w^r$$

where properties of permutation symbol from Rem. 6 were used. Multiplying it by orthogonal Q^{jr} we obtain (a) and therefore $\mathbf{w}$ is an axial vector.

Axiality of $\mathbf{w}$ is automatically achieved by the usual transformation ((c) in Rem. 4) of tensor $\mathbf{W}$. Therefore the skew-symmetric tensors instead of axial vectors and outer product (see Rem. 16) may be used and we do it this way at the moment of momentum balances in the Sects. 3.3, 4.3, cf. [7, 8, 14, 27]. Generalization of this Lemma to third-order tensors, made by M. Šilhavý, is published in Appendix of [28].

$$\dot{\mathbf{v}}^* = \mathbf{Q}\dot{\mathbf{v}} + \mathbf{i}^* \tag{3.44}$$

where $\mathbf{i}^*$ is defined by

$$\mathbf{i}^* \equiv 2\dot{\mathbf{Q}}\mathbf{v} + \ddot{\mathbf{c}} + \ddot{\mathbf{Q}}\mathbf{x} \tag{3.45}$$

Proof From the definition of acceleration in the new, starred frame and by (3.36), (3.28) we have

$$\begin{aligned}
(\dot{v}^j)^* &\equiv \frac{\partial \overset{*}{v}^j(X^J, t^*)}{\partial t^*} \\
&= \frac{\partial (Q^{ji}(t^* - b) v^i(X^J, t^* - b) + \dot{c}^j(t^* - b) \; + \; \dot{Q}^{ji}(t^* - b)\chi^i(X^J, t^* - b))}{\partial t^*} \\
&= Q^{ji}(t)\frac{\partial v^i(X^J, t)}{\partial t} + \frac{\mathrm{d}Q^{ji}(t)}{\mathrm{d}t} v^i(X^J, t) + \frac{\mathrm{d}\dot{c}^j(t)}{\mathrm{d}t} \\
&\quad + \frac{\mathrm{d}\dot{Q}^{ji}(t)}{\mathrm{d}t}\chi^i(X^J, t) + \dot{Q}^{ji}(t)\frac{\partial \chi^i(X^J, t)}{\partial t} \\
&= Q^{ji}\dot{v}^i + 2\dot{Q}^{ji}v^i + \ddot{c}^j + \ddot{Q}^{ji}x^i
\end{aligned}$$

which is (3.44), (3.45) with (3.37) and

$$\ddot{c}^j = \frac{\mathrm{d}\dot{c}^j(t)}{\mathrm{d}t}\,, \quad \ddot{Q}^{ji} = \frac{\mathrm{d}\dot{Q}^{ji}(t)}{\mathrm{d}t}$$

Q.E.D.

This *inertial acceleration* $\mathbf{i}^*$ (perceived in the new, starred frame) may be traditionally rewritten as (using (3.40), (3.41), (3.39), (3.27) and $\dot{\underline{\Omega}} + \underline{\Omega}^2 = \dot{\underline{\Omega}} - \underline{\Omega}\underline{\Omega}^T = \ddot{\mathbf{Q}}\mathbf{Q}^T$)

$$\mathbf{i}^* = 2\underline{\Omega}(\mathbf{v}^* - \dot{\mathbf{c}}) - \underline{\Omega}^2(\mathbf{x}^* - \mathbf{c}) + \dot{\underline{\Omega}}(\mathbf{x}^* - \mathbf{c}) + \ddot{\mathbf{c}} \tag{3.46}$$

The terms on the right-hand side of (3.46) are, subsequently, the Coriolis, centrifugal, and Euler accelerations and the last term is the acceleration of the origin.

For example of centrifuge (3.29) above (angular velocity is constant in time) the inertial acceleration $\mathbf{i}^*$ (3.46) in the place $\mathbf{x}^*$ perpendicular to the rotation axis and fixed with the rotor (starred frame, $\mathbf{v}^* = \mathbf{o}$) is therefore only the centrifugal one (see below (3.43) and Rem. 6)

$$\mathbf{i}^* = -\underline{\Omega}^2\mathbf{x}^* = \omega^2\mathbf{x}^* \tag{3.47}$$

Note that in Galileo transformation ($\mathbf{c}(t)$ linear, $\mathbf{Q}$ constant)

$$\mathbf{i}^* = \mathbf{o} \tag{3.48}$$

This zero inertial acceleration is assumed in the frame fixed with distant stars and therefore also in any inertial frame and at change between them. Therefore, in inertial frames the identity (3.48) is valid and the acceleration $\dot{\mathbf{v}}$ behaves objectively (frame indifferently).

Applying the change of frame (3.25), (3.26) on the further definitions of Sect. 3.1 and using the three precepts above we can decide about their frame indifference (objectivity); those remaining may be proved analogously.

Deformation gradient $\mathbf{F}$ (3.10) is not a frame-indifferent (objective) tensor, because it transforms as

$$\mathbf{F}^* = \mathbf{QF} \tag{3.49}$$

Namely, deformation gradient (3.10) in starred frame transforms by (3.33), (3.28)

$$\begin{aligned}\overset{*}{F}{}^{jJ} &\equiv \partial \overset{*}{\chi}{}^{j}(X^K, t^*)/\partial X^J = \partial(c^j(t^*-b) + Q^{ji}(t^*-b)\chi^i(X^K, t^*-b))/\partial X^J \\ &= Q^{ji}(t)\partial\chi^i(X^K, t)/\partial X^J = Q^{ji}F^{iJ}\end{aligned}$$

But the scalar J defined by (3.12) is the objective one

$$J^* \equiv \mid \det\mathbf{F}^* \mid = \mid \det\mathbf{Q} \mid\mid \det\mathbf{F} \mid = \mid \det\mathbf{F} \mid = J \tag{3.50}$$

Obviously, Grad$\mathbf{F}$ is an objective vector (cf. e.g., [28, 29])

$$(\mathrm{Grad}\mathbf{F})^* = \mathbf{Q}\,\mathrm{Grad}\mathbf{F} \tag{3.51}$$

(at fixed reference, $\mathbf{F}$ and Grad$\mathbf{F}$ may be considered as objective vectors (3.31), cf. (3.122)).

The velocity gradient $\mathbf{L}$ (3.14) is transformed at frame change as

$$\mathbf{L}^* = \mathbf{QLQ}^T + \underline{\Omega} \tag{3.52}$$

and therefore it is not an objective tensor (recall the skew-symmetry of $\underline{\Omega}$ (3.39)).

Proof We write transformation of velocity (3.38) in actual (Euler) description and use (3.27), (3.28):

$$\begin{aligned}\overset{*}{v}{}^i(\overset{*}{x}{}^l, t^*) &= Q^{ik}(t)v^k(x^l, t) + \dot{c}^i(t) + \Omega^{ik}(t)(\overset{*}{x}{}^k - c^k(t)) \\ &= Q^{ik}(t^*-b)v^k(Q^{ml}(t^*-b)(\overset{*}{x}{}^m - c^m(t^*-b)), t^*-b) \\ &\quad + \dot{c}^i(t^*-b) + \Omega^{ik}(t^*-b)(\overset{*}{x}{}^k - c^k(t^*-b))\end{aligned}$$

Using this and starting with definition (3.14) in the new, starred frame we obtain

$$\begin{aligned}\overset{*}{L}{}^{ij}(\overset{*}{x}{}^{l}, t^*) \equiv \frac{\partial \overset{*}{v}{}^{i}(\overset{*}{x}{}^{l}, t^*)}{\partial \overset{*}{x}{}^{j}} &= Q^{ik}(t^*-b)\frac{\partial v^k(Q^{ml}(t^*-b)(\overset{*}{x}{}^{m} - c^m(t^*-b)), t^*-b)}{\partial \overset{*}{x}{}^{j}} \\ &\quad + \Omega^{ik}(t^*-b)\frac{\partial(\overset{*}{x}{}^{k} - c^k(t^*-b))}{\partial \overset{*}{x}{}^{j}} \\ &= Q^{ik}(t)\frac{\partial v^k(x^l,t)}{\partial x^n}\,\frac{\partial(Q^{mn}(t^*-b)(\overset{*}{x}{}^{m} - c^m(t^*-b)))}{\partial \overset{*}{x}{}^{j}} + \Omega^{ik}(t^*-b)\delta^{kj} \\ &= Q^{ik}(t)L^{kn}(x^l,t)Q^{mn}(t)\delta^{mj} + \Omega^{ij}(t) = Q^{ik}(t)L^{kn}(x^l,t)Q^{jn}(t) + \Omega^{ij}(t)\end{aligned}$$

and this is (3.52). Q.E.D.

Using (3.15) in the starred frame we find with (3.52) that the spin $\mathbf{W}$ is not objective

$$\mathbf{W}^* = \mathbf{Q}\mathbf{W}\mathbf{Q}^T + \underline{\Omega} \tag{3.53}$$

but the stretching tensor $\mathbf{D}$ is objective (frame indifferent)

$$\mathbf{D}^* = \mathbf{Q}\mathbf{D}\mathbf{Q}^T \tag{3.54}$$

Transformation properties of some objects (mostly derivatives useful in the following chapters) formed from scalar a, vector $\mathbf{a}$, tensor $\mathbf{A}$ which are objective (frame indifferent) (3.30)–(3.32), will be discussed now. We must realize that these objective conditions must be valid at any $\mathbf{x}^*, t^*$ transforming by (3.25), (3.26) to $\mathbf{x}, t$ (the same event seen from different frames passing at the same particle $\mathbf{X}$); therefore[11]

$$a^*(\mathbf{X}, t^*) = a^*(\mathbf{x}^*, t^*) = a^* = a = a(\mathbf{x}, t) = a(\mathbf{X}, t) \tag{3.55}$$

$$\mathbf{a}^*(\mathbf{X}, t^*) = \mathbf{a}^*(\mathbf{x}^*, t^*) = \mathbf{a}^* = \mathbf{Q}\mathbf{a} = \mathbf{Q}(t)\mathbf{a}(\mathbf{x}, t) = \mathbf{Q}(t)\mathbf{a}(\mathbf{X}, t) \tag{3.56}$$

$$\mathbf{A}^*(\mathbf{x}^*, t^*) = \mathbf{A}^* = \mathbf{Q}\mathbf{A}\mathbf{Q}^T = \mathbf{Q}(t)\mathbf{A}(\mathbf{x}, t)\mathbf{Q}^T(t) \tag{3.57}$$

As a result, we obtain: If scalar a is objective (3.55) then its material derivative $\dot{a}$ and space gradient grad$a$ are objective while Grad$a$ and $\partial a/\partial t$ are not. If $\mathbf{a}$ is an objective vector, div$\mathbf{a}$, $\mathbf{a}.\mathbf{a} = \mathbf{a}^2$ are objective, while material derivative $\dot{\mathbf{a}}$ is not. Ultimately, with objective (second order) tensor $\mathbf{A}$, the vector div$\mathbf{A}$ and the scalars tr$\mathbf{A}$, det$\mathbf{A}$ are objective.

Proofs Transformation (frame change) of objective scalar a (3.55) with (3.28) gives the objectivity of scalar material derivative

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[11] Note that functions on both sides of $(3.55)_1$ are different: $a^*(\mathbf{x}^*, t^*) = a^*(\underline{\chi}^*(\mathbf{X}, t^*), t^*) \equiv a^*(\mathbf{X}, t^*)$. Remark that the assumption (3.30) is crucial for validity of (3.55); namely, the function $\alpha(\mathbf{x}, t)$, defined by (3.25), (3.26) as $a^*(\mathbf{x}^*, t^*) = a^*(\mathbf{c} + \mathbf{Q}\mathbf{x}, t + b) \equiv \alpha(\mathbf{x}, t)$ is generally different from function $a(\mathbf{x}, t)$. Similarly (3.31) and (3.32) are crucial for (3.56) and (3.57).

$$(\dot{a})^* \equiv \frac{\partial a^*(X^K, t^*)}{\partial t^*} = \frac{\partial a(X^L, t^* - b)}{\partial t^*} = \frac{\partial a(X^L, t)}{\partial t}\,\frac{\mathrm{d}(t^* - b)}{\mathrm{d}t^*} = \dot{a}$$

and also objectivity of vector grad$a$ (by (3.27), (3.28))

$$\begin{aligned}
\overset{*}{\overline{(\mathrm{grad}a)}}{}^{j} &\equiv \frac{\partial a^*(\overset{*}{x}{}^m, t^*)}{\partial \overset{*}{x}{}^j} \\
&= \frac{\partial a(x^n, t)}{\partial \overset{*}{x}{}^j} = \frac{\partial a(Q^{pn}(t^* - b)(\overset{*}{x}{}^p - c^p(t^* - b)), t^* - b)}{\partial \overset{*}{x}{}^j} \\
&= \frac{\partial a(x^n, t)}{\partial x^i}\,\frac{\partial (Q^{pi}(t^* - b)(\overset{*}{x}{}^p - c^p(t^* - b)))}{\partial \overset{*}{x}{}^j} \\
&= \frac{\partial a(x^n, t)}{\partial x^i}\,Q^{ji}(t) = Q^{ji}(\mathrm{grad}a)^i
\end{aligned}$$

But the vector Grad$a$ is not objective because

$$\overset{*}{\overline{(\mathrm{Grad}a)}}{}^{J} \equiv \frac{\partial a^*(X^K, t^*)}{\partial X^J} = \frac{\partial a(X^L, t)}{\partial X^J} = (\mathrm{Grad}a)^J$$

as well as $\partial a/\partial t$ (by (3.28), (3.27))

$$\begin{aligned}
(\partial a/\partial t)^* &\equiv \frac{\partial a^*(\overset{*}{x}{}^m, t^*)}{\partial t^*} = \frac{\partial a(x^n, t)}{\partial t^*} = \frac{\partial a(Q^{pn}(t^* - b)(\overset{*}{x}{}^p - c^p(t^* - b)), t^* - b)}{\partial t^*} \\
&= \frac{\partial a(x^n, t)}{\partial t}\,\frac{\mathrm{d}(t^* - b)}{\mathrm{d}t^*} + \frac{\partial a(x^n, t)}{\partial x^i}\,\frac{\partial (Q^{pi}(t^* - b)(\overset{*}{x}{}^p - c^p(t^* - b)))}{\partial t^*} \\
&= \frac{\partial a(x^n, t)}{\partial t} + \frac{\partial a(x^n, t)}{\partial x^i}\left(\frac{\mathrm{d}Q^{pi}(t)}{\mathrm{d}t}(\overset{*}{x}{}^p - c^p(t^* - b)) - Q^{pi}(t)\frac{\mathrm{d}c^p(t)}{\mathrm{d}t}\right) \\
&= \frac{\partial a}{\partial t} + (\mathrm{grad}a)^i(\dot{Q}^{pi}Q^{pj}x^j - Q^{pi}\dot{c}^p)
\end{aligned}$$

or (using time derivative of $Q^{pi}Q^{pj} = \delta^{ij}$)

$$(\partial a/\partial t)^* = \partial a/\partial t - Q^{pi}(\mathrm{grad}a)^i(\dot{Q}^{pj}x^j + \dot{c}^p)$$

i.e. the (space) time derivative of objective scalar a is not the objective scalar.

Transformation (frame change) of objective vector $\mathbf{a}$ (3.56) gives the objectivity of the scalar product $\mathbf{a}^2$

$$(\mathbf{a}^2)^* \equiv \mathbf{a}^*.\mathbf{a}^* = \overset{*}{a}{}^i\,\overset{*}{a}{}^i = Q^{ij}a^j\,Q^{ik}a^k = \delta^{jk}a^j\,a^k = a^j\,a^j = \mathbf{a}.\mathbf{a} = \mathbf{a}^2$$

and also the objectivity of the (space) divergence div**a** (scalar) using (3.27), (3.28), Rem. 8

$$\begin{aligned}(\mathrm{div}\mathbf{a})^* &\equiv \frac{\partial \overset{*}{a}{}^{i}(\overset{*}{x}{}^{l}, t^*)}{\partial \overset{*}{x}{}^{i}} = \frac{\partial (Q^{ij}(t)a^j(x^m, t))}{\partial \overset{*}{x}{}^{i}} \\ &= \frac{\partial (Q^{ij}(t^*-b)a^j(Q^{nm}(t^*-b)(\overset{*}{x}{}^{n} - c^n(t^*-b)), t^*-b))}{\partial \overset{*}{x}{}^{i}} \\ &= Q^{ij}(t)\frac{\partial a^j(x^m, t)}{\partial x^k}\,\frac{\partial (Q^{nk}(t^*-b)(\overset{*}{x}{}^{n} - c^n(t^*-b)))}{\partial \overset{*}{x}{}^{i}} \\ &= \frac{\partial a^j(x^m, t)}{\partial x^k}Q^{ij}(t)Q^{ik}(t) = \frac{\partial a^j(x^m, t)}{\partial x^j} = \mathrm{div}\,\mathbf{a}\end{aligned}$$

But the material derivative of objective vector $\dot{\mathbf{a}}$ is not objective: From (3.56), using (3.28), it follows

$$\begin{aligned}(\dot{a}^i)^* &\equiv \frac{\partial \overset{*}{a}{}^{i}(X^J, t^*)}{\partial t^*} = \frac{\partial (Q^{ij}(t^*-b)a^j(X^K, t^*-b))}{\partial t^*} \\ &= Q^{ij}(t)\frac{\partial a^j(X^K, t)}{\partial t}\,\frac{\mathrm{d}(t^*-b)}{\mathrm{d}t^*} \\ &\quad + \frac{\mathrm{d}Q^{ij}(t)}{\mathrm{d}t}\,\frac{\mathrm{d}(t^*-b)}{\mathrm{d}t^*}a^j(X^K, t) = Q^{ij}\dot{a}^j + \dot{Q}^{ij}a^j\end{aligned}$$

and therefore $\dot{\mathbf{a}}$ is not an objective vector.

Transformation (frame change) of objective (second order) tensor (3.57) gives the objectivity of the scalars tr**A** and det**A** :

$$(\mathrm{tr}\mathbf{A})^* = \mathrm{tr}\mathbf{A}^* = \overset{*}{A}{}^{ii} = Q^{ik}A^{kl}Q^{il} = \delta^{kl}A^{kl} = A^{ll} = \mathrm{tr}\mathbf{A}$$

$$(\mathrm{det}\mathbf{A})^* = \mathrm{det}\mathbf{A}^* = \mathrm{det}\mathbf{Q}\mathbf{A}\mathbf{Q}^T = \mathrm{det}\mathbf{Q}\mathrm{det}\mathbf{A}\mathrm{det}\mathbf{Q}^T = \mathrm{det}\mathbf{Q}\mathbf{Q}^T\mathrm{det}\mathbf{A} = \mathrm{det}\mathbf{A}$$

Also the vector div**A** is objective (from (3.57)) using

$$\begin{aligned}\overset{*}{\overline{(\mathrm{div}\mathbf{A})}}{}^{i} &\equiv \frac{\partial \overset{*}{A}{}^{ij}(\overset{*}{x}{}^{m}, t^*)}{\partial \overset{*}{x}{}^{j}} = \frac{\partial Q^{ik}(t)A^{kl}(x^n, t)Q^{jl}(t)}{\partial \overset{*}{x}{}^{j}} \\ &= \frac{\partial (Q^{ik}(t^*-b)A^{kl}(Q^{pn}(t^*-b)(\overset{*}{x}{}^{p} - c^p(t^*-b)), t^*-b)Q^{jl}(t^*-b))}{\partial \overset{*}{x}{}^{j}} \\ &= Q^{ik}(t)\frac{\partial A^{kl}(Q^{pn}(t^*-b)(\overset{*}{x}{}^{p} - c^p(t^*-b)), t^*-b)}{\partial \overset{*}{x}{}^{j}}Q^{jl}(t)\end{aligned}$$

$$= Q^{ik}(t)\frac{\partial A^{kl}(x^m,t)}{\partial x^q}\frac{\partial Q^{pq}(t^*-b)(\overset{*}{x}{}^p - c^p(t^*-b))}{\partial \overset{*}{x}{}^j}Q^{jl}(t)$$

$$= Q^{ik}(t)\frac{\partial A^{kl}(x^m,t)}{\partial x^q}Q^{jq}(t)Q^{jl}(t) = Q^{ik}(t)\frac{\partial A^{kl}(x^m,t)}{\partial x^l} = Q^{ik}(\mathrm{div}\mathbf{A})^k$$

Therefore, div**A** of objective tensor **A** is an objective vector. Q.E.D.

As we noted in the precepts above the remaining relations of Sect. 3.1 are also valid in all frames, e.g., (3.21), (3.22) or Reynolds theorem (3.24). Because of no influence of the change of frame on the reference configuration (and material points), no such influence may be also expected on material volume $\mathcal{V}$, material surface $\partial\mathcal{V}$ (they behave as objective scalars), and the outside normal **n** should be an objective vector.[12]

Objectivity of other quantities occurring in the remaining chapters may be obtained analogically.

Summary. The change of frame refers to the change (rotation, translation, etc.) of coordinate system used to describe space and time variations and the effects of this change on various (physical) quantities or functions. The change is mathematically described by (3.25) and (3.26). Special quantities which are in some sense invariant to this change were called objective or frame-indifferent, cf. (3.30)–(3.32), and are of special importance for the methodology of rational thermodynamics. The objectivity of several quantities or functions was tested; the most important conclusions are the objectivity of stretching tensor, cf. (3.54), and the nonobjectivity of velocity, cf. (3.35), and its gradient, cf. (3.52), and of deformation gradient, cf. (3.49).

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[12] Moreover, it should be expected that

$$\left(\int_{\mathcal{V}}\psi\,\mathrm{d}v\right)^* = \int_{\mathcal{V}}\psi^*\,\mathrm{d}v\ ,\quad \left(\int_{\partial\mathcal{V}}\psi\mathbf{n}\,\mathrm{d}a\right)^* = \int_{\partial\mathcal{V}}\psi^*\mathbf{Qn}\,\mathrm{d}a$$

because the objectivity of da, dv follows from the objectivity of space intervals (ψ may even be a component of a vector or a tensor).

Note also that the following relationships are valid in the starred frame for the time derivative of function $\varphi(t)$ (see (3.26), (3.28))

$$\overset{*}{\dot{\varphi}} \equiv \frac{\mathrm{d}\varphi^*(t^*)}{\mathrm{d}t^*} = \frac{\mathrm{d}\varphi^*(t^*)}{\mathrm{d}t}\frac{\mathrm{d}(t^*-b)}{\mathrm{d}t^*} = \frac{\mathrm{d}\varphi^*(t^*)}{\mathrm{d}t} = \dot{\overline{\varphi^*}}$$

Such a function φ may be, e.g., $\psi(\mathbf{X},t)$ or $\Psi(t)$ in (3.21); for the latter the relation (3.22) and the previous formula (with (3.50)) gives

$$\left(\dot{\overline{\int_{\mathcal{V}}\psi\,\mathrm{d}v}}\right)^* = \int_{\mathcal{V}_0}(\dot{\overline{\psi J}})^*\,\mathrm{d}V = \int_{\mathcal{V}_0}\dot{\overline{\overset{*}{\psi}\overset{*}{J}}}\,\mathrm{d}V = \dot{\overline{\int_{\mathcal{V}}\overset{*}{\psi}\ \mathrm{d}v}}$$

because $\mathcal{V}_0$ is a material volume in reference configuration.

3.3 Balances of Mass, Momentum, and Moment of Momentum

In this and in the following paragraphs, we formulate general postulates, mostly balances for a single substance [6–9, 11, 13, 23]. We use classical mechanics and formulate them in the inertial frame (specifically those fixed with distant, remote stars, see Sect. 3.2); generalization in other frames (even noninertial) will be shown at the end of the discussion of each special balance (for further developments, see end of Sect. 3.4).

To formulate the *balance of mass* let us consider the single (one-constituent) body in arbitrary actual configuration (in inertial frame noted above).

As a primitive we assign to each particle **X** of this body the *(mass) density* ρ—positive and (assuming) objective (frame indifferent) scalar. *Mass* of the body or its arbitrary part with material volume $\mathcal{V}$ is then

$$\int_{\mathcal{V}} \rho \,\mathrm{d}v \tag{3.58}$$

It follows that mass is continuous and additive with volume (cf. Rem. 7) and therefore we exclude the concentrated masses (mass points) from consideration. The *mass balance* is postulated by the conservation of mass of some part of the body (or body itself) containing the same particles during its motion. In other words, the mass of material volume $\mathcal{V}$ is not changed in time

$$\overline{\int_{\mathcal{V}} \rho \,\mathrm{d}v}^{\,\cdot} = 0 \tag{3.59}$$

Using Reynolds theorem (3.24), mass balance (3.59) may be written in (space) fixed volume V with surface ∂V as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V} \rho \,\mathrm{d}v + \int_{\partial V} \rho \mathbf{v}.\mathbf{n} \,\mathrm{d}a = 0 \tag{3.60}$$

i.e., mass in the fixed volume may be changed only by a flow through its (fixed) boundary. Using Gauss theorem (3.23) in (3.60) we have

$$\int_{V} \frac{\partial \rho}{\partial t} \,\mathrm{d}v + \int_{V} \mathrm{div}(\rho \mathbf{v}) \,\mathrm{d}v = 0 \tag{3.61}$$

We assume now validity of this mass balance for any part of the body, specifically for that whose volume V is sufficiently small. Then also the integrand here must be zero and we obtain the *local mass balance*

$$\frac{\partial \rho}{\partial t} + \mathrm{div} \rho \mathbf{v} = 0 \tag{3.62}$$

Another form of local mass balance follows using material derivative (3.8) of the density

$$\dot{\rho} + \rho \,\mathrm{div}\mathbf{v} = 0 \tag{3.63}$$

We note that using Euler relation (3.17) we can write the mass balance (3.63) as

$$\overline{\rho J}^{\,\boldsymbol{\cdot}} = 0 \tag{3.64}$$

which after time integration gives the mass balance in the form

$$\rho_0 = \rho J \tag{3.65}$$

Here ρ_0 is the density in the reference configuration (because $J = 1$ when $\mathbf{F} = \mathbf{1}$).

Assumed continuity and additivity of mass permits to introduce (cf. Rem. 7) the specific quantities φ related with densities ψ by

$$\psi = \rho\varphi \tag{3.66}$$

We note two useful formulae for specific quantities φ (which may also be a component of vector or tensor)

$$\frac{\partial \rho\varphi}{\partial t} + \mathrm{div}\rho\varphi\mathbf{v} = \rho\dot{\varphi} \tag{3.67}$$

$$\overline{\int_{\mathcal{V}} \rho\varphi \,\mathrm{d}v}^{\,\boldsymbol{\cdot}} = \int_{\mathcal{V}} \rho\dot{\varphi} \,\mathrm{d}v \tag{3.68}$$

which follows for (3.66) from (3.22), (3.63) in material volume $\mathcal{V}$.

Mass balances obtained so far were formulated and deduced in an inertial frame fixed with distant stars. But their form is the same in any frame (even a noninertial one), i.e., formulae (3.58)–(3.68) are independent of the frame. This may be seen from the assumption of objectivity of scalar mass density ρ ((3.30) is valid). Using the last formulae from Rem. 12 with objective density ρ as the scalar ψ we find general validity of mass balance (3.59) in any frame. In some new frame, Reynolds theorem (3.24) may be quite analogously deduced and used and then, by localization, all remaining formulae (3.60)–(3.68) are valid in any frame. Indeed, e.g., (3.63) is valid in any frame because of the objectivity of the material derivative of the objective scalar $\dot{\rho}$ and, see (3.16) $\mathrm{div}\mathbf{v} = \mathrm{tr}\mathbf{D}$, because the trace of objective tensor (3.54) is objective. Similarly, so is (3.65) with the same ρ_0 (reference is unique for all actual configurations) and by (3.50). This is also (3.68) for φ from such a new frame.

To postulate the *balance of momentum*, we define the *momentum* or *linear momentum* of a part of body (or the whole body) with material volume $\mathcal{V}$ in actual configuration in given (arbitrary) frame as

$$\int_{\mathcal{V}} \rho\mathbf{v} \,\mathrm{d}v \tag{3.69}$$

The postulate of the *balance of momentum* expresses the experience that the time change of momentum (3.69) is equal to the *forces* acting on the corresponding part of body with material volume $\mathcal{V}$ in actual configuration. Simple, classical formulation of this balance is done in an inertial frame, specifically that fixed with distant stars. The main reason for this is the nonobjectivity of velocity in (3.69), see (3.38); forces are a priori considered as objective. Below (3.78) we show that such formulation is the same in any inertial frame and that in a general frame the balance must be modified a little.

Forces are primitive quantities and we confine here two types of forces: the *external* or *body, volume, outer* forces exist inside material volume $\mathcal{V}$ but have their origin outside the (whole) body and are characterized by a vector of *body*, or *volume* forces $\mathbf{b}$ per mass unit (an example is the gravitation coming from the environment of the body). The second type are the *contact* or *surface* forces acting on the surface of the chosen part of the body. These imaginable forces come from the outside neighborhood of the surface considered ("short range interaction forces" from the outside part of the same body) and they are characterized by the *stress vector* or *traction* $\mathbf{t}$—force per unit surface of the chosen part coming from its outside.[13] Therefore, we exclude in the following a "long range interaction body forces" among distant parts of the same body like self-gravitation; for such a more general case see e.g., [18, 19, 30]. They might appear in ion mixtures, but in salt solution may be neglected by electroneutrality, cf. Rems. 6 and 32 in Chap. 4.

The *Balance of momentum* or *balance of linear momentum* for an arbitrary part of a body in actual configuration and in inertial frame (fixed on distant stars) is postulated as[14]

$$\overline{\int_{\mathcal{V}} \rho \mathbf{v}\, \mathrm{d}v}^{\,\boldsymbol{\cdot}} = \int_{\partial\mathcal{V}} \mathbf{t}\, \mathrm{d}a + \int_{\mathcal{V}} \rho \mathbf{b}\, \mathrm{d}v \tag{3.70}$$

where this part of the body has the material volume $\mathcal{V}$ with the material surface $\partial\mathcal{V}$. We shall assume in the following, that vectors $\mathbf{t}$, $\mathbf{b}$ are objective (frame indifferent).

Experience shows that the body force is a field (i.e., a function of position $\mathbf{x}$ and time t) but that traction depends not only on the $\mathbf{x}$ and t but also on the orientation of the surface; this is expressed by *Cauchy's postulate*[15]

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[13] On the real surface of the whole body the surface forces $\mathbf{t}$ (originated from the outside of the whole body) are given by boundary conditions; cf. Rems. 18 and 24 in this chapter, 9 in Chap. 1.

[14] Again [7, 10, 18–20] as we noted in Rem. 7, it would be more natural to postulate forces for any part of volume or surface (which bound them) and then to deduce $\rho\mathbf{b}$ or $\mathbf{t}$ as the volume or surface densities.

In fact, the formulation of balances in Sects. 3.3 and 3.4 for each part of the body is motivated by the *solidification principle*: we imagine the part of the body isolated from the remainder of the body and interactions with this remainder and surroundings of the body are expressed by appropriate (volume or surface) densities. This principle will be used also in the following, e.g., contact and body forces in formulation of (3.70) are such interactions.

[15] E.g., hydrostatic pressure (typical traction in steady fluid) is directed always perpendicularly to any orientation of the surface in a given place. Moreover, assumption (3.71) may be also proved

$$\mathbf{t} = \mathbf{t}(\mathbf{x}, t, \mathbf{n}) \tag{3.71}$$

where $\mathbf{n}$ is the outside normal to the surface $\partial\mathcal{V}$ in a given place $\mathbf{x}$ and instant t.

In fact, the dependence of $\mathbf{t}$ on $\mathbf{n}$ (3.71) is linear as the *Cauchy theorem* asserts

$$\mathbf{t} = \mathbf{T}\mathbf{n} \tag{3.72}$$

where the field $\mathbf{T} = \mathbf{T}(\mathbf{x}, t)$ is the *stress tensor*.

The Cauchy theorem may be proved by application of (3.70) to an infinitesimal tetrahedron at considered place $\mathbf{x}$ and instant t, the walls of which are formed by coordinate planes and a tangent plane perpendicular to considered $\mathbf{n}$. The estimate of the surface and volume integrals in (3.70) gives (using (3.68))

$$\rho\dot{\mathbf{v}}\,\Delta v = \mathbf{t}\,\Delta a + \mathbf{t}_j\,\Delta a^j + \rho\mathbf{b}\,\Delta v \tag{3.73}$$

Here Δv is the volume of the tetrahedron and $\mathbf{t}$ and $\mathbf{t}_j$ are the tractions on the surfaces Δa and Δa^j (the latter are formed by coordinate axes) respectively (summation rule is assumed). But $\Delta v = (1/3)h\,\Delta a$ (where h is the height of the tetrahedron) and $\Delta a^j = n^j\Delta a$ where n^j are components of $\mathbf{n}$. Inserting these relations into (3.73) and limiting $h \to 0$ (assuming continuity) we obtain $\mathbf{t} = -\mathbf{t}_j\mathbf{n}^j$ which is (3.72) in Cartesian components $t^i = T^{ij}n^j$ if we take T^{ij} as ith component of vector $-\mathbf{t}_j$. Moreover, $\mathbf{T}$ depends only on $\mathbf{x}$ and t because also $\mathbf{t}_j$ depends on $\mathbf{x}$ and t and not on $\mathbf{n}$ as follows from the construction of the tetrahedron. The sign of $\mathbf{T}$ is given by a convention which gives to $\mathbf{t}$ the meaning of tension by which the exterior of the surface $\partial\mathcal{V}$ acts on material inside (cf. e.g. [13]; modern versions of this proof [7, 30–32] show the much more general validity of (3.72)). The stress tensor $\mathbf{T}$ is objective because of the objectivity of $\mathbf{t}$ and (arbitrary) $\mathbf{n}$ (see end of Sect. 3.2); the deduction is similar to that of (3.32).

Inserting (3.72) into (3.70) we obtain the balance of momentum in the inertial frame (fixed on distant stars) as

$$\dot{\overline{\int_{\mathcal{V}} \rho\mathbf{v}\,\mathrm{d}v}} = \int_{\partial\mathcal{V}} \mathbf{T}\mathbf{n}\,\mathrm{d}a + \int_{\mathcal{V}} \rho\mathbf{b}\,\mathrm{d}v \tag{3.74}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\mathbf{v}\,\mathrm{d}v + \int_{\partial V} \rho\mathbf{v}(\mathbf{v}.\mathbf{n})\,\mathrm{d}a = \int_{\partial V} \mathbf{T}\mathbf{n}\,\mathrm{d}a + \int_V \rho\mathbf{b}\,\mathrm{d}v \tag{3.75}$$

where the last form (3.75) was obtained using (3.24) (Reynolds theorem obtainable in any frame) for the volume V with the surface ∂V fixed in the space. Because (3.74) and (3.75) are valid for any volume we can use the Gauss theorem to convert the surface integrals into those of volume(only those are permitted by stress field

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(Footnote 15 continued)
[7, 21, 30, 31]; from this proof it follows that $\mathbf{t}$ cannot depend on the other local properties of surface, like curvature, etc.

as distinct from traction (3.71)) and using (3.68) we obtain the local balances of momentum in the inertial frame

$$\rho\dot{\mathbf{v}} = \mathrm{div}\mathbf{T} + \rho\mathbf{b} \tag{3.76}$$

$$\frac{\partial\rho\mathbf{v}}{\partial t} + \mathrm{div}(\rho\mathbf{v}\otimes\mathbf{v}) = \mathrm{div}\mathbf{T} + \rho\mathbf{b} \tag{3.77}$$

(in components $(\mathrm{div}\mathbf{T})^i = \partial T^{ij}/\partial x^j$ and $(\mathrm{div}(\rho\mathbf{v}\otimes\mathbf{v}))^i = \partial\rho v^i v^j/\partial x^j$).

So far we have assumed that the inertial frame (fixed with distant stars) was used. To transform balances (3.70), (3.74)–(3.77) into another frame we note that the stress tensor $\mathbf{T}$ is objective (see below (3.72)). Considering any new (starred) frame and using (3.30)–(3.32), (3.44), (3.46) (note that div$\mathbf{T}$ is objective vector and ρ objective scalar) in (3.76) (multiplied by orthogonal transformation $\mathbf{Q}$ of coordinates in the inertial frame to the new one at considered instant) we obtain the *local balance of momentum* in any frame (stars denoting the new frame were removed)

$$\rho\dot{\mathbf{v}} = \mathrm{div}\mathbf{T} + \rho(\mathbf{b}+\mathbf{i}) \tag{3.78}$$

where the inertial acceleration $\mathbf{i}$ (3.46) in this new frame is

$$\mathbf{i} = 2\underline{\Omega}(\mathbf{v}-\dot{\mathbf{c}}) - \underline{\Omega}^2(\mathbf{x}-\mathbf{c}) + \dot{\underline{\Omega}}(\mathbf{x}-\mathbf{c}) + \ddot{\mathbf{c}} \tag{3.79}$$

Here, the tensor $\underline{\Omega}$ is the angular velocity (of original, inertial frame relative to new one) (3.39) and $\mathbf{c}$ is the position of origin, $\mathbf{v}$ is the velocity, $\mathbf{x}$ the position in the new frame at the considered instant.

Then it is not difficult to see that transformation of any momentum balance (3.70), (3.74)–(3.77) into an arbitrary frame means inserting $\mathbf{b}+\mathbf{i}$ instead of $\mathbf{b}$. Indeed, the starting postulate of momentum balance (3.70) has in an arbitrary new frame the form

$$\dot{\overline{\int_{\mathcal{V}} \rho\mathbf{v}\,\mathrm{d}v}} = \int_{\partial\mathcal{V}} \mathbf{t}\,\mathrm{d}a + \int_{\mathcal{V}} \rho(\mathbf{b}+\mathbf{i})\,\mathrm{d}v \tag{3.80}$$

because balance (3.78) in the new frame may be integrated in this frame through material volume (which is independent of the frame, cf. end of Sect. 3.2) and uses Gauss theorem (3.23), (3.72) and (3.68) (where φ is component of velocity) in the new frame (because these formulae are the same in all frames as well as the Reynolds theorem (3.24), mass balances above, etc.).

Repeating the previous procedure in the new frame we obtain all remaining balances in this new arbitrary frame, e.g.,

$$\dot{\overline{\int_{\mathcal{V}} \rho\mathbf{v}\,\mathrm{d}v}} = \int_{\mathcal{V}} \rho\dot{\mathbf{v}}\,\mathrm{d}v = \int_{\partial\mathcal{V}} \mathbf{T}\mathbf{n}\,\mathrm{d}a + \int_{\mathcal{V}} \rho(\mathbf{b}+\mathbf{i})\,\mathrm{d}v \tag{3.81}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\mathbf{v}\,\mathrm{d}v + \int_{\partial V}\rho\mathbf{v}(\mathbf{v}.\mathbf{n})\,\mathrm{d}a = \int_{\partial V}\mathbf{Tn}\,\mathrm{d}a + \int_V \rho(\mathbf{b}+\mathbf{i})\,\mathrm{d}v \tag{3.82}$$

$$\frac{\partial\rho\mathbf{v}}{\partial t} + \mathrm{div}(\rho\mathbf{v}\otimes\mathbf{v}) = \mathrm{div}\mathbf{T} + \rho(\mathbf{b}+\mathbf{i}) \tag{3.83}$$

Because of zero inertial acceleration (3.48), we can see from these general results (3.78)–(3.83), that the balances (3.70), (3.74)–(3.77) are valid in any inertial frame and not only in the one fixed with the distant stars. This assertion expresses the Galilean relativity principle about the impossibility of preference of any inertial frame.

Momentum balances (3.81), and (3.78) in the arbitrary frame may be written as (cf. [1, 7, 18–20, 22, 33])

$$\mathbf{o} = \int_{\partial\mathcal{V}}\mathbf{Tn}\,\mathrm{d}a + \int_{\mathcal{V}}\rho\underline{\beta}\,\mathrm{d}v \tag{3.84}$$

$$\mathbf{o} = \mathrm{div}\mathbf{T} + \rho\underline{\beta} \tag{3.85}$$

where the *total body force* $\underline{\beta}$ (coming from the outside of the body) is defined by

$$\underline{\beta} \equiv \mathbf{b} + \mathbf{i} - \dot{\mathbf{v}} \tag{3.86}$$

This force $\underline{\beta}$ is objective: indeed, (3.85) is valid in all frames, therefore

$$\underline{\beta}^* = (-(1/\rho)\mathrm{div}\mathbf{T})^* = \left(-(1/\rho^*)(\mathrm{div}\mathbf{T})^*\right) = \mathbf{Q}\,(-(1/\rho)\mathrm{div}\mathbf{T}) = \mathbf{Q}\underline{\beta} \tag{3.87}$$

where objectivity of scalar ρ and vector div$\mathbf{T}$ have been used (see Sect. 3.2; stress tensor $\mathbf{T}$ is objective).

Balance of momentum in the objective form (3.84), (3.85) may be interpreted as the general action and reaction law: sum of all forces is zero (in total body force (3.86) the force $\mathbf{i} - \dot{\mathbf{v}}$ caused by "distant, remote stars" is included).

To formulate another main principle—the balance of moment of momentum—we introduce for some part of body (or body itself) with material volume $\mathcal{V}$ in actual configuration of the considered frame the *moment of momentum* or *angular moment* related to the point $\mathbf{y}$ as follows[16]

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[16] We use the outer product $\wedge$ defined for two vectors $\mathbf{a}$, $\mathbf{b}$ as $\mathbf{a}\wedge\mathbf{b} \equiv \mathbf{a}\otimes\mathbf{b} - \mathbf{b}\otimes\mathbf{a}$, i.e. $(\mathbf{a}\wedge\mathbf{b})^{ij} = a^i b^j - a^j b^i$. This product is obviously the skew-symmetric tensor which, using the results from Rem. 10, is equivalent to the axial vector created by the vector product of these vectors, see Rem. 6

$$\mathbf{b}\times\mathbf{a} = -\mathbf{a}\times\mathbf{b}$$

Then, e.g., the balance of angular moment (3.90) may be written in a more traditional way as

$$\int_{\mathcal{V}}(\mathbf{x}-\mathbf{y})\times\rho\dot{\mathbf{v}}\,\mathrm{d}v = \int_{\partial\mathcal{V}}(\mathbf{x}-\mathbf{y})\times\mathbf{Tn}\,\mathrm{d}a + \int_{\mathcal{V}}(\mathbf{x}-\mathbf{y})\times\rho\mathbf{b}\,\mathrm{d}v$$

$$\int_{\partial\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho\mathbf{v}\,\mathrm{d}v \tag{3.88}$$

Here, $\mathbf{x}$ is the place where density ρ and $\mathbf{v}$ is considered and $\mathbf{y}$ is the point which may be outside of the body and usually fixed in the considered frame.

To obtain a simple form of the balance of moment of momentum, we confine its formulation to inertial frame with angular moment (3.88) having point $\mathbf{y}$ fixed here (although we use here the inertial frame fixed with distant stars, resulting formulations are valid in any inertial frame as will be shown at the end of this section). Again, the main reason for that is the nonobjectivity of $\mathbf{x}$, $\mathbf{y}$, $\mathbf{v}$ in (3.88), cf. (3.25), (3.38); generalization of this balance in the arbitrary frame will be discussed below but we note that the main local result—symmetry of stress tensor (3.93) below—is valid in the arbitrary frame.

Such a balance of the moment of momentum (balance of angular moment) asserts that the time change of the moment of momentum is equal to *torques* acting on a considered part of the body (or the body itself). Here we confine to the simplest case of (mechanically) nonpolar materials where torques are moments of forces (i.e., their outer products of Rem. 16 with $\mathbf{x}-\mathbf{y}$) used in the preceding balance of momentum.[17]

Therefore, the *balance of moment of momentum* or *balance of angular momentum* related to the fixed point $\mathbf{y}$ in actual configuration in the inertial frame (fixed with distant stars) for (arbitrary part of) body with material volume $\mathcal{V}$ and its surface $\partial\mathcal{V}$ is postulated as

$$\overline{\int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho\mathbf{v}\,\mathrm{d}v}^{\bullet} = \int_{\partial\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \mathbf{T}\mathbf{n}\,\mathrm{d}a + \int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho\mathbf{b}\,\mathrm{d}v \tag{3.89}$$

Traction $\mathbf{t}$ is here expressed through the stress tensor by (3.72). We also note that postulating (3.89) for one fixed point $\mathbf{y}$ the form (3.89) is valid for arbitrary but fixed point (say $\mathbf{y}_0$ as follows from the balance of linear momentum (3.74) multiplied by constant $(\mathbf{y}-\mathbf{y}_0)\wedge$ (i.e., as outer product in Rem. 16) and by summation with (3.89), of course all in our inertial frame). For this reason the origin $\mathbf{y} = \mathbf{o}$ is often used in formulations of this postulate, e.g., [16], without loss of generality.

Using (3.68), (3.7) (namely $\dot{\mathbf{x}} \wedge \mathbf{v} = \mathbf{0}$) and the assumption of fixed point, i.e., the time derivative $\dot{\mathbf{y}} = \mathbf{o}$ (note that (3.25) applied on point $\mathbf{y}$ shows that $\mathbf{y}$ may be at most a function of time in the arbitrary frame; cf. below (3.94)), we obtain

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[17] In more general (mechanically) *polar* materials [13, 34], the local result (3.93) must be changed (cf. also Rems. 32 in this chapter, 9 in Chap. 4). Namely, the balance (3.89) then contains (besides moments of forces) *torques* expressing the direct exchange of angular moment on a microscopic level (something like heat in energy exchange). These "microscopic" torques may be expressed by the objective field of density of skew-symmetric tensor $\mathbf{M}$ adding to the right-hand side of the postulate (3.89) the integral $\int_{\mathcal{V}} \mathbf{M}\,\mathrm{d}v$. Then instead of local result (3.93), we obtain

$$\mathbf{T} - \mathbf{T}^T = \mathbf{M}.$$

$$\int_{\mathcal{V}} (\mathbf{x}-\mathbf{y}) \wedge \rho \dot{\mathbf{v}} \, \mathrm{d}v = \int_{\partial \mathcal{V}} (\mathbf{x}-\mathbf{y}) \wedge \mathbf{T}\mathbf{n} \, \mathrm{d}a + \int_{\mathcal{V}} (\mathbf{x}-\mathbf{y}) \wedge \rho \mathbf{b} \, \mathrm{d}v \tag{3.90}$$

Using Gauss' theorem (cf. (3.23); note that the following skew-symmetric tensor is in components $(\mathrm{div}((\mathbf{x}-\mathbf{y}) \wedge \mathbf{T}))^{ij} = \partial((x^i - y^i)T^{jk} - (x^j - y^j)T^{ik})/\partial(x^k)$, cf. Rem. 16) and by localization using assumed validity of (3.90) for any $\mathcal{V}$, we obtain

$$(\mathbf{x}-\mathbf{y}) \wedge \rho \dot{\mathbf{v}} = \mathrm{div}((\mathbf{x}-\mathbf{y}) \wedge \mathbf{T}) + (\mathbf{x}-\mathbf{y}) \wedge \rho \mathbf{b} \tag{3.91}$$

Calculating divergence (simply in component form above, $\mathbf{y}$ is fixed) we obtain

$$\mathrm{div}((\mathbf{x}-\mathbf{y}) \wedge \mathbf{T}) = \mathbf{T}^T - \mathbf{T} + (\mathbf{x}-\mathbf{y}) \wedge \mathrm{div}\mathbf{T} \tag{3.92}$$

Inserting it in (3.91) and using in this inertial reference configuration the balance of momentum (3.76) multiplied by $(\mathbf{x}-\mathbf{y})\wedge$ from the left, we obtain the *local balance of moment of momentum* as

$$\mathbf{T} = \mathbf{T}^T \tag{3.93}$$

expressing the symmetry of the stress tensor (but see Rem. 17). Though our deduction was performed in the inertial frame fixed with distant stars, we can see that such symmetry of the stress tensor is valid in any frame, even a noninertial one, because the stress $\mathbf{T}$ is an objective tensor (see above and (3.32)).

Starting with (3.93) in any frame and tracing back the deduction we can obtain the integral form of the balance of angular momentum even in the noninertial frame; as may be expected such a result will be more complicated because of the nonobjectivity of $\mathbf{x}$, $\mathbf{y}$, $\mathbf{v}$ and objectivity of forces $\mathbf{T}$, $\mathbf{b}$, cf. e.g. [7, 14].

Namely, taking the outer product of $\mathbf{x}-\mathbf{y}$ with local momentum balance (3.78) in an arbitrary, even noninertial frame we have (we use (3.92) and the validity of moment of momentum balance (3.93) in any frame)

$$(\mathbf{x}-\mathbf{y}) \wedge \rho \dot{\mathbf{v}} = \mathrm{div}((\mathbf{x}-\mathbf{y}) \wedge \mathbf{T}) + (\mathbf{x}-\mathbf{y}) \wedge \rho(\mathbf{b}+\mathbf{i}) \tag{3.94}$$

where $\mathbf{y}$ may be an arbitrary function of time (at most, cf. our remark above (3.90); it would be better to denote all quantities in this new arbitrary frame say by stars as in Sect. 3.2, e.g. $\mathbf{y}^*$ may be obtained from $\mathbf{y}$ by (3.25) as $\mathbf{y}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{y}$ with fixed $\mathbf{y}$ (say from inertial frame fixed with distant stars above), but we do not use this mark for simplicity).

Integrating (3.94) through material volume $\mathcal{V}$ in this new arbitrary "starred" frame and using Gauss' theorem (3.23) we obtain (3.90) with $\mathbf{b}+\mathbf{i}$ instead of $\mathbf{b}$. Because $\dot{\overline{(\mathbf{x}-\mathbf{y}) \wedge \mathbf{v}}} = (\mathbf{x}-\mathbf{y}) \wedge \dot{\mathbf{v}} - \dot{\mathbf{y}} \wedge \mathbf{v}$ (namely $\dot{\mathbf{x}} \wedge \mathbf{v} = \mathbf{v} \wedge \mathbf{v} = \mathbf{0}$; scalar ρ is objective) we obtain by (3.68) ($\mathbf{y}$ is function of time at most) the balance of the moment of momentum related to even the nonfixed point $\mathbf{y}$ in an arbitrary (even noninertial) frame as

$$\dot{\overline{\int_{\mathcal{V}}(\mathbf{x}-\mathbf{y})\wedge\rho\mathbf{v}\,\mathrm{d}v}}+\dot{\mathbf{y}}\wedge\int_{\mathcal{V}}\rho\mathbf{v}\,\mathrm{d}v=\int_{\partial\mathcal{V}}(\mathbf{x}-\mathbf{y})\wedge\mathbf{Tn}\,\mathrm{d}a+\int_{\mathcal{V}}(\mathbf{x}-\mathbf{y})\wedge\rho(\mathbf{b}+\mathbf{i})\,\mathrm{d}v \tag{3.95}$$

Using here the Reynolds theorem (3.24) we can, e.g., write the balance of moment of momentum related to even a nonfixed point **y** in an arbitrary (even noninertial) frame for a fixed volume V in actual configuration as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{V}(\mathbf{x}-\mathbf{y})\wedge\rho\mathbf{v}\,\mathrm{d}v+\int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\rho\mathbf{v}(\mathbf{v}.\mathbf{n})\,\mathrm{d}a+\dot{\mathbf{y}}\wedge\int_{V}\rho\mathbf{v}\,\mathrm{d}v\\=\int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\mathbf{Tn}\,\mathrm{d}a+\int_{V}(\mathbf{x}-\mathbf{y})\wedge\rho(\mathbf{b}+\mathbf{i})\,\mathrm{d}v\end{aligned} \tag{3.96}$$

Therefore, as follows from (3.95), if point **y** is fixed (i.e., $\dot{\mathbf{y}}=\mathbf{o}$) the balances of moment of momentum (3.89) may be used also in an arbitrary (even noninertial) frame if body force **b** is enlarged by inertial acceleration **i** (3.79) (i.e., **b** is substituted by $\mathbf{b}+\mathbf{i}$). This is valid also for balance (3.90) (see deduction of (3.95)) and for local balance (3.91) (cf. (3.94)).

Balance of moment of momentum (3.93) expressed through the symmetry of a stress tensor (at least for mechanically nonpolar materials, cf. Rem. 17) is valid in any frame, even noninertial. Finally we can see that because (3.48) is valid for transformations between any inertial frames, the balances of angular moment related to fixed **y** (3.89)–(3.91) are valid in any inertial frame and not only in those fixed with distant stars.

Summary. The first three balance equations are formulated in this section. The balances are necessary conditions to be fulfilled not only in thermodynamics but generally (in continuum mechanics). The balance of mass was formulated locally in several alternatives—(3.62), (3.63), or (3.65). The most important consequence of the balance of momentum is the Cauchy theorem (3.72), which introduces the stress tensor. The local form of this balance is then expressed by (3.76) or (3.77). The most relevant outcome of the balance of moment of momentum is the symmetry of the stress tensor (3.93). Note that in this section also an important class of quantities—the specific quantities—was introduced by (3.66); note particularly their derivative properties (3.67) and (3.68).

3.4 Energy Balance and Entropy Inequality

In Chap. 1 we postulate the First Law as (1.3) which gives the existence of internal energy fulfilling (1.5). Similarly as in Sect. 2.1 we can write (1.5) as a balance: the time derivative of internal energy is equal to the sum of heating and power (cf. (2.1)) [11, 18, 22, 35]. This is applicable to the material volume of a (nonuniform) body or its arbitrary part consisting of a single substance. We postulate the existence of a *specific internal energy* u and assume that heating is composed of the *surface heating* q (exchange of heat between neighbourhood parts by conductivity) and the *volume heating* Q (exchange of heat by radiation from the outside of the body) which are surface and volume densities respectively.[18] Therefore assuming that power is given by forces from Sect. 3.3, i.e., by traction $\mathbf{t}$ (3.72) with symmetrical stress $\mathbf{T}$ (3.93) and the total body force $\underline{\beta}$ (3.86), we can postulate the *balance of energy* in the form

$$\overline{\int_{\mathcal{V}} \rho u \, \mathrm{d}v}^{\,\cdot} = \int_{\partial\mathcal{V}} q \, \mathrm{d}a + \int_{\mathcal{V}} Q \, \mathrm{d}v + \int_{\partial\mathcal{V}} \mathbf{v}.\mathbf{T}\mathbf{n} \, \mathrm{d}a + \int_{\mathcal{V}} \rho \underline{\beta}.\mathbf{v} \, \mathrm{d}v \tag{3.97}$$

for any material volume $\mathcal{V}$ with the surface $\partial\mathcal{V}$ but in actual configuration, cf. end of Sect. 3.1. The justification of the name *internal* energy on the left hand side follows from using all forces (including those inertial in $\underline{\beta}$) for the construction of power on the right-hand side, cf. discussion of (1.5).

We postulate also that u, q and Q are objective scalars (but see Rem. 21); then (3.97) is valid in all frames: by Rem. 12 the first three integrals in (3.97) are objective as well as the remaining scalar

$$\int_{\partial\mathcal{V}} \mathbf{v}.\mathbf{T}\mathbf{n} \, \mathrm{d}a + \int_{\mathcal{V}} \rho \underline{\beta}.\mathbf{v} \, \mathrm{d}v = \int_{\mathcal{V}} (\mathbf{v}.(\mathrm{div}\mathbf{T} + \rho \underline{\beta}) + \mathrm{tr}(\mathbf{L}\mathbf{T}))\mathrm{d}v = \int_{\mathcal{V}} \mathrm{tr}(\mathbf{D}\mathbf{T}) \, \mathrm{d}v \tag{3.98}$$

obtained by (3.23), (3.14), (3.85), (3.15), (3.93). Its objectivity follows from the objectivity of $\mathbf{D}$, $\mathbf{T}$ and therefore of $\mathbf{DT}$ (as may be easily seen) and its trace, see Sects. 3.2 and 3.3.

Densities in (3.97) are field quantities; but[19] we assume that the heating surface density q depends, in excess, on the external normal $\mathbf{n}$

$$q = q(\mathbf{x}, t, \mathbf{n}) \tag{3.99}$$

Then using the tetrahedron arguments (similarly as in deduction of (3.72)) we prove from (3.99), (3.97), that dependence on $\mathbf{n}$ is linear

$$q = -\mathbf{q}.\mathbf{n} \tag{3.100}$$

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[18] Exchange of radiation between distant parts of the same body is neglected; q on the real surface of body is given as a boundary condition. Assuming the validity of such a balance for each part of the body, we use again the principle of solidification and again volume and surface densities (ρu, Q, q etc.) could be deduced from more plausible primitives. Cf. Rems. 7, 13 and 14.

[19] Surface heating is scalar. Vectorial heat flux in (3.100) will be deduced quite similarly as the stress tensor was obtained from the traction in (3.72). Dependence of q on $\mathbf{n}$ may be expected, e.g., in a body under temperature gradient it may be expected in a given place that q on the surface perpendicular to such a gradient will be greater then on the surface parallel to it.

i.e., there exists a field[20] of the *heat flux* vector $\mathbf{q} = \mathbf{q}(\mathbf{x}, t)$. Indeed, if we apply (3.97) to a small tetrahedron (as in (3.73)) and use (3.68) and Gauss' theorem, we obtain

$$\rho \dot{u}\, \Delta v = q\, \Delta a + q^j\, \Delta a^j + Q\, \Delta v + (\operatorname{div}(\mathbf{vT}))\, \Delta v + \rho \underline{\beta}.\mathbf{v}\, \Delta v \tag{3.101}$$

Here $\Delta v = (1/3)h\, \Delta a$, h, Δa, $\Delta a^j = n^j \Delta a$ have the same meaning as in (3.73). Inserting these relations into (3.101) and limiting $h \to 0$ we obtain $q = -q^j n^j$ where $q^{\,j}$ (independent of $\mathbf{n}$) are components of the heat flux $\mathbf{q}$. Moreover, because of objectivities of q and (arbitrary) $\mathbf{n}$, the heat flux $\mathbf{q}$ is an objective vector (cf. motivation of (3.31) and below (3.72)).[21] Inserting (3.100) into (3.97) and using (3.68), (3.86) we obtain the balance of the whole energy (internal and kinetic) in the usual form

$$\begin{aligned}\overline{\int_{\mathcal{V}} \rho(u + (1/2)\mathbf{v}^2)\, \mathrm{d}v}^{\,\cdot} &= \int_{\mathcal{V}} \rho\overline{(u + (1/2)\mathbf{v}^2)}^{\,\cdot}\, \mathrm{d}v \\ &= -\int_{\partial\mathcal{V}} \mathbf{q}.\mathbf{n}\, \mathrm{d}a + \int_{\mathcal{V}} Q\, \mathrm{d}v + \int_{\partial\mathcal{V}} \mathbf{v}.\mathbf{Tn}\, \mathrm{d}a \\ &\quad + \int_{\mathcal{V}} \rho(\mathbf{b} + \mathbf{i}).\mathbf{v}\, \mathrm{d}v\end{aligned} \tag{3.102}$$

which is valid in an arbitrary frame (in inertial frame $\mathbf{i} = \mathbf{o}$). Balance (3.102) may be also written for fixed volume V with surface ∂V if we use the Reynolds theorem (3.24)

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}\int_{V} \rho(u + (1/2)\mathbf{v}^2)\, \mathrm{d}v + \int_{\partial V} \rho(u + (1/2)\mathbf{v}^2)\mathbf{v}.\mathbf{n}\, \mathrm{d}a \\ &\quad = \int_{\partial V} \mathbf{v}.\mathbf{Tn}\, \mathrm{d}a + \int_{V} \rho(\mathbf{b} + \mathbf{i}).\mathbf{v}\, \mathrm{d}v - \int_{\partial V} \mathbf{q}.\mathbf{n}\, \mathrm{d}a + \int_{V} Q\, \mathrm{d}v\end{aligned} \tag{3.103}$$

A special case follows when the body force has a potential Φ constant in the time[22]

$$\mathbf{b} + \mathbf{i} = -\operatorname{grad}\Phi, \quad \frac{\partial \Phi}{\partial t} = 0 \tag{3.104}$$

Inserting (3.104) into (3.102) and using (3.8), (3.68) we can interpret this special case as the balance of internal, kinetic and potential energy

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[20] The sign is in accord with convention mentioned in Rem. 7 in Chap. 1: negative heat q is emitted when $\mathbf{q}$ has direction of outer normal $\mathbf{n}$. Also Fourier law (3.187) directs heat flux $\mathbf{q}$ against temperature gradients, cf. [1, 14, 24, 27, 36, 37].

[21] Heat is based on molecular motion; therefore the possible nonobjectivity of heat flux has been discussed [24, 38–40]. Because of the molecular chaos this effect is probably negligible with the exception of very rarefied gases. Cf. also Rem. 33 in Chap. 4.

[22] Such is, e.g. the potential $\Phi = (1/2)\mathbf{x}^*.\underline{\Omega}^2\mathbf{x}^*$ giving centrifugal force (3.47); $\underline{\Omega}^2$ (as a product of the identical skew-symmetrical tensors) is symmetrical.

$$\dot{\overline{\int_{\mathcal{V}} \rho(u + (1/2)\mathbf{v}^2 + \Phi)\,\mathrm{d}v}} = \int_{\partial\mathcal{V}} \mathbf{v}.\mathbf{T}\mathbf{n}\,\mathrm{d}a - \int_{\partial\mathcal{V}} \mathbf{q}.\mathbf{n}\,\mathrm{d}a + \int_{\mathcal{V}} Q\,\mathrm{d}v \tag{3.105}$$

Now we can obtain the balance of energy in a local form using (3.68), Gauss' theorem and validity of (3.102) for all $\mathcal{V}$

$$\rho\dot{\overline{(u + (1/2)\mathbf{v}^2)}} = -\mathrm{div}\,\mathbf{q} + Q + \mathrm{div}(\mathbf{v}\mathbf{T}) + \rho(\mathbf{b} + \mathbf{i}).\mathbf{v} \tag{3.106}$$

From this we subtract the balance of "kinetic energy" obtained from (3.78) multiplying it by $\mathbf{v}$ and using (3.14), (3.15), (3.93) to get the *local energy balance*

$$\rho\dot{u} = -\mathrm{div}\,\mathbf{q} + Q + \mathrm{tr}(\mathbf{T}\mathbf{D}) \tag{3.107}$$

(this follows also by localization from (3.97), (3.68), (3.100), (3.98)). This result is valid in any frame because of objectivity of all members here, cf. Sect. 3.2.

We now apply the entropy inequality (1.42) to our continuous body (or arbitrary part of it). Because the integral in (1.42) may be understood (by definition of heat distribution) as time and space integral we can formulate an entropy inequality using the entropy rate, heating and corresponding densities of these quantities (cf. end of Sect. 1.4 and the way we obtained (2.2); again it is possible to proceed more naturally, see Rems. 7, 14 and 18) [11, 18, 35, 41]. Therefore entropy may be expressed if we introduce the *specific entropy* s as a primitive objective scalar. Because the heating now contains surface and volume parts with densities q and Q (cf. (3.97)) and because the absolute temperature is now scalar field $T = T(\mathbf{x}, t)$, assumed to be objective, it follows that the *entropy inequality* may be formulated as (we use (3.100))

$$\dot{\overline{\int_{\mathcal{V}} \rho s\,\mathrm{d}v}} \geq -\int_{\partial\mathcal{V}} (\mathbf{q}/T).\mathbf{n}\,\mathrm{d}a + \int_{\mathcal{V}} (Q/T)\,\mathrm{d}v \tag{3.108}$$

for the material volume $\mathcal{V}$ with the surface $\partial\mathcal{V}$ of a body or its arbitrary part.[23]

By Gauss' theorem and (3.68) we obtain entropy inequality in the local form called the *Clausius-Duhem inequality*

$$\sigma \equiv \rho\dot{s} + \mathrm{div}(\mathbf{q}/T) - Q/T \geq 0 \tag{3.109}$$

valid in any frame. The left-hand side of inequality (3.109) defines the *production of entropy* σ which is therefore never negative and by the objectivity of its defining quantities it is an objective scalar.

Using (3.68), Gauss' theorem (3.23) and definition (3.109) we can write entropy inequality (3.108) as

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[23] Using Reynolds theorem (3.24) in (3.108) we obtain quite naturally the entropy inequality for open systems in (single) continua. Cf. Rems. 14 in Chap. 2, 11 in Chap. 4 and the end of Sect. 3.1.

$$\int_{\mathcal{V}} \rho \dot{s}\, \mathrm{d}v + \int_{\mathcal{V}} \mathrm{div}(\mathbf{q}/T)\, \mathrm{d}v - \int_{\mathcal{V}} (Q/T)\, \mathrm{d}v = \int_{\mathcal{V}} \sigma\, \mathrm{d}v \geq 0 \tag{3.110}$$

Finally, we can eliminate **q** and Q from energy balance (3.107) and Clausius-Duhem inequality (3.109) and use the following definition of the *specific free energy* f and the *temperature gradient* **g**

$$f \equiv u - Ts \tag{3.111}$$

$$\mathbf{g} \equiv \mathrm{grad}\, T \tag{3.112}$$

(it follows that both are objective quantities, cf. Sect. 3.2) to get the *reduced inequality*

$$-T\sigma = \rho \dot{f} + \rho s \dot{T} + T^{-1}\, \mathbf{q}.\mathbf{g} - \mathrm{tr}(\mathbf{TD}) \leq 0 \tag{3.113}$$

This is again objective and will be useful later in Sect. 3.6.

At the end of these Sects. 3.3 and 3.4 we note that energy balance and entropy inequality motivated by procedures like those in Chap. 1 together with generalization of frame indifference (plausible objectivity is postulated not only for motion (Sect. 3.2) but also, e.g., for power of surface and body forces or heating) permit to deduce balances in Sect. 3.3 (i.e., for mass, linear and angular momentum), internal energy, entropy and their objectivity, etc. For details see, e.g., [1, 22, 42, 43] and other works on modern thermomechanics [7, 8, 18, 20, 41].

Summary. Energy balance containing heat transfer, and entropy inequality are typical thermodynamic conceptions. In fact, they constitute the (general forms of) First and Second Law of thermodynamics, respectively. Perhaps the most important for further development are the local energy balance in the form (3.107) and the Clausius-Duhem formulation of entropy inequality—(3.109). Introducing the (specific) free energy, (3.111), the latter is transformed to the reduced form (3.113).

3.5 Constitutive Principles and Constitutive Equations for the Single Substance

In preceding paragraphs, the balances and the entropy inequality in local form (3.63), (3.76), (3.93), (3.107), (3.109) have been obtained. Because of the general validity of balances (for broad class of nonuniform single continua in a given case; cf. similar situation in Sect. 2.1) these independent relations are not sufficient for determination of all fields (functions of **x**, t) occurring there

$$\underline{\chi}\,, \quad \rho\,, \quad T \tag{3.114}$$

$$u\,, \quad s\,, \quad \mathbf{q}\,, \quad \mathbf{T} \tag{3.115}$$

$$Q\,, \quad \mathbf{b}\,, \quad \mathbf{i} \tag{3.116}$$

We call the fields (3.114)–(3.116) fulfilling the balances of mass (3.63), (3.65), momentum (3.76), moment of momentum (3.93), and energy (3.107) a *thermodynamic process*, because only these are of practical interest. Then we denote the fields (3.114) as the *thermokinetic process* and the fields (3.115) as the *responses* (we limit to the models with symmetric **T** (3.93); in more general models we must introduce also the torque **M** into responses (3.115), cf. Rems. 17, 32). The fields (3.116) are controlled from the outside[24] (at least in principle). Just constitutive equations, which express the difference among materials, represent the missing equations and are relations between (3.114) and (3.115) [6, 7, 9, 10, 23, 34, 38, 40, 41, 44, 45]. Referring to Sect. 2.1 we briefly recall that *constitutive equations* are definitions of ideal materials which approximate real materials in the circumstances studied (i.e., at chosen time and space scales). Constitutive equations may be proposed in rational thermodynamics using the *constitutive principles* of[25]: *determinism, local action, memory, equipresence, objectivity, symmetry*, and *admissibility*.

The constitutive principle of *determinism* asserts that responses (3.115) in the present instant and given place are determined by thermokinetic process (3.114) in the past and present in all the body. But in single substances, the field of density is given by the motion through (3.65) (field ρ_0 is assumed to be known) and therefore response (3.115) is given by fields $\underline{\chi}$ and T only (in fact mass balance was used; this will be used also in the following applications of thermokinetic process, cf. Sects. 3.6, 4.5). Thus, the constitutive equations are functionals giving values of (3.115) in given particle **X** and present time t, independent variables of which are functions

$$\underline{\chi}(\mathbf{Y},\tau)\ , \quad T(\mathbf{Y},\tau) \tag{3.117}$$

in all the particles **Y** of the body and all times $\tau \leq t$. This very general material model is significantly reduced by the following two constitutive principles. The principle of *local action* asserts that responses (3.115) are influenced only by values of (3.117) in particles $\mathbf{Y} = \mathbf{X}$ and in immediate neighbourhood of **X** ("locality," cf. Rem. 12 in Chap. 2) and, similarly, the principle of *differential memory* asserts that the response (3.115) is given only by the values (3.117) in the present time t and in the immediate past. Mathematically we can express these principles in the following way (cf. Sect. 2.1 and Rem. 3 in Chap. 2 for memory effect only): we expand (3.117) in the Taylor series around the present time t and given particle **X**; then the response is influenced only by the values and several space and time derivatives taken at these t and **X**. This means that the response functionals are reduced to the following functions:

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \breve{\mathcal{F}}(\mathbf{x}, \mathbf{v}, \mathbf{F}, \mathrm{Grad}\mathbf{F}, \dot{\mathbf{F}}, T, \mathrm{Grad}T, \mathbf{X}, t) \tag{3.118}$$

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[24] Such are also boundary values **q**, **T** on the real surface of the whole body, cf. Rems. 13, 18, see also Rem. 36.

[25] Repeating those noted in Sects. 1.1 and 2.1 the name "principles" here is stilted a little: they are rather rules or recommendations which generalize motivation or proposals of such equations in the past [40], cf. exceptions in Rems. 21, 26, and 28.

We believe that the choice of derivatives is representative for the materials intended for study here. Note the elimination of temperature memory; otherwise the "local equilibrium" might be invalid (cf. Sects. 2.2, 4.5).

In (3.118), the concise form of writing of several constitutive equations with the same variables was used, i.e., here $\breve{\mathcal{F}}$ stands for constitutive functions $\breve{s}, \breve{u}, \breve{\mathbf{q}}, \breve{\mathbf{T}}$ respectively (overhead symbol $\smile$ differs function from its value; rare exclusion, see, e.g., Sect. 3.2). Because the response as well as the independent variables are functions of $\mathbf{X}$ and t, we add in (3.118) also explicit dependence on these quantities.[26] In formulation of constitutive equations (3.118) the constitutive principle of *equipresence* was used: in all constitutive equations (3.118) we used the same independent variables. This prevents the unjustified preference of some of such equations; it is a rather plausible rule, cf. Rem. 25, Sect. 2.1, which in special cases, e.g. [28, 60], may be left.

The explicit dependence on $\mathbf{X}$ in (3.118) means that in different particles of our body there may be different material of the same type (i.e., depending on the same variables but in different way). We eliminate for simplicity this dependence, i.e., our body consists of the same material in all particles.[27] Then we use (3.14), (3.15), (3.112) to write (3.118) in the form

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \breve{\mathcal{F}}(\mathbf{x}, \mathbf{v}, \mathbf{F}, \mathrm{Grad}\mathbf{F}, \mathbf{D}, \mathbf{W}, T, \mathbf{g}, t) \tag{3.119}$$

where $\breve{\mathcal{F}}$ means functions $\breve{s}, \breve{u}, \breve{\mathbf{q}}, \breve{\mathbf{T}}$.

Further reduction of constitutive equations (3.119) may be achieved by the constitutive principle of *frame indifference* or the principle of *objectivity*: the material properties and therefore also constitutive equations must be independent of the choice of frame. This principle is a generalization of common experience with mate-

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[26] Great numbers of more general models have been studied e.g. with long range memory (as *fading memory* or with *internal variables* mentioned in Sects. 2.1, 2.3), where differential memory is not suitable. Its analog for a space coordinate is the nonlocal material [46–50] where the local action is not sufficient. Another type are materials with a microstructure (*micromorphic* materials) in which the particles have a more complicated structure [11, 45, 48, 51, 52] (cf. Rem. 2). For simplicity we excluded in (3.118) the temperature memory studied in [23, 26, 53] (the influence of which was outlined in Sect. 2.2; cf. Rem. 31 in Chap. 4). The principle of determinism is modified in materials with *internal constraints* [6, 7, 10, 12, 54–58] manifested usually as some a priori limitation on the motion (but there are also nonmechanical constraints such as perfect heat conductivity). Most important are *incompressible* materials where the internal constraint is $J = 1$ (by (3.64) density of particles does not change and therefore only isochoric motions are allowed). The limitation is achieved by forces (pressure in incompressible material) which are not determined by the motion and do not work. The remaining part of the stress is given by the usual principle of determinism. Modification of determinism is also given by using pressure as an independent variable (usual in classical thermodynamics); then incompressibility may be also understood as pressure independence here [24, 59], cf. end of Sect. 3.7.

[27] Moreover a unique reference configuration was tacitly assumed in the whole body. But there are (nonfluid, usually solid) materials with *dislocations* which may be just described by nonunique references and dependence on $\mathbf{X}$ remains even if they are from the "same" material, cf. [6, 8, 41], cf. also Rem. 30.

rial properties.[28] Mathematically this principle means that the functions in (3.119) (considered in some frame) are the same in the arbitrary other "starred" frame

$$\{s^*, u^*, \mathbf{q}^*, \mathbf{T}^*\} = \breve{\mathcal{F}}(\mathbf{x}^*, \mathbf{v}^*, \mathbf{F}^*, (\mathrm{Grad}\mathbf{F})^*, \mathbf{D}^*, \mathbf{W}^*, T^*, \mathbf{g}^*, t^*) \tag{3.120}$$

where starred quantities in the new frame are transformed by (3.25), (3.26), (3.38), (3.49), (3.53), (3.54), (3.51) and (3.30)–(3.32) for objective $s, u, \mathbf{q}, \mathbf{T}, T, \mathbf{g}$.

In a special choice $\mathbf{Q} = \mathbf{1}$ and arbitrary $b, \mathbf{c}, \dot{\mathbf{c}}, \dot{\mathbf{Q}}$, these transformations must give the same values of responses in (3.119) and (3.120) (because $\breve{\mathcal{F}}$ is the same in both frames) and this is possible (change from (3.119) to (3.120) is valid for any values of independent variables) only if responses are independent of variables $\mathbf{x}, t, \mathbf{v}$ and $\mathbf{W}$. This means that two observers with a shift in origins of time and space and with different velocities of translation and rotation must obtain the same responses. Therefore, the constitutive equations (3.119) must be reduced by the principle of frame indifference (or objectivity) to the form

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \bar{\mathcal{F}}(\mathbf{F}, \mathrm{Grad}\mathbf{F}, \mathbf{D}, T, \mathbf{g}) \tag{3.121}$$

where again $\bar{\mathcal{F}}$ means functions $\bar{s}, \bar{u}, \bar{\mathbf{q}}, \bar{\mathbf{T}}$.[29] Because responses are given by (3.121) in the actual reference, the $\bar{\mathcal{F}}$ must be such that responses are the same if we only change reference configuration ($\mathbf{F}$ and Grad$\mathbf{F}$ change correspondingly but describe the same deformation; the other independent variables in (3.121) remain the same [6, 7, 41, 63], cf. Rem. 30 for application).

But this is not all. Using again the change of frame with arbitrary $\mathbf{Q}$ in the constitutive equations (3.121) we have (note that here all dependent and independent variables are objective; we can regard $\mathbf{F}$ and Grad$\mathbf{F}$ as objective vectors, cf. (3.49), (3.51))

$$\{s, u, \mathbf{Qq}, \mathbf{QTQ}^T\} = \bar{\mathcal{F}}(\mathbf{QF}, \mathbf{Q}\mathrm{Grad}\mathbf{F}, \mathbf{QDQ}^T, T, \mathbf{Qg}) \tag{3.122}$$

which must be identically valid for any values of independent variables and any orthogonal tensor $\mathbf{Q}$ from the full orthogonal group (see Rem. 8), i.e., at any rota-

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[28] E.g. we tacitly assume such a principle in the assertion that the same force extends by the same amount the loaded spring when it is suspended in gravitational field or it is attached in the centre of rotated disc. Namely, we assume that the constant of the Hook's law of the spring (i.e., its constitutive equation) is the same in these both frames [6, 7, 61]. But, cf. Rem. 25, even here they are exceptions [62] (from nonclassical physics).

[29] Namely, the substitution described below (3.120) gives

$$\{s, u, \mathbf{Qq}, \mathbf{QTQ}^T\} = \breve{\mathcal{F}}(\mathbf{Qx}+\mathbf{c}, \mathbf{Qv}+\dot{\mathbf{c}}+\underline{\Omega}\mathbf{Qx}, \mathbf{QF}, \mathbf{Q}\mathrm{Grad}\mathbf{F}, \mathbf{QDQ}^T, \mathbf{QWQ}^T+\underline{\Omega}, T, \mathbf{Qg}, t+b)$$

which by choice

$$\mathbf{Q} = \mathbf{1}, \mathbf{c} = -\mathbf{x}, \dot{\mathbf{c}} = -\mathbf{v} + \mathbf{Wx}, \underline{\Omega} = -\mathbf{W}, b = -t$$

gets

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \breve{\mathcal{F}}(\mathbf{o}, \mathbf{o}, \mathbf{F}, \mathrm{Grad}\mathbf{F}, \mathbf{D}, \mathbf{0}, T, \mathbf{g}, 0) \equiv \bar{\mathcal{F}}(\mathbf{F}, \mathrm{Grad}\mathbf{F}, \mathbf{D}, T, \mathbf{g})$$

valid for any independent variables, i.e., giving (3.121).

tion and inversion (also restriction on rotation only is used; cf. Rem. 9). This condition (3.122) restricts the form of functions to the so-called *isotropic functions*, the form of which in vector and tensor variables is very limited [6, 9, 64–66] (cf. also Appendix A.2 for linear functions on which we concentrate later, see Sect. 3.7). We name the model with constitutive equations (3.121) the *nonsimple* (or *second grade*) *material with heat conduction and viscosity*.

A special case is a *simple* material which does not depend on Grad**F**, cf. [67, 68]

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \bar{\mathcal{F}}(\mathbf{F}, \mathbf{D}, T, \mathbf{g}) \tag{3.123}$$

Such functions $\bar{\mathcal{F}}$ must again be isotropic (for **Q** from full orthogonal group)

$$\{s, u, \mathbf{Qq}, \mathbf{QTQ}^T\} = \bar{\mathcal{F}}(\mathbf{QF}, \mathbf{QDQ}^T, T, \mathbf{Qg}) \tag{3.124}$$

Further simplification of (3.123) is *thermoelastic* material (with heat conductivity, see Sect. 3.6)

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \bar{\mathcal{F}}(\mathbf{F}, T, \mathbf{g}) \tag{3.125}$$

(or *elastic* at T fixed, cf. Rem. 31) again isotropic, i.e., fulfilling analogical conditions (3.124).

The following constitutive principle of *material symmetry* demands that constitutive equations must be in accord with the inherent symmetry of the material studied.

Here we confine mainly to *fluids* (gases or liquids) defined as materials with maximal symmetry. Using this principle we find that dependence on **F** and Grad**F** may be in fluids expressed through dependence on density ρ and its gradient **h**

$$\mathbf{h} \equiv \mathrm{grad}\rho \tag{3.126}$$

respectively, and constitutive equations are independent of the reference. Other important materials are *solids*, mainly those *isotropic* (not to be confused with the isotropic function!), or crystals of different crystal classes, etc. For the purposes of this book, we plainly define the fluid using ρ instead of **F** in (3.125) for a simple fluid, and using ρ, **h** instead of **F**, Grad**F** in (3.121) for a nonsimple fluid. But such replacement may be deduced.[30]

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[30] How the principle of symmetry works we outline on simple material (3.123) (see [6, 7, 10, 14, 41, 63, 69] for details); for nonsimple fluid the similar procedure is more complicated, see [14, 70, 71]. Assume for simplicity a unique reference with reference density ρ_0 in the whole body (everywhere is uniform material without dislocations, see Rem. 27) and all responses behave equally (their symmetries are the same). The material symmetry may be expressed by (referential) tensor **H** (in components H^{JK}) which, changing deformation **F** to **FH** in constitutive relation (3.123), gives the same response

$$\bar{\mathcal{F}}(\mathbf{F}) = \bar{\mathcal{F}}(\mathbf{FH}) \qquad (a)$$

(nonchanging variables are omitted for brevity) and also the same (actual) density ρ at considered reference density ρ_0, i.e., by (3.65), (3.12), $\rho_0 = \rho|\mathrm{det}\mathbf{F}| = \rho|\mathrm{det}\mathbf{FH}|$. This latter condition limits tensors **H** to those which are unimodular

Also other criteria for classification of materials may be used.[31]

Therefore constitutive equations of *nonsimple fluid with viscosity and heat conduction* are

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \hat{\mathcal{F}}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \tag{3.127}$$

where $\hat{\mathcal{F}}$ stands for functions $\hat{s}$, $\hat{u}$, $\hat{\mathbf{q}}$, $\hat{\mathbf{T}}$ (independent variables including ρ and therefore $\mathbf{h}$ are objective, cf. Sect. 3.2). We repeat that response $\mathbf{T}$ here and in all mentioned constitutive functions is a symmetric tensor. Moreover, the principle of objectivity demands that functions $\hat{\mathcal{F}}$ must be isotropic, i.e., for any $\boldsymbol{Q}$ from full orthogonal group and all values of independent variables the following is valid

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(Footnote 30 continued)

$$|\ \det\mathbf{H}\ | = 1 \qquad (b)$$

E.g. indistinguishable rotation may be described by orthogonal $\mathbf{H}$ ((b) is valid, cf. Rem. 8).

All such $\mathbf{H}$ form the *symmetry group* $\mathcal{G}$ (e.g., two such rotations $\mathbf{H_1}$, $\mathbf{H_2}$ give indistinguishable rotation $\mathbf{H_1H_2}$) which characterize the inherent symmetry of studied material (3.123) in the considered reference configuration. For example, material is isotropic if any rotation (or even inversion) is indistinguishable, i.e., $\mathcal{G}$ contains a proper (or even full) orthogonal group.

Note that a symmetry group depends on a considered reference: its change (which may also alter referential density) generally changes the group. This is described by Noll's rule; for this and other details see, e.g. [10].

A symmetry group of *simple* material divides it in two parts (and each of them in isotropic and anisotropic subparts) [6, 7, 63]:

- simple solids: isotropic or anisotropic (crystal classes like cubic, hexagonal, triclinic etc.)
- simple liquid crystals: isotropic (simple fluids, i.e., gases or liquids) or anisotropic (liquid crystals).

E.g. in *simple solids* there exists a reference the symmetry group of which is contained in (full) orthogonal group; if they are identical then the material is the simple *isotropic* solid.

Simple fluid has a group of symmetry identical to a *unimodular group* (contains all $\mathbf{H}$ with $|\ \det\mathbf{H}\ | = 1$); this group is therefore the maximal one and fluids are isotropic (because they contain the orthogonal group, cf. Rem. 8; note that unimodular deformations (indistinguishable in fluids) need not be orthogonal, e.g., isochoric shear). Replacement of $\mathbf{F}$ by ρ follows from (a), (b) by the choice $\mathbf{H} = J^{1/3}\mathbf{F}^{-1}$ (unimodular for given $\mathbf{F}$: $|\ \det\mathbf{H}\ | = |\ \det(J^{1/3}\mathbf{F}^{-1})\ | = J\ |\ \det\mathbf{F}\ |^{-1} = 1$). Indeed, by (3.65), the response is

$$\bar{\mathcal{F}}(\mathbf{FH}) = \bar{\mathcal{F}}((\rho_0/\rho)^{1/3}) \equiv \hat{\mathcal{F}}(\rho) \qquad (c)$$

where $\hat{\mathcal{F}}$ is in fact independent of any reference (and its ρ_0) because the response (in actual configuration) must remain the same if the reference (and therefore $\mathbf{F}$, ρ_0) is changed (cf. remark under (3.121) valid also for (3.123)).

[31] Besides those based on symmetry in Rem. 30, see e.g., [8], another was used by Haupt [72] according to the size of memory for the stress tensor $\mathbf{T}$ in an isothermal body: materials (mostly solids) are

(i) elastic: $\mathbf{T}$ is (deformation) rate independent without hysteresis, e.g. (3.125).
(ii) plastic: $\mathbf{T}$ is rate independent with hysteresis (by appropriate internal variables, cf. Sect. 2.3).
(iii) viscoelastic: $\mathbf{T}$ is rate dependent without hysteresis, e.g. (3.123).
(iv) viscoplastic: $\mathbf{T}$ is rate dependent with hysteresis (possible even in equilibrium).

$$\{s, u, \mathbf{Qq}, \mathbf{QTQ}^T\} = \hat{\mathcal{F}}(\rho, \mathbf{Qh}, \mathbf{QDQ}^T, T, \mathbf{Qg}) \tag{3.128}$$

Analogously, starting from (3.123), *simple fluid with viscosity and heat conduction* has the constitutive equations

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \hat{\mathcal{F}}(\rho, \mathbf{D}, T, \mathbf{g}) \tag{3.129}$$

with analogical properties (3.128).

Finally the specialization of (3.125) on fluid leads to

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \hat{\mathcal{F}}(\rho, T, \mathbf{g}) \tag{3.130}$$

with analogical properties (3.128). This is the *thermoelastic fluid* or, in isothermal case, the *elastic fluid* or *ideal (Euler) fluid*.

The final form of constitutive equations for these models (3.125), (3.127), (3.129) will be given in Sect. 3.6 where we use the constitutive principle of admissibility.

Summary. A procedure really specific for the rational thermodynamics is introduced in this section in the form of several principles put forward to derive the thermodynamically consistent constitutive equations. In their most general form, the constitutive equations were proposed as functions (3.118) on the basis of the principles of determinism, local action, differential memory, and equipresence. They were further reduced to the form (3.121) considering the same material throughout the body and applying the principle of objectivity. Because of our interest in fluids only, the constitutive equations were further modified to this material type by means of the principle of material symmetry giving the final form (3.127). Two special types of fluid were defined by (3.129) and (3.130).

3.6 Principle of Admissibility — Constitutive Equations of Single Material. Fluid with Viscosity and Heat Conduction

The last constitutive *principle of admissibility* (or *dissipation* or *entropy principle*) proposed by Coleman and Noll [68] is the most typical for rational thermodynamics [6, 7, 9, 23, 24, 34, 38, 45, 63, 73] (cf. Sects. 2.2, 2.4, 2.5, 3.7, 4.5).

We call a thermodynamic process which is possible in a given material model, i.e., fields (like (3.114)–(3.116)) fulfilling all balances (like (3.65), (3.76), (3.93), (3.107)) combined with proposed constitutive equations an *admissible thermodynamic process*. Now, we want such a process to also fulfil entropy inequality. According to Coleman and Noll [68] (cf. Rem. 5 in Chap. 2) we leave the admissible thermodynamic process arbitrary and restrict the constitutive equations in such a way that the entropy inequality (3.109) is satisfied identically.

Therefore, the constitutive *principle of admissibility* (also called the *principle of dissipation* or *entropy*) may be formulated as follows: entropy inequality must be satisfied in any admissible thermodynamic process; mathematical justification of this principle was given by Muschik and Ehrentraut [74].

But, because of the validity of balances (3.107) (and remaining balances (3.93), (3.78), (3.63)), the entropy inequality (3.109) may be expressed as reduced inequality (3.113), the constitutive principle of admissibility may be alternatively formulated as follows: reduced inequality (3.113) must be satisfied in any admissible thermodynamic process.

Moreover, as we show in the following examples, an admissible process may be constructed from a thermokinetic process fulfilling the mass balance (using constitutive equations proposed so far and using outside controlled fields like (3.116)). Therefore, the results of the admissibility principle (i.e., simplifications and further properties of constitutive equations) follow from inequality obtained by inserting the constitutive equations into the reduced inequality and by using suitable thermokinetic process (fulfilling the mass balance, cf. above (3.117); there is also alternative method of I-Shih Liu explained in Appendix 5 avoiding the construction of admissible process in complicated cases. As was shown in Appendix 5, this method gives the same results for our fluid models of Sects. 2.2, 3.7, 4.5).

Although fluids are our main interest, first we demonstrate the admissibility principle on thermoelastic material (3.125).

Here the free energy (3.111) used in (3.113) has obviously the following constitutive equation

$$f = \bar{f}(\mathbf{F}, T, \mathbf{g}) \tag{3.131}$$

We calculate $\dot{f}$ using $\overset{\cdot}{\overline{\mathbf{F}\mathbf{F}^{-1}}} = 0$ and (3.13)–(3.15) and introducing result in (3.113) we obtain (in Cartesian components):

$$\begin{aligned}-T\sigma = {} & \rho \frac{\partial \bar{f}}{\partial F^{iJ}} F^{jJ} W^{ij} + \left(\rho \frac{\partial \bar{f}}{\partial F^{iJ}} F^{jJ} - T^{ji}\right) D^{ij} + \rho \left(\frac{\partial \bar{f}}{\partial T} + s\right) \dot{T} \\ & + \rho \overset{-1}{F}{}^{Ji} \frac{\partial \bar{f}}{\partial g^i} \overset{\cdot}{\overline{(\mathrm{Grad} T)^J}} - \rho \overset{-1}{F}{}^{Ki} \frac{\partial \bar{f}}{\partial g^i} (\mathrm{Grad} T)^J \overset{-1}{F}{}^{Jj} \dot{F}^{jK} + T^{-1} q^i g^i \leq 0\end{aligned} \tag{3.132}$$

According to the dissipation principle, this inequality must be valid at any admissible thermodynamic process, which in turn, may be obtained from the appropriate thermokinetic process (3.114) fulfilling the mass balance (cf. general procedure sketched above).

Namely, the inequality (3.132) must be valid in an arbitrarily chosen particle $\mathbf{X}$ and (say present) instant t ($\mathbf{x}$ is the place of $\mathbf{X}$ at t according to motion (3.1)) and the following thermokinetic process (cf. (3.114)) may be constructed in any particle $\mathbf{Y}$ and any time τ (with place $\mathbf{y}$) in the body as follows: for it we use the following expansions about considered $\mathbf{X}$ and present time t

$$\mathbf{y} = \underline{\chi}(\mathbf{Y}, \tau) = \mathbf{x} + \mathbf{F}(\mathbf{Y} - \mathbf{X}) + \dot{\mathbf{F}}(\mathbf{Y} - \mathbf{X})(\tau - t) \tag{3.133}$$

$$T(\mathbf{Y},\tau) = T + (\mathrm{Grad}T)(\mathbf{Y}-\mathbf{X}) + \overset{\cdot}{\overline{(\mathrm{Grad}T)}}(\mathbf{Y}-\mathbf{X})(\tau - t) \tag{3.134}$$

where $\mathbf{x}$, T, $\mathbf{F}$, $\dot{\mathbf{F}}$, Grad$T$, $\overset{\cdot}{\overline{(\mathrm{Grad}T)}}$ are values of these fields and its derivatives taken at $\mathbf{X}$, t, and the density field follows from mass balance (3.65)

$$\rho(\mathbf{Y},\tau) = \rho_0(\mathbf{Y}) / \mid \det\mathbf{F}(\mathbf{Y},\tau) \mid \tag{3.135}$$

(cf. above (3.117); it is valid by the field of density in the given reference configuration $\rho_0(\mathbf{Y})$ which is assumed to be known. The fixed mass of the body is then given by (3.58)).

The thermokinetic process (3.133)–(3.135) in thermoelastic material (3.125) fulfilling mass balance generates the admissible thermodynamic process. Indeed, for chosen values of $\mathbf{F}$, T and $\mathbf{g} = (\mathrm{Grad}T)\mathbf{F}^{-1}$ at $\mathbf{X}$ (or place $\mathbf{x}$) and t (see (3.13)) the fields of responses (3.115) follow by (3.125); the symmetric response $\mathbf{T}$ fulfils the balance of moment of momentum. Mass balance is satisfied by (3.135) and the balance of momentum (3.78) and energy (3.107) are satisfied by the appropriate choice of external body force $\mathbf{b}(\mathbf{Y},\tau)$ (or/and inertial force $\mathbf{i}(\mathbf{Y},\tau)$) and volume heating $Q(\mathbf{Y},\tau)$ because (3.116) are controlled from the outside.

Therefore, an admissible thermodynamic process exists and is caused by thermokinetic process (3.133)–(3.135); by the admissibility principle the inequality (3.132) must be satisfied. Then this inequality must be satisfied at (arbitrarily chosen) particle $\mathbf{X}$ and instant t by arbitrarily chosen values of mutually independent $\mathbf{F}$, T, $\mathbf{g}$ (or Grad$T$) and $\mathbf{W}$, $\mathbf{D}$, $\dot{T}$, $\overset{\cdot}{\overline{(\mathrm{Grad}T)}}$ (this follows from the independence of derivatives in expansions (3.133), (3.134) and (3.14), (3.15); note that T (and ρ) are positive scalars and $\mathbf{D}$, $\mathbf{W}$ are symmetric or skew-symmetric tensors, respectively). But the inequality (3.132) depends only linearly on the latter values and therefore members containing them must be zero because of Lemmas A.5.1, A.5.2 from Appendix 5.

Indeed, if we choose $\mathbf{F}$, T, $\mathbf{g}$ fixed, $\mathbf{D}$, $\mathbf{W}$, $\overset{\cdot}{\overline{(\mathrm{Grad}T)}}$ zero, the following relation follows from Lemma A.5.1

$$\frac{\partial \bar{f}}{\partial T} = -s \tag{3.136}$$

because $\dot{T}$ may be arbitrary scalar (and $\rho > 0$).

Similarly, if we choose $\overset{\cdot}{\overline{(\mathrm{Grad}T)}}$ arbitrary at $\mathbf{F}$, T, $\mathbf{g}$ fixed and $\mathbf{D}$, $\mathbf{W}$, $\dot{T}$ zero, the following vector must be zero

$$\frac{\partial \bar{f}}{\partial \mathbf{g}} = \mathbf{o} \tag{3.137}$$

by Lemma A.5.1 (applied on components, i.e., we choose the components of vector $\overset{\cdot}{\overline{(\mathrm{Grad}T)}}^{J}$ for $J = 1$ arbitrary and for $J = 2, 3$ as zeros; then the first component of vector $\rho \overset{-1}{F}{}^{Ji} \frac{\partial \bar{f}}{\partial g^i}$ must be zero. Repeating such application of Lemma A.5.1 for remaining $J = 2, 3$ we also obtain zeros for the remaining components of this last vector. Because matrix $\rho \overset{-1}{F}{}^{Ji}$ is regular we obtain result (3.137)).

Further, we use Lemma A.5.2 (with consequences for symmetric and skew-symmetric tensors). Namely, if we choose $\mathbf{D}$, $\dot{\overline{(\mathrm{Grad}T)}}$, $\dot{T}$ zero at arbitrary $\mathbf{F}$, T, $\mathbf{g}$, the first member in (3.132) must be zero at any skew-symmetric tensor $\mathbf{W}$, i.e., the following tensor in this member must be symmetric

$$\frac{\partial \bar{f}}{\partial \mathbf{F}} \mathbf{F}^T = \mathbf{F} \left(\frac{\partial \bar{f}}{\partial \mathbf{F}} \right)^T \tag{3.138}$$

By analogical arguments, we obtain from Lemma A.5.2 that the tensor standing at $\mathbf{D}$ in (3.132) must be skew-symmetric. But it is at the same time symmetric (see (3.138), (3.93)) and therefore it is zero.[32]

$$\mathbf{T} = \rho \frac{\partial \bar{f}}{\partial \mathbf{F}} \mathbf{F}^T \tag{3.139}$$

Moreover, these results (3.136)–(3.137) are valid identically: at any $\mathbf{F}$, T, $\mathbf{g}$ and any $\mathbf{X}$, t. Therefore, (3.131) is reduced to

$$f = \bar{f}(\mathbf{F}, T) \tag{3.140}$$

and (3.136) and (3.139) show that free energy is a potential for entropy and stress, i.e., the corresponding Gibbs equation is valid. Therefore also s (and by (3.111) also u) and $\mathbf{T}$ depend on $\mathbf{F}$, T only (only heat flux $\mathbf{q}$ depends on temperature gradient $\mathbf{g}$).

Production of entropy is caused only by heat conduction

$$\sigma = -T^{-2} \mathbf{q} . \mathbf{g} \geq 0 \tag{3.141}$$

and it is zero in the *equilibrium process* defined here by

$$\mathbf{g} = \mathbf{o} \tag{3.142}$$

(cf. the end of Sect. 2.1 and Rem. 11 in Chap. 1). But in equilibrium (3.142) the production of entropy $\sigma = \overline{\sigma}(\mathbf{F}, T, \mathbf{g})$ (cf. (3.125)) has a minimum and therefore

$$\frac{\mathrm{d}}{\mathrm{d}\lambda} \overline{\sigma}(\mathbf{F}, T, \lambda \mathbf{g}) \mid_{\lambda=0} = 0 \tag{3.143}$$

where λ is a real parameter. Inserting (3.141) into (3.143) gives

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[32] Note that by analogical calculation for (mechanically) polar materials Rem. 17, the result (3.139) is valid but its skew-symmetric part gives torque $\mathbf{M}$.

$$\mathbf{q}^o \equiv \overline{\mathbf{q}}(\mathbf{F}, T, \mathbf{o}) = \mathbf{o} \tag{3.144}$$

and therefore equilibrium value $\mathbf{q}^o$ of the heat flux is zero.

Without going into details we note also that sufficient conditions of minima of $\overline{\sigma}$ may be discussed and further simplifications of these results using objectivity (3.124) and material symmetry may be obtained: using Cauchy-Green tensors, Piola-Kirchhoff stress tensors, the known linearized constitutive equations of solids follow, e.g. Hook and Fourier laws with tensor (transport) coefficients which are reduced to scalars in isotropic solids (e.g. Cauchy law of deformation with Lamé coefficients) [6, 7, 9, 13, 14].

Results for thermoelastic fluid might be also obtained by the constitutive principle of symmetry but we get them directly from the following fluid model, cf. (3.182) and the end of this section.

Our main goal is to apply the admissibility principle to fluids [39, 53, 75–78], namely to nonsimple fluid (3.127) (the special cases of simple (3.129) and thermoelastic (3.130) fluids will be discussed at the end of this section but the most important are fluids with linear transport properties contained in Sects. 3.7 and 3.8). In nonsimple fluid (3.127) it is sufficient to use the field of velocity (instead of motion), cf. $(3.14)_1$, $(3.15)_1$. Therefore we define the *thermokinetic* process in fluids as the fields of (instead of (3.114))

$$\mathbf{v}, \quad \rho, \quad T \tag{3.145}$$

An admissible thermodynamic process in fluids is defined as fields of thermokinetic process (3.145), responses (3.115) (given by constitutive equations (3.127)), and outside fields (3.116) which fulfil balances (3.63), (3.78), (3.93), (3.107).

Although the spatial (Euler) description $\mathbf{x}$, t is simpler in fluids, the material (time) derivative, expressed by (3.8), is preferred below because it gives more concise results.

The principle of admissibility demands to fulfil entropy inequality (3.109) and therefore also the reduced inequality (3.113) by any admissible thermodynamic process. Here the free energy (3.111) is used for which, as follows from (3.127), we have the following constitutive equation

$$f = \hat{f}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \tag{3.146}$$

in our nonsimple fluid. Hence we can write

$$\dot{f} = \frac{\partial \hat{f}}{\partial \rho}\dot{\rho} + \frac{\partial \hat{f}}{\partial \mathbf{h}}.\dot{\mathbf{h}} + \mathrm{tr}\frac{\partial \hat{f}}{\partial \mathbf{D}}\dot{\mathbf{D}} + \frac{\partial \hat{f}}{\partial T}\dot{T} + \frac{\partial \hat{f}}{\partial \mathbf{g}}.\dot{\mathbf{g}} \tag{3.147}$$

Here $\mathrm{tr}\frac{\partial \hat{f}}{\partial \mathbf{D}}\dot{\mathbf{D}} = \frac{\partial \hat{f}}{\partial D^{ij}}\dot{\mathbf{D}}^{ij}$ where both tensors are symmetric. This is clear for $\dot{\mathbf{D}}$ but the symmetry of $\frac{\partial \hat{f}}{\partial \mathbf{D}}$ follows from the rule that the derivative of a scalar function with respect to a symmetric tensor is symmetric.[33]

Now we express $\dot{\rho}$ from (3.63) using (3.16) and $\dot{\mathbf{h}}$ from

$$\dot{\mathbf{h}} = -\mathbf{h}(\mathbf{D} + \mathbf{W}) - \mathbf{h}\,\mathrm{tr}\mathbf{D} - \rho\,\mathrm{grad}(\mathrm{tr}\mathbf{D}) \tag{3.148}$$

which may be obtained if we take the gradient from balance of mass (3.62) and use (3.126), (3.9), (3.14), (3.15). Both $\dot{\rho}$ and $\dot{\mathbf{h}}$ we use in (3.147) and then we insert $\dot{f}$ into reduced inequality (3.113). After rearrangement we obtain (in component form)

$$\begin{aligned} -T\sigma = & -\rho\frac{\partial \hat{f}}{\partial h^i}\left(h^j(D^{ji} + W^{ji}) + h^i D^{kk}\right) - \rho^2\frac{\partial \hat{f}}{\partial h^i}\frac{\partial D^{kk}}{\partial x^i} + \rho\frac{\partial \hat{f}}{\partial D^{ij}}\dot{D}^{ji} \\ & + \rho\frac{\partial \hat{f}}{\partial g^i}\dot{g}^i + \rho\left(\frac{\partial \hat{f}}{\partial T} + s\right)\dot{T} - \left(T^{ij} + \rho^2\frac{\partial \hat{f}}{\partial \rho}\delta^{ij}\right)D^{ji} + T^{-1}q^i g^i \le 0 \end{aligned} \tag{3.149}$$

---

[33] Let f be a scalar function $\tilde{f}$ of symmetric tensor D, i.e., a function of 6 independent variables:

$$\begin{aligned} f = \tilde{f}(\mathbf{D}) = \tilde{f}(D^{11}, D^{12}, D^{13}, D^{22}, D^{23}, D^{33}) = \tilde{f}\big(D^{11}, \tfrac{1}{2}(D^{12} + D^{21}), \\ \tfrac{1}{2}(D^{13} + D^{31}), D^{22}, \tfrac{1}{2}(D^{23} + D^{32}), D^{33}\big) \\ \equiv \hat{f}(D^{11}, D^{12}, D^{13}, D^{21}, D^{22}, D^{23}, D^{31}, D^{32}, D^{33}) = \hat{f}(\mathbf{D}) \end{aligned}$$

The last definition of function $\hat{f}$ of 9 variables (allowed by symmetry of $\mathbf{D}$) permits to employ the customary tensor (or matrix) descriptions, e.g. the summation convention in component form. This is the reason for using this definition of $\hat{f}$ in (3.146), (3.147) and other formulae in this book (similar definitions may be used for skew-symmetric tensor and vector and tensor functions [7, 14, 79]). As may be seen from the definition above, the main property of $\hat{f}$ is (when $\mathbf{D}$ is symmetrical and this is just such a case) that $\frac{\partial \hat{f}}{\partial \mathbf{D}}$ is indeed symmetrical, e.g.

$$\frac{\partial \hat{f}}{\partial D^{12}} = \frac{1}{2}\frac{\partial \tilde{f}}{\partial D^{12}} = \frac{\partial \hat{f}}{\partial D^{21}}$$

If $\mathbf{B}$ is a symmetric tensor then, as may be expected,

$$\begin{aligned} \mathrm{tr}\frac{\partial \hat{f}}{\partial \mathbf{D}}\mathbf{B} = \frac{\partial \hat{f}}{\partial D^{ij}}B^{ji} = \frac{\partial \tilde{f}}{\partial D^{11}}B^{11} + \frac{\partial \tilde{f}}{\partial D^{12}}B^{12} + \frac{\partial \tilde{f}}{\partial D^{13}}B^{13} \\ + \frac{\partial \tilde{f}}{\partial D^{22}}B^{22} + \frac{\partial \tilde{f}}{\partial D^{23}}B^{23} + \frac{\partial \tilde{f}}{\partial D^{33}}B^{33} = \frac{\partial \tilde{f}}{\partial \mathbf{D}}.\mathbf{B} \end{aligned}$$

and therefore this expression may be also written as an inner product in the space of symmetric tensors, i.e., as a scalar product (denoted by dot) of 6-dimensional vectors. This way is also often used; then, of course, we understand (in (3.146) etc.) f as a function in the space of symmetric tensor $\mathbf{D}$, i.e., as $\tilde{f}$. Similarly it may be proved that the derivative of a scalar function with respect to a skew-symmetric tensor is again skew-symmetric.

This inequality depends through constitutive equations (3.127), (3.146) on

$$\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g} \tag{3.150}$$

and linearly on

$$\mathbf{W}, \text{grad tr}\mathbf{D}, \dot{\mathbf{D}}, \dot{T}, \dot{\mathbf{g}} \tag{3.151}$$

In accord with our general procedure sketched in the beginning of this section we now construct the following thermokinetic process (assumed to fulfil mass balance) which generates an admissible thermodynamic process which in turn, by the admissibility principle, must fulfil the inequality (3.149). From this then further properties of constitutive equations (3.127), (3.146) will be obtained.

Namely, we construct the thermokinetic process (3.145) in arbitrary point $\mathbf{y}$ of the actual configuration of the body and arbitrary instant τ as bounded expansions of fields $\mathbf{v}(\mathbf{y}, \tau)$, $T(\mathbf{y}, \tau)$ around the arbitrarily selected place $\mathbf{x}$ in the body and (present) instant t

$$\begin{aligned} v^i(\mathbf{y}, \tau) = \; & v^i(\mathbf{x}, t) + (L^{ij}(\mathbf{x}, t))(y^j - x^j) + \left(\frac{\partial L^{ij}}{\partial t}(\mathbf{x}, t)\right)(y^j - x^j)(\tau - t) \\ & + \frac{1}{2}\left(\frac{\partial L^{ij}}{\partial x^k}(\mathbf{x}, t)\right)(y^j - x^j)(y^k - x^k) \end{aligned} \tag{3.152}$$

$$\begin{aligned} T(\mathbf{y}, \tau) = T(\mathbf{x}, t) + (\mathbf{g}(\mathbf{x}, t)).(\mathbf{y} - \mathbf{x}) + \left(\frac{\partial T}{\partial t}(\mathbf{x}, t)\right)(\tau - t) \\ + \left(\frac{\partial \mathbf{g}}{\partial t}(\mathbf{x}, t)\right).(\mathbf{y} - \mathbf{x})(\tau - t) \end{aligned} \tag{3.153}$$

Density field $\rho(\mathbf{y}, \tau)$ need not be formulated explicitly because mass balance is assumed to be valid (in fact it has been assumed at deduction of (3.149) in eliminations of $\dot{\rho}, \dot{\mathbf{h}}$ by (3.63), (3.148); note that $\dot{\rho}, \dot{\mathbf{h}}$ are not present in (3.150), (3.151)). It is satisfied, e.g. as (3.63) by choice $\dot{\overline{\ln \rho}} = \dot{\rho}/\rho = -\text{div}\mathbf{v}$ for appropriate velocity (3.152) at any $\mathbf{y}, \tau$.[34]

This thermokinetic process (with validity of mass balance) generates an admissible thermodynamic process: we can obtain the values of independent variables of constitutive equations (3.127), (3.146) in the whole body at any time (see (3.126), (3.112), (3.15)) and therefore also fields of responses (3.115) (with f). Further the balance of moment of momentum (3.93) is satisfied because of symmetric tensor $\mathbf{T}$

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[34] Construction of $\rho(\mathbf{y}, \tau)$ in Euler description is more complicated: in principle we can use current deformation of the body in present time t (assumed to be known as well as density fields $\rho(\mathbf{y}, t)$ in it) as the reference, calculate relative deformation function $\mathbf{y} = \underline{\chi}_t(\mathbf{x}, \tau)$ (cf. (3.1)) by integration of velocity field (3.152) and in turn the relative deformation gradient $\mathbf{F}_t = \text{grad}\underline{\chi}_t$ (see [8] p. 9 for details or [7, 10]). Then $\rho(\mathbf{y}, \tau) = \rho(\mathbf{y}, t)/ \mid \det\mathbf{F}_t(\mathbf{y}, \tau) \mid$ following analogy with (3.65).

in (3.127) and ultimately balances of momentum (3.78) and energy (3.107) may be fulfilled if we use appropriate fields of body force $\mathbf{b}$ (or/and inertial force $\mathbf{i}$) and body heating Q respectively.

Thus for each choice of obviously mutually independent values of $\mathbf{v}$ and T and its derivatives in (3.152), (3.153) taken in some $\mathbf{x}$ and t the admissible thermodynamic process exists and, according to the constitutive principle of admissibility, the reduced inequality (3.113) and therefore inequality (3.149) must be valid in this $\mathbf{x}$, t.

We choose these quantities in $\mathbf{x}$, t as follow: density and its gradient have the values ρ, $\mathbf{h}$, fields (3.152), (3.153) and its derivatives have values T, $\mathbf{g}$ and

$$\mathbf{v}(\mathbf{x},t)=\mathbf{o},\quad \mathbf{L}(\mathbf{x},t)=\mathbf{D}+\mathbf{W},\quad \frac{\partial \mathbf{L}}{\partial t}(\mathbf{x},t)=\dot{\mathbf{D}}$$

$$\frac{\partial L^{ij}}{\partial x^k}=\frac{1}{3}\frac{\partial D^{ll}}{\partial x^k}\delta^{ij}$$

(δ^{ij} is Kronecker delta),

$$\frac{\partial T}{\partial t}=\dot{T}\ ,\quad \frac{\partial \mathbf{g}}{\partial t}=\dot{\mathbf{g}}\ ,\quad \frac{\partial \rho}{\partial t}=-\rho\mathrm{tr}\mathbf{D}-\mathbf{v}.\mathbf{h}=-\rho\mathrm{tr}\mathbf{D}$$

This choice of (3.150), (3.151) may be arbitrary and independent (ρ, T are positive scalars, $\mathbf{D}$, $\dot{\mathbf{D}}$ are symmetric tensors, $\mathbf{W}$ skew-symmetric tensor and $\dot{T}$, $\mathbf{h}$, $\mathbf{g}$, grad tr$\mathbf{D}$, $\dot{\mathbf{g}}$ are arbitrary scalar or vectors); here the zero velocity in $\mathbf{x}$, t was used (see (3.8), (3.9)) and the choice of value $\frac{\partial\rho}{\partial t}$ (not needed in (3.149)) simply expresses the mass balance (3.62) at $\mathbf{x}$, t.

But because (3.149) depends on values (3.151) linearly, we can use Lemma A.5.1 from Appendix A.5, and the following restrictions on the constitutive equations follow

$$\frac{\partial \hat{f}}{\partial \mathbf{h}}=\mathbf{o},\quad \frac{\partial \hat{f}}{\partial \mathbf{D}}=\mathbf{0},\quad \frac{\partial \hat{f}}{\partial \mathbf{g}}=\mathbf{o} \tag{3.154}$$

$$\frac{\partial \hat{f}}{\partial T}=-s \tag{3.155}$$

$$-T\sigma=T^{-1}\mathbf{q}.\mathbf{g}-\mathrm{tr}\left(\left(\mathbf{T}+\rho^2\frac{\partial \hat{f}}{\partial \rho}\mathbf{1}\right)\mathbf{D}\right)\leq 0 \tag{3.156}$$

E.g. to prove $(3.154)_1$ we choose (3.150) and $\mathbf{W}$, $\dot{\mathbf{D}}$, $\dot{T}$, $\dot{\mathbf{g}}$ as some constants in Lemma A.5.1 applied on components (similarly as in proof of (3.137)): we choose the 1st component of grad tr$\mathbf{D}$ as arbitrary reals, while its 2nd and 3rd component are selected equal to zero. Then the result $\frac{\partial \hat{f}}{\partial h^1}=0$ follows from Lemma A.5.1 (ρ are always positive). By repetition of this procedure for remaining components 2,3 analogously we obtain the results $(3.154)_1$.

By a similar procedure we obtain (3.154)$_2$: we choose (3.150) and fixed $\mathbf{W}$, $\dot{T}$, $\dot{\mathbf{g}}$ (and grad tr$\mathbf{D}$ or we use the previous result) and because tr$\frac{\partial \hat{f}}{\partial \mathbf{D}}\dot{\mathbf{D}}$ may be considered as a 6-dimensional scalar product, cf. Rem. 33, we obtain by Lemma A.5.1 the result (3.154)$_2$ analogously as in the previous case. But we can use equivalently Lemma A.5.2 understanding $\mathbf{D}$ as 3×3 symmetric tensor: because $\dot{\mathbf{D}}$ is symmetric, the tensor $\frac{\partial \hat{f}}{\partial \mathbf{D}}$ is skew-symmetric but at the same time it is symmetric (cf. Rem. 33) and therefore zero (3.154)$_2$.

Quite similarly we obtain the remaining results (3.154)$_3$, (3.155). Thus the original entropy production (3.149) is simplified to inequality (3.156).

Note that the same results follow using the I-Shih Liu method of Lagrange multipliers (see Appendix A.5) and the discussion of mass balance in the construction of an admissible process is not needed. This method is described in Appendix A.5 in the example of thermoelastic simple fluid, cf. (3.11).

Relations (3.154), (3.155) are valid identically because values (3.150) and $\mathbf{x}$, t are chosen arbitrarily. Therefore the free energy f and also the entropy s (and by (3.111) also u) depend on ρ and T only in the nonsimple fluid

$$f = \hat{f}(\rho, T) \tag{3.157}$$

$$s = \hat{s}(\rho, T) \tag{3.158}$$

We say that in a given place and instant there is an *equilibrium process* when

$$\mathbf{D} = \mathbf{0}\,, \qquad \mathbf{g} = \mathbf{o} \tag{3.159}$$

The motivation for such definition is that the entropy production (3.156) is zero (cf. end of Sect. 2.1 and Rem. 12 in Chap. 1); we omit for simplicity more detailed discussion of equilibrium, reversibility, regularity (cf. Sect. 2.2), because this may be done analogously as in the special case of the linear fluid in Sect. 3.8.

We denote the equilibrium values of stress tensor and heat flux by $\mathbf{T}^o$ and $\mathbf{q}^o$ respectively

$$\mathbf{T}^o = \hat{\mathbf{T}}^o(\rho, \mathbf{h}, T) \equiv \hat{\mathbf{T}}(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) \tag{3.160}$$

$$\mathbf{q}^o = \hat{\mathbf{q}}^o(\rho, \mathbf{h}, T) \equiv \hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) \tag{3.161}$$

and we define the nonequilibrium stress tensor $\mathbf{T}_N$ by

$$\mathbf{T}_N = \hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \equiv \mathbf{T} - \mathbf{T}^o \tag{3.162}$$

We note that both stresses $\mathbf{T}^o$ and $\mathbf{T}_N$ are symmetrical and equilibrium value of $\mathbf{T}_N$ is zero

$$\mathbf{T}_N^o \equiv \hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) = \mathbf{0} \tag{3.163}$$

Inserting (3.162) into (3.156) we have

$$\sigma = T^{-1}\mathrm{tr}\left(\left(\mathbf{T}^o + \rho^2\frac{\partial \hat{f}}{\partial \rho}\mathbf{1}\right)\mathbf{D}\right) + T^{-1}\mathrm{tr}(\mathbf{T_N}\mathbf{D}) - T^{-2}\mathbf{q}.\mathbf{g} \geq 0 \tag{3.164}$$

Production of entropy $\sigma = \hat{\sigma}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g})$ is not only zero but also minimal at equilibrium (3.159). Therefore the following conditions must be fulfilled

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{\sigma}(\rho, \mathbf{h}, \lambda\mathbf{D}, T, \lambda\mathbf{g})\ |_{\lambda=0} = 0 \tag{3.165}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\lambda^2}\hat{\sigma}(\rho, \mathbf{h}, \lambda\mathbf{D}, T, \lambda\mathbf{g})\ |_{\lambda=0} \geq 0 \tag{3.166}$$

where λ is a real parameter (values of $\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}$ may be fixed arbitrarily).

Inserting (3.164) into (3.165) and using (3.163) we get

$$T^{-1}\mathrm{tr}\left(\left(\mathbf{T}^o + \rho^2\frac{\partial \hat{f}}{\partial \rho}\mathbf{1}\right)\mathbf{D}\right) - T^{-2}\mathbf{q}^o.\mathbf{g} = 0 \tag{3.167}$$

This equality is linear in arbitrary independent values of $\mathbf{D}$ and $\mathbf{g}$ and therefore we obtain, by Lemmas A.5.1, A.5.2, identities ((3.167) is valid for any $\rho, \mathbf{h}, T$)

$$\mathbf{T}^o = -P\mathbf{1} \tag{3.168}$$

$$P = \hat{P}(\rho, T) \equiv \rho^2\frac{\partial \hat{f}}{\partial \rho} \tag{3.169}$$

where P is called the (equilibrium) *pressure* which, as well as $\mathbf{T}^o$, is function of only ρ and T as follows from (3.157). Further it follows from (3.167) that the equilibrium value of the heat flux is zero

$$\mathbf{q}^o = \hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) = \mathbf{o} \tag{3.170}$$

The condition (3.166) gives some restrictions on the sign of derivatives of $\mathbf{T_N}$ and $\mathbf{q}$ but we omit them here (we elaborate on them only in the linearized model in Sect. 3.7).

As a result of all constitutive principles the constitutive equations of *nonsimple fluid* with (nonlinear) viscosity and heat conduction are (see (3.111), (3.127), (3.157), (3.158), (3.162), (3.168), (3.169))

$$f = \hat{f}(\rho, T), \quad s = \hat{s}(\rho, T), \quad u = \hat{u}(\rho, T) \tag{3.171}$$

$$\mathbf{q} = \hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \tag{3.172}$$

$$\mathbf{T} = -\hat{P}(\rho, T)\mathbf{1} + \hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \tag{3.173}$$

with the properties (3.155), (3.169):

$$\frac{\partial \hat{f}}{\partial T} = -s \tag{3.174}$$

$$\rho^2 \frac{\partial \hat{f}}{\partial \rho} = P \tag{3.175}$$

Functions $\hat{\mathbf{q}}$ and $\hat{\mathbf{T}}_N$ are isotropic (see (3.128), (3.173), Rem. 8), i.e., for every orthogonal tensor $\mathbf{Q}$ we have

$$\mathbf{Q}\hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) = \hat{\mathbf{q}}(\rho, \mathbf{Qh}, \mathbf{QDQ}^T, T, \mathbf{Qg}) \tag{3.176}$$

$$\mathbf{Q}\hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g})\mathbf{Q}^T = \hat{\mathbf{T}}_N(\rho, \mathbf{Qh}, \mathbf{QDQ}^T, T, \mathbf{Qg}) \tag{3.177}$$

Entropy production is caused by nonequilibrium stress (viscosity) and heat flux (conduction of heat) (see (3.164), (3.168), (3.169))

$$T\sigma = \mathrm{tr}(\mathbf{T}_N\mathbf{D}) - T^{-1}\mathbf{q}.\mathbf{g} \geq 0 \tag{3.178}$$

In the equilibrium process defined by $\mathbf{D} = \mathbf{0}$, $\mathbf{g} = \mathbf{o}$ (3.159), entropy production is zero $\sigma = 0$, stress is reduced on pressure P and heat flux is zero

$$\mathbf{T}^o = -P\mathbf{1} \qquad \text{or} \qquad \mathbf{T}^o_N = 0 \tag{3.179}$$

$$\mathbf{q}^o = \mathbf{o} \tag{3.180}$$

Isotropic functions (cf. (3.176), (3.177)) permit only a certain combination of vectors and tensors on which $\mathbf{q}$ and $\mathbf{T}$, may depend. This is described by the so called *representation theorems* [6, 9, 23, 64]; for general dependence see [65] (for full and proper orthogonal group from Rem. 8). An example for a simple fluid is given in Rem. 35 below, more details (as well as discussion of other results, e.g. (3.166)) we leave to the special model of linear fluid in Sect. 3.7.

The assertion that the results (3.171) with properties (3.174), (3.175) (in fact the same as in classical thermodynamics and proved in this model of nonsimple fluid) are valid even at nonequilibrium process (at nonzero σ in (3.178)) is known as *local equilibrium*. This was taken as a starting principle in the classical theories of nonequilibrium processes [36, 80]. But in more complicated models local equilibrium need not be valid, cf. Sect. 2.2.

Now we turn to the less complicated case of constitutive equations (3.129)—*simple fluid* with (nonlinear) viscosity and heat conduction in which an independence of the density gradient $\mathbf{h}$ was assumed from the start. By inspection of the results of the preceding more complicated model we obtain the same results (3.171)–(3.180) with the exceptions that the heat flux **q** and nonequilibrium stress $\mathbf{T}_N$ (Eqs. (3.172), (3.173)) are independent of density gradient **h**. Flows of such simple fluids are often studied in *rheology*.[35]

The last specialization is the *thermoelastic simple fluid* excluding also a dependence on **D** in constitutive equations of simple fluid (3.129) (independent of **h**). Then the results (3.171) are valid, heat flux in (3.172) is independent of **h** and **D** and nonequilibrium stress $\mathbf{T}_N$ are identically zero, i.e., instead of (3.173) we have

$$\mathbf{T} = -\hat{P}(\rho, T)\,\mathbf{1} \tag{3.181}$$

with (3.174) and (3.175). Production of entropy (3.178) is reduced to $T\sigma = -T^{-1}\mathbf{q}.\mathbf{g} \geq 0$. This model was used in Appendix A.5 to demonstrate I-Shih Liu method with more constraints giving the same results, cf. (A.158).

All the results for the thermoelastic fluid follow also from (3.136)–(3.144) for thermoelastic materials if we use the constitutive principle of symmetry (cf. Sect. 3.5 and Rem. 30). In this case the constitutive equations (3.125), (3.131) are realized through (3.65), (3.12), e.g.

$$\bar{f}(\mathbf{F}, T, \mathbf{g}) \equiv \hat{f}(\rho_0 \mid \det\mathbf{F} \mid^{-1}, T, \mathbf{g}) \tag{3.182}$$

Using (3.182) in (3.139) with the use of (e) from Rem. 4, we deduce (3.181), and (3.175) as well as the other results for thermoelastic fluid.

All these models may be specialized also to *incompressible* fluids, which practically model liquids (at nonextreme, say atmospheric, pressures). Such fluids may be defined mechanically by $J = 1$ [10, 83], cf. Rems. 26, 35 or thermodynamically [24, 43] and this will be discussed at the end of Sect. 3.7.

Further simplification of these fluid models (3.172)–(3.180) we obtain by linearization presented in Sect. 3.7. We note that the formulae (3.198)–(3.207) are valid also in the nonlinear model of this section.

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[35] Consider an example of the *non-Newtonian liquid* (e.g., solutions and melts of polymers, suspensions, etc.), isothermal and without heat conduction for simplicity. Isotropic nonequilibrium stress fulfils (cf. (3.177))

$$\mathbf{Q}\hat{\mathbf{T}}_N(\rho, \mathbf{D})\mathbf{Q}^T = \hat{\mathbf{T}}_N(\rho, \mathbf{Q}\mathbf{D}\mathbf{Q}^T)$$

for any $\mathbf{Q} \in \mathcal{O}$. Representation theorem of this symmetric isotropic nonlinear function of symmetric tensor is (see [9, 12, 64])

$$\mathbf{T}_N = \gamma_0\mathbf{1} + \gamma_1\mathbf{D} + \gamma_2\mathbf{D}^2$$

where coefficients $\gamma_0, \gamma_1, \gamma_2$ are (nonlinear) functions of ρ (T is constant) and tr**D**, tr$\mathbf{D}^2$, tr$\mathbf{D}^3$. Such nonNewtonian liquid is practically incompressible (tr$\mathbf{D} = 0$, see Rem. 26, (3.17), (3.16), below and end of Sect. 3.7), γ_0 may be included in the undetermined pressure and for small velocity gradients the last member may be neglected. Constitutive equation for nonequilibrium stress is reduced to [81]

$$\mathbf{T}_N = \gamma_1\mathbf{D}$$

where γ_1 depends nonlinearly on tr$\mathbf{D}^2$ (and ρ, T). For more complicated models see [8, 10, 82].

Ultimately these fluid models may still be reduced to the uniform models discussed in Chap. 2 mainly as the model A or B in Sects. 2.1 and 2.2. Due to the uniformity, the dependence on the gradient **g** must be eliminated and the dependence on **D** should be expressed through tr**D**, i.e., through $\dot{\rho}$ or equivalently $\dot{V}$ (see (3.63), (3.16)).

Because of neglecting the motion in the uniform models, the pressure (stress) on the boundary of the body (usually defined from the outside as a boundary condition, cf. Rem. 13) is given by the constitutive equation of material inside the body,[36] cf. Rems. 9 in Chap. 1, 1 in Chap. 2 and 37 in this chapter.

Generally, the results for simpler models may be obtained from a more general model by specialization of constitutive equations, but sometimes to get all the results, we must again use the admissibility principle on the remaining inequality (entropy production) of the more complicated model (cf. deduction of (3.181) and also Sect. 3.7).

Summary. This section finalizes the exemplification of rational thermodynamics methodology applying its most typical principle—the principle of admissibility. In fact, this principle represents the requirement of consistency of a material model (constitutive equations) with the Second Law or the entropy inequality. It was applied to finish the derivation of constitutive equations for a single fluid initiated in preceding sections of this chapter. Starting with the form (3.146) for the free energy we arrived at its final simplification in the form (3.157) which indicates also the final constitutive equations for the (specific) entropy and internal energy, see (3.171). In contrast the constitutive equation for the heat flux was not simplified and remained in the form (3.172). The same conclusion was found for the stress tensor but this could be decomposed to equilibrium and nonequilibrium parts, cf. (3.173), the former leading to the (equilibrium) pressure known from classical thermodynamics. Both, pressure and specific entropy are related to (specific) free energy in the form of its derivatives, see (3.174), (3.175). The final form of entropy inequality in this material model is (3.178); the definition of equilibrium, (3.159), is motivated by zero entropy production. Note that during the derivation of constitutive equations not only the entropy inequality as such was applied but also the fact of zero and minimum entropy in equilibrium was used, cf. (3.165) and (3.166). Several simplified fluid models were mentioned at the end of this section. The exposition is thus prepared to derive the key fluid model of our book in the subsequent section.

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[36] Namely, neglecting the motion and external fields ($\mathbf{v}$, $\dot{\mathbf{v}}$, $\mathbf{b}$, $\mathbf{i}$ are practically zeros) the momentum balance (3.81) of the thin layer along the real boundary reduces to $\int_{\mathcal{V}} \mathbf{T}\mathbf{n}\, \mathrm{d}v = \mathbf{o}$ with (mostly) pressure P, $\mathbf{T} = -P\mathbf{1}$ (cf. [84], figure on p. 108). In the limit of this narrow sub body this balance expresses the action-reaction law; therefore the pressure from the outside is given by the constitutive equation of the fluid inside (under the boundary). Pressure P in the model B is given by $(2.7)_3$ (the pressure may contain here a nonequilibrium part (2.34) given (in linear approximation) by the volume viscosity, cf. Rems. 9 in Chap. 1, 1 and 8 in Chap. 2, 37 in this chapter).

The equilibrium pressure part is given by the state equation, see (2.33), (2.32). This, in fact "equilibrium" pressure in "reversible" processes, forms the whole pressure $(2.6)_3$ of the "classical" thermodynamic model A (density of uniform body with constant mass is given by its volume V).

3.7 Fluid with Linear Transport Properties

In this paragraph we specialize the results for the nonsimple fluid (3.171)–(3.180) on the linear dependence in vectors and tensors i.e., in **D**, **g** and **h** (while the dependence on scalars ρ, T may be nonlinear) [9, 14, 23, 24, 27, 45]. We denote this model as a *linear fluid* or *fluid with linear transport properties* because the results describe the classical Navier-Stokes (Newtonian) and Fourier fluid with linear viscosity and heat conduction; at the same time the classical thermodynamic relations (local equilibrium) are valid.

From the principle of objectivity it follows that functions $\hat{\mathbf{q}}$ and $\hat{\mathbf{T}}_N$ must be isotropic (3.176), (3.177). In the linear case the most general form of such isotropic functions is given by the representation theorem (see Appendix A.2) of vector and tensor functions (3.172), (3.162) which are linear in vectors and tensors (cf. (A.58), (A.68)):

$$\mathbf{q} = -k\mathbf{g} + \chi\mathbf{h} \tag{3.183}$$

$$\mathbf{T}_N = \gamma_0\mathbf{1} + \gamma_1(\mathrm{tr}\mathbf{D})\mathbf{1} + \gamma_2\mathbf{D} \tag{3.184}$$

where all scalar coefficients $k, \chi, \gamma_0, \gamma_1, \gamma_2$ are (generally nonlinear) functions only of ρ and T. But in equilibrium (3.159) the nonequilibrium stress and heat flux must be zero (3.163), (3.170) at any ρ, T and **h** and therefore in (3.183) and (3.184) the following coefficients are identically (i.e., for all ρ, T) zero[37]

$$\chi \equiv 0 \tag{3.185}$$

$$\gamma_0 \equiv 0 \tag{3.186}$$

Therefore from (3.183) and (3.185) we obtain the *Fourier law* of heat conduction

$$\mathbf{q} = -k\mathbf{g} \tag{3.187}$$

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[37] As we note at the end of Sect. 3.6 all this and the subsequent results follow if the assumption of linearity has been used in a constitutive relation of a nonsimple fluid with viscosity and heat conduction (3.127), (3.146) (i.e., before application of admissibility principle). These constitutive relations are scalar, vector and symmetric tensor isotropic functions (3.128) (including f) which are linear in vector **g**, **h** and symmetrical tensor **D**.

The representation theorems for such linear functions (A.67), (A.58), (A.68) from Appendix A.2 then gives for scalar functions

$$s = s^{(0)} + s^{(1)}\mathrm{tr}\mathbf{D}\ , \qquad u = u^{(0)} + u^{(1)}\mathrm{tr}\mathbf{D}$$

$$f = f^{(0)} + f^{(1)}\mathrm{tr}\mathbf{D}$$

and (3.183) and (3.184) for vector and tensor functions. Similarly, as scalar coefficients here, the scalars $s^{(0)}, u^{(0)}, f^{(0)} \equiv u^{(0)} - Ts^{(0)}, s^{(1)}, u^{(1)}, f^{(1)} \equiv u^{(1)} - Ts^{(1)}$ are (generally nonlinear) functions of density ρ and temperature T. Using them in the reduced inequality (3.113) and by the admissibility principle, we obtain all the results (like (3.185), (3.186), etc.) of this section (namely $s^{(1)}, u^{(1)}, f^{(1)}$ are zeros identically), see [14, 27, 84].

where $k = \hat{k}(\rho, T)$ is the *heat conductivity* which is a function of ρ, T. Similarly from (3.186) and (3.184), using the divergenceless stretching tensor $\overset{\circ}{\mathbf{D}}$ defined as

$$\overset{\circ}{\mathbf{D}} \equiv \mathbf{D} - (1/3)\mathrm{tr}\mathbf{D}\mathbf{1}, \qquad \mathrm{tr}\,\overset{\circ}{\mathbf{D}} = 0 \tag{3.188}$$

and with $\zeta \equiv \gamma_1 + (1/3)\gamma_2$, $\eta \equiv (1/2)\gamma_2$, we obtain the *Newton law of viscosity*

$$\mathbf{T}_N = \zeta(\mathrm{tr}\mathbf{D})\mathbf{1} + 2\eta\,\overset{\circ}{\mathbf{D}} \tag{3.189}$$

where $\zeta = \hat{\zeta}(\rho, T)$ are the *volume (bulk) viscosity* and $\eta = \hat{\eta}(\rho, T)$ the (dynamical) *viscosity coefficients* respectively, both are (generally nonlinear) functions of ρ, T only. Note that tr$\mathbf{D}$ and $\overset{\circ}{\mathbf{D}}$ are mutually independent (choosing them arbitrarily and independently we obtain the corresponding $\mathbf{D}$ according to (3.188)).

The other constitutive equations are the same as in Sect. 3.6 (cf. (3.175), (3.171), (3.173))

$$f = \hat{f}(\rho, T) \tag{3.190}$$

$$s = \hat{s}(\rho, T) \tag{3.191}$$

$$u = \hat{u}(\rho, T) \tag{3.192}$$

$$\frac{\partial \hat{f}}{\partial T} = -s \tag{3.193}$$

$$\rho^2 \frac{\partial \hat{f}}{\partial \rho} = P = \hat{P}(\rho, T) \tag{3.194}$$

$$\mathbf{T} = -P\mathbf{1} + \zeta(\mathrm{tr}\mathbf{D})\mathbf{1} + 2\eta\,\overset{\circ}{\mathbf{D}} \tag{3.195}$$

where P, ζ, η are functions of ρ and T only. Production of entropy in the linear fluid follows from (3.178) inserting (3.187) and (3.189)

$$T\sigma = \zeta(\mathrm{tr}\mathbf{D})^2 + 2\eta\mathrm{tr}(\overset{\circ}{\mathbf{D}})^2 + T^{-1}k\mathbf{g}^2 \geq 0 \tag{3.196}$$

Because this quadratic form (of mutually independent variables) is positive semidefinite [85, 86], we obtain that the transport coefficients ζ, η, k are nonnegative for all ρ, T

$$\zeta \geq 0\,, \quad \eta \geq 0\,, \quad k \geq 0 \tag{3.197}$$

Equilibrium in the linear fluid will be thoroughly discussed in Sect. 3.8 in which we also confine this model to the *regular* one to avoid unusual situations or to achieve its stability (see (3.232)–(3.234), (3.256), (3.257), Rem. 42).

It is noteworthy that the independent variable **h** is not present at all in this linear model; therefore we would obtain the same results by analogous linearization of simple fluid (3.129), cf. end of Sect. 3.6 [9, 23, 24, 45] (but the presence of density gradients will be important in mixtures, see Sect. 4.8).

At the end we stress several characteristic features of the linear fluid. Though the thermodynamic quantities f, u, s, P as well as the transport coefficients k, ζ, η are functions of ρ and T only, no relationships exist between these two groups. Therefore it is impossible to obtain transport coefficients from equilibrium measurements. But such measurements suffice to obtain the thermodynamic functions, because the *Gibbs equation* is valid (by (3.193), (3.194))

$$\dot{f} = -s\dot{T} + (P/\rho^2)\dot{\rho} = -s\dot{T} - P\dot{v} \tag{3.198}$$

where the *specific volume* v was introduced

$$v \equiv 1/\rho \tag{3.199}$$

(remember that the same symbol used in dv in integrals has a different meaning, cf. (3.21), (3.275)).

These and other thermodynamic relations below are written in classical thermodynamics with differentials instead of material derivatives, e.g. dT instead of $\dot{T}$, cf. Sect. 4.6. As may be seen from Sect. 3.1 also $\partial/\partial t$ or grad may be used here.

Again, the (principle of) *local equilibrium* (cf. end of Sect. 3.6) which was deduced by the method of rational thermodynamics for the linear model (results (3.198)–(3.209) is also valid for the more general model of nonlinear fluid of preceding Sect. 3.6; cf. (3.157), (3.155), (3.169) [24, 75, 77, 78]); however, the local equilibrium is not to be expected as generally valid (cf. Sects. 2.2, 2.3).

Other forms of the Gibbs equation are

$$\dot{u} = T\dot{s} + (P/\rho^2)\dot{\rho} = T\dot{s} - P\dot{v} \tag{3.200}$$

$$\dot{g} = -s\dot{T} + v\dot{P} \tag{3.201}$$

Here (3.111) and the specific *Gibbs energy* (*free enthalpy*) or (specific) *chemical potential* g defined as

$$g \equiv \frac{\partial \rho \hat{f}}{\partial \rho} \tag{3.202}$$

have been used. Then, by (3.194), (3.199), a more classical form of this definition may be seen as in

$$g = f + Pv \tag{3.203}$$

It is well known that chemical potentials play an important role in many, usually more complicated models in the description of phase and chemical equilibria in mixtures (cf. Sects. 2.4, 2.5 and Chap. 4), surface phenomena, etc. Chemical potential may be generalized to more general material models (including, e.g. solids).[38]

Often the inversion of the function (3.194) $P = \hat{P}(\rho, T)$ for ρ is used

$$\rho = \tilde{\rho}(T, P) \tag{3.204}$$

assuming $\frac{\partial \hat{P}}{\partial \rho} \neq 0$ for every temperature T, cf. (3.234). This is practically fulfilled out of phase changes because of the stability criterion $\frac{\partial \hat{P}}{\partial \rho} > 0$, see (3.257).

Then P, T may be used instead of ρ, T as independent variables, e.g.

$$g = \hat{g}(\rho, T) = \tilde{g}(T, P)\ , \quad u = \tilde{u}(T, P)\ , \quad s = \tilde{s}(T, P) \tag{3.205}$$

Comparing (3.205) with (3.201) we have

$$\frac{\partial \tilde{g}}{\partial T} = -s \tag{3.206}$$

$$\frac{\partial \tilde{g}}{\partial P} = v \tag{3.207}$$

and from (3.200), (3.204), (3.205)

$$\begin{aligned} \dot{s} = (1/T)\dot{u} - (P/(T\rho^2))\dot{\rho} = (1/T)\left(\frac{\partial \tilde{u}}{\partial T} - (P/\rho^2)\frac{\partial \tilde{\rho}}{\partial T}\right)\dot{T} \\ + (1/T)\left(\frac{\partial \tilde{u}}{\partial P} - (P/\rho^2)\frac{\partial \tilde{\rho}}{\partial P}\right)\dot{P} \end{aligned} \tag{3.208}$$

From the last equation the form of derivatives $\tilde{s}(T, P)$ may be seen. Using them in the integrability condition $\partial^2\tilde{s}/\partial P \partial T = \partial^2 \tilde{s}/\partial T \partial P$ we obtain after some calculation

$$\frac{\partial \tilde{u}}{\partial P} = (T/\rho^2)\frac{\partial \tilde{\rho}}{\partial T} + (P/\rho^2)\frac{\partial \tilde{\rho}}{\partial P} \tag{3.209}$$

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[38] As the *configurational* or *material* forces [4, 87] (note that the density of chemical potential ρg has a pressure dimension). An analog of chemical potential is the *Eshelby tensor (of chemical potential)* $\underline{\Gamma}$ defined as $(\mathbf{F}^{-T} \equiv (\mathbf{F}^T)^{-1})$

$$\underline{\Gamma} \equiv f\mathbf{1} - (1/\rho)\mathbf{F}^T\mathbf{T}\mathbf{F}^{-T}$$

Note, that if stress is reduced to pressure P, $\mathbf{T} = -P\mathbf{1}$, (usual in fluids) this definition gives the classical result (3.203) $\underline{\Gamma} = g\mathbf{1}$, see (3.199). The Eshelby tensor, e.g. gives the condition of phase equilibria (Maxwell relation—equality of chemical potentials (2.116) in fluid phases), namely equality of $\underline{\Gamma}\mathbf{n}$ on both sides of equilibrated solid phases ($\mathbf{n}$ is the normal to phase boundary) and may be also used to describe surface phenomena, dislocations, etc. [1, 4, 87]. Eshelby tensors may also be defined in mixtures [2, 3].

With (3.204) we can write the transport coefficients k, ζ, η (functions of ρ and T) also as functions of P, T

$$k = \tilde{k}(T, P)\ , \quad \zeta = \tilde{\zeta}(T, P)\ , \quad \eta = \tilde{\eta}(T, P) \tag{3.210}$$

We also note that the vector or tensor responses (3.187), (3.189) depend only on the vector or tensor "driving forces" respectively. This fact is known in linear irreversible thermodynamics as the "Curie principle" [36, 80, 88, 89] (cf. discussion in [34, 38]). Present theory shows however, that this property follows from the isotropy of constitutive functions and from the representation theorems of such linear functions, see Appendix A.2, Eqs. (A.11)–(A.13) and (A.57)–(A.59). But representation theorems for nonlinear isotropic constitutive functions [64, 65] show that the "Curie principle" is not valid generally.

In processes with $\mathbf{g} = \mathbf{o}$ and $\overset{\circ}{\mathbf{D}} = \mathbf{0}$ the nonequilibrium stress is reduced to the nonequilibrium pressure P_N

$$\mathbf{T}_N = -P_N \mathbf{1}\ , \text{where} \quad P_N \equiv -\zeta \operatorname{tr}\mathbf{D} = -\zeta(T, v)\frac{\dot{v}}{v} \tag{3.211}$$

where (3.189), (3.63), (3.16), (3.199) have been used. Such nonequilibrium pressure exists even in a uniform system which is in fact the uniform model B from Sect. 2.2 (see (2.34); volume V is proportional to v) with linear dependence on $\dot{V}$ discussed in Rem. 8 in Chap. 2.

Recapitulating the results we need (from experiment or from molecular models) in this model of fluid

(i) to describe their transport behaviour: the heat conductivity k, volume viscosity ζ and viscosity η and their dependences on temperature and density;

(ii) to describe their thermodynamics: the *state equation* $P = \hat{P}(\rho, T)$ (3.194) and the *caloric state equation* $u = \hat{u}(\rho, T)$ (3.192). In fact, here we need the dependence on temperature only (usually in the form of dependence of heat capacity at constant volume) (see Appendix A.1, Rem. 5 in Appendix A) because dependence (3.192) on density may be calculated from the state equation (3.194) (namely, this gives, by interchangeability of mixed derivatives in (3.198), the dependence of s on density and therefore, by another form of Gibbs equation (3.200), the dependence of u on density).

In the simplest case of *ideal gas* (defined in Appendix A.1) the state (3.194) and caloric (3.192) equations are

$$P/\rho = Pv = (\mathrm{R/M})T \tag{3.212}$$

(see (A.3), (A.10) with use (3.199) and molar mass M) and (see Rems. 15 in Chap. 1, 5 in Appendix A)

$$u = \hat{u}(T) \tag{3.213}$$

As we explain in Appendix A.1 the experience shows that (3.212), (3.213) are valid for any gas in the limit of zero densities, even with nonlinear transport[39] and they were used for the definitions of absolute temperature and entropy (see (A.9), (1.28), (1.30), (1.31)).

Finally we can define the *incompressible* fluids which model *liquids* approximately because the dependence of liquids properties on the pressure may be neglected at nonextreme, say atmospheric, values of the pressure.

Incompressible fluids have been defined by mechanical internal constraint $J = 1$ in Rem. 5.3 but they may be defined (more specially and naturally) from previous thermodynamic formulae (3.204)–(3.209) neglecting their dependence on pressure [24]. Namely, we have by definition (instead of (3.204), (3.205))

$$\rho = \tilde{\rho}(T)\ , \quad s = \tilde{s}(T)\ , \quad u = \tilde{u}(T) \tag{3.214}$$

Then from integrability condition (3.209) it follows that density is independent of temperature

$$\rho \equiv \text{const.} \tag{3.215}$$

therefore density is a unique (positive) constant in this definition of incompressible fluid.

But then, by (3.16), (3.63), (3.65), we obtain

$$\text{div}\mathbf{v} = \text{tr}\mathbf{D} = 0\ , \quad J = 1 \tag{3.216}$$

which we have seen also in the mechanical definition. Note that even these formulae are valid for the linear fluid model and they are valid also in the nonlinear model from the previous Sect. 3.6 because thermodynamic formulae (3.204)–(3.209) are valid there too (cf. the discussion of local equilibrium above (3.200)).

Transport equations in the incompressible fluids are (see (3.187), (3.188), (3.195), (3.216))

$$\mathbf{q} = -k\mathbf{g} \tag{3.217}$$

$$\mathbf{T} = -P\mathbf{1} + 2\eta\mathbf{D} \tag{3.218}$$

where, by the definition of incompressible fluids, the thermal conductivity k and the viscosity η are functions of temperature only

$$k = \tilde{k}(T), \quad \eta = \tilde{\eta}(T) \tag{3.219}$$

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[39] If we assume that the ideal gas studied fulfils the local equilibrium (and this is the usual case: ideal gas may be from the linear fluid models discussed here, but it may be also from some nonlinear models fulfilling this principle, e.g. those in [78]), then property (3.213) follows from state equation (3.212). Indeed, the local equilibrium means the validity of Gibbs equations (3.200)$_1$, (3.198)$_1$, from which $\partial\hat{u}/\partial\rho = T\partial\hat{s}/\partial\rho + P/\rho^2$ and $\partial\hat{s}/\partial\rho = -\partial\widehat{\overline{(P/\rho^2)}}/\partial T$. By their combination and using state equation (3.212) we obtain identically $\partial\hat{u}/\partial\rho = 0$. Cf. also [27, Sect. 16], [90, 91].

and the pressure P is arbitrary scalar, cf. Rem. 26.

At the end we note that generalization of incompressibility on fluid mixtures is not straightforward, see Sect. 4.8.

Of course the results concerning nonlinear transport phenomena must be transformed correspondingly.

Summary. Section 3.7 derives the main model of interest in our book for the case of single fluid. This model of fluid with linear transport properties started with linearization of constitutive equations derived in preceding section for fluid vector and tensor quantities, i.e., for the heat flux and (nonequilibrium) stress tensor, taking into account that they are isotropic functions—see (3.183) and (3.184). Two classical laws immediately followed, viz. the Fourier law (3.187) and the Newton viscosity law (3.189). In the same time entropy inequality put some restrictions on the coefficients in these laws, cf. (3.197). It also followed that the Gibbs equation (3.198) is valid in this model and also the local equilibrium was proved. For our subsequent applications the definition of (specific) chemical potential (3.202) is important. Traditionally, the pressure is used as an independent variable in (chemical) thermodynamics. Though this was noted and used in paragraphs among Eqs. (3.204)–(3.210) the verification of this exchange of variables should be postponed to the next section. At the end the simplification to incompressible fluids is made which are defined by (3.214).

3.8 Equilibrium Processes in Linear Fluid

An *equilibrium process* in the linear fluid of Sect. 3.7 may be defined by (cf. (3.159))

$$\mathbf{D} = \mathbf{0} \tag{3.220}$$

$$\mathbf{g} = \mathbf{o} \tag{3.221}$$

because just these conditions give the zero entropy production

$$\sigma = 0 \tag{3.222}$$

as follows from (3.196), cf. discussion of (2.10), (2.11) and Rems. 12 in Chap. 1, 7 and 9 in Chap. 2.

Consider first an equilibrium process in the linear fluid model where (3.220), (3.221) are valid through all the body and persistently (at least for considered time interval); practically this is achieved by the *stability* discussed below [14, 18, 92–95].

The validity of (3.220) throughout the body is expressed by Killing's theorem (3.18), which is that the motion of a linear fluid body in an equilibrium process is rigid. This means that a frame fixed with such a body exists in which

$$\mathbf{v} = \mathbf{o} \tag{3.223}$$

through the body and persistently.[40] Such a frame, giving the zero velocity (3.223) in an equilibrium process, will be used in the following (among others it means that instead of material derivative we can use $\partial/\partial t$ in this frame). By persistence of (3.223) we have also

$$\dot{\mathbf{v}} = \mathbf{o} \tag{3.224}$$

through the body and persistently.

Constitutive equations (3.195), (3.188), (3.187) in such an equilibrium process are

$$\mathbf{T} = -P\mathbf{1} \tag{3.225}$$

$$\mathbf{q} = \mathbf{o} \tag{3.226}$$

With those equations the following forms of balances (3.63), (3.85), (3.107), (3.109) are valid ((3.93) is trivially satisfied)

$$\dot{\rho} = 0 \tag{3.227}$$

$$\operatorname{grad} P = \rho(\mathbf{b} + \mathbf{i}) \tag{3.228}$$

$$\rho\dot{u} = Q \tag{3.229}$$

$$\rho\dot{s} = Q/T \tag{3.230}$$

The persistence and validity of these equations through the body therefore give the behaviour of other formulae such as $\frac{\partial\rho}{\partial t} = 0$, $\frac{\partial\mathbf{g}}{\partial t} = \mathbf{o}$, $\frac{\partial\mathbf{h}}{\partial t} = \mathbf{o}$, etc.

Now, we restrict ourselves to some equilibrium process persisting in one equilibrium state of the linear fluid model in the sense of the property S4 from Sect. 1.2 (one equilibrium from those more possible which is compatible with the given boundary and external conditions).[41] Such an equilibrium state may be achieved if no radiation heat transfer is considered

$$Q = 0 \tag{3.231}$$

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[40] Cf. (3.18), Rem. 5 and deduction of (3.25). Because the change of frame describes the change of frame in a rigid motion to another one the result (3.223) is intuitively clear. Formally, inserting rigid motion from Rem. 5 into (3.25) we seek the (starred) frame in which $\mathbf{x}^* = \mathbf{X}$ (and therefore $\mathbf{v}^* = \mathbf{o}$, i.e., (3.223)) through the body. It may be seen that this need the change of frame by time functions $\mathbf{Q} = \underline{\Theta}^T$ and $\mathbf{c} = -\underline{\Theta}^T\underline{\gamma}$.

[41] Note that an equilibrium process (as the time succession of states with (3.220)–(3.222)) with nonzero radiation $Q \neq 0$, which is even reversible, is possible: in the "straight" part of the process the heating (defined by the first two members on the right-hand side of (3.97)) is given as $\int_V Q\,\mathrm{d}v$ by (3.226) (V is the volume of the body); see also

Moreover we add to the linear fluid model the following *regularity* conditions[42] valid at any ρ, T, i.e., at any state, not only in the equilibrium one:

Transport coefficients are always positive (as different from (3.197))

$$\zeta > 0\,, \quad \eta > 0\,, \quad k > 0 \tag{3.232}$$

and the following derivatives are nonzero

$$\frac{\partial \hat{u}}{\partial T} \neq 0 \tag{3.233}$$

$$\frac{\partial \hat{P}}{\partial \rho} \neq 0 \tag{3.234}$$

at any T, ρ.

Therefore, in this section, we study the *regular linear fluid body* or the *fluid with linear transport properties* with *regular responses* consisting of the linear fluid body of Sect. 3.7 to which we add the regularity properties (3.232)–(3.234).

In such *regular linear fluid* with no radiation (3.231) we define the *equilibrium* or *equilibrium state* by the zero entropy production (3.222) which is valid through all the body and persistently.

(Footnote 41 continued)
Sect. 1.2, models A, B in Sect. 2.2 and Rems. 12 in Chap. 1, 48 in this chapter.

Temperature may change in time but not in space (3.221) during such an equilibrium process in the rigid and not moving body, density does not change in time (3.227) (but may change in space); u, s change as the temperature changes, similarly P changes by a corresponding time change of $\mathbf{b}+\mathbf{i}$ (say by (3.192), (3.191), (3.194) in the linear fluid model). The reverse process may be imagined to exist as going through the same states of the equilibrium process, power and entropy production are again zero, heating is of reverse sign $-\int_V Q\,\mathrm{d}v$ (in comparison with the appropriate instant of "straight" equilibrium process).

Even this reversible process is rather a special one. We note it here to demonstrate that in the model of the linear fluid equality (in entropic inequality) is possible, see (1.35), and to show that entropy may be calculated with the precision of a constant, see (1.40), cf. application of reversible processes in Sect. 1.4. An equilibrium state is also an equilibrium process formed by a unique state with (3.231), cf. definition below (2.11).

[42] Similarly as in Rem. 11 in Chap. 1 and in Sects. 2.1, 2.2, we try to avoid in this way the unusual, often "pathological" situations of real complex materials in our simple models (as, e.g. zero values of some transport coefficients (3.197) at certain ρ, T); other motivation is the "practical realization of the persistence of the equilibrium state" which may be achieved through its stability (discussed below), e.g. regularity conditions (3.233), (3.234) are even intensified in such a stable equilibrium state (both derivatives are positive, see (3.256), (3.257) below).

Again we assume that the constitutive model together with regularities introduced is valid in all situations, e.g. the model of fluid with linear transport properties with regular response is assumed to be valid for all values of ρ, T. Namely, we study the (properties of) model even though we know that there are values of ρ, T for which a real fluid does not fulfil some regularities assumed (e.g. stability in the region of phase transformations); as usually, such difficulties are resolved by the appropriate limiting applications of the model studied.

Then "equilibrium conditions" (3.220), (3.221) are valid through the body and persistently because the quadratic form (3.196) is positive definite due to regularity conditions (3.232)[43] and, reversely, from (3.220), (3.221) equation (3.222) follows.

Therefore (3.225)–(3.228) are valid and, by (3.229)–(3.231), we have

$$\dot{u} = 0 \tag{3.235}$$

$$\dot{s} = 0 \tag{3.236}$$

From (3.235), (3.192), (3.227), and regularity (3.233) we have through the body and persistently

$$\dot{T} = 0\ , \text{ or by (3.223) } \frac{\partial T}{\partial t} = 0 \tag{3.237}$$

This, together with (3.221), means that a unique and constant (in time) temperature is everywhere in the body in this equilibrium (note that, reversely, Eq. (3.231) follows from (3.237), cf. (3.192), (3.227), (3.229) [76]).

Inserting constitutive equation for P (3.194) into (3.228) and using (3.221) we have

$$\frac{\partial \hat{P}}{\partial \rho}\mathbf{h} = \rho(\mathbf{b} + \mathbf{i}) \tag{3.238}$$

and making another time derivative of this equation (using zero time derivatives of $\rho, \mathbf{h}, T$) we obtain $\partial(\mathbf{b} + \mathbf{i})/\partial t = \mathbf{o}$, i.e., the body and/or inertial force must be constant in time in such an equilibrium process. Further, from (3.238), it follows that $\mathbf{h} \neq \mathbf{o}$ because of (3.234); in the special case $\mathbf{b} + \mathbf{i} = \mathbf{o}$ (no body and/or inertial forces), density gradient disappears $\mathbf{h} = \mathbf{o}$.

Therefore we can conclude that during such equilibrium process in the frame with persisting and everywhere zero velocity (3.223), the body is in one "persisting" equilibrium state in the sense of Sect. 1.2 in which density does not change in time but may change in space (if the body or inertial forces are nonzero constants in time), while temperature is everywhere the same persistent constant. Heating and power (the right-hand side of energy balances), e.g. of (3.103), (3.106) or (3.107) are zero (see (3.226), (3.231), (3.220), (3.223)) and in such an equilibrium state also all responses in the particles of the body do not change in time (cf. (3.227), (3.237), (3.225), (3.194)) but some of them (the density and properties depending on the density) may have nonzero space gradients (parallel to the time constant nonzero body and/or inertial forces; cf. (3.238), (3.221), (3.192)); temperature is a unique constant in all body.

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[43] Calculation of $\mathrm{tr}(\overset{\circ}{\mathbf{D}})^2$ in (3.196) gives $\mathrm{tr}(\overset{\circ}{\mathbf{D}})^2 = (\overset{\circ}{D}{}^{11})^2 + (\overset{\circ}{D}{}^{22})^2 + (\overset{\circ}{D}{}^{33})^2 + 2(\overset{\circ}{D}{}^{12})^2 + 2(\overset{\circ}{D}{}^{13})^2 + 2(\overset{\circ}{D}{}^{23})^2$ and therefore zero entropy production (3.222) and positivity (3.232) give from (3.196) the result (3.221) as well as $\mathrm{tr}\mathbf{D} = 0$ and $\overset{\circ}{D}{}^{11} = \overset{\circ}{D}{}^{22} = \overset{\circ}{D}{}^{33} = \overset{\circ}{D}{}^{12} = \overset{\circ}{D}{}^{13} = \overset{\circ}{D}{}^{23} = 0$ which with definition (3.188) of $\overset{\circ}{\mathbf{D}}$ gives (3.220).

The body force having a potential Φ is of practical importance; the potential, similarly as with this force, must be constant in time (3.104). In this case the chemical potential (3.205)–(3.207) is preferred (note use of regularity (3.234) here) because, by (3.221), (3.199), $\mathrm{grad}\, g = (1/\rho)\mathrm{grad}\, P$ and therefore the equilibrium result (3.228) with time constant potential Φ (3.104) may be written as

$$\mathrm{grad}(g + \Phi) = \mathbf{o} \tag{3.239}$$

in such an equilibrium state.[44] Probably the most important is this equilibrium in an inertial frame without the body force ($\mathbf{i} = \mathbf{o}, \mathbf{b} = \mathbf{o}$) because then space gradients disappear as we noted above and we obtain a *uniform equilibrium* state, not changing in time which, in fact, was exemplified by the uniform model A or by equilibrium in the model B of Sects. 2.1, 2.2, see also below.

Time persistence of an equilibrium state through the persistence of its conditions (like (3.220), (3.221), (3.227), (3.237)) may be realized in practice with great difficulties (or it is even impossible) because of molecular fluctuations. The practical persistence of an equilibrium state (and therefore also the assumption S4 in Sect. 1.2) may be achieved by its *stability* and this is analyzed in the rest of this section; we are inspired mainly by [1, 18, 92, 93], see also [94, 95, 97–102].

We concentrate here on the stability of our model of regular linear fluid (giving the classical Gibbs stability) modelling one-phase fluid.[45] We try to find such properties of constitutive equations which permit to realize equilibrium states in our model at some ρ, T (and also motivate some of the regularity conditions above). If such stability properties are not fulfilled then, typically, our (one-phase) fluid system disintegrates into more phases, cf. Rem. 45.

The *stability* of equilibrium state may be roughly defined as gradual return to the equilibrium after some disturbance from this state at fixed boundary and exterior conditions of the body. The mere removal of such disturbances (caused by molecular nature of studied material) causes the real persistence of the equilibrium state. As noted above, this property need not be valid generally in real material and depends on its formulation. Here we discuss sufficiently general stability of an isolated body resulting from the classical Gibbs stability [93–95, 97] which permits to obtain additional regularity properties—the *conditions of stability* of constitutive equations of our fluid model. Namely, consider an isolated body modelled by the linear fluid (3.187)–(3.196) with regular response (3.232)–(3.234) which is in an equilibrium

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[44] This result (3.239) may be generalized for Eshelby tensor $\underline{\Gamma}$ (generalization of chemical potential, e.g. for solids, see Rem. 38) as

$$\mathrm{Div}(\underline{\Gamma} + \Phi\mathbf{1}) = \mathbf{o}$$

cf. [1, 96] (Div is the divergence in referential description).

[45] But we omit the generalizations of equilibrium stabilities for phase transitions [1, 103–106] (for them typically criteria stability like (3.256), (3.257) are not valid), for more general materials (say solids), and the more complicated problem of stability of nonequilibrium states (e.g. the vast field of dissipative structures [24, 37, 80, 107–109]) because most of these issues do not concern our (one-phase) model or are now in the stage of intensive and not completely resolved research; see also Rem. 31 in Chap. 4.

state defined by (3.222) (or by (3.220), (3.221)) the persistence of which is achieved by the zero body heating (3.231), the zero inertial and body forces ($\mathbf{i} = \mathbf{o},\ \mathbf{b} = \mathbf{o}$) and the zero velocity $\mathbf{v} = \mathbf{o}$ (3.223) everywhere. The body is in the uniform equilibrium state mentioned above and as may be seen, such a state may be realized in the *isolated* body in which no exchange of heat, work and mass with environment exists and the boundary of which is fixed. Denoting constant (throughout the body and time) equilibrium values of temperature T^o density ρ^o and therefore also specific volume v^o, internal energy u^o and entropy s^o (cf. (3.191), (3.192), (3.199)) we can express the volume V^o, energy E^o and entropy S^o of the body in such equilibrium by

$$V^o = v^o m^o \tag{3.240}$$

$$E^o = u^o m^o \tag{3.241}$$

$$S^o = s^o m^o \tag{3.242}$$

where m^o is the mass of the body.

We say that such a uniform equilibrium state is *dynamically stable under isolation*, if an arbitrary "perturbed" state of the body compatible with isolation decays back to this equilibrium state. *Compatibility with isolation* means that during the whole return to the equilibrium state the energy and the volume is the same as in the original equilibrium state, E^o, V^o, further $\mathbf{b} = \mathbf{o}$, $Q = 0$ through the body and $\mathbf{v} = \mathbf{o}$, $\mathbf{q} = \mathbf{o}$ on the boundary (but generally nonzero inside the body). Therefore in an arbitrary state during this return (and including the original perturbed state as well) we have by (3.21) (with the density ρ and $\mathrm{d}m = \rho\,\mathrm{d}v$; cf. (3.199)), using the specific volume v, total energy and entropy and integrating through mass m^o of the body,

$$V^o = \int_{m^o} v\,\mathrm{d}m \tag{3.243}$$

$$E^o = \int_{m^o} \left(u + \frac{1}{2}\mathbf{v}^2\right)\,\mathrm{d}m \tag{3.244}$$

while the entropy S of an arbitrary state grows up (see (3.108)) to its maximum value S^o (3.242)

$$S = \int_{m^o} s\,\mathrm{d}m \leq S^o \tag{3.245}$$

i.e., in accord with the regular equilibrium response, we can conclude that the equality in (3.245) is valid only for a uniform equilibrium state (the stability of which is tested).

In fact, by the assertion that this equilibrium state is dynamically stable under isolation, we express an extra *postulate* that the state compatible with isolation and with the entropy S comes back to the equilibrium state with the entropy value S^o (3.242) in this isolated system.

This postulate is in agreement with traditional and reasonable expectation of achieving finite extremal values of entropy in a process occurring in an isolated system (an increase of entropy only follows from inequality (3.108)). Similarly, finite extremal values of other potentials at corresponding conditions, like the minimum of (say Gibbs) energies, etc., may be expected cf. [1, 37, 92, 110, 111].

In what follows we deduce the conditions of stability (3.256), (3.257) from this postulate. Then, in the remaining part of this section following mainly [18, 93], we try, on the contrary, to show that the stability conditions in the regular linear fluid lead to this postulate, see (3.266).

Result (3.245) is valid for any perturbed state and therefore also for such a state with zero velocity inside the body; then, instead of (3.244), we have in that perturbed state

$$E^o = \int_{m^o} u \, \mathrm{d}m \tag{3.246}$$

with volume and entropy given again by (3.243), (3.245) (in the following states of a body when approaching the equilibrium state the velocity need not be zero inside although it must be zero at the boundary). This special case of any perturbation with (3.243) and (3.246) (instead of (3.244)), considering (3.245), is in fact the classical definition of the *Gibbs stability* under isolation [92, 93]. Although the Gibbs stability is studied in classical thermodynamics with uniform model (like A of Sect. 2.2), its dynamical interpretation [18, 93, 97, 106] cannot be described in terms of such a uniform model, namely a nonuniform perturbed state permitting the nonequilibrium processes and therefore inequalities in (3.245) must be possible (in fact this is more or less explicitly expressed in classical proofs, see, e.g. [112, p. 82, Sect. 21]). This motivates the following procedure [93]:

Assume that a given uniform equilibrium state of the linear fluid with regular equilibrium response is dynamically stable under isolation. Therefore it is also Gibbs stable (namely its starting perturbed state may have zero velocity inside and (3.246) is valid). This suffices for the following result: the function

$$s = \bar{s}(u, v) \tag{3.247}$$

is *strict concave* in the corresponding domain (such function (3.247)[46] follows from (3.191) inserting inversion of (3.192) for T (which exists by (3.233)) and using (3.199)).

Indeed, let us choose a perturbed state with zero velocity inside in the following way: we divide the body on two parts with masses αm^o and $(1 - \alpha)m^o$ where $0 < \alpha < 1$; internal energies u^a, u^b and specific volumes v^a, v^b ($u^a \neq u^b$, $v^a \neq v^b$) are constant (uniform) but different in these parts and entropies s^a, s^b are given by

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[46] It follows from our intention to use the theorem of concave function from Appendix A.3 for the proof. This assumes the negative (or positive) definiteness of a matrix composed from second derivatives of such a function. This property has, besides (3.247), e.g. function $\tilde{g}(T, P)$ (3.205) (used also below in this section) but unfortunately not the more natural $\hat{f}(\rho, T)$ (3.190) or even $\check{f}(v, T)$ (see (3.199)); cf. [113, Sect. 39].

(3.247). Because of the compatibility with isolation of that perturbed state we have by (3.243), (3.246), (3.240), (3.241)

$$v^a \alpha m^o + v^b (1-\alpha) m^o = V^o \ , \quad u^a \alpha m^o + u^b (1-\alpha) m^o = E^o \tag{3.248}$$

Inserting (3.240), (3.241) and removing m^o we obtain

$$v^a \alpha + v^b (1-\alpha) = v^o \ , \quad u^a \alpha + u^b (1-\alpha) = u^o \tag{3.249}$$

But using such a perturbed state in (3.245)

$$s^a \alpha m^o + s^b (1-\alpha) m^o < S^o \tag{3.250}$$

(equality disappears because of the nonuniformity of the perturbed state; cf. (3.245)). By (3.242), (3.247) we have

$$\alpha \bar{s}(u^a, v^a) + (1-\alpha)\bar{s}(u^b, v^b) < \bar{s}(u^o, v^o) \tag{3.251}$$

By definition (i) in the theorem of concave functions (Appendix A.3), the function (3.247) is strict concave (see (A.70), (A.71), (A.72), (3.247), (3.249), (3.251) with $\vec{\omega} = (u, v)$ and $\Gamma = s$). Therefore property (iii) of this theorem is equivalently valid for function (3.247): the matrix of its second derivatives is negative definite at all corresponding u, v, i.e.,

$$\frac{\partial^2 \bar{s}}{\partial u^2} = -\big(T^2 \frac{\partial \hat{u}}{\partial T}\big)^{-1} < 0 \tag{3.252}$$

$$\frac{\partial^2 \bar{s}}{\partial u^2}\frac{\partial^2 \bar{s}}{\partial v^2} - \left(\frac{\partial^2 \bar{s}}{\partial u \partial v}\right)^2 = \frac{\partial(T,\rho)}{\partial(u,v)}\frac{\partial(T^{-1}, PT^{-1})}{\partial(T,\rho)} = \frac{\rho^2}{T^3}\frac{\partial \hat{P}}{\partial \rho}\left(\frac{\partial \hat{u}}{\partial T}\right)^{-1} > 0 \tag{3.253}$$

Here we use the properties of the negative definite matrix and Jacobians [85, 86], (3.192), (3.194) and (as follows from (3.200))

$$\frac{\partial \bar{s}}{\partial u} = \frac{1}{T} \tag{3.254}$$

$$\frac{\partial \bar{s}}{\partial v} = \frac{P}{T} \tag{3.255}$$

Thus it follows from (3.252), (3.253) (because $T > 0$, $\rho > 0$) that if the linear fluid body with regular equilibrium response is dynamically stable (or Gibbs stable) under isolation then at each corresponding T, ρ the following *stability conditions* are valid

$$\frac{\partial \hat{u}}{\partial T} > 0 \tag{3.256}$$

$$\frac{\partial \hat{P}}{\partial \rho} > 0 \tag{3.257}$$

in our models. In what follows we use these conditions (3.256), (3.257) instead of (3.233), (3.234) as regular conditions (besides (3.232)) to our model of fluid with linear transport properties because, as we shall show in the rest of this section, such models then have dynamical stability not only under isolation but even at other conditions.

It has been shown that results (3.256), (3.257) are necessary for dynamical stability of our linear fluid of Sect. 3.7 (with regularity (3.232)).

Now we try to prove also the sufficiency: assuming stability conditions (3.256), (3.257) we try to show that the body of regular linear fluid of Sect. 3.7 (with further regularities (3.232)), kept permanently in isolation (defined below) develops asymptotically to uniform equilibrium state. That is we prove the dynamical stability under isolation (and also Gibbs stability) for such a body. But the time behaviour of the perturbed system is generally a very complicated task—we need to solve the system of differential equations obtained by substitution of constitutive equations into balances.

For simplicity therefore we show only that the uniform equilibrium state (those given by (3.240)–(3.242)) is the possible one in which the perturbed state kept permanently in isolation (defined below) develops asymptotically as time goes to infinity [1, 18, 93, 97].

Let us have some perturbed state of a body made from the linear fluid (3.187)–(3.196) with regular equilibrium response ((3.232) is valid) and with stability conditions (3.256), (3.257), which is held permanently in an inertial frame without body force in isolation (no heat, work and mass exchange with surroundings). That is we have persistently through the body $\mathbf{i} = \mathbf{o}$ (3.48), $\mathbf{b} = \mathbf{o}$, no heat radiation $Q = 0$ (3.231) and on its boundary no heat exchange $\mathbf{q} = \mathbf{o}$ and zero velocity $\mathbf{v} = \mathbf{o}$.

Therefore the body, having permanently constant mass m^o, volume V^o and energy E^o given by (3.243), (3.244) with corresponding local specific volume v and energy u of the given state, develops asymptotically to a uniform equilibrium state with specific internal energy u^o and volume v^o given by

$$u^o \equiv E^o/m^o \tag{3.258}$$

$$v^o \equiv V^o/m^o \tag{3.259}$$

Because of assumed stability conditions (3.256), (3.257) we achieve from (3.252), (3.253) the fulfilment of property (iii) from Appendix A.3 for function (3.247). Therefore equivalently (A.73) is valid for this function (3.247), giving s^o for values u^o, v^o (3.258), (3.259) and s for values u, v in any place of the body in arbitrary state during the process, i.e.,

$$s < s^o + (1/T^o)(u - u^o) + (P^o/T^o)(v - v^o) \tag{3.260}$$

where T^o, P^o are values given by (3.254), (3.255). Equality in (3.260) is valid as

$$s = s^o \tag{3.261}$$

when (cf. in (A.73))

$$u = u^o \tag{3.262}$$

$$v = v^o \tag{3.263}$$

Now we add to the right-hand side of (3.260) the nonnegative quantity $(2T^o)^{-1}\mathbf{v}^2$ (with $\mathbf{v}$ in the same place and instant as in (3.260)) and integrate such inequality through the body at some instant; using (3.243), (3.244), (3.258), (3.259) we have

$$S(t) \equiv \int_{m^o} s \, \mathrm{d}m \leq \int_{m^o} s^o \, \mathrm{d}m \equiv S^o = s^o m^o \tag{3.264}$$

where the equality sign in the middle occurs if the system is a uniform one ((3.261)–(3.263) are valid in any place of the body; this is the final state with entropy S^o, see above (3.266)).

Before going further we note that result (3.264) for a special perturbed state with (3.243), (3.246) (i.e., (3.244) with zero velocity through the body) expresses the Gibbs stability of a uniform state with U^o, V^o, S^o (3.258), (3.259), (3.264), deduced from the stability conditions (3.256), (3.257).

Turning back to dynamical stability we can see from entropy inequality (3.110) and (3.68) in this isolation (3.226), (3.231) that at any moment t during the development

$$\dot{S}(t) \equiv \dot{\overline{\int_{m^o} s \, \mathrm{d}m}} = \int_{V^o} \sigma \, \mathrm{d}v \geq 0 \tag{3.265}$$

Therefore, during the process, the entropy function $S(t)$ has two properties: it does not decrease in time (3.265) and has the upper limit S^o (3.264) (in this connection $S(t)$ is called a *canonical function*). We add a simplifying (and in fact expected) assumption that whenever inequality in (3.264) is valid, the inequality in (3.265) is valid too (cf. [93, Rem. 4.5, Theor. 3]). Then in uniform equilibrium achieved at $t \to \infty$ entropy reaches the value S^o from (3.264)

$$\lim_{t \to \infty} S(t) = S^o \tag{3.266}$$

cf. [93, Eq. (4.40)].

Assuming also that $\lim_{t\to\infty} \dot{S}(t)$ exists it cannot be positive because of the upper limit S^o (3.264) and therefore by (3.265)

$$\lim_{t \to \infty} \dot{S}(t) = 0 \tag{3.267}$$

Moreover, motivated by (3.265), we assume that this limit (3.267) may be written as $\lim_{t\to\infty}\dot{S}(t) = \int_{V^o}\sigma^o\,\mathrm{d}v$ where σ^o are limits of (local) nonnegative entropy productions σ.

To localize these results we simply assume that all deductions may be repeated with any part of the considered body, i.e., with the corresponding part of mass, volume and other extensive quantities. Then result (3.267) may be written locally

$$\sigma^o = \lim_{t\to\infty}\sigma = 0 \tag{3.268}$$

in any place through the body.[47]

Therefore at $t \to \infty$ the body achieves the state where there is zero entropy production $\sigma = \sigma^0 = 0$ (3.222) in any place and permanently, and this is the equilibrium state defined with (3.240)–(3.242). In our linear fluid with regularity (3.232) we obtain from (3.196) (cf. Rem. 43) everywhere and permanently $\mathbf{D} = \mathbf{0}$ (3.220) and $\mathbf{g} = \mathbf{o}$ (3.221). Because of assumed zero velocity on the boundary of this equilibrium body, this rigid motion (3.18) gives zero velocity $\mathbf{v} = \mathbf{o}$ (3.223) everywhere and permanently inside. Constitutive equations (3.187), (3.195) give in this asymptotically equilibrium body (3.225), (3.226) and momentum balance (3.78) is then $\mathrm{grad}P = (\partial\hat{P}/\partial\rho)\mathbf{h} = \mathbf{o}$. By (3.257) we obtain $\mathbf{h} = \mathbf{o}$ and by mass balance (3.227), we can see that the density (and therefore also the specific volume v^o following from (3.259) because of the constant volume V^o) in this equilibrium body is everywhere and permanently constant, as is similarly temperature. The latter follows by (3.221) and (3.237) which is given by energy balance (3.235) at $Q = 0$ (3.231). From this and similarly from the entropy balance (3.236) and also from (3.192), (3.191) results that also the specific internal energy and entropy are everywhere and permanently constant with values u^o (following from constant energy E^o in (3.258)) and s^o obtainable then from (3.247), cf. (3.261).

Admitting the results (3.266), (3.268), the conditions (3.256), (3.257) are sufficient for the dynamical stability of a uniform equilibrium state compatible with isolation for a linear fluid body with regular equilibrium response.

Similarly as with classical Gibbs stability it may be shown that the stability conditions lead analogously to dynamical stability at other conditions. As another example of such a kind we discuss the fluid body of a constant volume immersed in a thermostat and in a body force field (and, also without it as special case). We use again the method similar to those giving (3.266), see also [94, 95] and Sect. 4.7.

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[47] Although assumptions giving (3.267), (3.268) look natural, this is not so, e.g. such $S(t)$ fulfilling (3.264), (3.265) may exist where $\dot{S}(t) > 0$ changes oscillatorily for any time and therefore a limit does not exist. Similarly the existence of limit (3.268) is not clear, e.g. σ^o in (3.267) may be nonzero on surfaces or lines (sets of zero measure) and such a situation may be obtained even by limitation from smooth function σ.

However, these difficulties may be avoided by other means, e.g. it is possible to prove (often with special types of material or with other potentials instead of entropy) the dynamical stability (even asymptotical one) but mostly in integral form (deviations are expressed by integral through the body). For further discussions see [1, 18, 93–95, 97–103, 114, 115].

Let us have a body consisting of linear fluid (of Sect. 3.7) with regular equilibrium response (3.232) with stability conditions (3.256), (3.257). The thermostatic boundary of this body has everywhere the same temperature T^o constant in time (the temperature inside the body may be arbitrary) and the boundary is fixed with $\mathbf{v} = \mathbf{o}$; therefore the volume of the body V^o is a constant. Heat may be exchanged but not by radiation, i.e., $Q = 0$ (3.231) through the body is valid. The mass of the body m^o is a constant which is independent of time

$$\int_{V^o} \rho \, \mathrm{d}v = m^o \tag{3.269}$$

The body is situated in the body force field $\mathbf{b}$ constant in time (e.g. earth gravitation), having the potential Φ

$$\mathbf{b} = -\mathrm{grad}\Phi \tag{3.270}$$

$$\frac{\partial \Phi}{\partial t} = 0 \text{ , i.e. } \quad \Phi = \Phi(\mathbf{x}) \tag{3.271}$$

but the frame is inertial, $\mathbf{i} = \mathbf{o}$ (cf. (3.104)).

We intend to show that a perturbed state compatible with these conditions may develop in $t \to \infty$ to the state which is in fact the *equilibrium* one: It has constant T^o and $\mathbf{v} = \mathbf{o}$ throughout the body, the stationary (equilibrium) pressure $P^o(\mathbf{x})$ is obtained by solution of (equilibrium) equation (3.228), (3.270)

$$\mathrm{grad} P^o(\mathbf{x}) = -\rho^o(\mathbf{x}) \, \mathrm{grad}\Phi(\mathbf{x}) \tag{3.272}$$

with stationary (equilibrium) density field $\rho^o(\mathbf{x}) \equiv \tilde{\rho}(T^o, P^o(\mathbf{x}))$. Such solution contains only one constant—pressure at one equipotential surface and this may be determined with the help of the known mass of the body (3.269) $m^o = \int_{V^o} \rho^o(\mathbf{x}) \, \mathrm{d}v$.

The balance of energy for such a body follows from (3.105)

$$\overline{\int_{V^o} \rho(u + \tfrac{1}{2}\mathbf{v}^2 + \Phi) \, \mathrm{d}v}^{\,\boldsymbol{\cdot}} = -\int_{\partial V^o} \mathbf{q}.\mathbf{n} \, \mathrm{d}a \tag{3.273}$$

where ∂V^o is the boundary of the body with fixed volume V^o. Because temperature T^o is a constant we can eliminate the surface integral from (3.273) using entropy inequality (3.108) (with the help of entropy production σ (3.109) and (3.68), (3.23)) for such a body with (3.231). After rearrangements we obtain

$$\begin{aligned} -\int_{\partial V^o} \mathbf{q}.\mathbf{n} \, \mathrm{d}a - \overline{\int_{V^o} \rho T^o s \, \mathrm{d}v}^{\,\boldsymbol{\cdot}} &= \overline{\int_{V^o} \rho(u - T^o s + \tfrac{1}{2}\mathbf{v}^2 + \Phi) \, \mathrm{d}v}^{\,\boldsymbol{\cdot}} \\ &= -T^o \int_{V^o} \sigma \, \mathrm{d}v \leq 0 \end{aligned} \tag{3.274}$$

Because field $P^o(\mathbf{x})$ and V^o are time independent we have (by (3.199) and below)

$$0 = \frac{\mathrm{d}}{\mathrm{d}t} \int_{V^o} P^o \, \mathrm{d}v = \frac{\mathrm{d}}{\mathrm{d}t} \int_{V^o} \rho v P^o \, \mathrm{d}v \tag{3.275}$$

Using the Reynolds theorem (3.24) in (3.275) for $\mathbf{v} = \mathbf{o}$ on the boundary and adding this to (3.274) we obtain (the volume V^o is fixed, the dot over the integral and $\frac{\mathrm{d}}{\mathrm{d}t}$ have the same meaning)

$$\dot{R}(t) = -T^o \int_{V^o} \sigma \, \mathrm{d}v \leq 0 \tag{3.276}$$

where the *canonical function* $R(t)$ is defined by

$$R(t) \equiv \int_{V^o} \rho(u - T^o s + P^o v + \tfrac{1}{2}\mathbf{v}^2 + \Phi) \, \mathrm{d}v \tag{3.277}$$

Because of conditions of stability (3.256), (3.257) we obtain again the inequality (3.260) ($u \neq u^o, s \neq s^o, v \neq v^o;\ T^o > 0$, using again (A.73) from Appendix A.3 for function (3.247)). This may be written as

$$u - sT^o + vP^o > u^o - s^o T^o + v^o P^o \equiv g^o \tag{3.278}$$

where (cf. (3.191), (3.192), (3.199), (3.111), (3.203)) we can choose u^o, s^o, v^o, g^o as the values at T^o, $\rho^o(\mathbf{x}) \equiv \tilde{\rho}(T^o, P^o(\mathbf{x}))$ in the given place $\mathbf{x}$ (calculated from (3.272)) and u, s, v are values at T, ρ in this place and some instant. Adding nonnegative quantity $\frac{1}{2}\mathbf{v}^2$ (the velocity is taken at this place and instant) to the left-hand side of (3.278) and adding the potential Φ to both sides, multiplying then the resulting inequality by $\rho > 0$ at this place and instant and integrating over the fixed volume V^o of the body in the given instant, we obtain

$$R(t) \geq R^o \tag{3.279}$$

(the equality is valid if $T = T^o$, $\rho = \rho^o$, $\mathbf{v} = \mathbf{o}$ through the body). Here the definition of canonical function (3.277) was used and R^o is defined by

$$R^o \equiv \int_{V^o} \rho(g^o + \Phi) \, \mathrm{d}v = (g^o + \Phi) m^o \tag{3.280}$$

The right-hand side of (3.280) and therefore R^o is constant; indeed, $g^o(\mathbf{x}) = \tilde{g}(P^o(\mathbf{x}), T^o)$, (3.278) was obtained using the solution $P^o(\mathbf{x})$ of (3.272) and therefore (remember that for time-constant potential Φ the equilibrium relation (3.239) is valid) $g^o + \Phi$ is constant as well as the mass (3.269).

Therefore we constructed the canonical function (3.277) which does not increase (3.276) and which has a lower bound (3.279). Using a similar simplifying assumption as at (3.266), namely, whenever the inequality in (3.279) is valid, the inequality in (3.276) is valid too (cf. [93, Rem. 4.5, Theor. 3]), we obtain

$$\lim_{t \to \infty} R(t) = R^o \tag{3.281}$$

i.e., the time limit of canonical function $R(t)$ achieves value R^o. Therefore this regular linear fluid achieves asymptotically the equilibrium state with constant temperature T^o and no movement inside $\mathbf{v} = \mathbf{o}$ (3.223) (such were permanent on the boundary). This is the equilibrium with equilibrium pressure $P^o(\mathbf{x})$ and density $\rho^o(\mathbf{x})$ fields given by (3.272). Adding similar simplifying assumptions leading to (3.267), (3.268), we obtain, in this equilibrium, e.g. the result (3.268) in such a nonuniform body.

The dynamical stability just described contains as a special case the zero body force $\mathbf{b} = \mathbf{o}$ (again $\mathbf{i} = \mathbf{o}$) which leads to a final uniform equilibrium state (noted below (3.239)) without potential (say $\Phi = 0$).

The stability conditions (3.256), (3.257) lead analogously to stability at further conditions, e.g. the stability of a fluid in a thermostatic cylinder closed by a piston under constant pressure, cf. [14, 95, 97]. This may be done similarly as for mixtures in the last example of Sect. 4.7.

The processes going asymptotically to equilibrium discussed in this section may be used for understanding the reversible equilibrium processes as those processes which pass so slowly that the entropy production in (3.265), (3.276) may be neglected, cf. Sects. 1.2, 2.1, 2.2, in models A, B, Rems. 12 in Chap. 1, 7 and 9 in Chap. 2, 41 in this chapter and [116] (for simplicity we use linear model of Sect. 3.7).[48]

Summary. This section shows the analysis of equilibrium state for a given system (single linear fluid in this case), which can be made once its final constitutive equations were derived. The equilibrium is defined so as to give the zero entropy production, cf. (3.220)–(3.222). To ensure the persistence of equilibrium (see the property S4 in Sect. 1.2), the regularity conditions (3.232)–(3.234) were added to the model of linear fluid. The majority of this section was devoted to the analysis of the stability of equilibrium; the concept of stable equilibrium was explained on page 127. The condition of stability called the Gibbs stability are (3.256) and (3.257). We

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[48] Namely, we discuss two examples of equilibrium reversible processes: the isothermal and then those which are adiabatic. Such processes with ideal gas (i.e., with real stable gas at sufficiently low pressures) are used in the Carnot cycle in Appendix A.1.

The uniform process described here for linear fluid (see below (3.239) and (3.211)) which is *isothermal* (temperature $T = T^0$ is permanently the same constant) may be considered as a special case of equilibrium reversible processes in the fluid model B of Sect. 2.2 if the entropy production (given by (2.36) or (3.196)) may be neglected. A stable equilibrium state in a given instant has (besides the constant temperature T^0) the volume V (with zero velocity everywhere (3.223)). The change of this state to another one with the volume $V + \mathrm{d}V$ (and the same temperature T^0 and zero velocity) by such a reversible process can be imagined as a sudden change of the volume by a small $\mathrm{d}V$ and as a development of this perturbed state isothermally to a new stable equilibrium state as described above (the second example without the body force: $\mathbf{b} = \mathbf{o}$ in (3.270)). A new equilibrium state will be practically achieved after a time interval much greater then the typical time scale in model B. Therefore the reversible process composed from sequences of such V to $V + \mathrm{d}V$ changes must be slow $\dot{V}$ is zero as well as the entropy production (2.36) and all this happens in the time scale of the model B. Heat exchange is nonzero and gives the entropy change, i.e., both members on the left-hand side of (3.274) compensate (similarly as in (2.10)) because the entropy production is zero (in (3.196) the second order contributions of heat and viscosity are neglected in fact, while in (3.274) the not neglected first order heat contribution is compensated).

want to stress that the latter condition enables the inversion of density as a function of pressure, i.e., it allows to use the pressure as an independent variable (in place of the density)—this condition was only supposed in preceding section and also in other thermodynamic approaches. During the evolution to the stable equilibrium state the entropy does not decrease in time, see (3.265) and also has an upper limit (3.264). Analogous conditions for the stability at different conditions (fluid of a constant volume maintained in a thermostat and under the effects of body forces) were derived in the form of canonical function defined by (3.277)—the conditions are given by (3.276) and (3.279).

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(Footnote 48 continued)

Quite analogously we can discuss the *adiabatic* reversible equilibrium process using the perturbation of the isolated body described above (the first example with persistent $\mathbf{i} = \mathbf{b} = \mathbf{o}$, $Q = 0$, $\mathbf{q} = \mathbf{o}$). Starting with a corresponding equilibrium state in a given instant with the volume V (with zero velocity everywhere (3.223)) we obtain the new perturbed state changing suddenly the volume to $V + \mathrm{d}V$ which develops as an isolated body into an equilibrium state with the new volume $V + \mathrm{d}V$, isolated and with zero velocity everywhere. An adiabatic reversible process is obtained, continuing in this way sequentially (analogously as in the previous isothermal example). Such V to $V + \mathrm{d}V$ changes must be again slow, with $\dot{V}$ nearly zero as well as the entropy production (all members in (3.196) are neglected, i.e., equality in (2.36) is valid in the time scale of model B). But then the left-hand side of (3.265) is nearly zero and entropy remains constant during such a reversible adiabatic process.

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Chapter 4
Continuum Thermodynamics of Mixture of Linear Fluids

This is the core chapter of our book. Here we discuss rational thermodynamics of mixtures and our main interest is the classical subject—the chemically reacting fluid mixture composed from fluids with linear transport properties (linear fluid mixture). In the last section, we discuss the relation of our results to those classical.

4.1 Principles of Mixture Theory

Thus far, with the exception of Sects. 2.4 and 2.5, we have studied only one-component system. In chemistry and its applications, multicomponent systems are much more encountered and the description of mixtures is much more important. The first systematic study of the non-equilibrium behaviour of mixtures was given in the linear thermodynamics of irreversible processes, mainly by Prigogine, Meixner and others [1–5]. It uses usually the properties of mixtures as primitives and it formulates balances (with the exception of those for mass) for mixture only. Also the newer extended thermodynamics (see Rem. 2 in Chap. 2) is studying mixtures [6–9].

Rational thermodynamics (the basic ideas of which have been presented in previous chapters) of mixtures has been promoted mainly by Truesdell [10–13], Bowen [14, 15], Müller [16–19], Williams [20, 21], see also reviews [15, 22, 23]. It also uses the classical approach [24–26] but most of its mixture theories [17, 27–73] use Truesdell's more detailed conception of mixture as superposing continua of its constituents [10, 11, 13]. These theories use the analogy with single (one constituent) material but because of the non-uniqueness of such analogy these theories differ sometimes in conceptions and details. Therefore, their comparison is often difficult but (because of limited knowledge of mixture properties) their results do not differ essentially [22, 23]. Mixtures studied by rational thermodynamics may be very different [13, 15, 17, 22, 23, 45, 54, 62, 74–78]. They include not only the one phase mixtures of fluids but also the more complicated (and therefore touched only marginally in this book) "heterogeneous mixtures" like porous solids filled with liquids

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and other phases, suspensions, emulsions, etc. (even non-linear in transport) [14, 15, 29–37, 54, 59, 60, 70–72, 79–81] and models with temperature memory effects (cf. Rems. 26 in Chap. 3, 31, Sect. 2.2 model D) [17, 18, 82, 83] (where the "local equilibrium" is invalid, cf. Sects. 2.2, 3.7 and 4.6), and systems with more temperatures (Rem. 2, [14, 15, 59]). Among them are also the mixtures with fading memory [35], mixture surfaces (waves and phase boundaries) [17, 40, 49, 51, 52, 55, 73, 84–92], Gibbs' phase rule [93, 94] and non-local materials [41, 95, 96]. Yet newer theories of mixtures are beginning to be developed based on modern concepts of continuum thermomechanics [97–100] and promoted mainly by Williams [20, 21, 67, 68, 101–103]. These theories use, in fact, only the solidification principle (in its broader form noted below) to construct the mixture, but so far they are elaborated mainly in mechanical aspects (cf. Rems. 7 in Chap. 3, 11).

In this book, we use Truesdell's conceptually most simple idea of mixture [10–12] and we confine ourselves to a classical task important in applications: we study the mixture of chemically reacting fluids (mechanically non-polar, cf. Sect. 4.3 and Rem. 17 in Chap. 3), with the same temperature of all constituents and with linear transport properties (like diffusion, heat conduction, viscosity; generalization on non-linear transport, see [60, 71, 72, 104]). This model, called shortly the *linear fluid mixture*, contains as special cases non-reacting fluid mixtures and some further ones (see Sect. 4.8).

At least for this linear fluids mixture, we (partially) overcome the usual objection to Truesdell's conception: how to find the thermodynamic partial properties taken as primitives in this theory. Namely, we show that such partial quantities may be calculated from the dependence of corresponding mixture properties on the composition using the so-called *mixture invariance* of balances [59], see Sects. 4.5 and 4.6.

To construct the theory of mixture, we use as a basis the following three "metaphysical" principles of Truesdell [12, 13]:

1. All properties of a mixture are consequences of properties of its constituents. By this principle, we introduce the properties of constituents as primitives and properties of mixture are then defined.
2. So as to describe the motion of a constituent, we may imagine it to be isolated from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it. This *solidification* principle (which is an extension of those noted in Rem. 14 in Chap. 3) permits us to formulate balances by analogy with pure materials.
3. The motion of the mixture is governed by the same equations as is a single body. By this principle, the properties and balances of mixture are formulated on the basis of pure substances.

Obviously, the interpretation of these principles is not unique. In this book, we interpret the third principle in the sense that if we neglect the *diffusion* (relative movement of one constituent towards the others—a phenomenon typical only for the mixture) the mixture must behave as a single substance (then even chemical reactions may be described with the use of internal variables); the balances in such a non-diffusing mixture must be the same as in Chap. 3.[1]

In the mixtures, we postulate two types of balances: balance for each constituent α and balance of mixture. Motivated by principles (1) and (2). we propose the balances for individual constituents (of mass, momentum and its moment, energy and entropy) similarly as for the single constituent (see Sects. 3.3 and 3.4), i.e. their left-hand sides form the change of corresponding partial quantity in a fixed volume and to the right-hand sides we add the interactions with the remaining constituents. Balances of mixtures we postulate as the sums of left-hand sides of individual constituent balances, putting the sums of interactions on right-hand sides equal to zero because of their assumed compensation, see Sects. 4.2, 4.3 and 4.4 for details. Entropy inequality is postulated for the mixture only (as may be expected physically; partial entropy inequalities seem to be too strong [15, 22, 23], cf. Rem. 2).

We simplify the mixture model in this book by assumption that all constituents (occupying simultaneously the same place of mixture, see below (4.1)) have the same temperature; then it suffices to formulate the energy and entropy balances for the mixture only, see Sect. 4.4.[2] Note that entropy, as a quantity depending on the material model (cf. Sect. 2.3), is not only the function of composition but also depends on the number of constituents (cf. Gibbs paradox: the presence of additional constituent discontinuously changes the entropy regardless of its (physical) proximity); therefore, we assume the number of constituents as firmly given in the following.

Concluding, it seems that the thermodynamics of mixtures has not yet been solved satisfactorily in spite of great endeavour and specific results. The main problems are rooted in distinguishing between heat and matter flowing simultaneously through (even imaginary) boundary which necessary appears in diffusing mixture exchanging mass (of different constituents by different velocities) and energy. While for single substance this difficulty has been removed by using the instrument of the "material volume" and this permits to construct the theory of single substance on the basis of Chap. 1 (namely, the First and Second Laws are postulated there for closed, i.e. not exchanging mass, system), this is impossible in diffusing and heat exchanging mixture. Here we must add rather intuitive postulates (on summing the left-hand sides of component balances or on the compensation of interactions) noted above. In spite of this, Truesdell's mixture theory seems to be simpler than the classical

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[1] Literal interpretation [12, 13] of the third principle is that "a body does not know if it is a mixture or not" which leads to complicated and not fully clear expressions in mixture when diffusion is present; cf. Rems. 3, 7, 10, 11, see also [60, 67, 68, 73].

[2] Energy and entropy balances may be formulated for individual constituents (and entropy inequality is given as the non-negativity of sums of entropy productions in individual entropy balances), cf. [14, 15, 59] but, even the constitutive equations for partial heat fluxes or energy interactions may be formulated, if the temperature of all constituents is the same, they play a role only through the sum of partial heat fluxes (i.e. through the heat flux for mixture as in Sect. 4.4) and the sum of energy interactions disappears by compensation, see [59, Sect. 3].

For mixtures with different temperatures, e.g. plasma is a mixture of electrons and ions with different temperatures, see [32, 59, 105].

theory [1, 3] with postulates for mixture only, where especially ad hoc proposition of energy and entropy balances is complicated and not unique, cf. Rems. 10, 11.

Properties of constituents which are of fixed number n will be denoted by the Greek subscript $\alpha = 1, 2, \dots, n$ (in this chapter, if it is not noted otherwise, subscripts $\alpha, \gamma, \epsilon = 1, 2, \dots, n$ and $\beta, \delta, \zeta = 1, 2, \dots, n-1$ are used).

For each constituent, we can use the same kinematic description as for the single substance in Sect. 3.1. Namely, for each constituent α invertible and smooth *motion* $\underline{\chi}_\alpha$ is defined as

$$\mathbf{x} = \underline{\chi}_\alpha(\mathbf{X}_\alpha, t) \qquad \alpha = 1, \dots, n \tag{4.1}$$

where $\mathbf{x}$ is the place of the particle $\mathbf{X}_\alpha$ of constituent $\alpha = 1, \dots, n$ in the instant t ($\mathbf{X}_\alpha$ is defined by its place in reference configuration of constituent α); see also [73, 90, 91, 106].

Mixture is an intersection of actual configurations of all n constituents, i.e. it is a superposition of such parts of actual configurations of every constituent that each place in the mixture is occupied simultaneously by n different particles each from every constituent of the mixture. The meaning of reference, actual configurations as well as other quantities for constituent α are quite analogous to those in Sect. 3.1. e.g. velocity $\mathbf{v}_\alpha$ of every constituent $\alpha = 1, \dots, n$, is defined by (cf. (3.7)):

$$\mathbf{v}_\alpha \equiv \partial\underline{\chi}_\alpha/\partial t = \overset{\backslash\alpha}{\underline{\chi}_\alpha} = \grave{\underline{\chi}}_\alpha \qquad \alpha = 1, \dots, n \tag{4.2}$$

where the second equality denotes the material derivative relative to constituent α; the last expression is the simplified description of this derivative when upper α is the same as in the lower index.

Each quantity—*field* φ—may be, by (4.1), described by the spatial as well as material (to some constituent α) description $\varphi = \varphi(\mathbf{x}, t) = \varphi(\mathbf{X}_\alpha, t)$; therefore the material derivative to the constituent α is also (cf. (3.8) and (3.9))

$$\overset{\backslash\alpha}{\varphi} \equiv \frac{\partial\varphi}{\partial t} + v^i_\alpha \frac{\partial\varphi}{\partial x^i} \tag{4.3}$$

and we have

$$\mathrm{Grad}\varphi = \mathrm{grad}\varphi\, \mathbf{F}_\alpha \tag{4.4}$$

Here the deformation gradient $\mathbf{F}_\alpha$ as well as the velocity gradient $\mathbf{L}_\alpha$, stretching $\mathbf{D}_\alpha$ and the spin $\mathbf{W}_\alpha$ for constituent are defined analogously as (3.10), (3.12), (3.14), (3.15) and (3.16), e.g.

$$\mathbf{F}_\alpha \equiv \partial\underline{\chi}_\alpha/\partial\mathbf{X}_\alpha \tag{4.5}$$

$$\mathbf{L}_\alpha \equiv \mathrm{grad}\mathbf{v}_\alpha = \mathbf{D}_\alpha + \mathbf{W}_\alpha = \grave{\mathbf{F}}_\alpha\mathbf{F}_\alpha^{-1} \tag{4.6}$$

$$\mathbf{D}_\alpha \equiv \frac{1}{2}(\mathbf{L}_\alpha + \mathbf{L}_\alpha^T), \qquad \mathbf{W}_\alpha \equiv \frac{1}{2}(\mathbf{L}_\alpha - \mathbf{L}_\alpha^T) \tag{4.7}$$

$$\mathrm{div}\mathbf{v}_\alpha = \mathrm{tr}\mathbf{D}_\alpha \tag{4.8}$$

Killing's theorem is valid for all constituents $\alpha = 1, \ldots, n$: The motion of the mixture is rigid if and only if for all α

$$\mathbf{D}_\alpha = \mathbf{0} \qquad \alpha = 1, \ldots, n \tag{4.9}$$

It is clear that analogues of (3.12), denoted J_α, are valid for each constituent as well as that of Euler relation (3.17) and Reynolds theorem (3.24) with $\backslash\alpha$ instead of the dot in the original equations, cf. (d) in Rem. 3, but material volume (containing the same particles of constituent α) is not as important as for the pure substance.

Results of Sect. 3.2 concerning the change of frame are possible to transfer to mixtures directly if we keep in mind that transformations (3.25),(3.26) concern all constituents of a mixture simultaneously ($\mathbf{c}(t), \mathbf{Q}(t), \mathbf{b}$ are the same for all constituents of the mixture). Velocities $\mathbf{v}_\alpha$ and accelerations $\grave{\mathbf{v}}_\alpha$ (concisely written like (4.2)) are transformed again by (3.38) and (3.44), i.e.

$$\mathbf{v}^*_\alpha = \mathbf{Q}\mathbf{v}_\alpha + \dot{\mathbf{c}} + \underline{\Omega}(\mathbf{x}^* - \mathbf{c}) \tag{4.10}$$

$$\grave{\mathbf{v}}^*_\alpha = \mathbf{Q}\grave{\mathbf{v}}_\alpha + \mathbf{i}^*_\alpha \tag{4.11}$$

where the inertial force of constituent $\alpha = 1, \ldots, n$ is

$$\mathbf{i}^*_\alpha \equiv 2\underline{\Omega}(\mathbf{v}^*_\alpha - \dot{\mathbf{c}}) - \underline{\Omega}^2(\mathbf{x}^* - \mathbf{c}) + \dot{\underline{\Omega}}(\mathbf{x}^* - \mathbf{c}) + \ddot{\mathbf{c}} \tag{4.12}$$

with $\underline{\Omega}$ given by (3.39) (cf. (3.46), see also (3.79) and (4.58)). The dot means the derivative of the function of time only. Note that in inertial frame $\mathbf{i}^*_\alpha = \mathbf{o}$ for the same reasons as (3.48). Stretching $\mathbf{D}_\alpha$ of constituent α is an objective tensor

$$\mathbf{D}^*_\alpha = \mathbf{Q}\mathbf{D}_\alpha\mathbf{Q}^T \tag{4.13}$$

(by the same arguments as in (3.54)) and similarly in other cases.

4.2 Balances of Mass and Stoichiometry of Chemical Reactions

In the mixture, in the given place and instant, we introduce the mass *density* ρ_α of constituent $\alpha = 1, \ldots, n$ as a primitive. It has the meaning of mass of constituent α in a volume unit of the whole mixture (in chemistry this quantity is called the mass or "weight" concentration). The (partial) densities $\rho_\alpha = \rho_\alpha(\mathbf{x}, t)$ are assumed to be objective and only positive—this is clearly a plausible model even when a "practically pure" constituent is formed as a result of chemical reactions. The density of mixture ρ (defined as the sum of partial densities through all constituents, cf. (4.21) and Rem. 3) has the usual meaning [11, 15, 17, 22, 23, 50].

Balances for constituent s and mixture (postulated in accord with in Sect. 4.1 proposed procedure) are as follows.

The *balance of mass for each constituent* α is

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho_\alpha \,\mathrm{d}v + \int_{\partial V} \rho_\alpha \mathbf{v}_\alpha.\mathbf{n}\,\mathrm{d}a = \int_V r_\alpha \,\mathrm{d}v \qquad \alpha = 1, \ldots, n \tag{4.14}$$

for each volume V fixed in space with the surface ∂V which is contained in mixture (cf. (3.60)). The first integral on the left-hand side is change of mass of constituent α in V, the second integral is flux of mass of α through ∂V (the left-hand side is the time change of mass in fixed volume) and the integral on the right-hand side expresses the change of mass of constituent α by chemical reactions: r_α is the mass produced ($r_\alpha > 0$) or consumed ($r_\alpha < 0$) by chemical reactions in the time and volume unit (the right-hand side is just interaction with the remaining constituents).

If identically

$$r_\alpha \equiv 0 \tag{4.15}$$

we denote such constituent α as the *non-reacting* one, cf. (4.28).

The *balance of mass for the mixture* asserts that in any fixed volume V of the mixture the whole mass (sum of mass of all constituents) can be changed only through the fixed surface ∂V as a result of the flow of each constituent α by the velocity $\mathbf{v}_\alpha$

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_{\alpha=1}^{n}\int_V \rho_\alpha \,\mathrm{d}v + \sum_{\alpha=1}^{n}\int_{\partial V} \rho_\alpha \mathbf{v}_\alpha.\mathbf{n}\,\mathrm{d}a = 0 \tag{4.16}$$

This postulate is in accord with the general proposal of construction of mixture balances given in Sect. 4.1: the left-hand side of (4.16) is the sum of the left-hand sides of (4.14) and the right-hand side of (4.16) expresses the compensation of interactions (cf. (4.20)).

Assuming, similarly as for pure substance in Sect. 3.3, the validity of these postulates for any part of the mixture we can localize them using Gauss' theorem (3.23) (cf. deduction of (3.62) from (3.60); note independency of V on constituents).

We obtain the local balances of mass for constituent

$$\frac{\partial \rho_\alpha}{\partial t} + \mathrm{div}\rho_\alpha \mathbf{v}_\alpha = r_\alpha \qquad \alpha = 1, \ldots, n \tag{4.17}$$

which may be rewritten with the use of material derivative of each constituent (4.3), (4.2)

$$\grave{\rho}_\alpha + \rho_\alpha \mathrm{div}\mathbf{v}_\alpha = r_\alpha \qquad \alpha = 1, \ldots n \tag{4.18}$$

Using (4.17), (4.3) the analogue of (3.67) may be obtained for field φ

$$\frac{\partial \rho_\alpha \varphi}{\partial t} + \mathrm{div}\rho_\alpha \varphi v_{\boldsymbol{\alpha}} = \rho_\alpha \overset{\backslash\alpha}{\varphi} + \varphi r_\alpha \tag{4.19}$$

Local balance of mass for mixture may be expressed as

$$\sum_{\alpha=1}^{n} r_\alpha = 0 \tag{4.20}$$

as follows from the local forms of (4.16) and (4.17).

We assume that r_α are objective scalars and therefore balances (4.18) and (4.20) are the same in any frame (cf. (4.8), (4.13); $\grave{\rho}_\alpha$ is objective which may be proved similarly as objectivity of the material derivative of the objective scalar in Sect. 3.2).

We introduce several definitions which will be useful later.[3]

Density of mixture ρ is defined as

$$\rho \equiv \sum_{\alpha=1}^{n} \rho_\alpha \tag{4.21}$$

Mass fraction w_α of constituent α (in physics denoted as "concentration")

$$w_\alpha \equiv \rho_\alpha / \rho \qquad \alpha = 1, \ldots, n \tag{4.22}$$

with property

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[3] Using density of mixture (4.21), mass fractions (4.22) and *barycentric velocity* $\mathbf{v}^w$, defined by

$$\mathbf{v}^w \equiv \sum_{\alpha=1}^{n} w_\alpha \mathbf{v}_\alpha \qquad (a)$$

in (4.16), we obtain the same form as (3.60) or locally the form of (3.62) or (3.63) with $\mathbf{v} = \mathbf{v}^w$

$$\frac{\partial \rho}{\partial t} + \mathrm{div} \rho \mathbf{v}^w = 0, \qquad \dot{\rho} + \rho\, \mathrm{div} \mathbf{v}^w = 0 \qquad (b)$$

where "dot" denotes the material derivative relative to barycentric velocity (cf. (3.8)), i.e.

$$\dot{\rho} \equiv \frac{\partial \rho}{\partial t} + \mathbf{v}^w . \mathrm{grad} \rho \qquad (c)$$

Using "dot" (like in Chap. 3) is natural if the all velocities $\mathbf{v}_\alpha$ are the same as in Sect. 4.7, see (4.322), (4.323).

Unfortunately, so simple a result is not obtainable with other balances (see Rems. 7, 10, 11) but even here, if all velocities are the same $\mathbf{v}_\alpha = \mathbf{v}$, they are in accord with the interpretation of the third principle in Sect. 4.1, cf. Rem. 1.

If we use material derivatives, balances (4.14) and (4.16) may be written

$$\overset{\backslash\alpha}{\overline{\int_{\mathcal{V}} \rho_\alpha \, \mathrm{d}v}} = \int_{\mathcal{V}} r_\alpha \, \mathrm{d}v, \qquad \sum_{\alpha=1}^{n} \overset{\backslash\alpha}{\overline{\int_{\mathcal{V}} \rho_\alpha \, \mathrm{d}v}} = 0 \qquad (d)$$

where the analogue of Reynolds theorem (3.24) for constituent α was used (cf. (3.59)); $\mathcal{V}$ is a material volume chosen the same for all constituents.

$$\sum_{\alpha=1}^{n} w_\alpha = 1 \tag{4.23}$$

In Sect. 4.1 we denoted as *diffusion* the relative motion of mixture constituents caused by their generally different velocities. Therefore, it is useful to define the *diffusion velocity* $\mathbf{u}_\beta$ *relative to the n-th constituent* (there are more possibilities of such definitions, cf. Rem. 7 and Sect. 4.10)

$$\mathbf{u}_\beta \equiv \mathbf{v}_\beta - \mathbf{v}_n \qquad \beta = 1, \dots, n-1, \qquad \mathbf{u}_n \equiv \mathbf{o} \tag{4.24}$$

The latter expression is useful in sums like (4.64). Note, see (4.10), that diffusion velocities (4.24) are objective (frame indifferent) as well as (4.21), (4.22).

In chemically reacting mixture $r_\alpha \neq 0$ (for several reacting constituents at least) due to chemical reactions among reacting constituents. The reactions are described by *stoichiometry*. Here we follow Bowen [14, 30, 31], see also [12, 48, 65], using non-orthogonal bases (see Appendix A.4); therefore, we use upper or lower indices for contravariant or covariant components. In stoichiometry, we assume that each constituent is composed of *atomic substances* (*atoms*—often chemical elements) in definite proportions. The constituent $\alpha = 1, \dots, n$ is characterized by a positive constant—the *molar mass* M_α, which is therefore a linear combination of *atomic masses* A^σ of atomic substances $\sigma = 1, 2, \dots, z$

$$M_\alpha = \sum_{\sigma=1}^{z} A^\sigma T_{\sigma\alpha} \qquad \alpha = 1, \dots, n \tag{4.25}$$

where $T_{\sigma\alpha}$ may be interpreted as the "number of atoms σ in one molecule of constituent α".

We define *reaction rate* J^α *of constituent* α (in mols in time and volume units) by

$$J^\alpha \equiv r_\alpha / M_\alpha \qquad \alpha = 1, \dots, n \tag{4.26}$$

expressing the number of mols of constituent α formed or destroyed by chemical reactions in a volume and time unit.

The basic postulate of stoichiometry is the *permanence of atomic substances*

$$\sum_{\alpha=1}^{n} T_{\sigma\alpha} J^\alpha = 0 \qquad \sigma = 1, \dots, z \tag{4.27}$$

which expresses the indestructibility of atoms in chemical reactions. This postulate is in accord with the balance of whole mass (4.20): summing r_α from (4.26) through constituents and using (4.25), (4.27), we obtain (4.20) (therefore, we could use (4.27) instead of (4.20)). In the following, the rank h of matrix $\|T_{\sigma\alpha}\|$ of dimension $z \times n$ plays an important role. According to its definition (rank h of a matrix is the dimension of the highest non-zero determinant formed from the matrix) $h \leq \min(z, n)$ and therefore $h \leq n$.

The case $h = n$ (this is possible if $z \geq n$) is the chemically *non-reacting* mixture because the solution of the system z equations (4.27) with n unknowns J^α is

$$J^\alpha = 0, \text{ i.e. } \quad r_\alpha = 0 \qquad \alpha = 1, \ldots, n \tag{4.28}$$

Note that if this is valid only for some constituents α (4.28) then those may be denoted as non-reacting, cf. (4.15).

In this section, we are interested mainly in chemical reactions where

$$h < n \tag{4.29}$$

The rank h of $\|T_{\sigma\alpha}\|$ gives the maximum number of the linear independent relations in (4.27) and $n - h$ gives the number of chemical reactions in the system (which are independent, namely no such chemical reaction follows by linear combination from those remaining), see below (4.33).[4] Therefore, only h independent relations from (4.27) (as well as any other system of h linearly independent relations obtained by linear combinations) are useful. Therefore, the permanence of atomic substances (4.27) may be expressed by

$$\sum_{\alpha=1}^{n} S_{\sigma\alpha} J^\alpha = 0 \qquad \sigma = 1, \ldots, h \tag{4.30}$$

where the matrix $\|S_{\sigma\alpha}\|$ of dimension $h \times n$ and of rank h is one from the matrices obtained from $\|T_{\sigma\alpha}\|$ in the way described above. If we use $S_{\sigma\alpha}$ instead of $T_{\sigma\alpha}$ in (4.25) we can write

$$M_\alpha = \sum_{\sigma=1}^{h} E^\sigma S_{\sigma\alpha} \qquad \alpha = 1, \ldots, n \tag{4.31}$$

where E^σ are certain linear combinations of atomic masses. Therefore, a "molecule" of constituent α is a combination of "atomic substances with atomic masses" E^σ (which are not generally the chemical elements, cf. examples at the end of this Sect. 4.2). With such interpretation Eqs. (4.30) and (4.31) will be used in the following instead of (4.27) and (4.25).

We introduce an abstract n-dimensional vector space $\mathcal{U}$ and we call it the *mixture space*. In it we select bases $\vec{e}_\alpha$ and $\vec{e}^\alpha$; for now it is sufficient to assume that these bases are othonormal, i.e. $\vec{e}_\alpha = \vec{e}^\alpha$, cf. Appendix A.4. In the space $\mathcal{U}$, we define the vectors of molar masses $\vec{M}$ and reaction rates $\vec{J}$ by

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[4] Results (4.28), (4.29) depend on the a priori choice of n constituents to obtain reasonable accord with chemistry: e.g. if we choose HCl and NaOH as constituents only we obtain non-reacting mixture ($z = 4, n = h = 2$); adding NaCl, H_2O ($n = 4, z = 4, h = 3$), one reaction is possible. On the other hand in practice, (4.28) may be valid even when (4.29) is valid ("frozen" reactions).

$$\vec{M} \equiv \sum_{\alpha=1}^{n} M_\alpha \vec{e}^{\alpha} \tag{4.32}$$

$$\vec{J} \equiv \sum_{\alpha=1}^{n} J^\alpha \vec{e}_\alpha \tag{4.33}$$

Then we define h independent (contravariant) vectors $\vec{f}_\sigma$ by

$$\vec{f}_\sigma \equiv \sum_{\alpha=1}^{n} S_{\sigma\alpha} \vec{e}^{\alpha} \qquad \sigma = 1, \ldots, h \tag{4.34}$$

which form a basis in h-dimensional subspace $\mathcal{W}$ of the mixture space $\mathcal{U}$. The subspace $\mathcal{W}$ uniquely determines a complementary, orthogonal and $n-h$ dimensional subspace in the space $\mathcal{U}$ which we will call the *reaction space* $\mathcal{V}$.

The postulate of *permanence of atomic substances* (4.30) may be equivalently expressed as follows [30]:

The vector of molar masses $\vec{M}$ is situated in the subspace $\mathcal{W}$ and the vector of reaction rates $\vec{J}$ is situated only in the reaction space $\mathcal{V}$, i.e.

$$\vec{M} \in \mathcal{W} \tag{4.35}$$

$$\vec{J} \in \mathcal{V} \tag{4.36}$$

where $\mathcal{W} \perp \mathcal{V}$ and $\mathcal{W} \oplus \mathcal{V} = \mathcal{U}$ ($\oplus$ means Cartesian sum).

Proof Necessity of (4.35): inserting (4.34), (4.31), (4.32) into the left hand side of following expression (4.37) we obtain

$$\sum_{\sigma=1}^{h} E^\sigma \vec{f}_\sigma = \vec{M} \tag{4.37}$$

i.e. $\vec{M}$ may be expressed in the basis of $\mathcal{W}$ and therefore (4.35) follows. The necessity of (4.36): using (4.33),(4.34),(4.30) in the left-hand side of following expression (4.38) we obtain

$$\vec{J}.\vec{f}_\sigma = 0 \qquad \sigma = 1, \ldots, h \tag{4.38}$$

i.e. $\vec{J}$ is orthogonal to the basis of $\mathcal{W}$ and therefore (4.36) follows. To prove the sufficiency, we show that (4.30), (4.31) follow from (4.35), (4.36): indeed, let $\vec{f}_\sigma$ ($\sigma = 1, \ldots, h$) be some basis of the h-dimensional subspace $\mathcal{W}$ and $S_{\sigma\alpha}$ are components of each $\vec{f}_\sigma$, in the basis $\vec{e}_\alpha$ ($\alpha = 1, \ldots, n$) of the mixture space $\mathcal{U}$, i.e. (4.34) is valid. According to (4.36), Eqs. (4.38) must be valid. Introducing (4.33), (4.34) into left-hand side of (4.38) we obtain (4.30). Further, let E^σ be components of $\vec{M}$ in the basis $\vec{f}_\sigma$ of subspace $\mathcal{W}$, i.e. (4.37) is valid. If $\vec{M}$ has components M_α in the space $\mathcal{U}$ according to (4.32), we can see, by substitution of (4.34) and (4.32) into (4.37), that (4.31) must be valid. Q.E.D.

From the permanence of atomic substances (4.35), (4.36) then follows

$$\vec{M}.\vec{J} = 0 \qquad \text{or} \qquad \sum_{\alpha=1}^{n} M_\alpha J^\alpha = 0 \tag{4.39}$$

which, according to (4.32), (4.33), (4.26), expresses again the mass balance for the mixture (4.20).

Now, let us choose $n - h$ linearly independent covariant vectors $\vec{g}^p$ as basis in the reaction subspace $\mathcal{V}$ and show that $n - h$ is the number of independent chemical reactions in the mixture, cf. below (4.45) and Rem. 4. These vectors can be written in the basis of $\mathcal{U}$ as

$$\vec{g}^p = \sum_{\alpha=1}^{n} P^{p\alpha} \vec{e}_\alpha \qquad p = 1, \ldots, n - h \tag{4.40}$$

where matrix $\|P^{p\alpha}\|$ of the dimension $(n - h) \times n$ is called the matrix of *stoichiometric coefficients* (of independent reactions noted above). Because of linear independency of $\vec{g}^p$, the rank of this matrix $\|P^{p\alpha}\|$ is $n - h$. From the orthogonality of subspaces $\mathcal{V}$ and $\mathcal{W}$ follows (with the use of (4.40) and (4.34))

$$\vec{f}_\sigma.\vec{g}^p = \sum_{\alpha=1}^{n} S_{\sigma\alpha} P^{p\alpha} = 0 \qquad \sigma = 1, \ldots, h, \quad p = 1, \ldots, n - h \tag{4.41}$$

Therefore, an arbitrary matrix of dimension $(n - h) \times n$ of the rank $n - h$ fulfilling the relations (4.41) for the given matrix $\|S_{\sigma\alpha}\|$ may be chosen as matrix $\|P^{p\alpha}\|$. If we use (4.40) and (4.32) then from (4.35), (4.36) it follows that

$$\vec{g}^p.\vec{M} = \sum_{\alpha=1}^{n} P^{p\alpha} M^\alpha = 0 \qquad p = 1, \ldots, n - h \tag{4.42}$$

From the permanence postulate (4.36) further follows

$$\vec{J} = \sum_{p=1}^{n-h} J_p \vec{g}^p \tag{4.43}$$

where J_p (components in chosen covariant basis $\vec{g}^p$ of reaction space $\mathcal{V}$) is called the *reaction rate* of p-th chemical reaction.

From (4.43) and (4.40), (4.33) we have

$$J^{\alpha} = \sum_{p=1}^{n-h} J_p P^{p\alpha} \qquad \alpha = 1, \ldots, n \tag{4.44}$$

On the other hand, the reaction rate J_r ($r = 1, \ldots, n - h$) may be obtained by multiplying (4.43) with vectors of contravariant basis $\vec{g}_r$ (see (A.89)). Inserting in such product from (4.33), from the relation between contra- and covariant bases in $\mathcal{V}$ (see (A.86)) and from (4.40), we obtain (by using of orthonormality of $\vec{e}_{\alpha}$) the relation between rates (reversal to (4.44))

$$J_r = \sum_{\alpha=1}^{n} \sum_{p=1}^{n-h} J^{\alpha} P^{p\alpha} g_{rp} \qquad r = 1, \ldots, n - h \tag{4.45}$$

(covariant metric tensor g_{rp} is obtained by the inversion of contravariant metric tensor $g^{rp} = \vec{g}^{r} . \vec{g}^{p}$ which follows fom (4.40) and chosen reactions; cf. (A.83)).

It follows therefore, that chemical changes can be described selecting basis $\vec{g}^{p}$ in the reaction space $\mathcal{V}$ (systematic choice see, e.g. [107, 108]). Such $n-h$ independent reactions may be seen from (4.42) if we use the corresponding chemical symbols instead of M_{α} and use the following convention: in the following, we call the products in p-th chemical reaction these constituents for which $P^{p\alpha} > 0$; constituents with $P^{p\alpha} < 0$ are the reactants in the reaction p. If $P^{p\alpha} = 0$ then constituent α does not take part in the reaction p; if this is valid in all reactions $p = 1, \ldots, n - h$ then such α is a non-reacting constituent (indeed, from (4.44) we obtain (4.28)).

The same reacting mixture may be described by infinite numbers of systems of $n-h$ independent chemical reactions equivalently (each of such systems corresponds to some choice of basis $\vec{g}^{p}$ in $\mathcal{V}$) which may be mutually recalculated by linear transformations of the type (A.87). Using (4.40), we recalculate the corresponding stoichiometry coefficients; zero column $P^{p\alpha}$ for non-reacting constituent α will be again zero. Therefore, reacting and non-reacting constituents are such in any choice of the system of independent chemical reactions.

Chemical kinetics is described by (constitutive equations for) rates J^{α} or J_p (see Sect. 4.9 for further details); note that $J_p P^{p\alpha}$ from (4.44) may be interpreted as the number of moles of constituent α produced (or consumed) in the time and volume unit in p-th reaction.

As an example of the preceding formulae, we consider the mixture of NO_2 ($\alpha = 1$) and N_2O_4 ($\alpha = 2$) with atoms N ($\sigma = 1$) and O ($\sigma = 2$). Then $\|T_{\sigma\alpha}\| = \begin{pmatrix} 1 & 2 \\ 2 & 4 \end{pmatrix}$ with $h = 1$ and therefore, e.g. $\|S_{\sigma\alpha}\| = (1 \;\; 2)$ (i.e. atomic substance is NO_2). As stoichiometric matrix, e.g. $\|P^{p\alpha}\| = (2 \;\; -1)$ may be chosen, corresponding to reaction

$$N_2O_4 = 2NO_2 \tag{4.46}$$

or $\|P^{p\alpha}\| = (-1 \;\; 1/2)$ with reaction

$$NO_2 = 1/2 N_2O_4 \tag{4.47}$$

Another example is again NO_2 and N_2O_4 but with atoms Q ($\alpha = 3 = n$). Correspondingly $\|T_{\sigma\alpha}\| = \begin{pmatrix} 1 & 2 & 0 \\ 2 & 4 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ with $h = 2$ and, e.g. $\|S_{\sigma\alpha}\| = \begin{pmatrix} 1 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$. Then, e.g. $\|P^{p\alpha}\| = (2 \ \ -1 \ \ 0)$ which corresponds to the reaction (4.46) with Q as non-reacting constituent.

The last example is O, O_2 ,O_3 ($\alpha = 1, 2, 3$) with atom O ($\sigma = 1$). Then $\|T_{\sigma\alpha}\| = (1 \ \ 2 \ \ 3) = \|S_{\sigma\alpha}\|$ (the last choice is possible). As the stoichiometric coefficients are, e.g. $\|P^{p\alpha}\| = \begin{pmatrix} 0 & 3 & -2 \\ 3 & 0 & -1 \end{pmatrix}$ corresponding to the reactions

$$2O_3 = 3O_2, \quad O_3 = 3O \tag{4.48}$$

Another equivalent set of these reactions is

$$O_3 = O_2 + O, \quad O_2 = 2O \tag{4.49}$$

See also Rem. 4 and Sect. 4.9.

Summary. The balance of mass can be written either for each component separately or for the mixture as a whole; both involve the mass density (mass concentration) of individual components. Their local forms are (4.17) or (4.18) and (4.20), respectively. The mass changes during chemical reactions are restricted by additional conditions resulting from the stoichiometry of chemical reactions or, in other words, by the permanence of atoms in reactions—see (4.27). Linear algebra of stoichiometry leads then to a restriction on rates by which the masses or molar amounts of reacting constituents are changed—see (4.39). Further it gives the stoichiometric matrix, (4.42), and translates the rates (of chemical transformations) of individual constituents to the rates of (independent) chemical reactions, cf. (4.45). Thus only the independent reactions are sufficient to be included in a model of chemically reacting mixture and to describe chemical transformations mathematically. Note also the definition of the density of mixture (4.21) and of the mass fraction (4.22).

4.3 Balances of Momentum and Moment of Momentum in Reacting Mixture

Postulation of momentum balances for constituents and for mixture [11, 12, 15, 17, 22, 23, 50, 65] is sufficient (similarly as for pure constituent in Sect. 3.3) to be done in the inertial frame because our main results—local balances (4.58), (4.63)—will be valid in any frame. For every fixed volume V with fixed surface ∂V in the mixture, we postulate the *balance of momentum of constituent* α in the inertial frame as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho_\alpha \mathbf{v}_\alpha \,\mathrm{d}v + \int_{\partial V} \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha.\mathbf{n})\,\mathrm{d}a = \int_{\partial V} \mathbf{t}_\alpha \,\mathrm{d}a + \int_V \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v + \int_V \mathbf{k}_\alpha \,\mathrm{d}v + \int_V r_\alpha \mathbf{v}_\alpha \,\mathrm{d}v \quad \alpha = 1,\ldots,n \tag{4.50}$$

(For modification for general, non-inertial frame see below (4.58)). On the left-hand side, there is the change of momentum of constituent α in the fixed volume V (momentum density is obviously $\rho_\alpha \mathbf{v}_\alpha$) and its flux through the fixed surface ∂V. On the right-hand side of (4.50), the forces on constituent α are postulated (according to principles discussed in Sect. 4.1): the first two represent surface and volume forces respectively (similarly as in pure material in Sect. 3.3) and those remaining describe interactions (but see Rem. 5). Namely, the first integral on the right side expresses through the *partial traction* $\mathbf{t}_\alpha$ the all contact forces (on surface unit) acting on the constituent α; these (partial stress) vectors are assumed to be objective (material frame indifferent). Such are the inner surface forces by which all constituents act from the outside (of V) on the constituent α on the surface ∂V (if ∂V, or its part, is a real boundary of the mixture they are outer surface forces from the outside given as boundary conditions) and also interaction surface forces coming from the remaining constituents acting from the inside (of V) on the constituent α on the surface ∂V.[5] The second integral on the right-hand side of (4.50) expresses the action of *body (volume, external and outer)* forces $\mathbf{b}_\alpha$ in the inertial frame (they have their sources in the outside the body); we assume that $\mathbf{b}_\alpha$ are objective vectors. The third integral on the right-hand side of (4.50) characterizes the volume interaction among constituents. Here the volume *interaction force* $\mathbf{k}_\alpha$ expresses the action of other constituents on the constituent α. It is assumed that $\mathbf{k}_\alpha$ are objective vectors. The last integral on the right-hand side of (4.50) expresses the time change of momentum caused by chemical reactions [11, 14, 25]; we assume that the velocity of reacting constituent α is $\mathbf{v}_\alpha$.[6]

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[5] These last forces from inside were introduced by more detailed mixture theory [101], see also [20, 67, 68, 109, 110], but we do not distinguish them in $\mathbf{t}_\alpha$ (or in partial stress $\mathbf{T}_\alpha$ (4.53) below). These therefore contain also surface interactions (analogues of volume interactions $\mathbf{k}_\alpha$ below) which compensate themselves in sum of tractions or stresses in (4.60), (4.61).

[6] This is not obvious but if it is not so this may be always achieved: let us assume that $\mathbf{v}^r_\alpha$ is a real velocity of chemically reacting constituent α and real interaction force is $\mathbf{k}^r_\alpha$. Then the last two members in (4.50) are

$$\int_V \mathbf{k}^r_\alpha \,\mathrm{d}v + \int_V r_\alpha \mathbf{v}^r_\alpha \,\mathrm{d}v = \int_V \mathbf{k}_\alpha \,\mathrm{d}v + \int_V r_\alpha \mathbf{v}_\alpha \,\mathrm{d}v$$

where the form postulated in (4.50) was achieved defining $\mathbf{k}_\alpha \equiv \mathbf{k}^r_\alpha + (\mathbf{v}^r_\alpha - \mathbf{v}_\alpha) r_\alpha$. Because the objectivity of $\mathbf{k}^r_\alpha$ and r_α may be assumed, the $\mathbf{k}_\alpha$ are also objective (in this way, the different formulations of these last two members used in the literature [12, 16, 22, 40, 41, 46, 49, 52, 95, 105, 111] may be transformed in the form used here in (4.50)).

Other possible forces are neglected in (4.50), e.g. long range body forces (cf. Sect. 3.3; they may occur in ionic salt solutions, but they may be neglected by electroneutrality, see Rem. 32), influence of (mechanically) polar components, cf. Rem. 9, hyperstresses [112].

The left-hand side of postulate (4.50) may be arranged by Gauss' theorem and with (4.19) using the component of partial velocity as φ; then the partial balance of momentum of constituent α is

$$\int_V \rho_\alpha \grave{\mathbf{v}}_\alpha \,\mathrm{d}v = \int_{\partial V} \mathbf{t}_\alpha \,\mathrm{d}a + \int_V \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v + \int_V \mathbf{k}_\alpha \,\mathrm{d}v \qquad \alpha = 1, \dots, n \tag{4.51}$$

To achieve momentum balance in a local form, we have the analogous difficulties with surface integral in the right-hand side of (4.50) as in Sect. 3.3. We therefore use analogical Cauchy's postulate and theorem but concerning here partial tractions and stresses (motivation and deductions are quite analogical as in Sect. 3.3): The *Cauchy postulate* for partial tractions is

$$\mathbf{t}_\alpha = \mathbf{t}_\alpha(\mathbf{x}, t, \mathbf{n}) \qquad \alpha = 1, \dots, n \tag{4.52}$$

i.e. partial traction depends (moreover) on the (outside) normal $\mathbf{n}$ to the chosen surface. *Cauchy's theorem* then asserts that such dependence is linear, that is

$$\mathbf{t}_\alpha = \mathbf{T}_\alpha \mathbf{n} \qquad \alpha = 1, \dots, n \tag{4.53}$$

where the *partial stress tensors* $\mathbf{T}_\alpha = \mathbf{T}_\alpha(\mathbf{x}, t)$ are fields (functions of position and time only) which are objective as follows from the objectivity of $\mathbf{t}_\alpha$ and $\mathbf{n}$ (similarly as by (3.32)).

Proof of (4.53) may be done analogously as of (3.72): we construct a similar infinitesimal tetrahedron on the tangent plane given by $\mathbf{n}$ on which we apply the balance (4.51)

$$\rho_\alpha \grave{\mathbf{v}}_\alpha \Delta v = \mathbf{t}_\alpha \Delta a + (\mathbf{t}_\alpha)_j \,\Delta a^j + (\rho_\alpha \mathbf{b}_\alpha + \mathbf{k}_\alpha)\Delta v \tag{4.54}$$

By limiting the volume of the tetrahedron to zero, we obtain result (4.53) quite analogously as (3.72) (components of stress tensor T_α^{ij} are components of vectors $-(\mathbf{t}_\alpha)_j$). Q.E.D.

Inserting (4.53) into (4.51) we obtain the balance of the momentum for constituent α in the inertial frame as

$$\int_V \rho_\alpha \grave{\mathbf{v}}_\alpha \,\mathrm{d}v = \int_{\partial V} \mathbf{T}_\alpha.\mathbf{n} \,\mathrm{d}a + \int_V \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v + \int_V \mathbf{k}_\alpha \,\mathrm{d}v \qquad \alpha = 1, \dots, n \tag{4.55}$$

Assuming its validity for any volume V the local formulation of momentum balance of constituent α in inertial frame may be obtained from (4.55) by Gauss' theorem

$$\rho_\alpha \grave{\mathbf{v}}_\alpha = \mathrm{div}\mathbf{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{k}_\alpha \qquad \alpha = 1, \dots, n \tag{4.56}$$

or (back by (4.19) choosing φ as velocity component)

$$\frac{\partial \rho_\alpha \mathbf{v}_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \operatorname{div}\mathbf{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha \qquad \alpha = 1, \ldots, n \quad (4.57)$$

Balances of momentum for constituents have been formulated in the inertial frame. Their form in a general (non-inertial frame) remains the same if we simply replace $\mathbf{b}_\alpha$ with $\mathbf{b}_\alpha + \mathbf{i}_\alpha$. Indeed, the local balance of momentum of constituent α in any frame may be obtained from (4.56) if we use (4.11) and the objectivity of remaining quantities assumed above (cf. analogous deduction of (3.78))

$$\rho_\alpha \grave{\mathbf{v}}_\alpha = \operatorname{div}\mathbf{T}_\alpha + \rho_\alpha(\mathbf{b}_\alpha + \mathbf{i}_\alpha) + \mathbf{k}_\alpha \quad \alpha = 1, \ldots, n \qquad (4.58)$$

where $\mathbf{i}_\alpha$ is given by (4.12) (without stars; other symbols as in (3.79)).

Starting with (4.58) in any frame (instead of (4.56) and going back through all previous formulae (as in inertial system) it may be seen (cf. analogous behaviour in Sect. 3.3 before (3.80)) that for transformation from inertial to non-inertial frame here, it suffices to use $\mathbf{b}_\alpha + \mathbf{i}_\alpha$ instead of $\mathbf{b}_\alpha$ in all preceding relations for the inertial frame including the starting postulate (4.50). Therefore, e.g. the integral momentum balance for constituent in an arbitrary (non-inertial) frame will be

$$\int_V \rho_\alpha \grave{\mathbf{v}}_\alpha \, \mathrm{d}v = \int_{\partial V} \mathbf{T}_\alpha.\mathbf{n} \, \mathrm{d}a + \int_V \rho_\alpha(\mathbf{b}_\alpha + \mathbf{i}_\alpha) \, \mathrm{d}v + \int_V \mathbf{k}_\alpha \, \mathrm{d}v \qquad \alpha = 1, \ldots, n \quad (4.59)$$

instead of (4.55) in an inertial frame.

In accord with the general procedure proposed in Sect. 4.1 (summing of l.h.s. of (4.50) and compensation of interactions) we postulate the *balance of momentum for the mixture* in the inertial frame as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha \, \mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha.\mathbf{n}) \, \mathrm{d}a = \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{t}_\alpha \, \mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \, \mathrm{d}v \quad (4.60)$$

for arbitrary fixed volume V with fixed surface ∂V in the mixture. Using here Cauchy's theorem (4.53) we can write momentum balance of mixture in the inertial frame as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha \, \mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha.\mathbf{n}) \, \mathrm{d}a = \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{T}_\alpha \mathbf{n} \, \mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \, \mathrm{d}v \quad (4.61)$$

Therefore, we assume that interaction forces (including the surface interaction forces assumed to be contained in the $\mathbf{t}_\alpha, \mathbf{T}_\alpha$) and exchange of momentum in chemical reactions compensate each other among the constituents.[7]

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[7] Postulate (4.61) is in accord with our interpretation of the third principle in Sect. 4.1: if the mixture is non-diffusive, i.e. velocities of all constituents are the same $\mathbf{v}_\alpha = \mathbf{v}$, then (4.61) has the form

Local momentum balance of mixture in the inertial frame follows from (4.61) with Gauss' theorem and arbitrary volume V (using (4.19))

$$\sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha \mathbf{v}_\alpha}{\partial t} + \operatorname{div} \sum_{\alpha=1}^{n} (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \sum_{\alpha=1}^{n} \rho_\alpha \grave{\mathbf{v}}_\alpha + \sum_{\alpha=1}^{n} r_\alpha \mathbf{v}_\alpha = \operatorname{div} \sum_{\alpha=1}^{n} \mathbf{T}_\alpha + \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \tag{4.62}$$

Summing (4.56) through the constituents and comparing it with $(4.62)_2$ we obtain the *local momentum balance of mixture* as

$$\sum_{\alpha=1}^{n} (\mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha) = \mathbf{o} \tag{4.63}$$

Although we have deduced this balance in the inertial frame, it is valid in all (even non-inertial) frames because both sums on the left-hand side are objective (for the second sum, this follows from (4.10) and (4.20)). This is also seen directly if we write the momentum balance of the mixture with the use of diffusion velocity (4.24) (which is an objective vector)

$$\sum_{\alpha=1}^{n} (\mathbf{k}_\alpha + r_\alpha \mathbf{u}_\alpha) = \mathbf{o} \tag{4.64}$$

The momentum balance for the mixture in integral forms (4.60), (4.61) may be written again in an arbitrary frame simply by substitution of $\mathbf{b}_\alpha$ with $\mathbf{b}_\alpha + \mathbf{i}_\alpha$. Indeed, adding $r_\alpha \mathbf{v}_\alpha$ to both sides of (4.58) and summing through all constituents we obtain, by (4.63), the result $(4.62)_2$ with aforementioned substitution. Going backward with the corresponding integration, we obtain integral momentum balances for the mixture in any frame with substitution mentioned above.

Postulation of *moment of momentum balances* for constituents and for mixture [11, 12, 15, 17, 22, 23, 50, 65] is sufficient (similarly as in Sect. 3.3, cf. Rem. 16 in Chap. 3) to be done in the inertial frame with the construction of moment against fixed point ($\mathbf{y}$ below) because our main results—local balances (4.70), (4.75)—are valid in any frame independently of $\mathbf{y}$ (for generalization, see Rem. 8).

For simplicity, we confine to models where all constituents as well as the mixture are mechanically non-polar (for polar models, see Rem. 9; cf. also Rem. 17 in Chap. 3), i.e. time changes of moment of momentum are equal only to moments of the

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of a momentum balance for pure substance(3.75); here (4.21) is used, and $\mathbf{T} \equiv \sum_{\alpha=1}^{n} \mathbf{T}_\alpha$ (4.94), $\rho \mathbf{b} \equiv \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha$ are defined.

In the general case of a diffusing mixture the interpretation noted in Rem. 1 is possible, i.e. we transform (4.61) in the form (3.75), if we use barycentric velocity $\mathbf{v}^w$ (see Rem. 3) and define the whole stress as $\sum_{\alpha=1}^{n} (\mathbf{T}_\alpha - \rho_\alpha \mathbf{u}_\alpha^w \otimes \mathbf{u}_\alpha^w)$ (i.e. different from (4.94)) where $\mathbf{u}_\alpha^w \equiv \mathbf{v}_\alpha - \mathbf{v}^w$ is the *diffusion velocity* relative to the barycentric velocity (note $\sum_{\alpha=1}^{n} \rho_\alpha \mathbf{u}_\alpha^w = \mathbf{o}$). Cf. [12, Lect. 5], [15, 18, 50].

forces introduced in the balances of momentum. Surface tractions will be expressed through stress tensors (4.53).

The *balance of moment of momentum for constituent* α in the inertial frame relative to the fixed point $\mathbf{y}$ is postulated in any fixed volume V with fixed surface ∂V in the mixture as (we use outer product from Rem. 16 in Chap. 3)

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V (\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{v}_\alpha\,\mathrm{d}v + \int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{v}_\alpha(\mathbf{v}_\alpha.\mathbf{n})\,\mathrm{d}a \\ = \int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha\mathbf{n}\,\mathrm{d}a + \int_V(\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{b}_\alpha\,\mathrm{d}v \\ + \int_V(\mathbf{x}-\mathbf{y})\wedge(\mathbf{k}_\alpha + r_\alpha\mathbf{v}_\alpha)\,\mathrm{d}v \qquad \alpha = 1,\dots,n\end{aligned} \tag{4.65}$$

To find the local moment of momentum balance for constituent α we use here Gauss' theorem (3.23) in surface integrals and by localization (validity of (4.65) is assumed for any volume V) we obtain

$$\begin{aligned}\frac{\partial\rho_\alpha(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha)}{\partial t} + \mathrm{div}(\rho_\alpha(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha\otimes\mathbf{v}_\alpha) \\ = \mathrm{div}((\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha) + (\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{b}_\alpha + (\mathbf{x}-\mathbf{y})\wedge\mathbf{k}_\alpha \\ + (\mathbf{x}-\mathbf{y})\wedge r_\alpha\mathbf{v}_\alpha \qquad \alpha = 1,\dots,n\end{aligned} \tag{4.66}$$

where both divergences with tensors $\mathbf{v}_\alpha\otimes\mathbf{v}_\alpha$ and $\mathbf{T}_\alpha$ are defined (in components) analogously as under (3.90). Using (4.19) in the left-hand side of (4.66) we find (an analogue of (3.91))

$$(\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\grave{\mathbf{v}}_\alpha = \mathrm{div}((\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha) + (\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{b}_\alpha + (\mathbf{x}-\mathbf{y})\wedge\mathbf{k}_\alpha \quad \alpha = 1,\dots,n \tag{4.67}$$

because

$$\overset{\grave{}}{\overline{(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha}} = (\mathbf{x}-\mathbf{y})\wedge\grave{\mathbf{v}}_\alpha \tag{4.68}$$

namely $\overset{\backslash\alpha}{\mathbf{x}}\wedge\grave{\mathbf{v}}_\alpha = \grave{\mathbf{v}}_\alpha\wedge\grave{\mathbf{v}}_\alpha = \mathbf{0}$ and $\overset{\backslash\alpha}{\mathbf{y}} = \mathbf{o}$ ($\mathbf{y}$ is fixed); for the same reason (cf. (3.92))

$$\mathrm{div}((\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha) = \mathbf{T}_\alpha^T - \mathbf{T}_\alpha + (\mathbf{x}-\mathbf{y})\wedge\mathrm{div}\mathbf{T}_\alpha \tag{4.69}$$

Inserting this result into (4.67) and subtracting (4.56) multiplied by $(\mathbf{x}-\mathbf{y})\wedge$ we obtain the *local partial moment of momentum balance* for constituent α as a symmetry of the partial stress tensor

$$\mathbf{T}_\alpha = \mathbf{T}_\alpha^T \qquad \alpha = 1,\dots,n \tag{4.70}$$

This is valid in any frame because of the objectivity of tensors $\mathbf{T}_\alpha$ (even (4.70) was deduced in the inertial frame); generalization for (mechanically) polar constituent see Rem. 9.

According to general procedure discussed in Sect. 4.1 (summing of l.h.s. of (4.65) and compensation of interactions), we postulate the *balance of moment of momentum for the mixture* in inertial frame relatively to the fixed place $\mathbf{y}$ for any fixed volume V with the surface ∂V in the mixture as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V (\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\rho_\alpha\mathbf{v}_\alpha\,\mathrm{d}v+\int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\rho_\alpha\mathbf{v}_\alpha(\mathbf{v}_\alpha.\mathbf{n})\,\mathrm{d}a\\ =\int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\mathbf{T}_\alpha\mathbf{n}\,\mathrm{d}a+\int_V(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\rho_\alpha\mathbf{b}_\alpha\,\mathrm{d}v\end{aligned}\tag{4.71}$$

To obtain the local moment of momentum balance for the mixture, we use Gauss' theorem in (4.71) and localization similarly as in (4.66). This result is

$$\begin{aligned}\sum_{\alpha=1}^{n}\left(\frac{\partial\rho_\alpha(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha)}{\partial t}+\mathrm{div}(\rho_\alpha(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha\otimes\mathbf{v}_\alpha)\right)\\ =\sum_{\alpha=1}^{n}\mathrm{div}((\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha)+(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\rho_\alpha\mathbf{b}_\alpha\end{aligned}\tag{4.72}$$

Using (4.19) in the left-hand side (φ are components of (skew symmetric) tensor) and (4.69) in the right-hand side of (4.72) we obtain

$$\begin{aligned}\sum_{\alpha=1}^{n}\rho_\alpha\grave{\overline{(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha}}+(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}r_\alpha\mathbf{v}_\alpha\\ =\sum_{\alpha=1}^{n}\mathbf{T}_\alpha^T-\sum_{\alpha=1}^{n}\mathbf{T}_\alpha+(\mathbf{x}-\mathbf{y})\wedge\mathrm{div}\sum_{\alpha=1}^{n}\mathbf{T}_\alpha+(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\rho_\alpha\mathbf{b}_\alpha\end{aligned}\tag{4.73}$$

Adding $(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\mathbf{k}_\alpha$ to both sides, using (4.68) and rearranging we obtain

$$\begin{aligned}(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}\left(\rho_\alpha\grave{\mathbf{v}}_\alpha-\mathrm{div}\mathbf{T}_\alpha-\rho_\alpha\mathbf{b}_\alpha-\mathbf{k}_\alpha\right)\;+\;(\mathbf{x}-\mathbf{y})\wedge\sum_{\alpha=1}^{n}(\mathbf{k}_\alpha+r_\alpha\mathbf{v}_\alpha)\\ =\sum_{\alpha=1}^{n}\mathbf{T}_\alpha^T-\sum_{\alpha=1}^{n}\mathbf{T}_\alpha\end{aligned}\tag{4.74}$$

But the left-hand side of this equation is zero because of the local momentum balance for each constituent (4.56) and for mixture (4.63). So, the *local balance of moment of momentum for the mixture* has been obtained

$$\sum_{\alpha=1}^{n} \mathbf{T}_\alpha = \sum_{\alpha=1}^{n} \mathbf{T}_\alpha^T = \left(\sum_{\alpha=1}^{n} \mathbf{T}_\alpha \right)^T \tag{4.75}$$

which is valid in any (even non-inertial) frame (on the same grounds as (4.70)).

Integral balances (4.71), (4.65) in any frame might be obtained by similar means as for a single substance (see end of Sect. 3.3) but we omit them here (for our applications, the local forms (4.70),(4.75) suffice).[8]

For our model of (mechanically) non-polar constituents and non-polar mixture[9] (4.75) is a trivial consequence of (4.70) and therefore the moment of momentum balance for mixture is not needed in this non-polar model (indeed, (4.71) follows by summing (4.65) and using (4.63)).

Summary. The balance of momentum postulated for individual constituents leads to the Cauchy's theorem for partial stress tensors (4.53) and the local form of this balance is given by (4.56) or (4.57). The balance of momentum for mixture as a whole is given by (4.63) or (4.64). The balance of moment of momentum postulated for individual constituents gives the symmetry of the partial stress tensor—see (4.70). Analogical balance for mixture as a whole gives "symmetry" of sum of these tensors, cf. (4.75). Note that in mixture conceptually new quantities entered these balances—especially partial quantities and the interaction forces between constituents.

4.4 Balance of Energy and Entropy Inequality in Reacting Mixture: Mixture Invariance

Because we study only mixtures with a unique temperature of all their constituents, we need only a balance of energy for the mixture as has been explained in Sect.4.1, cf. Rem. 2. Namely, in this case, the constitutive principles give no restrictions on energy interactions in energy balances for constituents [11, 15, 46, 50, 53, 65]. This is the difference with a more general mixture of constituents with different temperatures [10, 14, 37, 46, 59, 113].

We postulate the *balance of energy of a mixture* in the inertial frame motivating it by the energy balance of a single substance in the form (3.97). That is we postulate that the change of sum of kinetic energy (given by partial velocity $\mathbf{v}_\alpha$) and internal energy characterized by the primitive specific *partial internal energy* u_α of constituent α in fixed volume V of the mixture and the change of the total whole energy by the mass

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[8] In fact such calculation (see, e.g. [79, Sect. 30]) gives results similar to (4.65) or (4.71), only we must add $\dot{\mathbf{y}} \wedge \int_V \rho_\alpha \mathbf{v}_\alpha \, \mathrm{d}v$ or $\dot{\mathbf{y}} \wedge \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha \, \mathrm{d}v$ to their left-hand sides respectively and again $\mathbf{b}_\alpha$ must be substituted by $\mathbf{b}_\alpha + \mathbf{i}_\alpha$; note that by (3.25) $\mathbf{y}$ (fixed in some inertial frame) is in any frame function of time at most and $\dot{\mathbf{y}}$ is its time derivative like in the end of Sect. 3.3, cf. also (3.96).

[9] Often [13, Lect. 5], [27, 28, 37, 40, 46, 79] the mixture with polar constituents (containing partial torques $\mathbf{M}_\alpha$) which compensate themselves in the mixture is studied. Balance (4.65) then contains $\int_v \mathbf{M}_\alpha \, \mathrm{d}v$ on its right-hand side, balance (4.71) is the same. As the results we obtain $\mathbf{M}_\alpha = \mathbf{T}_\alpha - \mathbf{T}_\alpha^T$ (instead of (4.70)) and $\sum_{\alpha=1}^{n} \mathbf{M}_\alpha = \mathbf{0}$ (i.e. (4.75) remains valid), cf. Rems. 17, 32 in Chap. 3.

flux through the fixed surface ∂V is given by the power of all forces (in mixture, cf. balance (4.61); partial stress tensors (4.53) were used) and by heat exchange caused by the scalar *surface heating* q (heat exchanged by unit surface in time unit) and by the *volume heating* Q (heat exchanged by unit volume in time unit with external heat source by radiation):

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha(u_\alpha + (1/2)\mathbf{v}_\alpha^2)\,\mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha(u_\alpha + (1/2)\mathbf{v}_\alpha^2)\mathbf{v}_\alpha.\mathbf{n}\,\mathrm{d}a$$
$$= \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{v}_\alpha \mathbf{T}_\alpha.\mathbf{n}\,\mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha.\mathbf{v}_\alpha\,\mathrm{d}v + \int_{\partial V} q\,\mathrm{d}a + \int_V Q\,\mathrm{d}v \qquad (4.76)$$

Similarly as for the single substance in Sect. 3.4 we postulate that scalars u_α, q, Q are objective (frame indifferent) as well as $\rho_\alpha, \mathbf{b}_\alpha, \mathbf{T}_\alpha$.

Using Gauss' theorem in the left-hand side of balance (4.76) and then (4.19) we obtain the energy balance of mixture in the inertial frame in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha(u_\alpha + (1/2)\mathbf{v}_\alpha^2)\,\mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha(u_\alpha + (1/2)\mathbf{v}_\alpha^2)\mathbf{v}_\alpha.\mathbf{n}\,\mathrm{d}a$$
$$= \int_V \sum_{\alpha=1}^{n} \rho_\alpha \overset{\grave{}}{\overline{(u_\alpha + (1/2)\mathbf{v}_\alpha^2)}}\,\mathrm{d}v + \int_V \sum_{\alpha=1}^{n} r_\alpha(u_\alpha + (1/2)\mathbf{v}_\alpha^2)\,\mathrm{d}v$$
$$= \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{v}_\alpha \mathbf{T}_\alpha.\mathbf{n}\,\mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha.\mathbf{v}_\alpha\,\mathrm{d}v - \int_{\partial V} \mathbf{q}.\mathbf{n}\,\mathrm{d}a + \int_V Q\,\mathrm{d}v \qquad (4.77)$$

where the (field of) *heat flux* vector $\mathbf{q} = \mathbf{q}(\mathbf{x}, t)$, resulting from the (heat analogue of) Cauchy's theorem

$$q = -\mathbf{q}.\mathbf{n} \qquad (4.78)$$

was used.[10] This is obtained in the same way as (3.100) in Sect. 3.4, Rem. 20 in Chap. 3, from the (heat analogue of) the Cauchy postulate, i.e. that scalar heating q depends on the normal $\mathbf{n}$ to the chosen surface (cf. (3.99) with the same motivation)

$$q = q(\mathbf{x}, t, \mathbf{n}) \qquad (4.79)$$

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[10] We can transform (4.77) (see, e.g. [13, Lect. 5]) into the form (3.103)(with $\mathbf{i} = \mathbf{o}$) if we use the interpretation from Rem. 1 and define the internal energy as $\frac{1}{\rho}\sum_{\alpha=1}^{n} \rho_\alpha(u_\alpha + (1/2)(\mathbf{u}_\alpha^w)^2)$, the heat flux as $\mathbf{q} - \sum_{\alpha=1}^{n}(\mathbf{u}_\alpha^w \mathbf{T}_\alpha - \rho_\alpha(u_\alpha + (1/2)(\mathbf{u}_\alpha^w)^2)\mathbf{u}_\alpha^w)$, the heat source as $Q + \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha.\mathbf{u}_\alpha^w$ and use the following quantities (introduced in Rems. 3, 7, 11): $\mathbf{v}^w$ as the velocity, $\sum_{\alpha=1}^{n}(\mathbf{T}_\alpha - \rho_\alpha \mathbf{u}_\alpha^w \otimes \mathbf{u}_\alpha^w)$ as the (whole) stress, $\mathbf{u}_\alpha^w$ as the diffusion velocity and $\mathbf{b}$ as the body force.

Our interpretation of the third principle in Sect. 4.1 is then achieved in non-diffusing mixture with $\mathbf{u}_\alpha^w = \mathbf{o}$, with the internal energy u naturally given by (4.90), (4.22).

Namely, the balance (4.77)$_2$ with Gauss' theorem in the right-hand side applied on a small tetrahedron with volume Δv as in Sect. 3.4 is

$$\sum_{\alpha=1}^{n}\rho_\alpha \grave{\overline{(u_\alpha + (1/2)\mathbf{v}_\alpha^2)}}\,\Delta v + \sum_{\alpha=1}^{n} r_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2)\,\Delta v$$
$$= q\,\Delta a + q^j\,\Delta a^j + Q\,\Delta v + (\operatorname{div}\sum_{\alpha=1}^{n}\mathbf{v}_\alpha \mathbf{T}_\alpha)\,\Delta v + \sum_{\alpha=1}^{n}\rho_\alpha \mathbf{b}_\alpha.\mathbf{v}_\alpha\,\Delta v \quad (4.80)$$

from which (by limitation of tetrahedron volume to zero) we obtain result (4.78): components of vector **q** form scalar surface heatings q^j (independent of **n**) in the axes of the Cartesian system in tetrahedron, see Sect. 3.4.

Moreover, because q and (arbitrary) **n** are objective (see end of Sect. 3.2), then from (4.78) follows (similarly as below (3.101)) that the heat flux **q** in mixture is objective (frame indifferent) vector; cf. also Rem. 21 in Chap. 3.

By Gauss' theorem and by the arbitrariness of volume V, we obtain the local form of (4.77)$_2$ as

$$\sum_{\alpha=1}^{n}\rho_\alpha \grave{u}_\alpha + \sum_{\alpha=1}^{n}\rho_\alpha \frac{1}{2}\grave{\overline{\mathbf{v}_\alpha^2}} + \sum_{\alpha=1}^{n} r_\alpha u_\alpha + \sum_{\alpha=1}^{n} r_\alpha \frac{1}{2}\mathbf{v}_\alpha^2$$
$$= \operatorname{div}\sum_{\alpha=1}^{n}\mathbf{v}_\alpha \mathbf{T}_\alpha + \sum_{\alpha=1}^{n}\rho_\alpha \mathbf{b}_\alpha.\mathbf{v}_\alpha - \operatorname{div}\mathbf{q} + Q \quad (4.81)$$

Subtracting from this the local balance of kinetic energy (obtainable from momentum balance (4.56) by multiplying with $\mathbf{v}_\alpha$ and summing through constituents) and using (4.8), diffusion velocity (4.24) and mixture balances of momentum (4.64) and that of mass (4.20), we obtain from (4.81) the following local balance of (internal) energy in the mixture

$$\sum_{\alpha=1}^{n}\frac{\partial \rho_\alpha u_\alpha}{\partial t} + \sum_{\alpha=1}^{n}\operatorname{div}(\rho_\alpha u_\alpha \mathbf{v}_\alpha) = \sum_{\alpha=1}^{n}\rho_\alpha \grave{u}_\alpha + \sum_{\alpha=1}^{n} r_\alpha u_\alpha$$
$$= -\operatorname{div}\mathbf{q} + Q + \sum_{\alpha=1}^{n}\operatorname{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha - \sum_{\beta=1}^{n-1}\mathbf{k}_\beta.\mathbf{u}_\beta$$
$$- (1/2)\sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 \quad (4.82)$$

where the left-hand side follows from (4.19). Although the deduction of (4.82) was given in the inertial frame, this form is valid in any frame: indeed, (4.82)$_2$ contains only objective quantities (material derivative $\grave{u}_\alpha$ of objective scalar is objective; proof, with (4.3) here, is analogous to that below (3.57)).

Entropy inequality for the mixture [10, 14, 15, 17, 50, 65] is motivated by such inequality for single substance (3.108) (with (3.24)). We postulate it using two following primitive concepts (assumed to be objective scalars): the specific *partial entropy* s_α and the *absolute temperature* $T > 0$. Therefore, we confine ourselves to mixtures with only one temperature, the same for all constituents. For any fixed volume V in the mixture with fixed surface ∂V, we postulate the *entropy inequality* as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \,\mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \mathbf{v}_\alpha.\mathbf{n}\,\mathrm{d}a \geq -\int_{\partial V} (\mathbf{q}/T).\mathbf{n}\,\mathrm{d}a + \int_V (Q/T)\,\mathrm{d}v \tag{4.83}$$

Using Gauss' theorem, we can obtain the entropy inequality in the local form called the *Clausius-Duhem inequality*

$$\sigma \equiv \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha s_\alpha}{\partial t} + \sum_{\alpha=1}^{n} \operatorname{div}(\rho_\alpha s_\alpha \mathbf{v}_\alpha) + \operatorname{div}(\mathbf{q}/T) - Q/T \geq 0 \tag{4.84}$$

The left-hand side of this inequality is defined as the *entropy production* σ. Relation (4.84) (and in fact also (4.83)) is valid in any frame because of the objectivity of most quantities and because of

$$\sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha s_\alpha}{\partial t} + \sum_{\alpha=1}^{n} \operatorname{div}(\rho_\alpha s_\alpha \mathbf{v}_\alpha) = \sum_{\alpha=1}^{n} \rho_\alpha \grave{s}_\alpha + \sum_{\alpha=1}^{n} r_\alpha s_\alpha \tag{4.85}$$

which can be obtained quite analogously as Eq. $(4.82)_1$ (with similarly motivated objectivity of its right-hand side). Therefore also the entropy production σ is an objective quantity.[11]

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[11] So far no deduction of entropy inequality, entropy and absolute temperature in mixtures ("open" systems) as presented in Chap. 1 is known. Moreover, in formulation of entropy inequality in mixtures, there are discrepancies among the authors; here we follow the one of Truesdell [10] (cf. also [14, 15, 56, 59, 60, 79]) which seems to be the most simple; the other proposals see [2–4, 16–18, 24, 25, 51, 52]. As the most natural the theory of Williams [20, 21] can be considered which is based on a single body [100] but still an additional (even plausible) assumption (superadditivity of entropy production) must be added. The problem grows in mixtures with different temperatures of their constituents [10, 14, 37, 46, 59] where inequalities analogous to (4.84) for each constituent give too stringent results (in admissibility principle below) [22, 40, 43, 49] and therefore such partial inequalities are not considered here. The main source of discrepancies may be seen as follows: if we use the entropy of mixture s naturally defined by $\rho s = \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha$ (cf. (4.91), (4.22)) and barycentric $\mathbf{v}^w$ and diffusion $\mathbf{u}_\alpha^w$ velocities (see Rems. 3,7) we can write (4.83) as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho s \,\mathrm{d}v + \int_{\partial V} \rho s \mathbf{v}^w.\mathbf{n}\,\mathrm{d}a \geq -\int_{\partial V} T^{-1}(\mathbf{q} + \sum_{\alpha=1}^{n} \rho_\alpha T s_\alpha \mathbf{u}_\alpha^w).\mathbf{n}\,\mathrm{d}a + \int_V (Q/T)\,\mathrm{d}v$$

which, with $\psi = \rho s$, $\mathbf{v} = \mathbf{v}^w$, has the form (3.108) (with (3.24)) as the interpretation of the third principle in Rem. 1 demands. But here the heat flux $\mathbf{q} + \sum_{\alpha=1}^{n} \rho_\alpha T s_\alpha \mathbf{u}_\alpha^w$ and the heat source Q are

Later, another form of entropy inequality will be useful. To this end, we eliminate $\mathrm{div}\mathbf{q} - Q$ from balance (4.82) and inequality (4.84) using the specific *partial free energy* f_α

$$f_\alpha \equiv u_\alpha - T s_\alpha \qquad \alpha = 1, \ldots, n \tag{4.86}$$

and thus we obtain

$$\begin{aligned} -T\sigma = {} & \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha f_\alpha}{\partial t} + \sum_{\alpha=1}^{n} \mathbf{v}_\alpha.\mathrm{grad}(\rho_\alpha f_\alpha) + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \frac{\partial T}{\partial t} + \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha \,\mathrm{div}\mathbf{v}_\alpha \\ & + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \, \mathbf{v}_\alpha.\mathbf{g} + (1/T)\mathbf{q}.\mathbf{g} - \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{k}_\beta.\mathbf{u}_\beta \\ & + (1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 \le 0 \end{aligned} \tag{4.87}$$

Here we replace the velocities by diffusion velocities (4.24) and use (4.8) and the generalization of divergenceless tensor (3.188) in the mixture

$$\overset{\circ}{\mathbf{D}}_\alpha \equiv \mathbf{D}_\alpha - (1/3)\mathrm{tr}\mathbf{D}_\alpha \, \mathbf{1}, \quad \mathrm{tr}\, \overset{\circ}{\mathbf{D}}_\alpha = 0 \qquad \alpha = 1, \ldots, n \tag{4.88}$$

In this way, we obtain the *reduced inequality* for mixtures

$$\begin{aligned} -T\sigma = {} & \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha f_\alpha}{\partial t} + \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha \,\mathrm{tr}\mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{u}_\beta.\,\mathrm{grad}(\rho_\beta f_\beta) + \mathbf{v}_n \,\mathrm{grad} \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha \\ & + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \frac{\partial T}{\partial t} + \sum_{\beta=1}^{n-1} \rho_\beta s_\beta \, \mathbf{u}_\beta.\mathbf{g} + \mathbf{v}_n.\mathbf{g} \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha + (1/T)\mathbf{q}.\mathbf{g} \\ & - \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \, \overset{\circ}{\mathbf{D}}_\alpha - (1/3) \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathrm{tr}\mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{k}_\beta.\mathbf{u}_\beta \\ & + (1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 \le 0 \end{aligned} \tag{4.89}$$

(Footnote 11 continued)
different from these quantities in the energy balance noted in Rem. 10. In our formulation of (4.84), we use the weaker interpretation of the third principle from Sect. 4.1 which stresses the specific role of diffusion in a mixture (in non-diffusing mixture $\mathbf{u}_\alpha^w = \mathbf{o}$) and we obtain the accord of all these postulates. Moreover, discrepancies may also be understood in the light of "mixture invariance" [59] discussed below in this section 4.4. The formulation used in (4.83) (as well as in (4.76), (4.50), (4.60), (4.65), (4.71), (4.16), (4.14)) for such mass exchanging (open) systems follows naturally from Reynolds' theorem (3.24) for (fictive) surface ∂V, but for a real boundary exchanging the mass (especially with different velocities of different constituents and together with heat exchange) this is not as clear as it seems, cf. Rems. 14, 23 in Chaps. 2, 3 and the end of Sect. 3.1.

which we use in the following discussions of a (chemically) reacting fluid mixture with (mechanically) non-polar constituents with unique temperature, see Sect. 4.5.

Now, we write down the following useful definitions concerning the mixture (see (4.22)): the *specific total* (i.e. of the mixture) *internal energy* u, *entropy* s and *free energy* f are defined by

$$u \equiv \sum_{\alpha=1}^{n} w_\alpha u_\alpha \tag{4.90}$$

$$s \equiv \sum_{\alpha=1}^{n} w_\alpha s_\alpha \tag{4.91}$$

$$f \equiv \sum_{\alpha=1}^{n} w_\alpha f_\alpha \tag{4.92}$$

where (4.86) has been used; the following equation is then valid (cf. (3.111))

$$f = u - Ts \tag{4.93}$$

We also note that mixture properties (4.90)–(4.92) are objective (frame indifferent). For later applications, it is useful to define the *total stress* $\mathbf{T}$ by

$$\mathbf{T} \equiv \sum_{\alpha=1}^{n} \mathbf{T}_\alpha \tag{4.94}$$

In the following applications in fact only the local balances (4.18), (4.20), (4.58), (4.63), (4.70), (4.75), (4.82), (4.84), (4.85) are useful. They are valid, as has been proved in Sects. 4.2, 4.3 and 4.4, in any (even non-inertial) frame. But these balance equations have another interesting property, which we shall call the *mixture invariance* [56, 59, 65, 79, 114], (in older references called also the “form invariance”); its possibility is noted in [95, 112].

To discuss this property, we first rewrite local balances and rearrange balances of energy and entropy (inequality) into more appropriate forms:

$$\grave{\rho}_\alpha + \rho_\alpha \mathrm{tr}\mathbf{D}_\alpha = r_\alpha \qquad \alpha = 1, \ldots, n \tag{4.95}$$

$$\sum_{\alpha=1}^{n} r_\alpha = 0 \tag{4.96}$$

$$\rho_\alpha \grave{\mathbf{v}}_\alpha = \mathrm{div}\mathbf{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{k}_\alpha \quad \alpha = 1, \ldots, n \tag{4.97}$$

(as follows from (4.56), (4.58), in the non-inertial frame we change here $\mathbf{b}_\alpha$ for $\mathbf{b}_\alpha + \mathbf{i}_\alpha$),

$$\sum_{\alpha=1}^{n}(\mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha) = \mathbf{o} \tag{4.98}$$

$$\mathbf{T}_\alpha = \mathbf{T}_\alpha^T \qquad \alpha = 1, \dots, n \tag{4.99}$$

$$\sum_{\alpha=1}^{n} \mathbf{T}_\alpha = \sum_{\alpha=1}^{n} \mathbf{T}_\alpha^T \qquad \alpha = 1, \dots, n \tag{4.100}$$

$$\sum_{\alpha=1}^{n} \rho_\alpha \grave{u}_\alpha + \sum_{\alpha=1}^{n} r_\alpha u_\alpha = -\mathrm{div}\mathbf{q} + Q + \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha - \sum_{\alpha=1}^{n} \mathbf{k}_\alpha . \mathbf{v}_\alpha - (1/2) \sum_{\alpha=1}^{n} r_\alpha \mathbf{v}_\alpha^2 \tag{4.101}$$

$$\sigma = \sum_{\alpha=1}^{n} \rho_\alpha \grave{s}_\alpha + \sum_{\alpha=1}^{n} r_\alpha s_\alpha + \mathrm{div}(\mathbf{q}/T) - Q/T \geq 0 \tag{4.102}$$

(for (4.101) we use (4.24), (4.98), (4.96) in (4.82) and (4.102) follows from (4.84), (4.85)).

To discuss the mixture invariance, consider first a process described by the quantities occurring in the balance equations (4.95)–(4.102) and let

$$\varepsilon_\alpha, \quad \eta_\alpha \qquad \alpha = 1, \dots, n \tag{4.103}$$

be two sets of fields defined in the mixture, the ε_α having the physical dimension of energy, and the η_α having the physical dimension of entropy, such that identically

$$\sum_{\alpha=1}^{n} \rho_\alpha \varepsilon_\alpha = 0 \tag{4.104}$$

$$\sum_{\alpha=1}^{n} \rho_\alpha \eta_\alpha = 0 \tag{4.105}$$

Define fields φ_α by

$$\varphi_\alpha \equiv \varepsilon_\alpha - T\eta_\alpha \qquad \alpha = 1, \dots, n \tag{4.106}$$

so that

$$\sum_{\alpha=1}^{n} \rho_\alpha \varphi_\alpha = 0 \tag{4.107}$$

Now we replace u_α, s_α, $\mathbf{T}_\alpha$, $\mathbf{k}_\alpha$, $\mathbf{q}$ in (4.95)–(4.102) by the following primed quantities ($\alpha = 1, \ldots, n$)

$$u'_\alpha = u_\alpha + \varepsilon_\alpha \tag{4.108}$$

$$s'_\alpha = s_\alpha + \eta_\alpha \tag{4.109}$$

$$\mathbf{T}'_\alpha = \mathbf{T}_\alpha + \rho_\alpha \varphi_\alpha \mathbf{1} \tag{4.110}$$

$$\mathbf{k}'_\alpha = \mathbf{k}_\alpha - \mathrm{grad}(\rho_\alpha \varphi_\alpha) \tag{4.111}$$

$$\mathbf{q}' = \mathbf{q} - T \sum_{\alpha=1}^{n} \rho_\alpha \eta_\alpha \mathbf{v}_\alpha \tag{4.112}$$

while the remaining quantities in (4.95)–(4.102) are left unchanged, i.e.

$$\begin{aligned} &\rho'_\alpha = \rho_\alpha, \quad \mathbf{v}'_\alpha = \mathbf{v}_\alpha, \quad r'_\alpha = r_\alpha, \quad \mathbf{b}'_\alpha = \mathbf{b}_\alpha, \quad \rho' = \rho \\ &w'_\alpha = w_\alpha, \quad \mathbf{D}'_\alpha = \mathbf{D}_\alpha, \quad Q' = Q, \quad T' = T, \quad \sigma' = \sigma, \end{aligned} \tag{4.113}$$

We call the quantities with trivial transformations such as (4.113) the *mixture invariant* quantities. In what follows we assume that the definitions themselves are mixture invariant, e.g.

$$f'_\alpha = f_\alpha + \varphi_\alpha \tag{4.114}$$

$$f' = \sum_{\alpha=1}^{n} w'_\alpha f'_\alpha \tag{4.115}$$

(cf. (4.108), (4.109), (4.92), (4.86)), similarly u', s', $\grave{\mathbf{v}}'_\alpha = \grave{\mathbf{v}}_\alpha$, $\grave{\rho}'_\alpha = \grave{\rho}_\alpha$, $\grave{\mathbf{u}}'_\alpha = \grave{\mathbf{u}}_\alpha + \grave{\varepsilon}_\alpha$, $(\mathrm{tr}\mathbf{D}_\alpha)' = \mathrm{tr}\mathbf{D}_\alpha$ etc. Some of them are mixture invariant, cf. (4.116).

The *mixture invariance* may be described as follows [56, 59, 65, 79, 114]:

Consider a process in our mixture model described by the unprimed quantities in (4.108)–(4.113) that satisfy (4.95)–(4.102) and define the new primed quantities by (4.108)–(4.113). Then the primed quantities satisfy (4.95)–(4.102).

This means the change from the original, unprimed quantities to the primed quantities does not change the form of local balances (4.95)–(4.102) for arbitrary $2(n-1)$ independent fields (4.103).

Proof of mixture invariance follows by a direct substitution of (4.108)–(4.113) into (4.95)–(4.102). This proof is trivial for (4.95), (4.96) because of the mixture invariance of all quantities, for (4.99), (4.100) it is simple, (4.97) in primed quantities it follows by (4.110), (4.111) as $\rho_\alpha \grave{\mathbf{v}}_\alpha = \rho'_\alpha \grave{\mathbf{v}}'_\alpha = \mathrm{div}(\mathbf{T}'_\alpha - \rho_\alpha \varphi_\alpha \mathbf{1}) + \rho'_\alpha \mathbf{b}'_\alpha + \mathbf{k}'_\alpha + \mathrm{grad}(\rho_\alpha \varphi_\alpha \mathbf{1})$ and (4.98) we obtain by (4.107). To prove the remaining relationships (4.101), (4.102) in primed quantities we use

$$\sum_{\alpha=1}^{n} \rho_\alpha \grave{\varepsilon}_\alpha = \sum_{\alpha=1}^{n} \overset{\backslash\alpha}{\overline{\rho_\alpha \varepsilon_\alpha}} - \sum_{\alpha=1}^{n} \grave{\rho}_\alpha \varepsilon_\alpha = \sum_{\alpha=1}^{n} \mathbf{v}_\alpha.\mathrm{grad}(\rho_\alpha \varepsilon_\alpha) - \sum_{\alpha=1}^{n} \grave{\rho}_\alpha \varepsilon_\alpha$$

(which follow from (4.3), (4.104), (4.86)) and their analogues for η_α, namely using transformations (4.108)–(4.115) and (4.8), (4.106), (4.18). Q.E.D.

The possibility of changing systematically the values of certain quantities without breaking the validity of the balance equations indicates a certain degree of arbitrariness of the quantities in question. Using the mixture invariance property in the next section on the constitutive level, i.e. when the additional quantities (4.103) are given by constitutive equations similar to those for the main quantities, the new mixture with the new constitutive functions (4.108)–(4.112) leads to the same evolution equations for temperature, densities and motions of the constituents provided the same external fields of force and radiation are applied. Hence, the new mixture is indistinguishable from the original one. Therefore, the physical meaning of the mixture invariance consists in the fact that only the mixture invariant quantities have direct physical significance, i.e. they are expected to be measurable. Among them are the external fields of force and radiation, kinematical quantities, densities, chemical reaction rates, temperatures, etc. cf. (4.113), and total densities, total thermodynamic quantities and total stress (cf. (4.21), (4.92), (4.94)) as may be seen from (4.115), (4.114), (4.107), (4.110), (4.113)

$$f' = \sum_{\alpha=1}^{n} w_\alpha f'_\alpha = \sum_{\alpha=1}^{n} w_\alpha (f_\alpha + \varphi_\alpha) = f, \quad \text{similarly} \quad u' = u, \quad s' = s \tag{4.116}$$

$$\mathbf{T}' = \mathbf{T} \tag{4.117}$$

On the other side, partial quantities (4.108), (4.109), (4.110), (4.111), (4.112) are not mixture invariant in accord with their expected non-measurability. Note, that the heat flux (4.112), which may be also written as (see (4.105), (4.24))

$$\mathbf{q}' = \mathbf{q} - T \sum_{\alpha=1}^{n} \rho_\alpha \eta_\alpha \mathbf{u}_\alpha \tag{4.118}$$

is invariant in a non-diffusing mixture (when all constituents have the same velocities, the heat flux is measurable as in single material, cf. Rems. 14, 23, 11 in Chaps. 2, 3 and 4, respectively). This also reflects different choices of entropy flux in many classical and rational mixture theories, cf. [3, 14, 17, 18].

The property of mixture invariance will be used in the application of our model, see Sect. 4.6, namely, it gives the possibility of explicit calculations of partial thermodynamic properties similarly as in classical thermodynamics of solutions. Other applications (e.g. using mixture invariance as a constitutive principle permits to simplify constitutive equations for partial quantities) are discussed in [59, 60].

Summary. Balancing the energy introduced additional partial property—the partial internal energy. Because the different constituents do not have different temperatures in our model of mixture it is sufficient to write down the balance of energy only for the mixture as a whole. In the local form, this is expressed by (4.81); corresponding balance of internal energy is given by (4.82). Similarly it is sufficient to postulate the entropy inequality for the mixture as a whole. In the local form the Clausius-Duhem inequality is given by (4.84) and in the reduced form by (4.89). The (specific) partial quantities represent an essential instrument of rational thermodynamics approach to mixtures. Partial free energy was introduced by (4.86); corresponding properties of mixture can be obtained as indicated in (4.90)–(4.94). In our model these quantities are linked up with an interesting property of the mixture invariance, which is essential for the possibility of experimental determination of partial quantities. The mixture invariance simply means that only the mixture invariant quantities are measurable. Mathematically, it is expressed by the invariance of (local) balances to transformations of mixture invariant quantities; these transformations are indicated in (4.108)–(4.113).

4.5 Chemically Reacting Mixture of Fluids with Linear Transport Properties

We start this section by a brief explanation of the transfer of principles of rational thermodynamics, which have been explained for single component systems in Sects. 3.5 and 3.6, to mixtures. Similarly as in the case of the single fluid in Sect. 3.5, balances of Sects. 4.2–4.4 are not sufficient to solve any concrete problem: we must add the *constitutive equations*—further relations among fields in balances which describe the material model to be studied.

In models of fluid mixtures, cf. [16, 17, 27, 28, 56, 65], the following fields are called a *thermodynamic process*:
Thermokinetic process

$$\underline{\chi}_\gamma, \quad \rho_\gamma, \quad T \tag{4.119}$$

Responses

$$r_\beta,\ u_\alpha,\ s_\alpha,\ \mathbf{q},\ \mathbf{k}_\beta,\ \mathbf{T}_\alpha(\text{sym.}) \tag{4.120}$$

External fields

$$Q, \quad \mathbf{b}_\alpha, \quad \mathbf{i}_\alpha \tag{4.121}$$

with $\alpha, \gamma = 1, \ldots, n; \beta = 1, \ldots, n-1$, which fulfil (often through the fields deduced in Sects. 4.1, 4.2, like (4.2), (4.24)) the local form of mass (4.17), momentum (4.57) and energy (4.82) balances; the remaining balances (4.20), (4.63), (4.70) (and (4.75) trivially) are satisfied defining $r_n, \mathbf{k}_n$ and three components of $\mathbf{T}_\alpha$ for each constituent, respectively.

Because fields (4.121) are controlled from the outside (of the mixture), constitutive equations are relations between (4.119), (4.120): according to the constitutive principle of *determinism* their independent variables form the *thermokinetic process* (4.119) giving their values as *responses* (4.120). For simplicity, we restrict to recent past and nearest surroundings of the considered response by constitutive principles of *differential memory* and *local action*. Constitutive equations for responses (4.120) are then functions of the following values of thermokinetic process (4.119) and their (time and space) derivatives taken in a considered instant and place of response (in referential description introduced in Sect. 4.1 similarly as in Sect. 3.1, i.e. as (4.1), $\rho_\gamma = \rho_\gamma(\mathbf{X}_\gamma, t)$, $T = T(\mathbf{X}_\gamma, t)$), namely

$$\mathbf{x}, \mathbf{v}_\gamma, \mathbf{F}_\gamma, \mathrm{Grad}\mathbf{F}_\gamma, \grave{\mathbf{F}}_\gamma, \rho_\gamma, \mathrm{Grad}\rho_\gamma, T, \mathrm{Grad}T, t \qquad \gamma = 1, \ldots, n \tag{4.122}$$

(memory expressed through $\grave{\rho}_\gamma$ is superfluous, namely it may expressed through (4.122) as well, see (4.18), (4.8) and response for r_β); temperature memory is not studied at all (because local equilibrium would not be achieved, cf. Sects. 2.2 and 3.5) and dependences on $\mathbf{X}_\gamma$ expressing, e.g. “heterogeneous mixtures”, see Sect. 4.1, are not considered).

Using (4.6), (4.4) and the following definitions of space gradients of densities and temperature

$$\mathbf{h}_\gamma \equiv \mathrm{grad}\rho_\gamma \qquad \gamma = 1, \ldots, n \tag{4.123}$$

$$\mathbf{g} \equiv \mathrm{grad}T \tag{4.124}$$

the independent variables (4.122) may be chosen as

$$\mathbf{x}, \mathbf{v}_\gamma, \mathbf{F}_\gamma, \mathrm{Grad}\mathbf{F}_\gamma, \mathbf{L}_\gamma, \rho_\gamma, \mathbf{h}_\gamma, T, \mathbf{g}, t \tag{4.125}$$

and used, by the constitutive principle of *equipresence*, in all constitutive equations for responses (4.120).

By the constitutive principle of *symmetry*, we confine in this treatise to fluids mixtures only in which the independent variables of constitutive equations for (all) responses (4.120) reduce to[12]

$$\mathbf{x}, t, \rho_\gamma, \mathbf{h}_\gamma, \mathbf{v}_\gamma, \mathbf{L}_\gamma, T, \mathbf{g} \qquad \gamma = 1, \ldots, n \tag{4.126}$$

Now we restrict such constitutive equations—responses (4.120) as functions of (4.126)—by the principle of *objectivity* (or (material) *frame indifference*), cf. Sect. 3.5: constitutive equations cannot depend explicitly on (non-objective) $\mathbf{x}$ and t

---

[12] This may be looked upon as a definition of fluids mixture, but it may be deduced by the principle of symmetry defining the (non-simple) fluid (constituent) [79, 115–117] as the material with the greatest possible symmetry. If the fluid constituent γ is non-reacting, dependence on $\mathbf{F}_\gamma$, $\mathrm{Grad}\mathbf{F}_\gamma$ is performed through ρ_γ, $\mathbf{h}_\gamma$ (by mass balance like (3.65) similarly as for single substance; cf. Sect. 3.5 and Rem. 30 in Chap. 3); if fluid constituent α is a reacting one, then dependence on $\mathbf{F}_\alpha$, $\mathrm{Grad}\mathbf{F}_\alpha$ is completely eliminated [60, 115, 116, 118]. Then (4.126) follows from (4.125).

(cf. below (3.120)) and the dependence on the non-objective quantities $\mathbf{L}_\gamma$ and $\mathbf{v}_\gamma$ may be achieved through the objective quantities $\mathbf{D}_\gamma$, diffusion velocities (4.24) and *relative spins* $\underline{\Omega}_\delta$ (cf. difference with single substance in Sect. 3.5)

$$\underline{\Omega}_\delta \equiv \mathbf{W}_\delta - \mathbf{W}_n \qquad \delta = 1, \ldots, n-1 \tag{4.127}$$

Therefore, the constitutive equations of a mixture of reacting fluids are functions $\mathcal{F} = \hat{r}_\beta, \hat{u}_\alpha, \hat{s}_\alpha, \hat{\mathbf{q}}, \hat{\mathbf{k}}_\beta, \hat{\mathbf{T}}_\alpha$ as follows ($\alpha, \gamma = 1, \ldots, n$; $\beta, \delta = 1, \ldots, n-1$)

$$\{r_\beta, u_\alpha, s_\alpha, \mathbf{q}, \mathbf{k}_\beta, \mathbf{T}_\alpha(\text{sym.})\} = \mathcal{F}(\rho_\gamma, \mathbf{h}_\gamma, \mathbf{u}_\delta, \mathbf{D}_\gamma, \underline{\Omega}_\delta, T, \mathbf{g}) \tag{4.128}$$

Moreover it follows from the objectivity principle that functions (4.128) are isotropic, i.e.

$$\{r_\beta, u_\alpha, s_\alpha, \mathbf{Qq}, \mathbf{Qk}_\beta, \mathbf{QT}_\alpha\mathbf{Q}^T\} = \mathcal{F}(\rho_\gamma, \mathbf{Qh}_\gamma, \mathbf{Qu}_\delta, \mathbf{QD}_\gamma\mathbf{Q}^T, \mathbf{Q}\underline{\Omega}_\delta\mathbf{Q}^T, T, \mathbf{Qg}) \tag{4.129}$$

are valid for any orthogonal tensor $\mathbf{Q}$ (cf. Rem. 8 in Chap. 3 and discussion under (3.122)).

Note, that, as was shown by Müller [16–18], the presence of density gradients in a thermokinetic process is important for obtaining the classical thermodynamics of mixtures. Models without $\mathbf{h}_\gamma$, called *simple fluid mixtures* give vast simplifications of thermodynamics, e.g. partial free energies are independent of densities of other constituents (cf. Sect. 4.8), a simple gas mixture is reduced to the mixture of ideal gases only [61]. These and other special cases will be discussed in Sect. 4.8.

In this book, we confine ourselves only to the special case of fluids mixture (4.128) which is linear in vector and tensor variables.[13] We denote it as the *chemically reacting mixture of fluids with linear transport properties* or simply the *linear fluid mixture* [56, 57, 64, 65]. Then (see Appendix A.2) the scalar, vector and tensor isotropic functions (4.129) linear in vectors and tensors (symmetrical or skew-symmetrical) have the forms:

$$r_\beta = r_\beta^{(0)} + \sum_{\gamma=1}^{n} r_\beta^{(\gamma)} \mathrm{tr}\mathbf{D}_\gamma \qquad \beta = 1, \ldots, n-1 \tag{4.130}$$

(for non-reacting constituents coefficients $r_\beta^{(0)}, r_\beta^{(\gamma)}$ are identically zero),

$$u_\alpha = u_\alpha^{(0)} + \sum_{\gamma=1}^{n} u_\alpha^{(\gamma)} \mathrm{tr}\mathbf{D}_\gamma \qquad \alpha = 1, \ldots, n \tag{4.131}$$

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[13] For more complicated non-linear mixtures, even those non-fluid, see, e.g. [18, 60, 71, 72], the thermodynamic relations are similar (local equilibrium is valid) but constitutive equations for chemical reaction rates are not simplified as in the linear model here, cf. Sect. 4.9.

$$s_\alpha = s_\alpha^{(0)} + \sum_{\gamma=1}^{n} s_\alpha^{(\gamma)} \mathrm{tr}\mathbf{D}_\gamma \qquad \alpha = 1, \ldots, n \tag{4.132}$$

$$f_\alpha = f_\alpha^{(0)} + \sum_{\gamma=1}^{n} f_\alpha^{(\gamma)} \mathrm{tr}\mathbf{D}_\gamma \qquad \alpha = 1, \ldots, n \tag{4.133}$$

Constitutive equations (4.133) follow from definitions

$$f_\alpha^{(0)} \equiv u_\alpha^{(0)} - T s_\alpha^{(0)} \tag{4.134}$$

$$f_\alpha^{(\gamma)} \equiv u_\alpha^{(\gamma)} - T s_\alpha^{(\gamma)} \tag{4.135}$$

and (4.131), (4.132), (4.86).

The remaining constitutive equations are (with the use of (4.88))

$$\mathbf{q} = -k\,\mathbf{g} - \sum_{\delta=1}^{n-1} \lambda_\delta\,\mathbf{u}_\delta + \sum_{\gamma=1}^{n} \chi_\gamma\,\mathbf{h}_\gamma \tag{4.136}$$

$$\mathbf{k}_\beta = -\xi_\beta\,\mathbf{g} - \sum_{\delta=1}^{n-1} \nu_{\beta\delta}\,\mathbf{u}_\delta + \sum_{\gamma=1}^{n} \omega_{\beta\gamma}\,\mathbf{h}_\gamma \qquad \beta = 1, \ldots, n-1 \tag{4.137}$$

$$\mathbf{T}_\alpha = -p_\alpha\,\mathbf{1} + \sum_{\gamma=1}^{n} \zeta_{\alpha\gamma}\,(\mathrm{tr}\mathbf{D}_\gamma)\,\mathbf{1} + \sum_{\gamma=1}^{n} 2\eta_{\alpha\gamma}\,\overset{\circ}{\mathbf{D}}_\gamma \qquad \alpha = 1, \ldots, n \tag{4.138}$$

All coefficients in these constitutive equations $r_\beta^{(0)}$, $r_\beta^{(\gamma)}$, $u_\alpha^{(0)}$, $u_\alpha^{(\gamma)}$, $s_\alpha^{(0)}$, $s_\alpha^{(\gamma)}$, $f_\alpha^{(0)}$, $f_\alpha^{(\gamma)}$, k, λ_δ, χ_γ, ξ_β, $\nu_{\beta\delta}$, $\omega_{\beta\gamma}$, p_α, $\zeta_{\alpha\gamma}$, $\eta_{\alpha\gamma}$ are functions of the scalars $T, \rho_1, \rho_2, \ldots, \rho_n$ only (e.g. $f_\alpha^{(0)} = \hat{f}_\alpha^{(0)}(T, \rho_\gamma)$). We note that linear dependence on skew-symmetric tensors $\underline{\Omega}_\delta$ does not exist because $\mathbf{T}_\alpha$ are symmetric (this is not the case in mechanically polar constituents [27, 28]; cf. Rem. 9).

Of course this important reduction (known also as the "Curie principle" roughly asserting that response of given tensor rank (scalar, vector and tensor) depends on variables of the same tensor rank [2–4, 119, 120]) is valid only in this linear case [12, 13]. The non-linear case is much more complicated [79, 121–123].

It remains to apply the principle of *admissibility* to our material model of linear fluids mixture (cf. Sect. 3.6). According to the principle of admissibility [124] also the entropy inequality (4.84) must be fulfilled in an arbitrary *admissible thermodynamic process*. Such process is defined (cf. (3.145) and Sect. 3.6) by fields (4.120), (4.121), by thermokinetic process (4.119) (where instead of motions $\underline{\chi}_\gamma$ it is sufficient to use velocities $\mathbf{v}_\gamma$ as may be clear from the choice of independent variables in constitutive equations (4.128) for our fluids mixture) and fields of r_n, $\mathbf{k}_n$ and calculable three components of each symmetrical $\mathbf{T}_\alpha$, which fulfil all balances (of mass (4.17), (4.20), momentum (4.57), (4.63) and its moment (4.70) and energy (4.82)) in which responses (4.120) are given by constitutive equations of the studied model, i.e. in our case given by (4.130)–(4.133), (4.136)–(4.138).

The principle of admissibility demands also that reduced inequality (4.89) must be fulfilled in any admissible thermodynamic process (because (4.89) was constructed from all these balances, mainly those of energy and entropy inequality). Then, and this is the main idea of Coleman and Noll [124], inserting constitutive equations of the studied model into (4.89), the identical fulfilling of inequality obtained in this way at any admissible thermodynamic process permits to obtain further properties of the constitutive model (for this, it suffices to choose the thermodynamic processes appropriately).

We perform this procedure in detail for our linear fluids mixture. First, we insert the constitutive equations (4.130)–(4.133), (4.136)–(4.138) into reduced inequality (4.89).

Quantities $\rho_\alpha f_\alpha^{(0)}$ or $\rho_\alpha f_\alpha^{(\gamma)}$ in (see (4.133)) $\rho_\alpha f_\alpha = \rho_\alpha f_\alpha^{(0)} + \sum_{\gamma=1}^{n} \rho_\alpha f_\alpha^{(\gamma)} \mathrm{tr}\mathbf{D}_\gamma$ are functions of T and ρ_γ only. Their derivatives, written as $\partial\rho_\alpha \hat{f}_\alpha^{(0)}/\partial T$, $\partial\rho_\alpha \hat{f}_\alpha^{(\gamma)}/\partial T$, $\partial\rho_\alpha \hat{f}_\alpha^{(0)}/\partial\rho_\gamma$, $\partial\rho_\alpha \hat{f}_\alpha^{(\gamma)}/\partial\rho_\epsilon$ $(\alpha, \gamma, \epsilon = 1, \ldots, n)$, are used for calculation of the first two members on the right-hand side of (4.89). We eliminate $\partial\rho_\alpha/\partial t$ using the mass balances (4.17), (4.8), (4.123) and constitutive equations (4.130) and we deduce the part of the result (4.139) containing these derivatives. A further part is obtained using constitutive equations (4.130)–(4.133), (4.136)–(4.138) in the remaining part of (4.89).

After laborious rearrangements, we obtain inequality (Φ is the dissipation, cf. (2.11))

$$
\begin{aligned}
\Phi \equiv T\sigma = &- \left[\sum_{\beta=1}^{n-1}\Big(\sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial\rho_\beta} - \sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial\rho_n}\Big) r_\beta^{(0)}\right] - \left\{\sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial T} + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha^{(0)}\right\} \frac{\partial T}{\partial t} \\
&+ \sum_{\gamma=1}^{n}\left[\rho_\gamma \sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial\rho_\gamma} - \rho_\gamma f_\gamma^{(0)} - p_\gamma - \sum_{\beta=1}^{n-1}\Big(\sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(\gamma)}}{\partial\rho_\beta} - \sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(\gamma)}}{\partial\rho_n}\Big) r_\beta^{(0)}\right. \\
&\left.- \sum_{\beta=1}^{n-1}\Big(\sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial\rho_\beta} - \sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial\rho_n}\Big) r_\beta^{(\gamma)}\right] \mathrm{tr}\mathbf{D}_\gamma - \sum_{\gamma=1}^{n}\left\{\sum_{\alpha=1}^{n} \rho_\alpha f_\alpha^{(\gamma)}\right\} \frac{\partial \mathrm{tr}\mathbf{D}_\gamma}{\partial t} \\
&+ \sum_{\gamma=1}^{n}\sum_{\beta=1}^{n-1}\left\{\sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial\rho_\gamma}\delta_{\beta\gamma} - \frac{\partial\rho_\beta \hat{f}_\beta^{(0)}}{\partial\rho_\gamma} - \omega_{\beta\gamma}\right\} \mathbf{u}_\beta . \mathbf{h}_\gamma - \sum_{\alpha=1}^{n} \{\chi_\alpha/T\} \mathbf{h}_\alpha . \mathbf{g} \\
&- \left\{\sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(0)}}{\partial T} + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha^{(0)}\right\} \mathbf{v}_n . \mathbf{g} - \sum_{\gamma=1}^{n}\left\{\sum_{\alpha=1}^{n} \frac{\partial\rho_\alpha \hat{f}_\alpha^{(\gamma)}}{\partial T} + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha^{(\gamma)}\right\} \frac{\partial T}{\partial t} \mathrm{tr}\mathbf{D}_\gamma \\
&- \sum_{\gamma=1}^{n}\sum_{\beta=1}^{n-1}\left\{\rho_\beta f_\beta^{(\gamma)}\right\} \mathbf{u}_\beta . \mathrm{grad}\ \mathrm{tr}\mathbf{D}_\gamma - \sum_{\gamma=1}^{n}\left\{\sum_{\alpha=1}^{n} \rho_\alpha f_\alpha^{(\gamma)}\right\} \mathbf{v}_n . \mathrm{grad}\ \mathrm{tr}\mathbf{D}_\gamma + (k/T)\mathbf{g}^2 \\
&+ \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1}(\nu_{\beta\delta} - (1/2) r_\beta^{(0)} \delta_{\beta\delta}) \mathbf{u}_\delta . \mathbf{u}_\beta + \sum_{\beta=1}^{n-1}\left(\frac{\lambda_\beta}{T} + \xi_\beta - \frac{\partial\rho_\beta \hat{f}_\beta^{(0)}}{\partial T} - \rho_\beta s_\beta^{(0)}\right) \mathbf{u}_\beta . \mathbf{g}
\end{aligned}
$$

$$
\begin{aligned}
&+\sum_{\epsilon=1}^{n}\sum_{\gamma=1}^{n}\left[\rho_\epsilon\sum_{\alpha=1}^{n}\frac{\partial\rho_\alpha\hat{f}_\alpha^{(\gamma)}}{\partial\rho_\epsilon}-\sum_{\beta=1}^{n-1}\left(\sum_{\alpha=1}^{n}\frac{\partial\rho_\alpha\hat{f}_\alpha^{(\gamma)}}{\partial\rho_\beta}-\sum_{\alpha=1}^{n}\frac{\partial\rho_\alpha\hat{f}_\alpha^{(\gamma)}}{\partial\rho_n}\right)r_\beta^{(\epsilon)}\right.\\
&\left.-\rho_\epsilon f_\epsilon^{(\gamma)}+\zeta_{\epsilon\gamma}\right]\mathrm{tr}\mathbf{D}_\epsilon\,\mathrm{tr}\mathbf{D}_\gamma\\
&+\sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n}(2\eta_{\alpha\gamma})\mathrm{tr}(\overset{\circ}{\mathbf{D}}_\alpha\overset{\circ}{\mathbf{D}}_\gamma)+\sum_{\epsilon=1}^{n}\sum_{\gamma=1}^{n}\sum_{\beta=1}^{n-1}\left\{\sum_{\alpha=1}^{n}\frac{\partial\rho_\alpha\hat{f}_\alpha^{(\gamma)}}{\partial\rho_\beta}\delta_{\beta\epsilon}-\frac{\partial\rho_\beta\hat{f}_\beta^{(\gamma)}}{\partial\rho_\epsilon}\right\}\mathrm{tr}\mathbf{D}_\gamma\,(\mathbf{h}_\epsilon.\mathbf{u}_\beta)\\
&-\sum_{\beta=1}^{n-1}\sum_{\gamma=1}^{n}\left\{\frac{\partial\rho_\beta\hat{f}_\beta^{(\gamma)}}{\partial T}+\rho_\beta s_\beta^{(\gamma)}\right\}\mathrm{tr}\mathbf{D}_\gamma\,(\mathbf{u}_\beta.\mathbf{g})-\sum_{\gamma=1}^{n}\sum_{\beta=1}^{n-1}\{\frac{1}{2}r_\beta^{(\gamma)}\}\mathbf{u}_\beta^2\,\mathrm{tr}\mathbf{D}_\gamma\\
&-\sum_{\gamma=1}^{n}\left\{\sum_{\alpha=1}^{n}\frac{\partial\rho_\alpha\hat{f}_\alpha^{(\gamma)}}{\partial T}+\sum_{\alpha=1}^{n}\rho_\alpha s_\alpha^{(\gamma)}\right\}\mathrm{tr}\mathbf{D}_\gamma\,(\mathbf{v}_n.\mathbf{g})\geq 0
\end{aligned}
\tag{4.139}
$$

where $\delta_{\beta\gamma}$ is Kronecker delta (with $\delta_{\beta n}=0$ for all $\beta=1,\ldots,n-1$). According to the admissibility principle, this inequality (4.139) (obtained from entropy inequality (4.84) or reduced inequality (4.89) and from constitutive equations (4.130)–(4.133) and (4.136)–(4.138)) must be fulfilled at any place in mixture $\mathbf{x}$ and instant t with arbitrary values of the following mutually independent quantities

$$T,\rho_\gamma,\mathrm{tr}\mathbf{D}_\gamma,\mathbf{h}_\gamma,\mathbf{u}_\beta,\mathbf{g},\overset{\circ}{\mathbf{D}}_\gamma,\quad \gamma=1,\ldots,n;\beta=1,\ldots,n-1 \tag{4.140}$$

$$\frac{\partial T}{\partial t},\frac{\partial\mathrm{tr}\mathbf{D}_\gamma}{\partial t},\mathbf{v}_n,\mathrm{grad}\,\mathrm{tr}\mathbf{D}_\gamma\quad \gamma=1,\ldots,n \tag{4.141}$$

Namely, such values (4.140), (4.141) generate some admissible thermodynamic process as follows (cf. analogical procedure for fluid model in Sect. 3.6):

Temperature and velocities fields of the thermokinetic process in place $\mathbf{y}$ and time τ are constructed by bounded expansion about chosen place‘ $\mathbf{x}$ and instant t, i.e. as (cf. (3.152), (3.153))

$$T(\mathbf{y},\tau)=T(\mathbf{x},t)+(\mathbf{g}(\mathbf{x},t)).(\mathbf{y}-\mathbf{x})+(\frac{\partial T}{\partial t}(\mathbf{x},t))(\tau-t) \tag{4.142}$$

$$
\begin{aligned}
v_\gamma^i(\mathbf{y},\tau)=v_\gamma^i(\mathbf{x},t)+(L_\gamma^{ij}(\mathbf{x},t))(y^j-x^j)+\left(\frac{\partial L_\gamma^{ij}}{\partial t}(\mathbf{x},t)\right)(y^j-x^j)(\tau-t)\\
+\frac{1}{2}\left(\frac{\partial L_\gamma^{ij}}{\partial x^k}(\mathbf{x},t)\right)(y^j-x^j)(y^k-x^k)
\end{aligned}
\tag{4.143}
$$

where for values taken at $\mathbf{x}, t$ we choose $\mathbf{v}_\gamma=\mathbf{u}_\gamma+\mathbf{v}_n$, $\mathbf{L}_\gamma=(1/3)\mathrm{tr}\mathbf{D}_\gamma\mathbf{1}+\overset{\circ}{\mathbf{D}}_\gamma$, $\frac{\partial\mathbf{L}_\gamma}{\partial t}=(1/3)(\frac{\partial\mathrm{tr}\mathbf{D}_\gamma}{\partial t})\mathbf{1}$ and $\frac{\partial L_\gamma^{ij}}{\partial x^k}=(1/3)(\frac{\partial\mathrm{tr}\mathbf{D}_\gamma}{\partial x^i})\delta^{jk}$. This is motivated by (4.24), (4.6), (4.88) and choosing $\mathbf{W}_\gamma = \mathbf{0}$ ((4.139) is independent of $\mathbf{W}_\gamma$). These choices express possible (4.142), (4.143) through independent quantities (4.140), (4.141).

The density fields of the thermokinetic process are given by solutions of differential equations (4.17) (assuming their existence; we follow [14, 15, 125]) using fields of velocities (4.143) and constitutive equations (4.130) (r_n follows from (4.20)) with the following initial conditions for density fields at chosen instant t

$$\rho_\gamma(\mathbf{y}, t) = \rho_\gamma(\mathbf{x}, t) + (\mathbf{h}_\gamma(\mathbf{x}, t)).(\mathbf{y} - \mathbf{x}) \tag{4.144}$$

Therefore, mass balances (4.17), (4.20) are satisfied by such density fields.

It may be seen from this construction that any mutually independent choice of quantities (4.140), (4.141) gives some thermokinetic process (4.119) fulfilling the mass balances (4.17), (4.20). Using them in constitutive equations (4.130)–(4.133), (4.136)–(4.138), we obtain responses (4.120) and ultimately we fulfil the balances (4.58) and (4.82) by appropriate (4.121) (because these may be controlled from the outside the mixture) and balances (4.63) by appropriate $\mathbf{k}_n$ (there is only $n - 1$ constitutive equations (4.137)); fulfilling (4.70) (and therefore trivially (4.75)) is achieved by symmetric responses (4.138).

In this way, the admissible thermodynamic process may be obtained for any (mutually independent) values (4.140), (4.141) (in any chosen place $\mathbf{x}$ and instant t) and therefore it follows from the admissibility principle that (4.139) must be valid at any such values of (4.140), (4.141).[14]

The same results as (4.139) and its validity at any independent values of (4.140), (4.141) might be obtained directly by the method of Lagrange multipliers (see Appendix. A.5 with example of simple thermoelastic fluid from Sect. 3.6).

From the latter formulation of the admissibility principle, we obtain the necessary and sufficient validity of the following results concerning constitutive equations (identically for all $\mathbf{x}$ and t in mixture and for all values of fields ρ_γ, T in it):

$$\sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial T} + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha^{(0)} = 0 \tag{4.145}$$

$$f_\alpha^{(\gamma)} = 0 \tag{4.146}$$

$$s_\alpha^{(\gamma)} = 0 \tag{4.147}$$

$$r_\beta^{(\gamma)} = 0 \tag{4.148}$$

$$\chi_\gamma = 0 \tag{4.149}$$

---

[14] The weak point of argument above is that the arbitrary $\mathbf{b}_\alpha$ influencing only the constituent α is difficult to find (e.g. Coriolis force in $\mathbf{i}_\alpha$ (4.12) is specific on constituent α through $\mathbf{v}_\alpha$ but this cannot be maintained arbitrarily [126]).

$$\sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial \rho_\gamma}\delta_{\beta\gamma} - \frac{\partial \rho_\beta \hat{f}_\beta^{(0)}}{\partial \rho_\gamma} = \omega_{\beta\gamma} \tag{4.150}$$

where $\alpha, \gamma = 1, \dots, n$; $\beta = 1, \dots, n-1$ and

$$\begin{aligned} T\sigma = &-\sum_{\beta=1}^{n-1}\left(\sum_{\alpha=1}^{n}\frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial \rho_\beta} - \sum_{\alpha=1}^{n}\frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial \rho_n}\right) r_\beta^{(0)} \\ &+ \sum_{\gamma=1}^{n}(\rho_\gamma \sum_{\alpha=1}^{n}\frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial \rho_\gamma} - \rho_\gamma f_\gamma^{(0)} - p_\gamma)\mathrm{tr}\mathbf{D}_\gamma + \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n}\zeta_{\alpha\gamma}\mathrm{tr}\mathbf{D}_\alpha \mathrm{tr}\mathbf{D}_\gamma \\ &+ \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n}(2\eta_{\alpha\gamma})\mathrm{tr}(\overset{\circ}{\mathbf{D}}_\alpha \overset{\circ}{\mathbf{D}}_\gamma) + \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1}(\nu_{\beta\delta} - (1/2)r_\beta^{(0)}\delta_{\beta\delta})\mathbf{u}_\delta.\mathbf{u}_\beta + (k/T)\mathbf{g}^2 \\ &+ \sum_{\beta=1}^{n-1}\left(\frac{\lambda_\beta}{T} + \xi_\beta - \frac{\partial \rho_\beta \hat{f}_\beta^{(0)}}{\partial T} - \rho_\beta s_\beta^{(0)}\right)\mathbf{u}_\beta.\mathbf{g} \geq 0 \end{aligned} \tag{4.151}$$

Proof the sufficiency follows immediately and the necessity is proved, using mainly Lemma A.5.1 from Appendix A.5, as follows. For any fixed choice of ρ_γ, T (such fields of $\mathbf{x}, t$ in (4.144), (4.142) may be chosen arbitrarily; repeating the following procedures with other such choices and at any $\mathbf{x}, t$ we obtain identical validity of results noted above (4.145)) and zero choice of other quantities of (4.140) the inequality (4.139) depends linearly on $\frac{\partial T}{\partial t}$ or $\frac{\partial \mathrm{tr}\mathbf{D}_\gamma}{\partial t}$ (these numbers may be independently arbitrary reals). Therefore, the coefficients at these quantities in (4.139) must be identically zero to fulfil inequality (4.139) at all values of these quantities (coefficients which, as the result will be zero, are denoted in (4.139) by curly brackets and they will be discarded from it sequentially during the proof). From this (4.145) follows and

$$\sum_{\alpha=1}^{n} \rho_\alpha f_\alpha^{(\gamma)} = 0 \qquad \gamma = 1, \dots, n \tag{4.152}$$

Then, if we use (4.145) and (4.152), the inequality (4.139) depends linearly on grad $\mathrm{tr}\mathbf{D}_\gamma$; because $\mathbf{u}_\beta$ is arbitrary we have

$$f_\beta^{(\gamma)} = 0 \qquad \beta = 1, \dots, n-1 \qquad \gamma = 1, \dots, n \tag{4.153}$$

which in combination with (4.152) gives (4.146) (identical validity of these results noted above (4.145) which is obtained by repeating procedures with other values ρ_γ, T, give zero values of all derivatives of $\hat{f}_\alpha^{(\gamma)}$ and therefore to eliminating them from (4.139) in what follows). Further (4.139) is linear in $\mathbf{h}_\alpha$; choosing $\mathbf{g} \neq \mathbf{o}$ and $\mathbf{u}_\beta = \mathbf{o}$ we obtain (4.149) and then, by choice $\mathbf{u}_\beta \neq \mathbf{o}$, we have (4.150). In (4.139) there is another linear member in $\frac{\partial T}{\partial t}$; choosing $\mathrm{tr}\mathbf{D}_\gamma \neq 0$ and using (4.146) we have

$$\sum_{\alpha=1}^{n} \rho_\alpha s_\alpha^{(\gamma)} = 0 \qquad \gamma = 1, \dots, n \tag{4.154}$$

With (4.154), (4.145), (4.146) and choose $\mathbf{g} = \mathbf{o}$ the last member in remaining (4.139) is of the third order, i.e. it is necessary for (4.148) to be valid because otherwise, when $\mathbf{u}_\beta$ and $\mathrm{tr}\mathbf{D}_\gamma$ are sufficiently great, this member determines the sign of expression (4.139); see Lemma A.5.3 of Appendix A.5. By (4.154), (4.146) the remaining third order member in (4.139) (with non-zero $\mathbf{g}$) must be zero from the analogous reason and we obtain $s_\beta^{(\gamma)} = 0$ which with (4.154) gives (4.147). Finally using the results (4.145)–(4.150), we obtain inequality (4.151) from (4.139) and the proof of results (4.145)–(4.151) is finished. Q.E.D.

By (4.135), (4.146), (4.147), there is also

$$u_\alpha^{(\gamma)} = 0 \qquad \alpha, \gamma = 1, \dots, n \tag{4.155}$$

and therefore constitutive equations for scalar quantities (4.130)–(4.133) are (here and in the following we omit the index (0))

$$r_\alpha = \hat{r}_\alpha(T, \rho_1, \rho_2, \dots, \rho_n) = \hat{r}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.156}$$

For $\alpha = n$ this follows from those previous by balance (4.20). The last expression in (4.156) is the usual shortened form (used, e.g. in (4.128) and in the following). Similarly,

$$u_\alpha = \hat{u}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.157}$$

$$s_\alpha = \hat{s}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.158}$$

$$f_\alpha = \hat{f}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.159}$$

Using definitions of total specific quantities (of mixture) (4.90), (4.91), (4.92) it then follows (cf. (4.21), (4.22)) similarly

$$u = \hat{u}(T, \rho_\gamma), \quad s = \hat{s}(T, \rho_\gamma), \quad f = \hat{f}(T, \rho_\gamma) \tag{4.160}$$

Now we define the *specific chemical potential* g_α by[15]

$$\frac{\partial \rho \hat{f}}{\partial \rho_\alpha} \equiv g_\alpha = \hat{g}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.161}$$

---

[15] In Sect. 4.6 we shall see that this is the usual definition, cf. (4.194). Its density has a dimension of force; in some theories, using partial Eshelby tensors [88] as generalization of (4.161) (cf. Rem. 38 in Chap. 3), the "configurational" or "material" forces are introduced instead [127, 128].

and define (recall above (4.156))

$$\Delta p_\alpha \equiv \rho_\alpha(g_\alpha - f_\alpha) - p_\alpha \qquad \alpha = 1, \ldots, n \tag{4.162}$$

$$\vartheta_\beta \equiv \frac{\lambda_\beta}{T} + \xi_\beta - \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} - \rho_\beta s_\beta \qquad \beta = 1, \ldots, n-1 \tag{4.163}$$

Then we can write the results (4.145), (4.150) as

$$\frac{\partial \hat{f}}{\partial T} + s = 0 \tag{4.164}$$

$$g_\gamma \delta_{\beta\gamma} - \frac{\partial \rho_\beta \hat{f}_\beta}{\partial \rho_\gamma} = \omega_{\beta\gamma} \qquad \beta = 1, \ldots, n-1; \quad \gamma = 1, \ldots, n \tag{4.165}$$

and instead of (4.136), using (4.149), we have the constitutive equation for the heat flux

$$\mathbf{q} = -k\,\mathbf{g} - \sum_{\beta=1}^{n-1} \lambda_\beta\,\mathbf{u}_\beta \tag{4.166}$$

Constitutive equations (4.137), (4.138) are not changed. The remaining inequality (4.151) may be written as

$$\begin{aligned} T\sigma = &- \sum_{\beta=1}^{n-1} (g_\beta - g_n) r_\beta + \sum_{\gamma=1}^{n} \Delta p_\gamma \operatorname{tr}\mathbf{D}_\gamma + \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} \zeta_{\alpha\gamma} \operatorname{tr}\mathbf{D}_\alpha \operatorname{tr}\mathbf{D}_\gamma \\ &+ \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} 2\eta_{\alpha\gamma} \operatorname{tr}(\overset{\circ}{\mathbf{D}}_\alpha \overset{\circ}{\mathbf{D}}_\gamma) + \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1} (\nu_{\beta\delta} - (1/2) r_\beta \delta_{\beta\delta}) \mathbf{u}_\delta . \mathbf{u}_\beta + (k/T)\mathbf{g}^2 \\ &+ \sum_{\beta=1}^{n-1} \vartheta_\beta\, \mathbf{u}_\beta . \mathbf{g} \geq 0 \end{aligned} \tag{4.167}$$

This inequality may be written as the sum of two non-negative expressions

$$T\sigma = \Pi_1 + \Pi_2 \geq 0 \tag{4.168}$$

$$\Pi_1 \equiv \Pi_0 + \sum_{\alpha=1}^{n} \Delta p_\alpha \operatorname{tr}\mathbf{D}_\alpha + \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} \zeta_{\alpha\gamma} \operatorname{tr}\mathbf{D}_\alpha \operatorname{tr}\mathbf{D}_\gamma \geq 0 \tag{4.169}$$

$$\Pi_2 \equiv \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} (2\eta_{\alpha\gamma}) \operatorname{tr}(\overset{\circ}{\mathbf{D}}_\alpha \overset{\circ}{\mathbf{D}}_\gamma) + \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1} (\nu_{\beta\delta} - (1/2) r_\beta \delta_{\beta\delta}) \mathbf{u}_\delta . \mathbf{u}_\beta + (k/T)\mathbf{g}.\mathbf{g}$$

$$+\sum_{\beta=1}^{n-1} \vartheta_\beta \, \mathbf{u}_\beta . \mathbf{g} \geq 0 \tag{4.170}$$

where Π_0 is the dissipation (entropy production in fact) caused by chemical reactions

$$\Pi_0 \equiv -\sum_{\beta=1}^{n-1} (g_\beta - g_n) r_\beta \geq 0 \tag{4.171}$$

Inequalities (4.169) and (4.171) follow from (4.168) due to independence of quantities (4.140); note that Δp_α is generally non-zero, see below and cf. discussion of (A.98) in Appendix A.5. To prove (4.170) we fix T and all ρ_γ, set $\mathrm{tr}\mathbf{D}_\gamma = 0$, then (4.168) has the form: non-negative constant + real quadratic form ≥ 0. Transforming this quadratic form into canonical form we can see that all its coefficients must be non-negative (otherwise ≥ 0 is not fulfilled for some values of its variables) and therefore this form must be positive semidefinite.

Now we define the *molar chemical potential* μ_α

$$\mu_\alpha \equiv g_\alpha M_\alpha \quad \alpha = 1, \ldots, n \tag{4.172}$$

(where M_α is the molar mass (4.25)) and the *vector of chemical potentials* $\vec{\mu}$ in the mixture space $\mathcal{U}$ with Cartesian basis $\vec{e}^\alpha$

$$\vec{\mu} \equiv \sum_{\alpha=1}^{n} \mu_\alpha \, \vec{e}^\alpha \tag{4.173}$$

This vector may be uniquely decomposed in the orthogonal subspaces $\mathcal{V}$ and $\mathcal{W}$ (see Sect. 4.2)

$$\vec{\mu} = -\vec{A} + \vec{B}, \quad \vec{\mu} \in \mathcal{U}, \quad \vec{A} \in \mathcal{V}, \quad \vec{B} \in \mathcal{W}, \quad \mathcal{V} \perp \mathcal{W}, \quad \mathcal{V} \oplus \mathcal{W} = \mathcal{U} \tag{4.174}$$

The vector $\vec{A}$ is called a *vector of chemical affinities*

$$\vec{A} = \sum_{p=1}^{n-h} A^p \, \vec{g}_p \tag{4.175}$$

because, using (A.85), (4.40), (4.173)–(4.175), its components are the *chemical affinities* A^p of the p-th chemical reaction defined as [3, 4, 108, 129–131]

$$A^p = -\sum_{\alpha=1}^{n} \mu_\alpha \, P^{p\alpha} \quad p = 1, \ldots, n-h \tag{4.176}$$

with the usual convention about stoichiometric coefficients (Sect. 4.2); see also Rem. 15 in Chap. 2 and (2.94) (because of simple reaction (2.73) the mass units were used here) where the traditional definition of chemical affinity is discussed.

Decomposition $(4.174)_1$ may be expressed in component form as

$$\mu_\alpha = -\sum_{p=1}^{n-h}\sum_{q=1}^{n-h} A^p g_{pq} P^{q\alpha} + \sum_{\sigma=1}^{h} B^\sigma S_{\sigma\alpha} \quad \alpha = 1, \ldots, n \tag{4.177}$$

which follow from $\mu_\alpha = \vec{\mu}.\vec{e}^\alpha$ inserting (4.174) and using (4.175), (A.86), (4.40), expression of $\vec{B}$ in the subspace $\mathcal{W}$, namely $\vec{B} = \sum_{\sigma=1}^{h} B^\sigma \vec{f}_\sigma$, and (4.34). Cf. also stoichiometry in Sect. 4.2 and Appendix A.4.

The production of entropy by chemical reactions (4.171) may be written with (4.20), (4.172), (4.173), (4.26), (4.33), (4.174), (4.36) using rates J_p (4.43) and affinities A^p (4.175) of $n - h$ independent chemical reactions as

$$\Pi_0 = -\sum_{\alpha=1}^{n} g_\alpha r_\alpha = -\vec{\mu}.\vec{J} = \vec{A}.\vec{J} = \sum_{p=1}^{n-h} J_p A^p \geq 0 \tag{4.178}$$

It should be stressed that because the vectors $\vec{J}$ and $\vec{B}$ lie in orthogonal subspaces, cf. (4.41), (4.174), the product $\vec{B}.\vec{J}$ vanishes and $\vec{B}$ does not appear in (4.178). Consequently, theories of irreversible thermodynamics which try to find fluxes and forces from the production of entropy overlook the dependence of reaction rate (flux) on force $\vec{B}$, see also (4.179) below.

Note, that reaction rates J_p (see (4.45), (4.26)), similarly as rates r_α (4.156), (4.20), are functions (beside T) of ρ_γ and by the usual assumption of invertibility (see the third regularity condition at the end of Sect. 4.6) they may be expressed as functions $\bar{J}_p$ of chemical potentials (see (4.161), (4.172))

$$J_p = \hat{J}_p(T, \rho_\gamma) = \bar{J}_p(T, \mu_\gamma) = \tilde{J}_p(T, B^\sigma, A^r) \qquad \gamma = 1, \ldots, n; \quad \sigma = 1, \ldots, h;$$
$$p, r = 1, \ldots, n-h \tag{4.179}$$

The last function $\tilde{J}_p$ may be defined by insertion of (4.177) into the previous one: $\vec{B}, \vec{A}$ may be looked upon as independent vectors in $\mathcal{W}, \mathcal{V}$ respectively which by composition $(4.174)_1$ gives some vector $\vec{\mu}$.

The last quadratic form in (4.169) must be also positive semidefinite

$$\sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} \zeta_{\alpha\gamma}\, \mathrm{tr}\mathbf{D}_\alpha \mathrm{tr}\mathbf{D}_\gamma \geq 0 \tag{4.180}$$

This follows from (4.169) with (4.180) in the canonical form because this member of second order determines ultimately the sign of the whole (4.169). From the positive semidefinity[16] of quadratic forms (4.170) (such are also its two first quadratic forms by independency of (4.140)) and (4.180) there follows the non-negativity of certain determinants formed from their symmetrized matrices (e.g. symmetrized matrix of (4.180) is $\|(1/2)(\zeta_{\alpha\gamma} + \zeta_{\gamma\alpha}\|$) as, e.g.

$$k \geq 0, \quad \eta_{\alpha\alpha} \geq 0, \quad \zeta_{\alpha\alpha} \geq 0 \quad \alpha = 1, \ldots, n \tag{4.181}$$

$$\nu_{\beta\beta} \geq (1/2) r_\beta \quad \beta = 1, \ldots, n-1 \tag{4.182}$$

Relations (4.182) express the limitation of reaction rates by diffusion known in chemical kinetics [132] (roughly, inversions of $\nu_{\beta\beta}$ are proportional to diffusion coefficients, cf. Sect. 4.10).

We note that whenever

$$\Pi_0 = 0 \tag{4.183}$$

it must be also

$$\Delta p_\alpha = 0 \quad \alpha = 1, \ldots, n \tag{4.184}$$

as may be seen from (4.169), see (A.98) and Lemma A.5.4 from Appendix A.5.4. Important examples are non-reacting mixtures where $r_\alpha \equiv 0$ (4.15) (see Sect. 4.8) identically (by (4.178), (4.183), Lemma A.5.4, the (4.184) must be valid at any ρ_α, T) and (chemically reacting) mixtures in *chemical equilibrium* where (4.183) is valid at certain ρ_α, T giving, by Lemma A.5.4, Eq. (4.184) at these values (equilibrium in fluids mixture will be discussed in Sect. 4.7). Equation (4.184) is valid also in the case when coefficients $\zeta_{\alpha\gamma}$ are zero, e.g. in a mixture of monoatomic ideal gases [133] or if we neglect viscosity phenomena completely.

As we shall see in the next Sect. 4.6, Δp_α causes the difference between pressure p_α in stress (4.138) and the pressure used in thermodynamic formulae ("thermodynamic pressure", see (4.186)), e.g. in chemical kinetics out of equilibrium.

To estimate Δp_α, we choose some values of T, ρ_γ and therefore some values of Π_0, Δp_γ, $\zeta_{\alpha\gamma}$ are fixed. For simplicity, we assume that quadratic form (4.180) is positive *definite* with elements $\zeta_{\alpha\gamma}$ of symmetrized matrix and denote by $\zeta^{-1}_{\alpha\gamma}$ the elements of its inversion. Taking first derivative of Π_1 (4.169) (in arbitrary real $\text{tr}\mathbf{D}_\gamma$ at chosen T, ρ_γ) as zero we obtain the extremal values $\text{tr}\mathbf{D}_\gamma$ (in fact in minimum because second derivatives of (4.169) form positive definite matrix of (4.180), cf. [134, Sect.11.3-3]). Inserting this values into (4.169) (for which this inequality is valid too) we obtain the following minimal values of Π_1

$$\Pi_0 - (1/4) \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \zeta^{-1}_{\alpha\gamma} \Delta p_\alpha \Delta p_\gamma \geq 0 \tag{4.185}$$

---

[16] From this generally does not follow the symmetry of its coefficients. The skew-symmetric part of these coefficients disappears and to obtain them as zero we must add the new assumptions, namely Onsager reciprocity, cf. Sect. 4.10, Rem. 31.

valid for chosen T, ρ_γ (and therefore similarly for other values). This inequality may be used for the estimation of values Δp_α if we know volume viscosity coefficients and entropy production by chemical reactions.[17]

Summary. This section began with a short description of the application of principles of rational thermodynamics on mixtures. Then the principal model of our book—the mixture of fluids with linear transport properties—was defined generally by the linearization of constitutive equations (for fluids) in vector and tensor variables see (4.130)–(4.133), (4.136)–(4.138). The general forms were then modified and simplified by the admissibility principle. The final forms are given by (4.156)–(4.160) and (4.166); the constitutive equations (4.137) and (4.138) remained unchanged. The final form of entropy inequality is seen in (4.167) and can be separated into several relatively independent parts the most important of which is the part representing the entropy production by chemical reactions—(4.171) or in modified form (4.178). The entropy inequality put also the restrictions on transport coefficients, (4.181), and on reaction rates coupled with diffusion, (4.182). Note also the definition of (specific) chemical potential (4.161) and the decomposition of its molar counterpart into affinities (4.177). All this enables to formulate the reaction rates as functions of various sets of independent variables (4.179) though the necessary regularity conditions are given in the following sections only.

4.6 Thermodynamic Relationships in the Linear Fluid Mixture

We now deduce basic thermodynamic properties of the mixture of fluids with linear transport properties discussed in Sect. 4.5. Among others, we show that Gibbs equations and (equilibrium) thermodynamic relationships in such mixtures are valid also in any non-equilibrium process including chemical reactions (i.e. local equilibrium is proved in this model) [56, 59, 64, 65, 79, 138].

Besides the definitions (4.21), (4.22), (4.90)–(4.92), (4.161)–(4.163), we define the *partial thermodynamic pressure* P_α and the total *thermodynamic pressure* P of mixture

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[17] Though our model excludes by (4.120) influence of $\mathrm{tr}\mathbf{D}_\gamma$ on chemical reaction rate (usually discussed in classical linear non-equilibrium thermodynamics [3]) this influence remains indirect through the volume viscosity coefficients as may be seen from (4.185). We can estimate the (whole) pressure difference Δp for (chemical) reaction of hydrogen nuclear isomers $p-\mathrm{H}_2$ (1) to $o-\mathrm{H}_2$ (2) at 650 °C, 100 torr in which the rate is $J = 1.52 \times 10^{-3}$mol/m^{3}s at halftime 450 s [135]. Because of similarity of both isomers we take $\Delta p_1 = \Delta p_2 = \Delta p/2$ (cf. (4.186), (4.187)) and as $\zeta_{\alpha\alpha}$ (those which are diagonal; the remaining are neglected) we can take approximate volume viscosity ζ of pure H_2 for both isomers (estimated by $\zeta = 32\eta$ from usual viscosity $\eta = 1.9 \times 10^{-5}$ kg/m.s of pure H_2 [136]). Affinity A in halftime (the same concentrations of isomers) may be calculated by $A = \mathrm{R}T\ln K$ where the equilibrium constant is $K = 3$ [137], cf. (4.479), (4.481) and (*b*) from Rem. 28. Resulting Δp, calculated from $(\Delta p)^2 \leq 8\zeta J A$ (which is (4.185) with (4.178) in this example), is not greater then 0.25 Pa; unfortunately, for more realistic cases, we have difficulties in knowing the values of $\zeta_{\alpha\gamma}$.

$$P_\alpha \equiv p_\alpha + \Delta p_\alpha \qquad \alpha = 1, \ldots, n \tag{4.186}$$

$$P \equiv \sum_{\alpha=1}^{n} P_\alpha \tag{4.187}$$

the *partial volume* v_α, the *partial enthalpy* h_α ($\alpha = 1, \ldots, n$)

$$v_\alpha \equiv P_\alpha/(\rho_\alpha P) \tag{4.188}$$

$$h_\alpha \equiv u_\alpha + P v_\alpha \tag{4.189}$$

and the total specific *enthalpy* h, *volume* v and *free enthalpy (Gibbs energy)* g of mixture

$$h \equiv \sum_{\alpha=1}^{n} w_\alpha h_\alpha \tag{4.190}$$

$$v \equiv \sum_{\alpha=1}^{n} w_\alpha v_\alpha \tag{4.191}$$

(the same symbol used in dv in integrals, like (4.14), has another sense, cf. (3.199)),

$$g \equiv \sum_{\alpha=1}^{n} w_\alpha g_\alpha \tag{4.192}$$

All these quantities are functions of $T, \rho_1, \ldots \rho_n$ only.

By (4.186) and (4.162)

$$P_\alpha = \rho_\alpha (g_\alpha - f_\alpha) \tag{4.193}$$

and P_α, P play the role of pressures in the following thermodynamic relationships although P_α are generally different from "real pressures" p_α (cf. (4.138) and (4.186)). But when (4.184) is valid (e.g. chemical equilibrium or non-reacting mixture) both pressures are the same (cf. end of Sect. 4.5 and Rem. 17).

From (4.186)–(4.193), (4.21)–(4.23), (4.90)–(4.93), (4.161), (4.86) it may be obtained

$$g_\alpha = f_\alpha + P v_\alpha \qquad \alpha = 1, \ldots, n \tag{4.194}$$

$$v = 1/\rho \tag{4.195}$$

$$\sum_{\alpha=1}^{n} \rho_\alpha v_\alpha = 1 \tag{4.196}$$

$$f = u - Ts \tag{4.197}$$

$$g = f + Pv \tag{4.198}$$

$$h = u + Pv \tag{4.199}$$

$$P_\alpha = \sum_{\gamma=1}^{n} \rho_\alpha \rho_\gamma \frac{\partial \hat{f}_\gamma}{\partial \rho_\alpha} \qquad \alpha = 1, \ldots, n \tag{4.200}$$

From all these relations, the *Gibbs equations* may be obtained

$$\mathrm{d}(\rho f) = -\rho s \, \mathrm{d}T + \sum_{\alpha=1}^{n} g_\alpha \, \mathrm{d}\rho_\alpha \tag{4.201}$$

$$\mathrm{d}(\rho u) = T \, \mathrm{d}(\rho s) + \sum_{\alpha=1}^{n} g_\alpha \, \mathrm{d}\rho_\alpha \tag{4.202}$$

$$\mathrm{d}u = T \, \mathrm{d}s - P \, \mathrm{d}v + \sum_{\beta=1}^{n-1} (g_\beta - g_n) \, \mathrm{d}w_\beta \tag{4.203}$$

$$\mathrm{d}f = -s \, \mathrm{d}T - P \, \mathrm{d}v + \sum_{\beta=1}^{n-1} (g_\beta - g_n) \, \mathrm{d}w_\beta \tag{4.204}$$

$$\mathrm{d}h = T \, \mathrm{d}s + v \, \mathrm{d}P + \sum_{\beta=1}^{n-1} (g_\beta - g_n) \, \mathrm{d}w_\beta \tag{4.205}$$

$$\mathrm{d}g = -s \, \mathrm{d}T + v \, \mathrm{d}P + \sum_{\beta=1}^{n-1} (g_\beta - g_n) \, \mathrm{d}w_\beta \tag{4.206}$$

Because all these quantities are fields (i.e. functions of $\mathbf{x}$, t), we can use these equations with the time and space derivatives (gradients) instead of differentials (cf. below (3.199)).

From (4.206) and (4.192), the Gibbs-Duhem equation may be obtained

$$- s \, \mathrm{d}T + v \, \mathrm{d}P - \sum_{\alpha=1}^{n} w_\alpha \, \mathrm{d}g_\alpha = 0 \tag{4.207}$$

We can also deduce the following relationships from (4.165), (4.193), (4.187), (4.207), (4.22), (4.195), (4.92), (4.164)

$$\sum_{\gamma=1}^{n} \omega_{\beta\gamma}\, \mathrm{d}\rho_\gamma = \mathrm{d}P_\beta - \rho_\beta\, \mathrm{d}g_\beta + \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T}\, \mathrm{d}T \qquad \beta = 1, \ldots, n-1 \tag{4.208}$$

$$\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \omega_{\beta\gamma}\, \mathrm{d}\rho_\gamma = -\mathrm{d}P_n + \rho_n\, \mathrm{d}g_n - \rho_n \frac{\partial \hat{f}_n}{\partial T}\, \mathrm{d}T \tag{4.209}$$

We denote by y_α all specific *partial thermodynamic quantities* of constituents and by y corresponding specific *total* (or *for mixture*) *thermodynamic quantities*:

$$\begin{aligned} y_\alpha &= u_\alpha,\ s_\alpha,\ f_\alpha,\ g_\alpha,\ v_\alpha,\ h_\alpha, \qquad \alpha = 1, \ldots, n \\ y &= u,\ s,\ f,\ g,\ v,\ h \end{aligned} \tag{4.210}$$

Relations (4.90), (4.91), (4.92), (4.190), (4.191), (4.192), may be written as

$$y = \sum_{\alpha=1}^{n} w_\alpha y_\alpha \tag{4.211}$$

$$y = \hat{y}(T, \rho_\gamma) \tag{4.212}$$

$$y_\alpha = \hat{y}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.213}$$

Besides the independent variables $T, \rho_1, \ldots, \rho_n$, variables $T, P, w_1, \ldots, w_{n-1}$ are often used in classical thermochemistry (as well as their molar analogues, cf. (4.288) below). To obtain this change of variables we take (using (4.195), (4.22), (4.23))

$$\begin{aligned} P = \hat{P}(T, \rho_\gamma) &= \hat{P}(T, w_1/v, \ldots, w_{n-1}/v, (1 - \sum_{\beta=1}^{n-1} w_\beta)/v) \\ &\equiv \breve{P}(T, v, w_1, \ldots, w_{n-1}) \end{aligned} \tag{4.214}$$

and assume the existence of an inversion of $\breve{P}$ (4.214) for volume

$$v = \tilde{v}(T, P, w_1, \ldots, w_{n-1}) \tag{4.215}$$

(such assumption is fulfilled in the usual stable mixture where (4.358) is valid, see Sect. 4.7).

The arbitrary function of $T, \rho_1, \ldots, \rho_n$, may be transformed analogously as (4.214) and using (4.215) we obtain functions of $T, P, w_1, \ldots, w_{n-1}$ denoted by the tilde and written shortly as ($\alpha = 1, \ldots, n$; $\beta = 1, \ldots, n-1$)

$$y_\alpha = \tilde{y}_\alpha(T, P, w_\beta) \tag{4.216}$$

$$y = \tilde{y}(T, P, w_\beta) \tag{4.217}$$

Therefore, the classical relations of thermochemistry were obtained. Especially, the Gibbs equations (4.201)–(4.206) are valid in arbitrary process in this chemically reacting mixture of fluids with linear transport properties, i.e. the principle of local equilibrium is valid in this mixture. But we show in the following relations that this accord with classical thermochemistry (e.g. [138]) is not quite identical: indeed, if we differentiate (4.211) and use (4.22), (4.23) we obtain

$$\frac{\partial \tilde{y}}{\partial w_\beta} = y_\beta - y_n + \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}_\alpha}{\partial w_\beta} \qquad \beta = 1, \ldots, n-1 \tag{4.218}$$

and comparing the differentials from (4.211) and (4.217) and use (4.218) we obtain

$$\frac{\partial \tilde{y}}{\partial T}\,\mathrm{d}T + \frac{\partial \tilde{y}}{\partial P}\,\mathrm{d}P - \sum_{\alpha=1}^{n} w_\alpha\,\mathrm{d}y_\alpha + \sum_{\beta=1}^{n-1}\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}_\alpha}{\partial w_\beta}\,\mathrm{d}w_\beta = 0 \tag{4.219}$$

We can see that these relations (4.218), (4.219) are in accord with classical thermochemistry if the sum in the right hand side of (4.218) is zero (which is known as (generalized) Gibbs-Duhem equation) for all y_α (4.210). Exceptions are chemical potentials g_α and specific Gibbs energy g as may be seen from (4.206) and (4.217)

$$\frac{\partial \tilde{g}}{\partial w_\beta} = g_\beta - g_n \qquad \beta = 1, \ldots, n-1 \tag{4.220}$$

i.e. for chemical potentials the Gibbs-Duhem equations are valid

$$\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{g}_\alpha}{\partial w_\beta} = 0 \qquad \beta = 1, \ldots, n-1 \tag{4.221}$$

But we show now that validity of relations similar to (4.220), (4.221) (Gibbs-Duhem equations) may be achieved even for remaining y_α, y (4.210) and therefore the complete accord with classical thermodynamics of mixtures will be obtained (specifically, e.g. classical expressions (4.266), (4.267) will be valid).

For this, we use the *mixture invariance* discussed in Sect. 4.4 in the following programme with two Propositions (defined more precisely below):

- Proposition 23.1 gives by mixture invariance the equivalent description of linear fluid mixture (i.e. all constitutive equations and their properties from Sect. 4.5 remains valid) even with new “primed” quantities (introduced similarly as in Sect. 4.4) with arbitrary functions (4.222), (4.223) below (instead of arbitrary quantities (4.103)).
- All remaining hitherto obtained results of Sects. 4.5 and 4.6 of the linear fluid mixture will be shown to be valid also for primed quantities,

- Proposition 23.2 achieves (by appropriate choice of functions (4.222), (4.223), namely (4.257)) the (still absenting) validity of Gibbs-Duhem equations for all y_α, y (4.210).
- All these results then give the complete accord of thermodynamic relations with classical thermodynamics of mixtures.

Recall that the mixture invariance described in Sect. 4.4 means that all balances (4.95)–(4.102) remain valid with primed quantities defined by transformations (4.108)–(4.113). But here we proceed further: with functions (4.222), (4.223) instead of (4.103), the Eqs. (4.108)–(4.112) permit the formulation of linear constitutive equations with primed quantities by constitutive principles analogously[18] as in Sect. 4.5. Remaining parts of Sects. 4.5 and 4.6 will be done with analogous (but primed) definitions keeping the rule that the definitions themselves are mixture invariant (cf. above (4.114)). Procedure and description will be similar as in Sect. 4.4. Quantities or expressions which do not change by using (4.108)–(4.113) we denote as *mixture invariant*, e.g. quantities (4.113). For simplicity, we use the primes for mixture invariant quantities rather exceptionally.

Proposition 23.1 (*equivalent description of linear fluid mixture with primed quantities*). Assuming some a priori unprimed quantities u_α, s_α, $\mathbf{T}_\alpha$, $\mathbf{k}_\alpha$, $\mathbf{q}$ and some further (4.108)–(4.113) used in balances (4.95)–(4.102), we choose for the quantities (4.103) the following arbitrary (but differentiable) functions of (mixture invariant, see (4.113)) T and all ρ_γ

$$\varepsilon_\alpha = \hat{\varepsilon}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.222}$$

$$\eta_\alpha = \hat{\eta}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.223}$$

having the dimension of energy and entropy respectively, which fulfil (4.104) and (4.105) identically (for all T, ρ_γ). These functions may be written as

$$\zeta_\alpha = \hat{\zeta}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \dots, n \tag{4.224}$$

fulfilling identically (i.e. for all T, ρ_γ)

$$\sum_{\alpha=1}^{n} \rho_\alpha \zeta_\alpha = 0 \tag{4.225}$$

together with primed (specific) partial thermodynamic quantities $y'_\alpha = u'_\alpha$, s'_α, f'_α, g'_α, v'_α, h'_α defined as

$$y'_\alpha = y_\alpha + \zeta_\alpha \qquad \alpha = 1, \dots, n \tag{4.226}$$

where

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[18] This may be generalized also for non-linear models but then it seems plausible to give up the (principle of) equipresence [59, 60, 72, 114].

$$\zeta_\alpha = \varepsilon_\alpha,\ \ \eta_\alpha,\ \ \varphi_\alpha,\ \ 0,\ \ -\varphi_\alpha/P,\ \ T\eta_\alpha \tag{4.227}$$

corresponding to the original $y_\alpha = u_\alpha, s_\alpha, f_\alpha, g_\alpha, v_\alpha, h_\alpha$, respectively. Here the following definition was used:

$$\varphi_\alpha \equiv \varepsilon_\alpha - T\eta_\alpha = \hat{\varphi}_\alpha(T, \rho_\gamma) \qquad \alpha = 1, \ldots, n \tag{4.228}$$

Besides g_α, also the total thermodynamic pressure $P = P'$ is mixture invariant in (4.227), for which $P' = \sum_{\alpha=1}^n P'_\alpha$ (see (4.187)), with partial thermodynamic (primed) pressure obtainable from P_α (4.186) by transformation

$$P'_\alpha = P_\alpha - \rho_\alpha\varphi_\alpha \qquad \alpha = 1, \ldots, n \tag{4.229}$$

Total thermodynamic primed quantities y' are defined with (4.226) as (cf. (4.210), (4.211))

$$y' \equiv \sum_{\alpha=1}^n w_\alpha y'_\alpha = y \tag{4.230}$$

and they are mixture invariant (cf. (4.116)).

Transforming original unprimed quantities according (4.108)–(4.118) to corresponding primed quantities using some functions (4.222), (4.223), the resulting form of constitutive equations and their properties for primed quantities remains (cf. (4.157)–(4.159), (4.166), (4.137), (4.138))

$$u'_\alpha = \hat{u}_\alpha(T, \rho_\gamma) + \hat{\varepsilon}_\alpha(T, \rho_\gamma) = \hat{u}'_\alpha(T, \rho_\gamma) \quad \alpha, \gamma = 1, \ldots, n \tag{4.231}$$

$$s'_\alpha = \hat{s}_\alpha(T, \rho_\gamma) + \hat{\eta}_\alpha(T, \rho_\gamma) = \hat{s}'_\alpha(T, \rho_\gamma) \quad \alpha, \gamma = 1, \ldots, n \tag{4.232}$$

$$f'_\alpha = \hat{f}_\alpha(T, \rho_\gamma) + \hat{\varphi}_\alpha(T, \rho_\gamma) = \hat{f}'_\alpha(T, \rho_\gamma) \quad \alpha, \gamma = 1, \ldots, n \tag{4.233}$$

$$\mathbf{q}' = -k\mathbf{g} - \sum_{\beta=1}^{n-1} \lambda'_\beta \mathbf{u}_\beta \tag{4.234}$$

$$\mathbf{k}'_\beta = -\xi'_\beta \mathbf{g} - \sum_{\delta=1}^{n-1} \nu_{\beta\delta}\mathbf{u}_\delta + \sum_{\gamma=1}^{n} \omega'_{\beta\gamma}\mathbf{h}_\gamma \qquad \beta = 1, \ldots, n-1 \tag{4.235}$$

$$\mathbf{T}'_\alpha = -p'_\alpha \mathbf{1} + \sum_{\gamma=1}^{n} \zeta_{\alpha\gamma}(\mathrm{tr}\mathbf{D}_\gamma)\mathbf{1} + \sum_{\gamma=1}^{n} 2\eta_{\alpha\gamma}\, \overset{\circ}{\mathbf{D}}_\gamma \qquad \alpha = 1, \ldots, n \tag{4.236}$$

where primed quantities in their right-hand sides are transformed as

$$\lambda'_\beta = \lambda_\beta + \rho_\beta T \eta_\beta \tag{4.237}$$

$$\xi'_\beta = \xi_\beta + \rho_\beta \frac{\partial \hat{\varphi}_\beta}{\partial T} \tag{4.238}$$

$$\omega'_{\beta\gamma} = \omega_{\beta\gamma} - \frac{\partial \rho_\beta \hat{\varphi}_\beta}{\partial \rho_\gamma} \tag{4.239}$$

$$p'_\alpha = p_\alpha - \rho_\alpha \varphi_\alpha \tag{4.240}$$

Coefficients k, $\nu_{\beta\delta}$, $\zeta_{\alpha\gamma}$, $\eta_{\alpha\gamma}$ are mixture invariant. The remaining constitutive equations for reacting rates (4.156) are the same, because they contain the mixture invariant quantities only.

Chemical potentials g_α (4.161) are mixture invariant as well as quantities Δp_α (4.162), ϑ_β (4.163). Therefore resulting expressions (4.164), (4.167)–(4.171) are the same, i.e. Π_0, Π_1, Π_2, σ are mixture invariant in these inequalities. The result (4.165) is

$$g_\gamma \delta_{\beta\gamma} - \frac{\partial \rho_\beta \hat{f}'_\beta}{\partial \rho_\gamma} = \omega'_{\beta\gamma} \qquad \beta = 1, \ldots, n-1;\ \gamma = 1, \ldots, n \tag{4.241}$$

Proof Results follows by appropriate construction of constitutive equations and their properties (as in Sect. 4.5, i.e. starting with (4.128)) for primed quantities here proposed (i.e. as in Sect. 4.4):

Relations (4.226), (4.225) and mixture invariance (4.230) follow directly for $y = u, s$ as in Sect. 4.4 using (4.222), (4.223) instead of (4.103) (cf. (4.108), (4.109), (4.104), (4.105), (4.90), (4.91), (4.116)). For $y = f$, these relations and mixture invariance (4.230) then follow from definition (4.86) with primed quantities (definition formulae are mixture invariant) $f'_\alpha \equiv u'_\alpha - T s'_\alpha$ (cf. (4.106), (4.114), (4.107), (4.115), (4.116)). For the remaining $y = g, v, h$ these will be shown below.

Deduction of (4.231), (4.232), (4.233) follows from (4.108), (4.109), (4.114) inserting (4.131), (4.132), (4.133) and using $y_\alpha^{(0)'} = y_\alpha^{(0)} + \zeta_\alpha$ (for $y = u, s, f$ respectively) leaving their remaining parts $y_\alpha^{(\gamma)}$ mixture invariant (because such are r_β we leave mixture invariant all parts of (4.130)); that $y_\alpha^{(\gamma)} = 0$ will be shown below.

To obtain (4.234) we insert (4.136) into (4.118) and leaving here k, χ_γ mixture invariant while we choose (4.237) (this follows from members linear in diffusion velocities (4.24)); we have

$$\mathbf{q}' = -k\mathbf{g} - \sum_{\beta=1}^{n-1} \lambda'_\beta \mathbf{u}_\beta + \sum_{\gamma=1}^{n} \chi_\gamma \mathbf{h}_\gamma \tag{4.242}$$

(zero value of χ_γ is shown below).

To obtain constitutive equations (4.235), we insert (4.137) into (4.111); here $\mathrm{grad}(\rho_\beta \varphi_\beta) = \rho_\beta \frac{\partial \hat{\varphi}_\beta}{\partial T} \mathbf{g} + \sum_{\gamma=1}^{n} \frac{\partial \rho_\beta \hat{\varphi}_\beta}{\partial \rho_\gamma} \mathbf{h}_\gamma$ by (4.224) and therefore we choose (4.238), (4.239) leaving $\nu_{\beta\delta}$ mixture invariant.

Ultimately constitutive equations (4.236) follow inserting (4.138) into (4.110) leaving viscosities $\zeta_{\alpha\gamma}$, $\eta_{\alpha\gamma}$ mixture invariant; therefore (4.240) follows for mixture non-invariant partial pressures p_α.

Now, the proof of the final form of (4.231)–(4.236) will be given noting that constitutive equations obtained so far for primed quantities $r'_\beta, u'_\alpha, s'_\alpha, f'_\alpha, \mathbf{q}', \mathbf{k}'_\beta, \mathbf{T}'_\alpha$ have the same form as (4.130)–(4.133), (4.136)–(4.138). Similarly, reduced inequality with these primed quantities has the form (4.89) because this was obtained from an invariant form of balances (4.95)–(4.102) (cf. property of mixture invariance of balances in Sect. 4.4). Therefore, the great inequality may be constructed with primed quantities but otherwise is the same as (4.139), and because the arguments of the admissibility principle may be again used here analogously, all the results in Sect. 4.5 may be obtained also for primed quantities. Namely, zero results (4.146)–(4.149) are valid in accord with the assumed mixture invariance of all quantities here (see above and (4.113)), and the results (4.150), (4.151), (4.145) are valid with the corresponding primed quantities $y_\alpha^{(0)\prime}$,(4.237), (4.238), (4.239), (4.240). Therefore, constitutive equations (4.231), (4.232), (4.233) are obtained as analogues of (4.157), (4.158),(4.159) for primed quantities; the primed constitutive equation (4.156) is trivial by mixture invariance of rates r_β.

From mixture invariance (4.230) of $y = u, s, f$ (noted at the beginning of proof), the mixture invariance of result (4.164) also follows (in accord with that of (4.145)). By the same arguments, we can see that chemical potentials g_α (4.161) are mixture invariant and therefore $\zeta_\alpha = 0$ for this $y_\alpha = g_\alpha$ as we have noted in (4.227).

By zero value (4.149), we obtain from (4.242) constitutive equation for (primed) heat flux (4.234) (cf. (4.166)) and from (4.150) for primed quantities and chemical potential we obtain (4.241). With its original form (4.165) and (4.226), we obtain the transformation (4.239) again.

Definitions $\Delta p'_\alpha$ (4.162), ϑ'_β (4.163) for primed quantities are now mixture invariant because of (4.226) (for f_α, s_α), (4.240), (4.237), (4.238) and the mixture invariance of g_α

$$\Delta p'_\alpha \equiv \rho'_\alpha (g'_\alpha - f'_\alpha) - p'_\alpha = \rho_\alpha g_\alpha - \rho_\alpha (f_\alpha + \varphi_\alpha) - (p_\alpha - \rho_\alpha \varphi_\alpha) = \Delta p_\alpha$$

$$\begin{aligned} \vartheta'_\beta \equiv{}& \lambda'_\beta / T' + \xi'_\beta - \rho'_\beta \frac{\partial \hat{f}'_\beta}{\partial T'} - \rho'_\beta s'_\beta = \lambda_\beta / T + \rho_\beta \eta_\beta + \xi_\beta + \rho_\beta \frac{\partial \hat{\varphi}_\beta}{\partial T} - \rho_\beta \frac{\partial (\hat{f}_\beta + \hat{\varphi}_\beta)}{\partial T} \\ &- \rho_\beta (s_\beta + \eta_\beta) = \vartheta_\beta \end{aligned}$$

Finally it follows that σ, Π_0, Π_1, Π_2 are mixture invariant because all expressions for entropy productions are obtained for primed quantities are the same as (4.167)–(4.171) and contain the mixture invariant quantities only (see (4.113) and below, see also definitions (4.124), (4.88)).

Primed thermodynamic pressures are defined now, instead of (4.186), (4.187) (we recall that form of definitions is mixture invariant), as

$$P'_\alpha \equiv p'_\alpha + \Delta p'_\alpha \qquad \alpha = 1, \ldots, n \tag{4.243}$$

$$P' \equiv \sum_{\alpha=1}^{n} P'_\alpha \tag{4.244}$$

These definitions give, by mixture invariance of Δp_α above and (4.240) for p_α, the transformation (4.229) for partial thermodynamic pressures and mixture invariance of total thermodynamic pressure $P' = P$ (see (4.244), (4.229), (4.225) (cf. (4.107)).

It remains to show ζ_α (4.227) for $y = v, h$. Definitions of partial volumes (4.188) and enthalpies (4.189) for primed quantities are now ($\alpha = 1, \ldots, n$)

$$v'_\alpha \equiv P'_\alpha/(\rho'_\alpha P') = (P_\alpha - \rho_\alpha \varphi_\alpha)/(\rho_\alpha P) = v_\alpha - \varphi_\alpha/P \tag{4.245}$$

$$h'_\alpha \equiv u'_\alpha + P'v'_\alpha = u_\alpha + \varepsilon_\alpha + P(v_\alpha - \varphi_\alpha/P) = h_\alpha + T\eta_\alpha \tag{4.246}$$

where transformations follow by (4.229), (4.228) and (4.226), (4.227) for u_α (cf. (4.108), (4.106), (4.113)). These give the remaining values of ζ_α in (4.227). The mixture invariance of corresponding (and in fact also all) total thermodynamic (primed) quantities y' (4.230) follows from (4.225) (cf. (4.116), (4.90), (4.190), (4.191), (4.192), (4.211)), namely

$$y' \equiv \sum_{\alpha=1}^{n} w_\alpha y'_\alpha = \sum_{\alpha=1}^{n} w_\alpha y_\alpha + (1/\rho) \sum_{\alpha=1}^{n} \rho_\alpha \zeta_\alpha = y \tag{4.247}$$

Q.E.D.

According to our programme (see below (4.221)), it has been shown that all hitherto obtained results of Sects. 4.5 and 4.6 of a linear fluid mixture are valid for primed quantities (or to be the same for mixture invariant quantities). We show such validity for the remaining results.

Because molar masses and stoichiometric coefficients may be considered as mixture invariant, it is obvious that molar chemical potentials (4.172) and chemical affinities (4.176) are mixture invariant. Obviously, also the properties from the end of Sect. 4.5, (4.180)–(4.182) remain valid, including also special cases (4.183), (4.184).

To show it for the remaining formulae and quantities from Sect. 4.6 we use the primed quantities from Proposition 23.1 in the definitions. Some of them are valid trivially by the mixture invariance of the quantities in them (like Gibbs equations (4.201)–(4.206), (4.207), (4.195), (4.197)–(4.199) etc.), others, like (4.193), (4.194), (4.196), may be easily verified by previous results; we do it here with (4.200), (4.208), (4.209):

The validity of (4.200) for primed quantities follows because

$$\begin{aligned}
P'_\alpha &= \sum_{\gamma=1}^{n} \rho'_\alpha \rho'_\gamma \frac{\partial \hat{f}'_\gamma}{\partial \rho'_\alpha} = \sum_{\gamma=1}^{n} \rho_\alpha \rho_\gamma \frac{\partial(\hat{f}_\gamma + \hat{\varphi}_\gamma)}{\partial \rho_\alpha} \\
&= P_\alpha + \sum_{\gamma=1}^{n} \rho_\alpha \rho_\gamma \frac{\partial \hat{\varphi}_\gamma}{\partial \rho_\alpha} = P_\alpha + \rho_\alpha \frac{\partial \sum_{\gamma=1}^{n} \rho_\gamma \hat{\varphi}_\gamma}{\partial \rho_\alpha} - \sum_{\gamma=1}^{n} \rho_\alpha \varphi_\gamma \frac{\partial \rho_\gamma}{\partial \rho_\alpha} \\
&= P_\alpha - \rho_\alpha \varphi_\alpha
\end{aligned}$$

where (4.225) were used and this is indeed (4.229).

Inserting from (4.239), (4.229), (4.233) into (4.208) we have

$$\begin{aligned}
&\sum_{\gamma=1}^{n} \omega'_{\beta\gamma}\, \mathrm{d}\rho_\gamma + \sum_{\gamma=1}^{n} \frac{\partial(\rho_\beta \hat{\varphi}_\beta)}{\partial \rho_\gamma}\, \mathrm{d}\rho_\gamma \\
&\qquad = \mathrm{d}P'_\beta + \mathrm{d}(\rho_\beta \varphi_\beta) - \rho_\beta\, \mathrm{d}g_\beta + \frac{\partial \rho_\beta \hat{f}'_\beta}{\partial T}\, \mathrm{d}T - \frac{\partial \rho_\beta \hat{\varphi}_\beta}{\partial T}\, \mathrm{d}T
\end{aligned}$$

Calculating $\mathrm{d}(\rho_\beta \varphi_\beta)$ with function (4.228) and using the mixture invariance of g_α, ρ_α, T we obtain (4.208) in primed quantities:

$$\sum_{\gamma=1}^{n} \omega'_{\beta\gamma}\, \mathrm{d}\rho_\gamma = \mathrm{d}P'_\beta - \rho_\beta\, \mathrm{d}g_\beta + \rho_\beta \frac{\partial \hat{f}'_\beta}{\partial T}\, \mathrm{d}T \qquad \beta = 1, \ldots, n-1 \tag{4.248}$$

Similarly, inserting (4.239), (4.229), (4.233) into (4.209) we have

$$\begin{aligned}
\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \omega'_{\beta\gamma}\, \mathrm{d}\rho_\gamma + \sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \frac{\partial \rho_\beta \hat{\varphi}_\beta}{\partial \rho_\gamma}\, \mathrm{d}\rho_\gamma &= -\,\mathrm{d}P'_n - \mathrm{d}(\rho_n \varphi_n) + \rho_n\, \mathrm{d}g_n - \frac{\partial \rho_n \hat{f}'_n}{\partial T}\, \mathrm{d}T \\
&\quad + \frac{\partial \rho_n \hat{\varphi}_n}{\partial T}\, \mathrm{d}T
\end{aligned}$$

which with (4.225) (for $\zeta_\alpha = \varphi_\alpha$) gives (4.209) in primed quantities:

$$\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \omega'_{\beta\gamma}\, \mathrm{d}\rho_\gamma = -\mathrm{d}P'_n + \rho_n\, \mathrm{d}g_n - \rho_n \frac{\partial \hat{f}'_n}{\partial T}\, \mathrm{d}T \tag{4.249}$$

A change of independent variables from mixture invariant T, ρ_γ to mixture invariant T, P, w_β, may be done also for primed quantities, specifically for (4.224) $\zeta_\alpha = \tilde{\zeta}_\alpha(T, P, w_\beta)$ and therefore (4.216) is valid also for primed partial thermodynamic quantities y'_α (see (4.226))

$$y'_\alpha = \tilde{y}_\alpha(T, P, w_\beta) + \tilde{\zeta}_\alpha(T, P, w_\beta) \equiv \tilde{y}'_\alpha(T, P, w_\beta) \qquad \alpha = 1, \ldots, n \tag{4.250}$$

Relation (4.217) is valid for primed quantities

$$y' = \tilde{y}'(T, P, w_\beta) = y = \tilde{y}(T, P, w_\beta) \tag{4.251}$$

because of the mixture invariance of all quantities. Inserting from these results into (4.218) we have

$$\frac{\partial \tilde{y}'}{\partial w_\beta} = y'_\beta - \zeta_\beta - y'_n + \zeta_n + \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}'_\alpha}{\partial w_\beta} - \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{\zeta}_\alpha}{\partial w_\beta} \tag{4.252}$$

But identity (4.225) (divided by ρ) $\sum_{\alpha=1}^{n} w_\alpha \zeta_\alpha = 0$ may be understood as a function of T, P, w_β (see (4.23)) equal to zero identically; its derivative is therefore also zero

$$\frac{\partial \sum_{\alpha=1}^{n} w_\alpha \tilde{\zeta}_\alpha}{\partial w_\beta} = 0 \qquad \beta = 1, \ldots, n-1 \tag{4.253}$$

and from (4.253) it follows

$$\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{\zeta}_\alpha}{\partial w_\beta} = \frac{\partial \sum_{\alpha=1}^{n} w_\alpha \tilde{\zeta}_\alpha}{\partial w_\beta} - \sum_{\alpha=1}^{n} \zeta_\alpha \frac{\partial w_\alpha}{\partial w_\beta} = -\sum_{\eta=1}^{n-1} \zeta_\eta \frac{\partial w_\eta}{\partial w_\beta} - \zeta_n \frac{\partial w_n}{\partial w_\beta}$$
$$= -\zeta_\beta - \zeta_n \frac{\partial (1 - \sum_{\eta=1}^{n-1} w_\eta)}{\partial w_\beta} = -\zeta_\beta + \zeta_n$$

Therefore inserting this in the previous Eq. (4.252), we obtain (4.218) in primed quantities

$$\frac{\partial \tilde{y}'}{\partial w_\beta} = y'_\beta - y'_n + \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}'_\alpha}{\partial w_\beta} = \frac{\partial \tilde{y}}{\partial w_\beta} \tag{4.254}$$

which may be obtained also by differentiation of (4.230). Using (4.254) and differentials from (4.230), (4.251) analogously as in deduction (4.219) we obtain its analogue in primed quantities

$$\frac{\partial \tilde{y}}{\partial T} \mathrm{d}T + \frac{\partial \tilde{y}}{\partial P} \mathrm{d}P - \sum_{\alpha=1}^{n} w_\alpha \,\mathrm{d}y'_\alpha + \sum_{\beta=1}^{n-1} \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}'_\alpha}{\partial w_\beta} \mathrm{d}w_\beta = 0 \tag{4.255}$$

Ultimately (4.220) and Gibbs-Duhem equations (4.221) for chemical potentials remain unchanged because of their mixture invariance. Again, Gibbs-Duhem equations for all primed y'_α (i.e. zero value of the sum in (4.254)) are not generally valid.

All the results with primed quantities (including those in Proposition 23.1) starting with arbitrary functions (4.222), (4.223) therefore fulfil all results of mixture model achieved in Sect. 4.2–4.6.

From a physical point of view, it seems that measurable quantities are mixture invariant (cf. end of Sect. 4.4). Such are the properties of mixture like y, $\mathbf{T}$ (see (4.94), (4.236), (4.240), (4.225)) but also the chemical potentials g_α. Note that also heat flux is transformed as (4.118) (with functions (4.223)) and therefore heat flux is mixture invariant in a non-diffusing mixture (all $\mathbf{u}_\beta = \mathbf{o}$) in accord with its measurability. But heat flux is mixture non-invariant in a diffusing mixture, consistently with our expectation of difficulties in surface exchange (of masses) of different constituents with different velocities together with heat. We note that all formulations of heat flux used in linear irreversible thermodynamics [1–4, 120] (cf. Rems. 11 in this chapter, 14 in Chap. 2) are contained (by arbitrariness of η_β) in expression (4.118) for heat flux in a diffusing mixture.

Now we are ready to start the last part of our programme (outlined below (4.221)): by the following Proposition 23.2 we achieve the Gibbs-Duhem equations for all primed quantities y'_α because then, as we shall see, we obtain the complete accord of thermodynamic properties with classical thermodynamics of mixtures.

Proposition 23.2 (*general validity of Gibbs-Duhem equations* [56, 59, 139]). For every partial thermodynamic quantity y_α (4.210) of linear fluid mixture which may be expressed by (4.216) as $y_\alpha = \tilde{y}_\alpha(T, P, w_\beta)$ there are corresponding primed quantities (4.226), expressible as $y'_\alpha = \tilde{y}'_\alpha(T, P, w_\beta)$ (4.250), introduced and satisfying hypotheses of Proposition 23.1 which fulfil the Gibbs-Duhem equations

$$\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}'_\alpha}{\partial w_\beta} = 0 \qquad \beta = 1, \ldots, n-1 \tag{4.256}$$

Proof We begin (as in Proposition 23.1) with some $y_\alpha = u_\alpha, s_\alpha$ which may be expressed by (4.216) as $y_\alpha = \tilde{y}_\alpha(T, P, w_\beta)$. Based on them we now propose the primed quantities $y'_\alpha = u'_\alpha, s'_\alpha$ by (4.250) where for functions $\tilde{\zeta}_\alpha(T, P, w_\beta)$, $\zeta_\alpha = \varepsilon_\alpha, \eta_\alpha$, we choose the following special functions based on starting $\tilde{y}_\alpha(T, P, w_\beta)$ (we follow [59, Teor. 8.1, choice (8.36)]; another version is in [56, 139])

$$\begin{aligned} \zeta_n &= -\sum_{\beta=1}^{n-1}\sum_{\gamma=1}^{n} w_\beta w_\gamma \frac{\partial \tilde{y}_\gamma}{\partial w_\beta} \\ \zeta_\delta &= \sum_{\gamma=1}^{n} w_\gamma \frac{\partial \tilde{y}_\gamma}{\partial w_\delta} + \zeta_n \qquad \delta = 1, \ldots, n-1 \end{aligned} \tag{4.257}$$

This choice should have the basic property (4.225). Indeed

$$\sum_{\alpha=1}^{n} \rho_\alpha \zeta_\alpha = \sum_{\delta=1}^{n-1} \rho_\delta \zeta_\delta + \rho_n \zeta_n$$

$$= \rho \sum_{\delta=1}^{n-1} \sum_{\gamma=1}^{n} w_\delta w_\gamma \frac{\partial \tilde{y}_\gamma}{\partial w_\delta} + \rho \sum_{\delta=1}^{n-1} w_\delta \zeta_n + \rho w_n \zeta_n = -\rho \zeta_n + \rho \zeta_n = 0 \tag{4.258}$$

The relations (4.257) are then also valid for the remaining $y_\alpha = f_\alpha, g_\alpha, v_\alpha, h_\alpha$ because the corresponding ζ_α are combinations of ε_α, η_α, see (4.227) (for g_α trivially, see (4.221)). Indeed, by (4.257) for $y_\alpha = u_\alpha, s_\alpha$, we have for $y_\alpha = f_\alpha$ by (4.86)

$$\frac{\partial \tilde{f}_\gamma}{\partial w_\delta} = \frac{\partial \tilde{u}_\gamma}{\partial w_\delta} - T \frac{\partial \tilde{s}_\gamma}{\partial w_\delta} \tag{4.259}$$

which inserting into the right-hand side of $(4.257)_1$ gives by (4.106)

$$-\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} w_\beta w_\gamma \frac{\partial \tilde{f}_\gamma}{\partial w_\beta} = \varepsilon_n - T\eta_n = \varphi_n \tag{4.260}$$

Similarly, inserting into r.h.s. of $(4.257)_2$ we have by (4.106)

$$\sum_{\gamma=1}^{n} w_\gamma \frac{\partial \tilde{f}_\gamma}{\partial w_\delta} + \varphi_n = \varepsilon_\delta - \varepsilon_n - T(\eta_\delta - \eta_n) + \varphi_n = \varphi_\delta \tag{4.261}$$

The Gibbs-Duhem equation (4.221) gives $\zeta_\alpha = 0$ for (4.257) with $y_\alpha = g_\alpha$ (where $\alpha = \delta, n$). Inserting here from (4.194) we have by (4.260), (4.261) $0 = \varphi_n - P \sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} w_\beta w_\gamma \frac{\partial \tilde{v}_\gamma}{\partial w_\beta}$ which is $(4.257)_1$ (for $y_\alpha = v_\alpha$) with $\zeta_n = -\varphi_n/P$ and (inserting (4.194) into $(4.257)_2$ for $y_\alpha = g_\alpha$) $0 = \sum_{\gamma=1}^{n} w_\gamma \frac{\partial \tilde{f}_\gamma}{\partial w_\delta} + P \sum_{\gamma=1}^{n} w_\gamma \frac{\partial \tilde{v}_\gamma}{\partial w_\delta}$, i.e. $\sum_{\gamma=1}^{n} w_\gamma \frac{\partial \tilde{v}_\gamma}{\partial w_\delta} = -\varphi_\delta/P + \varphi_n/P$ from which $\zeta_\delta = -\varphi_\delta/P$; therefore result (4.257) follows for $y_\alpha = v_\alpha$.

Ultimately, we obtain by inserting (4.189) in the right hand side of (4.257) for $y_\alpha = h_\alpha$ using (4.257) for $y_\alpha = u_\alpha, v_\alpha$ and (4.106)

$$-\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} w_\beta w_\gamma \frac{\partial \tilde{h}_\gamma}{\partial w_\beta} = \varepsilon_n + P(-\varphi_n/P) = T\eta_n$$

$$\sum_{\gamma=1}^{n} w_\gamma \frac{\partial \tilde{h}_\gamma}{\partial w_\delta} + T\eta_n = \varepsilon_\delta - \varepsilon_n + P(-\varphi_\delta/P + \varphi_n/P) + T\eta_n = T\eta_\delta$$

which is for $y_\alpha = h_\alpha$ (4.227) and therefore (4.257).

Now we use the proposed choice (4.257) to show that partial thermodynamic quantities y'_α (4.250) with ζ_α given by (4.257) fulfil Gibbs-Duhem equations (4.256) for all of them (and not for chemical potentials only). Indeed, by (4.250) with (4.257) we have

$$\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}'_\alpha}{\partial w_\beta} = \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}_\alpha}{\partial w_\beta} + \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{\zeta}_\alpha}{\partial w_\beta} \tag{4.262}$$

Using identity (4.253) with (4.23), (4.257)$_2$

$$0 = \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{\zeta}_\alpha}{\partial w_\beta} + \sum_{\delta=1}^{n-1} \zeta_\delta \frac{\partial w_\delta}{\partial w_\beta} + \zeta_n \frac{\partial (1 - \sum_{\delta=1}^{n-1} w_\delta)}{\partial w_\beta} = \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{\zeta}_\alpha}{\partial w_\beta} + \zeta_\beta - \zeta_n$$
$$= \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{\zeta}_\alpha}{\partial w_\beta} + \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}_\alpha}{\partial w_\beta}$$

Inserting this into (4.262) we obtain (4.256)

$$\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}'_\alpha}{\partial w_\beta} = 0 \qquad \beta = 1, \ldots, n-1$$

i.e. Gibbs-Duhem equation (4.256) are valid for all such y'_α. Q.E.D.

Therefore, for such primed thermodynamic quantities, we have not only all the results of our theory of primed thermodynamic quantities but also the Gibbs-Duhem equations for all of them are valid.

In the following, we will *assume* that such primed thermodynamic quantities were achieved and hereafter we do *not use the prime* to denote these quantities. Therefore, all results of Sects. 4.2–4.6 (up to (4.217)) are valid but moreover also Gibbs-Duhem equations are valid for all partial thermodynamic quantities (i.e. (4.256) written without primes)

$$\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}_\alpha}{\partial w_\beta} = 0 \qquad \beta = 1, \ldots, n-1 \tag{4.263}$$

As a result of the validity of (4.263), we obtain from (4.218), (4.219) (in fact (4.254), (4.255) without primes) for all y_α another form of Gibbs-Duhem equations

$$\frac{\partial \tilde{y}}{\partial T} \, \mathrm{d}T + \frac{\partial \tilde{y}}{\partial P} \, \mathrm{d}P - \sum_{\alpha=1}^{n} w_\alpha \, \mathrm{d}y_\alpha = 0 \tag{4.264}$$

and

$$\frac{\partial \tilde{y}}{\partial w_\beta} = y_\beta - y_n \qquad \beta = 1, \ldots, n-1 \tag{4.265}$$

Moreover, from (4.265), (4.206), (4.211) we obtain the classical relationships (for them the general Gibbs-Duhem equation (4.263) are necessary)

$$\frac{\partial \tilde{g}_\alpha}{\partial T} = -s_\alpha \qquad \alpha = 1, \ldots, n \tag{4.266}$$

$$\frac{\partial \tilde{g}_\alpha}{\partial P} = v_\alpha \qquad \alpha = 1, \ldots, n \tag{4.267}$$

Indeed, to prove (4.266), we obtain from Gibbs equation (4.206) and Gibbs-Duhem Eq. (4.263)

$$\frac{\partial(\tilde{g}_\beta - \tilde{g}_n)}{\partial T} = -\frac{\partial \tilde{s}}{\partial w_\beta} = -(s_\beta - s_n) \quad \beta = 1, \ldots, n-1 \tag{4.268}$$

From Gibbs equation (4.206) it follows also $\partial \tilde{g}/\partial T = -s$ which with (4.211), (4.23) gives

$$\begin{aligned}\frac{\partial(\sum_{\beta=1}^{n-1} w_\beta \tilde{g}_\beta + (1 - \sum_{\beta=1}^{n-1} w_\beta)\tilde{g}_n)}{\partial T} &= \sum_{\beta=1}^{n-1} w_\beta \frac{\partial(\tilde{g}_\beta - \tilde{g}_n)}{\partial T} + \frac{\partial \tilde{g}_n}{\partial T} = -\sum_{\alpha=1}^{n} w_\alpha s_\alpha \\ &= -\sum_{\beta=1}^{n-1} w_\beta (s_\beta - s_n) - s_n\end{aligned}$$

Because of (4.268), we obtain (4.266) for $\alpha = n$ and therefore also (4.266) for remaining $\beta = 1, \ldots, n-1$.

Proof of (4.267) may be peformed quite analogously (using differentiation according to pressure instead of temperature).

Results (4.265) and (4.211) permit to obtain partial specific thermodynamic quantities y_α (fulfilling Gibbs-Duhem equations (4.263) of course) from specific thermodynamic quantities $y = \tilde{y}(T, P, w_\beta)$ of the mixture (measurable in accord with their mixture invariance) and their dependence on composition w_β as follows

$$y_n = y - \sum_{\beta=1}^{n-1} w_\beta \frac{\partial \tilde{y}}{\partial w_\beta} \tag{4.269}$$

$$y_\beta = y_n + \frac{\partial \tilde{y}}{\partial w_\beta} \qquad \beta = 1, \ldots, n-1 \tag{4.270}$$

While (4.270) is (4.265), Eq. (4.269) follows by multiplication of (4.270) with w_β, by summation through $\beta = 1, \ldots, n-1$ and using (4.23), (4.211).

Ultimately we note that using functions (4.213) (see (4.216), (4.214), (4.21), (4.22)), we have

$$g_\alpha = \tilde{g}_\alpha(T, P, w_\beta) = \tilde{g}_\alpha(T, \hat{P}(T, \rho_\gamma), \rho_\beta / \sum_{\gamma=1}^{n} \rho_\gamma) = \hat{g}_\alpha(T, \rho_\gamma) \tag{4.271}$$

Therefore $\partial\hat{g}_\alpha/\partial T = \partial\tilde{g}_\alpha/\partial T + (\partial\tilde{g}_\alpha/\partial P)(\partial\hat{P}/\partial T)$ and this gives by (4.266), (4.267), (4.194)

$$-s_\alpha = \frac{\partial\hat{g}_\alpha}{\partial T} - v_\alpha\frac{\partial\hat{P}}{\partial T} = \frac{\partial\hat{f}_\alpha}{\partial T} + P\frac{\partial\hat{v}_\alpha}{\partial T} \qquad \alpha = 1,\ldots,n \tag{4.272}$$

Therefore, a relation analogical to (4.164) for partial f_α does not follow (but this is possible in special cases, see (4.426)).

Analogues of (4.269), (4.270) for expressing the partial specific quantities through mixture properties in independent variables temperature and densities (4.213) are

- for partial specific volumes v_α

$$v_\alpha = (\frac{\partial\hat{P}}{\partial\rho_\alpha})/\left(\sum_{\gamma=1}^{n}\rho_\gamma\frac{\partial\hat{P}}{\partial\rho_\gamma}\right) \qquad \alpha = 1,\ldots,n \tag{4.273}$$

  where $P = \hat{P}(T,\rho_\gamma)$ is the (whole) thermodynamic pressure as the function of temperature and densities of all constituents.
- for remaining thermodynamic partial specific quantities $y_\alpha = u_\alpha, s_\alpha, f_\alpha, h_\alpha, g_\alpha$

$$y_\alpha = y + \rho\left(\frac{\partial\hat{y}}{\partial\rho_\alpha} - v_\alpha\sum_{\gamma=1}^{n}\rho_\gamma\frac{\partial\hat{y}}{\partial\rho_\gamma}\right) \qquad \alpha = 1,\ldots,n \tag{4.274}$$

  where v_α is given by (4.273) and the specific thermodynamic quantities of the mixture $y = \hat{y}(T,\rho_\gamma) = u, s, f, h, g$ are functions of temperature and densities of all constituents.

We prove (4.273), (4.274) using (4.269), (4.270) calculating $\partial\tilde{y}/\partial w_\beta$ appropriately. With (4.215), definition $\breve{P}$ (4.214), (4.195) we have

$$\frac{\partial\tilde{v}}{\partial w_\beta} = -\frac{\partial\breve{P}}{\partial w_\beta}/\frac{\partial\breve{P}}{\partial v} = \left(\frac{\partial\hat{P}}{\partial\rho_\beta} - \frac{\partial\hat{P}}{\partial\rho_n}\right)/\left(\sum_{\gamma=1}^{n}\rho_\gamma\frac{\partial\hat{P}}{\partial\rho_\gamma}\right) \qquad \beta = 1,\ldots,n-1 \tag{4.275}$$

because

$$\frac{\partial\breve{P}}{\partial v} = -\rho\sum_{\gamma=1}^{n}\rho_\gamma\frac{\partial\hat{P}}{\partial\rho_\gamma}$$

$$\frac{\partial\breve{P}}{\partial w_\beta} = \rho\frac{\partial\hat{P}}{\partial\rho_\beta} - \rho\frac{\partial\hat{P}}{\partial\rho_n} \qquad \beta = 1,\ldots n-1$$

Similarly, for the remaining $y = u, s, f, h, g$, we can define functions $y = \breve{y}(T, v, w_\beta)$ by

$$y = \hat{y}(T, \rho_\gamma) = \hat{y}(T, \frac{w_1}{v}, \ldots, \frac{w_{n-1}}{v}, \frac{1 - \sum_{\beta=1}^{n-1} w_\beta}{v}) \equiv \check{y}(T, v, w_1, \ldots, w_{n-1})$$
$$= \check{y}(T, \tilde{v}(T, P, w_\beta), w_\beta) = \tilde{y}(T, P, w_\beta) \tag{4.276}$$

From this we obtain analogously

$$\frac{\partial \tilde{y}}{\partial w_\eta} = \frac{\partial \check{y}}{\partial w_\eta} + \frac{\partial \check{y}}{\partial v}\frac{\partial \tilde{v}}{\partial w_\eta} = \rho(\frac{\partial \hat{y}}{\partial \rho_\eta} - \frac{\partial \hat{y}}{\partial \rho_n}) - \rho(v_\eta - v_n)\sum_{\gamma=1}^{n} \rho_\gamma \frac{\partial \hat{y}}{\partial \rho_\gamma} \qquad \eta = 1, \ldots n-1 \tag{4.277}$$

because (4.195), (4.265) and

$$\frac{\partial \check{y}}{\partial v} = -\rho \sum_{\gamma=1}^{n} \rho_\gamma \frac{\partial \hat{y}}{\partial \rho_\gamma}$$
$$\frac{\partial \check{y}}{\partial w_\eta} = \rho(\frac{\partial \hat{y}}{\partial \rho_\eta} - \frac{\partial \hat{y}}{\partial \rho_n}) \qquad \eta = 1, \ldots n-1$$

Inserting (4.275), (4.277) into (4.269), (4.270) (for $y = v$ and those remaining respectively) we obtain after rearrangement, the results (4.273), (4.274).

Result (4.273) gives that expressions $(\partial \hat{P}/\partial \rho_\alpha)/v_\alpha$ and therefore also (multiplying by $1/P$ and using (4.188) or (4.278)) $(\rho_\alpha/P_\alpha)(\partial \hat{P}/\partial \rho_\alpha)$ are the same for all constituents $\alpha = 1, \ldots, n$, cf. [61, Eq. 2.11]. This will be used in the next Sect. 4.8, see (4.415).

Application of (4.269), (4.270) on a specific volume (or mixture density ρ) permits to calculate partial specific volume v_α and therefore, by (4.188), to calculate partial thermodynamic pressures (see [140])

$$P_\alpha = \rho_\alpha v_\alpha P \qquad \alpha = 1, \ldots, n \tag{4.278}$$

which fulfil Dalton's law (4.187) generally. Note that $\rho_\alpha v_\alpha = c_\alpha M_\alpha v_\alpha$ in molar units (see below). In a mixture of ideal gases, $\rho_\alpha v_\alpha$ is the molar fraction and (4.278) is the classical Dalton law, see (4.423), (4.424).

Relations (4.217) are specifically (with the use of (4.195))

$$u = \tilde{u}(T, P, w_\beta), \qquad s = \tilde{s}(T, P, w_\beta), \tag{4.279}$$

$$v = \tilde{v}(T, P, w_\beta) \qquad \text{or} \qquad \rho = \tilde{\rho}(T, P, w_\beta), \tag{4.280}$$

From these relations and Gibbs equation (4.203), we obtain

$$\mathrm{d}s = \frac{1}{T}\,\mathrm{d}u - \frac{P}{T\rho^2}\,\mathrm{d}\rho - \sum_{\beta=1}^{n-1} \frac{(g_\beta - g_n)}{T}\,\mathrm{d}w_\beta = (1/T)\left(\frac{\partial \tilde{u}}{\partial T} - (P/\rho^2)\frac{\partial \tilde{\rho}}{\partial T}\right)\mathrm{d}T$$

$$+ (1/T)\left(\frac{\partial \tilde{u}}{\partial P} - (P/\rho^2)\frac{\partial \tilde{\rho}}{\partial P}\right) \mathrm{d}P$$
$$+ \sum_{\beta=1}^{n-1}\left(\frac{1}{T}\frac{\partial \tilde{u}}{\partial w_\beta} - \frac{P}{T\rho^2}\frac{\partial \tilde{\rho}}{\partial w_\beta} - \frac{(g_\beta - g_n)}{T}\right) \mathrm{d}w_\beta \tag{4.281}$$

Using the integrability conditions of (4.280), (4.279), namely $\partial^2\tilde{s}/\partial P\partial T = \partial^2\tilde{s}/\partial T\partial P$ we obtain, after some calculation

$$\frac{\partial \tilde{u}}{\partial P} = (T/\rho^2)\frac{\partial \tilde{\rho}}{\partial T} + (P/\rho^2)\frac{\partial \tilde{\rho}}{\partial P} \tag{4.282}$$

which is for the mixture an analogue of (3.209).

In classical thermodynamics of mixtures, the special case of the *uniform* (or *homogeneous*) *mixture* (i.e. without gradients of properties, cf. Sect. 2.4) is often studied. Denoting here by Y the following *extensive* quantities: volume V, entropy S, internal energy U, free energy F, Gibbs energy G and enthalpy H, we have the following relations between the extensive functions $Y = \check{Y}(T, P, m_\gamma), \gamma = 1, \ldots, n$ and the corresponding total specific thermodynamic quantities $y = \tilde{y}(T, P, w_\delta)$, $\delta = 1, \ldots, n-1$

$$Y = my = (\sum_{\gamma=1}^{n} m_\gamma)\tilde{y}(T, P, m_\delta/(\sum_{\gamma=1}^{n} m_\gamma)) \equiv \check{Y}(T, P, m_1, \ldots, m_n) \tag{4.283}$$

Here m is the mass of the uniform body which is the sum of masses of all constituents m_γ (cf. Sect. 2.4)

$$m = \sum_{\gamma=1}^{n} m_\gamma \tag{4.284}$$

and

$$\rho_\gamma = m_\gamma/V \qquad \gamma = 1, \ldots, n \tag{4.285}$$

$$w_\gamma = m_\gamma/m \qquad \gamma = 1, \ldots, n \tag{4.286}$$

((4.285) follows from the physical meaning of ρ_γ and (4.286) from (4.21), (4.22), (4.285), (4.284)).

Relations (4.283)–(4.286) in uniform mixture permit to express the partial specific thermodynamic quantities from extensive (4.283) as ([59], i.e. as an analogue of the molar “classical” definition [138, 141])

$$\frac{\partial \check{Y}}{\partial m_\alpha} = y_\alpha \qquad \alpha = 1, \ldots, n \tag{4.287}$$

(therefore they are also uniform analogue of (4.269), (4.270)). Indeed, (4.283) gives

$$\begin{aligned}\frac{\partial \check{Y}}{\partial m_\alpha} &= y + m\sum_{\beta=1}^{n-1}\frac{\partial \tilde{y}}{\partial w_\beta}\left(\frac{1}{m}\frac{\partial m_\beta}{\partial m_\alpha} - \frac{m_\beta}{m^2}\frac{\partial \sum_{\gamma=1}^{n} m_\gamma}{\partial m_\alpha}\right)\\ &= y + \sum_{\beta=1}^{n-1}\frac{\partial \tilde{y}}{\partial w_\beta}\delta_{\beta\alpha} - \sum_{\beta=1}^{n-1} w_\beta \frac{\partial \tilde{y}}{\partial w_\beta}\end{aligned}$$

which is the result (4.287) if we use (4.269), (4.270) because Kronecker delta $\delta_{\beta\alpha} \equiv \frac{\partial m_\beta}{\partial m_\alpha}$ here has the property $\delta_{\beta n} = 0,\ \beta = 1, \ldots, n-1$.

Examples of (4.287) are (2.100) and also Gibbs and Gibbs-Duhem equations (2.98), (2.104) are uniform analogues of (4.206), (4.207).

These and all previous results of thermodynamic mixture which also fulfil Gibbs-Duhem equations (4.263) show the complete agreement with the classical thermodynamic of mixtures but moreover all these relations are valid much more generally. Namely, they are valid in this material model—linear fluid mixture—in all processes whether equilibrium or not. Linear irreversible thermodynamics [1–4], which studies the same model, postulates this agreement as the *principle of local equilibrium*. Here in rational thermodynamics, this property is proved in this special model and it cannot be expected to be valid in a more general model. We stress the difference: in the cases when (4.184) is not valid—e.g. in a chemically reacting mixture out of equilibrium—the thermodynamic pressures P, P_α need not be the same as the measured pressure (as e.g. $\sum_{\alpha=1}^{n} p_\alpha$) and therefore applications of these thermodynamic formulae are not of much use in this case. This is probably the reason for difficulties in application of chemical thermodynamics in chemical kinetics, cf. Sect. 4.9.

Because of using these results in a non-equilibrium situation where momentum balances are important, specific variables have been used, while in (equilibrium) thermodynamics of mixtures molar units are prefered.

In chemical applications following molar quantities, based on molar mass (4.25), quantities ρ_α, ρ and w_α are introduced as analogues of "mass" quantities (in physical literature usually denoted as densities and concentrations). We define the *molar concentrations* c_α for constituents and for mixture c and the *molar fractions* x_α (cf. (4.25)) as follows ($\alpha = 1, \ldots, n$)

$$c_\alpha = \rho_\alpha / M_\alpha \tag{4.288}$$

$$c = \sum_{\alpha=1}^{n} c_\alpha \tag{4.289}$$

$$x_\alpha = c_\alpha / c \tag{4.290}$$

Because $M_\alpha > 0$ (constant molar mass), $\rho_\alpha > 0$ we have $c_\alpha > 0, c > 0$, $0 < x_\alpha < 1$ and

$$\sum_{\alpha=1}^{n} x_\alpha = 1 \tag{4.291}$$

$$w_\alpha = x_\alpha M_\alpha / M \tag{4.292}$$

where the average molar mass M (depending on composition) is defined by

$$M \equiv \sum_{\alpha=1}^{n} x_\alpha M_\alpha \tag{4.293}$$

and

$$\frac{1}{M} = \sum_{\alpha=1}^{n} \frac{w_\alpha}{M_\alpha} \tag{4.294}$$

$$1/c = vM \tag{4.295}$$

Equation (4.294) follows from (4.291), (4.292), and (4.295) asserts that the inverse of c is the molar volume Mv.

We now discuss relations between specific and molar description; as may be expected from the results above, the form of expressions remains if we change specific quantities y_α, y and mass fractions w_α by corresponding molar quantities $M_\alpha y_\alpha$, My and molar fractions x_α (cf., e.g. (4.172)). Such a simple change is understandable, because the application of molar quantities means in fact using different mass units for each constituent only. Change of specific and molar description may be sometimes simple, e.g. the expression for partial thermodynamic pressure (4.278) may be also written in a "molar" way as $P_\alpha = c_\alpha M_\alpha v_\alpha P$, the classical molar form of (4.287) which gives $M_\alpha y_\alpha$ follows using mols m_α / M_α in $\check{Y}$ (4.283), or inserting (4.292) into (4.211) we obtain its "molar analogue" $My = \sum_{\alpha=1}^{n} x_\alpha M_\alpha y_\alpha$. Sometimes the change is more complicated: multiplying "specific" Gibbs equation (4.206) (arranged with (4.23)) by M we obtain (using $\mathrm{d}w_\alpha = \frac{M_\alpha}{M}\,\mathrm{d}x_\alpha - \frac{x_\alpha M_\alpha}{M^2}\,\mathrm{d}M$ from (4.292))

$$\begin{aligned}
M\,\mathrm{d}g &= -Ms\,\mathrm{d}T + Mv\,\mathrm{d}P + \sum_{\alpha=1}^{n} Mg_\alpha\,\mathrm{d}w_\alpha \\
&= -Ms\,\mathrm{d}T + Mv\,\mathrm{d}P + \sum_{\alpha=1}^{n} g_\alpha M_\alpha\,\mathrm{d}x_\alpha - \sum_{\alpha=1}^{n} g_\alpha M_\alpha x_\alpha / M\,\mathrm{d}M
\end{aligned}$$

which is the "molar" Gibbs equation

$$\begin{aligned}
\mathrm{d}(Mg) &= -Ms\,\mathrm{d}T + Mv\,\mathrm{d}P + \sum_{\alpha=1}^{n} g_\alpha M_\alpha\,\mathrm{d}x_\alpha \\
&= -Ms\,\mathrm{d}T + Mv\,\mathrm{d}P + \sum_{\beta=1}^{n-1} (M_\beta g_\beta - M_n g_n)\,\mathrm{d}x_\beta
\end{aligned} \tag{4.296}$$

Another more complicated example is connected with a change of functions T, ρ_α or T, P, w_β to functions of T, c_α (see (4.288)) or T, P, x_β, $\beta, \delta = 1, \ldots, n-1$, e.g.

$$\begin{aligned} M_\alpha y_\alpha &= M_\alpha \tilde{y}_\alpha(T, P, w_\delta) = M_\alpha \tilde{y}_\alpha(T, P, x_\delta M_\delta/(M_n + \sum_{\delta=1}^{n-1} x_\delta(M_\delta - M_n))) \\ &\equiv \overline{M_\alpha y_\alpha}(T, P, x_\delta) \end{aligned} \tag{4.297}$$

where, according to (4.293), (4.291), $M = M_n + \sum_{\delta=1}^{n-1} x_\delta(M_\delta - M_n)$ was used.

With this M the expression (see (4.292))

$$\begin{aligned} \sum_{\alpha=1}^{n} x_\alpha \frac{\partial \overline{M_\alpha y_\alpha}}{\partial x_\beta} &= \sum_{\alpha=1}^{n} \frac{w_\alpha M}{M_\alpha} M_\alpha \sum_{\delta=1}^{n-1} \frac{\partial \tilde{y}_\alpha}{\partial w_\delta} \frac{\partial x_\delta M_\delta/(M_n + \sum_{\delta=1}^{n-1} x_\delta(M_\delta - M_n))}{\partial x_\beta} \\ &= M \sum_{\delta=1}^{n-1} \left(\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}_\alpha}{\partial w_\delta} \right) \frac{\partial x_\delta M_\delta/(M_n + \sum_{\delta=1}^{n-1} x_\delta(M_\delta - M_n))}{\partial x_\beta} \\ &= 0 \qquad \beta = 1, \ldots, n-1 \end{aligned} \tag{4.298}$$

is zero because of "specific" Gibbs-Duhem equation (4.263). But results (4.298) are Gibbs-Duhem equations in molar units.

From the "molar analogy" of (4.211) above we then see also that $My = \overline{My}(T, P, x_\delta)$ and from the derivative of it according to x_β we have (using molar Gibbs-Duhem equations (4.298))

$$\frac{\partial \overline{My}}{\partial x_\beta} = M_\beta y_\beta - M_n y_n \qquad \beta = 1, \ldots, n-1 \tag{4.299}$$

which is a molar analogue of (4.270). From these (by multiplication with x_β and summing) we obtain a molar analogue of (4.269)

$$M_n y_n = My - \sum_{\beta=1}^{n-1} x_\beta \frac{\partial \overline{My}}{\partial x_\beta} \tag{4.300}$$

By a similar means as in these examples, it may be proved that all thermodynamic relationships mentioned so far have their counterpart in molar units used in thermochemistry of mixtures.

At the end, we summarize the results of the model of a reacting mixture of fluids with linear transport properties from Sects. 4.5 and 4.6 (properties such as kinematics, stoichiometry and balances of mass, momentum and their moment, energy and entropy inequality are as in Sects. 4.2, 4.3 and 4.4). Constitutive equations, their properties and final form of entropy production are given in the end of Sect. 4.5 (from Eq. (4.156)), further thermodynamic quantities and properties are given at the beginning of Sect. 4.6 (up to Eq. (4.217)). But then we use only classical partial thermodynamic quantities fulfilling Gibbs-Duhem equations (Sect. 4.6 from Eq. (4.263)) which may be calculated by (4.269), (4.270) from corresponding properties of mixture; also corresponding molar description is presented. All these relations are valid in all equilibrium and non-equilibrium situations, (4.283)–(4.287) are valid in a uniform system.

Similarly as in preceding models (cf. Sect. 1.1, Rems. 6, 9, 8, 42 in Chaps. 2, 3, respectively) we exclude unusual situations by *regularity* conditions. Even though some exclusions are similar to those for pure materials and possible in (especially non-reacting) mixtures (e.g. disintegration of real fluid mixture to more phases which is outside of our models), the situation is much more complicated in chemical reacting mixtures because of non-linearity of chemical reaction rates in our model (transport phenomena are linear as in pure fluid of Sect. 3.7).

Regularity conditions (assumptions) 1, 2, 3 are chosen as follows:

1. Matrices of quadratic forms in (4.170), (4.180) are positive definite.
   This regularity means among others that transport coefficients in (4.181), (4.182) are only positive.
2. Matrices of derivatives $\partial \hat{r}_\alpha / \partial \rho_\gamma$ of function (4.156) ($\alpha, \gamma = 1, \ldots, n$) are regular.[19]
   Then the matrix of derivatives $\partial \hat{J}_p / \partial \rho_\gamma$ has (maximal) rank $n - h$. Here the chemical reaction rates are $J_p = \hat{J}_p(T, \rho_\gamma)$, (see (4.179)) $p = 1, \ldots, n - h$ is the number of independent chemical reactions chosen for description (any other reaction is their linear combination) and $\alpha, \gamma = 1, \ldots, n$ is the number of constituents.

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[19] Regular (quadratic) matrix means that its determinant is non-zero. Assertions in conditions 2, 3 about ranks $n - h$ (number of independent chemical reactions, see Sect. 4.2) follow with the use of *Lemma*: product of quadratic regular matrix with rectangular matrix of maximal rank has also this maximal rank (this follows from Sylvester's inequalities for rank of matrix product, see [134, 13.2.7]).

To prove assertion in regularity property 2 we make the derivative of (4.45) using (4.26)

$$\frac{\partial \hat{J}_p}{\partial \rho_\gamma} = \sum_{\alpha=1}^{n} \left(\sum_{r=1}^{n-h} g_{pr} P^{r\alpha} \right) \frac{\partial (\hat{r}_\alpha / M_\alpha)}{\partial \rho_\gamma}$$

Namely, by Lemma, the matrix in great parentheses has rank $n - h$ because such a rank has both metric tensor g_{pr} and rectangular matrix of stoichiometric coefficients $P^{r\alpha}$ (because chemical reactions chosen for description are independent, cf. Sect. 4.2). This is multiplied by last matrix $n \times n$ which is regular (as matrix product of regular diagonal matrix (with non-zero $1/M_\alpha$) and regular $\partial \hat{r}_\alpha / \partial \rho_\gamma$). Therefore, again by the Lemma, it follows the rank $n - h$ for $\partial \hat{J}_p / \partial \rho_\gamma$. Analogously, assertion 3 about the rank follows from derivative of (4.176) with (4.172)

$$\frac{\partial \hat{A}^p}{\partial \rho_\gamma} = - \sum_{\alpha=1}^{n} P^{p\alpha} \frac{\partial (M_\alpha \hat{g}_\alpha)}{\partial \rho_\gamma}$$

Namely, latter derivatives form a regular matrix (product of regular diagonal matrix (with non-zero M_α) and regular $\partial \hat{g}_\alpha / \partial \rho_\gamma$ has rank $n - h$. According to the Lemma the matrix $\partial \hat{A}_p / \partial \rho_\gamma$ has rank $n - h$.

3. Derivative (heat capacity, cf. (4.357), Sect. A.1) $\partial \hat{u}/\partial T$ is non-zero and the matrix of derivatives $\partial \hat{g}_\alpha/\partial \rho_\gamma$ of function (4.161) ($\alpha, \gamma = 1, \ldots, n$) is regular. In Sect. 4.7, we show that this property follows from stability, see (4.362).

Then it follows that the matrix of derivatives $\partial \hat{A}^p/\partial \rho_\gamma$ of corresponding affinities $A^p = \hat{A}^p(T, \rho_\gamma)$ (following from (4.176), (4.172), (4.161)) has (maximal) rank $n - h$.

Adding these regularities to our model of reacting fluid mixture with linear transport properties we formulate the most usable model called the *regular linear fluid mixture*. This model will be used in the remaining part of this book: in the discussion of equilibria and their stability Sect. 4.7 (condition 3. here follows from this stability), in chemical kinetics Sect. 4.9 and transport phenomena in Sect. 4.10.

As in the study of any model, we assume for simplicity that our model is valid at any values of the independent variables of its constitutive equations, e.g. at all positive temperatures and densities. Again, such behaviour is not fulfilled in reality and in fact this limits the range of application of such a model (cf. difference between real material and its mathematical model in Sect. 2.3).

From the model of (chemically) reacting (non-simple) mixture of fluids with linear transport properties simpler models may follow, e.g. the *non-reacting mixture* (where (4.15) is valid identically and regularity 2. plays no role), the *incompressible fluid mixture* (which should have similar properties as incompressible fluid from the end of Sect. 3.7.) or the *simple mixtures* (where density gradients are not a priori present in constitutive equations, see below (4.129) in Sect. 4.5). These simplified models will be thoroughly discussed in Sect. 4.8.

Summary. This section demonstrates mainly the relationships between our model of linear fluid mixture and classical chemical thermodynamics and investigated applicability of classics out of equilibrium. The Gibbs equations and the Gibbs-Duhem equation were obtained in specific quantities, cf. (4.201)–(4.206), (4.207), respectively, and are thus valid in non-equilibrium—in other words the local equilibrium was proved in this model. Alternative independent variable widely used in classical thermodynamics, i.e. the (thermodynamic) pressure, can be introduced as indicated in (4.214) but this needs a proof of invertibility of pressure as a function of volume which will be part of the subsequent section. However, introducing the pressure among independent variables disturbed the total harmony with classical thermodynamics as shown in (4.219) except the chemical potentials. This dissonance was remedied by means of the mixture invariance described in Sect. 4.4. This rather long procedure presented as the discussion of two Propositions (23.1 and 23.2) ended with the proof of (4.256) the non-zero value of which in unprimed quantities was the cause of that dissonance. The theoretical background for the measurability of partial quantities from measurements of mixture properties and their dependence on the composition is provided by (4.269) and (4.270) or by (4.273) and (4.274). Before the end we also made some notes on transfer from "specific" to molar description. At the end, we added three regularity conditions to exclude some strange situations and to prepare more detailed study of properties of linear fluid mixture in the following sections. Note also the definitions of thermodynamic pressures (4.186) and (4.187) and the partial volume (4.188), which were made to obtain the consistent results described in this section.

4.7 Equilibrium in the Linear Fluid Mixture

Definition of equilibrium is motivated similarly as in Sects. 1.2, 2.1, 2.2 and 3.8 [39, 52, 53, 56, 79, 98, 142, 143] (for non-linear models, see, e.g. [60, 71, 72]). For the regular linear fluid mixture model summarized at the end of previous Sect. 4.6, we define *equilibrium* by zero entropy production (4.301) as an equilibrium process going persistently through a unique equilibrium state, which is possible, as we shall see, if the body heat source is zero (4.303) and at zero rates of chemical reactions (4.302). By regularity conditions (see 1, 2, 3 at the end of Sect. 4.6), we exclude some unusual processes compatible with zero entropy production. We apply the regularity conditions on equilibrium states (moreover, regularity condition 3 follows for stable equilibrium states which will be discussed later in this Sect. 4.7).

In chemically reacting mixture (as different from the non-reacting one) the equilibrium may be achieved at any temperature T but only at certain densities ρ_γ^o (given by chemical equilibrium, see below (4.311)). We use sometimes the superscript o to denote the equilibrium values (because most quantities in this Sect. 4.7 are those of equilibrium we use o only for stressing this).

In the model of regular linear fluid mixture of Sects. 4.5 and 4.6 we define everywhere and permanently the *equilibrium* by zero entropy production

$$\sigma = 0 \tag{4.301}$$

and by zero chemical reaction rates r_α of all constituents (and therefore also zero of all J^α and J_p by (4.26), (4.45))

$$r_\alpha^o = 0, \quad J^{\alpha o} = 0 \qquad \alpha = 1, \ldots, n, \qquad J_p^o = 0 \qquad p = 1, \ldots, n-h \tag{4.302}$$

Body heating is assumed to be excluded

$$Q = 0 \tag{4.303}$$

We add the *regularity* assumptions 1, 2, 3 as they are formulated in the regular model at the end of previous Sect. 4.6; moreover, they mostly concern an equilibrium state and are used in it in this Sect. 4.7.

In a non-reacting mixture equations (4.302) are valid identically and regularity 2 plays no role. Moreover, as we show below in this Sect. 4.7, regularity 3 at equilibrium follows (even in more precise form with both $\partial\hat{u}/\partial T$ and determinant $\partial\hat{g}_\alpha/\partial\rho_\gamma$ being positive, see (4.357), (4.362)) from properties which assure that the equilibrium is *stable* (this concerns non-reacting mixture, too).[20]

This definition of the equilibrium process has the following consequences: in equilibrium it follows from (4.301) and (4.168) that

$$\Pi_1 = 0 \tag{4.304}$$

$$\Pi_2 = 0 \tag{4.305}$$

and from (4.302) (see (4.178)) we have zero production of entropy by chemical reactions Π_0 (chemical equilibrium (4.183))

$$\Pi_0 = 0 \tag{4.306}$$

From (4.306), (4.305) it follows that in equilibrium the condition (4.184) is fulfilled

$$\Delta p_\alpha = 0 \qquad \alpha = 1, \dots n \tag{4.307}$$

i.e. the (measurable) pressure in a chemically reacting mixture in (chemical) equilibrium is the same as the thermodynamic pressure (similarly for partial pressures, see (4.186), (4.187)); cf. end of Sect. 4.5. In a non-reacting mixture, the (4.307) is valid always, cf. Sect. 4.8.

But moreover we can see from (4.178) and (4.306) that Π_0 has a minimum in equilibrium and therefore, because $\Pi_0 = \hat{\Pi}_0(T, \rho_\gamma)$, $\gamma = 1, \dots n$ (as follows from functions $J_p = \hat{J}_p(T, \rho_\gamma)$ and $A^p = \hat{A}^p(T, \rho_\gamma)$ noted in regularity conditions 2, 3 at the end of Sect. 4.6), the necessary and sufficient conditions of minimum are

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{\Pi}_0(T^o + \lambda\beta, \rho^o_\gamma + \lambda\alpha_\gamma)|_{\lambda=0} = 0 \tag{4.308}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\lambda^2}\hat{\Pi}_0(T^o + \lambda\beta, \rho^o_\gamma + \lambda\alpha_\gamma)|_{\lambda=0} \geq 0 \tag{4.309}$$

Here ρ^o_γ, T^o are equilibrium values of densities and temperature at which (4.306) is valid, λ is a real parameter and α_γ, β are arbitrary constants. Calculation of (4.308) gives[21]

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[20] Defining here equilibrium by zero entropy production (4.301) with simultaneous zero of chemical rates (4.302) (together with regularity assumptions 1–3 giving simultaneously zero equilibrium affinities (4.311)) we exclude some (see (4.178)) rather pathological situations, giving zero entropy production (4.301) like non-zero chemical rates at zero affinities or perpendicularity of non-zero vectors $\vec{J}$ and $\vec{A}$ in reaction space (possible only for more chemical reactions). Our model of chemical equilibria excludes also by regularity 2 the case of "frozen reactions" where, even chemical affinities are non-zero, the chemical rates are zero (probably rather negligible in such observed cases) and it excludes, in accord with regularity 3, the instabilities of mixture (see below in this Sect. 4.7).

[21] We proceed similarly as in Sect. 1.2 , e.g. in (2.29), (2.31). Inserting (4.178) into (4.308)

$$\sum_{p=1}^{n-h}\left(\frac{\partial \hat{J}_p}{\partial \rho_\gamma}\right)^o A^{po} + \sum_{p=1}^{n-h} J_p^o \left(\frac{\partial \hat{A}^p}{\partial \rho_\gamma}\right)^o = 0 \qquad \gamma = 1, \dots, n \tag{4.310}$$

As follows from the assertions in regularity assumptions 2, 3 (see end of Sect. 4.6 and Rem. 19), the matrix of both derivatives in (4.310) has the (maximal) rank $n-h$ (equilibrium values are stressed here by the zero superscript, i.e. these are the values of corresponding quantities at ρ_γ^o, T^o). Therefore using now zero reaction rates (4.302) in the result (4.310) we obtain a system of homogeneous linear equations for $n-h$ equilibrium affinities with the matrix of rank $n-h$ formed by the equilibrium values of derivatives $\partial \hat{J}_p/\partial \rho_\gamma$. Therefore chemical affinities of independent chemical reactions (and, consequently, also of dependent reactions) must be zero in equilibrium

$$\vec{A}^o = \vec{0}, \quad A^{po} = 0 \qquad p = 1, \dots, n-h \tag{4.311}$$

The zero values of chemical affinities in equilibrium is the most important condition of *chemical equilibrium*. Namely

$$A^{po} = \hat{A}^p(T, \rho_\gamma^o) = 0 \qquad p = 1, \dots, n-h, \quad \gamma = 1, \dots, n \tag{4.312}$$

permit to calculate, through chemical potentials (see (4.176)), $n-h$ relations among n equilibrium values of densities ρ_γ^o at given $T = T^o$ (in practice, by using so called equilibrium constants, see Sect. 4.9).

Both properties (4.302), (4.311) are valid in the equilibrium simultaneously. Namely, both of them are equivalent: assume (4.311), then Π_0 has again minimal zero value and therefore (4.310) is valid. Because the matrix of (equilibrium) derivatives $\partial \hat{A}^p/\partial \rho_\gamma$ has rank $n-h$ (as follows from regularity 3, cf. Rem. 19) the zero reaction rates (4.302) of all reactions follow.

Note that from the split of the vector of chemical potential to the vector of affinities and the vector $\vec{B}$ (4.174) (or (4.177) in component form), we obtain in equilibrium

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(Footnote 21 continued)
and differentiating we have

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{\Pi}_0(T^o + \lambda\beta, \rho_\gamma^o + \lambda\alpha_\gamma)\\ &\quad = \beta\left(\sum_{p=1}^{n-h}\frac{\partial \hat{J}_p}{\partial T}A^p + \sum_{p=1}^{n-h} J_p \frac{\partial \hat{A}^p}{\partial T}\right) + \sum_{\gamma=1}^{n}\alpha_\gamma\left(\sum_{p=1}^{n-h}\frac{\partial \hat{J}_p}{\partial \rho_\gamma}A^p + \sum_{p=1}^{n-h} J_p\frac{\partial \hat{A}^p}{\partial \rho_\gamma}\right) \qquad (a)\end{aligned}$$

Because β, α_γ are arbitrary constants, the expressions staying at them must be zero at $\lambda = 0$ ((4.308) is valid in equilibrium). Such expressions at α_γ give result (4.310). Zero equilibrium value of the expression at β is then a trivial result of (4.302) and (4.311).

Sufficient condition of the minimum (4.309) may be calculated from (a). It gives some limits on equilibrium values of derivatives of functions $J_p = \hat{J}_p(T, \rho_\gamma)$, $A^p = \hat{A}^p(T, \rho_\gamma)$. We omit them here for simplicity; moreover practically the same limitation is given by (e) of Rem. 22 obtained analogously from (b) and (c) there.

by (4.311)

$$\vec{\mu}^o = \vec{B}^o \quad \text{in components} \quad \mu^o_\alpha = \sum_{\sigma=1}^{h} B^{\sigma o} S_{\sigma\alpha} \quad \alpha = 1, \ldots, n \tag{4.313}$$

i.e. the vector $\vec{B}$ is equal to the vector of chemical potential in equilibrium completely lying in the subspace $\mathcal{W}$ and composed from equilibrium values of chemical potentials (see Sects. 4.2 and 4.5). Indeed, inserting (4.313) into the definition of affinity (4.176) we obtain (4.312) because of (4.41), i.e. the projection of a chemical potential vector into the reaction space $\mathcal{V}$, i.e. the chemical affinity, is zero.[22] See examples in Sect. 4.9.

It is also necessary to distinguish between the equilibrium and the *steady state* (see, e.g. [144, 145]). The latter essentially embraces non-equilibrium chemical reaction processes where reaction rates of only some constituents are zero and do not contribute to the (non-zero) entropy production.

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[22] We can also start the (chemical) equilibrium definition with (4.311) (“strong” equilibrium instead of “weak” one used by (4.302) here, cf. [12, 13, 56, 79]). From (4.178), (4.179) it follows

$$\Pi_0 = \sum_{p=1}^{n-h} A^p \bar{J}_p(T, \mu_\gamma) = \sum_{p=1}^{n-h} A^p \tilde{J}_p(T, B^\sigma, A^r) \equiv \tilde{\Pi}_0(T, B^\sigma, A^r) \geq 0 \qquad (a)$$

The function $\tilde{\Pi}_0$ thus defined achieves zero value and also minimum in equilibrium (4.311) and therefore (cf. (4.308), (4.309) and similar consideration as in Rem. 21)

$$\frac{\mathrm{d}}{\mathrm{d}\lambda} \tilde{\Pi}_0(T^o + \lambda\beta, B^{\sigma o} + \lambda\epsilon^\sigma, \lambda A^r)|_{\lambda=0} = 0 \qquad (b)$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\lambda^2} \tilde{\Pi}_0(T^o + \lambda\beta, B^{\sigma o} + \lambda\epsilon^\sigma, \lambda A^r)|_{\lambda=0} \geq 0 \qquad (c)$$

where λ is the real parameter, $\beta, \epsilon^\sigma, A^r$ ($\sigma = 1, \ldots, h; r = 1, \ldots, n-h$) are the arbitrary real numbers and T^o, $B^{\sigma o}$ are the equilibrium values of temperature and $\vec{B}$, see (4.313). Calculation of (b) with the use (4.179), (4.177), (4.313) gives

$$\sum_{p=1}^{n-h} A^p \tilde{J}_p(T^o, B^{\sigma o}, A^{ro} = 0) = \sum_{p=1}^{n-h} A^p J^o_p = 0 \qquad (d)$$

because the equilibrium value of reaction rates is obviously $J^o_p = \tilde{J}_p(T^o, B^{\sigma o}, A^{ro} = 0)$ at such “strong” equilibrium in which, by arbitrariness of A^p, (d) gives the zero reaction rates $J^o_p = 0$ (4.302). Calculation of (c) gives (among others; β, ϵ^σ may be chosen zeros)

$$\sum_{p=1}^{n-h} \sum_{r=1}^{n-h} \left(\frac{\partial \tilde{J}_p}{\partial A^r} \right)^o A^p A^r \geq 0 \qquad (e)$$

where derivatives are taken in equilibrium, i.e. at T^o, $B^{\sigma o}$, $A^{ro} = 0$. Result (e) is valid in equilibrium of this section because of the simultaneous validity of (4.311), (4.302).

From the result (4.304) and from the regularity assumption 1 (the positive definite quadratic form is zero only if its variables are zero) it follows that in equilibrium (see (4.306), (4.307), (4.169), (4.170))

$$\mathrm{tr}\mathbf{D}_\alpha = 0 \qquad \alpha = 1, \dots n \tag{4.314}$$

$$\overset{\circ}{\mathbf{D}}_\alpha = \mathbf{0} \qquad \alpha = 1, \dots n \tag{4.315}$$

$$\mathbf{u}_\beta = \mathbf{o} \qquad \beta = 1, \dots n \tag{4.316}$$

$$\mathbf{g} = \mathbf{o} \tag{4.317}$$

From (4.314), (4.315) and (4.88), we have in equilibrium

$$\mathbf{D}_\alpha = 0 \qquad \alpha = 1, \dots n \tag{4.318}$$

Therefore in the equilibrium (with restrictions on equilibrium densities in the reacting mixture) the constitutive equations of the regular linear fluid mixture (cf. end of Sect. 4.6) are:

- constitutive equations for rates (4.156) are equal to zero (4.302), thermodynamic constitutive equations (4.157)–(4.159) and relations (4.164), (4.165) remain valid,
- heat flux (4.166) is zero in equilibrium (cf. (4.316), (4.317))

$$\mathbf{q}^o = \mathbf{o} \tag{4.319}$$

- interaction force (4.137) is in equilibrium

$$\mathbf{k}^o_\beta = \sum_{\gamma=1}^{n} \omega^o_{\beta\gamma} \mathbf{h}^o_\gamma \qquad \beta = 1, \dots, n-1 \tag{4.320}$$

  where $\omega^o_{\beta\gamma}$ is given by (4.165) (with equilibrium values),
- stress (4.138) is reduced in equilibrium to

$$\mathbf{T}^o_\alpha = -P^o_\alpha \mathbf{1} \qquad \alpha = 1, \dots, n \tag{4.321}$$

  where P^o_α are equilibrium values of partial thermodynamic pressures (4.186) (we use (4.307)–(4.318)).

As follows from (4.316), all constituents have the same velocity in equilibrium (denoted as $\mathbf{v}$); equilibrium superscript o is usually not used, cf. beginning of this Sect. 4.7.

$$\mathbf{v} = \mathbf{v}_\alpha \qquad \alpha = 1, \dots, n \tag{4.322}$$

Material derivatives (4.3) are all the same because of (4.322), and we can denote them by the dot; because of permanency the acceleration is everywhere zero in equilibrium

$$\dot{\mathbf{v}} = \dot{\mathbf{v}}_\alpha = \mathbf{o} \qquad \alpha = 1, \ldots, n \tag{4.323}$$

(namely, the "dot" denotes in this Sect. 4.7 the \α (4.3) which is the same for all constituents (4.322) in equilibrium, cf. (c) in Rem. 3).

Unique velocity (4.322) means the mixture is moving as a solid body and again permits to find a frame (similarly as in Sect. 3.8) where velocities are everywhere and permanently zero for all constituent in this equilibrium (see (4.318) and Killing's theorem (4.9)).

$$\mathbf{v} = \mathbf{v}_\alpha = \mathbf{o} \qquad \alpha = 1, \ldots, n \tag{4.324}$$

and we consider such a frame in equilibrium in the following. This may be the non-inertial one with inertial force (4.12). Therefore the material derivative (denoted by the dot, cf. (4.323)) may be identified with partial time derivatives $\partial/\partial t$ (at constant place).

The equilibrium valid everywhere in the mixture is also permanent in time as follows: by assumptions of zero body heating and chemical reaction rates (4.303), (4.302) and (4.301), (4.21), (4.90), the balances (4.18), (4.20), (4.58), (4.63), (4.82), (4.84) have the following forms in equilibrium (balance (4.70) is trivially satisfied by (4.321)), $\alpha = 1, \ldots, n$

$$\dot{\rho}_\alpha = 0 \tag{4.325}$$

$$\dot{\rho} = 0 \tag{4.326}$$

$$\operatorname{grad} P_\alpha = \rho_\alpha(\mathbf{b}_\alpha + \mathbf{i}_\alpha) + \mathbf{k}_\alpha \tag{4.327}$$

(permanence of $\mathbf{b}_\alpha + \mathbf{i}_\alpha$ is necessary; see above (4.334))

$$\sum_{\alpha=1}^{n} \mathbf{k}_\alpha = \mathbf{o} \tag{4.328}$$

$$\dot{u} = 0 \tag{4.329}$$

$$\dot{s} = 0 \tag{4.330}$$

Also from (4.329), (4.325), (4.213) (for $y = u$) and assumption 3 (non-zero heat capacity) we have in equilibrium

$$\dot{T} = 0 \tag{4.331}$$

Therefore, all properties are not changed in time in equilibrium but some of them, specifically pressures including the total one (see (4.187) and (4.323), (4.327), (4.328)), may change in space

$$\mathrm{grad}P^o = \sum_{\alpha=1}^{n} \rho_\alpha^o (\mathbf{b}_\alpha + \mathbf{i}_\alpha) \tag{4.332}$$

Similarly from (4.327), (4.320), (4.317), (4.328) and (4.208), (4.209) (for space gradient) we obtain

$$\mathrm{grad}g_\alpha^o = \mathbf{b}_\alpha + \mathbf{i}_\alpha \tag{4.333}$$

Equations (4.332), (4.333) are starting equations for deducing barometric and Svedberg formulae or calculation of chemical equilibrium in gravitational or centrifugal fields [3, 79].[23]

We can see from (4.333), (4.213) (for $y_\alpha = g_\alpha$), (4.317) and regularity assumption 3, that density gradients $\mathbf{h}_\alpha$ are not zero in the equilibrium state if $\mathbf{b}_\alpha + \mathbf{i}_\alpha$ are not zero. While temperature T is a constant fixed everywhere and permanently in equilibrium, densities ρ_α may change in space but are fixed in time as well as properties depending on them (like pressures) and also $\partial \mathbf{h}_\alpha/\partial t = \mathbf{o}$, $\partial \mathbf{g}/\partial t = \mathbf{o}$, etc. Then from (4.327),(4.320) it follows (similarly as in Sect. 3.8) that body and/or inertial forces $\mathbf{b}_\alpha + \mathbf{i}_\alpha$ must be constant in time in equilibrium. If they have potentials Φ_α, they do not change in time

$$\mathbf{b}_\alpha + \mathbf{i}_\alpha = -\mathrm{grad}\Phi_\alpha\,, \quad \frac{\partial \Phi_\alpha}{\partial t} = 0 \qquad \alpha = 1, \ldots, n \tag{4.334}$$

These forces must fulfil in equilibrium (because obviously $\mathrm{grad}A^{po} = \mathbf{o}$)

$$\sum_{\alpha=1}^{n} (\mathbf{b}_\alpha + \mathbf{i}_\alpha) M_\alpha P^{p\alpha} = \mathbf{o} \qquad p = 1, \ldots, n-h \tag{4.335}$$

as follows from (4.311), (4.333), (4.176), (4.172). Known gravitational and centrifugal forces have these properties (cf. (3.104)) because they are independent of α (cf. (4.12), (4.322), Rem. 13), i.e. (4.335) is satisfied by (4.42) (even in reactions of

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[23] Namely, (4.332) and then (4.333) may be written (see (4.213), (4.267), (4.331); equilibrium superscript o is omitted) in (time constant) gravitation or centrifugal fields which are independent of constituents $\mathbf{b}_\alpha = \mathbf{g}$ or $\mathbf{i}_\alpha = \mathbf{i}$ respectively ($\mathbf{g}$ is gravity acceleration, $\mathbf{i}$ is given by (4.12))

$$\mathrm{grad}P = \rho(\mathbf{g} + \mathbf{i})$$

$$\sum_{\beta=1}^{n-1} \frac{\partial \tilde{g}_\alpha}{\partial w_\beta} \mathrm{grad}w_\beta = (1 - \rho v_\alpha)(\mathbf{g} + \mathbf{i}) \quad \alpha = 1, \ldots, n$$

In an ideal binary solution, defined by (4.437), we obtain the Svedberg formula for measuring of molar mass M_1 (usually of macromolecular substance) in centrifuge with $\mathbf{i}$ above (see (4.292)–(4.294))

$$(1/x_1)\mathrm{grad}x_1 = (M_1/\mathrm{R}T)(1 - \rho v_1)\mathbf{i}$$

where v_1 of the ideal solution may be interpreted as specific volume of pure constituent 1 (cf. below (4.440)).

ions the electrostatic forces fulfil (4.335) by preservation of electrical charge in such reactions).

An important special case is the *uniform equilibrium* in the mixture. This is the case of the inertial frame and with zero body forces ($\mathbf{i}_\alpha = \mathbf{o}$ (3.48), $\mathbf{b}_\alpha = \mathbf{o}$) with (4.324), (4.323). Then from (4.332), (4.333) $\operatorname{grad} P^o = \mathbf{o}$, $\operatorname{grad} g^o_\alpha = \mathbf{o}$, and because of regularity (assumption 3) density gradients are also zero (besides (4.317)). Therefore in the uniform equilibrium we obtain all quantities not changing in time and space (thermodynamic properties are given by (4.283), (4.287)). Moreover, by (4.320), (4.328) we have

$$\mathbf{k}^o_\alpha = \mathbf{o} \qquad \alpha = 1, \ldots, n \tag{4.336}$$

in uniform equilibrium.

Definition of equilibrium here is difficult to achieve in practice because of molecular fluctuations; in fact the stability of equilibrium, i.e. its return back after its disturbance, must be achieved and thus the equilibrium may be realized. The problem of the *stability of equilibrium* will be discussed in the remaining part of this Sect. 4.7 proceeding similarly as in Sect. 3.8, although the problem is more complicated mainly due to chemical reactions, cf. [39, 98, 143, 146, 147].

Similarly as in Sect. 3.8 (cf. postulate of dynamical stability under isolation below (3.245)) our *postulate* is that the (body from) mixture under isolation, i.e. not exchanging work, heat or mass with the environment and without the presence of body forces ($\mathbf{i}_\alpha = \mathbf{o}$, $\mathbf{b}_\alpha = \mathbf{o}$) develops into the unique final uniform equilibrium state with time fixed properties with its entropy having achieved in this equilibrium state its maximal value (mixture body has the whole energy, volume and mass fixed, zero reaction rates, $Q = 0$ inside and $\mathbf{q} = \mathbf{o}$, $\mathbf{v}_\alpha = \mathbf{o}$ on the boundary).

This additional postulate seems physically plausible (note that from (4.83) applied to the whole mixture body, it follows the growth of entropy only).

Our programme will thus be completed in the remaining part of Sect. 4.7 by deduction, starting with this postulate, of the additional properties of the discussed constitutive model, namely *stability conditions* (4.357), (4.358), (4.359) (or (4.360), (4.362)), which assure the stability of the equilibrium state. At the end, reversely, assuming these stability conditions, we try to find the time development of some non-equilibrium states into corresponding equilibrium states, cf. (4.387), (4.400).

Therefore, using the just formulated postulate in the isolated mixture from our material model—the regular linear fluid mixture (cf. end of Sect. 4.6), we expect that an arbitrary perturbed state (obtainable, say, by molecular fluctuations) decays back to the final uniform equilibrium state with maximum entropy [39, 146] in which Eqs. (4.303), (4.302), (4.316)–(4.319), (4.321)–(4.326), (4.328)–(4.331), (4.336) are valid and gradients of pressures and chemical potentials are zero (see (4.327), (4.332), (4.333)). Let us denote by m^o the whole mass of such an equilibrium mixture, by m^o_α the mass of each constituent, by V^o its total volume, by E^o its total energy and by S^o its total (and maximum) entropy. Therefore (cf. (3.240)–(3.242))

$$V^o = v^o m^o \tag{4.337}$$

$$E^o = u^o m^o \tag{4.338}$$

$$m^o_\alpha = w^o_\alpha m^o \qquad \alpha = 1, \ldots, n \tag{4.339}$$

$$S^o = s^o m^o \tag{4.340}$$

where v^o, u^o, w^o_α, s^o, are constant equilibrium values of the specific volume (4.191), the internal energy (4.90), the mass fraction (4.22) and the entropy (4.91) respectively. Equations (4.339) are not independent: in a non-reacting mixture $n-1$ such equations are independent by (4.23) and in reacting mixture (with (4.29)) there is an additional dependence among w_α caused by $n-h$ relations (4.311). We also recall that in a uniform equilibrium mixture the rates of chemical reactions are zero (4.302).

Stability means that an arbitrary perturbed state under isolation decays into a unique final uniform equilibrium state (4.337)–(4.340) without exchange of heat, work and mass with the environment in the inertial frame with $\mathbf{b}_\alpha = \mathbf{o}$ and (4.303), i.e. with $\mathbf{v}_\alpha = \mathbf{o}$, $\mathbf{g} = \mathbf{o}$ on the boundary of the (body of) mixture. But now in the perturbed state v, w_α, u_α, $\mathbf{v}_\alpha$ are arbitrary fields but such that the whole volume and energy are obviously the same constants V^o, E^o as in (4.337), (4.338)

$$V^o = \int_{m^o} v \, \mathrm{d}m \tag{4.341}$$

$$E^o = \int_{m^o} \sum_{\alpha=1}^{n} w_\alpha (u_\alpha + (1/2)\mathbf{v}^2_\alpha) \, \mathrm{d}m \tag{4.342}$$

(here $\mathrm{d}m = \rho \mathrm{d}v$ with (4.21), (4.195) (see below (4.191)) and (4.77) are used).

In the perturbed state of a chemically reacting mixture reaction rates are generally non-zero, but the following relations are valid

$$\sum_{\alpha=1}^{n} (S_{\sigma\alpha}/M_\alpha) m^o_\alpha = \sum_{\alpha=1}^{n} (S_{\sigma\alpha}/M_\alpha) \int_{m^o} w_\alpha \, \mathrm{d}m \qquad \sigma = 1, \ldots, h \tag{4.343}$$

because they express the preservation of atomic substances during the chemical reactions, cf. Sect. 4.2 (we recall that atomic substances need not be the chemical elements). Indeed, Eq. (4.343) follow because from (4.14) for mixture with $\mathbf{v}_\alpha = \mathbf{o}$ on its boundary and from (4.26), (4.30) we have ($\rho_\alpha \mathrm{d}v = w_\alpha \rho \mathrm{d}v = w_\alpha \mathrm{d}m$)

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(E^\sigma \sum_{\alpha=1}^{n} (S_{\sigma\alpha}/M_\alpha) \int_{m^o} w_\alpha \, \mathrm{d}m \right) = 0 \qquad \sigma = 1, \ldots, h \tag{4.344}$$

i.e. quantities in outer parentheses—the masses of atomic substances with atomic masses E^σ—are preserved during chemical reactions in the course of decay of this perturbed state (masses of constituents in them are integrals in (4.344)).

But (4.343) are trivially satisfied even in a non-reacting mixture because then m^o_α from (4.339) are constants equal to integrals on the right-hand side of (4.343) (see (4.347) below).

According to (4.83) and (4.91) the entropy S of such an isolated perturbed state is not greater than the maximum entropy S^o (4.340) of the final equilibrium state as we discussed in our postulate above

$$S \equiv \int_{m^o} s\,\mathrm{d}m \leq S^o \tag{4.345}$$

and the equality may be expected in the equilibrium state stability of that is tested.

Because of the arbitrariness of the perturbed state, we (similarly as in Sect. 3.8) choose such a one in which Eqs. (4.341), (4.345) are valid while Eqs. (4.342), (4.343) are substituted by

$$E^o = \int_{m^o} u\,\mathrm{d}m \tag{4.346}$$

$$m^o_\beta = \int_{m^o} w_\beta\,\mathrm{d}m \qquad \beta = 1, \ldots, n-1 \tag{4.347}$$

i.e. we consider such a perturbed state which has zero velocities of all constituents and, in reacting mixtures, the masses of all constituents are the same as in the equilibrium state tested; this non-uniform perturbed state is not in chemical equilibrium and generally $w_\beta \neq w^o_\beta$ inside, while in non-reacting mixtures (4.347) are always valid (instead of (4.343) as we noted above). Of course, during the subsequent approach to the equilibrium state in an isolated system the velocities need not be zero as equally the masses of constituents need not be m^o_α (but they fulfil (4.343); in (4.347) we exclude the dependent mass by $m^o_n = m^o - \sum_{\beta=1}^{n-1} m^o_\beta$).

Using this type of perturbed state ((4.349)–(4.351)below) and assuming that each equilibrium state of a linear fluid mixture with regular response is stable under isolation (i.e. these perturbed states develop in isolation to the corresponding final equilibrium state as described above), we prove now that the function (cf. (3.247) and Rem. 46 in Chap. 3)

$$s = \bar{s}(u, v, w_\beta) \tag{4.348}$$

is *strict concave* in all equilibrium states (in chemical equilibrium, as different from a non-reacting mixture, w_β are not all independent). The existence of (4.348) follows from (4.212) written for s and u, inverting the last one for T (this is possible by regular response assumption 3 from the end of Sect. 4.6) and by inserting into the first one; then (4.22), (4.23) and (4.195) are used.

Proceeding analogously as in Sect. 3.8, we define the perturbed state with (4.341), (4.346), (4.347), (4.345) as follows: it is composed from two parts (denoted by superscripts a, b) with masses αm^o and $(1-\alpha)m^o$ (where $0 < \alpha < 1$; m^o is the mass of mixture) with different, but in these parts uniform, specific energies u^a, u^b, volumes v^a, v^b and mass fractions w^a_β, w^b_β and entropies s^a, s^b given by

(4.348). Using such division in (4.341), (4.346), (4.347), (4.345) and comparing with (4.337)–(4.340) we obtain (just the assumptions giving (4.346), (4.347) are important)

$$\alpha v^a + (1-\alpha)v^b = v^o, \quad \alpha u^a + (1-\alpha)u^b = u^o \tag{4.349}$$

$$\alpha w^a_\beta + (1-\alpha)w^b_\beta = w^o_\beta \qquad \beta = 1, \ldots, n-1 \tag{4.350}$$

$$\alpha \bar{s}(u^a, v^a, w^a_\beta) + (1-\alpha)\bar{s}(u^b, v^b, w^b_\beta) < \bar{s}(u^o, v^o, w^o_\beta) \tag{4.351}$$

According to the theorem of concave functions (Appendix A.3(i)), results (4.349)–(4.351) show that function (4.348) is strict concave. Therefore, according to Appendix A.3(ii), the matrix of its second derivatives in equilibrium is (equivalently) negative definite i.e. this matrix multiplied by -1 is positive definite. Then, according to the known theorem valid for such positive definite matrices [134, Sects. 13.5, 13.6], [148, Sect.1.29], its principal minors must be equivalently positive at equilibrium values u^o, v^o, w^o_β.

Then, according to the known theorem valid for such positive definite matrices [134, Sects.13.5–13.6], [148, Sect.1.29], its principal minors must be equivalently positive. Writing these determinants as jacobians and using (as follows from (4.203), (4.348))

$$\frac{\partial \bar{s}}{\partial u} = \frac{1}{T} \tag{4.352}$$

$$\frac{\partial \bar{s}}{\partial v} = \frac{P}{T} \tag{4.353}$$

$$\frac{\partial \bar{s}}{\partial w_\beta} = -\frac{g_\beta - g_n}{T} \qquad \beta = 1, \ldots, n-1 \tag{4.354}$$

the following determinants are positive (independent variables are here $u, v, w_1, \ldots, w_{n-1}$):

$$\frac{\partial - (1/T)}{\partial u} > 0, \quad \frac{\partial(-1/T, -P/T)}{\partial(u, v)} > 0 \tag{4.355}$$

$$\frac{\partial(-1/T, -P/T, (g_1 - g_n)/T, \ldots, (g_k - g_n)/T}{\partial(u, v, w_1, \ldots, w_k)} > 0 \qquad k = 1, \ldots, n-1 \tag{4.356}$$

From these inequalities (4.355), (4.356), the properties of the jacobians and using a "thermodynamic" way in writing some partial derivatives (see (4.214)) and functions (4.217), (4.216) (for $y = u, v, g$ respectively) we obtain

$$\frac{\partial \breve{u}}{\partial T} \equiv \left(\frac{\partial u}{\partial T}\right)_{v, w_\beta} = \frac{\partial \hat{u}}{\partial T} > 0 \tag{4.357}$$

which may be called the *heat capacity* at constant volume in mixture (cf. Appendix A.1),

$$\frac{\partial \check{P}}{\partial v} \equiv \left(\frac{\partial P}{\partial v}\right)_{T,w_\beta} < 0 \quad \text{or} \quad \frac{\partial \tilde{v}}{\partial P} < 0 \tag{4.358}$$

$$\frac{\partial(\tilde{g}_1 - \tilde{g}_n)}{\partial w_1} > 0, \ldots, \frac{\partial(\tilde{g}_1 - \tilde{g}_n, \ldots, \tilde{g}_k - \tilde{g}_n)}{\partial(w_1, \ldots, w_k)} > 0, \ldots, \frac{\partial(\tilde{g}_1 - \tilde{g}_n, \ldots, \tilde{g}_{n-1} - \tilde{g}_n)}{\partial(w_1, \ldots, w_{n-1}, P)} > 0 \tag{4.359}$$

Proof (cf. analogous deduction (3.256), (3.257)) Inequalities (4.355) (where all w_α are constants) give

$$0 < \frac{\partial - (1/T)}{\partial u} = \frac{1}{T^2}\left(1/\left(\frac{\partial u}{\partial T}\right)_{v,w_\beta}\right)$$

leading to (4.357) (we use (4.212) for $y = u$, (4.195), (4.23), (4.22)) and

$$\begin{aligned} 0 < \frac{\partial(-1/T, -P/T)}{\partial(u, v)} &= \frac{\partial(-1/T, -P/T)}{\partial(T, v)} \frac{\partial(T, v)}{\partial(u, v)} \\ &= \left((-1/T^3)\left(\frac{\partial P}{\partial v}\right)_{T,w_\beta}\right)\left(1/\left(\frac{\partial u}{\partial T}\right)_{v,w_\beta}\right) \end{aligned}$$

which by (4.357) gives $(4.358)_1$ (and from this following invertibility of (4.214) to (4.215) also $(4.358)_2$).

Further, from (4.356)

$$\begin{aligned} &\frac{\partial(-1/T, -P/T, (g_1 - g_n)/T, \ldots, (g_k - g_n)/T)}{\partial(u, v, w_1, \ldots, w_k)} \\ &= \frac{\partial(-1/T, -P/T, (g_1 - g_n)/T, \ldots, (g_k - g_n)/T)}{\partial(-1/T, -P/T, w_1, \ldots, w_k)} \cdot \frac{\partial(-1/T, -P/T, w_1, \ldots, w_k)}{\partial(u, v, w_1, \ldots, w_k)} \\ &= (1/T)^k \frac{\partial(g_1 - g_n, \ldots, g_k - g_n)}{\partial(w_1, \ldots, w_k)} \cdot \frac{\partial(-1/T, -P/T)}{\partial(u, v)} > 0 \quad k = 1, \ldots, n-1 \end{aligned}$$

from which follows, by (4.355) and $T > 0$

$$\frac{\partial(g_1 - g_n, \ldots, g_k - g_n)}{\partial(w_1, \ldots, w_k)} > 0 \quad k = 1, \ldots, n-1$$

Because here T, P and remaining w_β are constant we obtain (4.359) using (4.216) for $y_\alpha = g_\alpha$. Q.E.D.

Conditions of *stability* are therefore (4.357), (4.358), (4.359); from the latter it follows equivalently, by known theorem [134, Sects.13.5–13.6], that matrix $n-1 \times n-1$ from elements

$$\frac{\partial(\tilde{g}_\beta - \tilde{g}_n)}{\partial w_\delta} \qquad \beta, \delta = 1, \dots, n-1 \tag{4.360}$$

is positive definite. Therefore, the determinant of order $n-1$ of matrix (4.360) is also regular, i.e. non-zero, namely positive.

For binary mixture $n = 2$ it follows from (4.359) and Gibbs-Duhem equation (4.221) that

$$\frac{\partial \tilde{g}_1}{\partial w_1} > 0 \tag{4.361}$$

From these results, we obtain further consequences (again valid in equilibrium not stressed by index for brevity). Namely, we show that from regularity of matrix (4.360) it follows that matrix $n \times n$ with components

$$\frac{\partial \hat{g}_\alpha}{\partial \rho_\gamma} \qquad \alpha, \gamma = 1, \dots, n \tag{4.362}$$

is regular (i.e. its determinant of order n is non-zero, even positive), see results (4.375) below, cf. assumption 3 at the end of Sect. 4.6.[24] Indeed, the jacobian formed from (4.362) may be transformed as follows

$$\frac{\partial(g_1, \dots, g_n)}{\partial(\rho_1, \dots, \rho_n)} = \frac{\partial(g_1, \dots, g_n)}{\partial(w_1, \dots, w_{n-1}, P)} \frac{\partial w_1, \dots, w_{n-1}, P)}{\partial(w_1, \dots, w_{n-1}, v)} \frac{\partial(w_1, \dots, w_{n-1}, v)}{\partial(\rho_1, \dots, \rho_n)} \tag{4.363}$$

and its regularity follows, because all three jacobians here are non-zero as we prove now:

We start with the last jacobian in (4.363) which may be calculated as follows

$$\frac{\partial(w_1, \dots, w_{n-1}, v)}{\partial(\rho_1, \dots, \rho_n)} = (1/\rho)^{n-1}(-1/\rho^2) = -1/\rho^{n+1} = -v^{n+1} < 0 \tag{4.364}$$

because ρ, v are both positive. Namely, this jacobian contains derivatives

$$\frac{\partial w_\delta}{\partial \rho_\alpha} = \frac{1}{\rho}(\delta_{\delta\alpha} - w_\delta), \quad \frac{\partial v}{\partial \rho_\alpha} = -\rho^{-2} \quad \alpha = 1, \dots, n\,, \ \delta = 1, \dots, n-1 \tag{4.365}$$

obtained from functions $w_\delta = \rho_\delta / \sum_{\gamma=1}^n \rho_\gamma$ or $v = 1/\sum_{\gamma=1}^n \rho_\gamma$ of $\rho_1, \dots, \rho_n$ (cf. (4.21), (4.23), (4.195)). Inserting (4.365) into (4.364) and rearranging we have

$$\frac{\partial(w_1, \dots, w_{n-1}, v)}{\partial(\rho_1, \dots, \rho_n)} = (1/\rho)^{n-1}(-1/\rho^2) J \tag{4.366}$$

where determinant J (of order n) is defined as

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[24] Cf. [56, Sect. 24]; the unsuccessful proof of even positive definiteness of (4.362) in this reference obviously needs further assumptions.

$$J \equiv \begin{vmatrix} 1-w_1 & -w_1 & \dots & -w_1 & -w_1 \\ -w_2 & 1-w_2 & \dots & -w_2 & -w_2 \\ & & \vdots & & \\ & & \vdots & & \\ -w_{n-1} & -w_{n-1} & \dots & 1-w_{n-1} & -w_{n-1} \\ 1 & 1 & \dots & 1 & 1 \end{vmatrix} \tag{4.367}$$

Now, we prove that this $n \times n$ determinant J is equal to 1, see (4.370). Namely, $n-1$ negative mass fractions $(-1)^{n-1} w_1.w_2.....w_{n-1}$ we write before this determinant writing in its diagonal $1 - 1/w_k$ with $k = 1, \dots, n-1$ (remaining elements are 1) and from each line we substract the following line; the last line contains 1 only.

Expanding with respect to the last column we obtain J with determinant of order $n-1$

$$J = (-1)^{n-1} w_1.w_2.....w_{n-1} \begin{vmatrix} -1/w_1 & 1/w_2 & 0 & \dots & 0 & 0 \\ 0 & -1/w_2 & 1/w_3 & \dots & 0 & 0 \\ & & & \vdots & & \\ & & & \vdots & & \\ 0 & 0 & 0 & \dots & -1/w_{n-2} & 1/w_{n-1} \\ 0 & 0 & 0 & \dots & 0 & -1/w_{n-1} \end{vmatrix} \tag{4.368}$$

From the last line, we exclude $-1/w_{n-1}$ before determinant and develop according its last line. The order of determinant breaks down (to $n-2$) and we obtain

$$J = (-1)^{n-1} w_1.w_2.....w_{n-1} \frac{(-1)}{(w_{n-1})} \begin{vmatrix} -1/w_1 & 1/w_2 & 0 & \dots & 0 & 0 \\ 0 & -1/w_2 & 1/w_3 & \dots & 0 & 0 \\ & & & \vdots & & \\ & & & \vdots & & \\ 0 & 0 & 0 & \dots & -1/w_{n-3} & 1/w_{n-2} \\ 0 & 0 & 0 & \dots & 0 & -1/w_{n-2} \end{vmatrix} \tag{4.369}$$

This procedure (excluding $-1/w_{n-2}$ and developing the last line again; order of determinant breaks down) is repeated several times. So we obtain

$$\begin{aligned} J &= (-1)^{n-1} \frac{w_1.w_2.....w_{n-1}}{w_{n-1}.w_{n-2}....w_4} (-1)^{n-4} \begin{vmatrix} -1/w_1 & 1/w_2 & 0 \\ 0 & -1/w_2 & 1/w_3 \\ 0 & 0 & -1/w_3 \end{vmatrix} \\ &= (-1)^{n-1} \frac{w_1.w_2.....w_{n-1}}{w_{n-1}.w_{n-2}....w_4.w_3} (-1)^{n-3} \begin{vmatrix} -1/w_1 & 1/w_2 \\ 0 & -1/w_2 \end{vmatrix} \\ &= (-1)^{n-1} \frac{w_1.w_2.....w_{n-1}}{w_{n-1}.w_{n-2}....w_3.w_2.w_1} (-1)^{n-1} = 1 \end{aligned} \tag{4.370}$$

Therefore, because of this result (4.370), $J = 1$, we have from (4.366)

$$\frac{\partial(w_1, \ldots, w_{n-1}, v)}{\partial(\rho_1, \ldots, \rho_n)} = (1/\rho)^{n-1}(-1/\rho^2) < 0 \tag{4.371}$$

which is negative by the positivity of $\rho > 0$.

The central jacobian in (4.363) is

$$\frac{\partial(w_1, \ldots, w_{n-1}, P)}{\partial(w_1, \ldots, w_{n-1}, v)} = \left(\frac{\partial P}{\partial v}\right)_{T, w_\beta} < 0 \tag{4.372}$$

because the right-hand side of (4.372) is obvious and the negative sign follows from (4.358).

Ultimately we calculate the sign of the first jacobian in (4.363)

$$\frac{\partial(g_1, \ldots, g_n)}{\partial(w_1, \ldots, w_{n-1}, P)} = v.\frac{\partial(g_1 - g_n, \ldots, g_{n-1} - g_n)}{\partial(w_1, \ldots, w_{n-1})} > 0 \tag{4.373}$$

Its positivity may be obtained by rearranging the left-hand side by subtracting the last row of this jacobian from its 1 to $n - 1$ rows and adding to the last row these $1, \ldots, n - 1$ rows multiplied by $w_1, \ldots, w_{n-1}$ respectively (values of this jacobian are unchanged by such operations). Then the members of the last row are

$$\frac{\partial \tilde{g}_n}{\partial w_\delta} + \sum_{\beta=1}^{n-1} w_\beta \frac{\partial(\tilde{g}_\beta - \tilde{g}_n)}{\partial w_\delta} = 0 \qquad \delta = 1, \ldots, n-1, \quad \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{g}_\alpha}{\partial P} = v \tag{4.374}$$

as follows from Gibbs-Duhem equations (4.221) and (4.267), (4.191), (4.23). Developing a determinant obtained in this way according to the last row we obtain the right-hand side of (4.373), which is positive as follows from the important previous result (4.359) and $v > 0$.

By these partial results (4.371), (4.372), (4.373) we obtain from (4.363) that the jacobian

$$\frac{\partial(g_1, \ldots, g_n)}{\partial(\rho_1, \ldots, \rho_n)} > 0 \tag{4.375}$$

is positive and therefore the matrix (4.362) is regular. In other words, the result 3. from the end of Sect. 4.6 follows from the stability assumed in this section.

But we recall that these results are valid in equilibrium, specifically in a chemically reacting mixture only at (usually special) chemical equilibrium composition (as different from a non-reacting mixture where every composition may be the equilibrium one).

Therefore, the regularity of matrices (4.360), (4.362) or inequalities (4.357), (4.358), (4.359), are the *stability conditions* for the mixture.

Note that these results are valid not only in a stable reacting mixture in chemical equilibrium but also in a stable non-reacting mixture. It contains the known result that the chemical potential of a constituent increases with its concentration, cf. (4.361).

Now we try to show the reversal (similarly as in Sect. 3.8): any state of a regular linear fluid mixture with conditions of stability develops under conditions of isolation to a uniform equilibrium state. That is we show the dynamical stability under isolation (and also Gibbs stability) for such a mixture. We note that generally this goal is very complicated, especially in a chemically reacting mixture. For simplicity we therefore prove only that the uniform equilibrium state (those given by (4.337)–(4.340)) is a possible one in which the perturbed state kept permanently in isolation (defined below) develops asymptoticaly as time goes to infinity [39, 79, 143].

Thus, let us assume to have a regular linear fluid mixture with stability conditions ((4.357), (4.358), and (4.359)) which starts in an arbitrary non-equilibrium (initial) state held in isolation: there is no exchange of heat, work and mass with the environment, i.e. permanently $Q = 0, \mathbf{i}_\alpha = \mathbf{o}, \mathbf{b}_\alpha = \mathbf{o}$ (no external or non-inertial, e.g. centrifugal, forces) through the mixture and on its boundary there is $\mathbf{q} = \mathbf{o}$, $\mathbf{v}_\alpha = \mathbf{o}$, $\alpha = 1, \ldots, n$ (but they may be non-zero inside). Chemical reactions are going on, i.e. their rates are generally non-zero. From the known initial state we can calculate the whole energy E^o and volume V^o of the mixture by (4.341), (4.342) which are constant during the further development as well as the constant total mass m^o from the given masses of constituents m_α in the initial state

$$m^o = \sum_{\alpha=1}^{n} m_\alpha \tag{4.376}$$

We show now that such an initial state asymptotically develops to (a chemical) equilibrium uniform state (permanent with zero reaction rates) with values of the specific volume v^o and the internal energy u^o given by

$$v^o = V^o/m^o \tag{4.377}$$

$$u^o = E^o/m^o \tag{4.378}$$

At the same time, the masses m^o_α in a *non-reacting* mixture are equal to m_α, i.e. the equilibrium composition is then given for the independent masses by

$$w^o_\beta = m^o_\beta/m^o \qquad \beta = 1, \ldots, n-1 \tag{4.379}$$

However in the *reacting* mixture m^o_α need not be equal to m_α and w^o_β may be calculated as follows (in principle): chemical equilibrium (4.311) may be expressed in $n - h$ following relations if we use (4.176), (4.172) with (4.213) for $y_\alpha = g_\alpha$, eliminate T by $(4.160)_1$ (cf. (4.357)) and use (4.22), (4.23), (4.195)

$$A^p(u, v, w_1, \ldots, w_{n-1}) = 0 \qquad p = 1, \ldots, n-h \tag{4.380}$$

Putting (4.377), (4.378) for $u = u^o$, $v = v^o$ in equilibrium (4.380) we can express $n - h$ mass fractions $w_\alpha = w^o_\alpha$ as the functions of remaining h mass fractions in equilibrium; inserting them in (4.343), i.e. in

$$\sum_{\alpha=1}^{n}(S_{\sigma\alpha}/M_\alpha)m^o w^o_\alpha = \sum_{\alpha=1}^{n}(S_{\sigma\alpha}/M_\alpha)m_\alpha \qquad \sigma = 1, \dots, h \tag{4.381}$$

we can calculate the remaining h mass fractions from these h equations (m_α are prescribed) and therefore all (equilibrium) values w^o_β may be obtained.

We also recall that in the uniform state in chemical equilibrium (4.380) all rates (4.302) of chemical reactions are zero, cf. below (4.312).

Because of conditions of stability (4.357), (4.358), (4.359), Eqs. (4.355), (4.356) are valid (this is, in fact, a reversed proof of the former relations) and therefore a negative definiteness of the matrix of second derivatives of (4.348) follows. By (iii) and (ii) in Appendix A.3 we have equivalently for the values u^o, v^o (4.377), (4.378) and just calculated (chemical equilibrium) mass fractions w^o_β (cf. similar deduction of (3.260)):

$$s < s^o + (u - u^o)/T^o + (v - v^o)P^o/T^o - \sum_{\beta=1}^{n-1}(w_\beta - w^o_\beta)(g^o_\beta - g^o_n)/T^o \tag{4.382}$$

where (4.352)–(4.354) were used (remember, equilibrium values are denoted by zero superscript) and u, v, w_β, s are the values in mixture during the non-equilibrium process. We add to the right-hand side of (4.382) the non-negative quantity $\sum_{\alpha=1}^{n} w_\alpha \mathbf{v}^2_\alpha/(2T^o)$ (kinetic energies multiplied by $1/T^o$ with velocities $\mathbf{v}_\alpha$ in the mixture which are zeros in equilibrium) and integrate over the total mass m^o. We obtain

$$S \equiv \int_{m^o} s \,\mathrm{d}m \le \int_{m^o} s^o \,\mathrm{d}m = S^o = s^o m^o \tag{4.383}$$

where the equality occurs when in all the mixture

$$u = u^o, \quad v = v^o, \quad w_\beta = w^o_\beta \tag{4.384}$$

(this is the uniform final state with entropy S^o and constant s^o, cf. above (4.387)). The result (4.383) follows because integrals of the terms on the right-hand side in (4.382) (extended by kinetic energy) are zero: V^o, E^o in (4.377), (4.378) is given by (4.341), (4.342) for any state and the last integral may be calculated as follows

$$\begin{aligned}
&\int_{m^o} \sum_{\beta=1}^{n-1} \left(w_\beta - w^o_\beta\right) \frac{g^o_\beta - g^o_n}{T^o}\,\mathrm{d}m \\
&= \sum_{\alpha=1}^{n} \frac{g^o_\alpha}{T^o} \int_{m^o} \left(w_\alpha - w^o_\alpha\right)\mathrm{d}m = \sum_{\alpha=1}^{n} \left(m_\alpha - m^o_\alpha\right) \frac{g^o_\alpha}{T^o}
\end{aligned}$$

$$= \frac{1}{T^o} \sum_{\sigma=1}^{h} B^{\sigma o} \left(\sum_{\alpha=1}^{n} m_\alpha S_{\sigma\alpha}/M_\alpha - \sum_{\alpha=1}^{n} m_\alpha^o S_{\sigma\alpha}/M_\alpha \right) = 0 \tag{4.385}$$

where we use (4.23). For nonreacting mixture $m_\alpha = m_\alpha^o$ and these results follow immediately. For a reacting mixture the decomposition (4.177) for chemical equilibrium (4.313) has been used with (4.172) where $B^{\sigma o}$ are the equilibrium values of $\vec{B}$. Introducing (4.313) into (4.385) and using (4.381), (4.379) we obtain the result (4.385) and therefore also (4.383).

Before going further, we note that analogously as in Sect. 3.8 (i.e. all velocities are considered to be zero), we can define the Gibbs stability (under isolation) of the equilibrium state (usually for a non-reacting mixture) if for every state with (4.341), (4.346), (4.347), the inequality (4.345) is valid. From this definition, the stability conditions (4.357), (4.358), (4.359) may be deduced (similarly as shown above). Reversely, these conditions express the Gibbs stability.

Now, from the entropy inequality (4.83) for our isolated mixture we have (using entropy production (4.84) and (4.91); $\mathrm{d}m = \rho \mathrm{d}v$, cf. below (4.342))

$$\dot{S}(t) \equiv \frac{\mathrm{d}}{\mathrm{d}t} \int_{m^o} s \, \mathrm{d}m = \int_{V^o} \sigma \, \mathrm{d}v \geq 0 \tag{4.386}$$

Thus during the process the entropy S does not decrease in time (4.386) and has an upper bound (4.383). As the result, similarly as in Sect. 3.8 in (3.266), it may be obtained that in uniform equilibrium achieved at $t \to \infty$, the value of entropy reaches the value S^o from (4.383) and therefore also equality here is attained

$$\lim_{t\to\infty} S = S^o \tag{4.387}$$

In additional simplifying assumptions as in Sect. 3.8 we obtain even in this reacting mixture (cf. Rem. 47 in Chap. 3) analogues of (3.267), (3.268)

$$\lim_{t\to\infty} \dot{S}(t) = 0 \tag{4.388}$$

$$\sigma^o = \lim_{t\to\infty} \sigma = 0 \tag{4.389}$$

everywhere and persistently.

This limiting state with S^o, E^o, V^o, m^0 has been obtained as a result of time development from the starting state at $t \to \infty$ in fixed conditions $Q = 0, \mathbf{i}_\alpha = \mathbf{o}, \mathbf{b}_\alpha = \mathbf{o}$ through the (body of) the mixture and $\mathbf{q} = \mathbf{o}, \mathbf{v}_\alpha = \mathbf{o}$ on its boundary. The resulting equilibrium mixture (cf. beginning of this Sect. 4.7) is uniform with everywhere constant and time independent s^o, u^o, temperature, composition w_α^o in chemical equilibrium with zero affinities and chemical reaction rates. Zero entropy production $\sigma = \sigma^0 = 0$ (4.389) is valid in any place and permanently and similarly, by regularity conditions (mainly 1 and 3, see the end of Sect. 4.6 and beginning of this Sect. 4.7), permanently and everywhere (4.302)–(4.319) and (4.321), (4.322) (or (4.324) in the appropriate frame). Because of no inertial and/or body forces $\mathbf{i}_\alpha = \mathbf{o}$, $\mathbf{b}_\alpha = \mathbf{o}$ we have no densities gradients and (4.336) which is limiting equilibrium state is uniform.

The problem of approaching to a state of chemical equilibrium is solved and discussed in detail in Edelen's works [39, 143].

Again as in Sect. 3.8, conditions of stability give the dynamical stability at other conditions. Thus, similar asymptotic evolution to the equilibrium state of a chemically reacting linear fluid mixture in a closed vessel immersed in a thermostat and in an external gravitation field may be discussed [79, 143].

Here we show another example (cf. Edelen [39] for more details): asymptotic evolution to equilibrium of the linear fluid mixture with regular equilibrium response, fulfilling the stability conditions ((4.357), (4.358) and positive definiteness of (4.360)) and placed in a thermostated cylinder closed by piston under constant pressure. That is, the boundary of this mixture is under constant temperature T^o (over the whole boundary) and its movable part is under constant pressure P^o, i.e. the whole stress (4.94) is

$$\mathbf{T} = -P^o\mathbf{1} \tag{4.390}$$

Further, there are the same velocities of all constituents on the boundary: on its fixed part $\mathbf{v}_\alpha = \mathbf{o}$, on its movable part $\mathbf{v}_\alpha \equiv \mathbf{v}$, $\alpha = 1, \ldots, n$. We assume also that there is no radiation $Q = 0$ (4.303) (but exchange of heat by heat flux $\mathbf{q}$ through the boundary is possible), the frame is inertial $\mathbf{i}_\alpha = \mathbf{o}$ and there are no body forces $\mathbf{b}_\alpha = \mathbf{o}$. Total mass of the mixture m^o is constant but starting masses of constituents m_α can change by chemical reactions. We intend to show that an arbitrary (non-equilibrium) state of this mixture develops on conditions just given to an equilibrium state, i.e. that such a state is stable. The balance of energy (4.77) for such a mixture at these conditions is

$$\overset{\cdot}{\overline{\sum_{\alpha=1}^{n} \int_V (w_\alpha u_\alpha + w_\alpha (1/2)\mathbf{v}_\alpha^2)\rho \,\mathrm{d}v}} = -P^o \int_{\partial V} \mathbf{v}.\mathbf{n}\,\mathrm{d}a - \int_{\partial V} \mathbf{q}.\mathbf{n}\,\mathrm{d}a \tag{4.391}$$

where the left-hand side of (4.77) was transformed by Reynolds theorem (3.24) with the use of material derivative $\backslash\alpha$ (cf. below (4.9)); because V is the same for all constituents and on its surface $\mathbf{v}_\alpha = \mathbf{v}$ we use a dot instead of $\backslash\alpha$ in the sense used in this section, see below (4.323). By the same arguments, we can use (3.23), (3.22) (with $\psi = \rho v = 1$) on the first surface integral in (4.391) to obtain

$$P^o \int_{\partial V} \mathbf{v}.\mathbf{n}\,\mathrm{d}a = \overset{\cdot}{\overline{\int_V P^o \rho v\,\mathrm{d}v}} \tag{4.392}$$

and we put (4.392) to the left-hand side of (4.391). Moreover, we subtract the following quantity with constants g_α^o $(\alpha = 1, \ldots, n)$ from the left hand side of (4.391):

$$\overset{\boldsymbol{\cdot}}{\overline{\int_V \sum_{\beta=1}^{n-1} w_\beta (g^o_\beta - g^o_n)\rho \, \mathrm{d}v}} = \sum_{\beta=1}^{n-1} (g^o_\beta - g^o_n) \overset{\backslash\beta}{\overline{\int_V \rho_\beta \, \mathrm{d}v}} = \int_V \sum_{\alpha=1}^{n} g^o_\alpha r_\alpha \, \mathrm{d}v$$
$$= -\int_V \vec{A}^o . \vec{J} \, \mathrm{d}v = 0 \tag{4.393}$$

which is equal to zero by (4.311) (we use (4.16) in the form (d) in Rem. 3, (4.20) and the product from (4.178), see (4.174), (4.172), (4.26), (4.36)). Namely, in (4.393), w_β, ρ_β, ρ, $\vec{J}$, V are taken in an arbitrary state (say the initial one) but constants g^o_α are the chemical potentials in (uniform) chemical equilibrium mixture at its T^o, P^o and w^o_β (these values characterize the final equilibrium state in the evolution of the starting state at given conditions as we shall see below). Thus from (4.391), we obtain (using (4.90))

$$\overset{\boldsymbol{\cdot}}{\overline{\int_V \rho(u + P^o v - \sum_{\beta=1}^{n-1} w_\beta (g^o_\beta - g^o_n) + (1/2) \sum_{\alpha=1}^{n} w_\alpha \mathbf{v}^2_\alpha) \, \mathrm{d}v}} = -\int_{\partial V} \mathbf{q}.\mathbf{n} \, \mathrm{d}a \tag{4.394}$$

Now we write the entropy balance (4.83) for our mixture with fixed temperature T^o on the boundary (and $Q = 0$) using entropy production σ and Reynolds theorem (3.24) (with a dot instead of $\backslash\alpha$ argumenting similarly as below (4.391))

$$\overset{\boldsymbol{\cdot}}{\overline{\int_V \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \, \mathrm{d}v}} + (1/T^o) \int_{\partial V} \mathbf{q}.\mathbf{n} \, \mathrm{d}a = \int_V \sigma \, \mathrm{d}v \geq 0 \tag{4.395}$$

Multiplying (4.395) by T^o, using (4.91) and inserting here (4.394), we obtain

$$\dot{R}(t) = -T^o \int_V \sigma \, \mathrm{d}v \leq 0 \tag{4.396}$$

where we define the canonical function $R = R(t)$ as follows

$$R(t) \equiv \int_V \rho(u - T^o s + P^o v - \sum_{\beta=1}^{n-1} w_\beta (g^o_\beta - g^o_n) + (1/2) \sum_{\alpha=1}^{n} w_\alpha \mathbf{v}^2_\alpha) \, \mathrm{d}v \tag{4.397}$$

Now, because of conditions of stability ((4.357), (4.358) and the positive definiteness of matrix (4.360)), inequality (4.351), and therefore (cf. (A.72), (A.73)) equivalently (4.382), is valid in a chemical equilibrium state characterized by T^o, P^o, w^o_β (in (4.382) is $s^o = \tilde{s}(T^o, P^o, w^o_\beta)$ by (4.217)). This inequality (4.382) may be transformed by (4.197), (4.198), (4.192), (4.23) in the form

$$u - T^o s + P^o v - \sum_{\beta=1}^{n-1} w_\beta (g^o_\beta - g^o_n) > g^o_n \tag{4.398}$$

Adding to the left-hand side of (4.398) a non-negative quantity $(1/2)\sum_{\alpha=1}^{n} w_\alpha \mathbf{v}_\alpha^2$ (velocities are in the place and instant where u, s, v, w_β, etc. are considered), multiplying by $\rho > 0$ and integrating over the (material) volume of all the mixture we obtain

$$R(t) \geq R^o \equiv g^o_n \int_V \rho \, \mathrm{d}v = g^o_n m^o \tag{4.399}$$

where the definition of canonical function (4.397) was used (the integral in (4.399) is obviously the constant mass m^o of the whole mixture). Equality in (4.399) occurs when T^o, P^o, w^o_β and therefore u^o, s^o, v^o, etc. and also $\mathbf{v}_\alpha = \mathbf{o}$ for all constituents are valid throughout the mixture.

Thus we constructed, analogously as in previous examples in Sects. 4.7 and 3.8, the canonical function $R(t)$ which does not increase (4.396) and has a lower bound (4.399).

Therefore, similarly as by (4.387) or (3.266), it may be expected that also equality in (4.399) is achieved at $t \to \infty$.

$$\lim_{t\to\infty} R(t) = R^o \tag{4.400}$$

This is motivated similarly as (3.266), (3.281), (4.387). Other similar assumptions (giving (3.267), (3.268), (4.388),(4.389)) may be used to derive similar results $\lim_{t\to\infty} \dot{R} = 0$ and $\lim_{t\to\infty} \sigma = 0$, valid permanently and in all the mixture (with similar consequences as (4.389)).

We therefore find that the mixture of linear fluids with regular equilibrium response achieves a uniform equilibrium state with T^o, P^o everywhere in the mixture (because they were such permanently at the boundary) and therefore with w^o_β (calculated analogously as from (4.380) (using T, P, w_β as independent variables), (4.381)) and moreover with $\mathbf{v}_\alpha = \mathbf{o}$ in all the mixture (because this was permanently held on the part of its boundary).

Summary. This section analyses the equilibrium in the mixture of linear fluids equipped with the regularity condition introduced in the preceding section. The equilibrium was defined by zero entropy production, zero reaction rates and excluding the body heating, cf. (4.301)–(4.303), respectively. The entropy production or its parts given in Sect. 4.5 reach also a minimum in such equilibrium. From all these equilibrium characteristics, several important results can be derived. Chemical affinities of independent reactions are zero in equilibrium, cf. (4.312). The remark 22 contains an important restriction on rates of these reactions, the relation (*e*), as will be shown in Sect. 4.9. The constitutive equations which are changed in equilibrium are shown by (4.319)–(4.321), other remained unchanged, viz. (4.157)–(4.159). The equilibrium is permanent in time as shown on page 213 but the space changes are not excluded, unless the equilibrium is uniform, see pages 213–214. Most of this section is devoted to the analysis of stability of equilibrium. The dynamical stability is postulated on page 215 and the stability *per se* on page 216. The main results of the analysis of equilibrium are as follows: There is an upper—equilibrium—bound on entropy, see (4.345), and entropy as a function (4.348) is strictly concave; see also (4.383) and (4.386). The conditions of stability were derived in the form of (4.339)–(4.359). The condition (4.375) proves the regularity of the matrix (4.362) which was only supposed in previous section. Similarly, the conditions (4.358) prove the invertibility of the specific volume as a function of pressure and justify the introduction of pressure among independent variables which was done also in preceding section. Note that all these regularity conditions are valid in stable mixtures only, i.e. mixtures with stable equilibrium. This section concludes with the example analysing the approach to equilibrium of linear fluid mixture with regularity conditions placed in a thermostated cylinder with piston under constant pressure. The evolution to equilibrium is described by the canonical function defined in (4.397), see (4.396), (4.398), and (4.400).

4.8 Special Cases of Linear Fluid Mixtures. Chemical Potentials and Activities

Here we discuss some special cases of the (reacting, non-simple) fluid mixture with linear transport properties of Sect. 4.1–4.7 which may be often obtained by simplification of this model [16, 61, 65, 149–151]; simplified models for pure fluids were also discussed in Sects. 3.6–3.8. But simplification must be done carefully, e.g. the expression for entropy production should give additional results by admissibility, cf. end of Sect. 3.6, Rem. 25.

In this Sect. 4.8 we discuss also the results concerning chemical potentials and activities, studied mainly by classical equilibrium thermodynamics of mixtures [129, 138, 141, 152]. These are also valid in our models, among others in non-equilibrium (e.g. in transports or/and chemical reactions), because of the validity of local equilibrium, cf. Sect. 4.6.

While in the previous sections the difference between pure constituent and mixture was given by separated Chap. 3 and in this chapter (e.g. g in Sect. 3.7 concerns pure constituent (3.205) while in Sect. 4.6 the same symbol g concerns the mixture (4.192)) in the following we use both concepts together and therefore we use (namely in places where misunderstanding is possible) the following indexation:

$^\bullet$ means the pure fluid
^{0} means the pure ideal gas (note the difference from the equilibrium value ^{o})
s denotes the standard value or state (specified below, e.g. $^\ominus$ in (4.468))

Therefore, e.g. g or g_α is the Gibbs specific energy of the mixture or of constituent α in the mixture respectively, while $g^\bullet$ or even $g^\bullet_\alpha$ both are the *same* Gibbs specific energy of pure fluid (gas or liquid); by index α we only stress that we consider (in this case pure) constituent α. Moreover, $Mg^{\bullet} = \mu^{\bullet} = \mu_{\alpha}^{\bullet} = M_{\alpha} g_{\alpha}^{\bullet}$ is the molar Gibbs energy of the pure constituent α with the molar mass $M = M_{\alpha}$. We also often write for brevity $x_{\alpha} = 0, x_{\alpha} = 1, P = 0$, instead of limits $x_{\alpha} \to 0, x_{\alpha} \to 1, P \to 0$, etc. (cf. non-zero assumption of all densities at the beginning of Sect. 4.2), e.g. the (practically) pure constituent 1 follows from a binary mixture if $x_2 \to 0, x_1 \to 1$, (the presence of 2 is negligible).

(i) *Non-reacting Mixture of Non-simple Linear Fluids*

In this mixture, zero chemical reactions rates (4.15) are valid identically for all constituents

$$r_{\alpha} \equiv 0 \qquad \alpha = 1, \ldots, n \tag{4.401}$$

Therefore, the expressions containing r_{α} are eliminated from the results of Sect. 4.5–4.7. We note only that in a non-reacting mixture equations (4.184) are valid and therefore identically (see (4.186))

$$P_{\alpha} \equiv p_{\alpha} \qquad \alpha = 1, \ldots, n \tag{4.402}$$

i.e. the thermodynamic pressure P (4.187) is measurable through (4.94), (4.138) in principle. In the non-reacting mixture, all transport coefficients form positive semidefinite matrices, i.e. besides (4.181) we have instead of (4.182)

$$\nu_{\beta\beta} \geq 0 \tag{4.403}$$

Equilibrium discussions are more simple as was noted in Sect. 4.7; e.g. regularity (giving usual stability of equilibrium) demands inequality only in (4.403). For the case $n = 1$ we recover the results for the single linear fluid of Sect. 3.6.

(ii) *Incompressible Fluid Mixture* [104, 153]

which, as may be expected, should have similar properties (3.215), (3.216) as the incompressible fluid discussed at the end of Sect. 3.7. But the situation is not so simple because of the dependence on composition. Namely, using the Müller's concept [18] of incompressibility as independence of properties on pressure, elimination of the pressure P from the independent variables $T, P, w_1, \ldots, w_{n-1}$ (cf. (4.279), (4.280)) gives, from (4.282), $\frac{\partial \tilde{\rho}}{\partial T} \equiv 0$. Therefore, the density of the mixture (and by (4.195) also the specific mixture volume) remains dependent on mass fractions only

$$\rho = \tilde{\rho}(w_{\beta}), \qquad v = \tilde{v}(w_{\beta}) \tag{4.404}$$

(cf. the difference from (3.215) in pure incompressible fluid).

From the last result $(4.404)_2$ of an incompressible mixture, the formulae (4.269), (4.270) for $y = v$ give that partial volumes depend on w_{β} only, $v_{\alpha} = \tilde{v}_{\alpha}(w_{\beta})$, and also (4.191) is

$$v = \tilde{v}(w_{\beta}) = \sum_{\alpha=1}^{n} w_{\alpha} \tilde{v}_{\alpha}(w_{\beta}) \tag{4.405}$$

Therefore, the constant mixture density is not achieved (as in (3.215)), unless further assumptions are adopted:

The usual assumption is the independence of partial volumes on composition [58, 153]

$$v_\alpha = v^\bullet_\alpha = 1/\rho^\bullet = \text{const.} \tag{4.406}$$

where $\rho^\bullet = \rho^\bullet_\alpha$ may be interpreted as the constant density of the pure incompressible fluid constituent α before mixing (cf. (3.215)) and (4.405) expresses the Amagat law (incompressible fluid mixture is *volume-additive*), cf. (4.440) or (with (4.195), (3.199))

$$1/\rho = \sum_{\alpha=1}^{n} w_\alpha (1/\rho^\bullet_\alpha) \tag{4.407}$$

We again see that the constant mixture density is not achieved and further additional assumptions are needed, like (see [104]):

- Restriction to a (chemically) non-reacting incompressible mixture: mixture density (4.404) is constant because the composition is fixed ($w_\beta = \text{const.}$).
- Another possibility for a volume-additive incompressible (even reacting) mixture is (approximately) the same density $\rho^\bullet_\alpha$ of all constituents and therefore equal to the constant mixture density ρ

$$\rho^\bullet_\alpha = \rho = \text{const.} \qquad \alpha = 1, \ldots, n \tag{4.408}$$

- Another plausible assumption, e.g. in dilute (usually aqueous) solutions (water is the n-th constituent) where the mixture density is practically constant and equal to the density of pure water $\rho = \rho^\bullet_n = \text{const.}$ because $w_\beta \ll w_n$, $\beta = 1, \ldots, n-1$, see [104].

Therefore with such (or similar) additional assumptions, the constant density for incompressible fluid mixture should be achieved and also other properties are obtained (properties from Rem. 3 based on barycentric velocity are often used [58])

$$\rho = \text{const.} \qquad \dot{\rho} = 0 \qquad \operatorname{div} \mathbf{v}^w = 0 \tag{4.409}$$

Here ρ is the mixture density (4.21), $\dot{\rho}$ its material derivative relative to the barycentric velocity $\mathbf{v}^w$ defined as (c) in Rem. 3; the last expression follows from the previous one by mass balance (b) here.

(iii) *Mixture of Simple Linear Fluids (Simple mixture)*

As a simple fluid, we denoted a fluid, the response of which was independent of density gradient (cf. end of Sect. 3.6, [16–18, 56, 61]). Therefore a *mixture of simple linear fluids* or shortly a *simple mixture* of fluids is that from Sect. 4.6 (fulfilling, e.g.(4.263), (4.269), (4.270), (4.278)) defined by a priori absence of the density gradients $\mathbf{h}_\alpha$ in (4.136), (4.137) or equivalently (4.149) and identities

$$\omega_{\beta\gamma} = 0 \qquad \beta = 1, \ldots, n-1; \;\; \gamma = 1, \ldots, n \tag{4.410}$$

are valid. As a consequence, there is significant reduction of dependence of thermodynamic quantities on composition in the simple fluid mixture. Namely, from (4.410) identically follows

$$\frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \equiv 0 \qquad \alpha \neq \gamma, \quad \alpha, \gamma = 1, \ldots, n \tag{4.411}$$

because of (4.165) and (for $\alpha = n$) of (4.161),(4.92),(4.22) (recall that $\omega_{\beta\beta} = 0, \delta_{\beta n} = 0, \beta = 1, \ldots, n-1$). Then also (4.161) reduces to

$$\frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\alpha} = g_\alpha = \hat{g}_\alpha(T, \rho_\alpha) \qquad \alpha = 1, \ldots, n \tag{4.412}$$

Therefore, we found that in the mixture of simple fluids, the partial free energy of constituent α is independent of densities of other constituents (note the difference with (4.159))

$$f_\alpha = \hat{f}_\alpha(T, \rho_\alpha) \qquad \alpha = 1, \ldots, n \tag{4.413}$$

as well as the chemical potential (4.412). This surprising result (4.413) was shown first by Müller [16] for simple models with linear transport.[25]

The same simplifying property is valid by (4.200) for partial thermodynamic pressure

$$\rho_\alpha^2 \frac{\partial \hat{f}_\alpha}{\partial \rho_\alpha} = P_\alpha = \hat{P}_\alpha(T, \rho_\alpha) \qquad \alpha = 1, \ldots, n \tag{4.414}$$

From (4.194), (4.413), (4.412) it may be seen that also $P v_\alpha$ depends on corresponding ρ_α only (and T) in contrast with $P, v_\alpha, s_\alpha, u_\alpha, h_\alpha$ which generally depend on all

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[25] Therefore, simple models excluding density gradients from independent variables of constitutive equations a priori are not able to describe, e.g. classical thermodynamics of solutions [129, 138] (cf. Sect. 4.6); a gaseous simple mixture is in fact the mixture of ideal gases only [61], see (iv) below.

Result (4.411) may be valid in some more general but simple fluids [17, 18, 53]. For example, in non-linear (even reacting) simple fluid mixture from [72] where the density gradients $\mathbf{h}_\gamma$ are removed a priori: they are absent, e.g. in constitutive equations [72, (2.26)–(2.33)] and the "second" chemical potentials [72, (2.47)] they are zero. Therefore, the 4th and 5th term in the right-hand side of [72, (2.64)] are linear in $\mathbf{h}_\gamma$ in such a simple mixture and, consequently, again by the admissibility principle (using Lemma A.5.1 from Appendix A.5), the following identities are valid

$$(g_\alpha - f_\alpha)\mathbf{u}_\alpha - \sum_{\gamma=1}^{n} \rho_\gamma \frac{\partial \hat{f}_\gamma}{\partial \rho_\alpha} \mathbf{u}_\gamma = \qquad \alpha = 1, \ldots, n$$

(in [72, (2.64)] is a misprint: the 5th term should include a negative sign). Manipulating here with the independent diffusion velocities $\mathbf{u}_\alpha$ (note that $\mathbf{u}_n \equiv \mathbf{o}$, [72, (2.23), (2.46)]) we arrive at (4.411). Cf. also [79, Sect. 40]. Because the thermodynamic structure in this non-linear model is the same (cf. [72, (2.46), (3.28), (3.29)]) also other relations, like (4.412), (4.414) remain valid here.

$\rho_1, \ldots, \rho_n$ and T (cf. (4.413)–(4.414), (4.194), (4.187), (4.188), (4.189), (4.272), (4.86)).[26]

We can show that such a simple fluid mixture has a special form of "state equation" (4.414): indeed, we noted above (4.278) that expressions $(\rho_\alpha / P_\alpha)(\partial \hat{P} / \partial \rho_\alpha)$ are the same for all constituents $\alpha = 1, \ldots, n$ (cf. [61, Eq. (2.11)]) generally, but for a simple mixture, using (4.414) in (4.187) we have $\partial \hat{P} / \partial \rho_\alpha = \partial \hat{P}_\alpha / \partial \rho_\alpha$ depending, as well as P_α, only on the density of the considered constituent α (and on temperature). Therefore, there is a universal C (possibly a function of temperature)

$$\frac{\rho_\alpha}{P_\alpha} \frac{\partial \hat{P}_\alpha}{\partial \rho_\alpha} = C = C(T) \qquad \alpha = 1, 2, \ldots, n \tag{4.415}$$

in a simple mixture.

By integration, we obtain the following general form of dependence of partial pressures on densities in a simple fluid mixture (the state equation)

$$P_\alpha = K_\alpha (\rho_\alpha)^C \qquad \alpha = 1, 2, \ldots, n \tag{4.416}$$

where $K_\alpha = K_\alpha(T)$, as well as $C(T)$, are functions of temperature T only.

We note also that for such a simple fluid mixture we have from (4.415) and (4.414) that $\partial^2 \hat{f}_\alpha / \partial \rho_\alpha^2 = ((C-2)/\rho_\alpha) \partial \hat{f}_\alpha / \partial \rho_\alpha$ and therefore $\partial \hat{P}_\alpha / \partial \rho_\alpha = (C \rho_\alpha) \partial \hat{f}_\alpha / \partial \rho_\alpha$ and by (4.412) $\partial \hat{g}_\alpha / \partial \rho_\alpha = C\, \partial \hat{f}_\alpha / \partial \rho_\alpha$.

Using these and previous formulae, we can obtain from (4.273) for a simple fluid mixture (by (4.187))

$$\begin{aligned} v_\alpha &= (\frac{\partial \hat{P}_\alpha}{\partial \rho_\alpha}) / \left(\sum_{\gamma=1}^{n} \rho_\gamma \frac{\partial \hat{P}_\gamma}{\partial \rho_\gamma} \right) = \rho_\alpha (\frac{\partial \hat{f}_\alpha}{\partial \rho_\alpha}) / \left(\sum_{\gamma=1}^{n} \rho_\gamma^2 \frac{\partial \hat{f}_\gamma}{\partial \rho_\gamma} \right) = \frac{K_\alpha \rho_\alpha^{C-1}}{P} \\ &= \rho_\alpha (\frac{\partial \hat{g}_\alpha}{\partial \rho_\alpha}) / \left(\sum_{\gamma=1}^{n} \rho_\gamma^2 \frac{\partial \hat{g}_\gamma}{\partial \rho_\gamma} \right) \qquad \alpha = 1, \ldots, n \end{aligned}$$

The dependence of partial properties $f_\alpha, g_\alpha, P_\alpha, P v_\alpha$ only on the density of corresponding constituent α (besides T) in this simple mixture means (if we put $\rho_\gamma \to 0$ for other constituents) that such a partial property may be interpreted as a corresponding property of pure constituent α at the same density and temperature (as ρ_α, T in the mixture considered). E.g. relation (4.414) together with (4.187) expresses the classical Dalton law valid in this simple fluid mixture because we can interpret P_α as the pressures of pure constituents α at a given density and temperature before mixing, the sum (4.187) of which is the pressure P of the mixture at the same partial densities and temperature.

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[26] We stress that we use only the classical partial thermodynamic quantities, calculable (say) by (4.269), (4.270), but there are also other possible definitions, e.g. partial entropies by $-\frac{\partial \hat{f}_\alpha}{\partial T}$ (different by (4.272)), cf. [17, 18]. These are, however, not so useful as those classical.

(iv) *Mixture of Ideal Gases*

We show here that the mixture of ideal gases is equivalent to the simple fluid mixture from (iii), if its constituents and their mixture are gases [61] (modelling gas by linear fluid seems to be sufficient; moreover, the thermodynamic relations used here remain valid even in some models with non-linear transport as in [72], cf. Rem. 25).

The density and pressure of pure real gas (as different from liquid) goes to zero simultaneously, see Appendix A.1. Therefore, Pv_α considered for a pure gas constituent (i.e. as a product of the pressure P and the specific volume v_α of the pure constituent α; we omit symbols above with which we could write $P^\bullet = P^\bullet_\alpha, \rho^\bullet_\alpha = 1/v^\bullet_\alpha$, cf. (3.199)) has the property (A.1) permitting the introduction of absolute temperature based on any gas (see Appendix A.1; we use T (1.30) for temperature), that is

$$\lim_{\rho_\alpha \to +0} Pv_\alpha = \frac{\mathrm{R}T}{M_\alpha} = \lim_{\rho_\alpha \to +0} \frac{P_\alpha}{\rho_\alpha} \qquad \alpha = 1, \ldots, n \tag{4.417}$$

where R is the gas constant and M_α is the molar mass of the constituent.

Now, following the property of the simple mixture discussed at the end of (iii) above, we can interpret (4.417) and the quantities in it as those in a gaseous simple fluid mixture, i.e. $P_\alpha, \rho_\alpha, v_\alpha$ are corresponding partial quantities in this mixture fulfilling, e.g. (4.278), (4.188). Inserting (4.416) into (4.417) we obtain

$$\lim_{\rho_\alpha \to +0} (\rho_\alpha)^a = b \qquad \alpha = 1, \ldots, n \tag{4.418}$$

where $a \equiv C - 1, \quad b \equiv \mathrm{R}T/(K_\alpha M_\alpha)$.

But (4.418) is valid if and only if $a = 0, \quad b = 1$ (limits b for $a > 0$ or $a < 0$ are 0 or $+\infty$ respectively without physical sense; densities are only positive). Therefore $C = 1, \quad K_\alpha = \mathrm{R}T/M_\alpha$ and "state equation" (4.416) of the simple gas mixture is an *ideal* one

$$P_\alpha = \rho_\alpha \frac{\mathrm{R}T}{M_\alpha} \qquad \alpha = 1, \ldots, n \tag{4.419}$$

valid at any density and pressure (and not only in the limit (4.417)). This and the following relations show that the gaseous simple fluid mixture is the *ideal gas mixture*.

Moreover, for such a simple gas mixture, it follows by (4.419), (4.278) that partial molar volumes $v_\alpha M_\alpha$ of all constituents are the same

$$v_\alpha M_\alpha = \mathrm{R}T/P \qquad \alpha = 1, \ldots, n \tag{4.420}$$

From this, the independence of $v_\alpha = \tilde{v}_\alpha(T, P)$ on $w_1, \ldots, w_{n-1}$ follows (see (4.216)) which permits interpretation of v as the specific volume of the pure constituent α and (4.191) expresses the validity of Amagat's law in an ideal gas mixture (Amagat's law asserts that partial specific volumes in mixture in (4.191) are equal to specific volumes of pure constituents at the same P, T of the mixture, cf. (4.440) below); here, moreover, all molar partial volumes are the same (4.420).

Using (4.191), (4.420), (4.294) we obtain for the molar volume of mixture vM (4.295) the following state equation for the ideal gas mixture (which is the same as for pure ideal gas (A.3))

$$PvM = \mathrm{R}T \tag{4.421}$$

Equations (4.421) and (4.419), (4.420) are state equations of the ideal gas for the mixture and its constituents. Note, that interpreting (4.417) as valid for every constituent $\alpha = 1, \ldots, n$ in a simple gaseous mixture, multiplying each (4.417) by w_α and summing them we obtain (using (4.191), (4.294); the limit in all ρ_α with fixed w_α may be obviously substituted by the limit in P)

$$\lim_{P \to +0} Pv = \mathrm{R}T/M \tag{4.422}$$

But, following the discussion given at the end of iii. above and similarly as for the first "pure" interpretation of (4.417), we can interpret (4.422) as a limiting property of each real gas mixture of fixed composition, i.e. property (A.3) is valid also for mixtures of real gases which therefore in the limit of zero pressures behaves as an ideal gas mixture with state equation (4.421).

Inserting (4.419) through (4.187) into (4.278) we obtain

$$\rho_\alpha v_\alpha = (\frac{\rho_\alpha}{M_\alpha})/\left(\sum_{\gamma=1}^{n} \frac{\rho_\gamma}{M_\gamma}\right) = x_\alpha \qquad \alpha = 1, \ldots, n \tag{4.423}$$

i.e. $\rho_\alpha v_\alpha$ in the ideal gas mixture is equal to the molar fraction (see (4.288), (4.290)). From (4.278) the Dalton law for partial pressures for the mixture of ideal gases follows:

$$P_\alpha = x_\alpha P \qquad \alpha = 1, \ldots, n \tag{4.424}$$

which fulfils (another form of) Dalton's law (4.187).

From (4.423) (cf. (4.213)) we can also see that the partial specific volumes are independent of temperature in the ideal gas mixture

$$v_\alpha = \hat{v}_\alpha(\rho_\gamma) \qquad \alpha = 1, \ldots, n \tag{4.425}$$

and therefore instead of general result (4.272) we have

$$-\frac{\partial \hat{f}_\alpha}{\partial T} = s_\alpha = \hat{s}_\alpha(T, \rho_\alpha) \qquad \alpha = 1, \ldots, n \tag{4.426}$$

in the ideal gas mixture. This is not only an analogue of general result (4.164) but, moreover and much more importantly, it gives partial entropy as depending on the density ρ_α of the constituent α only (besides T; cf. also (4.434)). Then, according to the discussion at the end of (iii) above, the partial entropy s_α may be interpreted as specific entropy of *pure* (ideal) gas at a density equal to those in the mixture. This permits direct calculation of the *mixing entropy* (4.435) from pure ideal gases. This traditional calculation of mixing entropy in the ideal gas mixture is therefore well motivated by the fact that this mixture is the simple one.

Further, partial internal energies and enthalpies are functions only of temperature in the ideal gas mixture (simple gas mixture)

$$u_\alpha = \hat{u}_\alpha(T) \qquad \alpha = 1, \ldots, n \tag{4.427}$$

$$h_\alpha = \hat{h}_\alpha(T) \qquad \alpha = 1, \ldots, n \tag{4.428}$$

Equation (4.427) follows from (4.86) and from (4.426) by derivation with respect to ρ_α. Namely, $\frac{\partial \hat{u}_\alpha}{\partial \rho_\alpha} \equiv 0$ because it follows from (4.414) and (4.419)

$$\frac{\partial \hat{f}_\alpha}{\partial \rho_\alpha} = \frac{P_\alpha}{\rho_\alpha^2} = \frac{\mathrm{R}T}{M_\alpha \rho_\alpha} \qquad \alpha = 1, \ldots, n \tag{4.429}$$

Equation (4.428) then follows from (4.189), (4.427), (4.420).

Then, e.g. the internal energy u of the ideal gas mixture (and therefore, the heat capacity of the mixture (4.357)) depends on its composition in a simple way as may be seen from (4.427), (4.90).

The well-known logarithmic dependence of partial free energies, entropies or chemical potentials on composition in the ideal gas mixture (like densities, molar concentrations or fractions, partial pressures, etc.) follows as a consequence of the ideal state equation (4.419). For example, by integration of (4.429)

$$f_\alpha = \hat{f}^0_\alpha(T) + \frac{\mathrm{R}T}{M_\alpha} \ln \rho_\alpha \qquad \alpha = 1, \ldots, n \tag{4.430}$$

where $\hat{f}^0_\alpha(T)$, depending on temperature only, is the free energy of pure gas α at unit density (depending on its physical dimension). Inserting (4.430) with (4.419), (4.420) into (4.194) we have with classical partial pressure (4.424) in the ideal gas mixture

$$g_\alpha = \hat{g}^0_\alpha(T) + \frac{\mathrm{R}T}{M_\alpha} \ln P_\alpha \qquad \alpha = 1, \ldots, n \tag{4.431}$$

with $\hat{g}^0_\alpha(T) \equiv \hat{f}^0_\alpha(T) + (\mathrm{R}T/M_\alpha)(1 + \ln(M_\alpha/\mathrm{R}T))$ depending again on pressure units. Equation (4.431) is one of the proposed definitions of the mixture of ideal gases, cf. [154] (Chap. 3).

Here it has been shown that the property of the ideal gas mixture follows from the model of a simple fluid mixture of gases. In fact both these models are equivalent, because from (4.430), (4.431), (4.419) Eqs. (4.413), (4.412), (4.414) follow [61].

The result (4.431) may be written for the more usual molar chemical potential μ_α (4.172) using (4.424) as a logarithmic function of the molar fraction in the mixture of ideal gases

$$\mu_\alpha = (M_\alpha g_\alpha^0(T) + \mathrm{R}T\ln P) + \mathrm{R}T\ln x_\alpha = \mu_\alpha^0(T, P) + \mathrm{R}T\ln x_\alpha \qquad \alpha = 1, \dots, n \tag{4.432}$$

where $\mu_\alpha^0(T, P)$ is the molar chemical potential of pure ideal gas constituent α at T, P of the mixture (as follow from $x_\alpha \to 1$). Hence the mixture of ideal gases (or gaseous mixture of simple fluids) is an example of an *ideal mixture* defined by (4.437) below.

From (4.432), we obtain by (4.290), (4.295), (4.421) for a mixture of ideal gases

$$\mu_\alpha = (M_\alpha g_\alpha^0(T) + \mathrm{R}T\ln \mathrm{R}T) + \mathrm{R}T\ln c_\alpha = \mu_\alpha^0(T) + \mathrm{R}T\ln c_\alpha \qquad \alpha = 1, \dots, n \tag{4.433}$$

(as the simple mixture fulfils $(4.412)_2$ in molar units) used below, see (4.468), (4.469), Rem. 27.

Using (4.432) in (4.266) (with molar units (4.172); at constant w_δ is such also x_δ, see (4.292), (4.297)) we obtain for the molar entropy in the mixture of ideal gases

$$\frac{\partial \overline{\mu_\alpha}}{\partial T} = M_\alpha s_\alpha = M_\alpha s_\alpha^0(T, P) - \mathrm{R}\ln x_\alpha \qquad \alpha = 1, \dots, n \tag{4.434}$$

where $M_\alpha s_\alpha^0(T, P)$ is the molar entropy of pure ideal gas α at T, P of the mixture. Using (4.267) we obtain (4.420) analogously.

Equation (4.434) permits the calculation of *mixing entropy* (change of entropy at mixing of pure constituents to mixture) defined as the difference between the entropy of the mixture and the sum of entropies of pure constituents: molar mixing entropy (related to one mole of mixture, is therefore (using molar quantities in (4.434), (4.91), (4.292) at the same T, P of pure constituents and in mixture):

$$Ms - \sum_{\alpha=1}^{n} x_\alpha M_\alpha s_\alpha^0 = M \sum_{\alpha=1}^{n} w_\alpha (s_\alpha - s_\alpha^0) = -\mathrm{R} \sum_{\alpha=1}^{n} x_\alpha \ln x_\alpha \tag{4.435}$$

Just because this is the simple mixture, the partial entropy s_α may be interpreted as specific entropy of *pure* (ideal) gas at a density equal to those in the mixture (see (4.426) and below), and the mixing entropy may be calculated as the sum of entropy changes at the expansion of *pure* (ideal) gases α (with masses w_α) from starting density (before mixing) to final density (as in the mixture).

It is possible to define another mixing property in a similar way (besides s also for v, u, h, f, g), e.g. the specific *mixing volume* (related to mass unit of mixture) is defined as the left hand side of following equation

$$v - \sum_{\alpha=1}^{n} w_\alpha v_\alpha^0 = 0 \tag{4.436}$$

This mixing volume is zero for ideal gases because the specific volume of mixture is given by (4.421) and the specific volume of pure ideal gas α at the same T, P as in the mixture (w_α is its mass in mixture of unit mass) is $v_\alpha^0 = \mathrm{R}T/PM_\alpha$, cf. (A.3), (4.292), (4.291).

Mixing thermodynamic properties can be calculated in some simple models like (iv) or (v) here. In a general non-simple mixture, they are usually obtained experimentally.

(v) *Ideal Mixture*

Motivated by (4.432) we use in classical thermodynamics (e.g. [129, 138, 152, 155]) the *ideal mixture* or the *ideal solution* defined by the following expression for molar chemical potential of gas or liquid

$$\mu_\alpha = \mu_\alpha^\bullet(T, P) + \mathrm{R}T\ln x_\alpha \qquad \alpha = 1, \ldots, n \tag{4.437}$$

where $\mu_\alpha^\bullet(T, P)$ is the chemical potential of pure fluid (gas or liquid) at the same T, P as in the mixture, R is the universal gas constant (A.2).

An ideal mixture is generally *different* from a simple mixture; an exception is the ideal gas mixture which is also a simple mixture, see (4.432) and Rem. 27. But, on the other side, the ideal mixture (4.437) (and this is its main motivation) has many properties similar to the ideal gas mixture:

- molar mixing entropy follows from (4.266), (4.172) (cf. (4.434)), quite analogously as (4.435) but with (4.437) instead of (4.432): for molar entropy we have

$$M_\alpha s_\alpha = M_\alpha s_\alpha^\bullet(T, P) - \mathrm{R}\ln x_\alpha \qquad \alpha = 1, \ldots, n \tag{4.438}$$

  (where $M_\alpha s_\alpha^\bullet = -\partial\mu_\alpha^\bullet(T, P)/\partial T$ is the molar entropy of pure constituent α) and therefore

$$Ms - \sum_{\alpha=1}^{n} x_\alpha M_\alpha s_\alpha^\bullet = -\mathrm{R}\sum_{\alpha=1}^{n} x_\alpha \ln x_\alpha \tag{4.439}$$

  The mixing entropy in an ideal mixture is therefore the same as in an ideal gas mixture (4.435) but it is valid more generally, e.g. in the liquid the ideal mixture is formed from liquid pure constituents.
- Mixing volume is zero (i.e. no volume changes upon mixing) because *Amagat's law* is valid

$$v = \sum_{\alpha=1}^{n} w_\alpha v_\alpha^\bullet \tag{4.440}$$

  Here v is the specific volume of the mixture at given T, P, $w_1, \ldots, w_{n-1}$ and $v_\alpha^\bullet$ are the specific volumes of *pure* constituents at these T, P equal to v_α in (4.191). Indeed, this follows from (4.437) taking derivative (4.267) (with specific variables, cf. (4.172)) and using (3.207).
- Mixing enthalpy is zero (i.e. no enthalpy changes upon mixing). Indeed, by definition, the specific mixing enthalpy is the difference $h - \sum_{\alpha=1}^{n} w_\alpha h_\alpha^\bullet$ (cf. (4.435), (4.436)) where h is the specific enthalpy of the mixture and $h_\alpha^\bullet$ is the specific

enthalpy of pure α taken at the same T, P. But $h^\bullet_\alpha$ is equal to partial enthalpy h_α in the final mixture, indeed, by (4.189), (4.194), (4.86) (valid also for pure fluid, cf. (3.111), (3.203)) and by ideal mixture relations (4.437), (4.438)

$$\begin{aligned} h_\alpha &= g_\alpha + Ts_\alpha = \mu^\bullet_\alpha/M_\alpha + (\mathrm{R}/M_\alpha)T\ln x_\alpha + Ts^\bullet_\alpha - T(\mathrm{R}/M_\alpha)\ln x_\alpha \\ &= \mu^\bullet_\alpha/M_\alpha + Ts^\bullet_\alpha = h^\bullet_\alpha \end{aligned}$$

(of course enthalpy of pure fluid is defined similarly as (4.199)). Specific mixing enthalpy is therefore zero by (4.190).

- No internal energy changes upon mixing: specific mixing internal energy is zero as follows directly from the previous two results:

$$u - \sum_{\alpha=1}^{n} w_\alpha u^\bullet_\alpha = h - \sum_{\alpha=1}^{n} w_\alpha h^\bullet_\alpha - P(v - \sum_{\alpha=1}^{n} w_\alpha v^\bullet_\alpha) = 0$$

From these results it follows, that in an ideal mixture the partial Gibbs energy $g_\alpha = \mu_\alpha/M_\alpha$, the free energy $f_\alpha = g_\alpha - Pv_\alpha$ and the entropy s_α depend on T, P and on composition in a logarithmic way (see (4.437), (4.438)) but partial volume, enthalpy and internal energy v_α, h_α, $u_\alpha = h_\alpha - Pv_\alpha$ are functions of T, P only. All these results are valid also in special case of ideal gas mixture, cf. (4.433), (4.430), (4.434), (4.420) often even simpler (4.425), (4.427), (4.428).

If such mixing in the ideal mixture proceeds at constant temperature, pressure (and therefore at constant volume simultaneously), the system has constant energy (kinetic energy is usually neglected, cf. Rem. 9 in Chap. 1) and constant mass, no work is done and therefore no heat exchange is observed.

As we noted above, the ideal mixture is generally different from the simple mixture; the exception is the ideal gas mixture which is simple as well as ideal, cf. (4.432) with (4.437).[27]

In the remainder of this section, we discuss the important role of chemical potentials g_α or μ_α because they are sufficient to determine (through (4.266), (4.267), (4.86), (4.194), (4.189)) all other y_α (fulfilling Gibbs-Duhem equation (4.263)). Motivated by application in equilibrium thermodynamics [129, 138, 154, 156] (called *chemical thermodynamics*; but the following is valid also for non-equilibrium situations if local equilibrium is valid, e.g. for models presented in Sects. 4.5 and 4.6), instead of chemical potential μ_α of constituent α the *activity* a_α is used equivalently defined by

$$\mu_\alpha = \mu^s_\alpha + \mathrm{R}T\ln a_\alpha \tag{4.441}$$

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[27] The definition of ideal mixture (4.437) does not fulfil generally the property (4.412) of the simple mixture which should be $\mu_\alpha = \mu_\alpha(T, c_\alpha)$ (in molar units, cf. (4.172), (4.288)). Indeed, for the ideal mixture (by (3.205) $\mu^\bullet_\alpha(T, P) = \mu^\bullet_\alpha(T, c^\bullet_\alpha)$, where $c^\bullet_\alpha = \rho^\bullet_\alpha/M_\alpha$ is the molar density of pure constituent α; $\rho^\bullet_\alpha = \rho$ in Chap. 3)

where R is the gas constant (see Appendix A.1) and μ_α^s is the selected *standard* function (of T, P, w_β or some of them); usually it is called the *standard state*. Note that in the standard state (i.e. when $\mu_\alpha = \mu_\alpha^s$) activity is equal to one.

This special definition (4.441) is motivated by the fact that when a standard function is appropriately chosen, activities (and therefore chemical potentials) are (often at least approximately) expressible through easy measurable quantities like concentrations, pressures, etc. (besides this, μ_α must be determined relatively to some fixed level in practice). Note that activities are only positive, dimensionless and their relation to chemical potentials is unique (for the known standard function). Changing the standard function from μ_α^s to $\mu_\alpha^{s'}$ we can recalculate the corresponding activities from a_α to a'_α by

$$a'_\alpha = a_\alpha / a_\alpha^s \tag{4.442}$$

where a_α^s is the original activity of the new standard state given by $\mu_\alpha^{s'} = \mu_\alpha^s + \mathrm{R}T \ln a_\alpha^s$. (these formulae may be valid for all $\alpha = 1, \ldots, n$, but generally it is not necessary to choose as the standard state the same state for all constituents, cf. example below (4.446)).

Because of the many possibilities of selecting standard functions they must be clearly specified if an activity is to be used; due to practical and historical grounds some activities are called fugacities and, in fact, so-called activity or fugacity coefficients are also of this type [4, 79, 129]. These quantities and other examples of activities will be discussed in the following.

The basic properties of any activity and its use will be first demonstrated on the following classical example of fluid (gas or liquid) mixtures. As the standard function μ_α^s in (4.441) we choose $\mu_\alpha^\bullet(T, P)$ in (4.437), i.e. the chemical potential in the following standard state: pure constituent α at T, P and aggregation state as that

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(Footnote 27 continued)

$$\mu_\alpha = \mu_\alpha^\bullet(T, P) + \mathrm{R}T \ln x_\alpha = \mu_\alpha^\bullet(T, c_\alpha^\bullet) + \mathrm{R}T \ln c_\alpha + \mathrm{R}T \ln \sum_{\gamma=1}^{n} \left(c_\gamma / (\sum_{\varepsilon=1}^{n} c_\varepsilon) \right) (1/c_\gamma^\bullet)$$

where (4.290), (4.295), (4.440), (4.292), (4.289), (3.199) have been used. This is different from $\mu_\alpha = \mu_\alpha(T, c_\alpha)$ mainly because $c_\gamma^\bullet = (M_\gamma v_\gamma^\bullet)^{-1}$ are different for different γ. But in an ideal gas mixture where (at chosen T, P) molar densities are the same for all constituents as well for those which are pure, namely $c_\gamma = c_\gamma^\bullet = P/\mathrm{R}T$, see (4.420), (4.421), this equation (cf. (4.432)) gives (4.433) and this is the simple mixture.

There are attempts to motivate the definition of ideal mixture by a simpler way, e.g. it is possible to show [149, 150] that if the chemical potential of each constituent depends (besides temperature and pressure) only on the molar fraction of that constituent then this dependence is logarithmic as in (4.437) (it is assumed also that the partial internal energy and volume of at least one constituent depends on temperature and pressure only and that the number of constituents must be 3 as a minimum).

The alternative motivation of definition (4.437) for (real) gas mixtures comes from a statement that a mixture is ideal if Amagat's law (4.440) is valid at any T, P. Indeed, Amagat's laws means $v_\alpha = v_\alpha^\bullet$ and then by (4.454), (4.458) below, for fugacity coefficients also $\nu_\alpha = \nu_\alpha^\bullet$; therefore by (4.463), this is an ideal mixture.

in the mixture activity in which we try to find. The motivation follows from (4.437): if the mixture is ideal then activity a_α is equal to molar fraction $a_\alpha = x_\alpha$.

The behaviour of real fluid mixture may be described through deviations from ideal mixture [129, 138, 152, 154, 156] expressed by the *activity coefficient* γ_α defined by

$$a_\alpha = \gamma_\alpha x_\alpha \tag{4.443}$$

which is, similarly to the activity a_α, some function of $T, P, x_\beta,\ \beta = 1, \ldots, n-1$.

For this activity and activity coefficient equation (4.441) is written

$$\mu_\alpha = \mu_\alpha^\bullet(T, P) + \mathrm{R}T \ln a_\alpha = \mu_\alpha^\bullet(T, P) + \mathrm{R}T \ln x_\alpha + \mathrm{R}T \ln \gamma_\alpha \tag{4.444}$$

for the fluid (gas or liquid) constituent α.

Therefore, the activity coefficient is $\gamma_\alpha \equiv 1$ in ideal mixture (4.437), but, as follows from the choice of standard state, even in a real mixture, the activity coefficient has limiting property $\lim_{x_\alpha \to 1} \gamma_\alpha = 1$. (i.e. concentrations of all remaining constituents go to zero in such a limit). This may be also interpreted such that each real mixture behaves in the limit $x_\alpha \to 1$ as the ideal mixture (cf. (4.444) with (4.437) in this limit).

For a description of a dilute solution of constituents $\beta = 1, \ldots, n-1$ in nearly pure solvent n at given T, P we can use another limit: activity coefficients at infinitesimal dilution $\gamma_\beta^\infty = \lim_{x_\beta \to 0} \gamma_\beta$, practically depending only on T, P (the most simple case is one solute $\beta = 1$ in a solvent $n = 2$; also more complicated cases may be discussed when some solutes have got higher concentrations, e.g. when solvents are mixed, but we exclude for simplicity such cases from the following discussions). This permits to introduce another standard state (a “hypothetical” one based on Henry’s law (4.464), see (4.465)) giving new activities a'_β and new activity coefficients γ'_β fulfilling (cf. (4.443))

$$a'_\beta = x_\beta \gamma'_\beta \qquad \beta = 1, \ldots, n-1 \tag{4.445}$$

The (4.441) has the form

$$\mu_\beta = \mu_\beta^\infty + \mathrm{R}T \ln a'_\beta = \mu_\beta^\infty + \mathrm{R}T \ln x_\beta + \mathrm{R}T \ln \gamma'_\beta \qquad \beta = 1, \ldots, n-1 \tag{4.446}$$

which follows from Eq. (4.444) (applied on our dilute mixture with chemical potentials μ_α) by using the limiting γ_β^∞. Namely, we use the following definitions of new standard functions $\mu_\beta^\infty \equiv \mu_\beta^\bullet + \mathrm{R}T \ln \gamma_\beta^\infty$ and new activity coefficient $\gamma'_\beta \equiv \gamma_\beta / \gamma_\beta^\infty$. From this definition it follows that the new activity coefficient γ'_β has the following property $\lim_{x_\beta \to 0} \gamma'_\beta = 1$ (cf. difference from γ_β above).

Therefore in very dilute solution, the activities (4.445) of solutes a'_β may be substituted by molar fractions x_β and this is the main reason for using such a standard state, cf. (4.465). Note, that solvent n in such dilute solution is nearly a pure one and therefore it remains in the original standard state (4.444) for $\alpha = n$ (with nearly

$a_n = x_n = \gamma_n = 1$); this is an example of the use of different standard states for different constituents in the same mixture.

Both these standard states are used in thermodynamics of solutions (especially the last one also for other concentration units like (molar) concentrations or molalities, see end of this Sect. 4.8) but it is better to discuss them and other standard states in the following terms of fugacities.

The *fugacity* $\mathtt{f}_\alpha$ of constituent α is some type of activity in fluid (gas or liquid) mixture [152, 155]. It is a function of T, P and its composition defined by chemical potential μ_α of constituent α with the same conditions as

$$\mu_\alpha = \mu_\alpha^{0s}(T) + \mathrm{R}T\ln(\mathtt{f}_\alpha/P_s) \qquad \alpha = 1, \dots, n \tag{4.447}$$

Standard function $\mu_\alpha^{0s}(T) \equiv \mu_\alpha^{0s}(T, P = P_s)$ is the molar Gibbs energy of constituent α taken as a pure ideal gas at the considered temperature and the *standard pressure* P_s (usually 101.325 kPa); because of this constant, this standard function (and state) depends on temperature only (comparing with (4.441) this activity should be rather $\mathtt{f}_\alpha/P_s$ but for traditional reasons we keep the special name and dimension of pressure for $\mathtt{f}_\alpha$).

For *pure* fluid α the *fugacity* $\mathtt{f}_\alpha^\bullet$, a function of T, P, may be also defined through its molar Gibbs energy $\mu_\alpha^\bullet(T, P)$ (chemical potential of pure α) as

$$M_\alpha g_\alpha^\bullet = \mu_\alpha^\bullet = \mu_\alpha^{0s}(T) + \mathrm{R}T\ln(\mathtt{f}_\alpha^\bullet/P_s) \tag{4.448}$$

where $g_\alpha^\bullet$ is the (specific) Gibbs energy of pure fluid α, $\mu_\alpha^{0s}(T)$ is the molar Gibbs energy of (pure) ideal gas α at T and standard pressure P_s which is the same temperature function as in (4.447) for given α (cf. symbols introduced at the beginning of this Sect. 4.8).

The definitions are chosen in such a way that in an ideal gas or an ideal gas mixture

$$\mathtt{f}^\bullet = P, \qquad \mathtt{f}_\alpha = P_\alpha \qquad \alpha = 1, \dots, n \tag{4.449}$$

Indeed, inserting the partial pressure of ideal gas (4.424) into (4.431) we have

$$g_\alpha = \hat{g}_\alpha^0(T) + \frac{\mathrm{R}T}{M_\alpha}\ln P + \frac{\mathrm{R}T}{M_\alpha}\ln x_\alpha \qquad \alpha = 1, \dots, n \tag{4.450}$$

The first two members on the right-hand side form the specific Gibbs energy of pure ideal gas α at T, P, as may be seen from $x_\alpha = 1$ (note that in this limit the state equation of pure ideal gas α is valid, cf. (4.421)). Specifically, the molar Gibbs energy μ_α^{0s} of (pure) ideal gas α at standard pressure P_s (and the same T) is

$$\mu_\alpha^{0s}(T) = M_\alpha \hat{g}_\alpha^0(T) + \mathrm{R}T\ln P_s \tag{4.451}$$

where $\hat{g}_\alpha^0(T)$ are the same functions of temperature as in (4.450) or (4.431). Eliminating this function from (4.431) using (4.451) we obtain for ideal gas constituent α

$$\mu_\alpha = \mu_\alpha^{0s}(T) + \mathrm{R}T \ln(P_\alpha/P_s) \qquad \alpha = 1, \ldots, n \tag{4.452}$$

which comparing with (4.447) gives for an ideal gas mixture the result $(4.449)_2$ with partial pressure (4.424) of the ideal gas mixture. Limiting in (4.452) $x_\alpha \to 1$ we obtain a pure ideal gas, $P_\alpha \to P$ by (4.424), and, cf. (4.448), $(4.449)_1$ follows.

We introduce now the dimensionless *fugacity coefficients* $\nu^\bullet$ for pure fluid and ν_α for constituent α in mixture by

$$\mathtt{f}^\bullet = \nu^\bullet P, \qquad \mathtt{f}_\alpha = \nu_\alpha x_\alpha P \qquad \alpha = 1, \ldots, n \tag{4.453}$$

They express the deviation of fugacities from pressures and are equal to one for ideal gases, see (4.449).

Real gases and their mixtures have the property (see (4.422) and Appendix A.1) that at $P \to 0$ they behave as the ideal gases and their mixtures (4.421). This permits to calculate fugacity coefficients and therefore fugacities from state behaviour (equations like (3.204), (4.215)).

The fugacity coefficient ν_α for the real gas mixture may be calculated (at given composition x_α, temperature T and pressure P of which is ν_α function) from

$$\mathrm{R}T \ln \nu_\alpha = \int_0^P (M_\alpha v_\alpha - \mathrm{R}T/P)\,\mathrm{d}P \qquad \alpha = 1, \ldots, n \tag{4.454}$$

where $M_\alpha v_\alpha$ is the partial molar volume of constituent α in real gas mixture considered.

To deduce (4.454) we insert $(4.453)_2$ into (4.447) and we obtain

$$\mu_\alpha = \mu_\alpha^{id} + \mathrm{R}T \ln \nu_\alpha \tag{4.455}$$

where μ_α^{id} is the molar chemical potential in the ideal gas mixture (at the same T, P, composition) given by the right-hand side of (4.452) with (4.424). This quantity may be obtained by integration of (4.267) using (4.172) and partial molar volume in ideal gas mixture (4.420) (note that at both following integrations (4.456), (4.457) the composition is fixed no matter if it is expressed by mass or molar fractions; cf. similar "molar" integration of (4.266) in (4.434))

$$\mu_\alpha^{id} = \mu_\alpha^{00} + \int_0^P (\mathrm{R}T/P)\,\mathrm{d}P \tag{4.456}$$

Similarly, in a real gas mixture analogous integration of corresponding (4.267) gives for constituent α

$$\mu_\alpha = \mu_\alpha^{00} + \int_0^P M_\alpha v_\alpha\,\mathrm{d}P \tag{4.457}$$

It is important to note that the constant μ_α^{00} (molar chemical potential at the same T and composition and $P \to 0$) is the same in both (4.456),(4.457) because each real gas behaves as an ideal gas at $P \to 0$, see Appendix A.1,(4.422). Inserting (4.456), (4.457) into (4.455) we obtain result (4.454).

Fugacity coefficient $\nu^\bullet$ at T, P of real pure gas is calculated from

$$\mathrm{R}T \ln \nu^\bullet = \int_0^P (Mv^\bullet - \mathrm{R}T/P)\,\mathrm{d}P \tag{4.458}$$

where $Mv^\bullet$ is the molar volume of pure gas (M is the molar mass, $v^\bullet$ the specific volume (3.199)). Deduction of (4.458) is quite analogous to (4.454): inserting $(4.453)_1$ into (4.448) we obtain (index α is omitted) $Mg^\bullet = Mg^0 + \mathrm{R}T \ln \nu^\bullet$ where $Mg^0 = \mu^{0s}(T) + \mathrm{R}T \ln(P/P_s)$ is the molar Gibbs energy of pure ideal gas at P (and T). These Mg^0 and $Mg^\bullet$ may be again obtained by integration (3.207) (using the molar mass M), in the first case with the molar volume (3.212) of ideal gas, in the second one with the molar volume of pure real gas $Mv^\bullet$. We obtain $Mg^0 = Mg^{00} + \int_0^P (\mathrm{R}T/P)\,\mathrm{d}P, Mg^\bullet = Mg^{00} + \int_0^P (Mv^\bullet)\,\mathrm{d}P$. Here Mg^{00} (the molar Gibbs energy of pure gas at T and $P \to 0$) are the same for both cases again because a real gas behaves as an ideal one at $P \to 0$. Inserting both into first formula we obtain result (4.458).

Fugacities in the liquid phase may be defined as follows: they are equal to fugacities in a vapour (gas) phase which is in phase equilibrium and which may be calculated by (4.454) or (4.458). It is because fugacities of a given constituent are the same in both such phases (as follows from their definitions (4.447), (4.448), because the equality is valid for chemical potentials in phase equilibrium [152, 154] and the standard functions are the same for both phases).

The main importance of fugacities consists in the possibility to calculate arbitrary activity a_α in an arbitrary state from (4.442). Namely, taking here $\mathtt{f}_\alpha/P_s$ for activities, cf. below (4.447), we obtain

$$a_\alpha = \mathtt{f}_\alpha / \mathtt{f}_\alpha^s \tag{4.459}$$

and activity can be calculated if we know the fugacity $\mathtt{f}_\alpha$ in this state and the fugacity $\mathtt{f}_\alpha^s$ in the standard state on which the activity a_α is considered.

For the standard state and activities of classical example (4.444) the fugacity $\mathtt{f}_\alpha^s = \mathtt{f}_\alpha^\bullet$ of pure constituent α at T, P and the same aggregation state as in the mixture. That is, $\mathtt{f}_\alpha^\bullet = \mathtt{f}_\alpha^\bullet(T, P)$ is given by (4.448) with the chemical potential of standard state $\mu_\alpha^\bullet(T, P)$

$$\mu_\alpha^\bullet(T, P) = \mu_\alpha^{0s}(T) + \mathrm{R}T \ln(\mathtt{f}_\alpha^\bullet(T, P)/P_s) \tag{4.460}$$

Then (4.443) is valid and (4.459) in this standard state gives

$$\mathtt{f}_\alpha = x_\alpha \gamma_\alpha \mathtt{f}_\alpha^\bullet \tag{4.461}$$

where γ_α is the activity coefficient discussed at (4.444).

Because of the unit value of this activity coefficient in the ideal mixture (see (4.437), (4.444)) this may be expressed by fugacities through *Lewis'* or the *Lewis-Randall rule* equivalently as

$$\mathtt{f}_\alpha = x_\alpha \mathtt{f}^{\bullet}_\alpha \qquad \alpha = 1, \ldots, n \tag{4.462}$$

It gives the fugacity $\mathtt{f}_\alpha$ of constituent α in the ideal mixture with the molar fraction x_α from the fugacity $\mathtt{f}^{\bullet}_\alpha$ of pure constituent α at T, P of the mixture.

Equivalently to (4.462), the fugacity coefficient ν_α of constituent α in the ideal mixture is equal to that of the pure constituent (at the same T, P)

$$\nu_\alpha = \nu^{\bullet}_\alpha \qquad \alpha = 1, \ldots, n \tag{4.463}$$

and therefore is independent of composition. This follows by elimination of P from both relations (4.453) and comparing with (4.462).

Using limiting properties of activity coefficients γ in (4.461) (cf. discussion of (4.444)) we find that Lewis' rule is valid in the limit of high concentrations $x_\alpha \to 1$ at any real fluid mixture.

On the other hand, in the dilute solutions of solutes $\beta = 1, \ldots, n-1$ activity coefficients of which achieve in (4.461) their limits γ^{∞}_β (the value of which depend on T, P of the mixture which is nearly pure solvent n; we recall our simplification above (4.445), e.g. $\beta = 1, n = 2$) we obtain *Henry's law*

$$\mathtt{f}_\beta = x_\beta \gamma^{\infty}_\beta \mathtt{f}^{\bullet}_\beta \tag{4.464}$$

asserting that fugacities of very dilute solutions of constituent β are proportional to concentration, in this example to molar fraction x_β; quantity $\gamma^{\infty}_\beta \mathtt{f}^{\bullet}_\beta$ (depending on T, P only) is called the *Henry constant*. At the same time for solvent $\alpha = n$ Lewis' rule is valid because $x_n \to 1$ (this follows also from integration of Gibbs-Duhem equation (4.221), e.g. if linear Lewis' rule is valid for $n = 2$ at $x_2 \to 1$ then linearity of Henry's law is valid for $n = 1$ at $x_1 \to 0$ and reversely). But if the ideal mixture applies for all concentrations (as above in (v) *Ideal Mixture*), then the Lewis rule (4.462) and Henry's law (4.464) are equivalent (because activity coefficients are equal to one, e.g. $\gamma^{\infty}_\alpha = 1$).

Henry's law is traditionally expressed through pressure in (ideal gas) approximation of the type (4.449); with similar approximation the Lewis rule gives Dalton's law (4.424) in the gas phase or Raoult's law in the liquid phase used in vapour-liquid equilibria [152, 154].

Above (4.445) the "hypothetical" standard state was mentioned. This may be defined by the standard fugacity $\mathtt{f}^{s}_\beta = \gamma^{\infty}_\beta \mathtt{f}^{\bullet}_\beta$ because then (4.459) gives for activity (4.445) (with fugacity expressed through our first activity coefficient as (4.461))

$$a'_\beta = \frac{(\gamma_\beta \mathtt{f}^{\bullet}_\beta) x_\beta}{\gamma^{\infty}_\beta \mathtt{f}^{\bullet}_\beta} = \gamma'_\beta x_\beta \tag{4.465}$$

and this is (4.445) indeed. For very dilute solution (when Henry's law (4.464) is valid), also $\lim_{x_\beta \to 0} \gamma'_\beta = 1$ and the activities of solutes may be substituted by molar fractions $a'_\beta = x_\beta$; this is result below (4.446). The standard state is hypothetic because, as may be seen from (4.464), it has $x_\beta = 1$ but fugacity as in (an infinitely) diluted solution.

Because the molar fractions in (4.461) are proportional to other types of concentrations especially in dilute solutions we can obtain similar results for them. We demonstrate this in the case of molar concentration c_β (4.290) which may be inserted in (4.464); we use "dimensionless" concentration c_β/c_s where c_s is some fixed standard concentration (for liquid solution typically unit one, like $c_s = 1\,\text{mol/dm}^3$). Then Henry's law (4.464) in dilute solution of $\beta = 1, \ldots, n-1$ is

$$\mathtt{f}_\beta = H_\beta\, c_\beta/c_s \tag{4.466}$$

with the Henry constant $H_\beta \equiv c_s \gamma_\beta^\infty \mathtt{f}_\beta^\bullet / c^\infty$ in which we can include the molar volume of mixture $1/c^\infty$ which is in this dilute solution practically equal to the molar volume of pure solvent. Similarly as above, we choose the state with the fugacity $\mathtt{f}_\beta^s = H_\beta$ which depends on T, P, as another "hypothetic" standard state. Then, similarly as in the previous case (4.465), the (new) activity is given by (4.459), (4.461), (4.290)

$$a_\beta = (\gamma_\beta \mathtt{f}_\beta^\bullet c_\beta/c)/H_\beta = \gamma_\beta^c\, c_\beta/c_s \tag{4.467}$$

with another activity coefficient $\gamma_\beta^c \equiv (\gamma_\beta c^\infty)/(\gamma_\beta^\infty c)$. By diluting the solution $\gamma_\beta^c \to 1$ because if $c_\beta \to 0$ then $\gamma_\beta \to \gamma_\beta^\infty$, $c \to c^\infty$ and, as a result, we obtain that activity (4.467) in very dilute solution is equal to (dimensionless) concentration $a_\beta = c_\beta/c_s$.

Approximation of activities by corresponding concentrations in very dilute solutions is the main motivation for use of such "hypothetic" standard states.

These standard states are used, e.g. in dilute solutions of salt in water, where the Debye-Hückel theory exists for estimation [154] of these γ_β^c. Modern versions of this theory use molalities (number of mols in mass unit, namely 1 kg, of solvent) instead of concentrations with quite analogical, but different in principle, formulation of the standard state; at low concentrations the differences, e.g. in γ_β^c, are usually negligible.

A little similar but another choice of standard state, used e.g. in gas chemical kinetics, see Sect. 4.9, is the pure ideal gas at given temperature and at fixed standard molar concentration c_s (usually unit one, say $c_s = 1\,\text{mol/m}^3$). Therefore, by (4.433), the standard function (μ_α^s in (4.441)) is defined as $\mu_\alpha^\ominus(T) = \mu_\alpha^0(T) + \mathrm{R}T \ln c_s$ and depends only on temperature. Then (4.441) is (we use variables T, c_γ; see (4.212), (4.288))

$$\mu_\alpha = \mu_\alpha^\ominus(T) + \mathrm{R}T \ln a_\alpha(T, c_\gamma) \tag{4.468}$$

In the mixture of ideal gases, we have

$$a_\alpha = c_\alpha / c_s \tag{4.469}$$

as follows from (4.433).

Ultimately we note that the classical theory of mixtures presented here is used also for solids but with deformations limited on those only which may be described through density.

Summary. Following simplified models obtained from the linear fluids model are presented in this section: non-reacting mixture, incompressible mixture, simple mixture (independent of density gradients), mixture of ideal gases, and ideal mixture. In the non-reacting mixture the partial thermodynamic pressure is equal to "partial" pressure in stress tensor, cf. (4.402). The Amagat law was proved in the incompressible mixture, see (4.405). Although in classical (equilibrium) thermodynamics the chemical potential is defined as a partial derivative of Gibbs energy of mixture which is in general a function of molar amounts of all constituents, the chemical potential of a constituent is considered to be a function of only its concentration (molar or weight fraction). This independence of chemical potential from the concentration of other constituents was proved here only in the case of simple mixture—see (4.412); the same was shown for partial free energies, partial thermodynamics pressures, and for the product of partial volume and thermodynamic pressure. It was also shown that the simple mixture has a special constitutive (state) equation for partial thermodynamic pressures—(4.416). The mixture of ideal gases was shown to be a specific case of the simple mixture and the ideal gas state equation was derived, (4.419). The partial entropy of ideal gas constituent depends on the density of only this constituent (and temperature), cf. (4.426), what enabled the calculation of the mixing entropy (4.435). Classical logarithmic dependence of chemical potential on the composition naturally resulted from (4.429), cf. (4.431) and (4.432). The ideal mixture was defined on the basis of a specific type of just this logarithmic dependence, cf. (4.437). It is generally different from the simple mixture. The second part of this section discussed two important points related to chemical potential—the activity and standard states. The activity was defined by (4.441). The importance of selection of proper standard state and the use of activity coefficients and fugacities in calculating the activities was then described. In fact, this was not a specifically non-equilibrium or rational treatment but it operated on quantities and relationships the validity of which had been proved in our model of fluid mixture.

4.9 Chemical Reactions and their Kinetics

Chemical kinetics and its relation to chemical equilibrium is a subject of monographs and reviews [108, 131, 132, 154, 157]. Classical non-equilibrium thermodynamics [3, 4, 119, 120] studies this subject starting from entropy production (4.178) and therefore taking the affinity as a driving force of chemical reaction rates [158]; but this seems (at least) insufficient because of the decomposition (4.174), cf. discussion of (4.489), (4.493) below and references [108, 159, 160]. Chemical reactions are discussed also in rational thermodynamics [14, 18, 31, 75, 161].

To describe a chemically reacting system, it is sufficient to consider independent reactions only (see Sect. 4.2) because any other (dependent) chemical reactions may be obtained by their linear combinations.

In this Sect. 4.9 we discuss Eqs. (4.156), (4.171) concerning chemical reactions in a regular linear fluids mixture (see end of Sect. 4.6), i.e. with linear transport phenomena. This model gives the (non-linear) dependence of chemical reaction rates on temperature and densities (i.e. on molar concentrations (4.288)) only (4.156), which is (at least approximately) assumed in classical chemical kinetics [132, 157]. Here, assuming additionally polynomial dependence of rates on concentrations, we deduce the basic law of chemical kinetics (homogeneous, i.e. in one fluid (gas, liquid) phase) called also the *mass action law of chemical kinetics*, by purely phenomenological means [56, 66, 79, 162, 163].

In non-linear transport models, see e.g. [72], the chemical reaction rates depend on more parameters: not only on concentrations and temperature but also on deformation rates, gradients of concentrations, etc.; for a possible generalization of the presented procedure see [108, 164] and the end of this section.

Constitutive equations for rates of chemical reactions (4.156) in regular linear fluids mixture may be written with the use of molar quantities (4.26), (4.33) (cf. (4.179) and examples (4.487), (4.488), (*a*) of Rem. 30, below)

$$\vec{J} = \vec{J}(T, \vec{c}) = \vec{J}(T, \vec{\mu}) = \vec{J}(T, \vec{a}) \tag{4.470}$$

where $\vec{c}$ is the vector of (molar) concentrations c_α (4.288), $\vec{\mu}$ is the vector of molar chemical potentials μ_α (4.172), (4.173), and $\vec{a}$ is the vector of activities a_α (4.441) (in the mixture space $\mathcal{U}$, see Sect. 4.5). The second relation follows from the preceding one using inversion of function $\vec{\mu} = \vec{\mu}(T, \vec{c})$ (cf. (4.172), (4.161), (4.288)) which exists because the matrix with components $\partial\mu_\alpha/\partial c_\gamma = M_\alpha M_\gamma \partial\hat{g}_\alpha/\partial\rho_\gamma$ is regular by the regularity of (4.362) and diagonal matrix from non-zero M_α (we study rates (4.470) in stable, one-phase gas or liquid mixture). The last equation (4.470) follows from (4.441) where the form of this function depends on the form of the standard function; we limit ourselves to the most often used case (4.468) when the standard functions depend *only on temperature*.

In the regular linear fluids mixture, the production of entropy is caused by chemical reactions given by (4.178) and (chemical) equilibrium is given simultaneously by zero affinities (4.311) of independent chemical reactions chosen for their description of reacting system

$$\vec{A} = \vec{0} \tag{4.471}$$

and by the zero rate of these chemical reactions (4.302)

$$\vec{J} = \vec{0} \tag{4.472}$$

(see Sect. 4.7 for details). Equilibrium (4.471) may be expressed through the equilibrium values of activities a_α^o inserting (4.441) with the equilibrium chemical potentials $\mu_\alpha^o = \mu_\alpha^s + \mathrm{R}T \ln a_\alpha^o$ into (4.176) by

$$-\mathrm{R}T \ln \mathcal{K}_p = \sum_{\alpha=1}^{n} \mu_\alpha^s P^{p\alpha} \qquad p = 1, \ldots, n-h \tag{4.473}$$

where the so called *equilibrium constants* $\mathcal{K}_p$ of independent reaction p are defined as

$$\mathcal{K}_p = \prod_{\alpha=1}^{n} (a_\alpha^o)^{P^{p\alpha}} \qquad p = 1, \ldots, n-h \tag{4.474}$$

According to the limitation stated above, our standard functions $\mu_\alpha^s = \mu_\alpha^s(T)$ depend only on temperature and therefore also equilibrium constants depend on temperature only and by (4.474) give restrictions on the values of activities a_α^o in chemical equilibrium (denoted by superscript ^{o}; cf. Sect. 4.7). Equations (4.473) and (4.474) permit calculations of chemical equilibria: $\mathcal{K}_p$ may be calculated from the right-hand side of (4.473) (e.g. from thermodynamic data for pure constituents if they are taken as the standard state) and composition of equilibrium mixture is restricted by (4.474) if we know the relation of activities to composition; simple results follow for important case (4.469), which will be used below (4.475).

Chemical kinetics is given by constitutive equations (4.470). Their form must be valid in all processes and therefore also in equilibrium (4.471). But simultaneously we have a restriction (4.472) on the constitutive equations (4.470) in equilibrium. We find explicit consequences of this restriction for the approximation of constitutive equations (4.470) by a polynomial in activities a_α [66, 79, 162]. This was motivated by proportionality of activities to concentrations (e.g.(4.469)) and the empirically observed power dependency of reaction rates on concentrations. We denote such powers as *reaction orders* [132, 157]; often they are 1, 2 (rarely 3) but sometimes also fractions (see Rem. 17), cf. also end of this Sect. 4.9. Indeed, we show below that such approximation and restriction give the power law of chemical kinetics in activities which is, moreover, consistent with chemical equilibrium and which is then, by the activity-concentration proportionality just mentioned, consistent also with classical power law in concentrations (i.e. with the mass action law of chemical kinetics), cf. examples (4.476), (4.498) below.

Even though such power laws of chemical kinetics in activities were proposed [154, 156] the results are often controversial, cf. [165–168] and caused polemics between Haase and Hall [169–175], see detailed discussion in review [108]. These difficulties in application of activities and other thermodynamic concepts in chemical kinetics [131, 132, 157, 176], the dependence of chemical reaction rates on pressure (relatively small effect in comparison with temperature dependence [132, 157, 177]), problems related to not using T, P, w_β instead of T, ρ_γ as thermodynamic variables, etc., may be connected, as it seems, with the result of our theory that the thermodynamic pressures P_α and P are not the same as measured pressures (like p_α

or other quantities of such kind given by constitutive equations (4.138)). Namely, as follows from our theory (cf. end of Sect. 4.5 and (4.186),(4.187)), the non-zero values of such difference Δp_α (4.162) may be expected in a chemically reacting mixture out of equilibrium.

We demonstrate the procedure of obtaining the mass action law of chemical kinetics on special cases of regular linear fluids mixtures in which these activities (for standard states depending on temperature only) are equal to *dimensionless concentrations* (cf. end of Sect. 4.8, c_s is a fixed standard concentration)

$$a_\alpha = c_\alpha / c_s \qquad \alpha = 1, \ldots, n \tag{4.475}$$

specifically we limit ourselves to the mixture of ideal gases, see (4.468), (4.469).

Similar results may be obtained also for very dilute liquid solutions, see (4.467), but because the corresponding standard state may depend beside T also on the pressure P, we confine ourselves usually to chemical kinetics with constant, say atmospheric pressure (its small variation may be neglected in liquids).

As a first example, let us consider a linear mixture of two ideal gases NO_2 ($\alpha = 1$) and N_2O_4 ($\alpha = 2$) with reaction (4.46)

$$N_2O_4 = 2NO_2 \tag{4.476}$$

The rate of this reaction J_p ($p = 1$) is given by the first equation $(4.470)_1$.[28]

$$J_1 = J_1(T, c_1, c_2) \tag{4.477}$$

We note that this rate is in the relation with J^α (4.26) by (4.44)

$$J^1 = 2J_1, \quad J^2 = -J_1 \tag{4.478}$$

Chemical affinity (4.176) of this reaction (4.476) is

$$A^1 = -(2\mu_1 - \mu_2) = -(2\mu_1^\ominus(T) - \mu_2^\ominus(T)) - \mathrm{R}T \ln\left(\frac{1}{c_s}\frac{(c_1)^2}{c_2}\right) \tag{4.479}$$

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[28] We follow here the traditional chemical kinetics using concentrations c_α with their dimension giving more or less formal, dimensional complications, cf. Rem. 29, 30. Performing this example in dimensionless activities we have by $(4.470)_3$

$$J_1 = J_1(T, a_1, a_2) \qquad (a)$$

In equilibrium, cf. (4.480), (4.481), we have $J_1^o = J_1(T, a_1^o, a_2^o) = 0$ together with zero chemical affinity (4.479) $A^{1o} = -2\mu_1^o + \mu_2^o = 0$ which gives the dimensionless "real" equilibrium constant

$$\mathcal{K}_1 = \frac{(a_1^o)^2}{a_2^o} = \frac{1}{c_s}\frac{(c_1^o)^2}{c_2^o} \qquad (b)$$

(equilibrium values are denoted by superscript ^{o}, cf. below (4.474)).

where the last expression follows from chemical potentials of ideal mixture of gases (4.468) with activities (4.475).

In chemical equilibrium, Eqs.(4.471) and (4.472) are valid and with equilibrium concentrations c_1^o, c_2^o (at given temperature T) Eqs. (4.477) and (4.479) give

$$J_1^o = 0 = J_1(T, c_1^o, c_2^o) \tag{4.480}$$

$$-\,\mathrm{R}T \ln\left(\frac{1}{c_s}\frac{(c_1^o)^2}{c_2^o}\right) = 2\mu_1^{\ominus}(T) - \mu_2^{\ominus}(T) \tag{4.481}$$

where the dimensionless "real" equilibrium constant $\mathcal{K}_1$ is in logarithm, namely (b) in Rem. 28. This is depending on temperature only (because of such a dependence of the chosen standard state).

Because the number c_s is fixed (cf. Rem. 30), it can be included into the equilibrium constant:

$$c_s\mathcal{K}_1 = \frac{(c_1^o)^2}{c_2^o} \equiv K_1 \tag{4.482}$$

Motivated by traditional use in chemical kinetics, we denote K_1 also as an equilibrium constant of reaction (4.476) depending on temperature only, even it is different from dimensionless "real" equilibrium constant $\mathcal{K}_1$.

Now we assume that dependence (4.477) in concentrations may be approximated by a polynomial up to the second degree

$$J_1 = k_{00} + k_{10}c_1 + k_{01}c_2 + k_{20}c_1^2 + k_{11}c_1c_2 + k_{02}c_2^2 \tag{4.483}$$

where the coefficients $k_{00}, \ldots, k_{02}$ depend only on temperature.[29] This equation (4.483) must be valid also in equilibrium; therefore introducing (4.483) into (4.480) and eliminating c_2^o by (4.482) we obtain

$$0 = k_{00} + k_{10}c_1^o + (k_{01}/K_1 + k_{20})\,(c_1^o)^2 + (k_{11}/K_1)(c_1^o)^3 + (k_{02}/K_1^2)(c_1^o)^4 \tag{4.484}$$

which is a polynomial in independent equilibrium values of c_1^o. This value may be chosen arbitrarily in chemical equilibrium at a given temperature and Eq. (4.484) must be valid (the considered place in mixture is generally open to mass exchange,

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[29] The same form follows assuming that (a) of Rem. 28 is a polynomial in activities

$$J_1 = k_{00} + k_{10}a_1 + k_{01}a_2 + k_{20}a_1^2 + k_{11}a_1a_2 + k_{02}a_2^2 \qquad (a)$$

coefficients of which depend on T only and have the same dimension.

The corresponding polynomial in concentrations is obtained by substitution of (a) by (4.475), namely

$$J_1 = k_{00} + (k_{10}/c_s)c_1 + (k_{01}/c_s)c_2 + (k_{20}/c_s^2)c_1^2 + (k_{11}/c_s^2)c_1c_2 + (k_{02}/c_s^2)c_2^2 \qquad (b)$$

This is the same as (4.483) but with other coefficients than in (a), e.g. $k_{01} = k_{01}/c_s$; they have different dimensions but again they are functions of temperature only.

e.g. even in uniform equilibrium in a batch reactor this arbitrariness may be achieved by changing the initial composition of the mixture before chemical reactions start). Because a polynomial of finite degree may have only a finite number of roots, the requirement of arbitrariness of values c_1^o fulfilling (4.484) (e.g. its positive values from some interval) gives therefore that all coefficients in (4.484) must be identically zero, i.e.

$$k_{00} = k_{10} = k_{11} = k_{02} = 0 \tag{4.485}$$

$$k_{20} = -k_{01}/K_1 \tag{4.486}$$

Because these coefficients depend only on temperature, this result is valid also in the general expression (4.483). Therefore the final form of (4.483) is

$$J_1 = k_{01}c_2 - (k_{01}/K_1)c_1^2 = k_{20}(c_1^2 - K_1c_2) \tag{4.487}$$

Thus, the form of mass action law of chemical kinetics was recovered where k_{01} and k_{01}/K_1 may be interpreted as the rate constants in the forward and reversed directions of reaction (4.476) respectively; moreover, these constants depend only on temperature and fulfil the known relation (4.486) with the equilibrium constant.[30] Further, this form of mass action rate equation automatically satisfies the principle of detailed balance which is used as a thermodynamic restriction on chemical kinetics and which, in turn, seems to be a result of permanence of atoms [140] stated in Sect. 4.2. Conditions when this form transforms to traditional and experimentally supported mass action rate equations are discussed in Ref. [163]. In practice rate constants in the two directions often differ essentially (usually by extremely high or low values of equilibrium constants, cf. (4.486)) and we obtain the classical form of the chemical kinetic law for an "irreversible" one-directional reaction. From (4.487) and (4.478) (and this is valid by (4.44) more generally) the constitutive equations for

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[30] It may be seen that the same procedure may be performed formally quite analogously if we use activities instead concentrations (compare (a), (b) in Rem. 28 and (a) in Rem. 29 with corresponding (4.477), (4.482) and (4.483) even their difference in dimensions, cf. [79, 162]). Proceeding similarly, the analogue with activities (instead of concentrations) may be obtained, e.g. the analogue of (4.484) with equilibrium activity a_1^o. Therefore also the analogue of result $(4.487)_1$ in activities will be valid

$$J_1 = k_{01}a_2 - (k_{01}/\mathcal{K}_1)a_1^2 \qquad (a)$$

this time with coefficients (rate constants) coming from (a) of Rem. 29 with dimensionless equilibrium constant $\mathcal{K}_1$, see (b) of Rem. 28. Indeed, inserting (4.475) into (a) we obtain

$$J_1 = (k_{01}/c_s)c_2 - \left((k_{01}/c_s)\frac{c_2^o}{(c_1^o)^2}\right)c_1^2 \qquad (b)$$

which is $(4.487)_1$ with velocity constants as in (b) of Rem. 29 and with equilibrium constant (4.482) K_1.

Note, that if, as usually $c_s = 1$ mol/m^3 and concentrations are given in the same units, the numerical values of rate and equilibrium constants are the same even though their dimensions are different.

components J^{α} have also the form of (4.487) (with rate constants depending only on temperature) but this result is independent of the reaction chosen in contrast to rates J_p and equilibrium constants. E.g. for reaction (4.47) (with primed quantities) $K'_1 = K_1^{-0.5}$ and $J'_1 = -2J_1$ but J^{α} remains the same.

Substituting c_{α} in (4.487) from (4.475), (4.468) using (4.481) with (4.482) we obtain

$$\begin{aligned} J_1 &= c_s\, k_{01}(T) \exp[-\mu_2^{\ominus}(T)/(\mathrm{R}T)]\,(\exp[\mu_2/(\mathrm{R}T)] - \exp[2\mu_1/(\mathrm{R}T)]) \\ &= \bar{J}_1(T, \mu_1, \mu_2) \end{aligned} \tag{4.488}$$

which is the second relation (4.470) for this example (4.476), cf. (4.179) (the last one of (4.470) is (a) in Rem. 30)).

Eliminating μ_1 from (4.488) by (4.479), we have

$$J_1 = c_s\, k_{01}(T) \exp[-\mu_2^{\ominus}(T)/(\mathrm{R}T)] \exp[\mu_2/(\mathrm{R}T)] \left(1 - \exp[-A^1/(\mathrm{R}T)]\right) \tag{4.489}$$

Linearization of this equation in A^1 gives the "phenomenological" equation for reaction rate of linear irreversible thermodynamics [1, 3, 4, 130]. But there is a controversion here [159]: μ_2 is contained in affinity (4.479) as well as in the first part of (4.489) which is considered as constant in such linearization, cf. below (4.494), see also [158].

We show on this example (4.476) also the result of decomposition of vector of chemical potential from the 2-dimensional reaction space $\mathcal{U}$ into two 1-dimensional subspaces $\mathcal{V}$ and $\mathcal{W}$ (4.174), in component form (4.177):

$$\mu_{\alpha} = -A^1 g_{11} P^{1\alpha} + B^1 S_{1\alpha} \qquad \alpha = 1, 2 \tag{4.490}$$

Using matrices $\|P^{p\alpha}\| = (2 \quad -1)$, $\|S_{\sigma\alpha}\| = (1 \quad 2)$ for constituents in this reaction (4.476) (see above (4.46)) and $g_{11} = 1/5$ (because this is the inversion of $g^{11} = \vec{g}^1.\vec{g}^1 = 5$ calculated from (4.40)) we obtain the decomposition (4.490) as

$$\mu_1 = -(2/5)A^1 + B^1, \quad \mu_2 = (1/5)A^1 + 2B^1 \tag{4.491}$$

This gives the expression for affinity (4.479) and also

$$B^1 = (\mu_1 + 2\mu_2)/5 \tag{4.492}$$

Using this (1-dimensional) decompositions (4.479), (4.492) in (4.489) (inserting $(4.491)_2$) we obtain (4.470) with decomposition (4.174) as (4.179), i.e.

$$\begin{aligned} J_1 &= \bar{J}_1(T, \mu_1, \mu_2) = \tilde{J}_1(T, A^1, B^1) \\ &= c_s\, k_{01}(T) \exp[-\frac{\mu_2^{\ominus}(T)}{\mathrm{R}T}] \exp[\frac{2B^1}{\mathrm{R}T}] \exp[\frac{A^1}{5\mathrm{R}T}] \left(1 - \exp[-\frac{A^1}{\mathrm{R}T}]\right) \end{aligned} \tag{4.493}$$

At zero affinity $A^1 = A^{1o} = 0 = -2\mu_1^o + \mu_2^o$ (4.479) we obtain $J_1 = 0$ in equilibrium, indeed (where also $B^1 = B^{1o} = \mu_1^o = (1/2)\mu_2^o$ by (4.492), (4.479) with equilibrium values of chemical potentials μ_1^o, μ_2^o). Production of entropy (4.178) in this example is $\Pi_0 = J_1 A^1 \geq 0$ and therefore for $A^1 > 0$ it must be $J_1 > 0$ and it follows from (4.493) or (4.489) that ($c_s > 0$ of course)

$$k_{01} > 0 \tag{4.494}$$

Results of this type (signs of rate constants; equilibrium constants are only positive) follow generally from the sharp minimum of Π_0 (4.171) in equilibrium which is described in variables T, $\vec{A}$, $\vec{B}$ as (a) in Rem. 22. Namely, the first derivative (b) in it gives zero reaction rates (4.472) and the second derivative gives the inequality (e) in Rem. 22. The latter is (4.493) in our example and $(\partial \tilde{J}_1/\partial A^1)^o (A^1)^2 \geq 0$ gives (4.494) again.

As we noted below, the equation (4.489) the expressions (4.493) show that dependence of reaction rate on affinity is not so simple [158, 159] as it is assumed in classical non-equilibrium thermodynamics [1, 3, 4, 130] based on entropy production (by chemical reactions), i.e. as a product of “fluxes” and “driving forces” (4.178). Projection $\vec{B}$ of chemical potential vector $\vec{\mu}$ to the subspace $\mathcal{W}$ also plays a role in expression for reaction rates $\vec{J}$ as (4.493) in our example; the affinity $\vec{A}$ is projection of $\vec{\mu}$ into orthogonal reaction subspace $\mathcal{V}$ only, cf. (4.174). Cf. detailed discussion and criticism in review [108] and references [159, 160].

What happens if we use polynomials of different degrees in approximation of (4.477)?. For the zero and first degrees, we get by the same method $J_1 \equiv 0$ identically, for the third degree we obtain

$$J_1 = k_{20}(c_1^2 - K_1 c_2) + (k_{30} c_1 + k_{21} c_2)(c_1^2 - K_1 c_2) \tag{4.495}$$

The first member is the same as (4.487) (see (4.486)) and the second one may be interpreted as *autocatalysis* by both constituents of mixture (some rate constants may be neglected, cf. below (4.487)). Moreover, if we add a third constituent (say ideal gas) Q ($\alpha = 3$) to this mixture which formally does not take part in the reaction (4.476) but may have an influence on the reaction rate

$$J_1 = J_1(T, c_1, c_2, c_3) \tag{4.496}$$

then (using (4.482)) we obtain, approximating this dependence by polynomial of the 2nd degree, the same result as (4.487) and by the polynomial of the third degree we obtain a similar expression as (4.495) containing (besides autocatalysis members) also *catalysis* caused by the constituent Q ($\alpha = 3$)

$$J_1 = k_{200}(c_1^2 - K_1 c_2) + (k_{300} c_1 + k_{210} c_2 + k_{201} c_3)(c_1^2 - K_1 c_2) \tag{4.497}$$

Here again, as well as in (4.495), the coefficients $k_{200}, k_{300}, \ldots, K_1$ depend only on temperature. From (4.497) it follows, that in accord with experience, the autocatalysis and catalysis have influence on both directions of reaction (4.476).

As a last example, we consider the regular linear fluid mixture of atomic and molecular oxygen and ozone O, O_2, O_3 as ideal gases denoted by $\alpha = 1, 2, 3$ respectively, i.e. the simplification (4.475) is valid. Here two independent chemical reactions take place, e.g. (4.48)

$$2\mathrm{O}_3 = 3\mathrm{O}_2, \quad \mathrm{O}_3 = 3\mathrm{O} \tag{4.498}$$

denoted by $p = 1, 2$ respectively. Constitutive equations for reaction rates are (upper indices are $p = 1, 2$, the remaining are powers of concentrations)

$$\begin{aligned} J_p = J_p(T, c_1, c_2, c_3) = {} & k^p_{000} + k^p_{100}c_1 + k^p_{010}c_2 + k^p_{001}c_3 \\ & + k^p_{200}c_1^2 + k^p_{020}c_2^2 + k^p_{002}c_3^2 + k^p_{110}c_1c_2 + k^p_{011}c_2c_3 \\ & + k^p_{101}c_1c_3 \qquad p = 1, 2 \end{aligned} \tag{4.499}$$

where the approximation by polynomial of the 2nd degree was assumed. The equilibrium concentrations are connected by the equilibrium constants of reactions (4.498) respectively

$$K_1 = (c_2^o)^3/(c_3^o)^2, \quad K_2 = (c_1^o)^3/c_3^o \tag{4.500}$$

from which we express the equilibrium values (denoted by superscript ^{o})

$$c_2^o = (K_1/K_2^2)^{1/3}(c_1^o)^2, \quad c_3^o = (c_1^o)^3/K_2 \tag{4.501}$$

In equilibrium $J_p = 0 \quad p = 1, 2$ (with equilibrium concentrations $c_\alpha^o \quad \alpha = 1, 2, 3$) and we insert there from (4.501). We obtain two polynomials in (possible continuum of) c_1^o which must be zero; therefore, their coefficients must be zero:

$$\begin{aligned} & k^p_{000} = 0,\ k^p_{100} = 0,\ k^p_{002} = 0,\ k^p_{011} = 0,\ k^p_{010} = -k^p_{200}(K_2^{2/3}/K_1^{1/3}) \\ & k^p_{001} = -k^p_{110}(K_1K_2)^{1/3},\ k^p_{101} = -k^p_{020}(K_1^{2/3}/K_2^{1/3}) \quad p = 1, 2 \end{aligned} \tag{4.502}$$

Because coefficients in (4.499) and equilibrium constants (4.500) depend only on temperature, we obtain for reaction rates after inserting from (4.502) into (4.499):

$$J_p = k^p_{200}(c_1^2 - K_4c_2) + k^p_{110}(c_1c_2 - K_3c_3) + k^p_{020}(c_2^2 - K_5c_1c_3) \qquad p = 1, 2 \tag{4.503}$$

where (the upper indices mean powers as usual)

$$K_3^3 = K_1K_2,\ K_4^3 = K_2^2/K_1,\ K_5 = K_3/K_4 \tag{4.504}$$

which all are functions of temperature only (similarly as the rate constants k_{200}^{p}, k_{110}^{p}, k_{020}^{p}).

Note that we obtain the same result (using polynomial of the 2nd degree (4.499)) from an equivalent set of independent reactions, say (4.49). This may be seen directly from (4.503), (4.504) inserting (4.500): then K_3, K_4 are equilibrium constants of reactions (4.49) respectively. We also note that we can also eliminate c_1^o, c_3^o; then we must use the preceding method for polynomial of the type (4.484) but in $(c_2^o)^{0.5}$ and the result (4.503) may be obtained again. Therefore, chemical kinetics in the system O, O_2, O_3 may be described by two equilibrium and six rate constants when constitutive equations for reaction rates are approximated by a polynomial of the second order (a polynomial of the third order gives 20 rate constants [79]; equilibrium constants are again two because of two independent chemical reactions).

This method gives reaction orders as natural numbers only; for further details and discussion, see [79, 108, 162, 178]. Result (4.503) (written for J^{α} by (4.44)) may be interpreted also as a mechanism (e.g. $O_2 = 2O$, $O + O_2 = O_3$, $O_3 + O = 2O_2$) of some overall reaction (e.g. $2O_3 = 3O_2$) considering also unstable intermediate products as constituents, e.g. O in (4.498). Neglecting some rate constants and by standard methods of chemical kinetics [131, 132, 157], the mechanism may then explain the observed (even fractional) reaction orders. Therefore it seems that the method presented here is appropriate for (at least a possible) proposal of mechanisms, because the integer degrees of polynomials suffice giving 1, 2, or 3 for "molecularity" (the reaction order of "elementary" reactions (often linearly dependent) forming mechanism; their irreversibility follows ignoring some of rate constants as we noted below (4.487)). By this method (see also [108]) the mechanism of decomposition of N_2O has been discussed [178], as has the detailed balance in the "triangle" mechanism [179] and a possible application in heterogeneous kinetics [164] (the method presented here may be generalized on such more complex models if the reaction rates may be expressed through polynomial in concentrations (even though they depend on further parameters) and their equilibrium values are linked together, say by equilibrium constants).

We have seen above that expressions in a more general case with activities may be obtained simply using activities instead of concentrations (cf. Rems. 28, 29, 30), but the problem of their usefulness (and other thermodynamic notions) in chemical kinetics remains, as we noted above (4.475), because of the possible difference between measured and thermodynamic pressure in systems out of chemical equilibria.

Summary. The classical mass action law of chemical kinetics was proved, in fact, in the linear fluid mixture as the general constitutive equations for the reaction rates which were reproduced in this section as (4.470). This law generally states that the rates depend only on temperature and composition expressed by densities, molar concentrations or activities or, alternatively, even by (molar) chemical potentials. The equilibrium constant of independent reactions was defined by (4.474). Then we have shown on several reaction examples how the general function reaction rate-concentrations (or reaction rate-activities) can be approximated by a suitable polynomial in concentrations (or activities) and further modified to obtain the final equation for the reaction rate in the mass action form—cf., e.g. (4.477), (4.483) and (4.487). The traditional mass action kinetics was thus justified thermodynamically at least for our mixture model. We have also illustrated the proper transformation of reaction rate to a function of affinities (and temperature), which has not been done correctly in other works, see (4.493). This functional form also enables to find the restrictions put by the entropy inequality on the rate coefficients (mass action rate constants)—see (4.494).

4.10 Transport Phenomena in the Linear Fluid Mixture

We have studied a regular linear fluid mixture where most of the results for transport phenomena (4.137), (4.138), (4.165), (4.166) (viscosity, diffusion, heat conduction and cross effects) are not in a form useful in practice [76, 104, 180, 181]. In this section we transform them into a more convenient form which is also used in linear irreversible thermodynamics [1–4, 27, 28, 119, 120, 130, 182]. Onsager relations will be also noted and some applications, like Fick law and the electrical conductivity of electrolytes are discussed.

To account for *viscosity* effects [180, 183, 184], in a mixture of linear fluids we write the constitutive equations for stress (4.138) in the form (we use (4.186))

$$\mathbf{T}_\alpha = -P_\alpha \mathbf{1} + \mathbf{T}_\alpha^N \qquad \alpha = 1, \ldots, n \tag{4.505}$$

where P_α is the partial thermodynamic pressure and $\mathbf{T}_\alpha^N$ is the *partial non-equilibrium stress* defined by

$$\mathbf{T}_\alpha^N \equiv \Delta p_\alpha \mathbf{1} + \sum_{\gamma=1}^{n} \zeta_{\alpha\gamma} (\mathrm{tr}\mathbf{D}_\gamma)\mathbf{1} + \sum_{\gamma=1}^{n} 2\eta_{\alpha\gamma} \overset{\circ}{\mathbf{D}}_\gamma \qquad \alpha = 1, \ldots, n \tag{4.506}$$

Coefficients Δp_α and the partial volume viscosity coefficients $\zeta_{\alpha\gamma}$ and the partial viscosity coefficients $\eta_{\alpha\gamma}$ are functions of temperature and densities (composition) only. In applications $\mathbf{D}_\gamma$ of all constituents are often the same and the total stress (4.94) $\mathbf{T} = \sum_{\alpha=1}^{n} \mathbf{T}_\alpha$ is of interest; then (4.506) has the same form as for single fluids (3.189) with $\sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \zeta_{\alpha\gamma}$ and $\sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \eta_{\alpha\gamma}$ as viscosity coefficients of the mixture (and Δp_α (4.186) contributes to the pressure only in a chemically reacting mixture out of equilibrium; cf. Sects. 4.5 and 4.9).

To describe *diffusion*, *heat conduction* and *cross effects* [76–78, 180, 181], i.e. *thermodiffusion* and *Dufour effect*, we define the *diffusion flux* $\mathbf{j}_\beta$ as

$$\mathbf{j}_\beta \equiv \rho_\beta \mathbf{u}_\beta \qquad \beta = 1, \ldots, n-1 \tag{4.507}$$

where $\mathbf{u}_\beta$ is the *diffusion velocity* defined by (4.24) with the velocity of n-th constituent $\mathbf{v}_n$ as the referential one (for other diffusion velocities, see (4.539) and below).

To obtain the constitutive equations for fluxes $\mathbf{j}_\beta$, we express diffusion velocities from (4.137) and eliminate $\mathbf{k}_\beta$ by balance of momentum (4.58) using (4.505)

$$\sum_{\delta=1}^{n-1} \nu_{\beta\delta}\mathbf{u}_\delta = \sum_{\gamma=1}^{n} \omega_{\beta\gamma}\mathbf{h}_\gamma - \xi_\beta \mathbf{g} - \operatorname{grad} P_\beta + \operatorname{div}\mathbf{T}_\beta^N + \rho_\beta(\mathbf{b}_\beta + \mathbf{i}_\beta) \\ - \rho_\beta \grave{\mathbf{v}}_\beta \qquad \beta = 1, \ldots, n-1 \tag{4.508}$$

Writing (4.208) for space gradients we obtain

$$\sum_{\gamma=1}^{n} \omega_{\beta\gamma}\mathbf{h}_\gamma - \operatorname{grad} P_\beta = -\rho_\beta \operatorname{grad}_T g_\beta + \rho_\beta \left(s_\beta + \frac{\partial \hat{f}_\beta}{\partial T} \right) \mathbf{g} \tag{4.509}$$

where we used the *isothermal gradient of chemical potential* $\operatorname{grad}_T g_\alpha$ defined by [1–4, 120]

$$\operatorname{grad}_T g_\alpha \equiv \operatorname{grad} g_\alpha + s_\alpha \mathbf{g} \tag{4.510}$$

Note, that using variables (4.216) and (4.266), (4.267)

$$\operatorname{grad}_T g_\alpha = v_\alpha \operatorname{grad} P + \sum_{\beta=1}^{n-1} \frac{\partial \tilde{g}_\alpha}{\partial w_\beta} \operatorname{grad} w_\beta \tag{4.511}$$

Similarly, using variables (4.213), $\operatorname{grad} g_\alpha$ depends linearly on $\mathbf{g}, \mathbf{h}_\gamma$. Now the Eq. (4.509) is introduced into Eq. (4.508), the definition of the *driving force of diffusion* $\mathbf{y}_\beta$

$$\mathbf{y}_\beta \equiv \operatorname{grad}_T g_\beta - (\mathbf{b}_\beta + \mathbf{i}_\beta) + \grave{\mathbf{v}}_\beta - (1/\rho_\beta)\operatorname{div}\mathbf{T}_\beta^N \qquad \beta = 1, \ldots, n-1 \tag{4.512}$$

and (4.163) are used to obtain

$$-\sum_{\delta=1}^{n-1} \nu_{\beta\delta}\mathbf{u}_\delta = \rho_\beta \mathbf{y}_\beta + \left(\vartheta_\beta - \frac{\lambda_\beta}{T} \right) \mathbf{g} \qquad \beta = 1, \ldots, n-1 \tag{4.513}$$

Suppose that the matrix $\|\nu_{\beta\delta}\|$ is regular. It is usually the case because yet more is often assumed: the symmetry (4.521) (cf. Onsager relations below) and positive definiteness (see the assumption 1 of regular linear fluids mixture in the end of Sect. 4.6) at least in a non-reacting mixture (diffusion is mostly studied in a non-reacting mixture; rates in a reacting mixture are usually assumed to be negligible in (4.182)).

Then $\mathbf{u}_\delta$ may be eliminated from (4.513) and inserting them into (4.507) we obtain constitutive equations for diffusion fluxes

$$-\mathbf{j}_\delta = \sum_{\beta=1}^{n-1} L_{\delta\beta}\,\mathbf{y}_\beta + L_{\delta q}\,\frac{\mathbf{g}}{T} \qquad \delta = 1,\ldots,n-1 \tag{4.514}$$

$$-\mathbf{q} = \sum_{\delta=1}^{n-1} L_{q\delta}\,\mathbf{y}_\delta + L_{qq}\,\frac{\mathbf{g}}{T} \tag{4.515}$$

Equation (4.515) is deduced if we insert $\mathbf{u}_\beta$ just obtained into (4.166). Here the so called *phenomenological coefficients* are therefore defined by

$$L_{\delta\beta} \equiv \rho_\beta\rho_\delta\nu_{\delta\beta}^{-1} \qquad \beta,\delta = 1,\ldots,n-1 \tag{4.516}$$

$$L_{\delta q} \equiv \sum_{\beta=1}^{n-1} \rho_\delta T(\vartheta_\beta - \frac{\lambda_\beta}{T})\nu_{\delta\beta}^{-1} \qquad \delta = 1,\ldots,n-1 \tag{4.517}$$

$$L_{q\delta} \equiv -\sum_{\beta=1}^{n-1} \rho_\delta\lambda_\beta\,\nu_{\beta\delta}^{-1} \qquad \delta = 1,\ldots,n-1 \tag{4.518}$$

$$L_{qq} \equiv kT - \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1} T\lambda_\beta(\vartheta_\delta - \frac{\lambda_\delta}{T})\nu_{\beta\delta}^{-1} \tag{4.519}$$

where $\nu_{\delta\beta}^{-1}$ are the elements of the inverse matrix to the matrix of the transport coefficients $\nu_{\beta\delta}$ (i.e. $\sum_{\beta=1}^{n-1}\nu_{\delta\beta}^{-1}\nu_{\beta\eta} = \delta_{\delta\eta}$ is Kronecker delta, $\delta,\eta = 1,\ldots,n-1$) and subscript $_q$ denotes a relation to the heat flux. Therefore the phenomenological coefficients are, similarly to the coefficients in constitutive relations (4.137), (4.166), functions of $T, \rho_1, \ldots, \rho_n$ only (with usual invertibility, cf. (4.213), (4.217), also dependence on T, P, w_β or even on other variables, e.g. those in (4.551), are often used). In equilibrium, where (4.316), (4.317) is valid, it follows from (4.513) that the driving force of diffusion is zero $\mathbf{y}_\beta = \mathbf{o}$ (this follows also from (4.512); cf. (4.505), (4.321), (4.323), (4.333)).

Expressions (4.514), (4.515) are known as *phenomenological equations* of *linear irreversible* or *non-equilibrium thermodynamics* [1–5, 120, 130, 185–187], in this case for diffusion and heat fluxes, which represent the *linearity* postulate of this theory: "flows" ($\mathbf{j}_\delta, \mathbf{q}$) are proportional to "driving forces" ($\mathbf{y}_\beta, T^{-1}\mathbf{g}$) (irreversible thermodynamics studied also other phenomena, like chemical reactions, see, e.g. below (4.489)). Terms with phenomenological coefficients $L_{\delta\beta}, L_{\delta q}, L_{q\delta}, L_{qq}$, correspond to the *transport phenomena* of *diffusion*, *Soret effect* or *thermodiffusion*, *Dufour effect*, *heat conduction* respectively, discussed more thoroughly below.

In irreversible thermodynamics *Onsager reciprocity relations* are (usually) postulated which in our context (4.514), (4.515) are

$$L_{\delta\beta} = L_{\beta\delta}, \quad L_{\delta q} = L_{q\delta} \qquad \beta, \delta = 1, \ldots, n-1 \tag{4.520}$$

These reciprocity relations are valid if the following additional simple assumptions about our constitutive model is fulfilled

$$\nu_{\beta\delta} = \nu_{\delta\beta} \tag{4.521}$$

$$\vartheta_\beta = 0 \qquad \beta, \delta = 1, \ldots, n-1 \tag{4.522}$$

as may be seen from (4.516)–(4.519) (from (4.521) follows symmetry of $\nu^{-1}_{\beta\delta}$).

We motivate (4.521), (4.522) here[31] by plausible additional constitutive assumptions according to Truesdell [188], [13, Lect7] and Müller [18, Sect. 6.6]: Let us consider a non-reacting three-constituent linear fluids mixture ($n = 3$; generalization on more constituents is possible [188]). To prove (4.521) it suffices to consider the special case with $\mathbf{g} = \mathbf{o}, \mathbf{h}_\gamma = \mathbf{o}$ (in driving force (4.512) $\mathrm{grad}_T g_\beta = \mathbf{o}$, see below (4.511)) because $\nu_{\beta\delta}$ does not depend on them. Then by (4.137), (4.24)

$$\mathbf{k}_\beta = -\sum_{\delta=1}^{2} \nu_{\beta\delta}(\mathbf{v}_\delta - \mathbf{v}_3) \qquad \beta = 1, 2 \tag{4.523}$$

$$\mathbf{k}_3 = -\mathbf{k}_1 - \mathbf{k}_2 \tag{4.524}$$

where (4.524) expresses the balance of momentum (4.63) in such a non-reacting mixture. Introducing (4.523) into (4.524) and rearranging we can write Eqs. (4.523), (4.524) as

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[31] Besides the explanation of reciprocity relations through constitutive properties used here and proposed [188] and promoted by Truesdell [12], [13, Lect7], (for other examples of this type see Šilhavý [189], Wang [13, Appendix 7a]), most authors in irreversible thermodynamics consider them as a result of a more general principle like “dissipative potential” whose derivatives according to “driving forces” give the “fluxes” fulfilling the Onsager relation. Existence of such dissipative potentials is supported by plausible explanations of non-equilibrium states, as the steady non-equilibrium states and their stability, cf. minimum of entropy production by Onsager reciprocity [1, 129], see also [3, 5, 39, 190, 191]. Phenomenological theory [39, 143, 192–195] may give such dissipative potentials but with the condition that fluxes contain also parts not contributing to the entropy production, e.g. simply if such a part is zero (symmetry does not follow from positive semidefinity, see Rem. 16). To find such a part additional molecular arguments, at least in motivation, are necessary, e.g. from fluctuation theory with the principle of detailed balance or microscopic reversibility [1, 3, 5, 196] (originally Onsager’s idea), from molecular theories of transport phenomena (kinetic theory of gases) [133], from invariance entropy production against the time reversal [111, 197]; see also [22, 23, 111, 119, 182, 187, 196–201]. In addition, the symmetry (4.520) has been confirmed experimentally [181, 202].

$$\mathbf{k}_\alpha = \sum_{\gamma=1}^{3} F_{\alpha\gamma}(\mathbf{v}_\gamma - \mathbf{v}_\alpha) \qquad \alpha = 1, 2, 3 \tag{4.525}$$

where we define

$$\begin{gathered} F_{\alpha\alpha} = 0, \qquad \alpha = 1, 2, 3, \quad F_{12} = -\nu_{12}, \quad F_{21} = -\nu_{21}, \\ F_{13} = \nu_{11} + \nu_{12}, \quad F_{31} = \nu_{11} + \nu_{21}, \quad F_{23} = \nu_{22} + \nu_{21}, \quad F_{32} = \nu_{22} + \nu_{12} \end{gathered} \tag{4.526}$$

and therefore the scalar coefficients, the *diffusive drags* $F_{\alpha\gamma}$, are functions only of $T, \rho_1, \rho_2, \rho_3$. Forces $\mathbf{k}_\alpha$ (4.525) may be therefore interpreted as originating by transport of momentum from other constituents γ on a given constituent α. Because (4.524) is valid, we have

$$\sum_{\gamma=1}^{3} \mathbf{k}_\alpha = \sum_{\alpha=1}^{3}\sum_{\gamma=1}^{3}(F_{\gamma\alpha} - F_{\alpha\gamma})\mathbf{v}_\alpha = \mathbf{o} \tag{4.527}$$

But $F_{\alpha\gamma}$ are independent of velocities $\mathbf{v}_\alpha$ and therefore we have the following restriction from (4.527)

$$\sum_{\gamma=1}^{3}(F_{\gamma\alpha} - F_{\alpha\gamma}) = 0 \qquad \alpha = 1, 2, 3 \tag{4.528}$$

Splitting the matrix $\|F_{\alpha\gamma}\|$ uniquely to its symmetric $\|F^s_{\alpha\gamma}\|$ and skew-symmetric $\|F^a_{\alpha\gamma}\|$ parts, we have

$$\begin{aligned} F_{\alpha\gamma} = F^s_{\alpha\gamma} + F^a_{\alpha\gamma} \quad \alpha, \gamma = 1, 2, 3, \quad & F^s_{\alpha\gamma} \equiv (1/2)(F_{\alpha\gamma} + F_{\gamma\alpha}), \\ & F^a_{\alpha\gamma} \equiv (1/2)(F_{\alpha\gamma} - F_{\gamma\alpha}) \end{aligned} \tag{4.529}$$

Inserting (4.529) into (4.528) we obtain

$$\sum_{\alpha=1}^{3} F^a_{\alpha\gamma} = 0 \quad \text{or} \quad \sum_{\gamma=1}^{3} F^a_{\alpha\gamma} = 0 \tag{4.530}$$

i.e. the skew-symmetric matrix $\|F^a_{\alpha\gamma}\|$ must be such that sums of its columns and rows must be zero. Therefore, for $n = 3$ it must have the form

$$\|F^a_{\alpha\gamma}\| = \begin{pmatrix} 0 & +\alpha & -\alpha \\ -\alpha & 0 & +\alpha \\ +\alpha & -\alpha & 0 \end{pmatrix} \tag{4.531}$$

where α is a coefficient which is only a function of $T, \rho_1, \rho_2, \rho_3$. Plausible physical arguments are taken now as additional constitutive assumptions [188]:

1. $F_{\alpha\gamma}$ are independent of the density of constituent ε if $\varepsilon \neq \alpha, \gamma$. This may be regarded as a macroscopic definition of binary drags, i.e. the drag force between the constituents α and γ is independent of the presence of other constituents.
2. When $\rho_\gamma \to 0$ then $F_{\alpha\gamma} \to 0$ because it may be expected that the drag force from constituent γ on constituent α goes to zero when the mixture becomes more diluted in the constituent γ.

Then from assumption 1, we can see that the coefficient α is not dependent on ρ_1, ρ_2, ρ_3 altogether and from assumption 2 we have $\alpha = 0$, i.e. the skew-symmetric part of $\|F_{\alpha\gamma}\|$ is zero

$$\|F^a_{\alpha\gamma}\| = \|0\| \tag{4.532}$$

Then $\|F_{\alpha\gamma}\|$ is symmetrical and from (4.526) we obtain the symmetry (4.521), for this case

$$\nu_{12} = \nu_{21} \tag{4.533}$$

Thus from (4.516) the Onsager relation $L_{12} = L_{21}$ follows for this case.

To obtain the reciprocity relations (4.520), it suffices to add (4.522) (see (4.163)). This is valid in an ideal gas mixture (simple mixture of gases) where (4.426) is valid if we assume compensation $\lambda_\beta/T + \xi_\beta = 0$ (something like reciprocity in (4.166), (4.137)) or even $\lambda_\beta = 0$, $\xi_\beta = 0$ (no thermal drags); see discussion in [18, Sect. 6.6], [51, 75], cf. Rem. 26.

As we noted above, the phenomenological relations (4.514), (4.515) are starting equations for obtaining useful results for transport phenomena as diffusion, heat conduction and cross effects. This will be discussed in the remaining part of this Sect. 4.10; for details see [1–5].

Heat conduction [181] is described by the *Fourier law*

$$\mathbf{q} = -k\,\mathbf{g} \tag{4.534}$$

where the *heat conductivity k* depends on T, ρ_γ (cf. below (4.136), (4.519)). This follows from (4.166) at the absence of diffusion, cf. (3.187). Fourier law, understood as the proportionality of heat flux to temperature gradient, follows also from phenomenological equation (4.515) at zero diffusion driving force. But the "heat conductivity" L_{qq}/T, is changed a little, see (4.519), (4.545): the difference is caused by the most important cross effect, namely the *Soret effect (thermodiffusion)*: diffusion flux is caused by a temperature gradient because $\lambda_\beta \neq 0$, see (4.514) (cf. also (4.166)). Reversal to this cross effect is the *Dufour effect* (heat flux caused by diffusion), see (4.515), (4.518) and Onsager relations (4.520). For further details, see [9, 156].

The most important transport phenomenon—*diffusion* [76]—then remains. Using expression (4.511), we obtain for the driving force of diffusion (4.512)

$$\mathbf{y}_\beta = \sum_{\zeta=1}^{n-1} \frac{\partial \tilde{g}_\beta}{\partial w_\zeta} \operatorname{grad} w_\zeta + v_\beta \operatorname{grad} P - (\mathbf{b}_\beta + \mathbf{i}_\beta) + \grave{\mathbf{v}}_\beta - \frac{1}{\rho_\beta} \operatorname{div} \mathbf{T}_\beta^N \qquad \beta = 1, \ldots n-1 \tag{4.535}$$

Therefore, the diffusion driving force has three important parts which express the *concentration diffusion* (caused by composition gradient), the *barodiffusion* (by pressure gradient) and the third member is the *forced diffusion* by the body forces $\mathbf{b}_\beta + \mathbf{i}_\beta$. The remaining acceleration and friction parts are usually neglected (but see Rem. 33 below). While barodiffusion emerges rather by the choice of independent variables in (4.511), the forced diffusion explains the sedimentation (e.g. in centrifugal fields) and electrical conductivity.[32] Note, that these three types of diffusions are described by only one type of the phenomenological coefficient $L_{\delta\beta}$ (as the difference from thermodiffusion with special coefficient $L_{\delta q}$).

The most important case of *concentration diffusion* is that with isobaric diffusion driving force (4.535), without external forces and with corresponding neglection noted above, i.e. with the following driving force

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[32] E.g. (aqueous) solutions of electrolytes in electrochemistry. These may be described by our linear mixture model where constituents are ions of salts and water as solute. The volume force affecting ions is the electrical force which is such when acting on (for simplicity) a univalent positive ion in electrical field with intensity $\mathbf{E}$

$$\mathbf{b}_\beta = \frac{\partial \mathrm{F}}{\partial M_\beta} \mathbf{E} \qquad (a)$$

where F is the Faraday charge (product of elementary electrical charge and Avogadro number) and M_β is the molar mass of ion β. Then the diffusion flow at (electrical) conductivity measurement (mixture without temperature and concentration gradients) is according to (4.514), (4.512):

$$\mathbf{j}_\beta = L_{\beta\beta} \, \mathbf{b}_\beta \qquad (b)$$

with the force (a) (neglecting inertial forces, friction, acceleration and "cross" phenomenological coefficients $L_{\delta\beta}$). Inserting (4.507), (4.24), and assuming zero velocity $\mathbf{v}_n$ of solute (Hittorf referential system, see above the equation (4.539)) we obtain basic relation for electrical conductivity of solution

$$\mathbf{v}_\beta = u_\beta \, \mathbf{E} \qquad (c)$$

where the *mobility* u_β of univalent cation β is defined as

$$u_\beta \equiv L_{\beta\beta} \frac{\mathrm{F}}{\rho_\beta M_\beta} \qquad (d)$$

Mobility and electrical conductivity are therefore determined by the same phenomenological coefficient $L_{\beta\beta}$ as the diffusion, see (4.538). But the situation is much more complicated in such salt solutions because salt is composed from cations and anions and the mixture has at least three constituents. Moreover solutions are electroneutral with high precision and therefore measuring $L_{\beta\beta}$ of unique ion say by diffusion is difficult (difference between diffusion velocities of ions causes e.g. "diffusion potentials", etc.; see [3, 4, 203]). In fact the (near) electroneutrality of ionic solutions permits to use our theory here which neglect long-range electrical forces, cf. Rem. 6.

Experiments and molecular model show that the mobility u_β in the limit of zero concentration of β is constant; therefore $L_{\beta\beta}$ in such limit must be proportional to density ρ_β; this is an example that phenomenological coefficients need not be constant quantities, cf. below (4.519).

$$\mathbf{y}_\beta = \sum_{\zeta=1}^{n-1} \frac{\partial \tilde{g}_\beta}{\partial w_\zeta} \operatorname{grad} w_\zeta \qquad \beta = 1, \ldots, n-1 \tag{4.536}$$

and, moreover, under isothermal conditions. According to phenomenological equation (4.514), the diffusion flux is then given by the *Fick law*

$$-\mathbf{j}_\delta = \sum_{\zeta=1}^{n-1} D_{\delta\zeta}^{nw} \operatorname{grad} w_\zeta \qquad \delta = 1, \ldots, n-1 \tag{4.537}$$

where $D_{\delta\zeta}^{nw}$ are the *diffusion coefficients* or *diffusivities* (more precisely, as it is denoted by superscripts, relative to n-th constituent and for expression of concentration gradients through mass fractions) defined by

$$D_{\delta\zeta}^{nw} \equiv \sum_{\beta=1}^{n-1} L_{\delta\beta} \frac{\partial \tilde{g}_\beta}{\partial w_\zeta} \qquad \delta, \zeta = 1, \ldots, n-1 \tag{4.538}$$

They are therefore functions of temperature, pressure and composition (or temperature and partial densities) values of which are only partially determined by (equilibrium) thermodynamic quantities, namely by the dependence of chemical potentials on composition (usually expressed through the dependence of (logarithm of) the activity coefficient on composition, see (4.444), obtainable from equilibrium measurements).

Using Fick (4.537) and Fourier (4.534) laws in balances of mass and energy respectively gives the most commonly-used application.[33]

Fick's law of concentration diffusion understood as proportionality between the diffusion flow and the gradient of composition has many forms according to the choice of referential velocities and expressions of composition gradients; moreover also using molar instead of specific units plays a role (e.g. molar diffusion fluxes (4.560) instead of those from (4.507) which are specific). But the form of the Fick law remains the same with corresponding change in diffusion coefficients, cf. also labelling of diffusion flows or diffusion coefficients (see below and (4.537)). Their general recalculation may be found in [3, 4, 79], here we demonstrate this on examples of mainly binary non-reacting mixture used often in praxis.

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[33] Fick or Fourier laws, introduced into the mass or energy balances give (after known simplifications) parabolic differential equations for diffusion or heat conduction respectively. This leads to the "diffusion paradox": infinite velocity of concentration or temperature disturbance. It is possible to remove it if the influence of acceleration $\dot{\mathbf{v}}_\beta$ in diffusion driving force (4.535) is not neglected [16, 51, 52] or temperature memory is introduced [17, 82, 83]. This may be related to possible non-objectivity of heat flux sometimes discussed [13, 204] but as seems this effect is negligible in continuum theory [204], cf. Rem. 21 in Chap. 3. Moreover, Bright and Zhang [205] argumented that this paradox and preference of hyperbolic over parabolic differential equations are, in fact, a result of misperception.

In our theory, we mostly have used the *Hittorf referential system*, cf. (4.24), (4.507), Rem. 32, with the velocity of n-th constituent as the referential one. But also the *barycentric velocity* $\mathbf{v}^w$ (see Rem. 3) may be used as the referential one. Its molar analogue is the *molar average velocity* $\mathbf{v}^x$ defined by

$$\mathbf{v}^x \equiv \sum_{\alpha=1}^{n} x_\alpha \mathbf{v}_\alpha \tag{4.539}$$

where x_α is the molar fraction of constituent α.

Volume average velocity $\mathbf{v}^{\mathbf{o}}$ is defined by (cf. (4.196))

$$\mathbf{v}^{\mathbf{o}} \equiv \sum_{\alpha=1}^{n} \rho_\alpha v_\alpha \mathbf{v}_\alpha \tag{4.540}$$

and we can also define corresponding diffusion flows, e.g.

$$\mathbf{j}^{\mathbf{o}}_\alpha \equiv \rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\mathbf{o}}) \qquad \alpha = 1, \ldots, n \tag{4.541}$$

Motivation for these definitions is often rooted in experimental measurement of diffusion coefficient (we try here to use the referential velocity which is zero in the measuring device; movement of constituent relatively to it is just the diffusion). Usually, it is used (4.539) in gases, (4.540) in liquid, mixing of which is nearly ideal (4.440).

Only $n - 1$ diffusion flows and therefore also $n - 1$ Fick laws of any type are independent, e.g. because of (4.540), (4.541), (4.196),

$$\sum_{\alpha=1}^{n} v_\alpha \mathbf{j}^{\mathbf{o}}_\alpha = \mathbf{o} \tag{4.542}$$

or in Hittorf system with (4.507), (4.24) it should be $\mathbf{j}_n \equiv \rho_n(\mathbf{v}_n - \mathbf{v}_n) = \mathbf{o}$, cf. the binary diffusion below.

Results (4.516)–(4.519) for the binary mixture together with Onsager relations (4.520)

$$L_{1q} = L_{q1} \tag{4.543}$$

are valid if

$$\vartheta_1 = 0 \tag{4.544}$$

(see (4.517), (4.518); here the matrix $\nu^{-1}_{\delta\beta}$ is reduced to $1/\nu_{11}$); because of $\nu_{11} > 0$ (cf. (4.181), (4.182) and below (4.513) for a regular non-reacting mixture), (4.519), we obtain also

$$L_{11} > 0, \quad L_{qq} > 0 \tag{4.545}$$

For a binary mixture, the Fick law is therefore (4.537)

$$-\mathbf{j}_1 = D_{11}^{nw}\,\mathrm{grad}w_1 \tag{4.546}$$

where the diffusion coefficient is

$$D_{11}^{nw} \equiv L_{11}\,\frac{\partial \tilde{g}_1}{\partial w_1} \tag{4.547}$$

Because $L_{11} > 0$ (4.545) and in the stable mixture $\frac{\partial \tilde{g}_1}{\partial w_1} > 0$ (chemical potential increases with concentration, see (4.361)) we obtain $D_{11}^{nw} > 0$, i.e. diffusion leads to equalizing of concentration differences. In an unstable mixture $\frac{\partial \tilde{g}_1}{\partial w_1} \le 0$ and therefore $D_{11}^{nw} \le 0$ and the solution disintegrates to separate phases (diffusion enlarges the concentration difference).

The relation between $\mathbf{j}_1$ (Hittorf system) and diffusion flows $\mathbf{j}_\alpha^{\mathbf{o}}$ ($\alpha = 1, 2$) (relative to the volume average velocity) in a binary mixture follows from (4.541), (4.540), (4.196), (4.507), (4.24)

$$\mathbf{j}_1^{\mathbf{o}} = \rho_2 v_2\,\mathbf{j}_1 \tag{4.548}$$

Inserting the Fick law (4.546) here, we obtain again the Fick law but this time for the volume average diffusion flow with concentration gradient expressed by mass fraction again

$$-\mathbf{j}_1^{\mathbf{o}} = D_{11}^{\mathbf{o}w}\,\mathrm{grad}w_1 \tag{4.549}$$

where the new diffusion coefficient is defined as

$$D_{11}^{\mathbf{o}w} \equiv \rho_2 v_2\, D_{11}^{nw} \tag{4.550}$$

Superscripts denote referential velocities and gradient expressions respectively (cf. below (4.537)) and subscripts point to a binary mixture with one independent diffusion coefficient (sometimes the Fick law is also formulated for diffusion flow $\mathbf{j}_2^{\mathbf{o}}$ [76, 203] but this is not necessary by (4.542) for $n = 2$).

A more usual form of Fick law is obtained, if we use (in binary mixture) variables T, P, ρ_1 instead of T, P, w_1 (we recall that space gradients of T, P are zero at concentration diffusion), cf. (4.537). Assuming implicit definition of $w_1 = w_1(T, P, \rho_1)$ from $\rho_1 = w_1/\tilde{v}(T, P, w_1)$ (see (4.22), (4.195), (4.215)) we deduce with (4.191), (4.265) for $y = v$, (4.23), that

$$\left(\frac{\partial w_1}{\partial \rho_1}\right)_{T,P} = 1/(\rho^2 v_2) \tag{4.551}$$

$$\mathrm{grad}w_1 = \left(\frac{\partial w_1}{\partial \rho_1}\right)_{T,P} \mathrm{grad}\rho_1 \tag{4.552}$$

Inserting these relations into (4.549), we obtain the Fick law in the form traditionally used (e.g. for diffusion in liquid non-electrolyte mixtures)

$$-\mathbf{j}_1^{\mathbf{o}} = D\,\mathrm{grad}\rho_1 \tag{4.553}$$

giving the diffusion flow relatively to the volume average velocity with density gradients, i.e. with the diffusion coefficient $D_{11}^{\mathbf{o}\rho}$ (using also (4.550))

$$D \equiv D_{11}^{\mathbf{o}\rho} = D_{11}^{\mathbf{o}w}/(\rho^2 v_2) = (w_2/\rho)D_{11}^{nw} \tag{4.554}$$

Another often used Fick law for solutions (say of salts in water—solute, constituent 2) is

$$-\mathbf{j}_1 = D_{11}^{n\rho}\,\mathrm{grad}\rho_1 \tag{4.555}$$

and therefore, by (4.548), (4.553), we have

$$D = \rho_2 v_2\, D_{11}^{n\rho} = D_{11}^{ww}/\rho \tag{4.556}$$

The latter formula follows from the Fick law

$$-\mathbf{j}_1^{w} = D_{11}^{ww}\,\mathrm{grad}w_1 = \rho D\,\mathrm{grad}w_1 \tag{4.557}$$

written for the barycentric diffusion flow $\mathbf{j}_1^w \equiv \rho_1\mathbf{u}_1^w$ (with the barycentric diffusion velocity $\mathbf{u}_1^w$ from Rem. 7); namely then $\mathbf{j}_1^w = w_2\mathbf{j}_1$ and (4.557) follows by (4.546), (4.554).

The traditional symbol D is used because of frequent cases (4.553), (4.555) [76, 180]; moreover in dilute solutions (where solute 2 prevails $w_2 \to 1$ and $\rho_2 v_2 \to 1$) it follows from the transformations (4.556), (4.554), (4.550)

$$D \simeq D_{11}^{n\rho}, \quad \rho D \simeq D_{11}^{nw} \simeq D_{11}^{\mathbf{o}w} \tag{4.558}$$

With these approximations, the often used forms of Fick laws (4.553), (4.549), (4.546), (4.555) in dilute solutions are (usually $\mathbf{j}_1^{\mathbf{o}}$ for non-electrolytes and $\mathbf{j}_1$ for salt solutions)

$$-\mathbf{j}_1^{\mathbf{o}} = D\,\mathrm{grad}\rho_1 \ = \rho D\,\mathrm{grad}w_1, \quad -\mathbf{j}_1 = \rho D\,\mathrm{grad}w_1 = D\,\mathrm{grad}\rho_1 \tag{4.559}$$

(note that $(4.557)_2$ is valid generally).

But this is not all, the same diffusion coefficient D may be used if we use molar quantities in formulation of Fick law for this binary concentration diffusion, cf. (4.562) below. Specifically, using the *molar diffusion flow* of constituent 1 defined as the corresponding (specific) diffusion flow given above divided by the molar mass M_1 of the first constituent (molar quantities are denoted, in addition, by apostrophe $'$), e.g. the molar diffusion flow $\mathbf{j}_1'^{\mathbf{o}}$ relatively to volume average velocity as

$$\mathbf{j}'^{\mathbf{o}}_1 \equiv \mathbf{j}^{\mathbf{o}}_1/M_1 = c_1(\mathbf{v}_1 - \mathbf{v}^{\mathbf{o}}) \tag{4.560}$$

and expressing composition gradients through gradients of molar concentrations or molar fractions, we can write Fick law (4.553) in another classical way

$$-\,\mathbf{j}'^{\mathbf{o}}_1 = D\,\mathrm{grad}c_1 = D'^{\mathbf{o}x}_{11}\,\mathrm{grad}x_1 \tag{4.561}$$

with the same diffusion coefficient (4.554)

$$D \equiv D^{\mathbf{o}\rho}_{11} = D'^{\mathbf{o}c}_{11} \tag{4.562}$$

using our labelling above analogously. For this we use molar quantities from the end of Sect. 4.6 (4.288)–(4.295) and from them deduced relations like $\mathrm{grad}\rho_1 = M_1\mathrm{grad}c_1$, $\mathrm{grad}w_1 = (M_1M_2/M^2)\mathrm{grad}x_1$ for the binary mixture. With these results we can define similarly the molar diffusion flows $\mathbf{j}'_1 \equiv \mathbf{j}_1/M_1$, $\mathbf{j}'^{x}_1 \equiv \mathbf{j}^{x}_1/M_1 = c_1(\mathbf{v}_1 - \mathbf{v}^{x}) = (x_2/M_1)\mathbf{j}_1$ and analogously from the preceding "specific" Fick laws (4.555), (4.546) and analogue of (4.557) we obtain the "molar" Fick laws

$$-\,\mathbf{j}'_1 = D'^{nc}_{11}\,\mathrm{grad}c_1 = D'^{nx}_{11}\,\mathrm{grad}x_1 \tag{4.563}$$

$$-\,\mathbf{j}'^{x}_1 = D'^{xx}_{11}\,\mathrm{grad}x_1 = cD\,\mathrm{grad}x_1 \tag{4.564}$$

where diffusion coefficients are in analogous relations to D as in (4.554), (4.556), namely

$$D = D'^{\mathbf{o}c}_{11} = D'^{\mathbf{o}x}_{11}/(c^2v_2M_2) = (x_2/c)D'^{nx}_{11} = c_2M_2v_2D'^{nc}_{11} = D'^{xx}_{11}/c \tag{4.565}$$

Again, in dilute solutions ($x_2 \to 1$ and $c_2M_2v_2 \to 1$), we obtain analogously as (4.558) (with the same diffusivity D)

$$D \simeq D'^{nc}_{11}, \quad cD \simeq D'^{nx}_{11} \simeq D'^{\mathbf{o}x}_{11} \tag{4.566}$$

and in dilute solution "molar" Fick laws may be written analogously as (4.559)

$$-\,\mathbf{j}'^{\mathbf{o}}_1 = D\,\mathrm{grad}c_1 = cD\,\mathrm{grad}x_1, \quad -\mathbf{j}'_1 = cD\,\mathrm{grad}x_1 = D\,\mathrm{grad}c_1 \tag{4.567}$$

Note also, that for diffusion of gas mixtures where the molar average velocity $\mathbf{v}^{x}$ is used, it is possible to approximate such mixture by a mixture of ideal gases where, by (4.423), $\rho_\alpha v_\alpha = x_\alpha$ and therefore the volume average velocity is the same as the molar average one; it is therefore possible to use, e.g. Fick law in the form (4.561) (or (4.553) recalculated with constant M_1) with the same diffusion coefficient D.

These results demonstrate that the form of Fick law, as proportionality between diffusion flow and composition gradients, preserves in the different choice of concentration gradient and reference velocity.

Concluding, we can see that in the frequent practical cases of approximation by dilute solutions or ideal gases, that only one diffusion coefficient D can be used (or ρD or cD if we use for component the gradients of mass or molar fractions) and differences among different referential velocities can be neglected. This is the usual way in applications or/and at tabulation diffusion coefficients [76, 180, 206].

At the end we note concentration diffusion for more constituents, say for ternary system $n = 3$. Fick's law (4.537) is

$$-\mathbf{j}_\delta = \sum_{\zeta=1}^{2} D_{\delta\zeta}\, \mathrm{grad} w_\zeta \qquad \delta = 1, 2 \tag{4.568}$$

where diffusion flows in Hittorf system (4.507), (4.24) are

$$\mathbf{j}_\delta = \rho_\delta(\mathbf{v}_\delta - \mathbf{v}_3) \qquad \delta = 1, 2 \tag{4.569}$$

and diffusion coefficients (4.538) are

$$D_{\delta\zeta} \equiv \sum_{\beta=1}^{2} L_{\delta\beta} \frac{\partial \tilde{g}_\beta}{\partial w_\zeta} \qquad \delta, \zeta = 1, 2 \tag{4.570}$$

The Onsager relation of reciprocity is usually admitted

$$L_{21} = L_{12} \tag{4.571}$$

then (4.570) allows to express, e.g. D_{21} as the function of those remaining D_{11}, D_{22}, D_{12} and thermodynamic quantities $\partial\tilde{g}_\beta/\partial w_\zeta$ (cf. discussion of (4.538)). Therefore it is sufficient to measure the latter three independent diffusion coefficients only. Moreover, the "cross" diffusion coefficient D_{12} may be sometimes neglected in comparison with those which are "principal" D_{11}, D_{22}.

Summary. This section further elaborates on the description of transport phenomena, including their cross effects, in the linear fluid mixture. The equations derived for these phenomena in previous sections were transformed here into more practical forms. Some classical laws were thus disclosed. The diffusion fluxes were introduced by (4.507) and the isothermal gradient of chemical potential (4.510) was used to derive the constitutive equations for them—(4.514)—as well as the modified constitutive equation for the heat flux (4.515). All these new constitutive equations contain the driving force for diffusion (4.512) and their coefficients correspond to the phenomenological coefficients known from classical irreversible thermodynamics, cf. (4.516)–(4.519). These coefficients can be made to fulfill the Onsager reciprocity relations (4.520) as shown on pages 260–262. The Fourier law of heat conduction (4.534) was disclosed together with related cross effects with diffusion—Soret and Dufour effects. The driving force for diffusion was shown to include the concentration diffusion as well as the barodiffusion, the diffusion forced by the external body forces, by acceleration, and by friction—see (4.535). The most important part—the concentration diffusion—was treated in more details. The Fick law (4.537) was derived and some of its many forms, which depend on used velocity referential system, concentration (compositional) quantities and gradients, were demonstrated; for the most frequently used examples see (4.546), (4.553), or (4.561).

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Appendix

A.1 Empirical Temperature, Ideal Gas, and Carnot Cycle

Temperature is a quantity concerning macroscopic bodies only and may be introduced as follows:

Consider three systems having the corresponding measurable *thermometric properties* V, R, E, respectively, which change monotonously by heating or cooling such systems (e.g., in the first one, we measure the volume V, in the second one its (electrical) resistance R, and in the third one—electrochemical cell—its electromotive force E; other variables, like pressure or composition are assumed to be fixed). Putting each two of these systems in thermal contact (i.e., permitting mutually heat exchange), the experience shows that they achieve after sufficient time *thermal equilibrium*.[1] If the first and second systems achieve fixed values (in time) V_1 and R_1 in such equilibrium and the first and third achieve in their (separate) equilibrium (time fixed) values V_1 and E_1 (the value V_1 is chosen the same in both cases by corresponding heating or cooling of systems) and if we realize another equilibrium between the second and third system with the value R_1 (again achieved by heating or cooling), we find that the value in the third system is just E_1. This not self-evident empirical result expresses the *Zeroth Law of thermodynamics* (cf. [1, Sect. 1.4], [2, Sect. 1.05]): If two systems (our second and third such) are both in thermal equilibrium with another (the first in our case) system, then they are in thermal equilibrium with each other.

This means that these three systems have a common property called *empirical temperature*. Choosing, say, the first system as *thermometer*, we can take, in thermal equilibrium, as the numerical value of empirical temperature the thermometric property V of this first system because it is the same in all systems; in our experiments it has the value V_1.

Generally, measuring the empirical temperature ϑ (as we denote it in the following) of some system, therefore, consists in bringing it into thermal equilibrium with some thermometer and reading the thermometer value ϑ.

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[1] For simple systems, discussed in this book, achieving such equilibrium may follow from properties of systems, cf. Sects. 3.8, 4.7.

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The system in thermal equilibrium consists of one (usually great) subsystem—the *bath*—and several further subsystems—*calibrated* thermometers—serve to calibrate the thermometers according to one of them—the *calibrating* thermometer (and also for finding the relation between the different temperature scales if thermometric properties of the calibrated thermometers are different). For our purposes, we use only Kelvin units for empirical temperature ϑ using the *ideal gas thermometer* as the calibrating one which may be realized (in principle) as follows [3]: as a (real) calibrating thermometer, we use the *gas thermometer* containing a fixed number of mols n of (real) gas and measure its volume V (thermometric property in the example above) of the gas at fixed pressure P [2] and we repeat such measurements at lower and lower pressure. Then, the following limit for zero pressure $\lim_{P \to 0}(PV/n)$ which experience shows is the same for all gases (and, moreover, it is positive and rises with physiological "hotness") may be taken as the thermometric property. The empirical temperature ϑ of this *ideal gas thermometer* in Kelvin units K is given by

$$\vartheta = (\lim_{P \to 0} PV/n)/\mathrm{R} \tag{A.1}$$

where (positive) R $(= 8.31441\,\mathrm{J/K \cdot mol})$ is the *universal gas constant* [4]. This value was obtained by analogous measurement of the temperature of the triple point of water (equilibrium of (water) ice, liquid, and vapor) by the following relation

$$\mathrm{R} = (\lim_{P \to 0} PV/n)/273.16 \tag{A.2}$$

because the temperature of exactly 273.16 K was attributed to the triple point of water (the choice of this value is motivated by the practical invariability of data tabulated so far, e.g., the normal boiling point of water is by 0.026 K lower than the former value 373.15 K (100 °C)).

Because of laborious measurement with a gas thermometer, the International Temperature Scale (containing, e.g., melting or boiling temperatures of pure substances and obtained in principle on their basis) is used for practical calibrations.

Therefore, temperature and its measurement is joined with equilibrium the part of which is the thermal equilibrium (cf. unique temperature in equilibrium situations, e.g., (2.61), (3.237)).

The possibility of measuring empirical temperature ϑ in *nonequilibrium* situations is connected with the fact that the different calibrated thermometers noted above may have very different dimensions and very different relaxation times (the time intervals necessary to achieve practically thermal equilibrium). Then, a reliable empirical temperature in (even nonequilibrium) situations may be obtained if we use a thermometer with a dimension and relaxation time much less than the space and time of the observer's scales of this situation (cf. Sects. 1.1, 1.2, 2.3). Moreover, the right value of ϑ is assured if, by repeating identical measurement with other thermome-

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[2] Or the pressure P—thermometric property at a fixed volume V of thermometer.

ters with smaller and smaller dimensions and relaxation times, the same values (in Kelvins) are obtained.

The ideal gas thermometer realized by limitation (A.1) may be looked upon as a thermometer filled by *ideal gas* which is defined by

(i) the state equation

$$PV = n\mathrm{R}\vartheta \tag{A.3}$$

where ϑ is the temperature (A.1) measured in Kelvins and R is the universal gas constant (A.2).

(ii) its internal energy (of fixed gas amount) being an increasing function of temperature only.[3]

The state equation of ideal gas (A.3) and the limiting process in (A.1) express the experimental fact that every real gas in the limit of low pressure behaves as an ideal gas. Note, that the density and pressure of (real) gas goes to zero simultaneously and continuously (as different from liquids which achieve discontinuous phase change during such diminishing), cf. Sect. 4.8. Experience also confirms definition ii through the Joule experiment: the temperature of a gas (ideal in the limit of its zero pressure) does not change in adiabatic expansion to vacuum (i.e., without heat exchange against zero external force). Therefore, the internal energy of an ideal gas does not change even if its volume changes at constant temperature; moreover, the function in ii. is increasing, see Rem. 15 in Chap. 1, (3.213), (3.256). Properties i. and ii. are also in accord with the molecular picture of ideal gas as a gas with negligible interparticle influences (i.e., that its internal energy consists of the kinetic energy of molecular motions and its interparticle potential energy, is neglected). Moreover, as was shown by (4.421), (4.422), the state equation (A.3) of ideal gas is valid also for mixtures and the limiting property (A.1) is valid for any real gas mixture of constant composition.

In the remaining part of this Appendix A.1, we obtain the important result (A.9) using an ideal cyclic process from subset C of Sect. 1.2, namely the *Carnot cycle* [1, 2, 4, 5]. Carnot cycle is a cyclic process with (fixed number of mols, n, of) uniform ideal gas composed from isothermal and adiabatic (no heat exchange) expansions followed by isothermal (at lower temperature) and adiabatic compressions back to the starting state. All these processes pass the equilibrium (stable) states and they are reversible (cf. definition in Sect. 1.2), see also Rem. 48 in Chap. 3.

The Carnot cycle is an abstract construction because of ideal gas, namely this was used for obtaining temperature ϑ of the ideal gas thermometer in Kelvins (see (A.1)) and, through result (A.9) below, for obtaining the absolute temperature (1.30), see Sect. 1.4.[4] Also the balance of energy (1.5) contains only the volume work w (because the (macroscopic) kinetic and potential energy may be neglected, see Rem. 9

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[3] Internal energy is the (whole) energy diminished by kinetic energy of (macroscopic) flow or, moreover, by potential energy of external force fields (gravitation, e.g.); cf. Sect. 1.3.

[4] But, generally, such a cycle with adiabatic and isothermal irreversible processes may be realized with real gas (or even liquid). Those with real gas approximate the reversible Carnot cycle with ideal gas by a double limiting process as follows (i.e., we form the ideal cyclic process from set A (and also B and C), see motivation of postulate U2 in Sect. 1.2): running this cycle slower and slower

in Chap. 1) where, by reversibility, the pressure P is given by the state equation of ideal gas (A.3) (the external pressure is equal to the internal one in such a nearly nonmovable state, cf. Sect.2.1, Rem. 1). In this uniform (stable) equilibrium state, the internal energy U (of fixed number of mols, n) is given by an increasing function of temperature, cf. Rems. 15 in Chap. 1, 7 in Chap. 2, (3.213), (3.256).[5]

The Carnot cycle starts at state 1 with temperature ϑ_b , volume V_1 and internal energy $U_1 = U(\vartheta_b)$ and it expands reversibly and isothermally to state 2, volume V_2 with the same temperature ϑ_b. Internal energy $U_2 = U_1 = U(\vartheta_b)$ does not change during this isothermal expansion. Balance (1.5) (here and in the following we use $J = 1$), in the form (1.12) for this reversible expansion (pressure follows from the ideal gas state equation (A.3)) gives at this ϑ_b the heat Q_b (the component of heat distribution at ϑ_b of Carnot cycle)

$$Q_b = \int_{V_1}^{V_2} P \, \mathrm{d}V = n\mathrm{R}\vartheta_b \ln(V_2/V_1) = q^+ \tag{A.4}$$

which is, by expansion $V_2 > V_1$ and (1.14), the heat absorbed $q^+ > 0$.

From state 2, the adiabatic reversible expansion (i.e., with zero heat exchange) to state 3 follows, resulting in volume V_3 and temperature ϑ_a. Internal energy is $U_3 = U(\vartheta_a)$. Using the molar heat capacity C_V at constant volume (which is positive and may be a function of ϑ, see Rem. 5) as $nC_V = \mathrm{d}U/\mathrm{d}\vartheta$, the differential form of energy balance (1.13) gives with state equation (A.3) for this reversible adiabatic expansion

$$\mathrm{d}U = nC_V \; \mathrm{d}\vartheta = -P \, \mathrm{d}V = -n\mathrm{R}\vartheta \, \mathrm{d}V/V \tag{A.5}$$

Therefore $\mathrm{d}U < 0$, $\mathrm{d}\vartheta < 0$ (other quantities here are positive), i.e., internal energy and temperature fall and $\vartheta_b > \vartheta_a$ must be valid.

By integration of (A.5), we obtain

$$\int_{\vartheta_b}^{\vartheta_a} (nC_V/\vartheta) \, \mathrm{d}\vartheta = -n\mathrm{R} \ln(V_3/V_2) \tag{A.6}$$

(Footnote 4 continued)
the velocity of macroscopic motion may be neglected (external fields, like gravitation, are assumed to be not present), all states passed during this cycle are therefore uniform (without space gradients, cf. Sect. 3.8), and are (stable) equilibrium states (cf. Rems. 12 in Chap. 1, 7 in Chap. 2, 48 in Chap. 3). The sequence of such states is the reversible process which may be also homogeneous (changing mass, we change extensive w, $\vec{Q}$, cf. motivation of U2 in Sect. 1.2). Moreover, running this cycle in limits of lower and lower pressure, we obtain the Carnot cycle, because in the limit of low pressure any real gas behaves as the ideal one.

[5] Positive molar heat capacity $C_V \equiv \frac{1}{n}\mathrm{d}U/\mathrm{d}\vartheta$ depends generally on temperature (and it is not only constant as in discussions of Carnot cycle in many thermodynamic textbooks, cf. [1, exrc. 8 in Chap. 1].

From state 3 to 4, the isothermic reversible compression is running from volume V_3 to V_4 at (lower and constant) temperature ϑ_a and internal energy $U_3 = U(\vartheta_a) = U_4$. Heat exchanged Q_a (unique at ϑ_a) is given by (analogously as (A.4))

$$Q_a = \int_{V_3}^{V_4} P \,\mathrm{d}V = n\mathrm{R}\vartheta_a \ln(V_4/V_3) = -q^- \tag{A.7}$$

which, by compression $V_4 < V_3$ is the emitted heat $Q_a < 0$, i.e., by (1.15), $q^- > 0$. At last from state 4 to the initial state 1, we have reversible adiabatic compression from volume V_4 and temperature ϑ_a back to V_1 and ϑ_b and integration of (A.5) (at compression the temperature rises) gives

$$\int_{\vartheta_a}^{\vartheta_b} (nC_V/\vartheta)\,\mathrm{d}\vartheta = -n\mathrm{R}\ln(V_1/V_4) \tag{A.8}$$

Comparing the left hand sides of (A.8) and (A.6), we obtain $V_4/V_3 = V_1/V_2$. Using it in (A.4) divided by (A.7), we obtain the equality

$$Q_b/(-Q_a) = \vartheta_b/\vartheta_a = q^+/q^- \tag{A.9}$$

Note that the Carnot cycle has the heat distribution $\overrightarrow{Q}$, composed from only two nonzero members (of different signs) Q_a, Q_b, cf. (1.1); other members of heat distribution are zero (in adiabatic parts of the Carnot cycle or by definition—most temperatures are not present at all). Also note that from (A.9) follow $q^+ > q^-$ for our case $\vartheta_b > \vartheta_a$; therefore by (1.17) $q > 0$ and by (1.4) $w < 0$, i.e., in the Carnot cycle the work w is produced from “net absorbed” heat q; Second law (1.18) is valid.

Equality (A.9) is important for identification of empirical temperature of ideal gas thermometer ϑ with the absolute temperature T (see deduction of (1.30) in Sect. 1.4). In most parts of this book, we use this absolute temperature T. Therefore, e.g., the state equation of ideal gas (A.3) may be written as

$$PV = n\mathrm{R}T \tag{A.10}$$

A.2 Representations of Linear Isotropic Functions

In our treatise, we deal with the isotropic functions (Sects. 3.5, 3.7, 4.5) defined as follows: scalar a, vector $\mathbf{a}$ and tensor (of the second order) $\mathbf{A}$ in three dimensional space are given, respectively, by *isotropic* scalar $\hat{a}$, vector $\hat{\mathbf{a}}$ and tensor $\hat{\mathbf{A}}$ *function* of scalars y_γ ($\gamma = 1, \ldots, n$), vectors $\mathbf{y}_\alpha$ ($\alpha = 1, \ldots, r$) and (second order) tensors $\mathbf{Y}_\beta$ ($\beta = 1, \ldots, s$) if relations

$$a = \hat{a}(y_\gamma, \mathbf{y}_\alpha, \mathbf{Y}_\beta) = \hat{a}(y_\gamma, \mathbf{Q}\mathbf{y}_\alpha, \mathbf{Q}\mathbf{Y}_\beta\mathbf{Q}^T) \tag{A.11}$$

$$\mathbf{a} = \hat{\mathbf{a}}(y_\gamma, \mathbf{y}_\alpha, \mathbf{Y}_\beta) = \mathbf{Q}^T\hat{\mathbf{a}}(y_\gamma, \mathbf{Q}\mathbf{y}_\alpha, \mathbf{Q}\mathbf{Y}_\beta\mathbf{Q}^T) \tag{A.12}$$

$$\mathbf{A} = \hat{\mathbf{A}}(y_\gamma, \mathbf{y}_\alpha, \mathbf{Y}_\beta) = \mathbf{Q}^T\hat{\mathbf{A}}(y_\gamma, \mathbf{Q}\mathbf{y}_\alpha, \mathbf{Q}\mathbf{Y}_\beta\mathbf{Q}^T)\,\mathbf{Q} \tag{A.13}$$

are valid for any values of independent variables and any orthogonal tensor **Q** from the full orthogonal group $\mathcal{O}$ (i.e., for the set of all orthogonal transformations **Q** describing any rotation and inversion; cf. Rems. 8 in Chap. 3, 9 in Chap. 3). Independent variables in (A.11)–(A.13) are written by usual concise form (cf. (4.128), (3.1)), i.e., the number of independent scalars, vectors, and tensors (cf. Rem. 4 in Chap. 3) is n, r, s, respectively, (these numbers may be different in these three types of functions). The vectors are all usual, polar vectors (namely, axial vectors may be always expressed through corresponding skew-symmetric tensors of the second order, see Rem. 10 in Chap. 3) and if it is not stressed especially, by tensor we understand the tensor of the second order in the following.

It is clear that properties (A.11)–(A.13) restrict the functions $\hat{a}$, $\hat{\mathbf{a}}$, $\hat{\mathbf{A}}$ somehow and these restrictions concern only vector- and tensor-independent variables. Therefore, scalars y_γ play a role of parameters only and therefore they will not be written explicitly in the following. Of course in applications, where independent scalars are typically present, all coefficients in the subsequent formulae are functions of such scalars.

Restrictions of this type are studied by the theory of invariants [6] and for functions (A.11)–(A.13) are known as *representations of isotropic functions* [7, 8]; see these results in [9, 10] (quoted also in [11]). Deduction of these restrictions for the general case of nonlinear functions is complicated (we do it only in Cauchy's representation theorem below) and therefore, we discuss only the much more simple case of *linear isotropic functions* where dependence on vectors and tensors is only a linear one; of course, the dependence on scalar parameters is not restricted and is usually nonlinear.

As we noted in Rem. 9 in Chap. 3 sometimes only a proper group of orthogonal tensors (embracing only rotations) is used and as may be expected the resulting restrictions are not so strong. But for the linear case discussed mostly in this book such results are the same (see, e.g., representations in [10]) as for the full orthogonal group which is therefore preferred here.

Although the resulting representation theorem concerns 3-dimensional vectors and tensors, we note that the following Cauchy representation theorem and Lemma in its proof are valid for vectors of arbitrary dimension.

First, we deduce the *theorem of Cauchy about representation of scalar (nonlinear) functions of vectors* [12, Sect. 11]: If a scalar function $\hat{a}$ of r vectors $\mathbf{y}_\alpha$ ($\alpha = 1, \ldots, r$) is isotropic, i.e., if

$$a = \hat{a}(\mathbf{y}_1, \mathbf{y}_2, \ldots, \mathbf{y}_r) = \hat{a}(\mathbf{Q}\mathbf{y}_1, \mathbf{Q}\mathbf{y}_2, \ldots, \mathbf{Q}\mathbf{y}_r) \tag{A.14}$$

is valid for all $\mathbf{y}_\alpha$ and for all $\mathbf{Q}$ from the full orthogonal group $\mathcal{O}$, then it is necessary and sufficient that the dependence on these vectors $\mathbf{y}_\alpha$ is expressed through their scalar products $\mathbf{y}_\alpha.\mathbf{y}_\beta$ $(\alpha, \beta = 1, 2, \ldots, r; \quad \alpha \leq \beta)$.

Proof at the beginning, we note that here and in the following we shall write concisely $(\mathbf{y}_\alpha) = (\mathbf{y}_1, \mathbf{y}_2, \ldots, \mathbf{y}_r)$ and similarly we write the left hand side of (A.14) concisely $a = \hat{a}(\mathbf{y}_1, \ldots, \mathbf{y}_r) = \hat{a}(\mathbf{y}_\alpha)$ (in fact this concise form has been used also in (A.11)). We also assume that vectors $\mathbf{y}_\alpha$ are p-dimensional with Cartesian components y^i_α ($i = 1, \ldots, p$; for our 3-dimensional applications it is sufficient to consider $p \leq 3$).

First of all, we prove the following *Lemma*: Let us consider two r-tuples of nonzero vectors $(\mathbf{y}_\alpha)$ and $(\mathbf{x}_\alpha)$ such that

$$\mathbf{y}_\alpha.\mathbf{y}_\beta = \mathbf{x}_\alpha.\mathbf{x}_\beta \qquad \alpha, \beta = 1, 2, \ldots, r \tag{A.15}$$

Then Eq. (A.15) are valid if and only if an orthogonal tensor $\mathbf{Q} \in \mathcal{O}$ exists such that

$$\mathbf{Q}\mathbf{y}_\alpha = \mathbf{x}_\alpha \quad \alpha = 1, \ldots, r \tag{A.16}$$

For *proof of Lemma*, we start with its sufficiency: Let orthogonal tensor $\mathbf{Q}$ exist which for r-tuple of nonzero vectors $(\mathbf{y}_\alpha)$ gives r-tuple of vectors $(\mathbf{x}_\alpha)$ by (A.16). Then (A.15) follows (cf. Rem. 8 in Chap. 3):

$$\mathbf{y}_\alpha.\mathbf{y}_\beta = y^i_\alpha y^i_\beta = Q^{ji} x^j_\alpha Q^{ki} x^k_\beta = x^j_\alpha x^k_\beta \delta^{jk} = x^j_\alpha x^j_\beta = \mathbf{x}_\alpha.\mathbf{x}_\beta \quad \alpha, \beta = 1, 2, \ldots, r \tag{A.17}$$

Necessity of Lemma: Vectors $(\mathbf{y}_\alpha)$ form a subspace the dimension of which is given by a number p of linear independent vectors. We arrange $(\mathbf{y}_\alpha)$ in such a way that p linearly independent vectors are at the beginning.

Then the matrix from scalar products of the first p vectors is regular

$$\det \parallel \mathbf{y}_\gamma.\mathbf{y}_\varepsilon \parallel \neq 0 \quad \gamma, \varepsilon = 1, \ldots, p \tag{A.18}$$

which is a necessary and sufficient condition of their linear independence: indeed, (A.18) may be expressed as a product of two determinants, the rows of the first one and the columns of the second one are composed of p Cartesian components of (nonzero) vectors $(\mathbf{y}_1, \ldots, \mathbf{y}_p)$. Each of these determinants is nonzero if and only if these vectors are linearly independent and from this (A.18) follows.

If we insert (A.15) into (A.18), we obtain again the nonzero determinant with corresponding vectors $(\mathbf{x}_1, \ldots, \mathbf{x}_p)$ which are therefore also lineary independent.

Then there exists tensor $\mathbf{Q}$ unique for these both p-tuples of linear independent vectors giving

$$\mathbf{Q}\mathbf{y}_\gamma = \mathbf{x}_\gamma \quad \gamma = 1, \ldots, p \tag{A.19}$$

Namely, by linear independency of vectors $\mathbf{y}_\gamma$, unique cartesian components Q^{ij} $(i, j = 1, \ldots, p)$ of this tensor $\mathbf{Q}$ may be obtained if we solve p systems of linear equations (A.19) $Q^{ij}y^j_\gamma = x^i_\gamma$, $\gamma = 1, \dots, p$ (e.g., p components Q^{1j} follows uniquely from system $Q^{1j}y^j_\gamma = x^1_\gamma$, $\gamma = 1, \dots, p$ because its determinant is nonzero; similarly for remaining components of $\mathbf{Q}$).

Inserting (A.19) into (A.15) we have

$$\mathbf{y}_\gamma.\mathbf{y}_\varepsilon = \mathbf{Q}\mathbf{y}_\gamma.\mathbf{Q}\mathbf{y}_\varepsilon \quad \gamma, \varepsilon = 1, \dots, p \tag{A.20}$$

and therefore (with $\gamma = \varepsilon$ by definition, see Rem. 8 in Chap. 3) $\mathbf{Q}$ is an orthogonal tensor, $\mathbf{Q} \in \mathcal{O}$.

Result (A.19) proves the necessity of a Lemma for linear independent vectors (and in fact it transforms one basis $\mathbf{y}_\gamma$ of p-dimensional vector space to another one $\mathbf{x}_\gamma$ by linear transformation $\mathbf{Q}$). To prove this for the remaining linearly dependent vectors $\mathbf{y}_\eta$, we express them through those which are independent

$$\mathbf{y}_\eta = \sum_{\gamma=1}^{p} \alpha_{\eta\gamma}\mathbf{y}_\gamma \qquad \eta = p + 1, \dots, r \tag{A.21}$$

Scalar products

$$\mathbf{y}_\eta.\mathbf{y}_\varepsilon = \sum_{\gamma=1}^{p} \alpha_{\eta\gamma}\mathbf{y}_\gamma.\mathbf{y}_\varepsilon \quad \varepsilon = 1, \dots, p\,,\ \eta = p + 1, \dots, r \tag{A.22}$$

form $r - p$ systems of p linear equations with p unknowns which, by (A.18), may be solved uniquely by Cramer's rule for $(r - p) \times p$ quantities $\alpha_{\eta\gamma}$. Then $r - p$ vectors $\mathbf{x}_\eta$ from r-tuple $(\mathbf{x}_\eta)$ is given by first p vectors $(\mathbf{x}_\gamma)$ (linearly independent known from (A.19)) of this tuple as

$$\mathbf{x}_\eta = \sum_{\gamma=1}^{p} \alpha_{\eta\gamma}\mathbf{x}_\gamma \quad \eta = p + 1, \dots, r \tag{A.23}$$

where $\alpha_{\eta\gamma}$ are the same coefficients as in (A.21): indeed, forming the vectors $\mathbf{z}_\eta$ $(\eta = p + 1, \dots, r)$ by $\mathbf{z}_\eta = \sum_{\gamma=1}^{p} \alpha_{\eta\gamma}\mathbf{x}_\gamma$ using $\alpha_{\eta\gamma}$ calculated from (A.22) and known (linearly independent) $\mathbf{x}_\gamma$, we obtain, by multiplying these definitions by (again those linearly independent) $\mathbf{x}_\varepsilon$ $(\varepsilon = 1, \dots, p)$ and using (A.15) and (A.22), that $(\mathbf{z}_\eta - \mathbf{x}_\eta).\mathbf{x}_\varepsilon = 0$. Because $\mathbf{x}_\varepsilon$ are linearly independent, this system of homogeneous equations (for each fixed $\eta = p + 1, \dots, r$) gives $\mathbf{z}_\eta = \mathbf{x}_\eta$, i.e., (A.23) is proved.

From (A.23), (A.19), and (A.21), we can see

$$\mathbf{x}_\eta = \sum_{\gamma=1}^{p} \alpha_{\eta\gamma}\mathbf{Q}\mathbf{y}_\gamma = \mathbf{Q}\sum_{\gamma=1}^{p} \alpha_{\eta\gamma}\mathbf{y}_\gamma = \mathbf{Q}\mathbf{y}_\eta \quad \eta = p + 1, \dots, r \tag{A.24}$$

i.e., (A.16) is valid for vectors with indices $\alpha = \eta = p+1, \dots, r$ too. Therefore, (A.19) together with (A.24) gives the necessity of (A.16) and the Lemma is proved. Q.E.D.

Using this Lemma, we now *prove* the Cauchy theorem.

Sufficiency: let $a = \hat{a}(\mathbf{y}_\alpha)$ depend on $(\mathbf{y}_\alpha)$ through scalar products (left side of (A.15)). Choosing arbitrary orthogonal $\mathbf{Q} \in \mathcal{O}$, we find by (A.16) vectors $(\mathbf{x}_\alpha)$ and (A.15) is valid. Inserting (A.15) into $\hat{a}$ and using (A.16), we obtain (A.14).

Necessity: Let us assume (A.14) for all $\mathbf{Q} \in \mathcal{O}$ and we prove that a depends on $(\mathbf{y}_\alpha)$ through scalar products (left hand side of (A.15)) by contradiction. If such dependence does not exist, we find two r-tuples $(\mathbf{y}_{\alpha 1})$ and $(\mathbf{y}_{\alpha 2})$ giving the same values of scalar products $\mathbf{y}_{\alpha 1}.\mathbf{y}_{\gamma 1} = \mathbf{y}_{\alpha 2}.\mathbf{y}_{\gamma 2}$ (left hand side of (A.15)) but at the same time giving different values of (A.14) $\hat{a}(\mathbf{y}_{\alpha 1}) = a_1 \neq a_2 = \hat{a}(\mathbf{y}_{\alpha 2})$. Let us choose some $\mathbf{Q}' \in \mathcal{O}$ and by (A.16), we calculate two r-tuples $(\mathbf{x}_{\alpha 1})$ or $(\mathbf{x}_{\alpha 2})$ for the mentioned $(\mathbf{y}_{\alpha 1})$ or $(\mathbf{y}_{\alpha 2})$, respectively, (e.g., $(\mathbf{x}_{\alpha 2}) = \mathbf{Q}'(\mathbf{y}_{\alpha 2})$). By (A.15), these tuples give the same values of scalar products

$$\mathbf{x}_{\alpha 1}.\mathbf{x}_{\gamma 1} = \mathbf{y}_{\alpha 1}.\mathbf{y}_{\gamma 1} = \mathbf{y}_{\alpha 2}.\mathbf{y}_{\gamma 2} = \mathbf{x}_{\alpha 2}.\mathbf{x}_{\gamma 2} \tag{A.25}$$

and by (A.14) and (A.16) they give the same value

$$a_1 = \hat{a}(\mathbf{y}_{\alpha 1}) = \hat{a}(\mathbf{Q}'\mathbf{y}_{\alpha 1}) = \hat{a}(\mathbf{x}_{\alpha 1}) \tag{A.26}$$

or the same value

$$a_2 = \hat{a}(\mathbf{y}_{\alpha 2}) = \hat{a}(\mathbf{Q}'\mathbf{y}_{\alpha 2}) = \hat{a}(\mathbf{x}_{\alpha 2}) \tag{A.27}$$

respectively. But for two r-tuples $(\mathbf{y}_{\alpha 1})$ and $(\mathbf{x}_{\alpha 2})$ also (A.15) is valid as follows from (A.25) and therefore by Lemma there exists $\mathbf{Q} \in \mathcal{O}$ fulfilling (A.16) $\mathbf{Q}\mathbf{y}_{\alpha 1} = \mathbf{x}_{\alpha 2}$; but using this and (A.14) in (A.26)$_1$, we obtain equality of both (A.26) and (A.27) $a_1 = \hat{a}(\mathbf{y}_{\alpha 1}) = \hat{a}(\mathbf{Q}\mathbf{y}_{\alpha 1}) = \hat{a}(\mathbf{x}_{\alpha 2}) = a_2$. This contradicts the assumption $a_1 \neq a_2$ and therefore proves the necessity. Therefore, Cauchy's theorem is proved. Q.E.D.

Henceforth, we deal only with vectors and tensors in the three dimensional space.

Now, we define *isotropic tensors* of the first order (isotropic vectors) v^i, the second order U^{ij}, the third order R^{ijk} and the fourth order K^{ijkl} as tensors fulfilling

$$v^i = Q^{ij} v^j \quad \text{or} \quad \mathbf{v} = \mathbf{Q}\mathbf{v} \tag{A.28}$$

$$U^{ij} = Q^{ik} Q^{jl} U^{kl} \quad \text{or} \quad \mathbf{U} = \mathbf{Q}\mathbf{U}\mathbf{Q}^T \tag{A.29}$$

$$R^{ijk} = Q^{il} Q^{jm} Q^{kn} R^{lmn} \tag{A.30}$$

$$K^{ijkl} = Q^{im} Q^{jn} Q^{kp} Q^{lq} K^{mnpq} \tag{A.31}$$

for all orthogonal tensors $\mathbf{Q}$ from the full orthogonal group $\mathcal{O}$. In (A.28)–(A.31), Cartesian components are used and we stress that on both sides of these equations there are the same tensors with components in the one and the same Cartesian system.

The following *representation theorem of isotropic tensors* is valid: it is necessary and sufficient that isotropic tensors of odd orders (A.28), (A.30) are identically zero

$$v^i = 0 \tag{A.32}$$

$$\mathrm{R}^{ijk} = 0 \tag{A.33}$$

and isotropic tensors of even orders (A.29), (A.31) are of the form

$$U^{ij} = \eta\delta^{ij} \tag{A.34}$$

$$K^{ijkl} = \alpha\delta^{ij}\delta^{kl} + \beta\delta^{ik}\delta^{jl} + \gamma\delta^{il}\delta^{jk} \tag{A.35}$$

where η, α, β, γ are scalars (δ^{ij} are Kronecker's deltas).

Proof Sufficiency follows immediately by inserting (A.32)–(A.35) into (A.28)–(A.31) and using property of orthogonal tensors, see Rem. 8 in Chap. 3.

Necessity of (A.32) and (A.33) follows if we use $\mathbf{Q} = -\mathbf{1}$ in (A.28) and (A.30).

Necessity of (A.34), we prove forming the scalar function J of two arbitrary vectors $\mathbf{u}$, $\mathbf{w}$ by

$$J \equiv U^{ij}u^i w^j = J(\mathbf{u}, \mathbf{w}) \tag{A.36}$$

where U^{ij} is an isotropic tensor. Then

$$\frac{\partial^2 J}{\partial u^i \partial w^j} = U^{ij} \tag{A.37}$$

Now we take an arbitrary orthogonal tensor $\mathbf{Q} \in \mathcal{O}$ and we form a new tensor $\acute{\mathbf{U}}$ and vectors $\acute{\mathbf{u}}$, $\acute{\mathbf{w}}$ by the following linear transformations

$$\acute{U}^{kl} = Q^{ki}Q^{lj}U^{ij} \tag{A.38}$$

$$\acute{u}^k = Q^{km}u^m \tag{A.39}$$

$$\acute{w}^l = Q^{ln}w^n \tag{A.40}$$

Using properties of $\mathbf{Q}$ from Rem. 8 in Chap. 3 and (A.36), we have

$$\acute{U}^{kl}\acute{u}^k\acute{w}^l = Q^{ki}Q^{lj}U^{ij}Q^{km}u^m Q^{ln}w^n = U^{ij}u^i w^j = J \tag{A.41}$$

i.e., J is a scalar invariant at transformations (A.38)–(A.40). Using (A.29) in the r.h.s. of (A.41)$_1$, we obtain

$$J = J(\mathbf{u}, \mathbf{w}) = U^{kl}Q^{km}u^m Q^{ln}w^n = J(\mathbf{Q}\mathbf{u}, \mathbf{Q}\mathbf{w}) \tag{A.42}$$

Because this is valid for all $\mathbf{Q} \in \mathcal{O}$, we can see that J is a scalar isotropic function (A.14) of two vectors $\mathbf{u}$ and $\mathbf{w}$. According to Cauchy representation theorem for such a function (proved above), the dependence J on these vectors must be expressed through scalar products

$$\mathbf{u}.\mathbf{u}, \quad \mathbf{w}.\mathbf{w}, \quad \mathbf{u}.\mathbf{w} \tag{A.43}$$

But because (A.36) is linear and homogeneous in $\mathbf{u}$ and $\mathbf{w}$, this is possible only when J has a form

$$J = J(\mathbf{u}, \mathbf{w}) = \eta \mathbf{u}.\mathbf{w} \tag{A.44}$$

where η is a scalar. Using (A.37), we obtain the necessity of (A.34).

The necessity of (A.35) may be proved analogously: we form a scalar L of four arbitrary vectors

$$L \equiv K^{ijkl} u^i w^j x^k y^l = L(\mathbf{u}, \mathbf{w}, \mathbf{x}, \mathbf{y}) \tag{A.45}$$

where K^{ijkl} is an isotropic tensor. Then

$$\frac{\partial^4 L}{\partial u^i \partial w^j \partial x^k \partial y^l} = K^{ijkl} \tag{A.46}$$

Forming new tensor $\acute{K}^{mnpq}$ and new vectors $\acute{\mathbf{u}}$, $\acute{\mathbf{w}}$, $\acute{\mathbf{x}}$, $\acute{\mathbf{y}}$ by

$$\acute{K}^{mnpq} = Q^{mi} Q^{nj} Q^{pk} Q^{ql} K^{ijkl} \tag{A.47}$$

$$\acute{u}^m = Q^{mt} u^t \tag{A.48}$$

$$\acute{w}^n = Q^{nu} w^u \tag{A.49}$$

$$\acute{x}^p = Q^{pr} x^r \tag{A.50}$$

$$\acute{y}^q = Q^{qs} y^s \tag{A.51}$$

for some $\mathbf{Q} \in \mathcal{O}$, we obtain by properties of orthogonal tensor (see Rem. 8 in Chap. 3)

$$\begin{aligned} \acute{K}^{mnpq} \acute{u}^m \acute{w}^n \acute{x}^p \acute{y}^q &= Q^{mi} Q^{nj} Q^{pk} Q^{ql} K^{ijkl} Q^{mt} u^t Q^{nu} w^u Q^{pr} x^r Q^{qs} y^s \\ &= K^{ijkl} u^i w^j x^k y^l = L \end{aligned} \tag{A.52}$$

But using (A.31) in (A.52), we obtain (cf. (A.42))

$$L(\mathbf{u}, \mathbf{w}, \mathbf{x}, \mathbf{y}) = L(\mathbf{Q}\mathbf{u}, \mathbf{Q}\mathbf{w}, \mathbf{Q}\mathbf{x}, \mathbf{Q}\mathbf{y}) \tag{A.53}$$

for all $\mathbf{Q} \in \mathcal{O}$ and therefore L is a scalar isotropic function of vectors $\mathbf{u}$, $\mathbf{w}$, $\mathbf{x}$, $\mathbf{y}$. By Cauchy's representation theorem, L depends on the following scalar products

$$\mathbf{u}.\mathbf{u}, \quad \mathbf{w}.\mathbf{w}, \quad \mathbf{x}.\mathbf{x}, \quad \mathbf{y}.\mathbf{y}, \tag{A.54}$$

$$\mathbf{u}.\mathbf{w}, \quad \mathbf{u}.\mathbf{x}, \quad \mathbf{u}.\mathbf{y}, \quad \mathbf{w}.\mathbf{x}, \quad \mathbf{w}.\mathbf{y}, \quad \mathbf{x}.\mathbf{y} \tag{A.55}$$

But according to its definition (A.45), L depends on their vectors linearly and homogeneously and therefore has the following (most general) form (see (A.55))

$$\begin{aligned} L = {} & \alpha_1 \mathbf{u}.\mathbf{w} + \alpha_2 \mathbf{u}.\mathbf{x} + \alpha_3 \mathbf{u}.\mathbf{y} + \alpha_4 \mathbf{w}.\mathbf{x} + \alpha_5 \mathbf{w}.\mathbf{y} + \alpha_6 \mathbf{x}.\mathbf{y} + \alpha(\mathbf{u}.\mathbf{w})(\mathbf{x}.\mathbf{y}) \\ & + \beta(\mathbf{u}.\mathbf{x})(\mathbf{w}.\mathbf{y}) + \gamma(\mathbf{u}.\mathbf{y})(\mathbf{w}.\mathbf{x}) \end{aligned} \tag{A.56}$$

where $\alpha, \beta, \gamma, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6,$ are scalar constants. Inserting (A.56) into (A.46), we obtain the necessity of (A.35) and this finishes the proof of the representation theorem of isotropic tensors. Q.E.D.

Recalling the role of scalar parameters, we can also consider (A.28)–(A.31) as the definitions of isotropic functions (vector or tensor functions up to fourth order) of scalar variables only and relations (A.32)–(A.35) are representation theorems for such functions; then of course, scalars η, α, β, and γ are (not specified) functions of scalar variables (of course, some of these results follow as a special case of a more general representation theorem below).

Now we come to the main theorem of this Appendix concerning the representation of scalar, vector, and tensor linear isotropic functions of vectors and tensors (scalars as independent variables play the role of parameters).

Representation theorem of linear isotropic functions: Scalar, vector, and tensor (of second order) functions (with values $a, \mathbf{a}, \mathbf{A}$) depending linearly on r vectors $\mathbf{y}_\alpha$ $(\alpha = 1, \dots, r)$ and s tensors (of second order) $\mathbf{Y}_\beta$ $(\beta = 1, \dots, s)$ are isotropic (relative to the full orthogonal group $\mathcal{O}$) if and only if their (most general) forms are

$$a = a_0 + \sum_{\beta=1}^{s} \vartheta_\beta \operatorname{tr} \mathbf{Y}_\beta \tag{A.57}$$

$$\mathbf{a} = \sum_{\alpha=1}^{r} \varepsilon_\alpha \mathbf{y}_\alpha \tag{A.58}$$

$$\mathbf{A} = \tau \mathbf{1} + \sum_{\beta=1}^{s} \alpha_\beta (\operatorname{tr} \mathbf{Y}_\beta) \mathbf{1} + \sum_{\beta=1}^{s} (\beta_\beta \mathbf{Y}_\beta + \gamma_\beta \mathbf{Y}_\beta^T) \tag{A.59}$$

where $a_0, \vartheta_\beta, \varepsilon_\alpha, \tau, \alpha_\beta, \beta_\beta, \gamma_\beta$ are scalar constants.

Proof The most general forms of scalar, vector, and tensor functions depending on r vectors and s tensors linearly are

$$a = a_0 + \sum_{\alpha=1}^{r} v_\alpha^i y_\alpha^i + \sum_{\beta=1}^{s} U_\beta^{ij} Y_\beta^{ij} \tag{A.60}$$

$$a^i = a^i_0 + \sum_{\alpha=1}^{r} V^{ij}_\alpha y^j_\alpha + \sum_{\beta=1}^{s} R^{ijk}_\beta Y^{jk}_\beta \tag{A.61}$$

$$A^{ij} = A^{ij}_0 + \sum_{\alpha=1}^{r} S^{ijk}_\alpha y^k_\alpha + \sum_{\beta=1}^{s} K^{ijkl}_\beta Y^{kl}_\beta \tag{A.62}$$

where all coefficients, scalar a_0, vectors a^i_0, v^i_α, tensors of the second order A^{ij}_0, V^{ij}_α, U^{ij}_β, tensors of the third order R^{ijk}_β, S^{ijk}_α, and tensors of the fourth order K^{ijkl}_β are constants.

Now, these functions (A.60)–(A.62) must be isotropic and therefore by (A.11)–(A.13)

$$a_0 + \sum_{\alpha=1}^{r} v^i_\alpha y^i_\alpha + \sum_{\beta=1}^{s} U^{ij}_\beta Y^{ij}_\beta = a_0 + \sum_{\alpha=1}^{r} v^j_\alpha Q^{ji} y^i_\alpha + \sum_{\beta=1}^{s} U^{kl}_\beta Q^{ki} Q^{lj} Y^{ij}_\beta \tag{A.63}$$

$$Q^{il}\Big(a^l_0 + \sum_{\alpha=1}^{r} V^{lj}_\alpha y^j_\alpha + \sum_{\beta=1}^{s} R^{ljk}_\beta Y^{jk}_\beta\Big) = a^i_0 + \sum_{\alpha=1}^{r} V^{ik}_\alpha Q^{kj} y^j_\alpha + \sum_{\beta=1}^{s} R^{ilm}_\beta Q^{lj} Q^{mk} Y^{jk}_\beta \tag{A.64}$$

$$\begin{aligned} Q^{im}\Big(A^{mn}_0 + \sum_{\alpha=1}^{r} S^{mnk}_\alpha y^k_\alpha + \sum_{\beta=1}^{s} K^{mnkl}_\beta Y^{kl}_\beta\Big) Q^{jn} = A^{ij}_0 &+ \sum_{\alpha=1}^{r} S^{ijl}_\alpha Q^{lk} y^k_\alpha \\ &+ \sum_{\beta=1}^{s} K^{ijmn}_\beta Q^{mk} Q^{nl} Y^{kl}_\beta \end{aligned} \tag{A.65}$$

for all $\mathbf{Q}$ from the full group of orthogonal transformation $\mathcal{O}$ and for all values of the independent variables (components of all r vectors and s tensors). Adding here all coefficients standing at the same variables together, we may put such resulting coefficients to zero because of the independence of the variables (this concerns also the zero order members in (A.61), (A.62); a_0 is canceled). From this we can see, using the arbitrariness of $\mathbf{Q} \in \mathcal{O}$ and its properties from Rem. 8 in Chap. 3), that all vector and tensor (2-, 3-, 4- order) coefficients in (A.60)–(A.62) are isotropic tensors in the sense of (A.28)–(A.31). Therefore, representation theorems for such tensors (A.32)–(A.35) are valid, i.e.,

$$a^i_0 = 0, \quad v^i_\alpha = 0, \quad R^{ijk}_\beta = 0, \quad S^{ijk}_\alpha = 0$$

$$A^{ij}_0 = \tau\delta^{ij}, \quad V^{ij}_\alpha = \varepsilon_\alpha \delta^{ij}, \quad U^{ij}_\beta = \vartheta_\beta \delta^{ij}$$

$$K_\beta^{ijkl} = \alpha_\beta \delta^{ij}\delta^{kl} + \beta_\beta \delta^{ik}\delta^{jl} + \gamma_\beta \delta^{il}\delta^{jk} \qquad \alpha = 1, \dots, r \quad \beta = 1, \dots, s \tag{A.66}$$

where all τ, ε_α, ϑ_β, α_β, β_β, γ_β are scalar constants. Inserting (A.66) into (A.60)–(A.62), we obtain the necessity of (A.57)–(A.59).

The sufficiency of (A.57)–(A.59) follows immediately if we insert them into (A.11)–(A.13) and the proof of the representation theorem of linear isotropic functions is accomplished. Q.E.D.

This theorem is valid for any tensors but in applications there are tensors $\mathbf{A}$ or $\mathbf{Y}_\beta$ often symmetric or skew-symmetric. The most important case used in our treatise is that from s tensors $\mathbf{Y}_\beta$ the first h tensors $\mathbf{D}_\eta \quad (\eta = 1, \dots, h)$ are symmetric and the rest are skew-symmetric tensors $\mathbf{W}_\tau \quad (\tau = h + 1, \dots, s)$. Then, because $\mathrm{tr}\mathbf{W}_\tau = 0$, we have instead of (A.57)

$$a = a_0 + \sum_{\eta=1}^{h} \vartheta_\eta \mathrm{tr}\mathbf{D}_\eta \tag{A.67}$$

Moreover, if $\mathbf{A}$ is a symmetric tensor $\mathbf{B}$ given as a function (A.59), then by symmetrization of (A.59) (by which $\mathbf{B}$ is not changed)

$$\mathbf{B} = \tau \mathbf{1} + \sum_{\eta=1}^{h} \alpha_\eta (\mathrm{tr}\mathbf{D}_\eta)\mathbf{1} + \sum_{\eta=1}^{h} \sigma_\eta \mathbf{D}_\eta \tag{A.68}$$

where scalar constants $\sigma_\eta = \beta_\eta + \gamma_\eta \quad (\eta = 1, \dots, h)$.

Similarly, if $\mathbf{A}$ is a skew-symmetric tensor $\mathbf{M}$ given as a function (A.59), then skew-symmetrization of (A.59) (not changing $\mathbf{M}$) gives

$$\mathbf{M} = \sum_{\tau=h+1}^{s} \nu_\tau \mathbf{W}_\tau \tag{A.69}$$

with scalar constants $\nu_\tau = \beta_\tau - \gamma_\tau$ $(\tau = h + 1, \dots, s)$.

Therefore, Eqs. (A.57)–(A.59), (A.67)–(A.69) express the representation theorems of isotropic vector, scalar, and tensor (even symmetric or skew-symmetric) functions linear in vectors and (possibly symmetric or skew-symmetric) tensors. Of course, special cases of these representations follow, e.g., (A.68) is a representation theorem of the isotropic symmetric tensor function linear in symmetric tensors (this was used in Sects. 3.7, 4.5) or (A.34) is a special case of (A.59) as was noted above, etc.

Finally, we recall that if linear isotropic functions depend (even nonlinearly) also on scalars (and these are mostly our cases), then all the constants in representation theorems (A.57)–(A.59), (A.67)–(A.69), (A.34), and (A.35) are (unspecified, often nonlinear) functions of these scalars.

A.3 Concave Functions

In Sects. 3.8 and 4.7, certain properties of concave functions [13–15] are needed. At the same time, properties of convex functions are obtained because the convex functions differ from the concave by the sign only and therefore their properties are mostly obtainable by reversion of all following inequalities. For simplicity, we do not restrict the domain of independent variables (although possible restriction on some concave subset, i.e., having property (A.71) below, is nearly obvious) and we confine ourselves to strict concave functions which suffice for our purposes.

Theorem on concave functions: Let $\bar{\Gamma}$ be a (differentiable) function mapping m-dimensional vectors $\vec{\omega} = (\omega^1, \ldots, \omega^m)$ in real numbers Γ

$$\Gamma = \bar{\Gamma}(\vec{\omega}) \tag{A.70}$$

Then three following assertions are equivalent

(i) Function (A.70) is strictly concave in all its domain which means (by definition) that whenever $\vec{\omega}_0$, $\vec{\omega}_1$, and $\vec{\omega}_2$ are such that

$$\vec{\omega}_0 = \alpha\,\vec{\omega}_1 + (1-\alpha)\,\vec{\omega}_2 \quad \text{for} \quad 1 > \alpha > 0 \quad ; \quad \vec{\omega}_1 \neq \vec{\omega}_2 \tag{A.71}$$

the function (A.70) has the following property

$$\bar{\Gamma}(\vec{\omega}_0) > \alpha\bar{\Gamma}(\vec{\omega}_1) + (1-\alpha)\bar{\Gamma}(\vec{\omega}_2) \tag{A.72}$$

(of course equality instead of $>$ in (A.72) is valid if $\vec{\omega}_1 = \vec{\omega}_2$ or $\alpha = 0, 1$).

(ii) If $\vec{\omega}_1 \neq \vec{\omega}_2$ in (A.71) then

$$\bar{\Gamma}(\vec{\omega}_1) < \bar{\Gamma}(\vec{\omega}_0) + \sum_{p=1}^{m}(\omega_1^p - \omega_0^p)\frac{\partial\bar{\Gamma}}{\partial\omega^p}(\vec{\omega}_0) \tag{A.73}$$

where $\frac{\partial\bar{\Gamma}}{\partial\omega^p}(\vec{\omega}_0)$ is the value of the p-th component of gradient of the function $\bar{\Gamma}$ (in corresponding vector space) taken at $\vec{\omega}_0$ (of course if $\vec{\omega}_1 = \vec{\omega}_0$ the trivial equality instead of (A.73) is obtained).

(iii) The matrix of second derivatives of $\bar{\Gamma}$ (A.70) taken at arbitrary $\vec{\omega}_0$ (A.71)

$$\left\| \frac{\partial^2\bar{\Gamma}}{\partial\omega^p\partial\omega^q}(\vec{\omega}_0) \right\| \qquad p, q = 1, \ldots, m \tag{A.74}$$

is negative definite (therefore a matrix with elements $-\frac{\partial^2\bar{\Gamma}}{\partial\omega^p\partial\omega^q}$ is positive definite) [16, 13.5], [17, 1.29].

Proof It suffices to show that (iii) follows from (i), (i) follows from (ii), and (ii), (iii) are equivalent.

To prove that (iii) follows from (i), we choose (for arbitrary $\vec{\omega}_0$, $\alpha = 1/2$ and arbitrary vector $\vec{\tau} = (\tau^1, \ldots, \tau^m)$)

$$\vec{\omega}_1 = \vec{\omega}_0 + \vec{\tau}, \quad \vec{\omega}_2 = \vec{\omega}_0 - \vec{\tau} \tag{A.75}$$

Such choice fulfills (A.71) and inequality (A.72) is then

$$\bar{\Gamma}(\vec{\omega}_0 + \vec{\tau}) + \bar{\Gamma}(\vec{\omega}_0 - \vec{\tau}) < 2\bar{\Gamma}(\vec{\omega}_0) \tag{A.76}$$

We expand both terms on the left-hand side in the Taylor series around $\vec{\omega}_0$

$$\bar{\Gamma}(\vec{\omega}_0 + \vec{\tau}) = \bar{\Gamma}(\vec{\omega}_0) + \sum_{p=1}^{m} \tau^p \frac{\partial \bar{\Gamma}}{\partial \omega^p}(\vec{\omega}_0) + \sum_{p=1}^{m}\sum_{q=1}^{m} \tau^p \tau^q \frac{1}{2} \frac{\partial^2 \bar{\Gamma}}{\partial \omega^p \partial \omega^q}(\vec{\omega}_0) + o_1(\vec{\tau}^2),$$

$$\bar{\Gamma}(\vec{\omega}_0 - \vec{\tau}) = \bar{\Gamma}(\vec{\omega}_0) - \sum_{p=1}^{m} \tau^p \frac{\partial \bar{\Gamma}}{\partial \omega^p}(\vec{\omega}_0) + \sum_{p=1}^{m}\sum_{q=1}^{m} \tau^p \tau^q \frac{1}{2} \frac{\partial^2 \bar{\Gamma}}{\partial \omega^p \partial \omega^q}(\vec{\omega}_0) + o_2(\vec{\tau}^2) \tag{A.77}$$

where functions $o_1(\vec{\tau}^2)$, $o_2(\vec{\tau}^2)$ converge more rapidly to zero then preceding terms in (A.77). Inserting (A.77) into (A.76), we have

$$\sum_{p=1}^{m}\sum_{q=1}^{m} \tau^p \tau^q \frac{\partial^2 \bar{\Gamma}}{\partial \omega^p \partial \omega^q}(\vec{\omega}_0) + o_1(\vec{\tau}^2) + o_2(\vec{\tau}^2) < 0 \tag{A.78}$$

At sufficiently small vector $\vec{\tau}$, the left-hand side of (A.78) is a negative quadratic form and therefore iii follows for any $\vec{\omega}_0$.

Now we prove that (i) follows from (ii). We write (A.73) taking for $\vec{\omega}_1$, the vectors $\vec{\omega}_1, \vec{\omega}_2$ fulfilling (A.71), and multiplying such inequalities by α and $1 - \alpha$, respectively, we obtain

$$\alpha\bar{\Gamma}(\vec{\omega}_1) < \alpha\bar{\Gamma}(\vec{\omega}_0) + \sum_{p=1}^{m} \alpha(\omega_1^p - \omega_0^p) \frac{\partial \bar{\Gamma}}{\partial \omega^p}(\vec{\omega}_0),$$

$$(1-\alpha)\bar{\Gamma}(\vec{\omega}_2) < (1-\alpha)\bar{\Gamma}(\vec{\omega}_0) + \sum_{p=1}^{m} (1-\alpha)(\omega_2^p - \omega_0^p) \frac{\partial \bar{\Gamma}}{\partial \omega^p}(\vec{\omega}_0) \tag{A.79}$$

Adding these relations together, we have by (A.71)

$$\begin{aligned} \alpha\bar{\Gamma}(\vec{\omega}_1) + (1-\alpha)\bar{\Gamma}(\vec{\omega}_2) &< (\alpha + 1 - \alpha)\bar{\Gamma}(\vec{\omega}_0) \\ &\quad + \sum_{p=1}^{m} \left(\alpha\omega_1^p + (1-\alpha)\omega_2^p - (\alpha + 1 - \alpha)\omega_0^p\right) \frac{\partial \bar{\Gamma}}{\partial \omega^p}(\vec{\omega}_0) \\ &= \bar{\Gamma}(\vec{\omega}_0) \end{aligned} \tag{A.80}$$

and this is the result (A.72), i.e., (i) was proved.

Ultimately, we show that ii and iii are equivalent. We expand $\bar{\Gamma}(\vec{\omega}_1)$ in the Taylor series around $\vec{\omega}_0$ with the remainder of the second order

$$\bar{\Gamma}(\vec{\omega}_1) = \bar{\Gamma}(\vec{\omega}_0) + \sum_{p=1}^{m}(\omega_1^p - \omega_0^p)\frac{\partial\bar{\Gamma}}{\partial\omega^p}(\vec{\omega}_0) + \frac{1}{2}\sum_{p=1}^{m}\sum_{q=1}^{m}(\omega_1^p - \omega_0^p)(\omega_1^q - \omega_0^q)\frac{\partial^2\bar{\Gamma}}{\partial\omega^p\partial\omega^q}(\vec{\omega}_3) \tag{A.81}$$

where components ω_3^p of $\vec{\omega}_3$ are between ω_1^p and ω_0^p. Assuming (iii) for $\vec{\omega}_3$, we find that the last term in (A.81) is a negative definite quadratic form and we obtain (A.73) in (ii) for $\vec{\omega}_1 \neq \vec{\omega}_0$. Conversely, assuming (ii), i.e., (A.73), we find that the last term in (A.81) is a negative definite quadratic form and therefore (iii) follows.

A.4 Nonorthogonal Bases

In Sect. 4.2, we need vector space with a basis which is formed by k linear independent vectors $\vec{g}_p \quad (p = 1, \ldots, k)$ which are not generally perpendicular or of unit length [12, 18, 19]. Such nonorthogonal basis, we call a *contravariant* one. *Covariant* components of the so called *metric tensor* are defined by

$$g_{pq} = \vec{g}_p.\vec{g}_q \qquad p, q, = 1, \ldots, k \tag{A.82}$$

A metric tensor with matrix $\|g_{pq}\|$ is obviously symmetrical and regular (this last assertion is necessary and sufficient for the linear independence of $\vec{g}_p$: in the basis of k orthonormal vectors in this space, we obtain $\det\|g_{pq}\|$ as a product of two determinants first of them having the rows and second one having the columns formed from Cartesian components of $\vec{g}_p$ and $\vec{g}_q$. Because of the linear independence of these k vectors, every determinant and therefore also $\det\|g_{pq}\|$ is nonzero and conversely). *Contravariant* components g^{pq} of the metric tensor are defined by inversion

$$\|g^{pq}\| = \|g_{pq}\|^{-1} \quad \text{i.e.} \quad \sum_{q=1}^{k} g_{pq}\, g^{qr} = \delta_p^r \tag{A.83}$$

where δ_p^r is the Kronecker delta; $\|g^{pq}\|$ is regular and symmetrical.

The reciprocal *covariant* base $\vec{g}^p$ is defined by

$$\vec{g}^p = \sum_{q=1}^{k} g^{pq}\,\vec{g}_q \quad p = 1, \ldots, k \tag{A.84}$$

From (A.82)–(A.84), we have

$$\vec{g}^p.\vec{g}^r = g^{pr}, \quad \vec{g}^p.\vec{g}_r = \delta_r^p \tag{A.85}$$

$$\vec{g}_p = \sum_{q=1}^{k} g_{pq}\,\vec{g}^q, \quad \vec{g}_q = \sum_{p=1}^{k} \delta_q^p\,\vec{g}_p \tag{A.86}$$

The other basis $\vec{g}^{p'}$ is connected with $\vec{g}^r$ by regular tensor H_r^p

$$\vec{g}^{p'} = \sum_{r=1}^{k} H_r^p\,\vec{g}^r \tag{A.87}$$

and conversely, each regular transformation H_r^p defines a new basis (similar transformation is valid for $\vec{g}_r$).

It is possible to express an arbitrary vector $\vec{a}$ in k-dimensional vector space in both bases as

$$\vec{a} = \sum_{p=1}^{k} a^p\,\vec{g}_p = \sum_{q=1}^{k} a_q\,\vec{g}^q \tag{A.88}$$

where a^p and a_q are contravariant and covariant components, respectively. The following relations between them give (A.88), (A.82), (A.85) as

$$a^p = \vec{a}.\vec{g}^p = \sum_{q=1}^{k} g^{pq}\,a_q, \quad a_q = \vec{a}.\vec{g}_q = \sum_{p=1}^{k} g_{qp}\,a^p \tag{A.89}$$

A special (often used) case is the *orthonormal* basis where $\|g_{pq}\|$ is the unit matrix. Then both contravariant and covariant bases are the same unit vectors

$$\vec{g}_p = \vec{g}^p \tag{A.90}$$

as follows from (A.84); $\|g^{pq}\|$ is also the unit matrix.

A.5 Inequalities, Theorem of I-Shih Liu

Here, we present lemmas and the theorem containing inequalities as they have been used in the main text as the consequence of the Second Law (note that sometimes equivalent inequalities are used with reverse signs in premises and implications achieved by changing the signs of corresponding quantities, cf. (A.92) below).

Lemma A.5.1 ([20, Appendix 6.1]) If the following inequality with real constants a, b

$$a + bX \le 0 \tag{A.91}$$

is valid for any real X then it is necessary and sufficient that $b = 0$ and $a \leq 0$.

Proof of sufficiency is obvious and necessity follows by contradiction: if $b > 0$ at some real a then such real X may be found at which inequality is invalid. Analogously for $b < 0$. The remaining follows. Q.E.D.

If we define $a' \equiv -a, \quad b' \equiv -b$, we can obviously write Lemma A.5.1 equivalently as

$$a' + b'X \geq 0 \Leftrightarrow b' = 0, \;\; a' \geq 0 \tag{A.92}$$

In this form, Lemma A.5.1 has been also used (e.g. in (A.104) or in Sect. 4.5).

This Lemma has its generalization on matrices (3×3 in our application in Sect. 3.6):

Lemma A.5.2 If the following inequality with real matrix $\mathbf{B}$ and real constant a

$$a + \mathrm{tr}\mathbf{BX} \leq 0 \tag{A.93}$$

is valid for any real matrix $\mathbf{X}$, then it is necessary and sufficient that $a \leq 0$ and $\mathrm{tr}\mathbf{BX} = 0$.

Proof of sufficiency is obvious and necessity follows by contradiction: If it would be that $\mathrm{tr}\mathbf{BX}_1 \neq 0$ for some fixed matrix $\mathbf{X} = \mathbf{X}_1$ then (A.93) must be valid for $\mathbf{X} = \beta\mathbf{X}_1$ with any real β. But this is impossible because $a + \beta\mathrm{tr}\mathbf{B}X_1 \leq 0$ cannot be valid for some real β.

In the special case, it follows from $\mathrm{tr}\mathbf{BX} = 0$ that if arbitrary $\mathbf{X}$ is symmetric or skew-symmetric then $\mathbf{B}$ must be skew-symmetric or symmetric, respectively. This follows from the component form immediately choosing one independent element of corresponding $\mathbf{X}$ sequentially as a unit (and remaining as zero).

Lemma A.5.3 Let the following polynomial of the third degree in real X be given, where a is the real constant and $f(X)$ the polynomial of mostly second degree, and

$$aX^3 + f(X) \geq 0 \tag{A.94}$$

is valid for any real X. Then it is necessary and sufficient

$$a = 0, \quad f(X) \geq 0 \tag{A.95}$$

Proof Sufficiency is obvious. Necessity: If $a \neq 0$ then at $|X|$ of sufficient magnitude, the term of the third degree determines the sign of the left-hand side of (A.94) and its nonnegativity need not be fulfilled at some $X \in \Re$. The remaining follows immediately. Q.E.D.

Lemma A.5.4 If quadratic inequality with real constants b, a

$$bX + aX^2 \geq 0 \tag{A.96}$$

is valid for any real X then it is necessary and sufficient

$$b = 0, \quad a \geq 0 \tag{A.97}$$

Proof Sufficiency is obvious. Necessity: If $a = 0$ then obviously $b = 0$. If $a < 0$ then inequality (A.96) is not valid for sufficiently great $|X|$. If $a > 0$ and $b > 0$, then inequality (A.96), written as $X(X + b/a) \geq 0$, is not valid for $0 > X > -b/a$. Finally, if $a > 0$ and $b < 0$, then inequality (A.96), written as $X(X + b/a) \geq 0$, is not valid for $0 < X < -b/a$. Therefore, (A.97) is valid. Q.E.D.

We note that generalization of such a Lemma for more variables of X is deduced in [21, p. 240].

We also note that if quadratic inequality with real constants a, b and $c \neq 0$

$$c + bX + aX^2 \geq 0 \tag{A.98}$$

is valid for any real X then the previous result $b = 0$ is not generally valid. An example of such a case is $(1 + X)^2 = 1 + 2X + X^2 \geq 0$. Cf. Sect. 4.5, discussion of (4.169).

Method of Lagrange multipliers of I-Shih Liu [22], cf. also [23, 10]:

The use of the Coleman-Noll admissibility principle in complicated cases (mixtures , electromagnetic and surface systems) is often very difficult, because many gradients and time derivatives are bound together through some interrelations (mainly through balance equations) and the finding of an admissible process is therefore not easy. For these purposes, the method of Lagrange multipliers was proposed by I-Shih Liu [22] which simplifies such complicated situations (for many different applications see also [23], [10, mainly Sect. 5.4.3], [24–28]). The name originates from a certain analogy with the Lagrange method of finding extremes at additional constraints.

The basis for this method is formed by the following

Theorem of I-Shih Liu A.5.5 (cf. Lemma in [22] or [10, Sect. 5.4.3]):

Let it be given that $A = (A_{J\gamma})$ (the component form is in parentheses where $J = 1, \ldots, p, \gamma = 1, \ldots, n$) a real $p \times n$ matrix, $B = (B_J) \in \Re^p$, nonzero $\alpha = (\alpha_\gamma) \in \Re^n$ real vectors (of dimension p or n respectively) and real $\beta \in \Re$. Let S be the non-empty set of (mutually independent) vectors $X = (X_\gamma) \in \Re^n$ fulfilling equations (summing rules in γ, J are assumed)

$$A_{J\gamma} X_\gamma + B_J = 0 \qquad J = 1, \ldots, p \tag{A.99}$$

Then the following statements are equivalent:

(i)

$$\alpha_\gamma X_\gamma + \beta \geq 0 \qquad \text{for all} \quad X \in S \tag{A.100}$$

(ii) There exist nonzero Lagrange multipliers $\Lambda = (\Lambda_J) \in \Re^p$ such that

$$\alpha_\gamma X_\gamma + \beta - \Lambda_J (A_{J\gamma} X_\gamma + B_J) \geq 0 \quad \text{for all} \quad X_\gamma \in \Re^n \tag{A.101}$$

(iii) There exist nonzero Lagrange multipliers $\Lambda = (\Lambda_J) \in \Re^p$ such that

$$\alpha_\gamma - \Lambda_J A_{J\gamma} = 0 \quad \gamma = 1, \ldots, n \tag{A.102}$$

$$\beta - \Lambda_J B_J \geq 0 \tag{A.103}$$

Proof For the equivalence it is sufficient to prove, that (ii)⇒(i), (ii)⇔(iii), and (i)⇒(iii).

Result (ii)⇒(i) follows from (A.99).

Equivalence (ii)⇔(iii) follows writing (A.101)

$$(\alpha_\gamma - \Lambda_J A_{J\gamma})X_\gamma + (\beta - \Lambda_J B_J) \geq 0 \quad \forall X \in \Re^n \tag{A.104}$$

($\forall X \in \Re^n$ means for all vectors X (with components X_γ) from n-dimensional space $\Re^n$). Since X_γ are arbitrary reals, (A.104) is true if and only if (A.102), (A.103) is valid according to Lemma A.5.1 with reversal sign (A.92).

To complete the proof, it is sufficient to show that (i)⇒(iii): We define the following sets

$$H \equiv \{X \in \Re^n \qquad \text{fulfilling} \quad \alpha_\gamma X_\gamma + \beta \geq 0\} \tag{A.105}$$

i.e., H is the set of all those vectors $X = (X_\gamma)$ from $\Re^n$ fulfilling the (A.100) (but they need not fulfill (A.99), similarly in the following);

$$H_0 \equiv \{X \in \Re^n \qquad \text{fulfilling} \quad \alpha_\gamma X_\gamma = 0\} \tag{A.106}$$

$$H_0^\perp \equiv \{y \in \Re^n \qquad \text{fulfilling} \quad y_\gamma X_\gamma = 0, \quad \forall X \in H_0\} \tag{A.107}$$

(i.e., $H_0^\perp$ are those (n-dimensional) vectors $y = (y_\gamma)$ perpendicular to vectors from H_0). Similarly,

$$S_0 \equiv \{X \in \Re^n \qquad \text{fulfilling} \quad A_{J\gamma} X_\gamma = 0, \quad J = 1, \ldots, p\} \tag{A.108}$$

$$S_0^\perp \equiv \{y \in \Re^n \qquad \text{fulfilling} \quad y_\gamma X_\gamma = 0, \quad \forall X \in S_0\} \tag{A.109}$$

Observe that H_0, $H_0^\perp$, S_0, $S_0^\perp$ all are linear subspaces of $\Re^n$ (i.e., linear space in respect of its members, e.g., if $X, X' \in H_0$, then indeed $X + X' \in H_0$ and $\xi X \in H_0$ for $\xi \in \Re$ because $\alpha_\gamma(X_\gamma + X'_\gamma) = 0$ and $\alpha_\gamma \xi X_\gamma = 0$. The analogical proof is valid for $H_0^\perp$, S_0, $S_0^\perp$).

To continue the proof, we introduce two following auxiliary Lemmas:

Lemma 1: If $X \in S_0$ then for any $Y \in S$, we have $X + Y \in S$

This follows from the definition of S.

Lemma 2: By definition, (i) implies $S \subset H$, and from this it follows that $S_0 \subset H_0$.

This Lemma 2 will be proved as follows: Assuming that $S \subset H$ implies $S_0 \not\subset H_0$ (the opposite possibility), we obtain a contradiction:

Indeed, suppose that $S_0 \not\subset H_0$. Then there exists a $y \in S_0$ such that $y \notin H_0$, i.e., $A_{J\gamma} y_\gamma = 0, \quad \forall J = 1, \ldots, p$ and $\alpha_\gamma y_\gamma \neq 0$. Since S_0 is a linear subspace of

$\Re^n$, for any $a \in \Re$ it follows that $ay \in S_0$ (according to definition (A.108) $ay \in \Re^n$ and $A_{J\gamma} ay_\gamma = 0, \quad J = 1, \ldots, p$). Using Lemma 1 for $X = ay$, we obtain for any $Y \in S$ that $Y + ay \in S$. But

$$\alpha_\gamma (Y_\gamma + ay_\gamma) + \beta = a\alpha_\gamma y_\gamma + \alpha_\gamma Y_\gamma + \beta \tag{A.110}$$

and because $a\alpha_\gamma y_\gamma \neq 0$, there exists some $a \in \Re$ such that $\alpha_\gamma (Y_\gamma + ay_\gamma) + \beta < 0$, which means $Y + ay \not\subset H$ although $Y + ay \in S$ and this contradicts our assumption $S \subset H$. Lemma 2 is proved.

Result $S_0 \subset H_0$ of Lemma 2 implies $H_0^\perp \subset S_0^\perp$. Namely, taking some $y \in H_0^\perp$, this fulfills $y_\gamma X_\gamma = 0$ for all $X \in H_0$ (see (A.107)) and therefore also for all $X \in S_0$ (because of $S_0 \subset H_0$), i.e., such $y \in S_0^\perp$ (see (A.109)). This is valid for any such $y \in H_0^\perp$ and therefore $H_0^\perp \subset S_0^\perp$. According to the definition of H_0 (A.106), the vector $\alpha = (\alpha_\gamma)$ is one of vectors $y \in H_0^\perp$ (A.107), i.e. $\alpha \in H_0^\perp$. Therefore, according to the previous result $H_0^\perp \subset S_0^\perp$, we have also $\alpha \in S_0^\perp$. Analogically, considering the rows of matrix $(A_{J\gamma})$ as p vectors $\mathbf{A}_J$ (containing n elements), $J = 1, \ldots, p$, we can see from the definition of S_0 (A.108) that p vectors $\mathbf{A}_J$ are from $y \in S_0^\perp$, i.e., $\mathbf{A}_J \in S_0^\perp$.

By interpretation of matrix $(A_{J\gamma})$ through the vectors $\mathbf{A}_J \in S_0^\perp$, we can see that rank$(A_{J\gamma})$ gives the dimension of $S_0^\perp$, e.g., if rank$(A_{J\gamma}) = p$ then vectors $\mathbf{A}_J$, $J = 1, \ldots, p$, are linearly independent and form the basis of $S_0^\perp$. But even if rank $(A_{J\gamma}) < p$ (of course rank $(A_{J\gamma}) \leq n$), we can express the arbitrary vector from $S_0^\perp$ through p vectors $\mathbf{A}_J$, $J = 1, \ldots, p$, in this case even those linear dependent. Specifically for $\alpha_\gamma \in S_0^\perp$, there exists a nonzero vector $\Lambda = (\Lambda_J) \in \Re^p$ such that $= \Lambda_J \mathbf{A}_J$, or

$$\alpha_\gamma - \Lambda_J A_{J\gamma} = 0$$

Finally, for any $X \in S$ we have $A_{J\gamma} X_\gamma = -B_J, \quad J = 1, \ldots, p$, according to (A.99) and therefore from the previous result and (i) (A.100):

$$0 \leq \alpha_\gamma X_\gamma + \beta = \Lambda_J A_{J\gamma} X_\gamma + \beta = -\Lambda_J B_J + \beta$$

These last results are (A.102) and (A.103) of (iii) obtained from (i).

Finally, we note that if rank $A_{J\gamma} = p$ the Lagrange multipliers Λ_J are unique. Q.E.D.

At $p = 0$, the Theorem A.5.5 reduces to Lemma A.5.1 in the form (A.92).

Theorem A.5.5 (which is algebraic only) may be applied to the thermodynamics of our book, namely in the admissibility principle used on the models of differential type as we show in the examples below. The X_γ are here the time or space derivatives of deformation and temperature fields other than those contained in the independent variables of the constitutive equations and therefore all α_γ, β, Λ_J, $A_{J\gamma}$, B_J are functions of these independent variables. Constraint conditions (A.99) usually come from balances (of mass, momentum, energy) and (A.100) from the entropy inequality.

The advantage of I-Shih Liu's Theorem A.5.5 consists in the enlargement of the validity of inequality (ii) (A.101) (modified by Lagrange multipliers) to all X_γ ($\in \Re^n$)

while the original inequality (i) (A.100) has been valid only for X_γ fulfilling additional constraint equalities (A.99) (and just such limited $X_\gamma \in S$ are often difficult to find in classical procedure, see, e.g. Sect. 4.5). I-Shih Liu's Theorem A.5.5 then finds the Lagrange multipliers from (A.102) and therefore, the results of the admissibility principle including the remaining inequality from (A.103).

The strength of I-Shih Liu method, therefore, manifests itself at the more complicated constraints [24, 26]. The most complicated case in our book—the reacting mixture with linear transport properties—with the use of entropy inequality and all balances (of mass, momentum, energy) as (A.100), (A.99), would be laborious. Therefore, to demonstrate the application of the I-Shih Liu's Theorem A.5.5, we choose relatively simple examples of the uniform fluid model B from Sect. 2.2 and the simple thermoelastic fluid from the end of Sect. 3.6.[6]

The example of the *uniform fluid model* B discussed in the Sects. 2.1,2.2 uses entropy inequality (Second Law) (2.2) and balance of energy (First Law) (2.1) as a constraint (balances of mass and momentum may be ignored because they are fulfilled trivially: the mass of bodies is constant and velocity (and therefore also kinetic energy) is zero).

$$\dot{U} = Q - P\dot{V} \tag{A.111}$$

$$\dot{S} \geq Q/T \tag{A.112}$$

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[6] We note the special case of I-Shih Liu's Theorem A.5.5 when $p = n$ and the (quadratic) matrix $(A_{J\gamma}) = \mathbf{1}$ is unit matrix. Then, we have (A.99), (A.102) $(J = \gamma)$ as

$$X_\gamma + B_\gamma = 0, \qquad \alpha_\gamma = \Lambda_\gamma \qquad\qquad (a)$$

giving from inequality (A.100) the resulting inequality (A.103) of the I-Shih Liu Theorem. Such a procedure has been used in fact in our main text: using free energies the inequality (A.100) with constraint $(a)_1$ in special cases $p = n$, $(A_{J\gamma}) = \mathbf{1}$ may be constructed from which by elimination of X_γ, the unconstrained inequality (A.103) has been obtained (on which the standard Coleman-Noll admissibility method may be used).

We show it on our model B from Sect.2.2. Here, the basic inequality (A.100) is (2.2)

$$-Q + T\dot{S} \geq 0 \qquad\qquad (b)$$

with the additional constraint condition (A.99) given by energy balance (2.1) as

$$Q - (\dot{U} + P\dot{V}) = 0 \qquad\qquad (c)$$

We use I-Shih Liu Theorem A.5.5 choosing $n = p = 1$, $A_{11} = 1$, $B_1 = -(\dot{U} + P\dot{V})$, $\alpha_1 = -1$, $\beta = T\dot{S}$, $X_1 = Q$ and its results (A.102), (A.103) are $\Lambda_1 = -1$ and inequality

$$T\dot{S} - (\dot{U} + P\dot{V}) \geq 0 \qquad\qquad (d)$$

This inequality, using free energy $F = U - TS$ (2.12) and model B (2.7), specifically $F = \hat{F}(V, \dot{V}, T)$ (2.20), is the same as the inequality (2.21) (which has been obtained in Sect. 2.2 by elimination of Q from (2.2), (2.1)). From this it follows all results for model B by the same procedure as in Sect. 2.2.

Similarly, we can discuss results from Sects. 3.6, 4.5 using mass balances as $(a)_1$.

As a model, we use the uniform fluid with volume memory B (2.7) from Sects. 2.1, 2.2

$$U = \hat{U}(V, \dot{V}, T), \quad S = \hat{S}(V, \dot{V}, T), \quad P = \hat{P}(V, \dot{V}, T) \tag{A.113}$$

By (A.113) the constraint and inequality of the type (A.99), (A.100) in I-Shih Liu Theorem A.5.5 are

$$(\partial\hat{U}/\partial T)\dot{T} + (\partial\hat{U}/\partial\dot{V})\ddot{V} + \{[(\partial\hat{U}/\partial V) + P]\dot{V} - Q\} = 0 \tag{A.114}$$

$$(\partial\hat{S}/\partial T)\dot{T} + (\partial\hat{S}/\partial\dot{V})\ddot{V} + \{(\partial\hat{S}/\partial V)\dot{V} - Q/T\} \geq 0 \tag{A.115}$$

In this example $J = p = 1$ and $\gamma = 1, 2$ with $n = 2$ and with $X_\gamma = \dot{T}, \ddot{V}$. Matrix A is the vector $(A_{1\gamma}) = (\partial\hat{U}/\partial T, \partial\hat{U}/\partial\dot{V})$ and vector α is $(\alpha_\gamma) = (\partial\hat{S}/\partial T, \partial\hat{S}/\partial\dot{V})$.

Therefore, the results (A.102), (A.103) of I-Shih Liu Theorem A.5.5 are

$$(\partial\hat{S}/\partial T) - \Lambda(\partial\hat{U}/\partial T) = 0 \tag{A.116}$$

$$(\partial\hat{S}/\partial\dot{V}) - \Lambda(\partial\hat{U}/\partial\dot{V}) = 0 \tag{A.117}$$

$$\{(\partial\hat{S}/\partial V)\dot{V} - Q/T\} - \Lambda\left([(\partial\hat{U}/\partial V) + P]\dot{V} - Q\right) \geq 0 \tag{A.118}$$

with one Lagrange multiplier $\Lambda_1 \equiv \Lambda$ (which, similarly as other quantities here, may be a function of $V, \dot{V}, T$).

To calculate the Lagrange multiplier Λ, we write (A.118) as

$$\left((\partial\hat{S}/\partial V) - \Lambda(\partial\hat{U}/\partial V) - \Lambda P\right)\dot{V} + (\Lambda - 1/T)Q \geq 0 \tag{A.119}$$

and we express Q from (A.111) and (A.113)

$$Q = \dot{U} + P\dot{V} = (\partial\hat{U}/\partial V)\dot{V} + (\partial\hat{U}/\partial T)\dot{T} + (\partial\hat{U}/\partial\dot{V})\ddot{V} + P\dot{V} \tag{A.120}$$

Inserting (A.120) into (A.119), we obtain after rearrangement

$$\begin{aligned}\left((\partial\hat{S}/\partial V) - (1/T)(\partial\hat{U}/\partial V) - (P/T)\right)\dot{V} + (\Lambda - 1/T)(\partial\hat{U}/\partial T)\dot{T}\\ + (\Lambda - 1/T)(\partial\hat{U}/\partial\dot{V})\ddot{V} \geq 0\end{aligned} \tag{A.121}$$

This inequality is linear in $\dot{T}, \ddot{V}$ and therefore the coefficients at these must be zero (identically, i.e., at any independent variables of constitutive equations (A.113)). Therefore,

$$(\Lambda - 1/T)(\partial\hat{U}/\partial T) = 0 \tag{A.122}$$

But because $(\partial\hat{U}/\partial T) \neq 0$ (and is even positive, because this is the heat capacity at constant volume, cf. Rem. 9 in Chap. 2), we obtain for this Lagrange multiplier

$$\Lambda = 1/T \tag{A.123}$$

With this result (A.123), the inequality (A.121) gives

$$\Big((\partial\hat{S}/\partial V) - (1/T)(\partial\hat{U}/\partial V) - P/T\Big)\,\dot{V} \geq 0 \tag{A.124}$$

and the identities (A.116), (A.117) give

$$(\partial\hat{S}/\partial T) - (1/T)(\partial\hat{U}/\partial T) = 0 \tag{A.125}$$

$$(\partial\hat{S}/\partial\dot{V}) - (1/T)(\partial\hat{U}/\partial\dot{V}) = 0 \tag{A.126}$$

Using the free energy $F = U - TS = \hat{F}(V, \dot{V}, T)$ (2.12), (2.20) we obtain from (A.126), (A.125), (A.124)

$$\partial\hat{F}/\partial\dot{V} \equiv 0, \quad \text{i.e.,} \quad F = \hat{F}(V, T) \tag{A.127}$$

$$\partial\hat{F}/\partial T = -S \tag{A.128}$$

$$-(1/T)\Big((\partial\hat{F}/\partial V) + P\Big)\,\dot{V} \geq 0 \tag{A.129}$$

These are the same results as in Sect. 2.2, namely (2.22), (2.24), and (2.27). Therefore, the remaining results of model B in Sect. 2.2 follow.

The example of the *simple thermoelastic fluid*, noted in the end of Sect. 3.6 above (3.181) (cf. also example in [22]), has the constitutive equations for u, s, $\mathbf{T}$, $\mathbf{q}$ limited to independent variables ρ, T, $\mathbf{g} = \text{grad}T$ only. For simplicity, external body (or inertial) force and volume heating are not considered, $\mathbf{b} + \mathbf{i} = \mathbf{o}$, $Q = 0$. We have entropy inequality (3.109) (with (3.8))

$$\rho\frac{\partial s}{\partial t} + \rho v^j\frac{\partial s}{\partial x^j} + (1/T)\frac{\partial q^j}{\partial x^j} - (1/T^2)q^j g^j \geq 0 \tag{A.130}$$

constrained by balances of mass (3.63), momentum (3.78), and energy (3.107) (again with (3.8) and (3.15), (3.14)) assuming (3.93) (i.e., balance of moment of momentum has been used)

$$\frac{\partial\rho}{\partial t} + v^j\frac{\partial\rho}{\partial x^j} + \rho\frac{\partial v^j}{\partial x^j} = 0 \tag{A.131}$$

$$\rho\frac{\partial v^i}{\partial t} + \rho v^j\frac{\partial v^i}{\partial x^j} - \frac{\partial T^{ij}}{\partial x^j} = o^i \tag{A.132}$$

$$\rho\frac{\partial u}{\partial t} + \rho v^j\frac{\partial u}{\partial x^j} + \frac{\partial q^j}{\partial x^j} - T^{ij}\frac{\partial v^j}{\partial x^i} = 0 \tag{A.133}$$

We calculate derivatives of constitutive functions (denoted by hat) needed in (A.130)–(A.133)

$$\frac{\partial s}{\partial t} = \frac{\partial \hat{s}}{\partial \rho}\frac{\partial \rho}{\partial t} + \frac{\partial \hat{s}}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial \hat{s}}{\partial g^k}\frac{\partial g^k}{\partial t} \tag{A.134}$$

$$\frac{\partial s}{\partial x^j} = \frac{\partial \hat{s}}{\partial \rho}\frac{\partial \rho}{\partial x^j} + \frac{\partial \hat{s}}{\partial T}g^j + \frac{\partial \hat{s}}{\partial g^k}\frac{\partial g^k}{\partial x^j} \tag{A.135}$$

$$\frac{\partial u}{\partial t} = \frac{\partial \hat{u}}{\partial \rho}\frac{\partial \rho}{\partial t} + \frac{\partial \hat{u}}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial \hat{u}}{\partial g^k}\frac{\partial g^k}{\partial t} \tag{A.136}$$

$$\frac{\partial u}{\partial x^j} = \frac{\partial \hat{u}}{\partial \rho}\frac{\partial \rho}{\partial x^j} + \frac{\partial \hat{u}}{\partial T}g^j + \frac{\partial \hat{u}}{\partial g^k}\frac{\partial g^k}{\partial x^j} \tag{A.137}$$

$$\frac{\partial T^{ij}}{\partial x^j} = \frac{\partial \hat{T}^{ij}}{\partial \rho}\frac{\partial \rho}{\partial x^j} + \frac{\partial \hat{T}^{ij}}{\partial T}g^j + \frac{\partial \hat{T}^{ij}}{\partial g^k}\frac{\partial g^k}{\partial x^j} \tag{A.138}$$

$$\frac{\partial q^j}{\partial x^j} = \frac{\partial \hat{q}^j}{\partial \rho}\frac{\partial \rho}{\partial x^j} + \frac{\partial \hat{q}^j}{\partial T}g^j + \frac{\partial \hat{q}^j}{\partial g^k}\frac{\partial g^k}{\partial x^j} \tag{A.139}$$

Inserting (A.134)–(A.139) into (A.130)–(A.133), we obtain the inequality of the type (A.100) with constraints of the type (A.99) in I-Shih Liu Theorem A.5.5 choosing as X_γ the vector with $n = 26$ independent components

$$(X_\gamma) = \big(\frac{\partial \rho}{\partial t}, \frac{\partial v^j}{\partial t}, \frac{\partial T}{\partial t}, \frac{\partial g^k}{\partial t}, \frac{\partial \rho}{\partial x^j}, \frac{\partial v^j}{\partial x^k}, \frac{\partial g^{(k}}{\partial x^{j)}}\big) \quad \gamma = 1, \dots, 26 \tag{A.140}$$

(symmetrized tensor $\frac{\partial g^{(k}}{\partial x^{j)}} \equiv \frac{1}{2}(\frac{\partial g^k}{\partial x^j} + \frac{\partial g^j}{\partial x^k})$ is used because $\frac{\partial g^k}{\partial x^j} = \frac{\partial g^j}{\partial x^k}$ is symmetric with 6 independent components, cf. Rem. 7). The members containing g^j were excluded because of the choice of independent variables in our model; they are used in definitions β, B_J (A.142), (A.148).

Therefore, we obtain the inequality of the type (A.100) in I-Shih Liu Theorem A.5.5 by inserting (A.134), (A.135), and (A.139) into inequality (A.130)

$$\rho\frac{\partial \hat{s}}{\partial \rho}\frac{\partial \rho}{\partial t} + \rho\frac{\partial \hat{s}}{\partial T}\frac{\partial T}{\partial t} + \rho\frac{\partial \hat{s}}{\partial g^k}\frac{\partial g^k}{\partial t} + (\rho v^j\frac{\partial \hat{s}}{\partial \rho} + (1/T)\frac{\partial \hat{q}^j}{\partial \rho})\frac{\partial \rho}{\partial x^j}$$
$$+ (\rho v^{(j}\frac{\partial \hat{s}}{\partial g^{k)}} + (1/T)\frac{\partial \hat{q}^{(j}}{\partial g^{k)}})\frac{\partial g^{(k}}{\partial x^{j)}} + (\rho v^j\frac{\partial \hat{s}}{\partial T} + (1/T)\frac{\partial \hat{q}^j}{\partial T} - (1/T^2)q^j)g^j \geq 0 \tag{A.141}$$

from which we can see definitions[7]

$$\beta \equiv (\rho v^j \frac{\partial \hat{s}}{\partial T} + (1/T)\frac{\partial \hat{q}^j}{\partial T} - (1/T^2) q^j) g^j \tag{A.142}$$

$$(\alpha_\gamma) \equiv (\rho\frac{\partial \hat{s}}{\partial \rho}, o^j, \rho\frac{\partial \hat{s}}{\partial T}, \rho\frac{\partial \hat{s}}{\partial g^k}, \rho v^j\frac{\partial \hat{s}}{\partial \rho} + (1/T)\frac{\partial \hat{q}^j}{\partial \rho}, 0^{kj}, \rho v^{(j}\frac{\partial \hat{s}}{\partial g^{k)}} + (1/T)\frac{\partial \hat{q}^{(j}}{\partial g^{k)}}) \tag{A.143}$$

where, by symmetrization, the last six independent symmetrical quantities are written and o^i, 0^{ij} are 3 vector and 9 tensor zero components not used in (A.141), i.e., this vector (α_γ) has, similarly to (A.140), 26 components.

The choice of vectors (A.140) permits to obtain equalities of the type (A.99) in I-Shih Liu Theorem A.5.5 by inserting (A.136), (A.137), (A.138), (A.139) into balances (A.131), (A.132), (A.133) and rearranging:

$$\frac{\partial \rho}{\partial t} + v^j \frac{\partial \rho}{\partial x^j} + \rho\delta^{kj}\frac{\partial v^j}{\partial x^k} = 0 \tag{A.144}$$

$$\rho\delta^{ij}\frac{\partial v^j}{\partial t} - \frac{\partial \hat{T}^{ij}}{\partial \rho}\frac{\partial \rho}{\partial x^j} + \rho v^k \delta^{ij}\frac{\partial v^j}{\partial x^k} - \frac{\partial \hat{T}^{i(j}}{\partial g^{k)}}\frac{\partial g^{(k}}{\partial x^{j)}} - \frac{\partial \hat{T}^{ij}}{\partial T} g^j = o^i \tag{A.145}$$

$$\rho\frac{\partial \hat{u}}{\partial \rho}\frac{\partial \rho}{\partial t} + \rho\frac{\partial \hat{u}}{\partial T}\frac{\partial T}{\partial t} + \rho\frac{\partial \hat{u}}{\partial g^k}\frac{\partial g^k}{\partial t} + (\rho v^j \frac{\partial \hat{u}}{\partial \rho} + \frac{\partial \hat{q}^j}{\partial \rho})\frac{\partial \rho}{\partial x^j}$$

$$- T^{kj}\frac{\partial v^j}{\partial x^k} + (\rho v^{(j}\frac{\partial \hat{u}}{\partial g^{k)}} + \frac{\partial \hat{q}^{(j}}{\partial g^{k)}})\frac{\partial g^{(k}}{\partial x^{j)}} + \rho v^j \frac{\partial \hat{u}}{\partial T} g^j + \frac{\partial \hat{q}^j}{\partial T} g^j = 0 \tag{A.146}$$

---

[7] The term

$$(\rho v^{(j}\frac{\partial \hat{s}}{\partial g^{k)}} + (1/T)\frac{\partial q^{(j}}{\partial g^{k)}})\frac{\partial g^{(k}}{\partial x^{j)}} = (\rho v^j \frac{\partial \hat{s}}{\partial g^k} + (1/T)\frac{\partial q^j}{\partial g^k})\frac{\partial g^k}{\partial x^j} \tag{a}$$

in (A.141) is equal to those obtained by direct calculation of (A.141). This equality follows, from the definition of symmetrization, say of tensor N^{jk}, defined as $N^{(jk)} \equiv \frac{1}{2}(N^{jk} + N^{kj})$. Indeed, defining in ($a$) for brevity

$$N^{jk} \equiv \rho v^j \frac{\partial \hat{s}}{\partial g^k} + (1/T)\frac{\partial q^j}{\partial g^k}, \quad T_{,kj} \equiv \frac{\partial^2 T}{\partial x^k \partial x^j} = \frac{\partial g^k}{\partial x^j}$$

Because of symmetry $T_{,kj} = T_{,jk}$ we can write for the left hand side of (a)

$$\begin{aligned} N^{(jk)}T_{,(kj)} &= \frac{1}{2}(N^{jk} + N^{kj})\frac{1}{2}(T_{,kj} + T_{,jk}) = \frac{1}{2}(N^{jk} + N^{kj})T_{,kj} = \frac{1}{2}N^{jk}T_{,kj} + \frac{1}{2}N^{kj}T_{,jk} \\ &= \frac{1}{2}N^{jk}T_{,kj} + \frac{1}{2}N^{jk}T_{,kj} = N^{jk}T_{,kj} \end{aligned}$$

and this is the right hand side of (a).

Such symmetrization must be used in (A.141) (and in (A.140), (A.143), etc.) to stress the independence of X_γ, specifically the independence of only the six components of tensor $\partial g^k/\partial x^j$.

Because of the symmetry of $\frac{\partial g^k}{\partial x^j}$, the symmetrization from Rem. 7 has been used analogously giving $\frac{\partial \hat{T}^{i(j}}{\partial g^{k)}}\frac{\partial g^{(k}}{\partial x^{j)}} = \frac{\partial \hat{T}^{ij}}{\partial g^k}\frac{\partial g^k}{\partial x^j}$ and $(\rho v^{(j}\frac{\partial \hat{u}}{\partial g^{k)}} + \frac{\partial \hat{q}^{(j}}{\partial g^{k)}})\frac{\partial g^{(k}}{\partial x^{j)}} = (\rho v^j\frac{\partial \hat{u}}{\partial g^k} + \frac{\partial \hat{q}^j}{\partial g^k})\frac{\partial g^k}{\partial x^j}$.

Therefore, we have five equations of the type (A.99), $J = 1, \ldots, p = 5$ (2 scalar (A.144), (A.146), and 3 (in component i $= 1, 2, 3$) vector equations (A.145)).

From these form of Eqs. (A.144), (A.145), and (A.146) of the type (A.99), we can write explicitly the five components of the vector $B = (B_J)$:

$$(B_J) = (B_1, B_i, B_5) \qquad J = 1, \ldots, 5, \quad i = 1, 2, 3 \tag{A.147}$$

$$B_1 = 0, \quad B_i = -\frac{\partial \hat{T}^{ij}}{\partial T}g^j \qquad i = 1, 2, 3, \quad B_5 = \rho v^j\frac{\partial \hat{u}}{\partial T}g^j + \frac{\partial \hat{q}^j}{\partial T}g^j \tag{A.148}$$

and the matrix $A = (A_{J\gamma})$ of dimension (5×26):

$$\begin{array}{lllllll}
1 & o^j & 0 & o^k & v^j & \rho\delta^{kj} & 0^{(kj)} \\
o^i & \rho\delta^{ij} & o^i & \delta^{ik}o^k & -\frac{\partial \hat{T}^{ij}}{\partial \rho} & \rho v^k\delta^{ij} & -\frac{\partial \hat{T}^{i(j}}{\partial g^{k)}} \\
\rho\frac{\partial \hat{u}}{\partial \rho} & o^j & \rho\frac{\partial \hat{u}}{\partial T} & \rho\frac{\partial \hat{u}}{\partial g^k} & \rho v^j\frac{\partial \hat{u}}{\partial \rho} + \frac{\partial \hat{q}^j}{\partial \rho} & -T^{kj} & \rho v^{(j}\frac{\partial \hat{u}}{\partial g^{k)}} + \frac{\partial \hat{q}^{(j}}{\partial g^{k)}}
\end{array}$$

Therefore we obtain, as the result of I-Shih Liu Theorem A.5.5, the five Lagrange multipliers $\Lambda_1, \Lambda^i, i = 1, 2, 3, \Lambda_5$ in the resulting expressions (A.102), (A.103). These are in our example

$$\rho\frac{\partial \hat{s}}{\partial \rho} = \Lambda_1 + \Lambda_5\rho\frac{\partial \hat{u}}{\partial \rho} \tag{A.149}$$

$$o^j = \Lambda^i\rho\delta^{ij} \tag{A.150}$$

$$\rho\frac{\partial \hat{s}}{\partial T} = \Lambda_5\rho\frac{\partial \hat{u}}{\partial T} \tag{A.151}$$

$$\rho\frac{\partial \hat{s}}{\partial g^k} = \Lambda_5\rho\frac{\partial \hat{u}}{\partial g^k} \tag{A.152}$$

$$\rho v^j\frac{\partial \hat{s}}{\partial \rho} + (1/T)\frac{\partial \hat{q}^j}{\partial \rho} = \Lambda_1 v^j + \Lambda^i(-\frac{\partial \hat{T}^{ij}}{\partial \rho}) + \Lambda_5(\rho v^j\frac{\partial \hat{u}}{\partial \rho} + \frac{\partial \hat{q}^j}{\partial \rho}) \tag{A.153}$$

$$0^{kj} = \Lambda_1\rho\delta^{kj} + \Lambda^i\rho v^k\delta^{ij} + \Lambda_5(-T^{kj}) \tag{A.154}$$

$$\rho v^{(j}\frac{\partial \hat{s}}{\partial g^{k)}} + (1/T)\frac{\partial \hat{q}^{(j}}{\partial g^{k)}} = \Lambda^i(-\frac{\partial \hat{T}^{i(j}}{\partial g^{k)}}) + \Lambda_5(\rho v^{(j}\frac{\partial \hat{u}}{\partial g^{k)}} + \frac{\partial \hat{q}^{(j}}{\partial g^{k)}}) \tag{A.155}$$

$$(\rho v^j \frac{\partial \hat{s}}{\partial T} + (1/T)\frac{\partial \hat{q}^j}{\partial T} - (1/T^2)q^j)g^j - \Lambda^i(-\frac{\partial \hat{T}^{ij}}{\partial T}g^j) - \Lambda_5(\rho v^j \frac{\partial \hat{u}}{\partial T}g^j + \frac{\partial \hat{q}^j}{\partial T}g^j) \geq 0 \tag{A.156}$$

From these results, we calculate the following relations of our model (which are valid identically, i.e., for all independent variables ρ, T, $\mathbf{g}$ chosen in application of Theorem A.5.5 as fixed): Because $\rho \neq 0$, we obtain from (A.150) that all multipliers Λ^i are zeros. From this and because the symmetrized dyad formed by the multiplication of (A.152) with v^j is contained in (A.155), we obtain that Λ_5 is equal to the inverse of temperature

$$\Lambda^i = 0 \quad i = 1, 2, 3, \quad \Lambda_5 = 1/T, \quad \Lambda_1 = -P/(T\rho) \tag{A.157}$$

To obtain the last relation, we note that with the free energy (3.111) $f = u - Ts = \hat{f}(\rho, T, \mathbf{g})$, we find from (A.151), (A.152) that $\partial\hat{f}/\partial T = -s$ and f, and therefore s, u, are independent of $\mathbf{g}$. Then from (A.154) it may be seen that the stress tensor is reduced to $T^{kj} = \Lambda_1 T\rho\delta^{kj} = -P\delta^{kj}$ in our model, i.e., to the pressure P which may be expressed through Lagrange multipliers as $\Lambda_1 = -P/(T\rho)$. Using it and free energy in (A.149) we obtain that pressure is given by free energy $\partial\hat{f}/\partial\rho = P/\rho^2$ and therefore P depend on ρ, T only. Equation (A.153) is fulfilled identically. These relations reduce the inequality (A.156) to $-(1/T^2)q^j g^j \geq 0$.

The final results are, therefore,

$$f = \hat{f}(\rho, T), \quad s = \hat{s}(\rho, T), \quad u = \hat{u}(\rho, T), \quad P = \hat{P}(\rho, T)$$

$$\frac{\partial \hat{f}}{\partial T} = -s, \ \ \frac{\partial \hat{f}}{\partial \rho} = P/\rho^2, \ \ T^{kj} = -P\delta^{kj}, \ \ \mathbf{q} = \hat{\mathbf{q}}(\rho, T, \mathbf{g}), \ \ -(1/T^2)q^j g^j \geq 0 \tag{A.158}$$

We can see that the method of Lagrange multipliers in I-Shih Liu Theorem A.5.5 gives for the model of simple thermoelastic fluid exactly the same results as the classical procedure from Sect. 3.6, cf. (3.181), (3.174), (3.175), (3.171), and (3.172) (without $\mathbf{h}$, D).

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