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 $\alpha = 1, 2, \ldots, n$ (in this chapter, if it is not noted otherwise, subscripts $\alpha, \gamma, \epsilon = 1, 2, \ldots, n$ and $\beta, \delta, \zeta = 1, 2, \ldots, n-1$ 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

$$\mathbf{x} = \underline{\chi}_\alpha(\mathbf{X}_\alpha, t) \qquad \alpha = 1, \ldots, n \tag{4.1}$$

where $\mathbf{x}$ is the place of the particle $\mathbf{X}_\alpha$ of constituent $\alpha = 1, \ldots, n$ 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 $\alpha = 1, \ldots, n$, is defined by (cf. (3.7)):

$$\mathbf{v}_\alpha \equiv \partial \underline{\chi}_\alpha / \partial t = \overset{\backslash\alpha}{\underline{\chi}}_\alpha = \grave{\underline{\chi}}_\alpha \qquad \alpha = 1, \ldots, n \tag{4.2}$$

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 $\alpha = 1, \dots, n$: The motion of the mixture is rigid if and only if for all α

$$\mathbf{D}_\alpha = \mathbf{0} \qquad \alpha = 1, \dots, n \tag{4.9}$$

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 $\alpha = 1, \dots, n$ 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 $\alpha = 1, \dots, n$ 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)

$$\mathbf{u}_\beta \equiv \mathbf{v}_\beta - \mathbf{v}_n \qquad \beta = 1, \ldots, n-1, \qquad \mathbf{u}_n \equiv \mathbf{o} \tag{4.24}$$

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 $\alpha = 1, \ldots, n$ 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 $\sigma = 1, 2, \ldots, z$

$$M_\alpha = \sum_{\sigma=1}^{z} A^\sigma T_{\sigma\alpha} \qquad \alpha = 1, \ldots, n \tag{4.25}$$

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

$$J^\alpha \equiv r_\alpha / M_\alpha \qquad \alpha = 1, \ldots, n \tag{4.26}$$

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*

$$\sum_{\alpha=1}^{n} T_{\sigma\alpha} J^\alpha = 0 \qquad \sigma = 1, \ldots, z \tag{4.27}$$

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

$$\vec{M}.\vec{J} = 0 \quad \text{or} \quad \sum_{\alpha=1}^{n} M_\alpha J^\alpha = 0 \tag{4.39}$$

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

$$NO_2 = 1/2N_2O_4 \tag{4.47}$$

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. $\|P^{p\alpha}\| = (2 \quad -1 \quad 0)$ 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 $\|T_{\sigma\alpha}\| = (1 \quad 2 \quad 3) = \|S_{\sigma\alpha}\|$ (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

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho_\alpha \mathbf{v}_\alpha \,\mathrm{d}v + \int_{\partial V} \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha.\mathbf{n})\,\mathrm{d}a = \int_{\partial V} \mathbf{t}_\alpha \,\mathrm{d}a + \int_V \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v + \int_V \mathbf{k}_\alpha \,\mathrm{d}v + \int_V r_\alpha \mathbf{v}_\alpha \,\mathrm{d}v \quad \alpha = 1, \dots, n \tag{4.50}$$

(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

$$\int_V \rho_\alpha \grave{\mathbf{v}}_\alpha \,\mathrm{d}v = \int_{\partial V} \mathbf{t}_\alpha \,\mathrm{d}a + \int_V \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v + \int_V \mathbf{k}_\alpha \,\mathrm{d}v \qquad \alpha = 1, \ldots, n \tag{4.51}$$

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

$$\mathbf{t}_\alpha = \mathbf{t}_\alpha(\mathbf{x}, t, \mathbf{n}) \qquad \alpha = 1, \ldots, n \tag{4.52}$$

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

$$\mathbf{t}_\alpha = \mathbf{T}_\alpha \mathbf{n} \qquad \alpha = 1, \ldots, n \tag{4.53}$$

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

$$\int_V \rho_\alpha \grave{\mathbf{v}}_\alpha \,\mathrm{d}v = \int_{\partial V} \mathbf{T}_\alpha.\mathbf{n} \,\mathrm{d}a + \int_V \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v + \int_V \mathbf{k}_\alpha \,\mathrm{d}v \qquad \alpha = 1, \ldots, n \tag{4.55}$$

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

$$\rho_\alpha \grave{\mathbf{v}}_\alpha = \mathrm{div}\mathbf{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{k}_\alpha \qquad \alpha = 1, \ldots, n \tag{4.56}$$

or (back by (4.19) choosing φ as velocity component)

$$\frac{\partial \rho_\alpha \mathbf{v}_\alpha}{\partial t} + \mathrm{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \mathrm{div}\mathbf{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha \qquad \alpha = 1, \ldots, n \quad (4.57)$$

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))

$$\rho_\alpha \grave{\mathbf{v}}_\alpha = \mathrm{div}\mathbf{T}_\alpha + \rho_\alpha(\mathbf{b}_\alpha + \mathbf{i}_\alpha) + \mathbf{k}_\alpha \quad \alpha = 1, \ldots, n \qquad (4.58)$$

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

$$\int_V \rho_\alpha \grave{\mathbf{v}}_\alpha \,\mathrm{d}v = \int_{\partial V} \mathbf{T}_\alpha .\mathbf{n} \,\mathrm{d}a + \int_V \rho_\alpha(\mathbf{b}_\alpha + \mathbf{i}_\alpha) \,\mathrm{d}v + \int_V \mathbf{k}_\alpha \,\mathrm{d}v \qquad \alpha = 1, \ldots, n \qquad (4.59)$$

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

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha \,\mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha .\mathbf{n}) \,\mathrm{d}a = \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{t}_\alpha \,\mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v \qquad (4.60)$$

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

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha \,\mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha .\mathbf{n}) \,\mathrm{d}a = \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{T}_\alpha \mathbf{n} \,\mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v \qquad (4.61)$$

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)

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V (\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{v}_\alpha\,\mathrm{d}v + \int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{v}_\alpha(\mathbf{v}_\alpha.\mathbf{n})\,\mathrm{d}a \\ = \int_{\partial V}(\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha\mathbf{n}\,\mathrm{d}a + \int_V(\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{b}_\alpha\,\mathrm{d}v \\ + \int_V(\mathbf{x}-\mathbf{y})\wedge(\mathbf{k}_\alpha + r_\alpha\mathbf{v}_\alpha)\,\mathrm{d}v \qquad \alpha = 1,\ldots,n \qquad (4.65)\end{aligned}$$

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

$$\begin{aligned}\frac{\partial\rho_\alpha(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha)}{\partial t} + \mathrm{div}(\rho_\alpha(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha\otimes\mathbf{v}_\alpha) \\ = \mathrm{div}((\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha) + (\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{b}_\alpha + (\mathbf{x}-\mathbf{y})\wedge\mathbf{k}_\alpha \\ + (\mathbf{x}-\mathbf{y})\wedge r_\alpha\mathbf{v}_\alpha \qquad \alpha = 1,\ldots,n \qquad (4.66)\end{aligned}$$

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))

$$(\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\grave{\mathbf{v}}_\alpha = \mathrm{div}((\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha) + (\mathbf{x}-\mathbf{y})\wedge\rho_\alpha\mathbf{b}_\alpha + (\mathbf{x}-\mathbf{y})\wedge\mathbf{k}_\alpha \quad \alpha = 1,\ldots,n \qquad (4.67)$$

because

$$\overset{\grave{}}{\overline{(\mathbf{x}-\mathbf{y})\wedge\mathbf{v}_\alpha}} = (\mathbf{x}-\mathbf{y})\wedge\grave{\mathbf{v}}_\alpha \qquad (4.68)$$

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))

$$\mathrm{div}((\mathbf{x}-\mathbf{y})\wedge\mathbf{T}_\alpha) = \mathbf{T}_\alpha^T - \mathbf{T}_\alpha + (\mathbf{x}-\mathbf{y})\wedge\mathrm{div}\mathbf{T}_\alpha \qquad (4.69)$$

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

$$\mathbf{T}_\alpha = \mathbf{T}_\alpha^T \qquad \alpha = 1,\ldots,n \qquad (4.70)$$

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

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha \,\mathrm{d}v + \int_{\partial V} (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha . \mathbf{n}) \,\mathrm{d}a \\ = \int_{\partial V} (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \mathbf{T}_\alpha \mathbf{n} \,\mathrm{d}a + \int_V (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \,\mathrm{d}v \qquad (4.71)\end{aligned}$$

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

$$\begin{aligned}\sum_{\alpha=1}^{n} \left(\frac{\partial \rho_\alpha (\mathbf{x}-\mathbf{y}) \wedge \mathbf{v}_\alpha)}{\partial t} + \mathrm{div}(\rho_\alpha (\mathbf{x}-\mathbf{y}) \wedge \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) \right) \\ = \sum_{\alpha=1}^{n} \mathrm{div}((\mathbf{x}-\mathbf{y}) \wedge \mathbf{T}_\alpha) + (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \qquad (4.72)\end{aligned}$$

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

$$\begin{aligned}\sum_{\alpha=1}^{n} \rho_\alpha \grave{\overline{(\mathbf{x}-\mathbf{y}) \wedge \mathbf{v}_\alpha}} + (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} r_\alpha \mathbf{v}_\alpha \\ = \sum_{\alpha=1}^{n} \mathbf{T}_\alpha^T - \sum_{\alpha=1}^{n} \mathbf{T}_\alpha + (\mathbf{x}-\mathbf{y}) \wedge \mathrm{div} \sum_{\alpha=1}^{n} \mathbf{T}_\alpha + (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha \qquad (4.73)\end{aligned}$$

Adding $(\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \mathbf{k}_\alpha$ to both sides, using (4.68) and rearranging we obtain

$$\begin{aligned}(\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} \left(\rho_\alpha \grave{\mathbf{v}}_\alpha - \mathrm{div}\mathbf{T}_\alpha - \rho_\alpha \mathbf{b}_\alpha - \mathbf{k}_\alpha \right) + (\mathbf{x}-\mathbf{y}) \wedge \sum_{\alpha=1}^{n} (\mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha) \\ = \sum_{\alpha=1}^{n} \mathbf{T}_\alpha^T - \sum_{\alpha=1}^{n} \mathbf{T}_\alpha \qquad (4.74)\end{aligned}$$

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):

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2)\,\mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2)\mathbf{v}_\alpha.\mathbf{n}\,\mathrm{d}a \\ = \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{v}_\alpha \mathbf{T}_\alpha.\mathbf{n}\,\mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha.\mathbf{v}_\alpha\,\mathrm{d}v + \int_{\partial V} q\,\mathrm{d}a + \int_V Q\,\mathrm{d}v \qquad (4.76)\end{aligned}$$

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

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V \sum_{\alpha=1}^{n} \rho_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2)\,\mathrm{d}v + \int_{\partial V} \sum_{\alpha=1}^{n} \rho_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2)\mathbf{v}_\alpha.\mathbf{n}\,\mathrm{d}a \\ = \int_V \sum_{\alpha=1}^{n} \rho_\alpha \overset{\grave{}}{\overline{(u_\alpha + (1/2)\mathbf{v}_\alpha^2)}}\,\mathrm{d}v + \int_V \sum_{\alpha=1}^{n} r_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2)\,\mathrm{d}v \\ = \int_{\partial V} \sum_{\alpha=1}^{n} \mathbf{v}_\alpha \mathbf{T}_\alpha.\mathbf{n}\,\mathrm{d}a + \int_V \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha.\mathbf{v}_\alpha\,\mathrm{d}v - \int_{\partial V} \mathbf{q}.\mathbf{n}\,\mathrm{d}a + \int_V Q\,\mathrm{d}v \qquad (4.77)\end{aligned}$$

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

$$\sum_{\alpha=1}^{n} \rho_\alpha \grave{\overline{(u_\alpha + (1/2)\mathbf{v}_\alpha^2)}}\, \Delta v + \sum_{\alpha=1}^{n} r_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2)\, \Delta v$$
$$= q\, \Delta a + q^j\, \Delta a^j + Q\, \Delta v + (\mathrm{div} \sum_{\alpha=1}^{n} \mathbf{v}_\alpha \mathbf{T}_\alpha)\, \Delta v + \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha . \mathbf{v}_\alpha\, \Delta v \quad (4.80)$$

from which (by limitation of tetrahedron volume to zero) we obtain result (4.78): components of vector $\mathbf{q}$ form scalar surface heatings q^j (independent of $\mathbf{n}$) in the axes of the Cartesian system in tetrahedron, see Sect. 3.4.

Moreover, because q and (arbitrary) $\mathbf{n}$ are objective (see end of Sect. 3.2), then from (4.78) follows (similarly as below (3.101)) that the heat flux $\mathbf{q}$ 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

$$\sum_{\alpha=1}^{n} \rho_\alpha \grave{u}_\alpha + \sum_{\alpha=1}^{n} \rho_\alpha \frac{1}{2} \grave{\overline{\mathbf{v}_\alpha^2}} + \sum_{\alpha=1}^{n} r_\alpha u_\alpha + \sum_{\alpha=1}^{n} r_\alpha \frac{1}{2} \mathbf{v}_\alpha^2$$
$$= \mathrm{div} \sum_{\alpha=1}^{n} \mathbf{v}_\alpha \mathbf{T}_\alpha + \sum_{\alpha=1}^{n} \rho_\alpha \mathbf{b}_\alpha . \mathbf{v}_\alpha - \mathrm{div}\mathbf{q} + Q \quad (4.81)$$

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

$$\sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha u_\alpha}{\partial t} + \sum_{\alpha=1}^{n} \mathrm{div}(\rho_\alpha u_\alpha \mathbf{v}_\alpha) = \sum_{\alpha=1}^{n} \rho_\alpha \grave{u}_\alpha + \sum_{\alpha=1}^{n} r_\alpha u_\alpha$$
$$= -\,\mathrm{div}\mathbf{q} + Q + \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha - \sum_{\beta=1}^{n-1} \mathbf{k}_\beta . \mathbf{u}_\beta$$
$$-\,(1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 \quad (4.82)$$

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 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

$$\begin{aligned} -T\sigma = {} & \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha f_\alpha}{\partial t} + \sum_{\alpha=1}^{n} \mathbf{v}_\alpha.\mathrm{grad}(\rho_\alpha f_\alpha) + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \frac{\partial T}{\partial t} + \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha \,\mathrm{div}\mathbf{v}_\alpha \\ & + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \,\mathbf{v}_\alpha.\mathbf{g} + (1/T)\mathbf{q}.\mathbf{g} - \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{k}_\beta.\mathbf{u}_\beta \\ & + (1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 \leq 0 \end{aligned} \tag{4.87}$$

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

$$\begin{aligned} -T\sigma = {} & \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha f_\alpha}{\partial t} + \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha \,\mathrm{tr}\mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{u}_\beta.\,\mathrm{grad}(\rho_\beta f_\beta) + \mathbf{v}_n \,\mathrm{grad} \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha \\ & + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \frac{\partial T}{\partial t} + \sum_{\beta=1}^{n-1} \rho_\beta s_\beta \,\mathbf{u}_\beta.\mathbf{g} + \mathbf{v}_n.\mathbf{g} \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha + (1/T)\mathbf{q}.\mathbf{g} \\ & - \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \,\overset{\circ}{\mathbf{D}}_\alpha - (1/3) \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathrm{tr}\mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{k}_\beta.\mathbf{u}_\beta \\ & + (1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 \leq 0 \end{aligned} \tag{4.89}$$

(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 $\mathbf{b}_\alpha + \mathbf{i}_\alpha$),

$$\sum_{\alpha=1}^{n}(\mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha) = \mathbf{o} \tag{4.98}$$

$$\mathbf{T}_\alpha = \mathbf{T}_\alpha^T \qquad \alpha = 1, \ldots, n \tag{4.99}$$

$$\sum_{\alpha=1}^{n}\mathbf{T}_\alpha = \sum_{\alpha=1}^{n}\mathbf{T}_\alpha^T \qquad \alpha = 1, \ldots, n \tag{4.100}$$

$$\sum_{\alpha=1}^{n}\rho_\alpha \grave{u}_\alpha + \sum_{\alpha=1}^{n} r_\alpha u_\alpha = -\mathrm{div}\mathbf{q} + Q + \sum_{\alpha=1}^{n}\mathrm{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha - \sum_{\alpha=1}^{n}\mathbf{k}_\alpha.\mathbf{v}_\alpha - (1/2)\sum_{\alpha=1}^{n} r_\alpha \mathbf{v}_\alpha^2 \tag{4.101}$$

$$\sigma = \sum_{\alpha=1}^{n}\rho_\alpha \grave{s}_\alpha + \sum_{\alpha=1}^{n} r_\alpha s_\alpha + \mathrm{div}(\mathbf{q}/T) - Q/T \geq 0 \tag{4.102}$$

(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

$$\varepsilon_\alpha, \quad \eta_\alpha \qquad \alpha = 1, \ldots, n \tag{4.103}$$

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

$$\varphi_\alpha \equiv \varepsilon_\alpha - T\eta_\alpha \qquad \alpha = 1, \ldots, n \tag{4.106}$$

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 ($\alpha = 1, \ldots, n$)

$$u'_\alpha = u_\alpha + \varepsilon_\alpha \tag{4.108}$$

$$s'_\alpha = s_\alpha + \eta_\alpha \tag{4.109}$$

$$\mathbf{T}'_\alpha = \mathbf{T}_\alpha + \rho_\alpha \varphi_\alpha \mathbf{1} \tag{4.110}$$

$$\mathbf{k}'_\alpha = \mathbf{k}_\alpha - \operatorname{grad}(\rho_\alpha \varphi_\alpha) \tag{4.111}$$

$$\mathbf{q}' = \mathbf{q} - T \sum_{\alpha=1}^{n} \rho_\alpha \eta_\alpha \mathbf{v}_\alpha \tag{4.112}$$

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 $\rho_\alpha \grave{\mathbf{v}}_\alpha = \rho'_\alpha \grave{\mathbf{v}}'_\alpha = \operatorname{div}(\mathbf{T}'_\alpha - \rho_\alpha \varphi_\alpha \mathbf{1}) + \rho'_\alpha \mathbf{b}'_\alpha + \mathbf{k}'_\alpha + \operatorname{grad}(\rho_\alpha \varphi_\alpha \mathbf{1})$ and (4.98) we obtain by (4.107). To prove the remaining relationships (4.101), (4.102) in primed quantities we use

$$\sum_{\alpha=1}^{n} \rho_\alpha \grave{\varepsilon}_\alpha = \sum_{\alpha=1}^{n} \overset{\backslash\alpha}{\rho_\alpha \varepsilon_\alpha} - \sum_{\alpha=1}^{n} \grave{\rho}_\alpha \varepsilon_\alpha = \sum_{\alpha=1}^{n} \mathbf{v}_\alpha.\mathrm{grad}(\rho_\alpha \varepsilon_\alpha) - \sum_{\alpha=1}^{n} \grave{\rho}_\alpha \varepsilon_\alpha$$

(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),

$$u_\alpha = u_\alpha^{(0)} + \sum_{\gamma=1}^{n} u_\alpha^{(\gamma)} \mathrm{tr}\mathbf{D}_\gamma \qquad \alpha = 1, \ldots, n \tag{4.131}$$

---

[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 $\alpha, \gamma = 1, \ldots, n$; $\beta = 1, \ldots, n-1$ and

$$\begin{aligned} T\sigma = &- \sum_{\beta=1}^{n-1}\left(\sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial \rho_\beta} - \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial \rho_n}\right) r_\beta^{(0)} \\ &+ \sum_{\gamma=1}^{n}(\rho_\gamma \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha^{(0)}}{\partial \rho_\gamma} - \rho_\gamma f_\gamma^{(0)} - p_\gamma)\mathrm{tr}\mathbf{D}_\gamma + \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} \zeta_{\alpha\gamma}\mathrm{tr}\mathbf{D}_\alpha \mathrm{tr}\mathbf{D}_\gamma \\ &+ \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n}(2\eta_{\alpha\gamma})\mathrm{tr}(\mathring{\mathbf{D}}_\alpha \mathring{\mathbf{D}}_\gamma) + \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1}(\nu_{\beta\delta} - (1/2) r_\beta^{(0)}\delta_{\beta\delta})\mathbf{u}_\delta.\mathbf{u}_\beta + (k/T)\mathbf{g}^2 \\ &+ \sum_{\beta=1}^{n-1}\left(\frac{\lambda_\beta}{T} + \xi_\beta - \frac{\partial \rho_\beta \hat{f}_\beta^{(0)}}{\partial T} - \rho_\beta s_\beta^{(0)}\right)\mathbf{u}_\beta.\mathbf{g} \geq 0 \end{aligned} \tag{4.151}$$

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

$$\sum_{\alpha=1}^{n} \rho_\alpha f_\alpha^{(\gamma)} = 0 \qquad \gamma = 1, \ldots, n \tag{4.152}$$

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

$$f_\beta^{(\gamma)} = 0 \qquad \beta = 1, \ldots, n-1 \qquad \gamma = 1, \ldots, n \tag{4.153}$$

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

$$\sum_{\alpha=1}^{n} \rho_\alpha s_\alpha^{(\gamma)} = 0 \qquad \gamma = 1, \ldots, n \tag{4.154}$$

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

$$u_\alpha^{(\gamma)} = 0 \qquad \alpha, \gamma = 1, \ldots, n \tag{4.155}$$

and therefore constitutive equations for scalar quantities (4.130)–(4.133) are (here and in the following we omit the index (0))

$$r_\alpha = \hat{r}_\alpha(T, \rho_1, \rho_2, \ldots, \rho_n) = \hat{r}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.156}$$

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,

$$u_\alpha = \hat{u}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.157}$$

$$s_\alpha = \hat{s}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.158}$$

$$f_\alpha = \hat{f}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.159}$$

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]

$$\frac{\partial \rho \hat{f}}{\partial \rho_\alpha} \equiv g_\alpha = \hat{g}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.161}$$

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[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

$$\begin{aligned} T\sigma = {} & -\sum_{\beta=1}^{n-1}(g_\beta - g_n) r_\beta + \sum_{\gamma=1}^{n} \Delta p_\gamma \,\mathrm{tr}\mathbf{D}_\gamma + \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} \zeta_{\alpha\gamma}\,\mathrm{tr}\mathbf{D}_\alpha \mathrm{tr}\mathbf{D}_\gamma \\ & + \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} 2\eta_{\alpha\gamma}\,\mathrm{tr}(\overset{\circ}{\mathbf{D}}_\alpha \overset{\circ}{\mathbf{D}}_\gamma) + \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1}(\nu_{\beta\delta} - (1/2) r_\beta \delta_{\beta\delta})\mathbf{u}_\delta . \mathbf{u}_\beta + (k/T)\mathbf{g}^2 \\ & + \sum_{\beta=1}^{n-1} \vartheta_\beta\, \mathbf{u}_\beta . \mathbf{g} \geq 0 \end{aligned} \tag{4.167}$$

This inequality may be written as the sum of two non-negative expressions

$$T\sigma = \Pi_1 + \Pi_2 \geq 0 \tag{4.168}$$

$$\Pi_1 \equiv \Pi_0 + \sum_{\alpha=1}^{n} \Delta p_\alpha \,\mathrm{tr}\mathbf{D}_\alpha + \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} \zeta_{\alpha\gamma}\,\mathrm{tr}\mathbf{D}_\alpha \mathrm{tr}\mathbf{D}_\gamma \geq 0 \tag{4.169}$$

$$\Pi_2 \equiv \sum_{\alpha=1}^{n}\sum_{\gamma=1}^{n} (2\eta_{\alpha\gamma})\mathrm{tr}(\overset{\circ}{\mathbf{D}}_\alpha \overset{\circ}{\mathbf{D}}_\gamma) + \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1}(\nu_{\beta\delta} - (1/2) r_\beta \delta_{\beta\delta})\mathbf{u}_\delta . \mathbf{u}_\beta + (k/T)\mathbf{g}.\mathbf{g}$$

$$+\sum_{\beta=1}^{n-1} \vartheta_\beta \, \mathbf{u}_\beta . \mathbf{g} \geq 0 \tag{4.170}$$

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))

$$\begin{aligned} &J_p = \hat{J}_p(T, \rho_\gamma) = \bar{J}_p(T, \mu_\gamma) = \tilde{J}_p(T, B^\sigma, A^r) \qquad \gamma = 1, \ldots, n; \quad \sigma = 1, \ldots, h; \\ &p, r = 1, \ldots, n-h \end{aligned} \tag{4.179}$$

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.

$$k \geq 0, \quad \eta_{\alpha\alpha} \geq 0, \quad \zeta_{\alpha\alpha} \geq 0 \quad \alpha = 1, \dots, n \tag{4.181}$$

$$\nu_{\beta\beta} \geq (1/2) r_\beta \quad \beta = 1, \dots, n-1 \tag{4.182}$$

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

$$\Delta p_\alpha = 0 \quad \alpha = 1, \dots, n \tag{4.184}$$

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 $\Pi_0, \Delta p_\gamma, \zeta_{\alpha\gamma}$ 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 $\mathrm{tr}\mathbf{D}_\gamma$ at chosen T, ρ_γ) as zero we obtain the extremal values $\mathrm{tr}\mathbf{D}_\gamma$ (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

$$\Pi_0 - (1/4) \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \zeta^{-1}_{\alpha\gamma} \Delta p_\alpha \Delta p_\gamma \geq 0 \tag{4.185}$$

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[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 $p-H_2$ (1) to $o-H_2$ (2) at 650 °C, 100 torr in which the rate is $J = 1.52 \times 10^{-3}\mathrm{mol/m^3s}$ 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

$$\varepsilon_\alpha = \hat{\varepsilon}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.222}$$

$$\eta_\alpha = \hat{\eta}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.223}$$

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

$$\zeta_\alpha = \hat{\zeta}_\alpha(T, \rho_\gamma) \qquad \alpha, \gamma = 1, \ldots, n \tag{4.224}$$

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

$$y'_\alpha = y_\alpha + \zeta_\alpha \qquad \alpha = 1, \ldots, n \tag{4.226}$$

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 $\operatorname{grad}(\rho_\beta\varphi_\beta) = \rho_\beta\frac{\partial\hat{\varphi}_\beta}{\partial T}\mathbf{g} + \sum_{\gamma=1}^{n}\frac{\partial\rho_\beta\hat{\varphi}_\beta}{\partial\rho_\gamma}\mathbf{h}_\gamma$ 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

$$\begin{aligned}
\Delta p'_\alpha &\equiv \rho'_\alpha(g'_\alpha - f'_\alpha) - p'_\alpha = \rho_\alpha g_\alpha - \rho_\alpha(f_\alpha + \varphi_\alpha) - (p_\alpha - \rho_\alpha\varphi_\alpha) = \Delta p_\alpha\\
\vartheta'_\beta &\equiv \lambda'_\beta/T' + \xi'_\beta - \rho'_\beta\frac{\partial\hat{f}'_\beta}{\partial T'} - \rho'_\beta s'_\beta = \lambda_\beta/T + \rho_\beta\eta_\beta + \xi_\beta + \rho_\beta\frac{\partial\hat{\varphi}_\beta}{\partial T} - \rho_\beta\frac{\partial(\hat{f}_\beta + \hat{\varphi}_\beta)}{\partial T}\\
&\quad - \rho_\beta(s_\beta + \eta_\beta) = \vartheta_\beta
\end{aligned}$$

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

$$\frac{\partial(\sum_{\beta=1}^{n-1} w_\beta \tilde{g}_\beta + (1 - \sum_{\beta=1}^{n-1} w_\beta)\tilde{g}_n)}{\partial T} = \sum_{\beta=1}^{n-1} w_\beta \frac{\partial(\tilde{g}_\beta - \tilde{g}_n)}{\partial T} + \frac{\partial \tilde{g}_n}{\partial T} = -\sum_{\alpha=1}^{n} w_\alpha s_\alpha$$
$$= -\sum_{\beta=1}^{n-1} w_\beta (s_\beta - s_n) - s_n$$

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 $\check{P}$ (4.214), (4.195) we have

$$\frac{\partial\tilde{v}}{\partial w_\beta} = -\frac{\partial\check{P}}{\partial w_\beta}/\frac{\partial\check{P}}{\partial v} = \left(\frac{\partial\hat{P}}{\partial\rho_\beta} - \frac{\partial\hat{P}}{\partial\rho_n}\right)/\left(\sum_{\gamma=1}^{n}\rho_\gamma\frac{\partial\hat{P}}{\partial\rho_\gamma}\right) \qquad \beta = 1,\ldots,n-1 \tag{4.275}$$

because

$$\frac{\partial\check{P}}{\partial v} = -\rho\sum_{\gamma=1}^{n}\rho_\gamma\frac{\partial\hat{P}}{\partial\rho_\gamma}$$

$$\frac{\partial\check{P}}{\partial w_\beta} = \rho\frac{\partial\hat{P}}{\partial\rho_\beta} - \rho\frac{\partial\hat{P}}{\partial\rho_n} \qquad \beta = 1,\ldots n-1$$

Similarly, for the remaining $y = u, s, f, h, g$, we can define functions $y = \check{y}(T, v, w_\beta)$ by

$$\begin{aligned}y &= \hat{y}(T, \rho_\gamma) = \hat{y}(T, \frac{w_1}{v}, \ldots, \frac{w_{n-1}}{v}, \frac{1 - \sum_{\beta=1}^{n-1} w_\beta}{v}) \equiv \breve{y}(T, v, w_1, \ldots, w_{n-1}) \\ &= \breve{y}(T, \tilde{v}(T, P, w_\beta), w_\beta) = \tilde{y}(T, P, w_\beta)\end{aligned} \tag{4.276}$$

From this we obtain analogously

$$\frac{\partial \tilde{y}}{\partial w_\eta} = \frac{\partial \breve{y}}{\partial w_\eta} + \frac{\partial \breve{y}}{\partial v}\frac{\partial \tilde{v}}{\partial w_\eta} = \rho(\frac{\partial \hat{y}}{\partial \rho_\eta} - \frac{\partial \hat{y}}{\partial \rho_n}) - \rho(v_\eta - v_n)\sum_{\gamma=1}^{n} \rho_\gamma \frac{\partial \hat{y}}{\partial \rho_\gamma} \qquad \eta = 1, \ldots n-1 \tag{4.277}$$

because (4.195), (4.265) and

$$\begin{aligned}\frac{\partial \breve{y}}{\partial v} &= -\rho \sum_{\gamma=1}^{n} \rho_\gamma \frac{\partial \hat{y}}{\partial \rho_\gamma} \\ \frac{\partial \breve{y}}{\partial w_\eta} &= \rho(\frac{\partial \hat{y}}{\partial \rho_\eta} - \frac{\partial \hat{y}}{\partial \rho_n}) \qquad \eta = 1, \ldots n-1\end{aligned}$$

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 $Y = \check{Y}(T, P, m_\gamma)$, $\gamma = 1, \dots, n$ and the corresponding total specific thermodynamic quantities $y = \tilde{y}(T, P, w_\delta)$, $\delta = 1, \dots, n-1$

$$Y = my = (\sum_{\gamma=1}^{n} m_\gamma)\tilde{y}(T, P, m_\delta/(\sum_{\gamma=1}^{n} m_\gamma)) \equiv \check{Y}(T, P, m_1, \dots, m_n) \tag{4.283}$$

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

$$\rho_\gamma = m_\gamma/V \qquad \gamma = 1, \dots, n \tag{4.285}$$

$$w_\gamma = m_\gamma/m \qquad \gamma = 1, \dots, n \tag{4.286}$$

((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])

$$\frac{\partial \check{Y}}{\partial m_\alpha} = y_\alpha \qquad \alpha = 1, \dots, n \tag{4.287}$$

(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 $\delta_{\beta n} = 0,\ \beta = 1, \dots, n-1$.

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 ($\alpha = 1, \dots, n$)

$$c_\alpha = \rho_\alpha / M_\alpha \tag{4.288}$$

$$c = \sum_{\alpha=1}^{n} c_\alpha \tag{4.289}$$

$$x_\alpha = c_\alpha / c \tag{4.290}$$

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, $\beta, \delta = 1, \dots, n-1$, 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))

$$\begin{aligned} \sum_{\alpha=1}^{n} x_\alpha \frac{\partial \overline{M_\alpha y_\alpha}}{\partial x_\beta} &= \sum_{\alpha=1}^{n} \frac{w_\alpha M}{M_\alpha} M_\alpha \sum_{\delta=1}^{n-1} \frac{\partial \tilde{y}_\alpha}{\partial w_\delta} \frac{\partial x_\delta M_\delta / (M_n + \sum_{\delta=1}^{n-1} x_\delta (M_\delta - M_n))}{\partial x_\beta} \\ &= M \sum_{\delta=1}^{n-1} \left(\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{y}_\alpha}{\partial w_\delta} \right) \frac{\partial x_\delta M_\delta / (M_n + \sum_{\delta=1}^{n-1} x_\delta (M_\delta - M_n))}{\partial x_\beta} \\ &= 0 \qquad \beta = 1, \dots, n-1 \end{aligned} \tag{4.298}$$

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))

$$\frac{\partial \overline{My}}{\partial x_\beta} = M_\beta y_\beta - M_n y_n \qquad \beta = 1, \dots, n-1 \tag{4.299}$$

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

$$\Delta p_\alpha = 0 \qquad \alpha = 1, \ldots n \tag{4.307}$$

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 $\Pi_0 = \hat{\Pi}_0(T, \rho_\gamma)$, $\gamma = 1, \ldots n$ (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

$$\frac{\mathrm{d}}{\mathrm{d}\lambda} \hat{\Pi}_0(T^o + \lambda\beta, \rho_\gamma^o + \lambda\alpha_\gamma)|_{\lambda=0} = 0 \tag{4.308}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\lambda^2} \hat{\Pi}_0(T^o + \lambda\beta, \rho_\gamma^o + \lambda\alpha_\gamma)|_{\lambda=0} \geq 0 \tag{4.309}$$

Here ρ_γ^o, 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

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{\Pi}_0(T^o + \lambda\beta, \rho_\gamma^o + \lambda\alpha_\gamma)$$
$$= \beta\left(\sum_{p=1}^{n-h}\frac{\partial \hat{J}_p}{\partial T}A^p + \sum_{p=1}^{n-h} J_p \frac{\partial \hat{A}^p}{\partial T}\right) + \sum_{\gamma=1}^{n}\alpha_\gamma\left(\sum_{p=1}^{n-h}\frac{\partial \hat{J}_p}{\partial \rho_\gamma}A^p + \sum_{p=1}^{n-h} J_p \frac{\partial \hat{A}^p}{\partial \rho_\gamma}\right) \tag{a}$$

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)

$$\vec{\mu}^o = \vec{B}^o \quad \text{in components} \quad \mu^o_\alpha = \sum_{\sigma=1}^{h} B^{\sigma o} S_{\sigma\alpha} \quad \alpha = 1, \dots, n \tag{4.313}$$

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, $\beta, \epsilon^\sigma, A^r$ ($\sigma = 1, \dots, h; r = 1, \dots, n-h$) 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)

$$V^o = \int_{m^o} v \, \mathrm{d}m \tag{4.341}$$

$$E^o = \int_{m^o} \sum_{\alpha=1}^{n} w_\alpha (u_\alpha + (1/2)\mathbf{v}_\alpha^2) \, \mathrm{d}m \tag{4.342}$$

(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),

$$\frac{\partial \check{P}}{\partial v} \equiv \left(\frac{\partial P}{\partial v}\right)_{T,w_\beta} < 0 \qquad \text{or} \qquad \frac{\partial \tilde{v}}{\partial P} < 0 \tag{4.358}$$

$$\frac{\partial(\tilde{g}_1 - \tilde{g}_n)}{\partial w_1} > 0, \ldots, \frac{\partial(\tilde{g}_1 - \tilde{g}_n, \ldots, \tilde{g}_k - \tilde{g}_n)}{\partial(w_1, \ldots, w_k)} > 0, \ldots, \frac{\partial(\tilde{g}_1 - \tilde{g}_n, \ldots, \tilde{g}_{n-1} - \tilde{g}_n)}{\partial(w_1, \ldots, w_{n-1}, P)} > 0 \tag{4.359}$$

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

$$\frac{\partial(\tilde{g}_\beta - \tilde{g}_n)}{\partial w_\delta} \qquad \beta, \delta = 1, \ldots, n-1 \tag{4.360}$$

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

$$\frac{\partial \hat{g}_\alpha}{\partial \rho_\gamma} \qquad \alpha, \gamma = 1, \ldots, n \tag{4.362}$$

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

$$\frac{\partial(g_1, \ldots, g_n)}{\partial(\rho_1, \ldots, \rho_n)} = \frac{\partial(g_1, \ldots, g_n)}{\partial(w_1, \ldots, w_{n-1}, P)} \frac{\partial w_1, \ldots, w_{n-1}, P)}{\partial(w_1, \ldots, w_{n-1}, v)} \frac{\partial(w_1, \ldots, w_{n-1}, v)}{\partial(\rho_1, \ldots, \rho_n)} \tag{4.363}$$

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

$$\frac{\partial(w_1, \ldots, w_{n-1}, v)}{\partial(\rho_1, \ldots, \rho_n)} = (1/\rho)^{n-1}(-1/\rho^2) = -1/\rho^{n+1} = -v^{n+1} < 0 \tag{4.364}$$

because ρ, v are both positive. Namely, this jacobian contains derivatives

$$\frac{\partial w_\delta}{\partial \rho_\alpha} = \frac{1}{\rho}(\delta_{\delta\alpha} - w_\delta), \quad \frac{\partial v}{\partial \rho_\alpha} = -\rho^{-2} \quad \alpha = 1, \ldots, n\,, \ \delta = 1, \ldots, n-1 \tag{4.365}$$

obtained from functions $w_\delta = \rho_\delta / \sum_{\gamma=1}^{n} \rho_\gamma$ or $v = 1/\sum_{\gamma=1}^{n} \rho_\gamma$ of $\rho_1, \ldots, \rho_n$ (cf. (4.21), (4.23), (4.195)). Inserting (4.365) into (4.364) and rearranging we have

$$\frac{\partial(w_1, \ldots, w_{n-1}, v)}{\partial(\rho_1, \ldots, \rho_n)} = (1/\rho)^{n-1}(-1/\rho^2) J \tag{4.366}$$

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)

$$\frac{\partial(w_1, \dots, w_{n-1}, v)}{\partial(\rho_1, \dots, \rho_n)} = (1/\rho)^{n-1}(-1/\rho^2) < 0 \tag{4.371}$$

which is negative by the positivity of $\rho > 0$.

The central jacobian in (4.363) is

$$\frac{\partial(w_1, \dots, w_{n-1}, P)}{\partial(w_1, \dots, w_{n-1}, v)} = \left(\frac{\partial P}{\partial v}\right)_{T, w_\beta} < 0 \tag{4.372}$$

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)

$$\frac{\partial(g_1, \dots, g_n)}{\partial(w_1, \dots, w_{n-1}, P)} = v.\frac{\partial(g_1 - g_n, \dots, g_{n-1} - g_n)}{\partial(w_1, \dots, w_{n-1})} > 0 \tag{4.373}$$

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 $1, \dots, n-1$ rows multiplied by $w_1, \dots, w_{n-1}$ respectively (values of this jacobian are unchanged by such operations). Then the members of the last row are

$$\frac{\partial \tilde{g}_n}{\partial w_\delta} + \sum_{\beta=1}^{n-1} w_\beta \frac{\partial(\tilde{g}_\beta - \tilde{g}_n)}{\partial w_\delta} = 0 \qquad \delta = 1, \dots, n-1, \quad \sum_{\alpha=1}^{n} w_\alpha \frac{\partial \tilde{g}_\alpha}{\partial P} = v \tag{4.374}$$

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

$$\frac{\partial(g_1, \dots, g_n)}{\partial(\rho_1, \dots, \rho_n)} > 0 \tag{4.375}$$

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_α^o in a *non-reacting* mixture are equal to m_α, i.e. the equilibrium composition is then given for the independent masses by

$$w_\beta^o = m_\beta^o/m^o \qquad \beta = 1, \ldots, n-1 \tag{4.379}$$

However in the *reacting* mixture m_α^o need not be equal to m_α and w_β^o 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 $w_\alpha = w_\alpha^o$ as the functions of remaining h mass fractions in equilibrium; inserting them in (4.343), i.e. in

$$\sum_{\alpha=1}^{n} (S_{\sigma\alpha}/M_\alpha) m^o w_\alpha^o = \sum_{\alpha=1}^{n} (S_{\sigma\alpha}/M_\alpha) m_\alpha \qquad \sigma = 1, \ldots, h \tag{4.381}$$

we can calculate the remaining h mass fractions from these h equations (m_α are prescribed) and therefore all (equilibrium) values w_β^o 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_β^o (cf. similar deduction of (3.260)):

$$s < s^o + (u - u^o)/T^o + (v - v^o)P^o/T^o - \sum_{\beta=1}^{n-1} (w_\beta - w_\beta^o)(g_\beta^o - g_n^o)/T^o \tag{4.382}$$

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 $\sum_{\alpha=1}^{n} w_\alpha \mathbf{v}_\alpha^2/(2T^o)$ (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

$$S \equiv \int_{m^o} s \, \mathrm{d}m \leq \int_{m^o} s^o \, \mathrm{d}m = S^o = s^o m^o \tag{4.383}$$

where the equality occurs when in all the mixture

$$u = u^o, \quad v = v^o, \quad w_\beta = w_\beta^o \tag{4.384}$$

(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

$$\begin{aligned} &\int_{m^o} \sum_{\beta=1}^{n-1} \left(w_\beta - w_\beta^o\right) \frac{g_\beta^o - g_n^o}{T^o} \, \mathrm{d}m \\ &= \sum_{\alpha=1}^{n} \frac{g_\alpha^o}{T^o} \int_{m^o} \left(w_\alpha - w_\alpha^o\right) \mathrm{d}m = \sum_{\alpha=1}^{n} \left(m_\alpha - m_\alpha^o\right) \frac{g_\alpha^o}{T^o} \end{aligned}$$

$$= \frac{1}{T^o} \sum_{\sigma=1}^{h} B^{\sigma o} \left(\sum_{\alpha=1}^{n} m_\alpha S_{\sigma\alpha}/M_\alpha - \sum_{\alpha=1}^{n} m_\alpha^o S_{\sigma\alpha}/M_\alpha \right) = 0 \tag{4.385}$$

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

$$\dot{\overline{\sum_{\alpha=1}^{n} \int_V (w_\alpha u_\alpha + w_\alpha (1/2)\mathbf{v}_\alpha^2)\rho \, \mathrm{d}v}} = -P^o \int_{\partial V} \mathbf{v}.\mathbf{n} \, \mathrm{d}a - \int_{\partial V} \mathbf{q}.\mathbf{n} \, \mathrm{d}a \tag{4.391}$$

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

$$P^o \int_{\partial V} \mathbf{v}.\mathbf{n} \, \mathrm{d}a = \dot{\overline{\int_V P^o \rho v \, \mathrm{d}v}} \tag{4.392}$$

and we put (4.392) to the left-hand side of (4.391). Moreover, we subtract the following quantity with constants $g_\alpha^o \quad (\alpha = 1, \ldots, n)$ from the left hand side of (4.391):

$$\overset{\boldsymbol{\cdot}}{\overline{\int_V \sum_{\beta=1}^{n-1} w_\beta (g_\beta^o - g_n^o)\rho \, \mathrm{d}v}} = \sum_{\beta=1}^{n-1} (g_\beta^o - g_n^o) \overset{\backslash\beta}{\overline{\int_V \rho_\beta \, \mathrm{d}v}} = \int_V \sum_{\alpha=1}^{n} g_\alpha^o r_\alpha \, \mathrm{d}v$$
$$= -\int_V \vec{A}^o . \vec{J} \, \mathrm{d}v = 0 \qquad (4.393)$$

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_α^o are the chemical potentials in (uniform) chemical equilibrium mixture at its T^o, P^o and w_β^o (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))

$$\overset{\boldsymbol{\cdot}}{\overline{\int_V \rho(u + P^o v - \sum_{\beta=1}^{n-1} w_\beta (g_\beta^o - g_n^o) + (1/2)\sum_{\alpha=1}^{n} w_\alpha \mathbf{v}_\alpha^2) \, \mathrm{d}v}} = -\int_{\partial V} \mathbf{q}.\mathbf{n} \, \mathrm{d}a \qquad (4.394)$$

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))

$$\overset{\boldsymbol{\cdot}}{\overline{\int_V \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \, \mathrm{d}v}} + (1/T^o)\int_{\partial V} \mathbf{q}.\mathbf{n} \, \mathrm{d}a = \int_V \sigma \, \mathrm{d}v \geq 0 \qquad (4.395)$$

Multiplying (4.395) by T^o, using (4.91) and inserting here (4.394), we obtain

$$\dot{R}(t) = -T^o \int_V \sigma \, \mathrm{d}v \leq 0 \qquad (4.396)$$

where we define the canonical function $R = R(t)$ as follows

$$R(t) \equiv \int_V \rho(u - T^o s + P^o v - \sum_{\beta=1}^{n-1} w_\beta (g_\beta^o - g_n^o) + (1/2)\sum_{\alpha=1}^{n} w_\alpha \mathbf{v}_\alpha^2) \, \mathrm{d}v \qquad (4.397)$$

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_β^o (in (4.382) is $s^o = \tilde{s}(T^o, P^o, w_\beta^o)$ 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 $g_\alpha^\bullet$ 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, $Mg^{\bullet} = \mu^{\bullet} = \mu^{\bullet}_{\alpha} = M_{\alpha} g^{\bullet}_{\alpha}$ 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]

$$v_\alpha = v_\alpha^\bullet = 1/\rho^\bullet = \text{const.} \tag{4.406}$$

where $\rho^\bullet = \rho_\alpha^\bullet$ 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))

$$1/\rho = \sum_{\alpha=1}^{n} w_\alpha (1/\rho_\alpha^\bullet) \tag{4.407}$$

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 $\rho_\alpha^\bullet$ of all constituents and therefore equal to the constant mixture density ρ

$$\rho_\alpha^\bullet = \rho = \text{const.} \qquad \alpha = 1, \ldots, n \tag{4.408}$$

- 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 $\rho = \rho_n^\bullet = \text{const.}$ 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))

$$\begin{aligned} v_\alpha &= \Big(\frac{\partial\hat{P}_\alpha}{\partial\rho_\alpha}\Big)\Big/\left(\sum_{\gamma=1}^{n}\rho_\gamma\frac{\partial\hat{P}_\gamma}{\partial\rho_\gamma}\right) = \rho_\alpha\Big(\frac{\partial\hat{f}_\alpha}{\partial\rho_\alpha}\Big)\Big/\left(\sum_{\gamma=1}^{n}\rho_\gamma^2\frac{\partial\hat{f}_\gamma}{\partial\rho_\gamma}\right) = \frac{K_\alpha\rho_\alpha^{C-1}}{P} \\ &= \rho_\alpha\Big(\frac{\partial\hat{g}_\alpha}{\partial\rho_\alpha}\Big)\Big/\left(\sum_{\gamma=1}^{n}\rho_\gamma^2\frac{\partial\hat{g}_\gamma}{\partial\rho_\gamma}\right) \qquad \alpha = 1, \ldots, n \end{aligned}$$

The dependence of partial properties $f_\alpha, g_\alpha, P_\alpha, Pv_\alpha$ 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)

$$u_\alpha = \hat{u}_\alpha(T) \qquad \alpha = 1, \dots, n \tag{4.427}$$

$$h_\alpha = \hat{h}_\alpha(T) \qquad \alpha = 1, \dots, n \tag{4.428}$$

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)

$$\frac{\partial \hat{f}_\alpha}{\partial \rho_\alpha} = \frac{P_\alpha}{\rho_\alpha^2} = \frac{\mathrm{R}T}{M_\alpha \rho_\alpha} \qquad \alpha = 1, \dots, n \tag{4.429}$$

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)

$$f_\alpha = \hat{f}_\alpha^0(T) + \frac{\mathrm{R}T}{M_\alpha} \ln \rho_\alpha \qquad \alpha = 1, \dots, n \tag{4.430}$$

where $\hat{f}_\alpha^0(T)$, 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

$$g_\alpha = \hat{g}_\alpha^0(T) + \frac{\mathrm{R}T}{M_\alpha} \ln P_\alpha \qquad \alpha = 1, \dots, n \tag{4.431}$$

with $\hat{g}_\alpha^0(T) \equiv \hat{f}_\alpha^0(T) + (\mathrm{R}T/M_\alpha)(1 + \ln(M_\alpha/\mathrm{R}T))$ 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

$$\mu_\alpha = (M_\alpha g_\alpha^0(T) + \mathrm{R}T\ln P) + \mathrm{R}T\ln x_\alpha = \mu_\alpha^0(T, P) + \mathrm{R}T\ln x_\alpha \qquad \alpha = 1, \ldots, n \tag{4.432}$$

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

$$\mu_\alpha = (M_\alpha g_\alpha^0(T) + \mathrm{R}T \ln \mathrm{R}T) + \mathrm{R}T\ln c_\alpha = \mu_\alpha^0(T) + \mathrm{R}T\ln c_\alpha \qquad \alpha = 1, \ldots, n \tag{4.433}$$

(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

$$\frac{\partial \overline{\mu_\alpha}}{\partial T} = M_\alpha s_\alpha = M_\alpha s_\alpha^0(T, P) - \mathrm{R}\ln x_\alpha \qquad \alpha = 1, \ldots, n \tag{4.434}$$

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

$$\mu_\alpha = \mu_\alpha^\bullet(T, P) + \mathrm{R}T\ln x_\alpha \qquad \alpha = 1, \dots, n \tag{4.437}$$

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

  $$M_\alpha s_\alpha = M_\alpha s_\alpha^\bullet(T, P) - \mathrm{R}\ln x_\alpha \qquad \alpha = 1, \dots, n \tag{4.438}$$

  (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, $w_1, \dots, w_{n-1}$ 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 $\mu_\alpha^{s\prime}$ 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 $\mu_\alpha^{s\prime} = \mu_\alpha^s + \mathrm{R}T \ln a_\alpha^s$. (these formulae may be valid for all $\alpha = 1, \dots, n$, 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

$$\mu_\alpha = \mu_\alpha^{0s}(T) + \mathrm{R}T\ln(\mathtt{f}_\alpha/P_s) \qquad \alpha = 1, \ldots, n \tag{4.447}$$

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

$$\mathtt{f}^\bullet = P, \qquad \mathtt{f}_\alpha = P_\alpha \qquad \alpha = 1, \ldots, n \tag{4.449}$$

Indeed, inserting the partial pressure of ideal gas (4.424) into (4.431) we have

$$g_\alpha = \hat{g}_\alpha^0(T) + \frac{\mathrm{R}T}{M_\alpha}\ln P + \frac{\mathrm{R}T}{M_\alpha}\ln x_\alpha \qquad \alpha = 1, \ldots, n \tag{4.450}$$

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^o_α inserting (4.441) with the equilibrium chemical potentials $\mu^o_\alpha = \mu^s_\alpha + \mathrm{R}T \ln a^o_\alpha$ into (4.176) by

$$-\mathrm{R}T \ln \mathcal{K}_p = \sum_{\alpha=1}^{n} \mu^s_\alpha P^{p\alpha} \qquad p = 1, \ldots, n-h \tag{4.473}$$

where the so called *equilibrium constants* $\mathcal{K}_p$ of independent reaction p are defined as

$$\mathcal{K}_p = \prod_{\alpha=1}^{n} (a^o_\alpha)^{P^{p\alpha}} \qquad p = 1, \ldots, n-h \tag{4.474}$$

According to the limitation stated above, our standard functions $\mu^s_\alpha = \mu^s_\alpha(T)$ 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^o_α 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

$$J_1 = k_{00} + k_{10}a_1 + k_{01}a_2 + k_{20}a_1^2 + k_{11}a_1a_2 + k_{02}a_2^2 \tag{a}$$

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

$$J_1 = k_{00} + (k_{10}/c_s)c_1 + (k_{01}/c_s)c_2 + (k_{20}/c_s^2)c_1^2 + (k_{11}/c_s^2)c_1c_2 + (k_{02}/c_s^2)c_2^2 \tag{b}$$

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

$$J_1 = k_{01}c_2 - (k_{01}/K_1)c_1^2 = k_{20}(c_1^2 - K_1 c_2) \tag{4.487}$$

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)

$$2O_3 = 3O_2, \quad O_3 = 3O \tag{4.498}$$

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^p_{200}, k^p_{110}, k^p_{020}).

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^o_1, c^o_3; then we must use the preceding method for polynomial of the type (4.484) but in $(c^o_2)^{0.5}$ 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))

$$\mathbf{T}_\alpha = -P_\alpha \mathbf{1} + \mathbf{T}_\alpha^N \qquad \alpha = 1, \dots, n \tag{4.505}$$

where P_α is the partial thermodynamic pressure and $\mathbf{T}_\alpha^N$ is the *partial non-equilibrium stress* defined by

$$\mathbf{T}_\alpha^N \equiv \Delta p_\alpha \mathbf{1} + \sum_{\gamma=1}^{n} \zeta_{\alpha\gamma} (\mathrm{tr}\mathbf{D}_\gamma)\mathbf{1} + \sum_{\gamma=1}^{n} 2\eta_{\alpha\gamma} \overset{\circ}{\mathbf{D}}_\gamma \qquad \alpha = 1, \dots, n \tag{4.506}$$

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

$$\mathbf{j}_\beta \equiv \rho_\beta \mathbf{u}_\beta \qquad \beta = 1, \dots, n-1 \tag{4.507}$$

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) $\text{grad}_T g_\beta = \mathbf{o}$, 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

$$F_{\alpha\alpha} = 0, \qquad \alpha = 1, 2, 3, \quad F_{12} = -\nu_{12}, \quad F_{21} = -\nu_{21},$$
$$F_{13} = \nu_{11} + \nu_{12}, \quad F_{31} = \nu_{11} + \nu_{21}, \quad F_{23} = \nu_{22} + \nu_{21}, \quad F_{32} = \nu_{22} + \nu_{12} \tag{4.526}$$

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

$$F_{\alpha\gamma} = F^s_{\alpha\gamma} + F^a_{\alpha\gamma} \quad \alpha, \gamma = 1, 2, 3, \quad F^s_{\alpha\gamma} \equiv (1/2)(F_{\alpha\gamma} + F_{\gamma\alpha}),$$
$$F^a_{\alpha\gamma} \equiv (1/2)(F_{\alpha\gamma} - F_{\gamma\alpha}) \tag{4.529}$$

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)

$$\mathbf{y}_\beta = \sum_{\zeta=1}^{n-1} \frac{\partial \tilde{g}_\beta}{\partial w_\zeta} \operatorname{grad} w_\zeta + v_\beta \operatorname{grad} P - (\mathbf{b}_\beta + \mathbf{i}_\beta) + \dot{\mathbf{v}}_\beta - \frac{1}{\rho_\beta} \operatorname{div} \mathbf{T}_\beta^N \qquad \beta = 1, \ldots n-1 \tag{4.535}$$

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 **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*

$$-\mathbf{j}_\delta = \sum_{\zeta=1}^{n-1} D^{nw}_{\delta\zeta} \operatorname{grad} w_\zeta \qquad \delta = 1, \ldots, n-1 \tag{4.537}$$

where $D^{nw}_{\delta\zeta}$ 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

$$D^{nw}_{\delta\zeta} \equiv \sum_{\beta=1}^{n-1} L_{\delta\beta} \frac{\partial \tilde{g}_\beta}{\partial w_\zeta} \qquad \delta, \zeta = 1, \ldots, n-1 \tag{4.538}$$

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 $\grave{\mathbf{v}}_\beta$ 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 $\frac{\partial \tilde{g}_1}{\partial w_1} \leq 0$ and therefore $D_{11}^{nw} \leq 0$ 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)

$$-\mathbf{j}_1^{\mathbf{o}} = D\,\mathrm{grad}\rho_1 \quad = \rho D\,\mathrm{grad}w_1, \quad -\mathbf{j}_1 = \rho D\,\mathrm{grad}w_1 = D\,\mathrm{grad}\rho_1 \tag{4.559}$$

(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

$$\mathbf{j}_1'^{\mathbf{o}} \equiv \mathbf{j}_1^{\mathbf{o}}/M_1 = c_1(\mathbf{v}_1 - \mathbf{v}^{\mathbf{o}}) \tag{4.560}$$

and expressing composition gradients through gradients of molar concentrations or molar fractions, we can write Fick law (4.553) in another classical way

$$-\mathbf{j}_1'^{\mathbf{o}} = D\,\mathrm{grad}c_1 = D_{11}'^{\mathbf{o}x}\,\mathrm{grad}x_1 \tag{4.561}$$

with the same diffusion coefficient (4.554)

$$D \equiv D_{11}^{\mathbf{o}\rho} = D_{11}'^{\mathbf{o}c} \tag{4.562}$$

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 $\mathbf{j}_1' \equiv \mathbf{j}_1/M_1$, $\mathbf{j}_1'^{x} \equiv \mathbf{j}_1^{x}/M_1 = c_1(\mathbf{v}_1 - \mathbf{v}^{x}) = (x_2/M_1)\mathbf{j}_1$ and analogously from the preceding "specific" Fick laws (4.555), (4.546) and analogue of (4.557) we obtain the "molar" Fick laws

$$-\mathbf{j}_1' = D_{11}'^{nc}\,\mathrm{grad}c_1 = D_{11}'^{nx}\,\mathrm{grad}x_1 \tag{4.563}$$

$$-\mathbf{j}_1'^{x} = D_{11}'^{xx}\,\mathrm{grad}x_1 = cD\,\mathrm{grad}x_1 \tag{4.564}$$

where diffusion coefficients are in analogous relations to D as in (4.554), (4.556), namely

$$D = D_{11}'^{\mathbf{o}c} = D_{11}'^{\mathbf{o}x}/(c^2v_2M_2) = (x_2/c)D_{11}'^{nx} = c_2M_2v_2D_{11}'^{nc} = D_{11}'^{xx}/c \tag{4.565}$$

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)

$$D \simeq D_{11}'^{nc}, \quad cD \simeq D_{11}'^{nx} \simeq D_{11}'^{\mathbf{o}x} \tag{4.566}$$

and in dilute solution "molar" Fick laws may be written analogously as (4.559)

$$-\mathbf{j}_1'^{\mathbf{o}} = D\,\mathrm{grad}c_1 \; = cD\,\mathrm{grad}x_1, \quad -\mathbf{j}_1' = cD\,\mathrm{grad}x_1 = D\,\mathrm{grad}c_1 \tag{4.567}$$

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

$$-\mathbf{j}_\delta = \sum_{\zeta=1}^{2} D_{\delta\zeta} \operatorname{grad} w_\zeta \qquad \delta = 1, 2 \tag{4.568}$$

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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