

Some Consequences of an Analysis of the Kelvin-Clausius Entropy Formulation Based on Traditional Axiomatics

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Abstract: Recently, there have appeared interesting correctives or challenges [*Entropy* 1999, 1, 111-147] to the Second law formulations, especially in the interpretation of the Clausius equivalent transformations, closely related in area to extensions of the Clausius principle to irreversible processes [*Chem. Phys. Lett.* 1988, 143(1), 65-70]. Since the traditional formulations are central to science, a brief analysis of some of these newer theories along traditional lines is attempted, based on well-attested axioms which have formed the basis of equilibrium thermodynamics. It is deduced that the Clausius analysis leading to the law of increasing entropy does not follow from the given axioms but it can be proved that for irreversible transitions, the total entropy change of the system and thermal reservoirs (the “Universe”) is not negative, even for the case when the reservoirs are not at the same temperature as the system during heat transfer. On the basis of two new simple theorems and three corollaries derived for the correlation between irreversible and reversible pathways and the traditional axiomatics, it is shown that a sequence of reversible states can never be used to describe a corresponding sequence of irreversible states for at least closed systems, thereby restricting the principle of local equilibrium. It is further shown that some of the newer irreversible entropy forms given exhibit some paradoxical properties relative to the standard axiomatics. It is deduced that any reconciliation between the traditional approach and novel theories lie in creating a well defined set of axioms to which all theoretical developments should attempt to be based on unless proven not be useful, in which case there should be consensus in removing such axioms from theory. Clausius’ theory of equivalent transformations do not contradict the traditional

understanding of heat-work efficiency. It is concluded that the intuitively derived assumptions over the last two centuries seem to be reasonably well grounded, requiring perhaps some minor elaboration to the concepts of (i) system, (ii) the mechanism of heat transfer, and (iii) the environment, which would be expected to evolve with time in any case. If new generalizations at variance with Clausius' concepts are presented, then these ideas could be expected to require a different axiomatic basis than the one for equilibrium theory, and this difference must be stated at the outset of any new development. So far such empirically self-consistent axiomatic developments are not very much in evidence.

Keywords: Kelvin-Clausius Entropy, Irreversibility, Clausius Equivalent Transformation.

1. Introduction and Semantics

In order to determine potential “flaws” in the pioneering 19th century development of thermodynamics, one must highlight the well known presuppositions (stated below in axiomatic form) concerning the system under study. The axioms apply to closed systems.

- Axiom 1: The systems considered have (internal) states that are instantaneously defined and do not enter further into the entropy considerations [1].
- Axiom 2: For each pathway (defined as a mapping of thermodynamical variables to a line in the thermodynamical space of the system), there exists heat and work energy transfers between systems and reservoirs which can be carried out reversibly [2] during the transition from one equilibrium state to another; reversible here means that it is possible to arrange the physical conditions so that a transition from state A to state B involving transfers of energy of amount q for heat and w for work implies that a transition from state B to state A is also possible with the transfer of energy of amount $-q$ for heat and $-w$ for work, where the states A and B are arbitrarily close.
- Axiom 3: Where reversible transfers are concerned, bodies of unequal temperature should never be put together [3].
- Axiom 4: Total energy is conserved, and the net work output of a cyclical heat engine could be related to the net heat input over the cycle through the mechanical equivalent of heat conversion factor [4].
- Axiom 5: The *isothermal* transfer of heat between two bodies involves the presence of heat gradients which can be chosen to be vanishingly small to the point of being neglected, where heat is defined as that form of energy which is transferred by virtue of a temperature difference *only* between two regions of a system [5, 6] and is therefore the same form of energy as that due to Fourier heat conduction.
- Axiom 6: Work is that form of energy which is *not* temperature specific and which may be converted into other forms of energy completely without having to specify necessarily temperature variables; in particular it may completely or partially be converted during any stage of the cyclical

Carnot engine into heat which must be transferred to a body which has an associated temperature parameter. The work may be stored in principle without degradation (into heat) in a work reservoir that need not be specified by a temperature that can be used to effect changes on the component portions of an isolated system [7].

- Axiom 7: The system and thermal reservoirs used in thermal energy exchange may be in principal distinguished, even if they may form part of the same body.

- Axiom 8: The heat exchange in a closed loop along a thermodynamical pathway may be approximated to any degree of accuracy by a juxtaposition of an arbitrary number of virtual Carnot cycles working at either maximum or non-maximum efficiency where the heat absorption along the pathway corresponds to the isothermal heat transfer stage in the juxtaposed virtual Carnot engine sharing common adiabats [1-4].

For what follows, the systems are closed, such as obtains for the original Carnot engine; generalization to open systems were quantitatively and intuitively carried out most notably by Gibbs [8] in his pioneering work, which did not resort to the rigorous consideration of cyclical changes which lead to the entropy function of state definition in the first place, which was presumed to obtain for heterogeneous equilibria involving open systems as well.

We now illustrate by some examples how the traditional interpretation of the Kelvin-Clausius theorems, based on the above axiomatics differ from those recently postulated [9]; an instance is afforded by the Clausius definition of equivalent transformations. It turns out that the problem seems to be a divergence in how systems are categorized and understood.

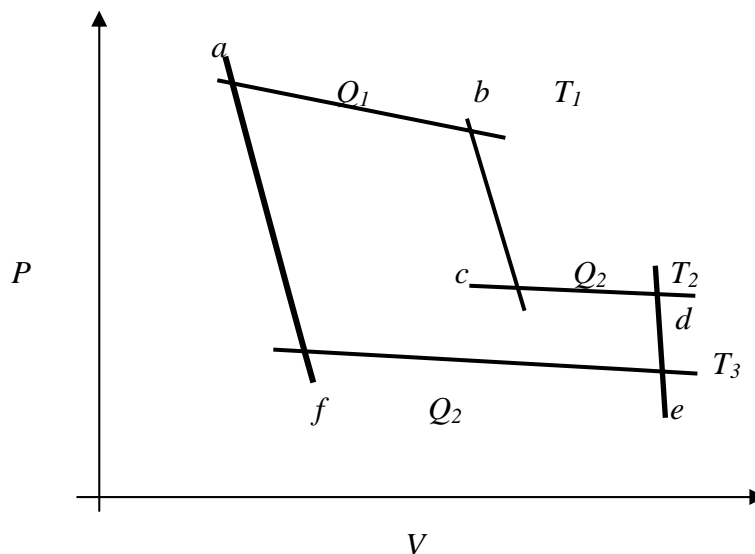


Figure 1. A closed system utilizing three heat reservoirs undergoing a cyclical change by changes in pressure (P), temperature (T) and volume (V). The adiabatic steps are represented by the vertical curves such as $a-f$, $b-c$ and $d-e$.

Fig. 1 depicts a closed system undergoing a cyclical transformation absorbing heat Q_1 and Q_2 at temperatures T_1 and T_2 and releasing amount Q_2 at temperature T_3 in isothermal transitions involving

heat reservoirs [10]. Fig. 1 above reduces to Fig. 1 of reference [11] if the adiabatic step $b-c$ is reduced to zero measure (zero external work done). Our Fig. 1 is adapted from a diagram concerned with a standard analysis of Clausius' equivalence transformations [10]. Let $Q_1.f(T_1)$ denote the Clausius equivalence value of the generation of heat Q_1 at temperature T_1 from mechanical energy, and $Q_2.f(T_2, T_3)$ as the equivalence value of the flow of heat energy Q_2 from T_2 to T_3 . Clausius, probably relying on Kelvin's 1854 paper on thermoelectric currents, makes the identities [10] $f(T) = 1/T$ and $f(T_2 - T_3) = (1/T_3) - (1/T_2)$, so that this equation for the total or net equivalence S between a flow of heat energy and the conversion of heat into mechanical energy becomes

$$S = \frac{-Q_1}{T_1} + \left(\frac{Q_2}{T_3} - \frac{Q_2}{T_2} \right) = 0 \quad (1)$$

for the above reversible cycle of Fig. 1; S in retrospect may be identified with the entropy. If the Universe U is viewed as a set composed of the union of the closed system C_s and n thermal reservoirs R_i with the set of all reservoirs given by $R = \{R_1 \cup R_2 \dots R_n\}$, then our Universe may be loosely denoted by $U = C_s \cup R$. Clausius views the heat increments as changes in the reservoirs, rather than the system, where for reversible transitions involving heat exchanges with the reservoirs,

$$S(U - C_s) = -S(U - R) \quad (2)$$

in set theory notation. Early workers, including Clausius, defined the heat absorbed according to Eq.(1) (or Fig.1 in [11]) as positive relative to the reservoirs, i.e. the entropy is measured in terms of heat absorptions experienced by the reservoirs, i.e. $S(U - C_s)$. The generalization of Eq.(1) as the number of reservoirs tend to infinity leads to the Second law deduction for closed systems over a cyclical loop-like transition between the same end-points written as

$$\lim_{n \rightarrow 0} \sum_{i=1}^n \frac{\delta Q_i}{T_i} = 0 \Rightarrow \lim_{n \rightarrow 0} \sum_{i=1}^n \frac{\delta Q_i}{T_i} = \oint \frac{\delta Q}{T} = 0 \quad (3)$$

The implication sign leading to the path integral in Eq.(3) requires a separate analysis which will not be attempted here, suffice to say that it has been the standard assumption throughout the history of thermodynamic analysis concerning the imperfect heat increment δQ , where the thermodynamical path is Riemann integrable with respect to this heat variable Q , which is assumed to be a continuous function.

Never in the traditional understanding and development has 'entropy' or equivalent transformations been interpreted as pertaining to $S(U)$, i.e. the entire Universe taken as a whole [12-13] and all logical and algebraic developments have assumed that $S(U)$ is not the whole Universe but the variables connected to the system (or the respective reservoirs, but not both). There is therefore a danger of extrapolating the basic thermodynamical development beyond its intentions if this and other basic presuppositions are not borne in mind. For instance, Iñiguez [11] writes for his Fig.1 transformations the following "So, the values of the transformations occurring in a reversible cyclical process instead of being

$$\Delta S [Q'(T_h) \rightarrow Q'(T_c)]_{rev} = Q'(T_h - T_c) / T_h T_c \text{ (his eqn.3) and } \Delta S [Q(T_h) \rightarrow w]_{rev} = -Q / T_h \text{ (his eqn.4)}$$

as the Clausius principle of the equivalence of transformations demand, they both turn out to be, as eqs. 1 and 2 show, equal to zero.” However, his eqs.1 and 2 refer to the algebraic sum of contributions from *both* system and reservoir (i.e. the entropy is essentially defined as $S(U)$ in our notation) and therefore differs in interpretation from the traditional development, including the definitions and axioms used traditionally. Indeed, the real significance of the non-composite sum $S(U - C_s) = Q'(T_h - T_c)/T_h T_c - Q/T_h$ from the Clausius and traditional point of view is that it is equal to zero; the generalization of which leads to the Second law statement of the existence of the entropy state function. Since the Iñiguez development does not use the same basic premises and axiomatics of the traditional Kelvin-Clausius thermodynamics, they are not comparable, and it is therefore questionable to speak of “flaws” in the traditional development when a common basis is absent. In isothermal exchanges of heat, clearly the algebraic sum of entropy increments must always cancel for system and reservoirs taken together, but no significant consequences may be deduced from this observation.

There have been attempts to create an irreversible thermodynamics with an entropy perfect differential based on considerations of “compensated heat” [14], which has been disproved [15] for isothermal processes; the analysis for the general case is given here in a subsequent section. Generally, concepts used in the attempts to extend thermostatics to nonequilibrium systems still rely on the structure and definitions used in equilibrium theory. In such developments, it is generally assumed that the Clausius inequality $\oint \delta q/T < 0$ obtains where the heat exchange is isothermal in the limit, even for irreversible transitions; clearly if this were not the case, then the ‘compensated heat’ entropy of the composite system would certainly break down, since the reservoir temperature variables are free to vary in this case [14]. It will be shown below that the statements concerning the law of increasing entropy for systems obeying the stated conditions is not jeopardized by non-isothermal heat transfers between system and reservoir. It is interesting that at least one text [7] has discussed the possibility of non-isothermal system-reservoir heat transfer as the basis or cause of irreversibility and the Clausius inequality, but in general the arguments seem to assume that the temperature parameter T is that registered at the heat reservoirs only which is the same as the system temperature when there is energy exchange with the reservoirs.

Another example of departure from tradition is due to the definition of quantities. Definitions (almost always) are not provable, but the effectiveness of definitions in scientific analysis is dependent on the rationality of the arguments used to create the definitions. For instance, whilst it is acknowledged that [16] the efficiency η of a cyclical process associated with heat transfers between temperatures T_h and T_c is given by $\eta = (T_h - T_c)/T_h$, it is also stated that if the “availability of energy for external purposes” is defined u as its quality, then the quality of loss $-\Delta\bar{c}$ will be proportional to the temperature of its cold reservoir, i.e. $-\Delta\bar{c} = \frac{T_c - T_h}{T_c T_h}$ since its “capacity for further work production will be lesser the lesser the temperature of the cold reservoir...”. Elementary considerations show that as $T_c \rightarrow 0, \eta \rightarrow 1$, so that the capacity for further work production increases as $T_c \rightarrow 0$. We note that there is a danger in utilizing ratios, proportions and reciprocals without establishing the value of the

exponents γ associated with a particular variable in expressions such as T^γ ; there is no proof why unity (± 1) should be the preferred exponent from the arguments presented for proportions, etc. (although it may eventually be proved as the correct choice). Notational confusion can also add to the obscurity [17] as when it is stated: “The true criterion of reversibility is embedded in eq.8 in the equation: $\int_A^B dS = -\int_B^A dS$ For every process that can in no way be completely reversed, it follows that: $\int_A^B dS \neq -\int_B^A dS$ ”. From the fundamental theorem of integration, if S possesses a differential dS (in multidimensional space) it follows that $\int_A^B dS + \int_B^A dS = \int_A^A dS = 0$ or $\int_A^B dS = -\int_B^A dS$, irrespective of pathway (whether irreversible or not, provided dS represents the entropy increment). Hence it is apparent [17] that the writer concerned has at the very least used an inappropriate notation in his explanations. Unreviewed grammar may also complicate the situation, when subject and predicate is not clearly distinguished, as when one writes [18]: “...it is learned that while the entropy change for the Universe of the reversible transfer of an amount of heat Q' from T_h to T_c is equal to zero, that of the irreversible transfer is equal to $Q'(T_h - T_c)/T_h T_c$. Looking back now at the principle of the equivalence of transformations one can only qualify as peculiar the fact that the entropy change *in it* associated to the reversible transfer of heat taking place in the *reversible* cyclical process to which such a principle refers, instead of being *zero*, as it should correspond to a *reversible* process, be $Q'(T_h - T_c)/T_h T_c$ which is the one associated to an *irreversible* heat transfer” (italics mine).

It is difficult to relate the above from the traditional perspective. Restricting the argument to closed systems delivering work W in one complete cycle, the entropy change of the reservoirs is given by $S(R) = -\frac{Q'}{T_h} + \frac{(Q' - W)}{T_c} = 0$ whereas for a completely dissipating system, $W=0$, and so $Q'(T_h - T_c)/T_h T_c > 0$. Thus the intentions of the writer is not so evident here.

(Needless to mention perhaps, vague and imprecise writing which does not trouble to relate historically to previously accepted practices and to persons, and which does not take pains to point out areas of departure from pre-existing or prevailing practices, could potentially masquerade as a TOE - “theory of everything”- by claims that what was mooted could subsume whatever another creates or postulates, thereby jeopardizing the anamnesis sequence within the living communion of investigators, so vital for its non-nihilistic functioning).

Apart from ambiguity of terminology, we next examine whether it is possible to extend the equilibrium Clausius entropy principle to irreversible systems.

2. Discussion of the Clausius Inequality and Some Definitions

The derivation of the Clausius inequality $\oint \delta q/T < 0$ for heat increments δq absorbed by a closed system in a closed loop transition is based on superimposing in the limit an infinite number of Carnot engines with common adiabatic steps between any two infinitesimal small loop transitions, such as discussed in [7]. Two general cases may be considered, when the thermal reservoirs are in the limit at the same temperature of the system (subparagraph a) below and when they are not (subparagraph b).

a) When system and reservoirs are in contact at almost the same temperature: Associated system

For conductive thermal energy transfer between system at temperature T_s and thermal reservoir at T_r the Fourier inequality $\mathbf{q} \cdot \nabla T < 0$ implies $|T_s - T_r| > \varepsilon$ for arbitrarily small positive ε (where \mathbf{q} is the heat current vector). On the other hand, a common assumption in the Carnot analysis is that there can be “isothermal” transfer of heat, so that $\varepsilon \rightarrow 0$. For what follows, we shall assume that these limits obtain.

For any one Carnot engine cycle in this summation process, let the optimum heat absorbed be δQ_2 (at temperature T_2) and that expelled be δQ_1 (at temperature T_1) where $T_2 > T_1$ and δW is the positive work done by the system (engine). The following definition will be required in due course.

Definition 1. Internally driven engine (system): An internally driven engine (system) i is one where $\delta W_i > 0$ for any engine E_i where the work refers to a cycle, and if the work increment $dw_i > 0$ for an element of path δC_i , the system or engine is internally driven along that path increment.

Definition 2. Externally driven engine (system): An externally driven engine (system) i is one where $\delta W_i < 0$ for any engine E_i where the work refers to a cycle, and if the work increment $dw_i < 0$ for an element of path δC_i , the system or engine is externally driven along that path increment.

Hence one necessary condition is that the system is not functioning as a refrigerator (where $\delta W_i < 0$) for $T_2 > T_1$ for an internally driven engine and where the system can never act as a source of work for an externally driven engine. From Axiom 1, the only way in which dissipation could be achieved is when work δW , representing the Carnot maximum work (see Fig. 2 below) is partly dissipated back by amounts δW_1 and δW_2 – where the subscripts (1,2) refer specifically to the interfacial ports of heat absorption and expulsion respectively – and held at temperatures T_1 and T_2 respectively.

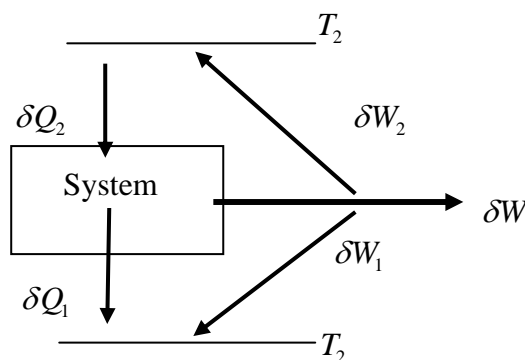


Figure 2. Typical energy exchange of a Carnot engine during a cycle with dissipation.

For internally driven engines, $0 < \delta W_q < \delta W$ ($q = 1, 2$) and $\delta W_1 + \delta W_2 < \delta W$, and for externally driven engines (e.g. refrigerating cycles), $\delta W_q \leq W_{ac} - \delta W$ ($q = 1, 2$) and $\delta W_1 + \delta W_2 = W_{ac} - \delta W$ where W_{ac} is the actual work done on the system. For the above, it will be noticed that the work term, as it so

far stands, is a globally relevant term, in that it represents the sum of all work increments over the cycle. It has been rigorously proven [19] that any transition along the adiabatic steps in the Carnot cycle (a device used to ensure that the working substance can absorb heat at at least two different temperatures) itself conforms to the Carnot theorem, and furthermore, it has been suggested [19] and proven [20] that the “isothermal” steps involving conductive heat with vanishingly small heat gradients also conforms to a Carnot theorem involving a “disintegrating” system [19, 20]. Hence it might be possible to derive the above inequalities by *not* concatenating “global” engines, but by a process involving local transitions, but this analysis is for the future; at present, on an *ad hoc* basis, one can suppose –without jeopardizing the traditional format– that the system is coupled to a “work reservoir” that can store pure work energy at each stage in the cycle, and at different times, and this work is available at all times to the system. Since the energy U is unchanged over a cyclic transition, then over the cycle $W = -Q$ where W is the total work done on the system and Q the total heat absorbed; i.e. $Q = Q_2 - Q_1$ in the notation of Fig. 2.

Therefore, for net work to be done to the environment, $|Q_2| > |Q_1|$; hence as $Q_2 \rightarrow 0$ for an infinitesimally small (arbitrary) cycle, an internally driven engine will always have the *capacity to do net work on the environment at any stage where the energy reservoir has zero work energy* if $Q_2 \neq 0$ provided the cycle begins at the upper temperature isotherm. Denoting the entropy differential $dS = \delta q/T$, with superscripts labeling the system or heat reservoir, and the subscripts denote whether the increment is due to an irreversible or reversible transition. Then according to the notation of Fig. 1

$$dS_{rev}^{sys} = \frac{\delta Q_2}{T_2} - \frac{\delta Q_1}{T_1} = 0 \quad (4)$$

for the system. If there is dissipation (irreversible change) we get

$$\delta S_{irr}^{sys} = \frac{(\delta Q_2 - \delta W_2)}{T_2} - \frac{(\delta Q_1 - \delta W_1)}{T_1} < 0 \quad (5)$$

where δS represents imperfect differentials and $\delta W_{1,2}$ is the potential work that is dissipated as heat to the thermal reservoir concerned through the system surface concerned. From Axioms {1-7}, a fundamental presupposition made for the Clausius inequality to obtain *for the system* is that the potential work energy must be dissipated to the thermal reservoirs interacting with the system, *and* that the dissipation of energy must be considered to flow through the system boundary to the thermal reservoir, or else inequality (5) would *never* obtain and so likewise the Clausius inequality $\oint \delta S_{irr}^{sys} \leq 0$ would also not obtain; by definition, we have excluded thermal energy transfer for the adiabatic steps, although in a more flexible theory, one might distinguish between system heat absorption through its own boundary and heat transfer from a work reservoir to the thermal reservoirs, through another boundary as distinct (and therefore allow for a specialized form of heat transfer during an adiabatic transition). Here we adhere to the conventional definitions. From inequality (5), since the δW 's are positive, the extra entropy gain for the reservoirs dS_{ex}^{res} would be $dS_{ex}^{res} = \frac{\delta W_1}{T_1} + \frac{\delta W_2}{T_2} > 0$ over the

cycle rather than zero; in particular even if the work were dissipated to another heat reservoir external to the system, the total entropy change of the reservoirs and system would be positive, as is

conventionally expected, since both the δW 's and T 's are positive. For permitted or accessible transitions from state A to B (denoted AB, and vice-versa BA for B to A transitions) the Clausius inequality reduces to

$$dS_{rev,BA}^{sys} + dS_{irr,AB}^{sys} < 0 \quad (6)$$

over a specified pathway. Integration yields $\int dS_{rev,BA}^{sys} = \Delta S_{AB}^{sys} = \alpha \Rightarrow \Delta S_{BA}^{sys} = -\alpha$ and $\int dS_{irr,AB}^{sys} = \Delta S_{irr,AB}^{sys} = \beta$ where the sign of β cannot change for a BA irreversible transition (unlike α since the transition is irreversible). Thus, inequality (6) yields $-\alpha + \beta < 0$ or $\alpha - \beta > 0$. Now, if we should allow Axiom 3 to obtain for the moment then the reservoirs involved in the heat interchange would be $\Delta S_{rev,BA}^{res} = +\alpha, \Delta S_{irr,AB}^{res} = -\beta$. For the AB transition, we have that the total entropy change of system and reservoir is given by $\Delta S_{AB}^{sys} + \Delta S_{irr,AB}^{res} = \alpha - \beta > 0$ from (6). This result is to be contrasted with Iñiguez who writes [21] “...That the entropy change for the universe of a process can be negative, a fact defined by Clausius work, is the reason the name chosen –negentropic—for the formulation herein presented.” The inequality is zero for reversible cyclic transitions, but it can never be negative.

b) When system and reservoirs are in contact at not the same temperature: Non-Associated system

Here, $|T_s - T_r| > \varepsilon$ where ε is any finite non-vanishing number for thermal energy exchange. The above result is not jeopardized if the condition given by Axiom 3 is relaxed, such as what Moore alleges [7], when he writes for the expression $\oint \frac{\delta q}{T} < 0$ (irreversible), the following: “We should note that the T ... is the temperature of the reservoir that supplies the heat, and not the temperature of the body to which the heat is supplied.” Clearly, this is in apparent contradiction to Axiom 3 as understood by other authorities; the above shows that for associated systems, (i.e. those for which the system and reservoir temperatures when in mutual contact possess a vanishingly small temperature gradient), Clausius’ inequality can still obtain if we postulate a back transfer of heat through the system surface due to work degradation; Moore’s postulate seems to not preclude the case where if the T variable were almost exactly the same for the system and reservoir, then the Clausius inequality would not obtain in general if the above back transfer suggestion is not included. But Moore’s definition may not be too helpful since if T were not the system temperature, then the inequality need not apply without further assumptions concerning the flow of (thermal) heat; hence it is imperative to consider Moore’s suggestion to define the limits of its applicability. If conductive heat transfer is envisaged [22, 23] where the inequality $\mathbf{q} \cdot \nabla T \leq 0$ obtains locally, (\mathbf{q} is the thermal heat conduction vector), then this fundamental inequality may be applied to any portion of a Carnot engine, at any stage in a cycle. Thus relative to Fig.3 below,

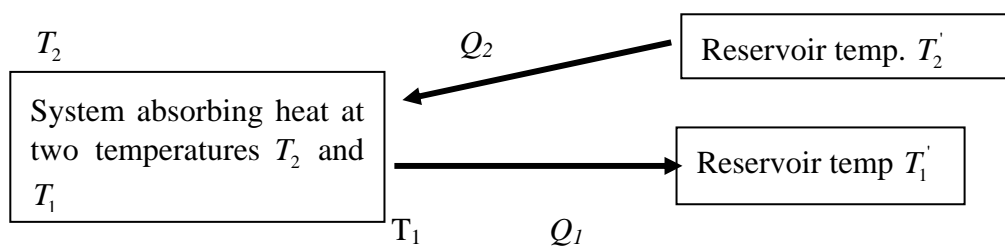


Figure 3. System absorbing thermal energy from heat reservoirs with dissimilar temperatures.

Q_2 is a positive increment of heat absorbed by the system whenever $T_2' > T_2$ and vice-versa, and Q_1 would be a negative quantum of heat absorbed (i.e. heat lost) of $T_1 > T_1'$. Now, in the traditional understanding, minute temperature differences $\pm\delta$ ($\text{Lim } \delta \rightarrow 0$) must exist with the condition $\delta > 0$, $T_2' = T_2 + \delta$ for heat absorption, or for work degradation into heat – by convention through the system boundary – whenever $\delta' < 0$, $T_2' = T_2 + \delta'$ at the same interface. Clearly the back transfer of work energy as dissipated heat through the same boundary as when heat was absorbed would involve the change of sign of δ and these processes *cannot* be simultaneously accomplished. If there exists a non-vanishing temperature difference $T_2' - T_2 > \alpha > 0$, where α is fixed, then the *isothermal absorption of heat by the system* at temperature T_2 and its conversion to work (e.g. in the isothermal expansion of a gas) along a segment AB of a thermodynamical path where $\delta q > 0$ (for the system) implies $\Delta S_{AB}^{sys} > 0$; if the transition along AB is along a pathway where the system boundary temperature is always less than the heat reservoir so that no work back-transfer can occur, then the curious result $\Delta S_{AB}^{sys} = \Delta S_{AB,rev}^{sys} > 0$ would obtain; the heat absorbed would correspond to the reversible heat absorbed. However, for such a transition, the entropy of both system and reservoir would increase since for each increment of heat δq absorbed by the system from the thermal reservoir,

$$dS_{irr}^U = \delta q \left(\frac{1}{T_2} - \frac{1}{T_2'} \right) > 0 \text{ for each } \delta q \text{ increment. For the segment of the system transition CD for which}$$

$\delta q < 0$, represented in general by Fig.3 by the heat transition Q_1 between temperatures T_1 and T_1' , the gradient is such that if $\delta q^{rev} (\equiv \delta q^{eq})$ represents the reversible transition increment, then by the external dissipation of work from the environment with increment $\delta W \equiv \delta q_{ex}$, there is the actual transfer of heat $\delta q^{ac} = \delta q^{eq} + \delta q_{ex} > \delta q^{eq}$, so that the entropy increment follows the overall entropy increment for the

system $dS^{sys} < \frac{\delta q^{ac}}{T}$ (in accordance with the Clausius inequality derived from cyclical considerations)

and the total entropy increase of the Universe $dS_{irr}^u > 0$ for each increment δq^{ac} because

$$dS_{irr}^u = \delta q^{ac} \left(\frac{1}{T_1'} - \frac{1}{T_1} \right) > 0. \text{ This illustration may be generalized.}$$

For a reversible transition between states A and B, the heat increments along a pathway can be represented by a sequence $\{\delta q_i\}$, where λ' is a generalized path parameter completely specifying the

path taken. From the First law statement $dU = dQ + dW$ (with Q and W representing the heat and work functions respectively), it is clear that an irreversible transition need not correspond to the same $\{\delta q_i\}$ sequence; a particular transitional pathway may be specified by the set $\{Q, \lambda, T\}$ with heat absorption increments $\{dQ\} = \{\delta q_1, \delta q_2 \dots \delta q_n\}, (n \rightarrow \infty)$; λ are all the other thermodynamical variables other than the temperature T and total heat content Q for transitions between states A and B; the temperature of the system is given by the sequence $\{T_i\}$ and time of transition by the sequence $\{\tau_i\}$; the temperature of the reservoirs is denoted by the sequence $\{T_i + \delta T_i\}$ where for the associated case $\delta T_i \rightarrow 0$. For this case

$$\Delta_A^B S_{assoc.}^{irr} = \sum_{i=1}^n \frac{\delta q_i}{T_i} < \Delta_A^B S^{rev} \quad (7)$$

as demonstrated previously. We partition the sequence $\{dQ\} = \{dQ^+\} \cup \{dQ^-\}$ where $\{dQ^+\} = \{\delta q_{n_1}, \delta q_{n_2}, \dots, \delta q_{n_r}\} (n_1 < n_2 \dots < n_r \dots)$ represents positive increments for heat absorption δq_i by the system with a similar notation for $\{dQ^-\}$, which represents the ordered (infinite) sequence with net heat loss by the system, the mechanism in both cases being purely Fourier heat conduction across a diathermal boundary[22,23]. The corresponding partitioned temperature sequences will be denoted $\{T^+\}$ and $\{T^-\}$ and similarly $\{\tau^+\}$ and $\{\tau^-\}$ are the corresponding time increments associated with the direction of heat transfer. For ‘associated’ heat transfers $\delta T_{n_i} \rightarrow 0$ for all members in $\{dQ\}$, and for such a case the reservoir entropy $\Delta_A^B S_{assoc.,reservoir}^{irr}$ clearly obeys

$$\Delta_A^B S_{assoc.,reservoir}^{irr} = -\Delta_A^B S_{assoc.,system}^{irr} \quad (8)$$

For the same specified path $\{Q, \lambda, T\}$ to be traversed for non-associated systems subjected to the Fourier inequality, it is sufficient to maintain the temperature gradients in the same direction as in the associated case where $\delta T_i'$ is a (small) finite and non-vanish quantity for a reservoir held at $\{T_i + \delta T_i'\}$ and this reservoir temperature is maintained until the amount of heat $\delta q_i \in \{dQ\}$ has been transferred; hence only the $\{\tau\}$ sequence will differ for the associated and non-associated case. Since (Axiom 1) the system is instantaneously defined, and $\delta T_i \rightarrow 0$ for any $\delta T_i'$ (it is as small as is specified), we can write $\delta T_i' > \delta T_i$ if $\delta T_i \in \{\delta T^+\}$ and $\delta T_i' < \delta T_i$ if $\delta T_i \in \{\delta T^-\}$. Thus for the same system pathway $\{Q, \lambda, T\}$, the reservoir entropies would obey the inequality

$$\Delta_{A non-assoc.reservoir}^{Birr} = -\left[\sum_{i=1}^{\infty} \frac{\delta q_{n_i}^+}{(T_{n_i} + \delta T_{n_i}')} + \sum_{r=1}^{\infty} \frac{\delta q_{n_r}^-}{T_{n_r} + \delta T_{n_r}'} \right] > -\left[\sum_{i=1}^{\infty} \frac{\delta q_{n_i}^+}{T_{n_i}} + \sum_{r=1}^{\infty} \frac{\delta q_{n_r}^-}{T_{n_r}} \right] \quad (9)$$

$$= \Delta_{A assoc.reservoir}^{Birr}$$

Since $\Delta_{A non-assoc.reservoir}^{Birr} > \Delta_{A assoc.reservoir}^{Birr}$, so $\Delta_{A non-assoc.reservoir}^{Birr} \neq \Delta_{A assoc.reservoir}^{Birr}$, for any definite pathway $\{Q, \lambda, T\}_A^B$, and in particular, Eq.(6) which yields $\Delta_{AB}^{sys} + \Delta_{irr,AB}^{res} = \alpha - \beta > 0$ clearly implies $\Delta_{AB}^{sys} + \Delta_{A,non-assoc.reservoir}^{B,irr} > \alpha - \beta > 0$ for the same AB transition and so even here the entropy of the Universe is positive. For such constructs, the Iñiguez result [21] cannot obtain. The reservoir variables

are free to vary in Moore's characterization, so it is not necessarily true –subjected to further elaboration– to suppose that a “compensated entropy” may be described to create a new function of state because of the ambiguity of the temperature value, where we suppose for the time being that such theories are true [14] for associated systems. However, even for associated systems, it has been proved that such a scheme does not exist for isothermal systems with no work transitions [15]. Hence it is imperative to study the case of non-equilibrium transitions for associated systems to determine whether any new function(s) of state are implicated as a generalization of Clausius' result.

3. Investigation on whether a Nonequilibrium Entropy may be Deduced from the Clausius Inequality of Equilibrium Thermodynamics

(a) Formal theoretical construct

The lucid arguments of Benofy and Quay [22] make a case for the global nature of the descriptions provided by the traditional Kelvin-Clausius development, which must be contrasted to its reduction to a supposed local form from total system interactions involving circular integrals [24]; the resolution of these conflicting viewpoints is attempted here. Writing the Clausius integral as $-N$ and integrating between thermodynamical variable space points A and B located on the thermodynamical path of the loop yields the following “global” [22] result

$$-N = \oint_{\text{irrev}} \frac{dQ}{T} \leq 0 \quad (10a)$$

$$N = \Delta S - \int_{A,\text{irr}}^B \frac{dQ[P'_{AB}]}{T} \geq 0 \quad (10b)$$

where $\Delta S = \int_{A,\text{rev}}^B \frac{dQ[P_{AB}]}{T}$ is the reversible entropy change between states A and B; where P_{AB} denotes a reversible path and P'_{AB} an irreversible pathway, and the state variables for the system is \mathbf{Q} for each equilibrium state.

Lemma 1: The variable N must be a functional of the variable A,B and path P'_{AB} , i.e. $N = N(A, B, P'_{AB})$.

Proof: Since ΔS is the integral of a perfect differential, it is a function of the endpoints of the integral, and the irreversible integration along P'_{AB} is path dependent, hence the result.

In order to develop the global properties of the Kelvin-Clausius theory, we need to state some elementary theorems, where the first theorem is more obvious than the second.

Theorem 1: There exists an infinite number of irreversible heat exchange pathways P'_{AB} even if during the irreversible transition from A to B, the system traverses arbitrarily closely along a reversible pathway P^+_{AB} where the pathway is described by a sequence of equilibrium state variables \mathbf{Q} .

Proof: From Axiom 1 the system state is instantaneously defined, so that the isothermal heat exchanges are due to the dissipation of heat about the system boundary due to the system work or the external work reservoir, and likewise at each point in the time sequence, the virtual reversible

transition may be characterized by an equilibrium state variable, the entire set constituting P^+_{AB} . In accordance with the well-known Axiom 8, the dissipation of work to heat through the boundaries of the system is bounded by W_{op} , the optimum work which the cycle can perform. However, if the external environment were to dissipate energy in addition to W_{op} , the result below would still obtain by considering the dissipation inequalities below. Now, consider the loop formed by the reversible path P_{BA} followed by the irreversible transition P'_{AB} , such as depicted in Fig. 4 below. By Axiom 1 and 8, we may consider one elementary Carnot cycle with corners at (a_1, b_1, b_2, a_2) where heat Q_1 is absorbed along reversible segment a_1 - b_1 and $|Q_2|$ ejected about irreversible segment a_2 - b_2 .

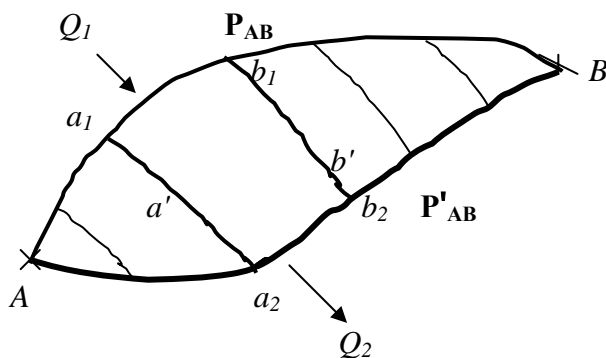


Figure 4. A thermodynamical circular pathway with the reversible portion maintained at a higher temperature than the irreversible segment, and where heat is absorbed, with elementary Carnot engine superimposed with isotherms and adiabats meeting at a_1, b_1, b_2 and a_2 .

The system here corresponds to an internally driven engine; the arguments for an externally driven engine are similar (and will be omitted). At the optimum (op) level, $Q_{1,op} + Q_{2,op} = -W_{op}$, where W_{op} is the work done on the system for the reversible cycle about (a_1, b_1, b_2, a_2) and $W_{op} = Q_1(f(T_1, T_2))$ as stated previously. Since segment (a_1, b_1) is reversible, the amount of heat ejected $|Q_2(P'_{BA})|$ about the (a_2, b_2) segment would be $|Q_2| = Q_1 + W_{op} + \delta(a_2, b_2)$ where $\delta(a_2, b_2)$ is the dissipation function about segment (a_2, b_2) where $0 < \delta(a_2, b_2) \leq |W_{op}|$ and if there is extra work provided externally, then the preceding condition reduces to $0 < \delta(a_2, b_2)$. Clearly δ is not dependent on the P^+_{AB} or P^+_{BA} sequence of path variables and an infinite number of separate values for δ exists for each infinitesimal segment (a_2, b_2) . Hence an entire set of dissipation functions obtain for this infinitesimal segment, and thus for the entire pathway P'_{BA} which corresponds to the system having a particular set of equilibrium variable sequences, we can write $P'_{BA} = \{P^+_{BA}; \Delta\}$, where Δ are the variables along P^+_{AB} connected to the dissipation function δ about the boundary of the system.

Theorem 2: Subject to the (system) conditions of the preceding theorem, it is impossible for the irreversible pathway P'_{AB} (for any finite length) to contain the same sequence of points as P_{AB} (in the opposite direction) for any fixed, predetermined path P_{AB} in a closed loop Clausius integral.

Remark: The above theorem precludes the localization of the irreversible and reversible connected segments of the Clausius closed loop integral.

Proof: Any segment P'_{AB} (see Fig. 4) may be completed by the reversible pathway P_{BA} to form a closed loop, where P'_{AB} possesses at each point the state variables belonging to the reversible pathway P^+_{AB} ($\equiv P^+_{BA}$ in terms of the sequence of points) as in the preceding theorem. We now distort the contour P_{AB} such that $P_{AB} \rightarrow P^+_{AB}$, where $P'_{AB} \equiv \{P^+_{AB}, \Delta\}$ as described previously. Then for each virtual Carnot cycle, the adiabatic paths b' and $a' \rightarrow 0$ in length, so that $W_{op} = 0$, because $W_{op} = Q_1 \cdot f'(T_1, T_2)$ where $f' \rightarrow 0$ as $T_1 \rightarrow T_2$ and $0 < \delta \leq W_{op}$ (along the entire irreversible segment) $\Rightarrow \delta = 0$. Hence the opposite direction pathway P'_{BA} is a reversible pathway with $Q_2 = -Q_1$ for each infinitesimal isotherm, and since $\Delta = 0$, P'_{AB} cannot therefore be irreversible.

Corollary 1: The Clausius inequality of the closed loop integral under the conditions of Axiom 8 precludes the non-trivial existence of a local infinitesimal excess quantity dN for any of the following definitions of dN : (a) $dN = \lim_{A \rightarrow B} N$, (b) $dN = \lim_{P_{AB} \rightarrow P'_{AB}} N$ and (c) $dN = \lim_{\substack{A \rightarrow B \\ P_{AB} \rightarrow P'_{AB}}} N$ where N is defined

as in Eqs.(10a,b).

Proof: Case (a) If $A \rightarrow B$, then since $\Delta S \rightarrow 0$, we have

$$N(= dN) = \lim_{A \rightarrow B} \left[- \int_{A, irr, P'_{AB}}^B \frac{dQ}{T} \right] \leq 0 \tag{11}$$

The general possibilities for (11) imply a cusp-like topology as in Fig. 5 (or its generalizations to intersecting looped chains) or line for the path.

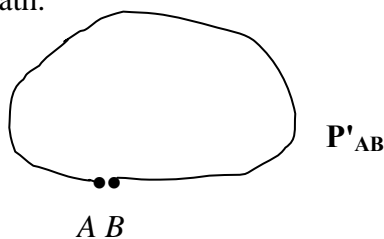


Figure 5. A simple cusp or loop path as $A \rightarrow B$.

If a cusp or cusps are implied, then in the limit as $A \rightarrow B$, we get $dN = N(P'_{AB})$, where dN is a finite, non-vanishing number if dQ/T in (11) and the length of the path is bounded, and so dN is dependent on P'_{AB} and is clearly *not* a differential element since it is a finite number. If the condition $|P'_{AB}| \rightarrow 0$ applies, then from Theorem 2, since P'_{AB} is irreversible, it cannot contain the same sequence of points as P_{AB} , and so is a non-local path dependent parameter. Writing the heat absorption increment as $dQ = \mathbf{H}(\mathbf{R}, \delta) \cdot d\mathbf{R}$ where $d\mathbf{R}$ is the element of length in thermodynamic space and \mathbf{H} a bounded function specific to the pathway implies that as $|P'_{AB}| \rightarrow 0$, $d\mathbf{R} \rightarrow 0$, so $dN \rightarrow 0$ and in the limit, $dN = 0$.

Case (b): From (a), if $P'_{AB} \rightarrow P_{AB}$, then from Theorem 2, $dN = 0$ trivially since an irreversible path would not exist.

Case (c): From (a) and (b), $dN = 0$.

Corollary 2: N is at most a constant function *locally* since $dN = 0$ when there is a coincidence of paths from Corollary 1 and Theorems 1 and 2.

Corollary 3: It is not possible to have a (continuous) sequence of states which are known to be nonequilibrium states be described by a continuous sequence of thermodynamical equilibrium states for if this was the case, Theorem 2 would be contradicted.

We now investigate whether (10a) rewritten as

$$\oint \frac{dQ}{T} + N = 0 \quad (12)$$

and the expression $N = \oint dN$ (circular integral) leading to

$$\oint \left(\frac{dQ}{T} + dN \right) = 0 \quad (13a)$$

implies the existence of a new entropy exact differential $d\Sigma$ such that

$$d\Sigma = \frac{dQ}{T} + dN . \quad (13b)$$

The formal development above indicates clearly that $dN > 0$ if a cusp-like non-local loop is involved from Corollary 1 where dN is a finite number and is not a differential, and therefore $d\Sigma$ is not a differential. If locality (implying coincidence of the thermodynamical variables) is imposed as in Corollary 2, then $d\Sigma = \frac{dQ}{T}$ is a perfect differential, where $\frac{dQ}{T}$ must be defined as the reversible heat increment, which is *not* obvious from (13b). Hence the formal development based on traditional axiomatics does not in general support (13b) as a candidate for a new irreversible entropy differential [24]. In order to confirm the above for the general case, we resort to a direct evaluation.

(b) Direct analysis of irreversible entropy increment

The integral $N = \oint dN$ is not arbitrary but has a form which must always conform to the defining relations (10a), where the pathways for the reversible and irreversible portion of the integral must be carefully distinguished, i.e.

$$N(A, B, P'_{AB}) = \int_A^B \frac{dQ[P_{AB}]}{T} - \int_A^B \left(\frac{dQ[P'_{AB}]}{T} \right)_{irr} \geq 0 . \quad (14)$$

Hence generalizations of (14) include expressions such as

$$dN(A, B, P'_{AB})_{rev} = - \frac{dQ(A, B, P_{AB})}{T} \quad (15a)$$

where

$$\oint dN(A, A, P'_{AA})_{rev} = - \oint \frac{dQ(A, A, P_{AA})}{T} = 0 \quad (15b)$$

for a cyclical *reversible* path AA and a similar expression obtains for irreversible paths, i.e.

$$dN(A, B, P'_{AB})_{irr} = - \frac{dQ(A, B, P'_{AB})}{T} \quad (16a)$$

and

$$\oint dN(A, A, P'_{AA})_{irr} = - \oint \frac{dQ(A, A, P'_{AA})}{T} \geq 0 . \quad (16b)$$

Eqs.(15-16) makes it clear that Eqs.(10a,b) are not arbitrary circular integrals over all thermodynamical spaces such that $\oint dN = N$, but that N must be defined always in terms of the reversible and irreversible paths traversed, i.e.

$$\oint dN = N = -\int_A^B \left(\frac{dQ}{T}\right)_{irr} + \int_A^B \left(\frac{dQ}{T}\right)_{rev} \quad (17)$$

leading to Eq.(10a)

$$N(A, B, P_{AB}, P'_{AB}) = -\int_A^B \frac{dQ}{T} + \Delta S_A^B \quad (18)$$

Reference [14] for instance has $\oint dN = N$ (Eq.(10) there, denoted (10') here) and $N + \oint \frac{dQ}{T} = 0$ (Eq.(9) there, denoted (9') here) so that substitution of (10') into (9') apparently yields

$$\oint \left(\frac{dQ}{T} + dN\right) = 0 \quad (19)$$

From (14), retracing the substitutions leading to (19) leads exactly to

$$\begin{aligned} \oint \frac{dQ(A, B, P_{AB}, P'_{AB})}{T} - \int_A^B \left(\frac{dQ}{T}\right)_{irr} + \int_A^B \left(\frac{dQ}{T}\right)_{rev} &= 0 \\ \int_A^B \left(\frac{dQ}{T}\right)_{irr} - \int_A^B \left(\frac{dQ}{T}\right)_{irr} &\text{ or } - \int_A^B \left(\frac{dQ}{T}\right)_{rev} + \int_A^B \left(\frac{dQ}{T}\right)_{rev} &= 0. \end{aligned} \quad (20)$$

So, exactly the same equations are subtracted i.e. $N - N = 0$, from which a perfect differential was deduced in reference [14]; this tautology cannot imply that $\frac{dQ_{irr}}{T}$ and dN are conjugate variables, in the sense that dQ and dW are in thermostatics, (which incidentally are experimentally distinguishable and defined differently theoretically). It is deduced that since $\oint \left(\frac{dQ}{T} + dN\right) = 0$, then

$d\Sigma = \frac{dQ_{irr}}{T} + dN$ is a perfect differential. This is true if $\left(\frac{dQ_{irr}}{T} + dN\right)$ were defined over all

completely arbitrary pathways, but since dQ , N and dN are all specifically characterized by the pathways and points (A, B, P_{AB}, P'_{AB}) , there being different functionals dQ , N and dN for different (A, B, P_{AB}, P'_{AB}) , it does not follow in general that the same infinitesimal quantities (e.g. dQ and dN) obtain for different pathways; if they did, i.e. if these quantities were defined independently of the variation of thermodynamical space, then $d\Sigma$ would be a perfect differential, but this has not been explicitly demonstrated. Further, it is clear that the infinitesimals such as $\frac{dQ}{T}$ and dN are not

simultaneously defined for exactly the same thermodynamical space coordinate, which must obtain if a test is to be performed for their sum being a perfect differential; Corollary 2 give examples of the resulting value of dN when the contour is localized. In particular, if points A and B are considered

fixed then (10b) yields $dN(A, B, P'_{AB}) = -\frac{dQ(A, B, P'_{AB})_{irr}}{T}$ from which it would be not true to state that $dN > 0$ for every irreversible segment, despite $N \geq 0$ since the irreversible heat exchange has indeterminate sign. Hence the statement "The differential $dN > 0$ for every irreversible segment, or it would be possible to contrive..." [14] need not obtain for non-local situations, whereas Corollary 2 shows that for the limits mentioned, the local result reduces to $d\Sigma = \frac{dQ_{irr}}{T}$ since $dN = 0$, where clearly dQ_{irr} must represent the *reversible* heat increment for $d\Sigma$ to be a perfect differential.

Conclusion

The above shows that investigators of new entropy forms should clarify further the topological structure of the space that they are utilizing if they are to avoid some of the paradoxes that might arise if they utilized traditional concepts without carefully distinguishing and relating these to their own definitions concerning primary concepts such as *heat*, *work*, *Universe* and *environment*. Another related point concerns the use of entropy vectors in modern developments, where traditionally, the reversible entropy increment dS has been defined as $dS = \frac{dQ}{T}$ where $\frac{dQ}{dt} = \int_{\partial C} \mathbf{J}_q \cdot d\mathbf{s}$ where \mathbf{J}_q is the thermal conductive vector integrated over the ∂C surface of the system with area increment $d\mathbf{s}$ and time parameter t . The entropy then is a scalar quantity here [19]. A preliminary general irreversible theory has been attempted (in the presence of a temperature field) where the entropy is considered to be scalar [25], according to classical definition. The common modern view [26], on the other hand, views entropy as a caloric vector fluid flow, described by balance equations and "internal" entropy production. The paradoxes associated with these descriptions have been examined in relation to the traditional axioms [19,25]. Of immediate practical significance is the often used local equilibrium hypothesis in modeling nonequilibrium processes, where it is assumed that each neighborhood of a point in the nonequilibrium system corresponds to an equilibrium state, so that certain conserved quantities (such as particles with invariant mass), if described as a subsystem flowing through a streamline within the system though a sequence of equilibrium states, would violate Corollary 3, implying that such subsystems can never be described fully by utilizing the local equilibrium hypothesis.

Finally, the above analysis of systems have as a presupposition an inertial frame of reference through which all elements (system, Universe, environment, source and sink reservoirs of thermophysical quantities) are related to each other via the dynamical coordinates, which involves the transfer of quantities such as impulse, energy and momentum between the sub-elements. It may be anticipated that modifications to the traditional axiomatics would involve considerations concerning frames of reference.

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