Does Clausius' Inequality Analogue Exist for Open Discrete Systems ?

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Abstract

We derive two versions of Clausius inequality for open discrete systems, one formulated for the non-equilibrium system itself using contact quantities, the other one using equilibrium quantities belongs to the system's environment. Consequently Bhalekar's conjecture that there is no Clausius inequality for open systems is disproved.

1 Introduction

A.A. Bhalekar stated [1]: "...that no Clausius inequality can be arrived at for open systems" and "that the Clausius inequality is primarily a statement for a global closed system", and especially "adiabaticity has no locus standii in the case of open sytems". Because these statements are in contradiction to the Clausius inequality for open systems derived in [2] we want to investigate the question again, if there exists such an inequality for open discrete systems. Because the answer is not independent of the formulation of the first law for open systems, we will discuss it first of all. The first law for open systems contains an arbitrary split of the heat exchange into a mass-dependent part and a temperature-dependent one. In contradiction to Bhalekar's conjecture we derive Clausius inequality of open systems for arbitrary splits in two different versions: One version is formulated in quantities

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belonging to the non-equilibrium system, such as contact temperature and dynamical chemical potentials, the other version is using quantities of the system's equilibrium environment, such as its thermostatic temperature and its chemical equilibrium potentials.

2 First law for open systems

The first law for open discrete systems contains a term which describes the change of internal energy due to external mass exchange [3]. This term can be defined differently, thus determining the heat exchange for open systems [4]. First of all we will not fix this expression -we will do that in section 4- and we write down the time rate of the internal energy in the following form

$$\dot{U} = \dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) + \dot{W} + \boldsymbol{\zeta} \cdot \dot{\boldsymbol{n}}^e. \tag{1}$$

Here the heat exchange $\dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e)$ depends on the quantities $\boldsymbol{\zeta}$ which describes the change of the internal energy due to external mole number exchange $\dot{\boldsymbol{n}}^e$ and which we call the *split*. The power exchange $\dot{W}$ between the open system and its environment is independent of this split. Of course, the split is a theoretical concept, because measuring devices only indicate mass exchanges and temperatures. Consequently we have to define what a "heat" exchange between open systems should be. This definition is made by fixing the split $\boldsymbol{\zeta}$. From this consideration follows, that physical statements must be independent of the special split. Therefore changing the $\boldsymbol{\zeta}$ to $\boldsymbol{\zeta}'$ (that means choosing another split) (1) becomes

$$\dot{U} = \dot{Q}(\boldsymbol{\zeta}', \dot{\boldsymbol{n}}^e) + \dot{W} + \boldsymbol{\zeta}' \cdot \dot{\boldsymbol{n}}^e, \tag{2}$$

and we obtain by subtraction of (1) and (2)

$$\dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e) = \dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) + \boldsymbol{\zeta} \cdot \dot{\boldsymbol{n}}^e = \dot{Q}(\boldsymbol{\zeta}', \dot{\boldsymbol{n}}^e) + \boldsymbol{\zeta}' \cdot \dot{\boldsymbol{n}}^e. \tag{3}$$

This relation shows, that different splits of the internal energy per mole number can be related to the time rate of mole number. Even the whole change of internal energy per mole number can be added to the "heat" exchange $\dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e)$ which is independent of the split according to (3). For closed systems (cl, $\dot{\boldsymbol{n}}^e = \mathbf{o}$) (3) results in

$$\dot{Q}^{cl} := \dot{Q}(\mathbf{o}, \mathbf{o}) = \dot{Q}(\boldsymbol{\zeta}, \mathbf{o}) = \dot{Q}(\boldsymbol{\zeta}', \mathbf{o}). \tag{4}$$

That means, that in closed systems the value $\dot{Q}^{cl}$ of the heat exchange is of course the same for all splits.

The first law for closed systems writes

$$\dot{U}^{cl} \;=\; \dot{Q}^{cl} \;+\; \dot{W}^{cl}. \tag{5}$$

We now state that the power exchange is defined as equal for closed and for open systems, that means the power is independent of $\dot{\boldsymbol{n}}^e$ [4]

Axiom:

$$\dot{W} \;\equiv\; \dot{W}^{cl}. \tag{6}$$

Consequently (1) and (5) result in

$$\dot{U} \;=\; \dot{U}^{cl} \;+\; \dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) \;-\; \dot{Q}^{cl} \;+\; \boldsymbol{\zeta}\cdot\dot{\boldsymbol{n}}^e, \tag{7}$$

and we obtain for $\boldsymbol{\zeta} = \mathbf{o}$

$$\dot{U} \;=\; \dot{U}^{cl} \;+\; \dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e) \;-\; \dot{Q}^{cl}. \tag{8}$$

Because the difference between $\dot{U}$ and $\dot{U}^{cl}$ is caused by opening the system a special split $\boldsymbol{\zeta}^0$ exists, so that from (8) follows

$$\dot{U} \;-\; \dot{U}^{cl} \;=\; \dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e) \;-\; \dot{Q}^{cl} \;=:\; \boldsymbol{\zeta}^0\cdot\dot{\boldsymbol{n}}^e. \tag{9}$$

The special value of $\boldsymbol{\zeta}^0$ will be calculated in section 4. By use of (5), (9), and (3) we can write down a different formulation of the first law for open systems (1)

$$\dot{U} \;=\; \dot{Q}^{cl} \;+\; \dot{W} \;+\; \boldsymbol{\zeta}^0\cdot\dot{\boldsymbol{n}}^e. \tag{10}$$

A comparison of (10) with (1) results in

$$\dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) \;=\; \dot{Q}^{cl} \;+\; (\boldsymbol{\zeta}^0 - \boldsymbol{\zeta})\cdot\dot{\boldsymbol{n}}^e. \tag{11}$$

As (9) this expression describes the difference between the heat exchanges of open and closed systems. If we choose $\boldsymbol{\zeta} = \boldsymbol{\zeta}^0$, we obtain from (11)

$$\dot{Q}(\boldsymbol{\zeta}^0, \dot{\boldsymbol{n}}^e) \;=\; \dot{Q}^{cl} \;=\; \dot{Q}(\boldsymbol{\zeta}^0, \dot{\boldsymbol{n}}^e_I) \;=\; \dot{Q}(\boldsymbol{\zeta}^0, \dot{\boldsymbol{n}}^e_{II}). \tag{12}$$

That means, that the heat exchange in open systems which belongs to the special split $\boldsymbol{\zeta}^0$ has independently of the external mass exchange the same value which is, as if the system would be closed.

3 Second law for open systems

The time rate of non-equilibrium entropy is defined by [5]

$$\dot{S} \ = \ \frac{1}{\Theta}\left[\dot{Q}(\,\boldsymbol{\zeta},\,\dot{\boldsymbol{n}}^e) \ + \ \boldsymbol{\zeta}\cdot\dot{\boldsymbol{n}}^e\right] \ - \ \frac{\boldsymbol{\mu}}{\Theta}\cdot\ \dot{\boldsymbol{n}} \ + \ \Sigma, \tag{13}$$

or according to (3)

$$\dot{S} \ = \ \frac{1}{\Theta}\dot{Q}(\ \mathbf{o},\,\dot{\boldsymbol{n}}^e) - \ \frac{\boldsymbol{\mu}}{\Theta}\cdot\ \dot{\boldsymbol{n}} \ + \ \Sigma. \tag{14}$$

Here Θ is the contact temperature of the open system, $\boldsymbol{\mu}$ its dynamical chemical potentials, $\boldsymbol{n}$ the mole numbers of the components contained in the system, and Σ the entropy production [6]. The contact temperature and the dynamical chemical potentials are defined by the inequalities [7]

$$\dot{Q}^{cl}\left[\frac{1}{\Theta} \ - \frac{1}{T^\star}\right] \ \geq \ 0, \qquad \dot{\boldsymbol{n}}^e \ = \ \mathbf{o}, \quad \dot{W} \ = \ 0, \tag{15}$$

$$\dot{\boldsymbol{n}}^e\cdot(\ \boldsymbol{\mu}^\star \ - \ \boldsymbol{\mu}) \ \geq \ \mathbf{o}, \qquad \Theta \ = \ T^\star, \quad \dot{W} \ = \ 0. \tag{16}$$

Here the asterisks refer to the equilibrium environment of the system: $T^\star$ is its thermostatic temperature and $\boldsymbol{\mu}^\star$ the chemical equilibrium potentials of the environment. If we presuppose, that $\dot{Q}^{cl}$ is a continuous and strictly monotone function of the difference $1/\Theta - 1/T^\star$, then according to (15) we can prove [8]

$$\Theta \ = \ T^\star \qquad \Longleftrightarrow \qquad \dot{Q}^{cl} \ = \ \dot{Q}(\,\boldsymbol{\zeta},\ \mathbf{o}) \ = \ 0. \tag{17}$$

Therefore the contact temperature of a discrete system is the thermostatic temperature of that equilibrium environment for which the net heat exchange between the closed system and the environment vanishes. The inequality (16) is valid for each component, that means, that the mole number exchange of the j-th component $\dot{n}_j^e$ vanishes, iff the chemical potentials of the system μ_j and of its environment $\mu_j^\star$ are equal.

Splitting the rate of the mole numbers into their external parts $\dot{\boldsymbol{n}}^e$ due to mass exchange of the open system and their internal parts $\dot{\boldsymbol{n}}^i$ due to chemical reactions

$$\dot{\boldsymbol{n}} \ = \ \dot{\boldsymbol{n}}^e + \dot{\boldsymbol{n}}^i, \tag{18}$$

(13) and (14) yield

$$
\begin{aligned}
\dot{S} &= \frac{1}{\Theta}\dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) + \frac{1}{\Theta}(\boldsymbol{\zeta} - \boldsymbol{\mu}) \cdot \dot{\boldsymbol{n}}^e - \frac{\boldsymbol{\mu}}{\Theta} \cdot \dot{\boldsymbol{n}}^i + \Sigma, && (19)\\
\dot{S} &= \frac{1}{\Theta}\dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e) - \frac{1}{\Theta}\boldsymbol{\mu} \cdot \dot{\boldsymbol{n}}^e - \frac{\boldsymbol{\mu}}{\Theta} \cdot \dot{\boldsymbol{n}}^i + \Sigma. && (20)
\end{aligned}
$$

By definition the entropy production σ in a discrete system is the entropy rate of the isolated system ($\dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) = 0, \quad \dot{\boldsymbol{n}}^e = \mathbf{o}$), that means according to (19)

$$
\sigma = -\frac{\boldsymbol{\mu}}{\Theta} \cdot \dot{\boldsymbol{n}}^i + \Sigma. \tag{21}
$$

Here we now use an extended formulation of the second law (2nd law IV in [9]) which states, that the entropy production is not negative for all times

$$
\sigma(t) \geq 0. \tag{22}
$$

By integrating (19) along an arbitrary cyclic process performed by the considered system which contains at least one equilibrium state, we obtain

$$
{}^{+}\!\!\oint \dot{S}dt = {}^{+}\!\!\oint \frac{1}{\Theta}\left[\dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) + (\boldsymbol{\zeta} - \boldsymbol{\mu}) \cdot \dot{\boldsymbol{n}}^e\right] dt + {}^{+}\!\!\oint \sigma dt. \tag{23}
$$

Here $^+$ indicates, that the chosen cyclic process contains at least one equilibrium state. The non-equilibrium entropy S satisfies the *Embedding Axiom* [10]:

$$
{}^{+}\!\!\oint \dot{S}dt = 0 \tag{24}
$$

which states, that the equilibrium entropy is a unique state function on the equilibrium sub-space. According to (22) (2nd law III in [9])

$$
{}^{+}\!\!\oint \sigma dt \geq 0 \tag{25}
$$

holds, and we obtain from (23) and (24) the extended Clausius inequality for open systems

$$
{}^{+}\!\!\oint \frac{1}{\Theta}\left[\dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) + (\boldsymbol{\zeta} - \boldsymbol{\mu}) \cdot \dot{\boldsymbol{n}}^e\right] dt \leq 0 \tag{26}
$$

which already was derived in [2] by a simulation procedure presupposing a weak formulation of Clausius inequality for open systems. The extended

Clausius inequality (26) follows here from the strong formulation of the second law (22). But even if σ is not definite, the extended Clausius inequality follows also from the weaker formulation of the second law (25). In any way (26) is valid for an arbitrary splitting $\boldsymbol{\zeta}$ of the heat exchange. Introducing (11) the extended Clausius inequality (26) becomes

$$^{+}\oint \frac{1}{\Theta}\left[\dot{Q}^{cl} \ + \ (\boldsymbol{\zeta}^{0} - \ \boldsymbol{\mu})\cdot \dot{\boldsymbol{n}}^{e}\right] dt \ \leq \ 0 \tag{27}$$

containing $\boldsymbol{\zeta}^0$ which is derived in section 4.

Heat and mass exchange between the considered system and its environment depends on the properties of the partition between them. There may be active partitions, heating system and environment, or mass absorbing partitions. Here the interaction between system and environment is achieved by a so-called *inert partition* which is defined by

$$\dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^{e}) \ = \ -\dot{Q}^{\star}(\mathbf{o}, \dot{\boldsymbol{n}}^{e\star}), \tag{28}$$

$$\dot{\boldsymbol{n}}^{e} \ = \ -\dot{\boldsymbol{n}}^{e\star}. \tag{29}$$

This means, that inert partitions do not absorb or emit energy and mass and do not cause chemical surface reactions.

The inequalities (15) and (16) are only valid taking the constraints on their right-hand sides into account. The question arises: What is the shape of these inequalities in the general case? The entropy rate of the reversible environment is according to (20)

$$\dot{S}^{\star} \ = \ \frac{1}{T^{\star}}\dot{Q}^{\star}(\mathbf{o}, \dot{\boldsymbol{n}}^{e\star}) \ - \ \frac{1}{T^{\star}}\,\boldsymbol{\mu}^{\star}\cdot\dot{\boldsymbol{n}}^{e\star}. \tag{30}$$

Presupposing that the compound system composed of the system in consideration and its environment is isolated, and that the entropy is an additive quantity, we obtain from (20) and (30) taking (28) and (29) into account

$$\begin{aligned} \dot{S}^{com} &:= \dot{S} + \dot{S}^{\star} = \\ &= \dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^{e})\left[\frac{1}{\Theta} - \frac{1}{T^{\star}}\right] - \left[\frac{\boldsymbol{\mu}}{\Theta} - \frac{\boldsymbol{\mu}^{\star}}{T^{\star}}\right]\cdot\dot{\boldsymbol{n}}^{e} - \frac{\boldsymbol{\mu}}{\Theta}\cdot\dot{\boldsymbol{n}}^{i} + \Sigma. \end{aligned} \tag{31}$$

The entropy rate in isolated systems is not negative according to the second law (2nd law Va in [9])

$$\dot{S}^{com} \ \geq \ 0. \tag{32}$$

Consequently (31) becomes an inequality which consists of two parts: The second part describes the entropy production in the considered system which is not negative according to (21) and (22). The first part in (31) describes the irreversible exchange of heat and mass between the system and its environment. Because this part is independent of $\dot{\boldsymbol{n}}^i$ and Σ and because the special reversible limit $\sigma = 0$ is included in (31), also the first part is not negative

$$\dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e)\left[\frac{1}{\Theta} - \frac{1}{T^\star}\right] - \left[\frac{\boldsymbol{\mu}}{\Theta} - \frac{\boldsymbol{\mu}^\star}{T^\star}\right] \cdot \dot{\boldsymbol{n}}^e \geq 0. \tag{33}$$

This inequality is the wanted one. For the special cases mentioned on the right-hand sides of (15) and (16) we recover these two inequalities. We will now investigate what the consequences of (33) with respect to Clausius inequality are.

According to (9) we obtain from (28) and (29)

$$\dot{Q}^{cl} + \boldsymbol{\zeta}^0 \cdot \dot{\boldsymbol{n}}^e = -\dot{Q}^{\star cl} + \boldsymbol{\zeta}^{\star 0} \cdot (-\dot{\boldsymbol{n}}^{e\star}) = -\dot{Q}^{\star cl} + \boldsymbol{\zeta}^{\star 0} \cdot \dot{\boldsymbol{n}}^e. \tag{34}$$

This yields

$$-\dot{Q}^{\star cl} + (\boldsymbol{\zeta}^{\star 0} - \boldsymbol{\mu}^\star)\cdot(-\dot{\boldsymbol{n}}^{e\star}) = \dot{Q}^{cl} + (\boldsymbol{\zeta}^0 - \boldsymbol{\mu})\cdot \dot{\boldsymbol{n}}^e + (\boldsymbol{\mu} - \boldsymbol{\mu}^\star)\cdot \dot{\boldsymbol{n}}^e. \tag{35}$$

Dividing this equation by $T^\star$ and generating the first two term on the right-hand side we obtain

$$\begin{aligned} -\frac{\dot{Q}^{\star cl}}{T^\star} + \frac{\boldsymbol{\zeta}^{\star 0} - \boldsymbol{\mu}^\star}{T^\star} \cdot (-\dot{\boldsymbol{n}}^{e\star}) &= \frac{\dot{Q}^{cl}}{\Theta} + \frac{\boldsymbol{\zeta}^0 - \boldsymbol{\mu}}{\Theta} \cdot \dot{\boldsymbol{n}}^e + \\ + \left[\frac{1}{T^\star} - \frac{1}{\Theta}\right] [\dot{Q}^{cl} + (\boldsymbol{\zeta}^0 - \boldsymbol{\mu}) \cdot \dot{\boldsymbol{n}}^e] &+ \frac{1}{T^\star}(\boldsymbol{\mu} - \boldsymbol{\mu}^\star) \cdot \dot{\boldsymbol{n}}^e. \end{aligned} \tag{36}$$

The last three terms can be transformed by (9)

$$\begin{aligned} \left[\frac{1}{T^\star} - \frac{1}{\Theta}\right] [\dot{Q}^{cl} + (\boldsymbol{\zeta}^0 - \boldsymbol{\mu}) \cdot \dot{\boldsymbol{n}}^e] + \frac{1}{T^\star}(\boldsymbol{\mu} - \boldsymbol{\mu}^\star) \cdot \dot{\boldsymbol{n}}^e &= \\ = \left[\frac{1}{T^\star} - \frac{1}{\Theta}\right] \dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e) + \left(\frac{\boldsymbol{\mu}}{\Theta} - \frac{\boldsymbol{\mu}^\star}{T^\star}\right) \cdot \dot{\boldsymbol{n}}^e. \end{aligned} \tag{37}$$

According to (33) this expression is not positive. Consequently we obtain from (36) the inequality

$$-\frac{\dot{Q}^{\star cl}}{T^\star} + \frac{\boldsymbol{\zeta}^{\star 0} - \boldsymbol{\mu}^\star}{T^\star} \cdot (-\dot{\boldsymbol{n}}^{e\star}) \leq \frac{\dot{Q}^{cl}}{\Theta} + \frac{\boldsymbol{\zeta}^0 - \boldsymbol{\mu}}{\Theta} \cdot \dot{\boldsymbol{n}}^e. \tag{38}$$

Integrating over a cyclic process which is performed by the system, (38) yields

$$^{+}\oint\left[-\frac{\dot{Q}^{\star cl}}{T^{\star}}+\frac{\boldsymbol{\zeta}^{\star 0}-\ \boldsymbol{\mu}^{\star}}{T^{\star}}\cdot(-\,\dot{\boldsymbol{n}}^{e\star})\right]dt\ \leq\ ^{+}\oint\left[\frac{\dot{Q}^{cl}}{\Theta}\ +\ \frac{\boldsymbol{\zeta}^{0}-\ \boldsymbol{\mu}}{\Theta}\cdot\ \dot{\boldsymbol{n}}^{e}\right]dt. \tag{39}$$

Using the extended Clausius inequality (27) we obtain from (39) a version of Clausius inequality in wich appear only quantities of the system's environment

$$^{+}\oint\frac{1}{T^{\star}}\left[-\dot{Q}^{\star cl}\ +(\,\boldsymbol{\zeta}^{\star 0}-\ \boldsymbol{\mu}^{\star})\cdot(-\,\dot{\boldsymbol{n}}^{e\star})\right]dt\ \leq\ 0. \tag{40}$$

The quantities $-\dot{Q}^{\star cl}$ and $-\,\dot{\boldsymbol{n}}^{e\star}$ are heat and mole number exhanges belonging to the environment of the system, $T^{\star}$ is the thermostatic temperature of the environment. Like the extended Clausius inequality (27) also (40) is valid for arbitrary splits (3) of the heat flux. A more familiar shape of (40) can be written down by (29) and the following redefinition

$$\dot{Q}^{\diamond cl}\ \equiv\ -\dot{Q}^{\star cl}\ \neq\ \dot{Q}^{cl}, \tag{41}$$

$$^{+}\oint\frac{1}{T^{\star}}\left[\dot{Q}^{\diamond cl}\ +(\,\boldsymbol{\zeta}^{\star 0}-\ \boldsymbol{\mu}^{\star})\cdot\ \dot{\boldsymbol{n}}^{e}\right]dt\ \leq\ 0. \tag{42}$$

Here in general the inequality in (41) is valid in open systems according to (28). The special quantity $\boldsymbol{\zeta}^{0}$ is determined by (9), and now we will find out in the next section, what meaning it has.

4 Heat exchange for open sytems

According to (1) and (2) the "heat" exchange $\dot{Q}(\,\boldsymbol{\zeta},\,\dot{\boldsymbol{n}}^{e})$ for open systems is arbitrary and can be fixed by choice of $\boldsymbol{\zeta}$. In contrast to that free choice $\boldsymbol{\zeta}^{0}$ is determined by its definition (9). Its meaning is now derived. We introduce the work variables $\boldsymbol{a}$ and the generalized forces $\boldsymbol{A}$, so that the power exchange in (1) can be written as

$$\dot{W}\ =\ \ \boldsymbol{A}\cdot\dot{\boldsymbol{a}}. \tag{43}$$

Then the time rate of the enthalpy is defined by

$$\dot{H}\ :=\ \Theta\dot{S}\ -\ \ \boldsymbol{a}\cdot\dot{\boldsymbol{A}}\ +\ \ \boldsymbol{\mu}\cdot\dot{\boldsymbol{n}}. \tag{44}$$

Inserting (19) we obtain

$$\dot{H} = \dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) + \boldsymbol{\zeta} \cdot \dot{\boldsymbol{n}}^e - \boldsymbol{a} \cdot \dot{\boldsymbol{A}} + \Theta\Sigma. \tag{45}$$

Because the split $\boldsymbol{\zeta}$ is arbitrary, we choose here $\boldsymbol{\zeta} = \boldsymbol{\zeta}^0$ and obtain by taking (12) into account

$$\dot{H} = \dot{Q}^{cl} + \boldsymbol{\zeta}^0 \cdot \dot{\boldsymbol{n}}^e - \boldsymbol{a} \cdot \dot{\boldsymbol{A}} + \Theta\Sigma. \tag{46}$$

From this equation we can read off the meaning of $\boldsymbol{\zeta}^0$

$$\dot{H}(\boldsymbol{A}, \Theta, \boldsymbol{n})\Big|_{\substack{\dot{Q}(\mathbf{o},\,\mathbf{o}) = 0 \\ \boldsymbol{A} = \mathbf{o} \\ \Sigma = 0}} = \boldsymbol{\zeta}^0 \cdot \dot{\boldsymbol{n}}^e \longrightarrow \tag{47}$$

$$\longrightarrow \boldsymbol{\zeta}^0 = \left(\frac{\partial H}{\partial \boldsymbol{n}}\right)_{\substack{\dot{Q}(\mathbf{o},\mathbf{o}) = 0 \\ \boldsymbol{A} = \mathbf{o} \\ \Sigma = 0}} =: \boldsymbol{h}. \tag{48}$$

Consequently $\boldsymbol{\zeta}^0$ is the reversible partial molar enthalpy for constant generalized forces and for vanishing heat exchange of the closed system. According to (17) this heat exchange vanishes, if the contact temperature of the system and the thermostatic temperature of its environment are equal: $\Theta = T^\star$. This is the condition for adiabaticity in case of open systems.

By (48) (9) results in the heat exchange for open systems

$$\dot{Q}(\mathbf{o}, \dot{\boldsymbol{n}}^e) = \dot{Q}(\boldsymbol{\zeta}, \dot{\boldsymbol{n}}^e) + \boldsymbol{\zeta} \cdot \dot{\boldsymbol{n}}^e = \dot{Q}^{cl} + \boldsymbol{h} \cdot \dot{\boldsymbol{n}}^e, \tag{49}$$

and the first law (10) writes

$$\dot{U} = \dot{Q}^{cl} + \dot{W} + \boldsymbol{h} \cdot \dot{\boldsymbol{n}}^e. \tag{50}$$

The split $\boldsymbol{\zeta}$ remains arbitrary, but the difference between the heat exchanges for open and closed systems is now determined by (49). Introducing the molar entropies belonging to the system and its environment

$$\boldsymbol{s} := \frac{\boldsymbol{h} - \boldsymbol{\mu}}{\Theta}, \quad \boldsymbol{s}^\star := \frac{\boldsymbol{h}^\star - \boldsymbol{\mu}^\star}{T^\star} \tag{51}$$

the Clausius inequalities (27) and (42) for open systems become

$$+\oint \left[\frac{\dot{Q}^{cl}}{\Theta} \ + \ \boldsymbol{s} \cdot \dot{\boldsymbol{n}}^e \right] dt \ \leq \ 0, \tag{52}$$

$$+\oint \left[\frac{\dot{Q}^{\diamond cl}}{T^\star} \ + \ \boldsymbol{s}^\star \cdot \dot{\boldsymbol{n}}^e \right] dt \ \leq \ 0. \tag{53}$$

These are Clausius inequalities whose existence were doubted in [1]. A more detailled discussion can be found in the next section.

5 Discussion

Starting out with the strong formulations (22) and (32) of the second law [9] we derived two versions (52) and (53) of Clausius inequality for open systems. In the first version (52) the exchange quantities belong to the open non-equilibrium system of contact temperature Θ. In the second version (53) the exchange quantities refer to the open system's equilibrium environment of thermostatic temperature $T^\star$. In (53) the sign of the exchanges are written down with respect to the system itself.

Because in [1] no contact quantities are used, this paper deals only with Clausius inequality of type (53). The split (2) is unknown to the author. His starting point ((13) in [1]) is an unproved, and perhaps not provable inequality. Because Bhalekar does not introduce the concept of the inert partition, he cannot remark, that the split can be different for system and environment according to (28). Because in general the molar enthalpies of system and environment are different $\boldsymbol{h} \neq \boldsymbol{h}^\star$, also the corresponding heat exchanges $\dot{Q}^{cl} \neq \dot{Q}^{\diamond cl}$ are different in open systems according to (34). Therefore $\dot{Q}^{\diamond cl}$ does not belong to the first law of the system, but to that of the environment.

The inequality (21) in [1] is the correct one according to (53), if one refers to the first law of the system's environment. That is also very clear from a more logical point of view: Because Bhalekar is using equilibrium quantities, such as thermostatic temperature and molar entropies of the reservoir, one has also to use the first law with respect to the environment, as it was already done in [2].

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