

EXPLOITATION OF A SPECIAL-RELATIVISTIC ENTROPY IDENTITY FOR ONE COMPONENT OF A MULTI-COMPONENT SYSTEM

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ABSTRACT. Non-equilibrium and equilibrium thermodynamics of an interacting component of a special-relativistic multi-component system is discussed by using an entropy identity. The special case of the corresponding free component is considered.

1. Introduction

The treatment of multi-component systems is often restricted to transport phenomena in chemically reacting systems, that means, the mixture consisting of different components is described by 1-component quantities such as temperature, pressure and energy which are not retraced to corresponding quantities of the several components. That is the case in non-relativistic physics (De Groot and Mazur 1962) as well as in relativistic physics (Kluitenberg *et al.* 1953a,b; Israel 1976; Havas and Swenson 1979; Neugebauer 1980). In this paper, the single component as an interacting member of the mixture is investigated. Thus, each component of the mixture is equipped with its own temperature, pressure, energy and mass density which all together generate the corresponding quantities of the mixture.

Considering a multi-component system, three items have to be distinguished: a component of the system which interacts with all other components of the system, the same component as a free 1-component system separated from the multi-component system and finally the multi-component system itself as a mixture which is composed of components. Here, the interacting and the free component are discussed, both in a special-relativistic framework. For finding out the entropy-flux, -supply, -production and -density, a special tool is used: the entropy identity which constrains the possibility of an arbitrary choice of these quantities (Borzeszkowski and Chrobok 2003; Muschik and Borzeszkowski 2009, 2015). The specific entropy and the corresponding Gibbs and Gibbs-Duhem equations are derived. By use of the entropy identity, accessory variables are introduced belonging to the balance equations which are taken into account in the entropy identity: those of the energy-momentum tensor, the rest mass density and the diffusion flux. Equilibrium is defined by equilibrium conditions which are divided into necessary ones given by vanishing entropy-flux, -supply and -production and into supplementary ones such as vanishing diffusion flux, vanishing

heat flux and rest mass production. The Killing relation of the 4-temperature is shortly discussed. Constitutive equations are out of scope of this paper.

The paper is organized as follows. After this introduction, the kinematics of a multi-component system is considered for introducing the mass flux density and the diffusion flux. The energy-momentum tensor is decomposed into its (3+1)-split, and the non-equilibrium thermodynamics of an interacting component in the mixture and those of the corresponding free component is discussed. The equilibrium belonging to both kinds of components finishes the paper together with a summary.

2. Kinematics

2.1. The components. We consider a multi-component system consisting of Z components. The component index A runs from 1 to Z . Each component has its own rest frame \mathcal{B}^A in which the rest mass density ρ^A is locally defined. These rest mass densities are relativistic invariants, that means the ρ^A are scalars.

In general, the components have different 4-velocities: u_k^A , $A = 1, 2, \dots, Z$ which all are tensors of first order. We now define the mass flux density

$$N_k^A := \rho^A u_k^A, \quad N^{Ak},{}_{,k} = \Gamma^A. \quad (1)$$

Here, $(1)_2$ is the mass balance equation of the A -component. Consequently, we introduce the basic fields of the components

$$\{\rho^A, u_k^A\}, \quad A = 1, 2, \dots, Z. \quad (2)$$

2.2. The mixture. As each component, also the multi-component system has a mass density ρ and a 4-velocity u_k which are determined by the partial quantities of the components. For deriving ρ and u_k , we apply the

■ Mixture Axiom: The balance equation of a mixture looks like the balance equation of an one-component system. ■

According to the mixture axiom, the mass balance of the mixture looks like

$$N^k{}_{,k} = \Gamma, \quad \Gamma = 0, \quad (3)$$

with vanishing production, if the mass of the mixture is conserved.

Now the question arises: which quantities of the components are additive? Obviously, neither the mass densities ρ^A nor the component 4-velocities u_k^A are additive quantities according to their definitions. Consequently, we demand in accordance with the mixture axiom that the mass flux densities are additive¹

Setting I:

$$\sum_A N_k^A \stackrel{\bullet}{=} N_k := \rho u_k = \sum_A \rho^A u_k^A \longrightarrow u_k = \sum_A \frac{\rho^A}{\rho} u_k^A. \quad (4)$$

¹The sign $\stackrel{\bullet}{=}$ stands for a setting and $:=$ for a definition.

For the present, ρ and u_k are unknown. Of course, they depend on the basic fields of the components (2). Contraction with u^k and use of (4)_{2,3} results in

$$\rho = \frac{1}{c^2} \sum_A \rho^A u_k^A u^k = \frac{1}{c^2} N_k u^k = \frac{1}{c^2} N_k \frac{1}{\rho} N^k \longrightarrow \rho = \pm \frac{1}{c} \sqrt{N_k N^k}, \quad (5)$$

or in more detail

$$\rho = \pm \frac{1}{c} \sqrt{\sum_{A,B} \rho^A \rho^B u_k^A u^{Bk}}. \quad (6)$$

The mass density ρ and the 4-velocity u_k of the mixture are expressed by those of the components according to (6) and (4)₄. According to (4)₄, the 4-velocity of the mixture is a weighted mean value of the 4-velocities of the components. For the mass density, we have according to (5)₁ also a weighted mean value of the mass density components

$$f^A := \frac{1}{c^2} u_k^A u^k \longrightarrow \rho = \sum_A f^A \rho^A = \sum_A f^A (u_k^A, u^k) \rho^A, \quad (7)$$

resulting in the entanglement of ρ and u_k which are not independent of each other

$$\rho = R(\rho^A, u_k^A, u_k), \quad u_k = U_k(\rho^A, u_k^A, \rho). \quad (8)$$

According to (4)₁ and (1)₂, we obtain the additivity of the mass production terms

$$N^k_{,k} = \sum_A N^{Ak}_{,k} = \sum_A \Gamma^A = \Gamma. \quad (9)$$

2.3. The diffusion flux. From (4)₃ and (7)₂ follows

$$0 = \sum_A \rho^A u_k^A - u_k \sum_A f^A \rho^A = \sum_A \rho^A (u_k^A - f^A u_k). \quad (10)$$

Introducing the diffusion flux density using (10)₂

$$J_k^A := \rho^A (u_k^A - f^A u_k) = N_k^A - \rho^A f^A u_k \longrightarrow \sum_A J_k^A =: J_k = 0, \quad (11)$$

we obtain

$$J_k^A u^k = \rho^A (u_k^A u^k - f^A c^2) = 0, \quad (12)$$

$$J_k^A u^{Ak} = c^2 \rho^A [1 - (f^A)^2] =: c^2 \rho^A w^A = w^A N_k^A u^{Ak} \quad (13)$$

By introducing the projectors

$$h_l^{Am} := \delta_l^m - \frac{1}{c^2} u^m u_l^A, \quad h_l^m := \delta_l^m - \frac{1}{c^2} u^m u_l, \quad (14)$$

we obtain the following properties of the diffusion flux density:

$$J^{Am} h_m^k = J^{Ak} = N^{Am} h_m^k \quad (15)$$

$$J^{Ak} = J^{Am} h_m^{Ak} + \rho^A w^A u^{Ak} = J^{Am} h_m^{Ak} + w^A N^{Ak} \quad (16)$$

$$J^{Ak}_{,k} = (J^{Am} h_m^{Ak})_{,k} + (\rho^A w^A)_{,k} u^{Ak} + \rho^A w^A u^{Ak}_{,k}. \quad (17)$$

According to (15)₂, the diffusion flux density is that part of the mass flux density which is perpendicular to the 4-velocity of the mixture. The diffusion flux density vanishes in 1-component systems ($u_k^A \equiv u_k$) according to $f^A = f = 1$ and (11)₁.

3. The Energy-Momentum Tensor

3.1. Free and interacting components. The energy-momentum tensor T^{Akl} of the A -component consists of two parts

$$T^{Akl} = \overset{0}{T}{}^{Akl} + \sum_B W_B^{Akl}, \quad W_B^{Bkl} = 0. \quad (18)$$

Here, $\overset{0}{T}{}^{Akl}$ is the energy-momentum tensor of the free A -component, that is the case, if there are no interactions between the A -component and the other ones. W_B^{Akl} describes the interaction between the B - and the A -component. The interaction between the environment and the A -component is given by the force density k^{Al} which appears in the energy-momentum balance equation

$$T^{Akl}{}_{,k} = k^{Al}, \quad (19)$$

and in the balance equations of

$$\text{energy:} \quad u_l^A T^{Akl}{}_{,k} = u_l^A k^{Al}, \quad (20)$$

$$\text{momentum:} \quad h_l^{Am} T^{Akl}{}_{,k} = h_l^{Am} k^{Al}. \quad (21)$$

Consequently, the interaction of the A -component with the other components of the mixture modifies the energy-momentum tensor of the free A -component. Additionally, its interaction with the environment shows up in the source of the energy-momentum balance. According to its definition, T^{Akl} is the energy-momentum tensor of the “ A -component in the mixture”.

3.2. (3+1)-split. The (3+1)-split of the energy-momentum tensor of the A -component is

$$T^{Akl} = \frac{1}{c^2} e^A u^{Ak} u^{Al} + \frac{1}{c} u^{Ak} p^{Al} + \frac{1}{c^2} q^{Ak} u^{Al} + t^{Akl}. \quad (22)$$

The (3+1)-components of the energy-momentum tensor are²

$$e^A := \frac{1}{c^2} T^{Ajm} u_j^A u_m^A, \quad p^{Al} := \frac{1}{c} h_m^{Al} T^{Ajm} u_j^A, \quad (23)$$

$$q^{Ak} := h_j^{Ak} T^{Ajm} u_m^A, \quad t^{Akl} := h_j^{Ak} T^{Ajm} h_m^{Al}, \quad (24)$$

$$q^{Ak} u_k^A = 0, \quad p^{Al} u_l^A = 0, \quad t^{Akl} u_k^A = 0, \quad t^{Akl} u_l^A = 0. \quad (25)$$

If the stress tensor is decomposed into pressure p^A and viscous tensor π^{Akl}

$$t^{Akl} = -p^A h^{Akl} + \pi^{Akl}, \quad (26)$$

we obtain for the physical dimension of the pressure³

$$[p] = \frac{N}{m^2} = \frac{Nm}{m^3} = \text{energy density}. \quad (27)$$

According to (14) and (7)₁, we have

$$[h_m^{Al}] = 1, \quad [f^A] = 1, \quad (28)$$

²the (3+1)-split is made by taking the physical meaning of (23) and (24) into account, see (29) to (31)

³the bracket $[\boxtimes]$ signifies the physical dimension of \boxtimes

and by taking (26), (22) and (28) into account we obtain

$$[\pi^{Akl}] = [t^{Akl}] = [T^{Akl}] = [e^A] = [p^{Al}] = \frac{Nm}{m^3} = \text{energy density} \quad (29)$$

$$[p^A] = \frac{N}{m^2} = \frac{kg}{s^2} \frac{m}{m^2} = kg \frac{m}{s} \frac{1}{m^3} \frac{m}{s} = \text{momentum flux density}, \quad (30)$$

$$[q^{Ak}] = [T^{Akl}] \frac{m}{s} = \frac{Nm}{m^3} \frac{m}{s} = \text{energy flux density}. \quad (31)$$

4. Thermodynamics (Interacting Component)

4.1. The entropy identity. For establishing the entropy balance equation, we use a special procedure starting out with an identity (Muschik and Borzeszkowski 2009), the so-called *entropy identity*. This tool helps to restrict arbitrariness for defining entropy density, entropy flux density, entropy production and supply. In the sequel, we establish the entropy identity for the A -component. Starting out with the (3+1)-split of the entropy 4-vector

$$S^{Ak} = s^A u^{Ak} + s^{Ak}, \quad (32)$$

we lay down s^A as entropy density and s^{Ak} as entropy flux density

$$s^A := \frac{1}{c^2} S^{Ak} u_k^A, \quad s^{Ak} := S^{Am} h_m^{Ak}, \quad (33)$$

$$[s^A] = [e^A] \frac{1}{K} = \frac{Nm}{m^3} \frac{1}{K}, \quad [s^{Ak}] = [q^{Ak}] \frac{1}{K} = \frac{Nm}{m^3} \frac{m}{s} \frac{1}{K}. \quad (34)$$

Before writing down the entropy identity, we have to choose the quantities which are essential for formulating the four entropy quantities mentioned above. The choice is: all quantities appearing in the (3+1)-split of the energy-momentum tensor (22) and additional the mass flux density (1)₁ and the diffusion flux density (16)₂ have to be included because we are dealing with a multi-component system. Consequently, the entropy identity is

$$\begin{aligned} S^{Ak} \equiv & s^A u^{Ak} + s^{Ak} + \chi^A \left(J^{Ak} - J^{Am} h_m^{Ak} - w^A N^{Ak} \right) + \kappa^A \left(N^{Ak} - \rho^A u^{Ak} \right) \\ & + \Lambda_l^A \left(T^{Akl} - \frac{1}{c^2} e^A u^{Ak} u^{Al} - \frac{1}{c} u^{Ak} p^{Al} - \frac{1}{c^2} q^{Ak} u^{Al} - t^{Akl} \right). \end{aligned} \quad (35)$$

Here χ^A and κ^A are scalars, undefined for the present, and the (3+1)-split of the likewise arbitrary vector Λ_l^A is

$$\Lambda_l^A = \lambda^A u_l^A + \lambda_l^A, \quad \lambda_l^A u^{Al} = 0, \quad \lambda_j^A h_l^{Aj} = \lambda_l^A, \quad (36)$$

$$\Lambda_l^A u^{Al} = c^2 \lambda^A, \quad \Lambda_l^A h_m^{Al} = \lambda_m^A. \quad (37)$$

We denote χ^A , κ^A , λ^A and λ_l^A as “accessory variables” because they help to formulate the entropy identity. An identification of these auxiliary variables is given below after the definitions of entropy flux density, entropy production, density and supply in section 4.3.

By use of (26) and (36), the entropy identity (35) becomes

$$\begin{aligned}
 S^{Ak} \equiv & u^{Ak} \left(s^A - \chi^A \rho^A w^A - \kappa^A \rho^A - \lambda^A e^A - \frac{1}{c} \lambda_l^A p^{Al} \right) + \kappa^A N^{Ak} \\
 & + s^{Ak} + \chi^A J^{Ak} - \chi^A J^{Am} h_m^{Ak} - \lambda^A q^{Ak} + \lambda^{Ak} p^A - \lambda_l^A \pi^{Akl} + \\
 & + \left(\lambda^A u_l^A + \lambda_l^A \right) T^{Akl}. \quad (38)
 \end{aligned}$$

This identity becomes an other one by differentiation and by taking the entropy balance equation

$$S^{Ak}_{,k} = \sigma^A + \varphi^A \quad (39)$$

into account

$$\begin{aligned}
 S^{Ak}_{,k} \equiv & \left[u^{Ak} \left(s^A - \chi^A \rho^A w^A - \kappa^A \rho^A - \lambda^A e^A - \frac{1}{c} \lambda_l^A p^{Al} \right) \right]_{,k} + \\
 & + \left[s^{Ak} - \chi^A J^{Am} h_m^{Ak} - \lambda^A q^{Ak} + \lambda^{Ak} p^A - \lambda_l^A \pi^{Akl} \right]_{,k} + \\
 & + \kappa^A \Gamma^A + \kappa^A_{,k} N^A + \chi^A_{,k} J^{Ak} + \chi^A J^{Ak}_{,k} + \\
 & + \left(\lambda^A u_l^A \right)_{,k} T^{Akl} + \lambda^A u_l^A T^{Akl}_{,k} + \lambda^A_{,l,k} T^{Akl} + \lambda_l^A T^{Akl}_{,k} = \sigma^A + \varphi^A. \quad (40)
 \end{aligned}$$

Here, σ^A is the entropy production and φ^A the entropy supply of the A -component. The identity (40) changes into the entropy production, if s^A , s^{Ak} and φ^A are specified below.

The terms of the last row of (40) are scalars which do not contribute to the interior of the second bracket of (40). This bracket contains the entropy flux density s^{Ak} and additionally further tensors which all are perpendicular to the 4-velocity u^{Ak} . The scalars of the last row of (40) do also not contribute to the first row of (40) because the factor u^{Ak} times a scalar is missing.

The first and the third term of the fourth row of (40) become

$$\begin{aligned}
 (\lambda^A u_l^A)_{,k} T^{Akl} &= \\
 &= \left(\lambda^A_{,k} u_l^A + \lambda^A u^A_{l,k} \right) \left(\frac{1}{c^2} e^A u^{Ak} u^{Al} + \frac{1}{c} u^{Ak} p^{Al} + \frac{1}{c^2} q^{Ak} u^{Al} + t^{Akl} \right) = \\
 &= \lambda^A_{,k} u^{Ak} e^A + \frac{1}{c} \lambda^A u^A_{l,k} u^{Ak} p^{Al} + \lambda^A_{,k} q^{Ak} - \underline{p^A \lambda^A u^{Ak}_{,k}} + \lambda^A u^A_{l,k} \pi^{Akl}, \quad (41)
 \end{aligned}$$

and taking (26) and (14)₁ into account⁴

$$\begin{aligned}
 \lambda^A_{l,k} T^{Akl} &= \lambda^A_{l,k} \left(\frac{1}{c^2} e^A u^{Ak} u^{Al} + \frac{1}{c} u^{Ak} p^{Al} + \frac{1}{c^2} q^{Ak} u^{Al} + t^{Akl} \right) = \\
 &= \lambda^A_{l,k} u^{Ak} \frac{1}{c^2} e^A u^{Al} + \lambda^A_{l,k} u^{Ak} \frac{1}{c} p^{Al} + \frac{1}{c^2} \lambda^A_{l,k} q^{Ak} u^{Al} - \\
 &\quad - \underbrace{\lambda^A_{l,k} p^A h^{Akl}} + \lambda^A_{l,k} \pi^{Akl}. \quad (42)
 \end{aligned}$$

⁴the signs \square , $\widehat{\square}$, $\underbrace{\square}$ and $\widetilde{\square}$ mark terms which are related to each other in the sequel

Summing up (41) and (42) results in

$$\begin{aligned}
 (\lambda^A u_l^A)_{,k} T^{Akl} + \lambda^A_{l,k} T^{Akl} &= \\
 &= \left(\lambda^A_{,k} + \lambda^A_{l,k} \frac{1}{c^2} u^{Al} \right) \left(q^{Ak} + e^A u^{Ak} \right) + \\
 &+ \left(\lambda^A u^A_{l,k} + \lambda^A_{l,k} \right) \left(\pi^{Akl} + u^{Ak} \frac{1}{c} p^{Al} \right) - \underline{p^A \lambda^A u^{Ak}}_{,k} - \overbrace{\lambda^A_{l,k} p^A h^{Akl}}. \quad (43)
 \end{aligned}$$

The terms which contain the pressure p^A do not fit in the brackets. Evidently, the term $\underline{p^A \lambda^A u^{Ak}}_{,k}$ belongs to the first row of (40), and the second term can be split by taking (14)₁ into account

$$-\overbrace{\lambda^A_{l,k} p^A h^{Akl}} = -\lambda^{Ak}_{,k} p^A + \frac{1}{c^2} \lambda^A_{l,k} p^A u^{Ak} u^{Al}. \quad (44)$$

In the next section, we now specify s^A , s^{Ak} and φ^A .

4.2. Exploitation of the entropy identity.

4.2.1. Entropy density, Gibbs and Gibbs-Duhem equations. Performing the derivation in the first row of (40) and inserting the underlined term of (41) into the first row of (40), we obtain by use of (1)₁⁵

$$\begin{aligned}
 u^{Ak}_{,k} \left(s^A - \chi^A \rho^A w^A - \kappa^A \rho^A - \lambda^A e^A - \underline{p^A \lambda^A} - \frac{1}{c} \lambda_l^A p^{Al} \right) + \\
 + \left(s^A - \chi^A \rho^A w^A - \kappa^A \rho^A - \lambda^A e^A - \underline{p^A \lambda^A} - \frac{1}{c} \lambda_l^A p^{Al} \right)^{\bullet} + \left(p^A \lambda^A \right)^{\bullet} = \\
 = \left[u^{Ak} \left(s^A - \chi^A \rho^A w^A - \kappa^A \rho^A - \lambda^A e^A - p^A \lambda^A - \frac{1}{c} \lambda_l^A p^{Al} \right) \right]_{,k} + \left(\widetilde{p^A \lambda^A} \right)^{\bullet}. \quad (45)
 \end{aligned}$$

We now define the entropy density s^A according to the round bracket in (45)₂

Setting II:

$$s^A \stackrel{\bullet}{=} \chi^A \rho^A w^A + \kappa^A \rho^A + \lambda^A e^A + p^A \lambda^A + \frac{1}{c} \lambda_l^A p^{Al}. \quad (46)$$

The specific entropy with regard to the mass density of the mixture is

$$c^A := \frac{\rho^A}{\rho} : \quad \frac{s^A}{\rho} = (\chi^A w^A + \kappa^A) c^A + \lambda^A \frac{e^A}{\rho} + p^A \lambda^A \frac{1}{\rho} + \frac{1}{c} \lambda_l^A \frac{p^{Al}}{\rho} \quad (47)$$

which corresponds to the non-equilibrium state space which does not contain the accessory variables (Schellstede 2016)

$$\mathbf{z} = \left(c^A, \frac{1}{\rho}, \frac{e^A}{\rho}, \frac{p^{Al}}{\rho} \right). \quad (48)$$

These state space variables have the following meaning: c^A , $1/\rho$ and e^A/ρ are equilibrium variables, p^{Al}/ρ is a non-equilibrium variable extending the equilibrium sub-space in the

⁵ \bullet is the "component time derivative" $\boxplus^A := \boxplus^A_{,k} u^{Ak}$

sense of Extended Thermodynamics. The corresponding Gibbs equation according to (47) and (48) is

$$\left(\frac{s^A}{\rho}\right)^\bullet = (\chi^A w^A + \kappa^A)^\bullet c^A + p^A \lambda^A \left(\frac{1}{\rho}\right)^\bullet + \lambda^A \left(\frac{e^A}{\rho}\right)^\bullet + \frac{1}{c} \lambda_l^A \left(\frac{p^{Al}}{\rho}\right)^\bullet. \quad (49)$$

Differentiation of (47) results in the Gibbs-Duhem equation by taking (49) into account

$$0 = (\chi^A w^A)^\bullet c^A + \dot{\kappa}^A c^A + (p^A \lambda^A)^\bullet \frac{1}{\rho} + \dot{\lambda}^A \frac{e^A}{\rho} + \frac{1}{c} \dot{\lambda}_l^A \frac{p^{Al}}{\rho}, \quad (50)$$

$$\rightarrow (\widetilde{p^A \lambda^A})^\bullet = -(\chi^A w^A)^\bullet \rho^A - \dot{\kappa}^A \rho^A - \dot{\lambda}^A e^A - \frac{1}{c} \dot{\lambda}_l^A p^{Al}. \quad (51)$$

According to (45) and (46), the first row of (40) becomes $(\widetilde{p^A \lambda^A})^\bullet$.

4.2.2. Entropy flux, supply and production. According to the second row of (40), we define the entropy flux density

Setting III:

$$S^{Ak} \equiv \lambda^A q^{Ak} + \chi^A J^{Am} h_m^{Ak} - \lambda^{Ak} p^A + \lambda_l^A \pi^{Akl}. \quad (52)$$

Consequently, the second row of the entropy identity vanishes and (40) becomes by taking (51), (52), (43) and (44) into account

$$\begin{aligned} S^{Ak}{}_{,k} \equiv & - (\chi^A w^A)^\bullet \rho^A - \underbrace{\dot{\kappa}^A \rho^A}_{\text{marked}} - \underbrace{\dot{\lambda}^A e^A}_{\text{marked}} - \frac{1}{c} \underbrace{\dot{\lambda}_l^A p^{Al}}_{\text{marked}} + \\ & + \underbrace{\kappa^A \Gamma^A + \kappa^A{}_{,k} N^{Ak}}_{\text{marked}} + \chi^A{}_{,k} J^{Ak} + \chi^A J^{Ak}{}_{,k} + \lambda^A u_l^A T^{Akl}{}_{,k} + \lambda_l^A T^{Akl}{}_{,k} + \\ & + \left(\lambda^A{}_{,k} + \lambda^A{}_{l,k} \frac{1}{c^2} u^{Al} \right) \left(q^{Ak} + \frac{e^A u^{Ak}}{c} \right) + \\ & + \left(\lambda^A u^A{}_{l,k} + \lambda^A{}_{l,k} \right) \left(\pi^{Akl} + u^{Ak} \frac{1}{c} p^{Al} \right) - \\ & - \lambda^{Ak}{}_{,k} p^A + \frac{1}{c^2} \lambda^A{}_{l,k} p^A u^{Ak} u^{Al} = \sigma^A + \varphi^A. \end{aligned} \quad (53)$$

The marked terms cancel each other, and we obtain

$$\begin{aligned} S^{Ak}{}_{,k} \equiv & - (\chi^A w^A)^\bullet \rho^A + \chi^A{}_{,k} J^{Ak} + \\ & + \kappa^A \Gamma^A + \chi^A J^{Ak}{}_{,k} + \lambda^A u_l^A T^{Akl}{}_{,k} + \lambda_l^A T^{Akl}{}_{,k} + \\ & + \left(\lambda^A{}_{,k} + \lambda^A{}_{l,k} \frac{1}{c^2} u^{Al} \right) q^{Ak} + \lambda^A{}_{l,k} \frac{1}{c^2} u^{Al} e^A u^{Ak} + \\ & + \left(\lambda^A u^A{}_{l,k} + \lambda^A{}_{l,k} \right) \pi^{Akl} + \lambda^A u^A{}_{l,k} u^{Ak} \frac{1}{c} p^{Al} - \\ & - \lambda^{Ak}{}_{,k} p^A + \frac{1}{c^2} \lambda^A{}_{l,k} p^A u^{Ak} u^{Al} = \sigma^A + \varphi^A. \end{aligned} \quad (54)$$

We now split the entropy identity (54) into the entropy production and the entropy supply. For this end, we need a criterion to distinguish the production from the supply. Such a criterion is clear for discrete systems: a local isolation suppresses the entropy supply but not the entropy production. Here for systems in field formulation, we cannot apply the local

isolation. Instead of that, we define the entropy supply by terms which contain the energy and momentum supply, (20) and (21) and beyond that divergencies. The entropy production is characterized by gradients and fluxes. Consequently, we define the entropy supply

Setting IV:

$$\begin{aligned} \chi^A J^{Ak}{}_{,k} + \lambda^A u_l^A T^{Akl}{}_{,k} + \lambda_l^A T^{Akl}{}_{,k} - \lambda^{Ak}{}_{,k} p^A &= \\ &= \chi^A J^{Ak}{}_{,k} + \lambda^A u_l^A k^{Al} + \lambda_m^A k^{Am} - \lambda^{Ak}{}_{,k} p^A \doteq \varphi^A. \end{aligned} \quad (55)$$

Taking (16)₁ into account, the first row of (54) results in

$$\chi^A{}_{,k} J^{Ak} - \dot{\chi}^A p^A w^A - \chi^A \dot{w}^A p^A = \chi^A{}_{,k} J^{Am} h_m^{Ak} - \chi^A \dot{w}^A p^A, \quad (56)$$

and according to (55), the entropy identity changes in the entropy production

$$\begin{aligned} \sigma^A &= \chi^A{}_{,k} J^{Am} h_m^{Ak} - \chi^A \dot{w}^A p^A + \kappa^A \Gamma^A + \\ &+ \left(\lambda^A{}_{,k} + \lambda^A{}_{l,k} \frac{1}{c^2} u^{Al} \right) q^{Ak} + \lambda^A{}_{l,k} \frac{1}{c^2} u^{Al} e^A u^{Ak} + \\ &+ \left(\lambda^A u^A{}_{l,k} + \lambda^A{}_{l,k} \right) \pi^{Akl} + \lambda^A u^A{}_{l,k} u^{Ak} \frac{1}{c} p^{Al} - \\ &+ \frac{1}{c^2} \lambda^A{}_{l,k} p^A u^{Ak} u^{Al}. \end{aligned} \quad (57)$$

A rearranging results in

$$\begin{aligned} \sigma^A &= \chi^A{}_{,k} J^{Am} h_m^{Ak} - \chi^A \dot{w}^A p^A + \kappa^A \Gamma^A + \\ &+ \lambda^A{}_{,k} q^{Ak} + \lambda^A{}_{l,k} \frac{1}{c^2} u^{Al} \left(q^{Ak} + e^A u^{Ak} \right) + \\ &+ \lambda^A u^A{}_{l,k} \left(\pi^{Akl} + u^{Ak} \frac{1}{c} p^{Al} \right) + \lambda^A{}_{l,k} \pi^{Akl} + \\ &+ \frac{1}{c^2} \lambda^A{}_{l,k} p^A u^{Ak} u^{Al}, \end{aligned} \quad (58)$$

and finally, the entropy production becomes

$$\begin{aligned} \sigma^A &= \chi^A{}_{,k} J^{Am} h_m^{Ak} + \kappa^A \Gamma^A + \\ &+ \lambda^A{}_{,k} q^{Ak} + \lambda^A u^A{}_{l,k} \left(\pi^{Akl} + u^{Ak} \frac{1}{c} p^{Al} \right) - \\ &- \chi^A \dot{w}^A p^A + \lambda^A{}_{l,k} \left[\pi^{Akl} + \frac{1}{c^2} u^{Al} \left(q^{Ak} + (e^A + p^A) u^{Ak} \right) \right]. \end{aligned} \quad (59)$$

The first four terms of the entropy production describe the classical four reasons of irreversibility: diffusion, chemical reactions, heat conduction and internal friction with a modified viscous tensor according to the chosen state space (48). To these irreversible processes belong the following four accessory variables: χ^A , κ^A , λ^A and λ_l^A . The last two terms⁶ are typical for an interacting 1-component system as a part of the mixture.

The expressions of entropy density, production and supply and the entropy flux density contain these accessory variables which are introduced for formulating the entropy identity

⁶which vanish in equilibrium and for free 1-component systems as we will see below

playing up to here the role of place-holders. Their physical meaning is discussed in the next Section.

4.3. Accessory variables. Starting out with (46), we have the following equation of physical dimensions

$$[s^A] = [\lambda^A][e^A]. \quad (60)$$

Taking (34)₁ and (29) into account, we obtain

$$\frac{N}{m^2} \frac{1}{K} = [\lambda^A] \frac{N}{m^2} \longrightarrow [\lambda^A] = \frac{1}{K}, \quad (61)$$

that means, λ^A is a reciprocal temperature belonging to the A -component. Therefore, we accept the following

Setting V:

$$\lambda^A \doteq \frac{1}{\Theta^A}. \quad (62)$$

Here, Θ^A is the temperature of the A -component⁷.

Starting out with (52), we have the following equation of physical dimensions

$$[s^{Ak}] = [\chi^A][J^{Am}][t_m^{Ak}]. \quad (63)$$

Taking (34)₂, (11)₂ and (28)₁ into account, we obtain

$$\frac{N}{ms} \frac{1}{K} = [\chi^A] \frac{kg}{m^3} \frac{m}{s} 1 \longrightarrow [\chi^A] = \frac{m^2}{s^2} \frac{1}{K} = \frac{N}{m^2} \frac{m^3}{kg} \frac{1}{K} = [\kappa^A], \quad (64)$$

and according to the the first row of (38), the physical dimensions of χ^A and κ^A are equal. We know from the non-relativistic Gibbs equation that the chemical potentials μ^A have the physical dimension of the specific energy e^A/ρ

$$[\mu^A] = \frac{[e^A]}{[\rho]} = \frac{N}{m^2} \frac{m^3}{kg} = K[\chi^A] = K[\kappa^A]. \quad (65)$$

Because χ^A belongs to diffusion and κ^A to chemical reactions, we make the following choice by taking (65) into consideration

Setting VI:

$$\chi^A \doteq \kappa^A \doteq -\lambda^A \mu^A. \quad (66)$$

Starting out with (52), we have the following equation of physical dimensions

$$[s^{Ak}] = [\lambda^{Ak}][p^A]. \quad (67)$$

Taking (34)₂ and (30) into account, we obtain

$$\frac{N}{ms} \frac{1}{K} = [\lambda^{Ak}] \frac{N}{m^2} \longrightarrow [\lambda^{Ak}] = \frac{m}{s} \frac{1}{K}. \quad (68)$$

⁷This temperature is a non-equilibrium one, the contact temperature Muschik 1977; Muschik and Brunk 1977 which should not be confused with the thermostatic equilibrium temperature T^A .

By taking (36)₂ into account, we define

Setting VII:

$$\lambda^{Ak} \doteq \lambda^A u^m h_m^{Ak}. \quad (69)$$

According to (66)₁ and (69), we obtain

$$\chi^A_{,k} = -\lambda^A_{,k} \mu^A - \lambda^A \mu^A_{,k}, \quad (70)$$

$$\lambda^A_{l,k} = (\lambda^A u_m h_l^{Am})_{,k} = \lambda^A_{,k} u_m h_l^{Am} + \lambda^A (u_m h_l^{Am})_{,k} \quad (71)$$

Inserting (70) and (71) into (59), the entropy production change in another expression

$$\begin{aligned} \sigma^A = & -\lambda^A \mu^A_{,k} J^{Am} h_m^{Ak} - \lambda^A \mu^A (\Gamma^A - \dot{w}^A \rho^A) + \\ & + \lambda^A_{,k} (q^{Ak} - \mu^A J^{Am} h_m^{Ak} + u_m h_l^{Am} \pi^{Akl}) \\ & + \lambda^A u^A_{l,k} (\pi^{Akl} + u^{Ak} \frac{1}{c} p^{Al}) + \\ & + \lambda^A (u_m h_l^{Am})_{,k} [\pi^{Akl} + \frac{1}{c^2} u^{Al} (q^{Ak} + (e^A + p^A) u^{Ak})]. \end{aligned} \quad (72)$$

This expression for the entropy production is composed of following parts:

- diffusion and chemical reactions with a modified mass production term in the first row of (72),
- heat conduction with a modified heat flux density in the second row,
- internal friction with a modified viscous tensor in the third row and
- an additional term describing the fact that the ^A-component is a component of the mixture.

Inserting the accessory variables in the expression of entropy density (46), of entropy flux density (52) and of entropy supply (55) we obtain

$$s^A = -\lambda^A \mu^A (w^A + 1) \rho^A + \lambda^A e^A + p^A \lambda^A + \frac{1}{c} \lambda^A u_m h_l^{Am} p^{Al}, \quad (73)$$

$$s^{Ak} = \lambda^A q^{Ak} - \lambda^A \mu^A J^{Am} h_m^{Ak} - \lambda^A u^m h_m^{Ak} p^A + \lambda^A u_m h_l^{Am} \pi^{Akl} \quad (74)$$

$$\varphi^A = -\lambda^A \mu^A J^{Ak}_{,k} + \lambda^A u^A_l k^{Al} + \lambda^A u_p h_m^{Ap} k^{Am} - (\lambda^A u^m h_m^{Ak})_{,k} p^A. \quad (75)$$

The transition from the interacting ^A-component to the free 1-component system is considered in sect.5. All quantities introduced up to here are non-equilibrium ones, because we did not consider equilibrium conditions up to now. This will be done in the next section.

4.4. Equilibrium conditions. Equilibrium is defined by *equilibrium conditions* which are divided into necessary and *supplementary* ones (Muschik and Borzeszkowski 2009, 2015). The necessary equilibrium conditions are given by vanishing entropy production, vanishing entropy flux density and vanishing entropy supply⁸:

$$\sigma_{eq}^A \doteq 0 \quad \wedge \quad s_{eq}^{Ak} \doteq 0 \quad \wedge \quad \varphi_{eq}^A \doteq 0. \quad (76)$$

⁸The sign \doteq stands for a setting which implements an equilibrium condition.

A first supplementary equilibrium condition is the vanishing of all diffusion flux densities. According to (11)₁, we obtain

$$J_k^{Aeq} \doteq 0 \quad \longrightarrow \quad u_k^{Aeq} = f_{eq}^A u_k^{eq} \quad \longrightarrow \quad c^2 = f_{eq}^A u_k^{eq} u_{eq}^{Ak}. \quad (77)$$

Taking (7)₁ into account, (77)₃ results in

$$(f_{eq}^A)^2 = 1 \quad \longrightarrow \quad f_{eq}^A = \pm 1. \quad (78)$$

Consequently, we have to demand beyond (77)₁ the supplementary equilibrium condition that the mass densities are additive in equilibrium

$$\rho_{eq} \doteq \sum_A \rho_{eq}^A \quad \longrightarrow \quad f_{eq}^A = 1 \quad \longrightarrow \quad w_{eq}^A = 0, \quad (79)$$

according to (7)₂ and (13)₂. Taking (77)₂ and (69) into account, (79)₂ yields

$$u_k^{Aeq} = u_k^{eq} \quad \longrightarrow \quad \lambda_{eq}^{Ak} = 0. \quad (80)$$

Further supplementary equilibrium conditions are given by vanishing covariant time derivatives, except that of the four-velocity:

$$\boxplus_{eq}^\bullet \doteq 0, \quad \boxplus \neq u^l, \quad (81)$$

that means \dot{u}_{eq}^l is in general not zero in equilibrium. Consequently, the time derivatives of all expressions which contain the 4-velocity must be calculated separately, as we will see below.

According to (81)₁, we obtain

$$\dot{\rho}_{eq}^A = 0, \quad \dot{\lambda}_{eq}^A = 0, \quad (82)$$

and the (3+1)-components of the energy-momentum tensor, (23) and (24), satisfy

$$\dot{e}_{eq}^A = 0, \quad \dot{p}_{eq}^{Al} = 0, \quad \dot{q}_{eq}^{Ak} = 0, \quad \dot{p}_{eq}^A = 0, \quad \dot{\pi}_{eq}^{Akl} = 0. \quad (83)$$

Starting out with (7)₁, we have

$$\dot{f}_{eq}^A = \frac{1}{c^2} \left(\dot{u}_m^{Aeq} u_{eq}^m + u_m^{Aeq} \dot{u}_{eq}^m \right). \quad (84)$$

Taking (80)₁ into account, this results in

$$\dot{f}_{eq}^A = 0 \quad \longrightarrow \quad \dot{w}_{eq}^A = 0. \quad (85)$$

According to (69), we obtain

$$\lambda_{l,k}^A = \left(\lambda^A u_m h_l^{Am} \right)_{,k} = \lambda_{,k}^A u_m h_l^{Am} + \lambda^A u_{m,k} h_l^{Am} + \lambda^A u_m h_{l,k}^{Am}. \quad (86)$$

In equilibrium, we have according to (80)₁ and (14)

$$h_{l,eq}^{Am} = h_{l,eq}^m. \quad (87)$$

Consequently, the first term of the RHS of (86) vanishes in equilibrium, and only the δ_l^m remains in the second term. Thus, we obtain

$$\lambda^{Aeq}{}_{l,k} = \lambda_{eq}^A u_{l,k}^{eq} - \frac{1}{c^2} \lambda_{eq}^A u_m^{eq} \left(u_{,k}^{meq} u_l^{eq} + u_{eq}^m u_{l,k}^{eq} \right) = 0. \quad (88)$$

Consequently, the time derivatives of the accessory variables vanish in equilibrium, and according to (49) and (50), Gibbs and Gibbs–Duhem equations are identically satisfied in equilibrium.

Taking (79)₃ and (87) into account, the entropy density (73) becomes in equilibrium

$$s_{eq}^A = \lambda_{eq}^A \left(e_{eq}^A + p_{eq}^A - \mu_{eq}^A \rho_{eq}^A \right). \quad (89)$$

This is the usual expression for the entropy density in thermostatics. The energy density and the pressure are here defined by the (3+1)-decomposition (22) of the energy-momentum tensor. The chemical potential is as well as the temperature introduced as an accessory variable.

Taking (76)₂, (77)₁ and (87) into account, the entropy flux density (74) results in

$$0 = q_k^{Aeq}, \quad (90)$$

and finally taking (77)₁, (87) and (88) into account, the entropy supply (75) results in

$$0 = u_l^{Aeq} k_{eq}^{Al}, \quad (91)$$

that means, the power vanishes in equilibrium.

Another supplementary equilibrium condition is the vanishing of the production term in (1)₂

$$\Gamma_{eq}^A \doteq 0. \quad (92)$$

Thus, we obtain from (1), (82)₁ and (92)

$$\rho^A{}_{,k} u^{Ak} + \rho^A u^{Ak}{}_{,k} = \Gamma^A \quad \longrightarrow \quad u_{eq}^{Ak}{}_{,k} = 0. \quad (93)$$

The entropy production (72) has to vanish in equilibrium according to the necessary equilibrium condition (76)₁. Taking (77)₁, (90), (83)₂ and (88) into account, we obtain

$$0 = u^{Aeq}{}_{l,k} \pi_{eq}^{Akl}. \quad (94)$$

As demonstrated in this section, the non-equilibrium expressions of the A component in the mixture for the entropy density, flux, production and supply are compatible with the corresponding equilibrium expressions. According to (80)₁, the mixture looks like an 1-component system in equilibrium. But different is, how to deal with free 1-component systems in non-equilibrium which are considered in the next section.

5. Thermodynamics (Free Component)

A free 1-component system⁹ can be described by setting equal all component indices of a multi-component system

$$A, B, C, \dots, Z \longrightarrow 0, \quad (95)$$

and for shortness, we omit this common index 0. Then the basic fields are according to (2)

$$\text{rest mass density and 4-velocity: } \{\rho, u_k\}. \quad (96)$$

The equations (4) of Setting I change in identities. According to (7)₁, (11)₁, (13)₂ and (19), we have

$$f = 1, \quad J_k = 0, \quad w = 0, \quad T^{kl},{}_{,k} = k^l. \quad (97)$$

The accessory variables become according to (62), (66) and (69)

$$\lambda = \frac{1}{\Theta}, \quad \chi = \kappa = -\lambda\mu, \quad \lambda^k = 0. \quad (98)$$

The state space (48) and the entropy density (73) are as in equilibrium of the A -component (89)

$$z = \left(\frac{1}{\rho}, \frac{e}{\rho}, \frac{p^l}{\rho} \right), \quad s^A = \lambda^A \left(e^A + p^A - \mu^A \rho^A \right). \quad (99)$$

The entropy flux (73), the entropy supply (75) and the entropy production (72) are

$$s^k = \lambda q^k, \quad \varphi = \lambda u_l k^l, \quad \sigma = \lambda_{,k} q^k + \lambda u_{l,k} \left(\pi^{kl} + u^k \frac{1}{c} p^l \right) - \lambda \mu \Gamma. \quad (100)$$

Another expressions for the entropy production (100)₃ is according to (22)

$$\sigma = \lambda_{,k} q^k + \lambda u_{l,k} \left(T^{kl} - \frac{1}{c^2} e u^k u^l - \frac{1}{c^2} q^k u^l + p h^{kl} \right) - \lambda \mu \Gamma. \quad (101)$$

This expression can be transformed by taking

$$-\lambda u_{l,k} \frac{1}{c^2} q^k u^l = 0 \quad (102)$$

into account. Consequently, (101) yields

$$\sigma = \lambda_{,k} q^k + \left[(\lambda u_l)_{,k} - \lambda_{,k} u_l \right] \left(T^{kl} - \frac{1}{c^2} e u^k u^l + p h^{kl} \right) - \lambda \mu \Gamma. \quad (103)$$

Taking according to (22)

$$u_l T^{kl} = e u^k + q^k \quad (104)$$

into account, the entropy production (103) becomes

$$\sigma = (\lambda u_l)_{,k} \left(T^{kl} - \frac{1}{c^2} e u^k u^l + p h^{kl} \right) - \lambda \mu \Gamma. \quad (105)$$

⁹that is not a mixture which is treated elsewhere

We now consider the three terms in the bracket of (105) separately. Taking (22) into account, (105) becomes

$$\begin{aligned} (\lambda_{,k}u_l + \lambda u_{l,k}) \left(\frac{1}{c^2} e u^k u^l + \frac{1}{c} u^k p^l + \frac{1}{c^2} q^k u^l - p h^{kl} + \pi^{kl} \right) = \\ = \dot{\lambda} e - \lambda u_l \frac{1}{c} \dot{p}^l + \lambda_{,k} q^k - \lambda p u^k_{,k} + \lambda u_{l,k} \pi^{kl}, \end{aligned} \quad (106)$$

$$-(\lambda_{,k}u_l + \lambda u_{l,k}) \frac{1}{c^2} e u^k u^l = -\dot{\lambda} e, \quad (107)$$

$$(\lambda_{,k}u_l + \lambda u_{l,k}) p h^{kl} = \lambda p u^k_{,k}. \quad (108)$$

The necessary equilibrium conditions are (76)₁ and (92), and (105) yields

$$0 = (\lambda u_l)_{,k}^{eq} \left(T^{kl} - \frac{1}{c^2} e u^k u^l + p h^{kl} \right)^{eq}. \quad (109)$$

According to (106) to (108), this equilibrium condition is satisfied by

$$\begin{aligned} (\lambda u_l)_{,k}^{eq} \neq 0: \\ (\lambda u_l)_{,k}^{eq} T^{kl} = 0, \quad (\lambda u_l)_{,k}^{eq} e^{eq} u_{eq}^k u_{eq}^l = 0, \quad (\lambda u_l)_{,k}^{eq} p^{eq} h_{eq}^{kl} = 0. \end{aligned} \quad (110)$$

Consequently, (109) does not enforce $(\lambda u_l)_{,k}^{eq} = 0$. Also the setting

$$T_{eq}^{kl} \stackrel{?}{=} \frac{1}{c^2} e^{eq} u_{eq}^k u_{eq}^l - p^{eq} h_{eq}^{kl} \quad (111)$$

would demand further supplementary equilibrium conditions according to (22):

$$p_{eq}^l \stackrel{?}{=} 0, \quad \pi_{eq}^{kl} \stackrel{?}{=} 0 \quad (112)$$

which both are beyond (83)₂ and (94). Therefore we deny (111) and (112), and $(\lambda u_l)_{,k}^{eq} = 0$ is not an equilibrium condition because of the validity of (110). This property carries over to the Killing relation of the 4-temperature λu_l

$$\left((\lambda u_l)_{,k} + (\lambda u_k)_{,l} \right)^{eq} \stackrel{?}{=} 0 \quad (113)$$

in case of a symmetric energy-momentum tensor. The derivative of the 4-temperature and the Killing relation are rather conditions for reversible processes because they enforce the entropy production to be zero without existing equilibrium

$$(\lambda u_l)_{,k}^{rev} = 0, \quad \text{or } T^{kl} = T^{lk}: \left((\lambda u_l)_{,k} + (\lambda u_k)_{,l} \right)^{rev} = 0. \quad (114)$$

A comparison of (110) with (114) points out the difference between equilibrium and reversible processes.

6. Summary

Starting out with the rest mass densities of the components of the multi-component system, the mass flux densities of the components are defined by introducing their different 4-velocities. The mixture of the components is characterized by several settings. The first one is the additivity of the component's mass flux densities to the mass flux density of the mixture. In combination with the mixture axiom, this setting allows to define mass density and 4-velocity of the mixture and the diffusion fluxes of the components. The

non-symmetric energy-momentum tensor of one component interacting with the mixture is introduced, and its (3+1)-split together with the component's mass and diffusion flux densities are generating the entropy identity Muschik and Borzeszkowski 2009. The exploitation of the entropy identity requires additional settings: the entropy density, flux and supply. These settings are led by physical interpretations of entropy density, flux and supply. The entropy production follows from the entropy identity which restricts possible arbitrariness of defining.

The use of the entropy identity introduces so-called accessory variables. These are temperature, chemical potential and an additional non-equilibrium variable which characterizes the considered component to be a part of the mixture. Beside the classical irreversible processes –diffusion, chemical reactions, heat conduction and friction– an additional irreversible process appears due to the embedding of the considered component into the mixture. Different from the classical case, the mass production term, the heat flux density and the viscous tensor are modified, so-called effective quantities.

Equilibrium is defined by equilibrium conditions which are divided into necessary and supplementary ones (Muschik and Borzeszkowski 2009; Borzeszkowski *et al.* 2010; Muschik and Borzeszkowski 2015). The necessary equilibrium conditions are given by vanishing entropy production, vanishing entropy flux density and vanishing entropy supply. Supplementary equilibrium conditions are: vanishing diffusion flux densities, vanishing component time derivatives¹⁰ and vanishing of the mass production terms. Presupposing these equilibrium conditions, we obtain: all components have the same 4-velocity, all heat flux densities are zero, the power as well as the divergence of the 4-velocity of each component vanish, and the viscous tensor is perpendicular to the velocity gradient.

The corresponding free component is defined by undistinguishable component indices¹¹. This 1-component system represents the easiest classical case serving as a test, if the interacting component in the mixture is correctly described. The vanishing of the entropy production in equilibrium is shortly investigated: the so-called Killing relation of the vector of 4-temperature is neither a necessary nor a sufficient condition for equilibrium. Also the statement that materials are perfect in equilibrium cannot be confirmed.

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¹⁰except that of the 4-velocity

¹¹that is not the mixture which is a multi-component system

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