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Thermodynamic foundations of physical chemistry: reversible processes and thermal equilibrium into the history

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Abstract

In the history of science, the birth of classical chemistry (1789) and thermodynamics (1824) produced an anomaly within Newtonian mechanical paradigm: force and acceleration were no longer citizens of new cited sciences. Scholars tried to reintroduce them within mechanistic approaches, as the case of the kinetic gas theory. Nevertheless, Thermodynamics, in general, and its Second Law, in particular, gradually affirmed their role of dominant not-reducible cognitive paradigms for various scientific disciplines: more than twenty formulations of Second Law—a sort of indisputable intellectual wealth—are conceived after 1824 Sadi Carnot's original statement and a multitude of entropy functions are proposed after 1865 Clausius' former definition. Furthermore, at the end of nineteenth century, thermodynamics extended its cognitive domain to chemistry. Mainly thanks to Gibbs, a *brand new* discipline—*chemical thermodynamics* or *physical chemistry*—gradually affirmed its role inside the scientific community. This paper reports the former results of collaborative research program in the History and Epistemology of Science (chemistry, physics and mathematics relationship) as well as Nature of Science Teaching aimed at retracing the foundations of the *physical chemistry*. Specifically, the research is structured in three parts: (1) historical-epistemic reflections on fundamental thermodynamic concepts and principles—such as reversible process, heat, temperature, thermal equilibrium and Clausius' Second Law—that play a structural role inside modern *physical chemistry*; (2) panoramic overview on the *entropy*, whose polysemy makes it one of the most demanding concepts for scholars, teachers and students while approaching thermodynamics; (3) conceptualization of chemical equilibrium as complex entity according to the dual epistemological approach offered by Gibbs' *thermodynamic* model and the *kinetic* standpoint by Guldberg and Waage. In particular, the present work details an original reading of thermodynamic principles with the aim of setting forth a rationalized multidisciplinary substrate whereon the foundational concepts of *reversible process* and *thermal equilibrium* can be set.

Keywords Thermodynamics · Chemistry · Physics · Principles · Entropy · Energy · Carnot · Clausius · Prigogine · Gibbs · Foundations · Nature of Science (NoS) · Teaching

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Introduction

> There is not a discovery in science, however revolutionary, however sparkling with insight that does not arise out of what went before. 'If I have seen further than other men', said Isaac Newton, 'it is because I have stood on the shoulders of giants.' (Asimov 1966, p. xi).

More generally, according to Isaac Asimov's (1920–1992) *Understanding Physics*—science needs an historical approach that allows—nowadays—contextualizing scientific discoveries and ideas within the cultural–intellectual background wherein they developed.

This approach is particularly useful when dealing with *physical chemistry*, resulting from a sort of merge of two distinct disciplines: chemistry and thermodynamics. Despite epistemic similarities (such as the not mechanistic approach marking their difference from mechanics, electricity or magnetism of the nineteenth century), thermodynamics (Müller 2007; Hess 1842; Leicester 1951; Médard and Tachoire 1994; Kragh and Weininger 1996; Truesdell 1980; Buchdahl 1966; Boudenot 2001; Cochran and Heron 2006) and chemistry (Causey 1971; Scerri 2001, 2007a, b, 2013; Scerri and Worrall 2001; Hartely 1971) follow truly different cognitive paths. Thermodynamics (within Clausius' approach) mathematically interprets transformations in terms of state functions (energy and entropy) and process functions (work and heat) (Clausius 1850; Müller 2007; Callen 1985). Conversely, chemistry—along with the tradition of nineteenth-century French school (Berthollet 1803; Lavoisier 1789, 1862–1893; Lavoisier and Laplace 1784; Kapoor 1970–1980; Nash 1957)—relies its foundations on the notion of *affinity*, a fundamental concept explaining the chemical reactivity (Waage and Guldberg 1864, 1867, 1986). At the end of nineteenth century, following Gibbs' seminal works on equilibrium of heterogeneous substances (Gibbs 1892, 1899, 1902, 1906, 1990), thermodynamics undergoes a huge cognitive evolution. From pretty *engineeristic* discipline, aimed at optimizing the efficiency of heat engines (Carnot 1824, 1897, 1986; Fox 1971; Clapeyron 1834), it oriented its focus on more complex systems undergoing chemical transformations. This thermodynamics' evolution—leaning on Gibbs's works on chemical equilibrium—can be seen as the foundational act of the brand new *physical chemistry*.

In other words, current physical chemistry—based on Gibbs' general theory of equilibrium (Gibbs 1892, 1899, 1902, 1906, 1990)—actually stems as the last conceptual brick of an almost 50-year-long cognitive process, which was ignited by Carnot's (1824) paper (Carnot 1824), continued by Clausius with thermodynamics' fundamental equation (Clausius 1867) hence extended by Gibbs (1892, 1899) to chemically reactive systems through the introduction of potentials (i.e.: *chemical potential*). In addition, the socio-historical foundations of both thermodynamics (Pisano 2009b, 2011a, b) and industrial chemistry (Pellegrino et al. 2016) seem also to be necessary for conceptualizing these nineteenth-century discoveries. In fact, whilst the development of thermodynamics in the nineteenth century (from Sadi Carnot to Clausius) is intimately linked to the study of heat machines (Pisano and Bussotti 2015, 2016, 2017a), the origin of Gibbs' equilibrium theory can be retraced among the technological needs of former chemical industries (Pellegrino et al. 2016).

It remains that the scientific roots of *physical–chemistry* stand among the foundations of nineteenth-century thermodynamics. Clarifying the conceptualisation process of entropy, energy, heat as well as of thermodynamic fundamental principles represents a necessary step for contextualizing the modern chemical thermodynamics inside the Epistemology of

Science and Nature of Science (Anakkar 2014; Nagels 2017). This process of contextualisation as well as its cognitive implications constitutes the object of the present paper.[1]

Scientific foundations of the *thermodynamic paradigm* and Nature of Science's problematic implications

Generally speaking, physics and chemistry—like other natural sciences—consist in observing nature, in quantifying the observations and in summarizing the results by means of a formal language. This latter is the syntactic structure that allows, for example, mathematically codifying physical laws and symbolically representing chemical formulas. However, in educational context the formal language necessarily intertwines with the natural language whereon the oral and written communication depends. Hence, as Williams (1999) pinpoints, language difficulties inevitably have implications in education, even though the role of language—in Nature of Science—is often underestimated. Examples of these criticisms are the definition of concepts such as *quasi-static process*, *reversible (and irreversible) process*, the conceptual characterization of *Temperature, Heat and Energy* and the conceptual relation between the *Second Law, entropy* and *thermal equilibrium* (Pisano 2010; Anakkar 2014; Pellegrino 2016; Nagels 2017). Our thesis is that a historical-epistemological approach, leaning on the study of primary sources, allows clarifying the meaning of such problematic concepts, hence avoiding common misconceptions. In particular, in the following sections, we analyse two paradigmatic cases. First, we critically develop the notion of *reversible process* by framing it inside Clausius' mathematical model (Clausius 1867) and inside critical Prigogine's approach (Prigogine 1967, 1996, 1997). *Secondo*, we deliver an original example—not yet developed in textbooks—useful to conceptualize the *thermal equilibrium* and to explain how it is intertwined with the Temperature, the Heat, the Entropy and the Second Law.

Quasi-static, reversible processes and Clausius' framework

A *quasi-static process* is a theoretical instance: *no* real process is quasi-static. A real process approximately behaves as *quasi-static* if it evolves infinitesimally slowly. *However, what does it mean from empirical standpoint?* A process cannot be static (equilibrium

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[1] Authors' scientific collaboration allows retracing an historical—and—historical epistemology *fil rouge* inside nineteenth–twentieth century scientific debate; particularly, intertwining *paradigmatical anomalies* from mechanics to thermodynamics, and from thermodynamics to statistical mechanics until to the *quanta* at beginning of the twentieth century (Planck 1901). Actually, this collaboration relies on a multidisciplinary conceptual framework resulting from authors' interdisciplinary specializations/research: Pisano from his teaching physics and mathematics, history of physics–mathematics research-NoS, Anakkar from his teaching physics studies, Pellegrino from his doctoral studies (2016. Torino University, Italy. Co-supervisor Prof. Pisano. Examination committee, Prof. Anakkar) and Nagels from his doctoral studies (2017. Lille University. Supervisor Prof. Anakkar and examination committee, Prof. Pisano). Particularly, this paper also adopts an advanced—structured reorganization of a short self-sufficient interlude and spots-ideas on history of mechanics and history of thermodynamics presented in previous publications of one us (RP). Therefore, theoretical advancements as cases study—are cited from them as a self-citation. For example: *Sadi Carnot: A Scientific and Filial Relationship* (Gillispie and Pisano 2014, 197–199, 353–356, 375–381), *Tartaglia's science of weights* (Pisano and Capecchi 2015, 224–225), *The Emergencies of Mechanics and Thermodynamics in the Western Society during 18th–19th Century* (Pisano and Bussotti 2015, 412–413).

situation) and dynamic (non-equilibrium situation or dynamical one) at one time. Nevertheless, this instance becomes meaningful by referring to the mathematical concept of *infinitesimal*, a quantity, which is smaller than any feasible measurement, but not zero in size; and at one time, so small that it cannot be distinguished from zero by any available means.[2] *Again, what does it mean in an empirical physics?* Moreover, *if we do not use strict empirical procedures and instruments*, *what kind of physics are we talking about?* In effect, this scientific approach—i.e. leaning on infinitesimal calculus—is far from a *measurable physics. Quasi-static* processes interpreted as infinitesimal entities do not correspond to any real entity and their meaning can be only contextualized inside the theoretical structure of infinitesimal analysis. Conversely, the *quasi-static* concept can also be interpreted by constructive mathematics where each point is a range of values: in that case, the notion can be explained in terms of *measurable physics.*

Reversible process is another conceptual entity whose definition—in NoS context—is truly demanding (Thomsen and Bers 1996; Tolmann and Fine 1948; Prigogine and Stengers 1992; Prigogine and Kondepudi 1999; Méheut et al. 2004; Hertz 2004; Samiullah 2007). Reversible processes do not exist in nature (Pisano 2010; Gillispie and Pisano 2014, Chapters IX–XI): their behaviour can be approximated—for example—by infinitesimally slow transformations or by processes in which dissipative effects are negligible. Despite their ideal nature, reversible processes played a key role within the epistemic process that led Sadi Carnot to conceive (*Ibidem)* his theory:

> The necessary condition of the maximum is, then, *that in the bodies employed to realize the motive power of heat there should not occur any change of temperature which may not be due to a change of volume.* Reciprocally, every time that this condition is fulfilled the maximum will be attained. This principle should never be lost of sight in the construction of heat-engines; it is its fundamental basis. If it cannot be strictly observed, it should at least be departed from as little as possible (Carnot 1978, p. 28).

Moreover, reversible processes represent ideal circumstances wherein certain physical quantities, such as the efficiency of heat engines or the maximum work that can be obtained from a heat machine, have their optimum value.

> Sadi Carnot does not employ the concept of reversibility in his *posthumous manuscript*. We maintain that if he had completed his manuscript, he would have only obtained value W as a consequence of the variables characterizing a heat machine. However, with regard to natural phenomena, he states that these machines, even having the same values of variables, produce very different work. These are not mere approximations; they represent a preventative problem for the use of mathematics to interpret a phenomenon. Thus, Carnot is addressing the problem of the relationship between mathematics and physics in the theory. In the discursive part of *Réflexions sur la puissance motrice du feu* (Carnot 1978, pp. 1–73), Sadi Carnot introduces his original concept of the cycle, both as a method of reasoning and a method of calculation alternative to infinitesimal analysis. He dedicates several pages (Carnot 1978,

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[2] Generally speaking, in constructive mathematics a point is a range (not an infinitesimal point) typical of empirical measurements in physics. Of course this mathematical approach did not obtain properly the entire *power of calculus* such as possible to have by means of infinitesimal analyses (Pisano 2011a, b, 2013a, b, c; Pisano and Bussotti 2012).

pp. 14–22) to presenting his reasoning regarding the first demonstration for a three-phase cycle and goes on to discuss the cycle of inverse operations (Carnot 1978, p. 19). He then presents the first expression of his theorem (Carnot 1978, pp. 21–22).[3]

The conceptual notion of reversible—and—irreversible process inside advanced thermodynamics and its interplay with the Second Law of Thermodynamics was not a matter of fairly scientific agreement among the authors (i.e., see Prigogine 1967, 1996, pp. 68–71). For, from historical and nature of science standpoints, it could be interesting the following discussion.

Clausius' main reasoning leading to the famous mathematical expression of the Second Law does not correspond to a simple mathematical opening to new physical and logical paths, but it is the result of elaborated progressive cognitive processes, almost 15-year long, which can be retraced throughout most Clausius' scientific writings.[4] In particular, 1872 Clausius' paper (Clausius 1872) presents a summary of the main steps of this process and, specifically, reports the following conclusions,[5] for *non-cyclic processes*. For completeness, in the following, we quote the main reasoning until to the 1872—*Memoir*:

1. Clausius provides a dual conceptual distinction of work by defining two physical quantities: *innere Arbeit* and *äußere Arbeit*, which can be translated as *interior* and *exterior work*, respectively. The physical meaning of this two instances explicitly relies on Clausius atomistic idea of matter wherein constituent particles are subjected to attractive forces. Hence, according to this model, a change of aggregation state, e.g. from liquid to gaseous one, takes place since heat wins the attractive forces among particles. In this frame of ideas, the *innere Arbeit* is defined as the quantity of work necessary to overcome the mutual attraction of the particles and to separate them to the distance they occupy in a state of vapor. In Clausius' words this reads as follows:

   > The work produced is of a twofold nature. First, a certain quantity of work is necessary to overcome the mutual attraction of the particles, and to separate them to the distance that they occupy in a state of vapour. Secondly, the vapour during its development must, in order to procure room for itself, force back an outer pressure. We name it innere Arbeit […]. (Clausius 1850, p. 375; Pellegrino's translation)

   Conversely, the *äußere Arbeit*—whose meaning is very close to the notion of macroscopic mechanical work as used in current thermodynamics—is defined as follows:

   > Secondly, the vapour during its development must, in order to procure room for itself, force back an outer pressure. We name this latter äußere Arbeit. (Clausius 1850, p. 375; Pellegrino's translation)

   At this point, we would like to specify that Clausius does not use the script δ to distinguish non-total differentials. Hence, he writes dI and dW to designate interior (total differential) and exterior work (non-total differential), respectively.

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[3] Cf. Gillispie and Pisano (2014, p. 404).

[4] Clausius (1850, 1865, 1867, 1872). See also Thomson (1848–1849, 1851a, b, 1852, 1882–1911), Mayer (1842a, b), Saint-Robert (1865, 1870a, b, c) and Fox 1969, 1971).

[5] On the subject, see recently Pellegrino (2016) and Gillispie and Pisano (2014, chaps. 6–8).

2. Likewise, Clausius provides a conceptual distinction of heat into two categories: *freie Wärme* and *latente Wärme* that can be translated in English as *free heat* and *hidden heat*, respectively. The discriminant between these two entities stands in the fact that *freie Wärme* (symbolically represented with the letter) corresponds to the quantity of heat that cannot be transformed into work and that is dispersed in the outside. Conversely, *latente Wärme* (designated by the letter) corresponds to the quantity of heat that can actually be transformed into work.[6]
3. It remains that *latente Wärme* and *innere Arbeit* are pre-modern quantities. They are no more used in current thermodynamics as well as the *Disgregation*, that Clausius defined as follows:

   > By disgregation is represented […] the degree of dispersion of the body. Thus, for example, the disgregation of a body is greater in the liquid state than in the solid, and greater in the aeriform than liquid state. (Clausius 1867, p. 226)

4. Based on these premises, Clausius mathematically formulates the *second fundamental* theorem of the Mechanical Theory of Heat and provides the truly former definition of entropy. He writes:

   > With the aid of this quantity [disgregation[7]] and of that indicated with H, the heat actually available in the system, instead of the above relation I could obtain the following general statement
   > The sum $\int \frac{\mathrm{dH}}{\mathrm{T}} + \int \mathrm{dZ}$ is that to which I have given name of Entropy of a system.
   >
   > $$\int \frac{dQ + dH}{T} + \int dZ \geq 0 \tag{1}$$
   >
   > (Clausius 1872, pp. 145–146; Pellegrino's translation)

Clearly, entropy assumption given by $\int \frac{\mathrm{dH}}{\mathrm{T}} + \int \mathrm{dZ}$ in terms of disgregation (dZ) and hidden heat (dH) needs to be interpreted. The key hermeneutic passage (Pellegrino et al. 2015) is to formally consider infinitesimals elements (i.e. ignoring integrals) and to give entropy definition equal to dS, hence writing:

$$\frac{dH}{T} + dZ = dS \tag{2}$$

By substituting it into the previous inequality (1) written by ignoring the integrals, that is to say:

$$\frac{dQ + dH}{T} + dZ \geq 0 \tag{3}$$

we obtain

$$\frac{dQ}{T} + dS \geq 0 \tag{4}$$

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[6] Clausius writes dH (total differential) and dQ (non-total differential) for *Latente Wärme* and *Freie Wärme* respectively.

[7] 1862—*sixth Memoir—On the Application of the Theorem of the Equivalence of Transformations to Interior Work.*

Hence, changing the sign of heat[8] and rearranging it follows

$$dS \geq \frac{dQ}{T} \tag{5}$$

It is worth noticing that in his 1867—*Memories*, Clausius does not report this latter inequality. Instead, in his ninth-*Memoir* he delivers a mathematical expression for entropy, in case of reversible processes, through a truly different path that we quote and comment:

> In fact if [...] the integral $\int \frac{dQ}{T}$ vanishes whenever the body, starting from any initial condition, returns thereto after its passage through any other conditions, then the expression $\frac{dQ}{T}$ under the sign of integration must be the complete differential of a magnitude which depends only on the present existing condition of the body, and not upon the way by which it reached the latter. Denoting this magnitude by S, we can write
>
> $$dS = \frac{dQ}{T} \tag{6}$$
>
> or, if we conceive this equation to be integrated for any reversible process whereby the body can pass from the selected initial condition to its present one, and denote at the same time by S_0 the value which the magnitude S has in that initial condition,
>
> $$S = S_0 + \int \frac{dQ}{T} \tag{7}$$
>
> (Clausius 1867, p. 355).

Actually, the logical premise of this reasoning relies on his 1854 discoveries on *cyclic processes* (Clausius 1854, 1872, p. 144) proving that a quantity *N:*

$$N = \int \frac{dQ}{T} \tag{8}$$

(that he named *uncompensated transformation*; *Ibidem*), cannot be negative in cyclic boundary conditions; at least N can be zeros in case of reversibility. Hence, since the integral $\int \frac{dQ}{T}$ vanishes in case of cyclic reversible processes, then Clausius concludes that the integrand $\frac{dQ}{T}$ is an exact differential (Clausius 1867, p. 355). The next passage is crucial to extend the reasoning to *non-cyclic reversible processes*: he says that $\frac{dQ}{T}$ has to be the exact differential of a physical quantity that in current language we can define as *state quantity*; in fact, according to Clausius this quantity value does not depend on the path but "on the present existing condition of the body" (*Ibidem*). For, Clausius designates by S this quantity (*Ibidem*). He says that it corresponds to what he called *Entropie*[9] hence writing its differential as (*Ibidem*):

$$dS = \frac{dQ}{T} \tag{9}$$

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[8] Clausius assumes the opposite convention; in fact, as regard to the heat element, he specifies that "*dQ* is the heat element that flows from the body under transformation towards a heat reservoir." (Clausius 1872, p. 144) (Pellegrino's translation).

[9] See also *moment of activity* in Carnot (1803a, b) and Gillispie and Pisano (2014).

By integrating above Eq. (9), he obtains the following definition for entropy in *non-cyclic reversible conditions:*

$$S = S_0 + \int \frac{dQ}{T} \tag{10}$$

What about entropy in irreversible processes? Clausius does finish his *ninth—and last—memoir* without discussing this subject (Pisano and Pellegrino 2019, pre-print). His ultimate implications of Entropy definition—that we find in the Appendix to the *Ninth-Memoir* published in 1866—is to

> […] show how the equations which serve for the determination of energy and entropy may be derived directly from the fundamental equations of the mechanical theory of heat. (Clausius 1867, p. 366)

In addition, he specifies:

> We have, therefore,
>
> $$dQ = dU + dw$$
>
> $$dQ = TdS$$
>
> The first of these two equations applies to reversible as well as to non-reversible changes; the second, on the contrary, holds good for reversible changes solely. But in order to be able to bring the two equations into conjunction, we will suppose that they relate to one and the same reversible change of a body. In this case the thermal element dQ is the same in both equations, hence we can eliminate it from the equations, whereby we obtain $TdS = dU + dw$ (Clausius 1867, p. 366).[10]

To continue the discussion on the irreversible changes, based on Clausius' inequality, let us consider a general case of non-cyclic process:

$$\int dS \geq \int \frac{dQ}{T} \tag{11}$$

In case of irreversibility and considering infinitesimals processes Eq. (11) reduces to:

$$dS > \frac{dQ}{T} \tag{12}$$

Now, let us introduce a strictly non-negative quantity d_iS, which is zero in case of reversibility and positive otherwise. Hence, above inequality can be written as:

$$dS = \frac{dQ}{T} + d_iS \tag{13}$$

In fact,

$$\text{if } d_iS = 0 \text{ (i.e. reversible process) then } dS = \frac{dQ}{T}$$

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[10] It is worth noticing that few years later Gibbs uses this latter equation (i.e.: $TdS = dU + dw$) as the foundational element of his thermodynamic theory (Gibbs 1906).

Table 1 Syntactic discussion on the sign of entropy by using Clausius' Second Law in irreversible processes

Type of process	Entropy variation[a]		
Adiabatic process	$\frac{dQ}{T} = 0$	$dS > 0$	
Endothermic process	$\frac{dQ}{T} > 0$	$dS > 0$	
Exothermic process	$\frac{dQ}{T} < 0$	$dS > 0$ if	$\left\|\frac{dQ}{T}\right\| < \|d_iS\|$
		$dS = 0$ if	$\left\|\frac{dQ}{T}\right\| = \|d_iS\|$
		$dS < 0$ if	$\left\|\frac{dQ}{T}\right\| > \|d_iS\|$

[a] In order to avoid misunderstanding for our historical scientific analysis, we maintain the absolute values

$$\text{if } d_iS > 0 \text{ (i.e. irreversible process) then } dS > \frac{dQ}{T}$$

In this theoretical framework—and according to the *physical and mathematical* nature of the irreversible process (i.e. adiabatic, exothermic and endothermic)—we present the panorama as is Table 1:

In case of irreversible process either adiabatic or endothermic, the sign of entropy variation is known and strictly positive. Conversely, in case of exothermic irreversible processes entropy variation can be null, positive or negative, depending on the concurrence between the absolute values of $\frac{dQ}{T}$ and d_iS. Nevertheless, the absolute value of the term d_iS is unknown. Hence, the sign of entropy variation for irreversible exothermic process cannot definitely be known.

To conclude this historical path on entropy and irreversibility it is interesting to mention Prigogine's approach. Ilya Prigogine (1917–2003), starting from above Clausius' equations (Clausius 1872, pp. 145–146) expressing the second law for adiabatically isolated systems ($dS \geq 0$), developed a model aimed at extending the second law to not isolated systems. More specifically, he modeled the thermodynamic behavior of an arbitrary open system by considering the entity made of the system and its outside. According to entropy extensive nature, in this case

> The change of entropy dS can be split into two parts. Denoting by d_eS the flow of entropy, due to intersections with the exterior, and by d_iS the contribution due to changes inside the system, we have[11]
>
> $$dS = d_eS + d_iS \tag{3.3}$$
>
> The entropy increase d_iS due to changes inside the system is never negative. It is zero when the system undergoes reversible changes only, but it is positive if the system is subject to irreversible processes as well.
>
> $$d_iS = 0 \quad \text{(reversible process)} \tag{3.4}$$
>
> $$d_iS > 0 \quad \text{(irreversible process)} \tag{3.5}$$
>
> (Prigogine 1955, p. 16).

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[11] Numbering of this quotation are the ones of original Prigonine's text.

hence attaining a principle (valid for open systems only) stating that:

> The only *general criterion* of irreversibility is given by the entropy production according to (3.4) and (3.5). (Prigogine 1955, p. 17).

In addition, Prigogine also observed a certain weakness[12] within De Donder's (1870–1957) results. In *The End of Certainty* (Prigogine 1997), he wrote:

> In Chapter 1, we mentioned the classical formulation of the second law of thermodynamics attributed to Clausius. The law is based on in inequality: The entropy, S, of an isolated system increases monotonically until it reaches its maximum value at thermodynamic equilibrium. We therefore have $dS \geq 0$ for the change in entropy over the course of time. How can we extend this statement to systems that are not isolated, but which exchange energy and matter with the outside world? We must then distinguish two terms in the entropy change, dS: the first, d_eS, is the transfer of entropy across the boundaries of the system; the second, d_iS, is the entropy produced within the system. As result, we have $dS = d_eS + d_iS$. We can now express the second law [attributed to Clausius as above] by stating that whatever the boundary conditions, the entropy production d_iS is positive, that is, $d_iS \geq 0$. *Irreversible processes are creating entropy*. De Donder (Donder and Rysselberghe 1936) went even farther: He expressed the production of entropy per unit time $P = d_iS/dt$ in terms of the rates of various irreversible processes (chemical reaction rates, diffusion, etc.) and thermodynamics forces. In fact, he considered only chemical reactions, but further generalizations was easy (by bibliographical footnote, he cites Donder and Rysselberghe 1936). De Donder himself did not go very far along this road. He was concerned mainly with equilibrium and neighbourhood of equilibrium. Limited as it was, his work represented an important step in the formulation of non-equilibrium thermodynamics, even if it seemed to lead nowhere for considerable length of time. I still remember the hostility with de Donder's work met. For the vast majority of scientists, thermodynamics had to be limited *strictly* to equilibrium. That was the opinion of J. Willard Gibbs, as well as of Gilbert N. Lewis, the most renowned thermodynamicist of his day. Lewis went so far as to write "We shall see that nearly everywhere the physicist has purged from his science the use of one-way … alien to the ideals of physics."[by bibliographical footnote, he cites Lewis's *The Symmetry of Time in Physics*[13]] (Prigogine 1997, pp. 60–61; author's italics, ellipsis and quotations)

To summarize, the Eq. (13), in spite of its mathematical similarity with the famous Prigogine's equation (see above Prigogine 1955, Eq. 3.3), also corresponds to a formal passage necessary for our next hermeneutic reading of Clausius' equation as above presented (Eq. 1). In fact, taking into account above cited

- Clausius' second principle and entropy reasoning (1850, 1865, 1867, 1872)

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[12] As remarked in the running text the matter is object of discussion, especially from physics-mathematics standpoint. Unfortunately, we have not so much room to deal with this interesting aspect of the thermodynamics of the second half of the nineteenth century and the beginning of the twentieth century.

[13] This is full the Lewis's arguing: "We shall see that nearly everywhere the physicist has purged from his science the use of one-way time, as though aware that this idea introduces an anthropomorphic element alien to the ideals of physics. Nevertheless, in several important cases unidirectional time and unidirectional causality have been invoked, but always, as we shall proceed to show in support of some false doctrine." (Lewis 1930, p. 570; see also Prigogine and Stengers 1984, p. 233).

- Prigogine's[14] researches (Prigogine 1967, pp. 27–29, 1996, pp. 69–70)
- And related arguments by Théofile de De Donder's (1870–1957)[15]

then, Clausius' Second Law reasoning (Clausius 1872, pp. 145–146) can be written as equality (Eq. 32) by introducing a differential d_iS strictly non-negative—corresponding to the *irreversible part* of entropy. This step has to be logically read as a premise of the above hermeneutical reading of Clausius' equation (Table 1).

We conclude this section by means of a brief foundational discussion on how our aforementioned historical findings can be used to contextualize the notion of Clausius' inequality,[16] entropy and the second principle of thermodynamics. More specifically, we deliver a historical-epistemological discussion of the basic thermodynamic elements reported in the following chart and which are often source of problems in Nature of Science (physics, chemistry, mathematics).

In order to sweep away a common source of misconceptions regarding Clausius' inequality and the Clausius' Second Law, it is useful to consider that these two conceptual entities result from a long process that went through a number of subsequent steps reflecting the evolution of Clausius' thought (Pisano and Pellegrino 2019, pre-print). In particular, it is important to be aware that, at first, Clausius dealt with cyclic transformations, hence delivering what we call Clausius' inequality, and only subsequently, he provided the *extension of his second fundamental theorem* to non-cyclic processes through the definition of entropy, hence establishing the bases for the modern second principle. In fact, concerning cyclic processes, in 1862 Clausius writes:

> […] I have further completed the analysis. The previous expression for the uncompensated transformation concerning only cyclic processes, can also be written as follows:
>
> $$\int \frac{dQ}{T} \geq 0 \tag{14}$$
>
> that holds only for a cyclic process. (Clausius 1872, p. 145) (Pellegrino's translation)

The Eq. (14) is the former expression of what we currently call Clausius' inequality but it needs to be correctly read. As first, it is necessary to take into account that Clausius, even if he acknowledges the nature of non-total differential for Q, does not use the current script δ to designate the differential of Q. Hence dQ has to be replaced by δQ. Then, Clausius in this context does not use the symbol $\oint$ for cyclic integral: he simply specifies it in the text. Hence, an undefined integral $\int$ has to be replaced by a cyclical $\oint$.

Finally, Clausius uses a convention of sign for heat that is opposite to the current one. In order to have a positive sign when heat is absorbed by the system, inequality has to be inversed. For that, Clausius previous inequality (Eq. 14) also known as *Clausius' theorem* (Clausius 1872, pp. 145–146), in currently modern notation, corresponds—for *cyclic processes*—to:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{15}$$

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[14] See also Tolman and Fine (1948), Tishin and Spichkin (2016), Pellegrino (2016) and Nagels (2017).

[15] Donder and Rysselberghe (1936); see also the quotation by Prigogine on De Donder (Prigogine 1996, p. 70) and De Donder's *Leçons* and related studies on the affinities (De Donder 1920, 1928, 1931, 1934).

[16] The subject is part of a larger current research (Pisano and Pellegrino 2019, pre-print).

Table 2 Synopsis comparing Clausius' inequality and entropy inequality

Clausius' inequality	Entropy	Entropy inequality
$\oint \frac{\delta Q}{T} \leq 0$	$dS = \frac{\delta Q}{T}$	$dS \geq \frac{\delta Q}{T}$

By commenting the Eq. (15), it is worth mentioning how Clausius recognizes that the quantity under integral is an exact differential in case of cyclic and reversible process. We report again Clausius' words:

> The integral $\int \frac{dQ}{T}$ vanishes whenever the body, starting from any initial condition, returns thereto after its passage through any other conditions, then the expression $\frac{dQ}{T}$ under the sign of integration must be the complete differential of a magnitude which depends only on the present existing condition of the body, and not upon the way by which it reached the latter (Clausius 1867, p. 355).

Alternatively, in current thermodynamics this same reasoning can be developed by considering that, in case of reversible and cyclic process, the quantity $\frac{1}{T}$ plays the role of integrating factor with respect to the non-total differential δQ.

In Nature of Science contexts, usually it is said that there is a relationship-proof between *Clausius inequality* and the *entropy*. For sake of brevity, is said that a certain quantity is added to a system during a cyclical process: this quantity is a potential function and it is defined such as

$$dS = \frac{dQ}{T}, \text{ or such as } \Delta S = \oint \frac{\delta Q}{T}. \tag{16}$$

Actually, in Clausius' works we can perceive a relationship between the epistemic content of the inequality for cyclic processes and the entropy but the reasoning is slightly different. Clausius investigates cyclic processes within a logical framework grounded on the idea of *Aequivalenzwerth* and *uncompensirte Verwandlung (uncompensated transformation)*, this latter being a quantity that is added during an irreversible cycle and is mathematically defined, in 1854 (Clausius 1872, p. 144), as a quantity N:

$$N = \oint \frac{\delta Q}{T} \tag{17}$$

named as *uncompensirte Verwandlung* (*Ibidem*). This quantity, even if its definition is formally equivalent to aforementioned ΔS definition, is not the entropy but it may be seen as a conceptual precursor of entropy. Actually, entropy is historically defined 11 years later inside the context of non-cyclic process investigations. Nevertheless, it remains that this quantity N shares two properties with entropy: it is a state function and it has the same dimensions [J/K].

To summarize, Clausius' inequality can be correctly contextualized as the mathematical expression of the second law for infinitesimal cycles and heat changes whilst the scientific roots of entropy can be found within its conceptual content. Furthermore, the definition of entropy and the *entropy inequality* as reported in the previous Table 2, historically emerged from Clausius' treatment of non-cyclic processes. As briefly discussed before, they result from a complex cognitive activity that we can summarize by saying that in Clausius' Memoires there are two definitions of entropy. One is defined in terms of disgregation and hidden heat (Clausius 1867, p. 226, 1872, pp. 145–146; see also above Eq. 1). The second one is delivered through the following expression (18), that is valid for reversible process only.

$$dS = \frac{\delta Q}{T} \tag{18}$$

In this same historical framework, the expression of the second principle—as exactly presented above by Table 2—expressed as $dS \geq \frac{\delta Q}{T}$ is not explicitly discussed in Clausius' memoires. Conversely, as it has been shown, its origin can be retraced by considering the former expression of Clausius' second theorem of *Mechanical Theory of Heat* extended to non-cyclic processes and formulated in terms of pre-modern quantities disgregation and hidden heat (Eq. 3).

Thermal equilibrium, entropy and the second law: a subtle mutual relationship

A critical point in Nature of Science is the conceptual distinction between temperature, heat and energy.[17] It is worth quoting how Max Planck introduced the difference between Temperature and Heat at the beginning of chapter III of his Treatise of Thermodynamics:

> If we plunge a piece of iron and a piece of lead, both of equal weight and at the same temperature (100 °C), into two precisely similar vessels containing equal quantities of water at 0 °C, we find that, after thermal equilibrium has been established in each case, the vessel containing the iron has increased in temperature much more than that containing the lead. Conversely, a quantity of water at 100 °C is cooled to a much lower temperature by a piece of iron at 0 °C, than by an equal weight of lead at the same temperature. This phenomenon leads to a distinction between temperature and heat. (Planck 1917, p. 34)

Planck's empirical approach (Planck 1914, 1991) actually suggests leaning the definitions of these problematic quantities on *measurable physics*. In this perspective, we can synthetically deliver the following assumptions.

Temperature can be presented as the physical quantity measured by the thermometer (Chang 2004, 2012), and given by the thermometry equation:

$$l_f = l_0(1 + \alpha \Delta T). \tag{19}$$

Heat can be presented as the physical quantity measured with the calorimeter (Duprez and Méheut 2007; Iacona et al. 2012) by leaning on the calorimetric fundamental equation that, at constant volume, reads as:

$$Q = mc\Delta T \tag{20}$$

Finally, *energy* definition (Smith and Wise 1989; Ngô 2009) can be (only) introduced by discussing First Law of Thermodynamics (Clausius 1850) for *non-cyclic processes* as in term of internal energy:

$$\Delta U = Q \pm W \tag{21}$$

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[17] Baierlein (1994) indicates that students find it difficult to distinguish properly between the internal energy U and heat transfer Q. Cannon (2004) shows that the physical meaning generally attributed to thermodynamic potentials (enthalpy, Helmholtz energy, Gibbs energy denoted respectively H, F and G) also is not clear. Williams (1999) and Anakkar (2014) confirmed that textbooks have semantic problems: unclear or contradictory definitions, including statement of the principles that normally should no longer be an issue of divergence.

or, for infinitesimal *quasi-static processes,*[18] as in term of energy:

$$dE = \delta Q \pm \delta W \tag{22}$$

Furthermore, heat and temperature were physical quantities that play a central role to define the *thermal equilibrium* (Fourier 1822; Laplace 1822; Lamé 1836, 1861a, b; Reech 1853, 1854). In 1807, Joseph Black (1728–1799) in the second volume of his *Lectures on the elements of chemistry* describes the attainment of thermal equilibrium as follows:

> In this manner, therefore, and upon all occasions without exceptions, is heat communicated from hotter bodies to colder ones, when they are in contact, or in the vicinity of one another; and the communication goes on until the bodies are reduced to an equal temperature, indicating an equilibrium of heat with one another. (Black 1807, p. 25)

and about the process of heat exchange—using a pre-modern language that today sounds incorrect—he writes:

> even without the help of thermometers, we can perceive a tendency of heat to diffuse itself from any hotter body to the cooler around, until it be distributed among them, in such a manner that none of them are disposed to take any more heat from the rest. The heat is thus brought into a state of equilibrium. (Black 1807, p. 76)

To summarize, it is by leaning on measurements of temperature that Black concludes that the *heat* flows exclusively from higher temperature to lower temperature—*from hotter to colder bodies*, in his words—until the attainment of the equilibrium. Equilibrium is then the circumstance in which any thermal process stops and the temperature is the same everywhere in the observed system. This kind of phenomenological approach leaves the problematic question of making explicit and mathematically translating how the condition of *equilibrium* is connected with the temperature and how—more generally—can be framed inside modern thermodynamics and intertwined with the entropy and the Second Law. The Second Law of Thermodynamics is usually introduced in classroom lectures by underlying the necessity of a general principle to treat irreversibility (Ebeling 2008; Foussard and Julien 2005; Kiréev 1975; Mahan 1977; Marcella 1992; Rosenfeld 1941, 1999; Riollet 1992), with reference to some paradigmatic cases.[19] In the context of our research, we have developed an alternative approach—not reported in textbooks—by mathematically describing the case of two solid systems in thermal contact (Pellegrino 2016, pp. 169–177). This example also provides an original way to mathematically describe thermal equilibrium

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[18] dE (also written as dU, exact differential) is the exchanges in internal energy of a system for infinitesimal *quasi-static process*. E is an abstraction to justify mathematically the process. δQ (also expressed as TdS, where S is the entropy and T is the temperature) is the infinitesimal quantity of heat supplied/lacking and δW (also expressed as pdV) is the mechanical work on/from the system/surroundings. The signs convention *plus* and *minus* remind this aspect of the Eqs. (21 and 22); i.e., the heat supplied to the system as opposed to by the system (see also Clausius 1850, or later on, Planck 1897–1903). The latter two quantities, δQ and δW, are not exact differentials and for, they do not describe the state of the system. The Eq. (22), for *non-cyclic processes*, was introduced by heat machines researches for producing the maximum of efficiency (Pisano 2010). We also remark that for *cyclical processes*, that is when $\Delta U = 0$, the Eq. (21) become an idealistic (and inaccurate) complete conversion from heat into work. The second principle of thermodynamics makes clear this according to both historical and scientific standpoints (Pisano 2004; Gillispie and Pisano 2014).

[19] Among them Joule–Gay-Lussac relaxation (i.e.: expansion of a gas in vacuum) can be mentioned as well as the diffusion process of two different gases (Gay-Lussac 1802).

phenomenology and, at one time, to clarify how it is intertwined with the entropy, the temperature and the Second Law. The following section develops this case in details.

Let us consider two identical solid samples (A_1) and (A_2) containing the same amount of matter (let us say n moles), hence having the same heat capacity C_V. These two systems, with different initial equilibrium temperatures T_1 and T_2, are mutually brought into thermal contact (i.e.: heat can be exchanged between the two samples). The overall Σ system consisting of A_1 and A_2 is, then, isolated from the outside by a rigid athermanous wall and undergoes an isochoric ($V=$const.) irreversible transformation until a new thermal equilibrium state is reached. T_1' and T_2' are final absolute temperatures of the two samples. In the following reasoning we will show that at equilibrium T_1' and T_2' have the same value, as necessary consequence of the Second Law. As first, applying the First Law to such an isolated system Σ implies that its internal energy variation zeroes:

$$\Delta U_{\Sigma} = \Delta U_1 + \Delta U_2 = 0 \tag{23}$$

For each sub-system, infinitesimal variation of internal energy can be made explicit as follows:

$$dU_1 = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{24}$$

and, since heat capacity at constant volume is defined by the following expression:

$$nC_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{25}$$

then, in the assumed isochoric conditions (i.e.: $dV = 0$), Eq. (24) can be written as:

$$dU_1 = nC_V dT \tag{26}$$

Hence, Eq. (26), integrated between initial state with temperature T_1 and the final state with temperature T_1', gives:

$$\Delta U_1 = nC_V\left(T_1' - T_1\right) \tag{27}$$

The same applies for the second sample. Hence, for the overall isolated system Σ, Eq. (23) can be written as follows:

$$nC_V\left(T_1' - T_1\right) + nC_V\left(T_2' - T_2\right) = 0 \tag{28}$$

Equation (28) deserves some comments. First, it represents a formal expression of the First Law in the particular case of the Σ system evolving from thermal non-equilibrium state towards an equilibrium state. Then, Eq. (28) does not imply that, in the final equilibrium state, the temperature is the same in both subsystems (i.e. throughout the entire isolated system), as experimentally observed at equilibrium. Instead, the maximal information that can be inferred from Eq. (28) is that it does not contradict the phenomenological evidence that—in the case of two solid samples at different temperature that are brought into thermal contact—*the temperature of the subsystem with higher temperature can only decrease and the temperature of the subsystem with lower temperature can only* *increase*[20] *per* effect of the irreversible process leading these two subsystems towards thermal equilibrium.

Since the First Law alone does not offer enough elements to describe the evolution of a system towards thermal equilibrium, this limitation of the First Law can be presented to students as disclosing the need of another fundamental law (i.e. the Second Law of Thermodynamics) and new physical quantities (i.e. Entropy) to describe the thermodynamic process towards equilibrium.[21]

With these premises, the Second Law of Thermodynamics can be formulated—in the school books—by proposing, for example, the following statement:

> For any thermodynamic system it is possible to define a state function named entropy and formally represented by the letter S. For any isolated system, per effect of any thermodynamic state change, the entropy function (S) can only increase until it attains a maximum corresponding to a state of thermodynamic rest—named thermodynamic equilibrium—wherein no further transformation are allowed. For any infinitesimal thermodynamic change, the foregoing statement mathematically translates into:
>
> $$dS \geq 0 \tag{29}$$
>
> being the equality referred to equilibrium.

After having introduced the Second Law, it is worth recalling the definition of entropy. Concerning any thermodynamic system, entropy variation following any infinitesimal reversible process is given by:

$$dS = \frac{\delta Q}{T} \tag{30}$$

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[20] A formal justification of this non-contradiction statement can be found as follows. The phenomenological proposition stating that *"per effect of a thermal process leading Σ system towards equilibrium, temperature of the subsystem at higher temperature can only decrease and the temperature of the subsystem at lower temperature can only increase"* can be analytically represented by the following relation:

$$T_1' < T_1 < T_2 < T_2' \tag{I}$$

if we assume that $T_1 < T_2$—that is to say that (A_2) is at higher temperature than (A_1). Condition (I) mathematically implies that:

$$\left(T_2' - T_2\right) > 0 and \left(T_1' - T_1\right) < 0 \tag{II}$$

By combining inequalities (II) with Eq. (28), this latter translates into the algebraic sum of two terms with opposite sign—whose result may be logically zero (note that this condition is necessary but not sufficient). This implies that the phenomenological proposition stating that the *"temperature of the subsystem at higher temperature can only decrease and the temperature of the subsystem at lower temperature can only increase"* does not contradict the First Law (as expressed by Eq. 28). This is the maximal information—concerning the thermal evolution of an isolated system towards equilibrium—that can be made explicit from the First Law.

[21] To introduce entropy and the Second Law starting from this framework, it can be also useful to recall to students an analogy with mechanics. In mechanics (Pisano and Capecchi 2015) a stationary object is in a stable equilibrium state if its potential energy (denoted Ψ) corresponds to a minimum. From a cognitive standpoint, mechanics owns a function—the potential energy—standing as *steering variable* whereby equilibrium conditions are formalized. Similarly, in thermodynamics, a physical quantity named entropy is defined and it plays the similar role of *steering variable* as the potential energy does in mechanics.

Whilst dS is an exact differential, δQ indicates the infinitesimal thermal exchange (that is not an exact differential) and T is the absolute temperature of the outside (that is supposed thermally homogeneous). At constant volume (under the hypothesis that work is only mechanical *PV-work*, hence being $=0$) internal energy change is equal to . Hence, it holds true:

$$dS = \frac{dU}{T} \tag{31}$$

Furthermore, dS can be generally made explicit, through the following Eq. (32) by considering that is function of and as:

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \tag{32}$$

By comparing Eqs. (31) and (32), it follows:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \tag{33}$$

that holds true for infinitesimal reversible processes only. Coming back to the example of the isolated system Σ, the Second Law can be applied to it, hence giving:

$$dS_{\Sigma} \geq 0 \tag{34}$$

Since entropy is an additive quantity, Eq. (34) can be equivalently written as:

$$dS_1 + dS_2 \geq 0 \tag{35}$$

and, by using Eq. (32), the differential dS_1 can be made explicit as follows:

$$dS_1 = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1} dU_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1} dV_1 \tag{36}$$

In isochoric conditions (i.e. $dV_1 = 0$) Eq. (36) becomes:

$$dS_1 = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1} dU_1 \tag{37}$$

and, by substituting Eq. (33) into (37) it follows:

$$dS_1 = \frac{1}{T_1} dU_1 \tag{38}$$

The same applies for subsystem A_2, giving:

$$dS_2 = \frac{1}{T_2} dU_2 \tag{39}$$

For the overall isolated system, internal energy does not vary as consequence of any thermodynamic process, hence $_{\Sigma}$ zeroes. It follows that:

$$dU_2 = -dU_1 \tag{40}$$

In addition, Eq. (39) can be written as:

$$dS_2 = -\frac{1}{T_2} dU_1 \tag{41}$$

hence, the entropy variation of the overall system is given by the following expression:

$$dS_{\Sigma} = dS_1 + dS_2 = \frac{1}{T_1}dU_1 - \frac{1}{T_2}dU_1. \tag{42}$$

or equivalently:

$$dS_{\Sigma} = dS_1 + dS_2 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dU_1 \tag{43}$$

By combining inequality (35) (i.e. the Second Law for isolated systems) with expression (43) it finally follows:

$$dS_{\Sigma} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dU_1 \geq 0 \tag{44}$$

Equation (44) deserves some comments. There are two possibilities:

1. When the set of two systems evolves towards equilibrium (i.e. Σ is not yet at equilibrium) the total entropy increases since $dS_{\Sigma} > 0$, and the following inequality holds true:

$$dS_{\Sigma} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dU_1 > 0 \tag{45}$$

Just to fix the ideas, it is arbitrary considered the case wherein $T_1 < T_2$, condition that corresponds to the following inequality:

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0 \tag{46}$$

Under the hypothesis (46), the inequality (45) holds true if and only if dU_1 is positive, then:

$$dU_1 > 0 \tag{47}$$

At constant volume (i.e. $\delta W_1 = 0$, when ignoring non-mechanical work) $dU_1 = \delta Q_1$; hence Eq. (47) can be written as follows:

$$\delta Q_1 > 0, \tag{48}$$

meaning that, *per* effect of the thermal process leading the overall system towards equilibrium, there is heat exchange[22] between the constituent subsystems whose direction is from the sample A_2 (higher temperature) towards A_1 (lower temperature). In other words, Eq. (48) means that *per* effect of thermal processes leading the system towards equilibrium, heat transfer takes place from the portion at higher temperature towards the one at lower temperature. This conclusion recalls Clausius' formulation of the Second Law that reads as:

> This principle [*later named the Second Law]* is in its shortest form: *the heat cannot flow by itself from a colder to a warmer body* (Clausius 1872, p. 136).

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[22] The positive sign of heat exchange means that heat flows towards the system, in this case sample A_1.

As final remark, it is worth noticing that the temperature difference between the two bodies (corresponding to portions of an isolated system), not the difference between their energies, sets the direction of heat transfer.

2. When thermodynamic equilibrium is established then $dS_\Sigma = 0$, that is to say that entropy stops increasing or, in other words, any further change of state variables of the system does not imply a variation of entropy. This latter circumstance—referring to internal energy as state variable—can be formally expressed as follows:

$$\frac{dS_\Sigma}{dU_1} = 0 \tag{49}$$

At equilibrium, Eq. (44) can be formally rearranged giving the expression:

$$\frac{dS_\Sigma}{dU_1} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{50}$$

and by combining Eqs. (49) and (50), it results:

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = 0; \tag{51}$$

hence:

$$T_1 = T_2 \tag{52}$$

Finally, the Eq. (52) means that when two bodies—that are in thermal contact and constitute in their whole an isolated system—are in thermal equilibrium then they have the same temperature. This conclusion is obtained as logical consequence of Thermodynamic Second Law, as expressed by Eq. (35).

Concluding remarks

In conclusion, the foregoing analyses and discussions explored crucial conceptual *topoi* whose complexity always represents a challenge for scholars, teachers and students. In particular, our historical-epistemological approach allowed outlining the hermeneutical strength of Clausius' works and identifying it with the introduction of the *calculus* in thermodynamics. We have seen how the mathematical model of the *new* Mechanical Theory of Heat opened the way to mathematically represent—even if within certain limits—foundational concepts such as reversibility and irreversibility that formerly emerged as problematic entities in Sadi Carnot. It is in Sadi Carnot that we seminally find what will be called the second principle of thermodynamics while it is inside Clausius' model that the second principle is mathematically expressed—as Clausius' inequality and entropy inequality. From the results of this analytical–epistemic approach we could also perceive the emergence of a new concept, the entropy, that can be seen as the *symbolic entity* around which modern thermodynamics started taking shape. In spite of its clear-cut definition stemming from Clausius' memories, the notion of entropy underwent a huge semantic enrichment during nineteenth and twentieth century (Čápek and Sheehan 2005; Nelson 1994; Boltzmann 1866; Cercignani 1998; Frigg 2008; Jaynes 1965; Nernst 1907, 1921, 1926; Shannon

1948; Strehlow 2005; Tonnelat 1978; Tribus and MacIrvine 1971; Brosseau and Viard 1992; Brunhes 1991; Christensen et al. 2009; Tachray 1970; Balian 1982; Diu et al. 1996; Hill 1986; Landau and Lifchitz 1984) by going beyond the strictly thermodynamic cognitive domain. This epistemic opening (Pellegrino et al. 2014)—that translates into the use of entropy in disparate fields from chemistry to biology, from Information Theory (Shannon 1948) to cosmology (Hawking 1988)—has serious implications in Epistemology of Science and Nature of Science. Deepening this wide conceptualization of entropy remains a fundamental step to correctly set up thermodynamics' foundations, in general, and to avoid misconceptions, in particular. This latter conclusion confirms the necessity of a panoramic overview on the notion of entropy in the follow-up of our research program.

Furthermore, these conclusions open to fundamental Nature of Science questions and reflections. Dealing with historical and philosophical aspects of science represents a crucial—but actually underestimated—task in Nature of Science (Kuhn 1962; Klein 1980; Martinez 2005; Lakoff and Nunez 2000; Meltzoff et al. 2009; Lederman 2001; Osborne and Dillon 2008; Osborne 2010, 2014; Osborne and Patterson 2011; Osborne and Collins 2003). *How is it possible to keep on teaching sciences being unaware of their origins, cultural reasons and eventual conflicts and values? How is it possible to teach and comment on the contents and certainties of chemistry, physics and mathematics as sciences without having first introduced sensible doubt about the inadequacy and fluidity of such sciences in particular contexts?* Education needs to revaluate scientific knowledge as an integral part of human (humanistic and scientific mixed) culture that could build up an autonomous scientific cultural trend in schools (Pisano 2009b). *In this sense, what about the importance of introducing the history of science as an integral part of the culture of teaching education to the extent of considering such a discipline—in its turn—as an indissoluble pedagogical element of history and culture?* It would be useful to pay particular attention to the elaboration of the *teaching–learning* process based on the reality observed by students (inductively), by a continuing critical reflection, e.g. by means of studying the historical foundations of modern sciences. Therefore, turning from *teaching based on principles* to *teaching (also) based on broad and cultural themes* would be crucial. It would mean teaching scientific education as well, this latter being a kind of education that poses *problems*. As for physics and chemistry, this new attitude would imply a contextualisation within a historical and philosophical perspective. It would be helpful to practically support processes on a multidisciplinary or even on co operational level, a kind of pedagogy able to re-consider, from this point of view, the relationship between theory and experience, history and foundations. For example, the insights on the foundations of thermodynamics through the historical-epistemological analysis of Clausius writings, as above, which we have presented in this paper actually are helpful to correctly contextualise concepts and to use the adequate language. It is the case of conceptual relationship between Clausius' inequality and the second principle, very often source of issues for students.

From cognitive–epistemological point of view (George and Vellema 2002; Pisano 2001, 2007a, b, 2009a, 2015; Pisano et al. 2017a, b) people do not naturally and scientifically reason by means of deductive or inductive processes only. In this regard, scientific reasoning (Lakoff and Nunez 2000) is not a part of our common knowledge reasoning, although we often intuitively compare events, tables etc. Instead, generally speaking, we daily reason mainly by a cognitive association of *ideas*, far from the scientific conceptualisation, e.g., heat and temperature, mass, weight and force–weights, the solar system and atomic orbital system (Pisano and Bussotti 2017b) in quantum mechanics, the kinetic model of gases and thermodynamics (McQuarrie and Simon 2000), parallel straight, material points, etc. Thus, the current scientific teaching system paradoxically changes the logical basis of reasoning.

A hypothetical proposal—of course not the only one possible—could be (within a structured and interdisciplinary educational programme) to select ad hoc readings on mathematics–physics and chemistry. For example, Aristotelian mechanics, (*Problemata mechanica*), Euclid (*Elements*), Archimedes (*On equilibrium of planes*), Tartaglia (*Quesiti*), Galilei (*Discorsi*), Torricelli (*Opera*), Lazare Carnot (*Essai*; see also Carnot 1778, 1780, 1803a, b; Gillispie and Pisano 2014; Gillispie 1970–1979, 1971), Lavoiser (*Traité*) Sadi Carnot (*Réflexions*), Faraday (*Experimental Researches*), etc. By reading such passages, together with pre-arranged and effective work shared by several disciplines, (1) *the student is placed before a problematic situation and driven to realise the inadequacy of his/her basic knowledge with regard to problem solving*, (2) *can build up a scientific-aptitude education.* The result could be a scientific pedagogy according to which science education (Osborne and Collins 2001) essentially means *setting and solving problems* and teaching means re-evaluating the relationship between theory and experience and between history and foundations. They could come together with well-structured and practical interdisciplinary work by means of the history of science. International debate should take into account pedagogical research on foundations for history and learning–teaching science, discovering science teaching and informal learning activities as well. In this way, a student is the *protagonist,* both formally and informally (*hands-on*), of his *learning*. We feel the same about schools training experts, as these also should provide a setting that favours teaching research aimed at the critical re-construction of scientific meanings along with ideas, opinions and proper contents. In the end, this briefly proposed reflection should convey that it is urgent to establish the basis for a debate that ethically appears correct and professionally necessary. Maybe, operating in a different way, we could also contribute to building a school (or university) linked to the new perspectives of science, its image and teaching without limitations on specializations, pushing past disciplinary competences.

A multidisciplinary teaching based on large themes–problems toward a scientific education based on different formulations of the same theory would be appreciated. Some of the following case-studies may be discussed reading a textbook related with history of science: e.g., lack of relationship physics–logics, space and time in mechanics, mechanics and thermodynamics, *ad absurdum* proofs, non-Euclidean geometries and the space in physics, planetary model (Bussotti and Pisano 2014, 2017; Pisano and Bussotti 2013, 2014a, b, c) and quantum mechanics, infinite–infinitesimal and measures in laboratory (Mellone and Pisano 2012), heat–temperature–friction, and reversibility phenomena (Pisano and Capecchi 2009), concept of set and field, continuum–discrete models in mechanics and theory of elasticity of the nineteenth (Pisano and Capecchi 2013) hypothesis ad hoc in the theory, local–global interpretation and differential equations–integral, point–range and physical phenomena, mechanics, kinetic model of gases and thermodynamics.

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