

# Non-redundant and natural variables definition of heat valid for open systems

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## Abstract

Although an unambiguous definition of heat is available in the classical thermodynamics for closed systems, the question of how best to define heat transfer in open systems is not yet settled.

After an introduction to the basic formalism of modern thermodynamics, this article reviews the different definitions of heat for open systems used by CALLEN, CASAS-VÁZQUEZ, DEGROOT, FOX, HAASE, JOU, KONDEPUDI, LEBON, MAZUR, MISNER, PRIGOGINE, SMITH, THORNE, and WHEELER, emphasizing their main pros and cons.

A posterior section deals with the main objective of this article and introduces a new definition of heat that avoids the main difficulties of the existent definitions, providing us (i) a complete distinction between open and closed systems, (ii) high non-redundancy, (iii) natural variables for the thermodynamic potentials, and (iv) a sound and complete but intuitive generalization of classical thermodynamic expressions. The application of the new definition of heat to termoelectricity is used for showing new advantages over the previous definitions, including corrections to misleading and contradictory expressions for the density of production of entropy obtained by other authors for solid conductors. Finally, some consequences of this generalization of classical thermodynamic expressions to open systems are given and misleading recent comments done in black hole literature are corrected.

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## 1 Introduction

The true nature of heat, as a form of energy that can interconvert to other forms of energy, was established after much debate in the last part of the 19th century [1]. However, an unambiguous definition was lacking until BORN introduced his definition in 1921 [2, 3]

$$Q \equiv \Delta E - W, \quad (1)$$

with  $E$  and  $W$  being the total energy and work, respectively. This classical thermodynamics definition can be restated in differential form –with the help of imperfect differentials [4]–

$$\delta Q \equiv dE - \delta W. \quad (2)$$

Although the BORN definition (1) and its differential version (2) are *not valid for open systems* [1, 2] –i.e., for systems that can interchange matter as well as energy–, this restriction has not been, in practice, a difficulty for its usage in the classical thermodynamic theory of equilibrium; essentially, because the basic problem of classical thermodynamics is, according to CALLEN, «*the determination of the equilibrium state that eventually results after the removal of internal constraints in [an isolated], composite system*» [5, 6].

The difficulties begin with the extension of classical thermodynamics to irreversible processes. In modern thermodynamics [1], systems in a nonequilibrium thermodynamic state are divided into small elements of volume and each element is assumed to be locally at equilibrium [7]. Now, these elements of volume can interchange matter with adjacent elements, which requires *a new definition of heat valid for open systems as well*.

The importance of a generalization of the closed-systems definition of heat has been emphasized many years ago; however, in despite of the existence of several proposed generalizations, the question of how best to define heat transfer in open systems is not yet settled [8].

The next section gives an introduction to the basic formalism of modern thermodynamics, including balance equations for general thermodynamic quantities. The section 3 reviews the available definitions of heat for open systems in irreversible thermodynamics, emphasizing their main pros and cons for simple thermodynamic systems. The section 4 emphasizes the non-equivalence between the different definitions proposed in the literature up to now.

This author introduces, in the section 5, a new definition of heat for simple thermodynamic systems that avoids the main difficulties of the existent definitions and, in the section 6 presents the new definition for general thermodynamic systems. The application of the new definition of heat to termoelectricity is discussed in the section 7, where new advantages over the previous definitions are shown, including corrections to misleading and contradictory expressions for the density of production of entropy obtained by other authors for solid conductors.

Finally, some consequences of the generalization of the classical thermodynamic expressions to open systems are commented and misleading recent comments done in black hole physics literature corrected.

## 2 Basic formalism of modern thermodynamics

In this section, we follow closely «*Modern Thermodynamics*» by KONDEPUDI & PRIGOGINE. Readers would consult [1] for details.

Consider a general thermodynamic quantity  $Y$ , its variation can be expressed as a sum of two parts

$$dY = d_i Y + d_e Y, \quad (3)$$

in which  $d_e Y$  is the change in  $Y$  due to exchanges with the exterior and  $d_i Y$  is the change produced by processes in the interior of the thermodynamic system. If the density of  $Y$  is denoted by  $y$ , the change in the amount of  $Y$  in a volume  $V$  can be written as

$$\int_V \frac{\partial y}{\partial t} dV = \int_V \sigma_Y dV - \int_A \mathbf{J}_Y \cdot d\mathbf{A}, \quad (4)$$

where  $\mathbf{J}_Y$  is the flux of  $Y$ ,  $d\mathbf{A}$  the vector representing an area element, and  $\sigma_Y$  the amount of  $Y$  produced per unit volume per unit time [1]. Applying GAUSS' theorem to (4) gives the usual local form of the balance equation for  $Y$

$$\frac{\partial y}{\partial t} = \sigma_Y - \nabla \cdot \mathbf{J}_Y. \quad (5)$$

Specific expressions for  $\sigma_Y$  for several quantities as internal energy, amount of substance, entropy, and others are given in the literature [1].

Finally, it must be emphasized that modern thermodynamics does not rely in the use of imperfect differentials because is defined over an extended thermodynamic space that includes time [4]. This means that classical thermodynamics expressions as (2) are modernized to

$$dQ \equiv dE - dW, \quad (6)$$

with both  $dQ$  and  $dW$  well-defined and measurable physical quantities. Of course, this modern definition of heat continues being valid for closed systems only.

## 3 Review of available definitions of heat flux

We start by considering one-component elements of volume that can interchange internal energy and matter, without chemical reactions  $\sigma_N = 0$ , for which internal energy is conserved  $\sigma_U = 0$ , and that verify the generalized GIBBS equation [2, 7]

$$Tds = du - \mu dn, \quad (7)$$

for thermodynamic temperature  $T$ , density of entropy  $s$ , density of internal energy  $u$ , chemical potential  $\mu$ , and mole unit per unit volume  $n$ . This kind of simple thermodynamic systems is enough for the purposes of this section, more general systems will be considered in a posterior section.

Taking partial derivatives  $\partial/\partial t$  in the generalized GIBBS equation (7) and using the local balance equations for internal energy and composition we obtain the well-known balance equation for entropy [1, 5]

$$\frac{\partial s}{\partial t} = \sigma_S - \nabla \cdot \mathbf{J}_S, \quad (8)$$

with the density of production of entropy  $\sigma_S$  and the entropy flux  $\mathbf{J}_S$  given by

$$\sigma_S = \mathbf{J}_U \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{J}_N \cdot \nabla \left( \frac{\mu}{T} \right) \quad (9)$$

and

$$\mathbf{J}_S = \frac{\mathbf{J}_U - \mu \mathbf{J}_N}{T}. \quad (10)$$

In the above expressions,  $\mathbf{J}_U$  and  $\mathbf{J}_N$  are the flows of internal energy and matter, respectively.

The density of production of entropy (9) is the usual product of flows and thermodynamic forces [1]. This will be our starting point to revise the different definitions of heat flux proposed up to now.

A first definition of heat flux follows from considering it as the flux associated with the gradient of temperature in the first product of (9), i.e.,  $\mathbf{J}_{Q^{[1]}} \equiv \mathbf{J}_U$ . Using this definition, the density of production of entropy (9) can be rewritten as

$$\sigma_S = \mathbf{J}_{Q^{[1]}} \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{J}_N \cdot \nabla \left( \frac{\mu}{T} \right) \quad (11)$$

and (10) as

$$\mathbf{J}_S = \frac{\mathbf{J}_{Q^{[1]}} - \mu \mathbf{J}_N}{T}. \quad (12)$$

Notice that  $T\mathbf{J}_S = \mathbf{J}_{Q^{[1]}}$  *only holds for closed systems*, which means that the flux  $\mathbf{J}_{Q^{[1]}}$  *allows a physical distinction between open and closed systems at the entropic level*. Effectively, integrating (12) over the area  $A$  of an isothermal system, and multiplying by  $dt$  we obtain DEDONDER entropic term for open systems [1, 2, 9]

$$d_e S = dt \int_A \mathbf{J}_S \cdot d\mathbf{A} = \frac{dQ^{[1]}}{T} + (d_e S)_{matter}. \quad (13)$$

For closed systems  $\mathbf{J}_N = 0$  and (13) reduces to DEDONDER [10] entropic term for closed systems –see equation (III.4) in DEGROOT & MAZUR [9]–

$$d_e S = dt \int_A \mathbf{J}_S \cdot d\mathbf{A} = \frac{dQ^{[1]}}{T}. \quad (14)$$

This first definition  $\mathbf{J}_{Q^{[1]}}$  is used by DEGROOT & MAZUR [9], FOX [11] and JOU, CASAS-VÁZQUEZ, & LEBON in irreversible thermodynamics [12]; by JOU, CASAS-VÁZQUEZ, & LEBON in extended thermodynamics [12] –in this case with equations (11) and (12) being generalized to an extended thermodynamic space–; and is the standard in kinetic theory of gases [9, 13].

The main advantages of this first definition of heat flux,  $\mathbf{J}_{Q^{[1]}}$ , are its use of natural variables for the thermodynamic potentials and its distinction between open and closed systems through DEDONDER entropic term: (13) *versus* (14). The main disadvantages of  $\mathbf{J}_{Q^{[1]}}$  are found in its

redundancy and that does *not distinguish between open and closed systems at the energetic level*. Both disadvantages are analyzed with detail below.

In the first place,  $\mathbf{J}_{Q[1]}$  is highly redundant. Effectively, any instance of  $\mathbf{J}_{Q[1]}$  in the equations could be substituted by  $\mathbf{J}_U$  without physical or mathematical changes, just as any instance of «*heat flux*» in the text of the above references [9, 11, 12] could be reverted to «*internal energy flux*» without any appreciable change, doing unneeded the introduction of the concept of heat in the formalism. Notice the difference with the rest of definitions considered in this work, which are non-redundant and really introduce a *physical concept of heat flux different from the concept of internal energy flux*.

In the second place,  $\mathbf{J}_{Q[1]}$  does not completely distinguish between open and closed systems. This disadvantage can be shown by using  $\mathbf{J}_{Q[1]}$  in the balance equation for the internal energy of a homogeneous thermodynamic system, at rest and in absence of external field,

$$\frac{\partial u}{\partial t} = \sigma_U - \nabla \cdot \mathbf{J}_{Q[1]} \quad (15)$$

integrating over the volume  $V$  of the system and multiplying by  $dt$  for obtaining

$$dU = dQ^{[1]} - pdV. \quad (16)$$

According to this expression, the only possible changes in the internal energy  $U$  are due to flow of heat and to mechanical work  $dW \equiv -pdV$  [9]. There is not possibility to modify the internal energy of the system by a flow of mass. However as SMITH remarks [8]:

*«It is therefore expected that the usual version of the first law of thermodynamics for closed systems, namely  $dU = dQ + dW$ , will not be valid for open systems.»*

Notice that for the kind of systems considered here  $dE = dU$ ; therefore, the restriction of (16) to closed systems is directly related to the same restriction for the BORN definition (2) and for its modern thermodynamic version (6). Below we will show how the extension of the first law to open systems has to be performed.

The underlying physical reason for the inadequacy of  $\mathbf{J}_{Q[1]}$  to distinguish between open and closed systems, at the energetic level, must be traced to the important fact that *internal energy  $U$  is an extensive thermodynamic quantity* and, therefore,  $\mathbf{J}_U = \mathbf{J}_{Q[1]}$  does not differentiate between changes in internal energy due to flows of mass –transferring the internal energy per particle in the flow– and changes due to genuine heat flows.

The two disadvantages of  $\mathbf{J}_{Q[1]}$  reported here are a motivation for the search of improved definitions for open systems. A second definition of heat follows by separating the gradient of  $\mu$  from the gradient of  $(1/T)$  in (9). Using

$$\nabla \left( \frac{\mu}{T} \right) = \mu \nabla \left( \frac{1}{T} \right) + \left( \frac{1}{T} \right) \nabla \mu, \quad (17)$$

the density of production of entropy (9) can be rewritten as

$$\sigma_S = \mathbf{J}_{Q[2]} \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{J}_N \cdot \left( \frac{\nabla \mu}{T} \right) \quad (18)$$

and the entropy flux (10) as

$$\mathbf{J}_S = \frac{\mathbf{J}_{Q^{[2]}}}{T}, \quad (19)$$

where  $\mathbf{J}_{Q^{[2]}} \equiv \mathbf{J}_U - \mu\mathbf{J}_N$ . This new definition of heat flux is only used by CALLEN [5], although MISNER, THORNE, & WHEELER use a weird variant [14] in curved spacetime thermodynamics –in this case with equations (11) and (12) being formulated in curved spacetime– [15].

The main advantages of this second definition are its use of natural variables for the thermodynamic potentials, its non-redundancy, and that differentiates between changes in internal energy due to flows of mass and due to genuine heat flows:  $\mathbf{J}_U = \mathbf{J}_{Q^{[2]}} + \mu\mathbf{J}_N$ . The main disadvantage being that *does not distinguish closed from open systems at the entropic level*.

Effectively, integrating (19) over the area  $A$  of an isothermal system, and multiplying by  $dt$  we obtain the following DEDONDER entropic term

$$d_e S = dt \int_A \mathbf{J}_S \cdot d\mathbf{A} = \frac{dQ^{[2]}}{T}, \quad (20)$$

which is *not valid for open systems* [1, 2, 9] because is missing a  $(d_e S)_{matter}$  term for matter exchange –compare with (13) for open systems and with (14) for closed systems–.

The underlying physical reason for the inadequacy of  $\mathbf{J}_{Q^{[2]}}$  to distinguish between open and closed systems, at the entropic level, must be traced to the important fact that *entropy  $S$  is an extensive thermodynamic quantity* and, therefore, (19) does not differentiate between changes in entropy due to flows of mass –transferring the entropy per particle in the flow– and changes due to genuine heat flows.

Precisely CALLEN introduces his  $\mathbf{J}_{Q^{[2]}} = T\mathbf{J}_S$  «*in analogy*» [5] with  $\delta Q = TdS$  for classical thermodynamics. The problem is that the classical  $\delta Q = TdS$  is not valid for open systems [10] by the same reason that modern (20) is not valid, and the same physical defect is inherited by  $\mathbf{J}_{Q^{[2]}} = T\mathbf{J}_S$ .

Although  $\mathbf{J}_{Q^{[2]}}$  has a pair of advantages over  $\mathbf{J}_{Q^{[1]}}$ , its main disadvantage is a motivation for the search of improved definitions for open systems. It is interesting to remark a kind of complementarity between  $\mathbf{J}_{Q^{[1]}}$  and  $\mathbf{J}_{Q^{[2]}}$ : the first fails at the energetic level, whereas the second does at the entropic level. A new definition of heat working at both levels is evidently needed.

A third definition of heat can be obtained by noticing that the gradient of chemical potential  $\nabla\mu$  in (17) is still a function of the temperature  $T$ . This means that extra heating effects due to gradients of temperature were not included in the previous definitions of heat flow.

Introducing the next separation [1], where  $\mu = \mu(T, n)$  and  $s_n \equiv (\partial s / \partial n)_T$  is a pseudo-molar entropy [16],

$$\nabla\mu = (\nabla\mu)_T - s_n \nabla T \quad (21)$$

in (17), the density of production of entropy (9) can be rewritten as

$$\sigma_S = \mathbf{J}_{Q^{[3]}} \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{J}_N \cdot \frac{(\nabla\mu)_T}{T} \quad (22)$$

and the entropy flux (10) as

$$\mathbf{J}_S = \frac{\mathbf{J}_{Q^{[3]}}}{T} + s_n \mathbf{J}_N \quad (23)$$

for a heat flux  $\mathbf{J}_{Q^{[3]}} \equiv \mathbf{J}_U - (\mu + Ts_n)\mathbf{J}_N$ .

Notice that  $T\mathbf{J}_S = \mathbf{J}_{Q^{[3]}}$  only holds for closed systems, which means that  $\mathbf{J}_{Q^{[3]}}$  allows a physical distinction between open and closed systems at the entropic level. Effectively, integrating (23) over the area  $A$  of an isothermal system, and multiplying by  $dt$  we obtain DeDonder entropic term for open systems [1, 2, 9]

$$d_e S = dt \int_A \mathbf{J}_S \cdot d\mathbf{A} = \frac{dQ^{[3]}}{T} + (d_e S)_{matter}. \quad (24)$$

For closed systems  $\mathbf{J}_N = 0$  and (24) reduces to DeDonder [10] entropic term for closed systems –see equation (3.4.9) in Kondepudi & Prigogine [1]–

$$d_e S = dt \int_A \mathbf{J}_S \cdot d\mathbf{A} = \frac{dQ^{[3]}}{T}. \quad (25)$$

This new  $\mathbf{J}_{Q^{[3]}}$  also allows a physical distinction between open and closed systems at the energetic level. This advantage, regarding the first law of thermodynamics, can be shown by using  $\mathbf{J}_{Q^{[3]}}$  in the balance equation for the internal energy of a homogeneous thermodynamic system, at rest and in absence of external field,

$$\frac{\partial u}{\partial t} = \sigma_U - \nabla \cdot \mathbf{J}_{Q^{[3]}} - \nabla \cdot (u_n \mathbf{J}_N). \quad (26)$$

A pseudo-molar internal energy  $u_n = \mu + Ts_n$  has been used [1, 16]. Integrating over the volume  $V$  of the system and multiplying by  $dt$  we obtain –see equation (2.2.12) in [1]–

$$dU = dQ^{[3]} + dW^{[3]} + dU_{matter}. \quad (27)$$

«For open systems, there is an additional contribution due to the flow of matter  $dU_{matter}$ » [1] in the first law of thermodynamics –see also the Smith quotation, reproduced after (16), emphasizing how the term  $dU_{matter}$  is missing in (16)–.

Unlike the previous definitions, this new  $\mathbf{J}_{Q^{[3]}}$  completely distinguishes between open and closed systems, at both energetic and entropic levels, because  $\mathbf{J}_{Q^{[3]}}$  considers the extensive thermodynamic character of both entropy  $S$  and internal energy  $U$ . Notice that (23) is able to distinguish changes in entropy due to flows of mass from changes due to genuine heat flows, whereas  $\mathbf{J}_U = \mathbf{J}_{Q^{[3]}} + u_n \mathbf{J}_N$  distinguishes between changes in internal energy due to flows of mass and those due to genuine heat flows. As a consequence,  $\mathbf{J}_{Q^{[3]}}$  provides the needed  $(d_e S)_{matter}$  term at the entropic level [1, 2, 9] plus a waited  $dU_{matter}$  term at the energetic level [8]. The heat flux  $\mathbf{J}_{Q^{[3]}}$  is used by Kondepudi & Prigogine [1], Haase [2] and by Smith [8].

The main advantages of this  $\mathbf{J}_{Q^{[3]}}$  over the two previous definitions  $\mathbf{J}_{Q^{[1]}}$  and  $\mathbf{J}_{Q^{[2]}}$  are its complete distinction between closed and isolated systems and its high non-redundancy. The main disadvantage being that  $\mathbf{J}_{Q^{[3]}}$  is not defined in natural variables.

Indeed, the above expressions explicitly involve the use of  $s_n = s_n(T, n)$ ,  $u_n = u_n(T, n)$ , and  $\mu = \mu(T, n)$ . Precisely Kondepudi & Prigogine [1] introduce the definition  $\mathbf{J}_{Q^{[3]}}$  after a

change of variables  $(s, n) \rightarrow (T, n)$  in the internal energy balance equation. As is well-known internal energy is not a thermodynamic potential in a temperature-composition state space and when considering expressions that use  $\mathbf{J}_{Q[3]}$ , this important fact has to be taken into account.

Moreover, their change of variables introduces a divergence with ordinary thermodynamic expressions. For instance, (27) cannot be directly reduced to the usual first law for closed systems  $dU = dQ - pdV$ , because  $dW^{[3]} \equiv (\partial U / \partial V)_{T, N} dV \neq -pdV$  –see their boxed equation (2.2.12) in [1]–.

Although  $\mathbf{J}_{Q[3]}$  has advantages over both  $\mathbf{J}_{Q[1]}$  and  $\mathbf{J}_{Q[2]}$ , its main disadvantage is a motivation for the search of an improved definition, not only for open systems but even also for closed! A new definition of heat working at both entropic and energetic levels, which directly reduces to ordinary classical thermodynamic expressions, and maintains natural variables is evidently needed, but before presenting our new definition it will be interesting to review the reasons for the non-equivalence between the different definitions of heat flux considered up to now.

## 4 Non-equivalence of the different definitions of heat

Although it is sometimes stated that different definitions of heat are 'equivalent', this really means that the density of production of entropy  $\sigma_S$  is invariant when is expressed in terms of  $\mathbf{J}_{Q[1]}$ ,  $\mathbf{J}_{Q[2]}$ , or  $\mathbf{J}_{Q[3]}$ . Effectively, (11), (18), and (22) are equivalent to the original density of production (9). However, the equivalence of the production of entropy *does not imply a complete equivalence of the different definitions of heat flux*.

Different instances of the *non-equivalence of the different definitions of heat flux* were given in the previous section. For instance, the flux  $\mathbf{J}_{Q[2]}$  introduced by CALLEN is not compatible with DEDONDER entropic term for an open system, whereas the flows used by DEGROOT & MAZUR and by KONDEPUDI & PRIGOGINE, SMITH, and HAASE are compatible.

As was emphasized in the previous section, this deficiency of  $\mathbf{J}_{Q[2]}$  must be traced to its neglect of the important fact of that entropy  $S$  is an *extensive thermodynamic quantity* and, therefore, entropy can vary due to flows of mass and due to genuine heat flows. This deficiency of  $\mathbf{J}_{Q[2]}$  cannot be perceived in the density of production of entropy (18), because is therein being compensated by the  $\mathbf{J}_N \cdot (\nabla \mu / T)$  term; however, the deficiency is detected in (20), because (20) relies exclusively on  $\mathbf{J}_S$  where the compensation term is lost –see (19)–.

It is not a surprise that neither DEGROOT & MAZUR nor KONDEPUDI & PRIGOGINE consider that  $\mathbf{J}_{Q[2]}$  was a valid heat flux and that all these authors avoid even to name it [1, 9]. SMITH and HAASE also avoid  $\mathbf{J}_{Q[2]}$  completely [2, 8].

Another instance of the *non-equivalence of the different definitions of heat flux* follows from the demonstration, done in the previous section, of that  $\mathbf{J}_{Q[1]}$  is not compatible with the first law of thermodynamics for open systems, whereas the flow used by KONDEPUDI & PRIGOGINE, SMITH, and HAASE is compatible.

As was emphasized then, this deficiency of  $\mathbf{J}_{Q[1]}$  must be traced to its neglect of the important



*extensive thermodynamic character* of the internal energy  $U$ , which can vary due to flows of mass and due to genuine heat flows. This deficiency of  $\mathbf{J}_{Q[1]}$  cannot be perceived in the density of production of entropy (11), because is therein being compensated by the  $\mathbf{J}_N \cdot \nabla(\mu/T)$  term; however, this deficiency is detected in (16), because (16) relies exclusively on  $\mathbf{J}_U = \mathbf{J}_{Q[1]}$  where the compensation term  $\mathbf{J}_N \cdot \nabla(\mu/T)$  is lost.

By all these technical reasons, both SMITH and HAASE avoid  $\mathbf{J}_{Q[1]}$  completely and only use  $\mathbf{J}_{Q[3]}$  [2, 8]. In his own analysis of different definitions of heat, SMITH confirms the non-equivalence:

*«In irreversible thermodynamics [...] there exist several definitions of heat flux [...] although many authors employ non-equivalent definitions (see e.g. deGroot and Mazur 1962)»*

In its turn,  $\mathbf{J}_{Q[3]}$  has deficiencies as well.  $\mathbf{J}_{Q[3]}$  obligates us to work always in a different state space –where internal energy is not thermodynamic potential, for instance– and with non-ordinary thermodynamic expressions such as  $dW^{[3]} \equiv (\partial U/\partial V)_{T,N}dV \neq -pdV$  even for closed systems. Of course, one can work in a  $(T, n)$  state space in thermodynamics, but the LEGENDRE transformation was precisely invented to obtain the corresponding thermodynamic potentials in new state spaces and no such transformation is applied in the definition of  $\mathbf{J}_{Q[3]}$ . Of course, there is not any objective reason which one has to work in another state space exclusively to use the concept of heat! Additional disadvantages of  $\mathbf{J}_{Q[3]}$  are given in the section 7 for the case of thermoelectricity. The deficiencies shown in this work were not reported previously in the literature [1, 2, 8, 9].

Evidently if all the definitions were equivalent, thermodynamicians would not waste their time analyzing the existent definitions, identifying their weak points, and providing new definitions. For instance, KONDEPUDI & PRIGOGINE do not use an old definition introduced by PRIGOGINE and criticized by SMITH and others [8], but use the definition introduced by HAASE [2]. That defective old definition has been completely abandoned in the literature and has not been even considered here.

After showing that the available definitions of heat flux are completely redundant ( $\mathbf{J}_{Q[1]}$ ), do not properly generalize the thermodynamic expressions to open systems ( $\mathbf{J}_{Q[1]}$  and  $\mathbf{J}_{Q[2]}$ ), and do not use natural variables for the thermodynamic potentials –introducing a divergence with many classical thermodynamic expressions– ( $\mathbf{J}_{Q[3]}$ ), we will propose a new definition without such deficiencies.

## 5 New definition of heat flux

We will continue with the simple system considered in the section 3 for the sake of comparison with the previous definitions. More general systems will be considered in the next section.

A new definition of heat can be obtained by considering extra heating effects in the chemical potential, due to gradients of temperature, that were not included in the previous definitions  $\mathbf{J}_{Q[1]}$  and  $\mathbf{J}_{Q[2]}$ . Starting with the GIBB & DUHEM like equation corresponding to (7)

$$s\nabla T - \nabla p + n\nabla\mu = 0 \quad (28)$$

and considering a system at mechanical equilibrium, we obtain the next identity

$$\left(\frac{1}{T}\right)\nabla\mu = \left(\frac{Ts}{n}\right)\nabla\left(\frac{1}{T}\right). \quad (29)$$

Notice that we continue working in a natural variables state space  $(u, n)$ , because  $\mu = \mu(u, n)$ ,  $s = s(u, n)$ , and  $T = T(u, n)$  hold in the above identity.

Using (29) together with (17), the density of production of entropy (9) can be rewritten as

$$\sigma_S = \mathbf{J}_Q \cdot \nabla\left(\frac{1}{T}\right) \quad (30)$$

and the entropy flux (10) as

$$\mathbf{J}_S = \frac{\mathbf{J}_Q}{T} + \left(\frac{s}{n}\right)\mathbf{J}_N, \quad (31)$$

using a new heat flux defined as

$$\mathbf{J}_Q \equiv \mathbf{J}_U - \left(\mu + \frac{Ts}{n}\right)\mathbf{J}_N. \quad (32)$$

The physical interpretation of this new definition of heat is sound and complete, but intuitive because the parenthesized term in (31) is a molar entropy, whereas the parenthesized term in (32) is a molar internal energy. For instance, (31) is saying us that  $\mathbf{J}_Q$  is proportional to an entropy flow  $\mathbf{J}_S^*$  where the entropy transferred through a mass flow has been subtracted

$$\mathbf{J}_Q = T\mathbf{J}_S^* \equiv T\left[\mathbf{J}_S - \left(\frac{s}{n}\right)\mathbf{J}_N\right]. \quad (33)$$

Notice that  $T\mathbf{J}_S = \mathbf{J}_Q$  *only holds for closed systems*, which means that  $\mathbf{J}_Q$  *allows a physical distinction between open and closed systems at the entropic level*. Effectively, integrating (31) over the area  $A$  of an isothermal system, and multiplying by  $dt$  we obtain DEDONDER entropic term for open systems [1, 2, 9]

$$d_e S = dt \int_A \mathbf{J}_S \cdot d\mathbf{A} = \frac{dQ}{T} + (d_e S)_{matter}. \quad (34)$$

For closed systems  $\mathbf{J}_N = 0$  and (34) reduces to DEDONDER [10] entropic term for closed systems

$$d_e S = dt \int_A \mathbf{J}_S \cdot d\mathbf{A} = \frac{dQ}{T}. \quad (35)$$

The new  $\mathbf{J}_Q$  *also allows a physical distinction between open and closed systems at the energetic level*. This advantage regarding the first law of thermodynamics can be shown by using  $\mathbf{J}_Q$  in the balance equation for the internal energy of a homogeneous thermodynamic system, at rest and in absence of external field,

$$\frac{\partial u}{\partial t} = \sigma_U - \nabla \cdot \mathbf{J}_Q - \nabla \cdot \left(\frac{u}{n}\mathbf{J}_N\right), \quad (36)$$

where the molar internal energy  $(u/n) = \mu + T(s/n)$  has been used [16]. Integrating over the volume  $V$  of the system and multiplying by  $dt$  we obtain

$$dU = dQ + dW + dU_{matter} \quad (37)$$

in agreement with extensive discussions and quotations, about the first law for open systems, reproduced on the section 3.

Unlike other definitions, this new  $\mathbf{J}_Q$  is able to distinguish between open and closed systems completely, at both energetic and entropic levels, because  $\mathbf{J}_Q$  considers the *extensive thermodynamic character of entropy  $S$  but also of internal energy  $U$* . Notice that (31) distinguishes changes in entropy due to flows of mass from changes due to genuine heat flows, whereas  $\mathbf{J}_U = \mathbf{J}_Q + (u/n)\mathbf{J}_N$  distinguishes between changes in internal energy due to flows of mass and those due to genuine heat flows. As a consequence,  $\mathbf{J}_Q$  provides the needed  $(d_e S)_{matter}$  term at the entropic level [1, 2, 9] plus a waited  $dU_{matter}$  term at the energetic level [8].

Moreover,  $\mathbf{J}_Q$  is defined in natural variables space and allows for a smooth generalization of classical thermodynamic expressions to open systems. For instance, (37) can be directly reduced to the ordinary first law for closed systems  $dU = dQ - pdV$  because  $dW \equiv -pdV$ . This contrasts with the equation (27), using  $\mathbf{J}_{Q[3]}$ , which could not be directly reduced because in it  $dW^{[3]} \neq -pdV$ .

The main advantages of  $\mathbf{J}_Q$  over the previous definition are **(i)** complete distinction between open and closed systems, **(ii)** its high non-redundancy, **(iii)** its use of natural variables, and **(iv)** that properly generalizes classical thermodynamic expressions.

In the following section, we will present the general definition of heat and will show other important advantages over the previous definitions.

## 6 Heat for general thermodynamic systems

Instead considering a simple system as we did in the section 3, we will consider now a generic kind of thermodynamic systems. We start our analysis with a multi-component element of volume that can interchange internal energy, matter, and a collection of «*work coordinates*» [2] –whose densities are  $z_j$ –. This thermodynamic element of volume verifies a generalized GIBBS equation [2, 7]

$$Tds = du - \sum_j \zeta_j dz_j - \sum_k \mu_k dn_k \quad (38)$$

for thermodynamic temperature  $T$ , density of entropy  $s$ , density of internal energy  $u$ , and chemical potential  $\mu_k$  and mole unit per unit volume  $n_k$  of component  $k$ . The coefficients  $\zeta_j$ , conjugate to the densities  $z_j$ , are «*work coefficients*» [2]. Examples of work coefficients and work coordinates are given in the literature for specific thermodynamic interactions, such as those due to transfer of density of charge  $dq$  across a potential difference  $\phi$ , change of density of electric dipole moment  $d\mathbf{p}$  in the presence of an electric field  $\mathbf{E}$ , and change of density of magnetic dipole moment  $d\mathbf{m}$  in the presence of a magnetic field  $\mathbf{B}$  [1, 2]

$$\sum_j \zeta_j dz_j = \phi dq - \mathbf{E} \cdot d\mathbf{p} - \mathbf{B} \cdot d\mathbf{m} + \dots \quad (39)$$

Taking partial derivatives  $\partial/\partial t$  in the generalized GIBBS equation (38) and using the local balance equations for internal energy, composition, and work coordinates, we obtain the

balance equation (8) for entropy but now with a generalized density of production of entropy

$$\sigma_S = \frac{\sigma_U - \sum_j \zeta_j \sigma_{z_j} - \sum_k \mu_k \sigma_{N_k}}{T} + \mathbf{J}_U \cdot \nabla \left( \frac{1}{T} \right) - \sum_j \mathbf{J}_{z_j} \cdot \nabla \left( \frac{\zeta_j}{T} \right) - \sum_k \mathbf{J}_{N_k} \cdot \nabla \left( \frac{\mu_k}{T} \right) \quad (40)$$

and with a generalized entropy flux

$$\mathbf{J}_S = \frac{\mathbf{J}_U - \sum_j \zeta_j \mathbf{J}_{z_j} - \sum_k \mu_k \mathbf{J}_{N_k}}{T}. \quad (41)$$

In the above expressions,  $\mathbf{J}_U$ ,  $\mathbf{J}_{z_j}$ , and  $\mathbf{J}_{N_k}$  are the flows of internal energy, work coordinate  $j$ , and component  $k$ , respectively; whereas  $\sigma_U$ ,  $\sigma_{z_j}$ , and  $\sigma_{N_k}$  are their corresponding densities of production. For instance, the density of production of component  $k$  by chemical reactions can be expressed in terms of the reaction velocities  $v_\alpha$  and the corresponding stoichiometric coefficients  $\nu_{\alpha k}$  as  $\sigma_{N_k} = \sum_\alpha v_\alpha \nu_{\alpha k}$ .

Once again, the production of entropy (40) contains the usual product of flows and thermodynamic forces [1]. This will be our starting point for the introduction of a new definition of heat.

The new definition of heat flux follows by separating the gradient of  $(1/T)$  from the gradient of  $\zeta_j$

$$\nabla \left( \frac{\zeta_j}{T} \right) = \zeta_j \nabla \left( \frac{1}{T} \right) + \left( \frac{1}{T} \right) \nabla \zeta_j \quad (42)$$

and from the gradient of  $\mu_k$

$$\nabla \left( \frac{\mu_k}{T} \right) = \mu_k \nabla \left( \frac{1}{T} \right) + \left( \frac{1}{T} \right) \nabla \mu_k, \quad (43)$$

and by using the identity

$$\left( \frac{1}{T} \right) \nabla \mu_k = \left( \frac{T s}{n_k} \right) \nabla \left( \frac{1}{T} \right) + \left( \frac{\gamma_k}{T} \right), \quad (44)$$

with  $\gamma_k \equiv \nabla \mu_k + (s/n_k) \nabla T$ . This  $\gamma_k$  can be explicitly worked out using the GIBB & DUHEM like equation corresponding to (38)

$$s \nabla T - \nabla p + \sum_j z_j \nabla \zeta_j + \sum_k n_k \nabla \mu_k = 0, \quad (45)$$

but, in general, leads to a too convoluted expression, which is not really needed for applications where  $\gamma_k$  can be directly computed from a measurement of the densities of entropy  $s$  and composition  $n_k$ , and of the gradients  $\nabla \mu_k$  and  $\nabla T$ . An exception are mono-component isobaric systems without any work coordinate  $j$ , because then (45) can be used to reduce (44) to the simple identity (29).

Using (42), together with (43) and (44), the density of production of entropy (40) can be rewritten as

$$\sigma_S = \frac{\sigma_U - \sum_j \zeta_j \sigma_{z_j} - \sum_k \mu_k \sigma_{N_k}}{T} + \mathbf{J}_Q \cdot \nabla \left( \frac{1}{T} \right) - \sum_j \mathbf{J}_{z_j} \cdot \left( \frac{\nabla \zeta_j}{T} \right) - \sum_k \mathbf{J}_{N_k} \cdot \left( \frac{\gamma_k}{T} \right) \quad (46)$$

and the entropy flux (41) as

$$\mathbf{J}_S = \frac{\mathbf{J}_Q}{T} + \sum_k \left( \frac{s}{n_k} \right) \mathbf{J}_{N_k}, \quad (47)$$

for a heat flux

$$\mathbf{J}_Q \equiv \mathbf{J}_U - \sum_j \zeta_j \mathbf{J}_{Z_j} - \sum_k \left( \mu_k + \frac{Ts}{n_k} \right) \mathbf{J}_{N_k}. \quad (48)$$

Notice that the factor  $(s/n_k)$  continues having units of molar entropy, which implies that  $(\mu_k + Ts/n_k)$  continues having units of molar energy. This allows us to directly apply the sound, complete, and intuitive physical interpretation of our new definition of heat for simple systems –previously presented in the section 5– also to multi-component generalized thermodynamic systems. Effectively, (47) is saying us that  $\mathbf{J}_Q$  for generalized thermodynamic systems continues being proportional to an entropy flow  $\mathbf{J}_S^*$  where the entropy transferred through the mass flows has been subtracted

$$\mathbf{J}_Q = T \mathbf{J}_S^* \equiv T \left[ \mathbf{J}_S - \sum_k \left( \frac{s}{n_k} \right) \mathbf{J}_{N_k} \right]. \quad (49)$$

We can use the definition (48) of the new heat flux for generalizing classical thermodynamics as well. Integrating the definition (48) of the new heat flux  $\mathbf{J}_Q$  over the area  $A$  of the whole system and over the time interval  $dt$  needed to achieve a final equilibrium state –from an initial equilibrium state–, downgrading from modern to classical thermodynamic space [4], and considering the relation between total energy and internal energy, gives a generalization of the classical BORN definition of heat (2) for open systems

$$\delta Q \equiv dE - \delta W - \sum_k \left( \frac{TS}{N_k} \right) \delta_e N_k. \quad (50)$$

In this expression  $E$  and  $W$  are the total energy and work, respectively. Although in modern thermodynamics, (50) is really a derived result, it can be used *in classical thermodynamics as definition of heat, instead of (2)*. Evidently (50) reduces to (2) for closed systems, satisfying the requirement number (iv), for any reliable definition of heat. Analogously, we can obtain, from (47), the generalization of the classical CLAUSIUS theorem to open systems

$$dS \geq \frac{\delta Q}{T} + \sum_k \left( \frac{S}{N_k} \right) \delta_e N_k. \quad (51)$$

## 7 Application to thermoelectricity

Although the main advantages of the new definition of heat have been presented in previous sections, further advantages can be shown by application to thermoelectric phenomena. We will consider a conductor at mechanical equilibrium  $\nabla p = 0$  with both electric and heat flux –the electric flux being carried by electrons. This is a system where the only thermodynamic variables in (38) will be the density of internal energy  $u$ , the density of charge  $q$  –see the first term in (39)–, and the mole unit per unit volume  $n$  of electrons. Substituting all in (46) and using (45), we obtain the density of production of entropy for this system

$$\sigma_S = \mathbf{J}_Q \cdot \nabla \left( \frac{1}{T} \right). \quad (52)$$

This concise form predicts zero production of entropy under isothermal conditions. Now we will show how the other definitions of heat flux can give, and in fact give, misleading and self-contradictory conclusions under the same conditions.

Using again the GIBBS & DUHEM relation (45) –recall that  $\nabla p = 0$ –, we can write the alternative expression

$$\sigma_S = \left( \mathbf{J}_Q + \frac{T_S}{n} \mathbf{J}_N \right) \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{J}_N \cdot \left( \frac{\nabla \mu + q/n \nabla \phi}{T} \right). \quad (53)$$

Using now the relation (47), the definitions for the electric field  $\mathbf{E} \equiv -\nabla \phi$  and the electric current  $\mathbf{I} \equiv q/n \mathbf{J}_N$ , and multiplying both sides by temperature, we obtain

$$T\sigma_S = -\mathbf{J}_S \cdot \nabla T - \mathbf{I} \cdot \left[ \nabla \left( \frac{\mu}{q/n} \right) - \mathbf{E} \right]. \quad (54)$$

This last expression is, with a slightly different notation, the basic equation XIII.61 used by DEGROOT & MAZUR in their analysis of the same system [9]. Their study of thermoelectricity is twice interesting; first, because they apply equation (54) under isothermal conditions –see their equation XIII.62–

$$T\sigma_S = \mathbf{I} \cdot \left[ \mathbf{E} - \nabla \left( \frac{\mu}{q/n} \right) \right]. \quad (55)$$

*without noticing the zero production of entropy* under such conditions (52) and, second, because of their lengthy and convoluted derivation.

Regarding the first point, DEGROOT & MAZUR are considering thermoelectric systems at mechanical equilibrium which implies, for isothermal conditions and electronic monocomponent, the following constraint –see their equation XIII.50–

$$\nabla \mu - q/n \mathbf{E} = 0. \quad (56)$$

Substituting this back into (55) –i.e., into their equation XIII.62–, we obtain  $\sigma_S = 0$ , in complete agreement with the prediction done by (52) under the same isothermal conditions. DEGROOT & MAZUR *do not notice that their equation XIII.62 trivially vanishes, which would lead to confusions about the dissipative character of the system under study.*

Regarding the second point –i.e., their lengthy and convoluted derivations [9]–, it is important to notice that DEGROOT & MAZUR start by re-defining internal energy –see their equation XIII.32– in presence of electromagnetic fields. There exists a difficulty, their redefinition is not compatible with the usual meaning of internal energy. Internal energy is the energy that has a system at rest in absence of *external* fields [2]; however, their redefinition is not considering the COULOMB interaction energy between particles *within* the system, for example. As is now well-known, the VAN DER WAALS equation for internal energy contains a term due to the interactions between molecules in a gas.

DEGROOT & MAZUR redefinition of the well-established concept of internal energy is clearly motivated by their need to identify  $\mathbf{J}_{Q[1]}$  with  $\mathbf{J}_U$  –see the corresponding redefinition of heat flux in XIII.33–. It must be further emphasized that DEGROOT & MAZUR propose BOLTZMANN kinetic theory of gases as foundation for their approach to irreversible thermodynamics [9]. Within such restricted framework, their definition of heat flux is consistent with a special

concept of internal energy which consists, entirely, of the kinetic energy of translation of particles.

Nevertheless, there are not objective reasons which we would use two different concepts of internal energy at once: one in classical thermodynamics –where internal energy includes the interaction energies between particles– and other concept in irreversible thermodynamics when using  $\mathbf{J}_{Q[1]}$ . Our new definition of heat flux  $\mathbf{J}_Q$  maintains the traditional concept of internal energy [2] and this universality must be considered as another advantage.

DEGROOT & MAZUR give the density of production of entropy for thermoelectric phenomena in their equation XIII.39. Next, they recognize that their own expression, using  $\mathbf{J}_{Q[1]}$ , is not adequate «for the discussion of irreversible phenomena connected with electrical conduction» [9] and then eliminate  $\mathbf{J}_{Q[1]}$  from the equations. After several pages of technical developments, they finally obtain their basic equation XIII.61 –i.e., equation (54) above–. The relevant fact here is that the same expression (54) has been obtained in a much more simple way from (52) thanks to our new  $\mathbf{J}_Q$ .

Similar difficulties arise with the use of  $\mathbf{J}_{Q[3]}$  by KONDEPUDI & PRIGOGINE [1]. Their study of thermoelectricity is twice interesting as well; first, because they propose, by fiat, a density of production of entropy without noticing the incompatibility with their own theory and, second, because of their somewhat convoluted derivations.

Regarding the first point, KONDEPUDI & PRIGOGINE begin with their general expression for the density of production of entropy –see their equation A15.1.13–

$$\sigma_S = \mathbf{J}_{Q[3]} \cdot \nabla \left( \frac{1}{T} \right) - \sum_k \frac{\mathbf{J}_{N_k} \cdot (\nabla \mu_k)_T}{T} + \frac{\mathbf{I} \cdot \mathbf{E}}{T} - \sum_k \frac{\mu_k \sigma_{N_k}}{T}. \quad (57)$$

Readers would be warned that their approach is full of typos and inconsistencies [17]. Readers would also maintain in mind that their expression (57) is not so general as our (46).

In the section «16.3 Thermoelectric phenomena», and without any explanation, KONDEPUDI & PRIGOGINE present the following density of production –see their 16.3.1–

$$\sigma_S = \mathbf{J}_{Q[3]} \cdot \nabla \left( \frac{1}{T} \right) + \frac{\mathbf{I} \cdot \mathbf{E}}{T}. \quad (58)$$

Evidently, the last term in (57) vanishes in absence of chemical reactions, but the elimination of the  $(\nabla \mu_k)_T$  term is not that evident. In fact, KONDEPUDI & PRIGOGINE are considering solid conductors at rest, and these systems verify the constrain –see equation XIII.49 in [9]–

$$(\nabla \mu_k)_T - q/n \mathbf{E} = 0. \quad (59)$$

This constraint implies that the  $\mathbf{I} \cdot \mathbf{E}$  term in (58) must be eliminated as well, because the electric current  $\mathbf{I} \equiv q/n \mathbf{J}_N$ . Otherwise, (58) would predict  $\sigma_S \neq 0$  under isothermal conditions. A nonzero density of production of entropy would be not only in disagreement with our (52), but also in disagreement with the equation XIII.62 by DEGROOT & MAZUR –i.e., with equation (55)–.

Effectively, the thermoelectric expressions (58) by KONDEPUDI & PRIGOGINE and the (54) by DEGROOT & MAZUR only can hold together, under isothermal conditions –see also the constrains (56) and (59)–, if both vanish in agreement with our (52).

Regarding the second point –the convoluted derivations by KONDEPUDI & PRIGOGINE [1]–, it is worth to mention that the tandem of authors begin with a redefinition of their heat flux  $\mathbf{J}_{Q^{[3]}}$  in presence of electromagnetic fields –see their equation 15.4.20–. There exists a difficulty, initially they consider a definition that satisfies  $\mathbf{J}_U = \mathbf{J}_{Q^{[3]}} + u_n \mathbf{J}_N$ , but in their redefinition of heat for systems in presence of fields, this changes to  $\mathbf{J}_U = \mathbf{J}_{Q^{[3]}} + u_n^0 \mathbf{J}_N$ , where  $u_n^0$  is computed in absence of fields! Their redefinition implies a mixture of field-dependent and field-less terms in their formalism. Our new definition (48) avoids such mixtures of terms.

There are more difficulties with their approach. For instance, since their definition of  $\mathbf{J}_{Q^{[3]}}$  has changed, their previous relation (23) separating the entropy transferred by a heat flux from the entropy transferred by a matter flux is no longer valid in presence of fields. This is in contrast with our new definition of heat flux  $\mathbf{J}_Q$ , which maintains the separation (31) also valid in presence of fields (47) and this fact must be considered as another advantage.

Although technical reasons for the rejection of CALLEN's heat flux  $\mathbf{J}_{Q^{[2]}}$  were given in sections 3 and 4, it is worth to analyze the density of production of entropy proposed by him for thermoelectricity under isothermal conditions, because in this case  $\mathbf{J}_{Q^{[2]}}$  is absent. He proposes the following expression

$$\sigma_S = -\mathbf{J}_N \cdot \left( \frac{\nabla \tilde{\mu}}{T} \right), \quad (60)$$

with  $\tilde{\mu} \equiv \mu + q\phi/n$  being the electrochemical potential –see 14.50 in [5]–. Using the definitions for the electric field  $\mathbf{E} \equiv -\nabla\phi$  and the electric current  $\mathbf{I} \equiv q/n \mathbf{J}_N$ , we rewrite it as

$$\sigma_S = -\frac{\mathbf{I}}{T} \cdot \left[ \nabla \left( \frac{\mu}{q/n} \right) - \mathbf{E} \right]. \quad (61)$$

Once again, we can check that (61) coincides with (58) –by KONDEPUDI & PRIGOGINE– and with (54) –by DEGROOT & MAZUR–, under isothermal conditions –see also the constraints (56) and (59)–, only if all them vanish at once, in complete agreement with our (52) for the same system and identical conditions.

## 8 Final remarks

Finally, some consequences of the generalization of the classical thermodynamic expressions to open systems –equations (50) and (51)– deserve to be commented.

For an isolated system, the integration of (51) between an initial and a final equilibrium state predicts that the entropy  $S$  of the system never decreases with time  $\Delta S \geq 0$ . This is a well-known result, but is often misunderstood. For instance, for an open system transporting isothermally energy and matter to the surroundings, and in absence of chemical reactions, the integration of the general expression (51) yields

$$\Delta S - \left[ \frac{Q}{T} + \sum_k \left( \frac{S}{N_k} \right) \Delta N_k \right] \geq 0. \quad (62)$$

Effectively, *the venerable second law of thermodynamics*,  $\Delta_i S \geq 0$ , *continues to hold for open systems* [1, 2, 9], but now the entropy  $S$  can increase, decrease, or remain constant in



function of the flow term  $\Delta_e S$  enclosed in brackets. Contrary to a common confusion, *the decreasing of entropy  $S$  in an open system is perfectly compatible with the second law of thermodynamics.*

Fortunately, this kind of confusions about the second law of thermodynamics for open systems have been successfully corrected in the literature in biological thermodynamics. It is now well-understood that living systems are open systems with maintain *dissipative structures*, in full agreement with the second law of thermodynamics, thanks to flows of entropy  $\Delta_e S$  with the surrounds.

Unfortunately, such confusions still remain in black holes physics. For instance, the general relativist ROBERT M. WALD writes [18]:

*«Even in classical general relativity, there is a serious difficulty with the ordinary second law of thermodynamics when a black hole is present, as originally emphasized by J.A. Wheeler: One can simply take some ordinary matter and drop it into a black hole, where, according to classical general relativity, it will disappear into a spacetime singularity. In this process, one loses the entropy initially present in the matter, and no compensating gain of ordinary entropy occurs, so the total entropy,  $S$ , of matter in the universe decreases. One could attempt to salvage the ordinary second law by invoking the bookkeeping rule that one must continue to count the entropy of matter dropped into a black hole as still contributing to the total entropy of the universe. However, the second law would then have the status of being observationally unverifiable [...] the ordinary second law will fail when matter is dropped into a black hole.»*

This is incorrect. As already mentioned at the start of this section, the second law of thermodynamics does not predict that the entropy of an open system must always increase. Indeed, a simple analysis of (62) shows that a decrease in the total entropy,  $S$ , of matter in universe offers absolutely no difficulty for the ordinary second law. Moreover, the second law continues being observationally verifiable in open systems, with all the known observations up to the date –including laboratory experiments– being in complete agreement with the predictions done by ordinary thermodynamics for open systems [1, 2, 9].

We must accept that such claims as *«the ordinary second law will fail when matter is dropped into a black hole»* [18] must be traced to the insistence of some general relativists to apply the expression of the second law for isolated systems  $\Delta S \geq 0$  to systems which are not isolated! WALD and others would be consistent and *apply the open systems expression of the second law to open systems.*

If we consider ordinary matter plus a black hole, it is interesting to note that the total entropic flow term  $\Delta_e S$  is proportional to the area  $A$  separating the matter system from the black hole –see (3) and (4)–. Precisely an entropic term proportional to the area of the black hole is postulated in black hole physics [18], but this is completely misleading for the following reasons.

First, the presence of an entropic term proportional to area is not related to the exotic nature of black holes, but a mere consequence of ordinary thermodynamics for non-isolated systems.

Second, the total flow  $\Delta_e S$  is *not* minus the total variation in the black hole entropy, but only the entropy transferred between black hole and matter outside. The true total variation,  $\Delta S_{BH}$ , would contain the production term due to dissipative processes within the black hole. WALD, as many others, confounds  $\Delta S_{BH}$  with  $\Delta_e S_{BH} = -\Delta_e S$ .

Third, since  $\Delta_e S$  is not a production of entropy, but a flow term, it can be positive, negative or zero. For instance, if there is not flow of matter –i.e., we are considering a closed black hole [19]– and if the black hole is radiating heat away, then  $Q > 0$  in (62), and can be written as

$$\Delta S + \Delta_e S_{BH} \geq 0, \quad (63)$$

where, evidently,  $\Delta_e S_{BH} \propto \Delta A < 0$ .

By confounding  $\Delta_e S_{BH}$  with  $\Delta S_{BH}$ , general relativist are obligated to consider that the evaporation of a black hole via emission of radiation is not a dissipative process! Moreover, by the same confusion, general relativists claimed for decades that one of the fundamental laws of black hole physics was the law of increasing of area  $\Delta A \geq 0$  [18]; although presented then as the black hole analogue of the second law of thermodynamics is now currently accepted that the area law is violated during evaporation [18]. From the perspective of the thermodynamics of open systems, a result as  $\Delta_e S_{BH} < 0$  for a radiating heat process is perfectly valid and understandable.

There are many more fundamental issues with the traditional literature on black hole physics, but a discussion goes beyond the scope of this work.

Summarizing, the new definition  $\mathbf{J}_Q \equiv \mathbf{J}_U - \sum_j \zeta_j \mathbf{J}_{Z_j} - \sum_k (\mu_k + Ts/n_k) \mathbf{J}_{N_k}$  provides us (i) a complete distinction between open and closed systems, (ii) high non-redundancy, (iii) natural variables for the thermodynamic potentials, and (iv) a sound and complete but intuitive generalization of classical thermodynamic expressions –such as CLAUSIUS  $TdS \geq \delta Q$  and the BORN definition (2)– to open systems.

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- [2] Survey of fundamental laws **1971**: *In Physical Chemistry, An Advanced Treatise; Volume I Thermodynamics; Academic Press, Inc.; London; Wilhelm Jost (Editor)*. HAASE, R.
- [3] IUPAC recommendation for the signs –work is considered positive if increases the energy of the system– is used in this article as in most of the literature. See, for instance, [1, 2, 5, 8, 12].
- [4] Classical thermodynamics is defined over a timeless thermodynamic space associated to «idealized, infinitely slow, reversible processes» [1]. This obligates to the use of imperfect differentials  $\delta$ , for such quantities as heat and work. Modern thermodynamics is defined in an extended thermodynamic space without such idealizations, which «avoids the use of imperfect differentials» [1].

- [5] Thermodynamics and an Introduction to Thermostatistics; Second Edition **1985**: *John Wiley & Sons Inc.; New York*. CALLEN, HERBERT B.
- [6] CALLEN uses the old term «closed» instead of the more modern and accurate term «isolated» for referring to systems that cannot interchange energy or matter with the surrounds [1, 2].
- [7] This is an excellent approximation for systems where there are not large gradients and/or fast processes. When the local approximation does not hold, the formalism of extended thermodynamics is needed. See [12] and references cited therein.
- [8] Definition of Heat in Open Systems **1980**: *Aust. J. Phys.*,33, 95–105. SMITH, D. A.
- [9] Non-equilibrium thermodynamics **1984**: *Courier Dover Publications*. DEGROOT, SYBREN RUURDS; MAZUR, PETER.
- [10] DEDONDER equation  $d_e S = dQ/T$ , associated to modern thermodynamics, would not be confused with the CLAUSIUS equation  $dS = \delta Q/T$  of classical thermodynamics.  
 In the first place, DEDONDER equation is for  $d_e S$ , whereas the CLAUSIUS equation uses  $dS$ . In general,  $d_e S \neq dS$ . This means that CLAUSIUS equation is only valid for reversible processes, whereas DEDONDER equation is valid for irreversible processes as well.  
 In the second place,  $dQ$  in DEDONDER equation uses perfect differentials, whereas the CLAUSIUS equation, relies on imperfect differentials as  $\delta Q$ . See [4] for details.
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- [14] MISNER, THORNE, & WHEELER only consider simple thermodynamic systems and in absence of chemical reactions. They begin by introducing a «heat-flux 4-vector»  $\mathbf{q}$  with components  $(0, q^1, q^2, q^3)$  defined in the rest-frame of the element of volume; they loosely define the spatial components as «energy per unit time crossing unit surface» –see their 22.16.b–, without specifying what energy, although we can guess from their formulation of the first law of thermodynamics that by «energy» they really mean internal energy. Next, they define an «entropy 4-vector» as  $\mathbf{s} \equiv \mathbf{su} + \mathbf{q}/T$  –their 22.16.e– and postulate the «second law of thermodynamics» as  $\nabla^4 \cdot \mathbf{s} \geq 0$  –their 22.16.g–, with  $\nabla^4$  the four-divergence [15].  
 This is all weird and inconsistent. In the first place, the 4-vector  $\mathbf{s}$  cannot be an entropy because has units of flow;  $\mathbf{s}$  is an «entropy-flux 4-vector». In the second place, the trio of authors mix local and material flows when define  $\mathbf{s}$  as their heat-flux 4-vector plus an entropic convective term. This means that the internal energy flux 3-vector associated to the entropy flux 3-vector is measured locally, at a given spacetime point, whereas the heat-flux 3-vector associated to their four-vector  $\mathbf{q}$  cannot be measured locally. Compare with CALLEN and his use of a local heat-flux 3-vector, which is locally measured [5].
- [15] Gravitation **1973**: *W. H. Freeman & Co.; San Francisco*. MISNER, C.; THORNE, K.; WHEELER, J.

- [16] True molar quantities are defined as  $Y/N$ . IUPAC recommends the notation  $Y_m$  for molar quantities. Notice that  $Y/N = y/n$ .
- [17] Detailed analysis of their work reveals that 15.4.20 and 15.4.23, defining the heat flux and the source of heat respectively, contain  $u_k$  instead of the guessed  $u_k^0$ ; both definitions contain extra  $\sum_i$  that have to be eliminated; the tandem of authors give 15.5.12 in terms of an electric current  $\mathbf{I}$  which they define in the text; however, when restating the density of production of entropy –A15.1.13– in terms of their  $\mathbf{J}_{Q^{[3]}}$  they introduce a  $\mathbf{I}_k$  nowhere defined –we can easily guess that  $\mathbf{I}_k$  represents the contribution of ion  $k$  to the electric current–; they use everywhere  $-\nabla\psi$  for the electric field, except in table 15.1 where use  $-\nabla\phi$ ; several expressions in the same chapter contains typos as  $\partial/dt$ ; their 15.5.11 is dimensionally incorrect, but following the text we can guess that the typo is corrected by substituting  $\mathbf{J}_k^\psi$  by  $\mathbf{J}_U$ ; in section 16.3 they start using  $\mathbf{I}_e$  for «*electric current*», but after nine equations suddenly change to the older notation  $\mathbf{I}$ , which then rename as «*current density*»; a  $T$  is missing in 10.1.15 for electrical conduction; both figure 10.3 and equation 10.1.11 confound chemical and electrochemical potentials; etcetera.
- [18] The Thermodynamics of Black Holes **2001**: *Living Rev. Relativity* 4(6), 2012 February 16 (access): <http://www.livingreviews.org/lrr-2001-6>. WALD, ROBERT M.
- [19] although WALD writes «*isolated black hole will radiate away*» [18], this is incorrect, because an isolated system cannot, by definition, radiate anything [6].