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The Contradictions between the Total-Entropy and the Gibbs Energy When Applied to the Evolving Path and State of Equilibrium of Thermodynamically-Reversible Chemical Reactions

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Abstract

This paper, an addendum to "Dialectical Thermodynamics' solution to the conceptual imbroglio that is the reversible path", this journal, **10**, 775-799, was written in response to the requests of several readers to provide further evidence of the said "imbroglio". The evidence here presented relates to the incompatibility existing between the total-entropy and the Gibbs energy prescriptions for the reversible path. The previously published proof of the negentropic nature of the transformation of heat into work is here included to validate out conclusions about the Gibbs energy perspective.

Keywords

Total-Entropy, Gibbs Energy, Evolving Path, Equilibrium, Contradictory Prescriptions for Thermodynamically Reversible Chemical Reactions

1. Antecedents

1) From J. C. Maxwell [1] [2]: "Work is done when resistance is overcome, and the quantity of wok done is measured by the product of the resisting force and the distance through which that force is overcome … The idea of work implies a fund of energy, from which the work is supplied."

Complementing the previous quote, let us add, to be specific, that the work done by the expansion of a gas against an external resisting pressure p through an infinitesimal change of volume dV is pdV. Under reversible conditions, however, the external pressure p differs only infinitesimally from the pressure of the gas, P. Being this so, the work done may be calculated solely in terms of properties of the gas (the system) as PdV.

2) From Maron & Prutton [3]: "All changes in nature are due to the tendency on the part of systems to reach a condition of maximum stability commensurate with the state of each system, *i.e.*, equilibrium. Once equilibrium has been reached, the propensity toward further changes disappears, and we say that the system is stable… Work results only when the tendency of systems to attain equilibrium is harnessed in some way. From a system in equilibrium no work can be obtained… The amount of work that can be recovered from any system undergoing a change depends both on the nature of the change and the manner in which the system is harnessed. However, for each particular process there is a maximum amount of work the system can possibly do, and this maximum amount of work may be taken as a measure of the tendency of the system in question to undergo change. A system undergoing change can perform maximum work only when the change is carried on reversibly. If the process is not completely reversible, the amount of work obtainable is always below the maximum, the difference appearing as heat. The driving force behind the change is still, however, the maximum work difference between the final and initial states."

3) From Denbigh [4]: "The reversible path must be one for which the internal forces of the system differ only infinitesimally from the external forces, and for which all heat transfers take place over temperature differences which are only infinitesimal… a path between two states A and B of a system (is) defined as being reversible if the cycle $A \to B \to A$ could be completed without leaving a change in any other body."

4) Those processes with the potential to output work along their transit towards equilibrium are called spontaneous. They have been defined as those "…which take place of their own accord" [5]. Non-spontaneous processes are, on their part, those which need to be forced to take place. By forced we mean that work needs to be spent on them. Both, spontaneous, and non-spontaneous processes can take place either reversibly or irreversibly.

5) For a closed, isothermal, isobaric, and reversible reaction system, like the one numerically analyzed in the paper to which the present one is an addendum, the equation of the first law takes the following form:

$$\Delta U = T\Delta S - P\Delta V - W_{rev} \tag{1}$$

In the previous equation $T\Delta S$ represents the (reversible) heat exchanged by the reaction system with its heat bath; $P\Delta V$ the work of displacement, that is, the work exchanged by the system with its environment in order to accommodate its change in volume [6], and W_{rev} the "chemical work" which originating in the reaction system's continuous change of composition, is exchanged by it with its associated work or mechanical reservoir; "This is … the 'chemical work' which can be attained by the use of the van't Hoff equilibrium box …" [7]. It is important to note that the chemical and PV works are accounted separately. It will be assumed that the previous equation corresponds to full conversion, that is, for $\xi = 1$, with ξ representing the degree of advancement or extent of reaction, [8]. The reader should note that for the first law, as written above, work transferred by the system outside its boundaries, as well as heat taken in by the system from its associated heat bath are positive magnitudes; their respective inverses, negative.

If in Equation (1) the terms $T\Delta S$, and $P\Delta V$ are sent to its left-hand side, we will get: $\Delta U + P\Delta V - T\Delta S = -W_{rev}$. The facts that for an isobaric system $\Delta U + P\Delta V = \Delta H$, and for an isothermal one $\Delta H - T\Delta S = \Delta G$, we can finally write, for our isothermal and isobaric reaction system, the following equation:

$$-\Delta G_{T,P} = W_{rev} \tag{2}$$

The previous equation finds its general representation, valid for any given degree of the reaction's advancement, $0 \le \xi \le 1$, in the following manner:

$$-\xi\Delta G_{T,P} = W_{rev} \tag{3}$$

As should be obvious, in the previous equation W_{rev} represents the work output associated to the transit $\xi = 0$ to ξ.

Let us now recognize that the transference of work by the reaction system under consideration to its mechanical reservoir will be possible as long as the $\Delta G_{T,P}$ term represents a negative magnitude, that is $\Delta G_{T,P} < 0$, as it is only in this case that in Equations (2) and (3) we can get: $(-)(-) = (+)$. Read from left to right, while the first negative sign of the previous signs-expression is the one coming with Equation (2), the second one is the one required from $\Delta G_{T,P}$ to produce $W_{rev} > 0$; This in accord with the expression of the first law used to obtain Equation (2), for which any such work is a positive magnitude. Recall here that ξ is a positive number. This result enlightens the fact that any work W_{rev} outputted by the reversible reaction system originates in an equivalent decrease of its Gibbs energy. This is what identifies the Gibbs energy change for isothermal, and isobaric processes with what Maxwell calls work's energy fund.

Let us now recognize that on reason of its state function nature, the Gibbs energy change for the transit of a reaction system between given initial and final states will be the same with independence of the nature of the path, reversible or irreversible, connecting said states. The difference between one path and the other is that while, as indicated by Equation (3), any depletion in Gibbs energy experienced by the reversible system ends up as work in its mechanical reservoir, the equivalent depletion experienced by the irreversible system ends up, however, as previously noted in the quote of Maron & Prutton, as heat in its heat reservoir. This wasted work-production potential, of the same magnitude as W_{rev}, is what is commonly called the lost work, W_{lost}.

The previous considerations permit writing the following extended version of Equation (3) for both, the reversible and irreversible versions of a spontaneous, isothermal, and isobaric reaction system:

$$-\xi\Delta G_{T,P} = W_{rev} = W_{lost} \tag{4}$$

That the reversible and irreversible versions of a given spontaneous, isobaric, and isothermal reaction experience identical Gibbs energy changes ΔG for identical advancements $\Delta\xi$ from any given and common point ξ to $\xi+\Delta\xi$ along their respective paths, can be equivalently expressed by saying that the value of the ratio $\frac{\Delta G}{\Delta\xi}$ for the said transit is, necessarily, common to both paths. This fact, which as noted above originates in the state function nature of the Gibbs energy, can be re-expressed, via $\lim_{\Delta\xi\to 0}\frac{\Delta G}{\Delta\xi}$, by saying that the infinitesimal quotient $\frac{\mathrm{d}G}{\mathrm{d}\xi}$ valued at any given point ξ is also common to both paths. Said fact, it should be clear, can only emerge from a common equation of the path $G=f(\xi)$, or, equivalently, from a common graph G *vs.* ξ for one path and the other; The reason being that only identical graphs can have tangents with identical slopes at every point in their common domain. From another perspective, the said infinitesimal quotients can also be interpreted by saying that the thermodynamic rate—a rate referred to ξ, not to time—at which the Gibbs energy fund is being depleted at any point along the reaction's path, is identical for both its reversible and irreversible versions. The previous considerations find summary by saying that the same concave-up curve, with its minimum identifying the state of chemical equilibrium, rules for one path and the other.

Denbigh [9], speaking about the reaction taking place in a Daniel cell, states the following:

"This change of G is, of course, the same for the same initial and final states of the reaction system, whether the process is conducted reversibly or not. It is the output of work which varies and, in the limiting case where the cell is short-circuited, the work falls to zero and all the energy is liberated as heat. This is equivalent to carrying out the reaction irreversibly without the use of a galvanic cell, as when a piece of zinc is dropped into copper sulphate solution." Also from Denbigh [10], we learn that "The criterion of equilibrium of a system which is held at constant temperature and pressure is therefore that G has reached its minimum value."

6) The potential for work-production is the distinctive characteristic of spontaneous processes. The fact that this characteristic finds equivalent expression, as evinced by our previous discussion, in a negative Gibbs energy change, is the reason for the use of $\Delta G<0$ as the criterion of spontaneity for all isothermal and isobaric process. Conversely, the negative work done on a reversible, non-spontaneous, isothermal, and isobaric system to force its occurrence ends up producing a positive change in the system's Gibbs energy, *i.e.*, $\Delta G>0$. This situation is easy to understand when Equation (2) is written in the following general manner: $\Delta G=-W$. Since work done on the system is, as above noted, negative, then signwise we will have $+=-(-)$.

Summarizing, for isothermal and isobaric processes, the conditions for spontaneity and non-spontaneity, expressed in differential form, are as follows:

$$\text{Spontaneous}: \mathrm{d}G<0$$

$$\text{Non-spontaneous}: \mathrm{d}G > 0$$

The two previous criterions will be accompanied with the following one:

$$\text{Equilibrium}: \mathrm{d}G = 0$$

The criterion of equilibrium is the mathematical expression of the fact that, as noted above by Maron & Prutton: "From a system in equilibrium no work can be obtained."

With specific reference to chemical reactions, the previous criterions can be given their most precise representation by referring them to the reaction's degree of advancement ξ, in the following manner:

$$\text{Spontaneous}: \frac{\mathrm{d}G}{\mathrm{d}\xi} < 0 \tag{5}$$

$$\text{Non-spontaneous}: \frac{\mathrm{d}G}{\mathrm{d}\xi} > 0 \tag{6}$$

$$\text{Equilibrium}: \frac{\mathrm{d}G}{\mathrm{d}\xi} = 0 \tag{7}$$

2. Planck's Statement of the Second Law

From Planck [11]:

> "The significance of the second law of thermodynamics depends on the fact that it supplies a necessary and far-reaching criterion as to whether a definite process which occurs in nature is reversible or irreversible … *Every physical or chemical process in nature takes place in such a way as to increase the sum of the entropies of all the bodies taking any part in the process. In the limit, i.e. for reversible processes, the sum of the entropies remains unchanged.* This is the most general statement of the second law of Thermodynamics."

The sum of the entropies referred to in the previous quote is what has been here called the "total-entropy."

The previous statement finds symbolic representation in the expression:

$$\Delta S_{tot} \geq 0 \tag{8}$$

where the equality refers to reversible processes, and the inequality to all others.

In reference to the total-entropy criterion, Pitzer & Brewer [12] state that "… any actual, or irreversible, process is characterized by an increase in the total entropy of all systems concerned. Therefore a system is subject to spontaneous change if there is any conceivable process for which $\sum dS > 0$, where the sum covers all the systems affected. On the other hand, a state of equilibrium is one in which every possible infinitesimal process is reversible, or one in which the total entropy remains constant. It is therefore a necessary condition for equilibrium that, for any process, $\sum dS = 0$.This is the most general criterion of equilibrium which thermodynamics offers. Indeed for many purposes it is too general. It is not always as easy to study the change in entropy of all the systems which may be affected by a given process as to focus our attention upon some one system. It is for this reason that numerous "thermodynamic functions" have been invented which are less fundamental and less general than the entropy but which are of more practical convenience in the study of some concrete problems."

Among the invented thermodynamic functions referred to by these authors we find the Gibbs and Helmholtz (free) energy functions.

3. The Limitations of the Law of Increasing Entropy and Its Associated Magnitude, the Total-Entropy

In reference to spontaneity, we find the law of increasing entropy incapable of discriminating between spontaneous and non-spontaneous processes. If reversible, both are assigned a zero total-entropy change; if irreversible, both are assigned a positive total entropy change. There is just no way to establish a total-entropy supported distinction between reversible spontaneous and reversible non-spontaneous processes, or between irreversible spontaneous and irreversible non-spontaneous. The members of each of these pairs being, entropy-wise, identical to one another.

With reference to the subject matter of this discussion, it can be said that *the only discriminating function of interest of the total-entropy criterion reduces to that it performs between the reversible and irreversible versions of spontaneous chemical reactions.* Thus, while an irreversible spontaneous chemical reaction evolves along a total-entropy increasing path which culminates in the total-entropy maximum recognized as its state of equilibrium, its reversible version evolves, on the other hand, along a constant total-entropy path, condition which according to the previous quote of Pitzer & Brewer, and in the words of Callen [13], makes of this path "… a dense succession of equilibrium states," and in those of Schmidt [14] "… a series of states of equilibrium which follow one another…" It must be recognized that if a state of equilibrium is, as defined by Pitzer & Brewer, one for which $\sum dS = 0$, then no other explanation but that given by Callen is possible for a path, the reversible path, defined as one of constant total-entropy.

The problem at the core of this dictum of the law of increasing entropy is that the state of equilibrium of a reversible reaction is, entropy-wise, indistinguishable from any other state preceding it. Here we have a state essentially different from any other state along the reversible path, yet indistinguishable from any of them. Another absurdity arising in this regard is that, as noted above by Maron & Prutton, no work can be obtained from a system in equilibrium. How is then the efficient work-production characteristic of spontaneous reversible processes to be explained given that no work comes out of them at any point along their path?

Another aspect of the previous objections to the law of increasing entropy (*LIE*) stems from the fact that it fails to discriminate, total-entropy-wise, between a reaction system *evolving* reversibly towards its state of equilibrium, and the same system *in* equilibrium, as for the law of increasing entropy these two irreconcilable different situations share a constant total-entropy condition. Just like a given body cannot be simultaneously at rest and in motion, however small its rate of motion might be, neither can a thermodynamic system be in equilibrium and out of equilibrium at the same time. While at equilibrium all gradients have vanished, and all the state variables are in a way of speaking, frozen, a situation that has been concisely described by Reiss [15] as: "… equilibrium precludes change"; in its way to equilibrium, however, even if some variables might remain unchanged (the constraints imposed on the process, if any), others, like the system's concentration in a chemical reaction, will change concomitant to the transit of the reversible system from one state to another.

Unless we are ready to accept that the state of rest is identical with the state of motion, or that a thermodynamic system can be in equilibrium and out of equilibrium at the same time, or capable of experiencing change without changing, we will have to accept that if $\sum dS = 0$ is the descriptor of equilibrium, then $\sum dS \neq 0$ must be the one describing the path leading reversible systems to their state of equilibrium.

Assigning the constant total-entropy condition to both, systems in equilibrium and systems on their way to equilibrium, is the tangible manifestation of the essential contradictory nature—the imbroglio—of Planck's second law.

Additional discussions on this subject can be found in [16].

4. A Contrast between the Total-Entropy and the Gibbs Energy

From Pitzer & Brewer's quote on Section 2 about certain thermodynamic functions being invented, among which we can identify the so-called free energies, which even if "… less fundamental and less general than the entropy … are of more practical convenience in the study of some concrete problems", one gets the impression that these new functions are to provide us with alternative but equivalent expressions in terms, say, of A or G, to those the law of increasing entropy provide in terms of total-entropy. This interpretation ends up, however, not being correct, as the description provided by these new functions for the evolution of reversible and irreversible processes *frontally contradict* those of the law of increasing entropy.

Along the transition from total-entropy to the Gibbs energy the emphasis shifts from reversibility to spontaneity, or from total-entropy to work. The following three facts will be here noted about the application of the Gibbs energy to spontaneous chemical reactions:

1) The Gibbs energy is capable of performing, for isothermal and isobaric processes, the discrimination the total-entropy could not, as for it, reversible spontaneous processes differ from those reversible and non-spontaneous in the sign of their Gibbs energy changes, negative for the spontaneous, and positive for the non-spontaneous. This same criterion applies for the distinction between irreversible spontaneous from irreversible non-spontaneous processes. This ability of

the Gibbs energy comes from its connection with that thermodynamic magnitude, *work*, which we find at the center of Carnot's pioneering work on the second law, the same that Planck practically erased from his second law because of his crusade against anthropomorphism in physical theory. Spontaneous processes, reversible or not, are recognized as such on reason of their potential to produce work; non-spontaneous processes, reversible or not, find identification in the fact that their occurrence demands the consumption of work.

2) That in opposition to the different paths prescribed by the law of increasing entropy (*LIE*) for the reversible and irreversible versions of a given spontaneous, isothermal, and isobaric chemical rection, namely a constant total-entropy path for the reversible version, and an increasing total-entropy path for the irreversible one, with the state of equilibrium defined exclusively for the latter; the Gibbs energy criterion asserts, on its part, that both versions, namely spontaneous reversible and spontaneous irreversible, share a *common path of decreasing Gibbs energy* which culminates in a minimum corresponding to the state of equilibrium, which stands this way *clearly and unambiguously* defined for both reversible and irreversible spontaneous processes.

3) That under the perspective of the Gibbs energy the *reversible path* is not one of equilibrium, which in terms of the graph of G *vs.* ξ would take the form of a horizontal line of slope equal to zero at any point along the path, *i.e.*, $\frac{\mathrm{d}G}{\mathrm{d}\xi} = 0, \forall \xi$, but one infinitesimally close to equilibrium, that is, one in which the Gibbs energy for any intermediate state of the system between the initial and equilibrium conditions is infinitesimally smaller than the previous state, and infinitesimally larger than the succeeding one, but certainly not equal to that of any of these states. These facts are evinced by the concave-up G *vs.* ξ curve representing both, the reversible and irreversible paths. For it, it is true that:

$$G(\xi) - G(\xi - \mathrm{d}\xi) < 0,\ 0 < \xi \le \xi_{eq}$$

or, equivalently:

$$\frac{\mathrm{d}G}{\mathrm{d}\xi}(\xi) < 0,\quad 0 < \xi < \xi_{eq}$$

With:

$$\frac{\mathrm{d}G}{\mathrm{d}\xi}(\xi_{eq}) = 0$$

Note then that the Gibbs energy criterion subsumes no more the absurd notion of making the reversible path "… a dense succession of equilibrium states." In the perspective provided by *G*, the change experienced by the spontaneous reversible system in its transit from one state to another finds reflection in a corresponding change in its Gibbs energy. The irreducible difference existing between the 'system in its way to equilibrium' and 'the system in its state of equilibrium' finds here mathematical expression in the corresponding difference between $\frac{\mathrm{d}G}{\mathrm{d}\xi} < 0$ and

$$\frac{\mathrm{d}G}{\mathrm{d}\xi}=0\,.$$

The previous discussion evinces the fact that for the second law of thermodynamics as currently understood, changing the description of reversible processes from the Gibbs energy to the total-entropy miraculously change the way reversible processes take place: while driven by an infinitesimal force in the former; they become driven by a non-existing force in the latter: *an effect without a cause*! The transit from the description provided by the Gibbs energy to that of the total-entropy becomes this way a transit from physics to metaphysics, from science to magic, from the natural to the supernatural.

In order to understand the form that the alternative perspective generated by the Gibbs energy adopts in terms of total-entropy, we have to take into account the essential notion provided by Dialectical Thermodynamics. This is the matter of the next section

5. Thermodynamically-Reversible Chemical Reactions at the Light of Dialectical Thermodynamics

For Dialectical Thermodynamics the total-entropy change for an isobaric, isothermal, and reversible reaction system finds, in terms of the energy transformations there taking place, the following representation:

$$\Delta S_{tot}\left[\text{chem. react.}\right]_{rev}=\Delta S_{tot}\left[Q\left(T\right)\to Q\left(T\right)\right]+\Delta S_{tot}\left[\Delta G\to W_{rev}\right] \tag{9}$$

The previous equation reflects the fact that two are the transformations taking place along the reversible evolution of the said reaction. The first term of the right-hand side represents the transformation of the amount of heat $Q=T\Delta S_{sys}$ between the reaction system and its heat bath, with both these bodies at temperature T. As shown in Equation (10) below, this transformation finds equivalent representation in terms of the entropy changes sustained by these two bodies, ΔS_{sys} and $\Delta S_{bath,rev}$, on reason of the said exchange. The second term represents, on its part, the transformation of an amount of heat ΔG into an equivalent amount of work W_{rev} [17].

$$\Delta S_{tot}\left[\text{chem. react.}\right]_{rev}=\Delta S_{sys}+\Delta S_{bath,rev}+\Delta S_{tot}\left[\Delta G\to W_{rev}\right] \tag{10}$$

The obvious fact that the entropy changes of system and bath are of identical magnitudes but opposite signs, combining this way to a value of zero, reduces the previous equation to the following form:

$$\Delta S_{tot}\left[\text{chem. react.}\right]_{rev}=\Delta S_{tot}\left[\Delta G\to W_{rev}\right] \tag{11}$$

The fact that the remaining transformation represents the *upgrading* of the lower-quality heat represented by ΔG into the equivalent amount of higher-quality energy W_{rev} [18] [19], makes its total entropy change, in accord with the results of the formal proof soon to be provided, acquire the value given by the equation below:

$$\Delta S_{tot}\left[\text{chem. react.}\right]_{rev}=\Delta S_{tot}\left[\Delta G\to W_{rev}\right]=-\frac{W_{rev}}{T}=\frac{\Delta G}{T}<0 \tag{12}$$

Now, the total entropy change for the *irreversible version* ($W_{irr}=0$) of the reaction being considered, same initial and final states, can be calculated with Equation (10) once its rightmost term is eliminated, and in that form the equation is referred to the irreversible case. This term is redundant when there is no production of work out of heat. As noted in my previous works on this matter, it is in this instance, when the work-producing potential ends up being wasted as heat, that Dialectical Thermodynamics reduces to the thermodynamics of Planck

Thus modified, Equation (10) becomes:

$$\Delta S_{tot}\left[\text{chem. react.}\right]_{irr}=\Delta S_{sys}+\Delta S_{bath,irr} \tag{13}$$

Getting at the value of this total-entropy change starts by writing the here applicable form of the first law of thermodynamics, in the following manner:

$$\Delta U=Q_{irr,sys}-P\Delta V \tag{14}$$

In the previous equation $Q_{irr,sys}$ represents the heat exchanged by the system with its heat bath in this irreversible case.

The fact that for an isobaric reaction we have that $\Delta H=\Delta U+P\Delta V$ allows us to write Equation (14) as follows:

$$\Delta H_{sys}=Q_{irr,sys} \tag{15}$$

The previous equation indicates that in the case at hand the heat transferred from the reaction system to the heat bath is numerically identical with the reaction's enthalpy change.

The fact that heat lost by the system is heat gained by the bath, and vice-versa, finds expression in the following equation:

$$Q_{irr,bath}=-Q_{irr,sys}=-\Delta H_{sys} \tag{16}$$

With this result at hand, the equation for the total-entropy change of the irreversible version of the reaction under consideration takes the following form:

$$\begin{aligned}\Delta S_{tot}\left[\text{chem. react.}\right]_{irr}&=\Delta S_{sys}+\Delta S_{bath,irr}=\Delta S_{sys}-\frac{\Delta H_{sys}}{T}\\&=\frac{-\left(\Delta H_{sys}-T\Delta S_{sys}\right)}{T}=-\frac{\Delta G}{T}=\frac{W_{lost}}{T}>0\end{aligned} \tag{17}$$

Note that the entropy change of the system ΔS_{sys} in the previous equation is identical to the one associated to the reversible reaction. The reasons being the state function nature of the entropy combined with the fact that the initial and final states defining the transit of the reaction system are identical for both paths. The entropy change of the bath is, as should be known, determined by the heat by it exchanged, with independence of the nature of the process, reversible or not, with which the exchange takes place [20]. Regarding the W_{lost} term let me remind the reader that in the irreversible version an identical amount of energy to that appearing as work in the reversible case, appears a heat in the heat reservoir.

This is the work that could have been produced, but was not.

Equation (12) is the form prescribed by Dialectical Thermodynamics for any spontaneous, reversible, and constant (*T, P*) chemical reaction producing work out of heat. The negative total-entropy change is a consequence of the fact that the transformation of heat into work is an energy-upgrading process. The lower the temperature of the heat converted into work, the larger the negentropic effect.

In agreement with the reduction of Dialectical thermodynamics to Planck's formulation in the case of irreversible processes where no energy upgrading takes place, we find the positive total-entropy change for the energy-degrading, irreversible version of the reaction to be proportional to the amount of work degraded, and inversely proportional to the temperature of the heat coming out of said degradation. The lower the temperature of this heat, the larger the degradation and, consequently, the larger the entropic effect.

The equations establishing the functional connection between $\Delta S_{tot}\left[\text{chem. react.}\right]_{rev}$ and $\Delta S_{tot}\left[\text{chem. react.}\right]_{irr}$ with the reaction's degree of advancement ξ, that is, the equations defining their respective paths in graphs ΔS_{tot} *vs.* ξ follow from the substitution of the corresponding equation establishing the connection between ΔG and ξ, here represented as $\Delta G\left(\xi\right)$, in Equations (12) and (17), as shown below:

$$\Delta S_{tot}\left(\xi\right)\left[\text{chem. react.}\right]_{irr} = -\frac{\Delta G\left(\xi\right)}{T} \tag{18}$$

$$\Delta S_{tot}\left(\xi\right)\left[\text{chem. react.}\right]_{rev} = \frac{\Delta G\left(\xi\right)}{T} \tag{19}$$

The fact that $\Delta G\left(\xi\right)$ in the two previous equations is the same function means that the graph associated to Equation (19) is the reflection across the ξ-axis of the graph of Equation (18), in other words, the one associated to the reversible reaction will take the form of a concave-up curve with its minimum appearing at the same ξ at which the maximum of that associated to Equation (18) occurs, both of these extrema complying with the condition $\frac{\partial \Delta S_{tot}\left(\xi\right)}{\partial \xi} = 0$. Take notice then that the linear, constant total-entropy path dictated by the law of increasing entropy for reversible processes no longer holds under the perspective of Dialectical Thermodynamics.

6. The Negentropic Nature of the Transformation of Heat into Work

The arguments of Sections 6.1-6.3 have been excerpted from [21]; See also [22], and [23].

6.1. From One Cycle of a Reversible Engine to a Couple of Irreversible Transformations of Heat

In **Figure 1**, (implicit) reversible engine (*a*) is shown transferring to the cold reservoir of temperature T_c the portion Q_c of the cyclical amount of heat Q_h

received by it from the hot reservoir of temperature T_h, as well as transforming the remaining portion Q into an equivalent amount of work W. Note then that $Q_h = Q_c + Q$, and $Q = W$.

The concatenation of one cycle of this engine's operation with that process shown in (*b*) in which the work output (W) of the engine is irreversibly transformed via a frictional mechanism into the equivalent amount of heat Q at the temperature of the cold reservoir, reduces the said concatenation to the two irreversible transformations of heat depicted in (*c*).

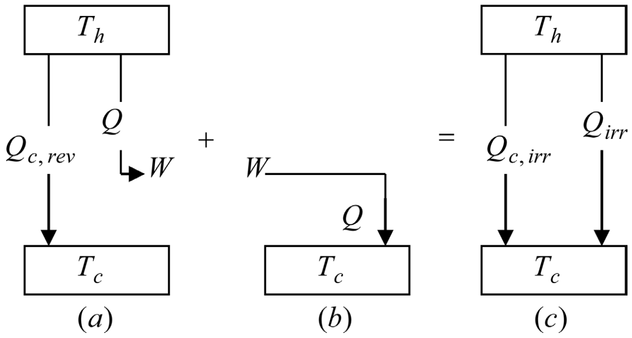

Figure 1. In transformation notation, the effects of processes (*a*), (*b*), and (*c*) take, in that order, the following form: $\left[Q_c(T_h)\to Q_c(T_c)\right]_{rev}$, $\left[Q(T_h)\to W\right]_{rev}$; $\left[W\to Q(T_c)\right]_{irr}$; and $\left[Q_c(T_h)\to Q_c(T_c)\right]_{irr}$, and $\left[Q(T_h)\to Q(T_c)\right]_{irr}$.

The transit from [(*a*) + (*b*)] to (*c*) finds explanation in the following two considerations:

1) The final and sole effect of the concatenation of the reversible heat-to-work transformation $\left[Q(T_h)\to W\right]_{rev}$ shown in (*a*), with the irreversible work-to-heat transformation $\left[W\to Q(T_c)\right]_{irr}$ shown in (*b*), is the irreversible transfer of Q from the hot to the cold reservoir: $\left[Q(T_h)\to Q(T_c)\right]_{irr}$. Having left the hot reservoir of temperature T_h to be transformed into W in (*a*), Q reappears in (*b*) entering the cold reservoir following the frictional transformation of W back into heat there taking place. Therefore:

$$\left[Q(T_h)\to W\right]_{rev} + \left[W\to Q(T_c)\right]_{irr} = \left[Q(T_h)\to Q(T_c)\right]_{irr} \tag{20}$$

2) Just like the availability of W in (*a*) is the reason behind the reversible condition of the two transformations there taking place—the feeding of W to the inverse cycle has the effect of restoring the initial condition without additional changes setting in; It is the unavailability of work at the conclusion of work-degrading step (*b*) what explains the new irreversible condition of the two transformations of heat into which the combination (*a*) + (*b*) has been reduced to, namely $\left[Q_c(T_h)\to Q_c(T_c)\right]_{irr}$ and $\left[Q(T_h)\to Q(T_c)\right]_{irr}$. The reason is simple. The transfer back of Q_{irr} or $Q_{c,irr}$ or both from the cold to the hot reservoir demands the expenditure of work. The fact that none is now available means that the only possibility left for restoration of the initial condition without additional changes setting in, is represented by the spontaneous transit of these amounts of

heat from the cold to the hot reservoir; the fact that this possibility is denied by experience explains their irreversible conditions.

That no other change remains at the conclusion of concatenation (*a*) + (*b*) but the ones shown in (c) finds the following explanation in regard to the two other bodies taking part in it; 1) No change remains in the engine's variable body on reason of the fact that at the end of every cycle it returns to its initial condition, and 2) No change remains in the work reservoir as the work originally deposited there by engine (*a*) has been retrieved from it and transformed into heat in process (*b*).

The previous considerations, in combination with the fact that $Q_h = Q_c + Q$, allows us to assert that the entropy changes sustained by the hot and cold reservoirs in (*c*) are, in that order, the following $\Delta S_{hr} = -\frac{Q_h}{T_h}$, and $\Delta S_{cr} = +\frac{Q_h}{T_c}$, and if so, that the total-entropy change for the combined irreversible transfers of heat there depicted amounts to:

$$\Delta S_{total}\left[(c)\right]_{irr} = Q_h\left(\frac{T_h - T_c}{T_h T_c}\right) \tag{21}$$

This expression, for the purposes of the argument that follows, will be written in the following manner:

$$\Delta S_{total}\left[(c)\right]_{irr} = \left(Q_c + Q\right)\left(\frac{T_h - T_c}{T_h T_c}\right) \tag{22}$$

6.2. Proof of the Negentropic Nature of the Transformation of Heat into Work

In terms of the transformations by it subsumed, the total-entropy change for process (*c*) can be expressed in the following manner:

$$\Delta S_{total}\left[(c)\right]_{irr} = \Delta S_{total}\left[Q_c\left(T_h\right) \to Q_c\left(T_c\right)\right]_{irr} + \Delta S_{total}\left[Q\left(T_h\right) \to Q\left(T_c\right)\right]_{irr} \tag{23}$$

The combination of equations (22) and (23) produces the following expression:

$$\Delta S_{total}\left[Q_c\left(T_h\right) \to Q_c\left(T_c\right)\right]_{irr} + \Delta S_{total}\left[Q\left(T_h\right) \to Q\left(T_c\right)\right]_{irr} = \left(Q_c + Q\right)\left[\frac{T_h - T_c}{T_h T_c}\right] \tag{24}$$

The fact that apart from the temperatures, the total-entropy changes for the transfers of $Q_{c,irr}$ and Q_{irr} can only be functions of Q_c, and Q, respectively, leads to the following identifications:

$$\Delta S_{total}\left[Q\left(T_h\right) \to Q\left(T_c\right)\right]_{irr} = -\left(Q/T_h\right) + \left(Q/T_c\right) \tag{25}$$

And

$$\Delta S_{total}\left[Q_c\left(T_h\right) \to Q_c\left(T_c\right)\right]_{irr} = -\left(Q_c/T_h\right) + \left(Q_c/T_c\right) \tag{26}$$

The total-entropy change for the irreversible transfer of Q depicted in (*c*) can, in attention to equation (20), be written as follows

$$\Delta S_{total}\left[Q\left(T_h\right)\rightarrow Q\left(T_c\right)\right]_{irr}=\Delta S_{total}\left[Q\left(T_h\right)\rightarrow W\right]_{rev}+\Delta S_{total}\left[W\rightarrow Q\left(T_c\right)\right]_{irr} \quad (27)$$

The further combination of the previous equation with equation (25) produces:

$$\Delta S_{total}\left[Q\left(T_h\right)\rightarrow W\right]_{rev}+\Delta S_{total}\left[W\rightarrow Q\left(T_c\right)\right]_{irr}=-\left(Q/T_h\right)+\left(Q/T_c\right) \quad (28)$$

The evident facts that the entropy changes of the transformations represented from left to right in the left-hand side of the previous equation can only be functions of the amount and temperature of the heat transformed into work, or generated out of work allows us, via a term-by-term comparison across the equal sign in this equation, to perform the following identifications:

$$\Delta S_{total,DT}\left[Q\left(T_h\right)\rightarrow W\right]_{rev}=-\frac{Q}{T_h}=-\frac{W_{rev}}{T_h}<0 \quad \blacksquare \quad (29)$$

and:

$$\Delta S_{total,DT}\left[W\rightarrow Q\left(T_c\right)\right]_{irr}=\frac{Q}{T_c}=\frac{W_{lost}}{T_c}>0 \quad (30)$$

The insertion of the work-quotients in the previous equations finds explanation in the fact indicated in Figure 1(a) and Figure 1(b) that $Q=W_{rev}=W_{lost}$.

The "*DT*" (for Dialectical Thermodynamics) subindex added to the two previous equations identify their total-entropy changes as the ones coming out of our own correction of Planck's or post-Clausius' thermodynamics.

It is the just proven negentropic nature of the transformation of heat into work shown by Equation (29), the one providing the up-to-now pending justification for equation (12).

6.3. The Failure of the Law of Increasing Entropy, and the Inevitability of the Negentropic Nature of the Transformation of Heat into Work

In order to exhibit the incapability of the law of increasing entropy to explain the total-entropy change for $\left[Q\left(T_h\right)\rightarrow Q\left(T_c\right)\right]_{irr}$ as it takes place in Figure (c), it is required, in addition to the *fiat* constituting the foundation of Planck's thermodynamics (*PT*), namely $\Delta S_{total,PT}\left[Q\left(T_h\right)\rightarrow W\right]_{rev}=0$, of that other notion which identical to our own just proven value given by Equation (30), forms also part of both Clausius' and Planck's thermodynamics:

In the words of Clausius [24]:

If…a quantity of heat Q is generated by any process such as friction, and this is finally imparted to a body of temperature T, the uncompensated transformation thus produced has the value Q/T

From Pitzer and Brewer [25]:

If an amount of work δW is degraded to heat at temperature T, the increase in entropy is $\delta W/T$

From Schmidt [26]:

…If we now allow the weight to sink back to its original level and if its energy is simultaneously transformed into heat by friction, the heat of friction $Q_f=W$ being added to the source T_o, the entropy of the latter will increase by

$\Delta S = Q_f / T_o = W/T_o$

In transformation notation, the previous statements find the following representation

$$\Delta S_{total,PT}\left[W \to Q\left(T_c\right)\right]_{irr} = Q/T_c \tag{31}$$

The failure of the law of increasing entropy comes to light when these two notions, namely $\Delta S_{total,PT}\left[Q\left(T_h\right) \to W\right]_{rev} = 0$ and $\Delta S_{total,PT}\left[W \to Q\left(T_c\right)\right]_{irr} = Q/T_c$, are used to calculate, via Equation (27), the total entropy change for the irreversible transformation of Q taking place in (c):

$$\begin{aligned}
&\Delta S_{total,PT}\left[Q\left(T_h\right) \to Q\left(T_c\right)\right]_{irr} \\
&= \Delta S_{total,PT}\left[Q\left(T_h\right) \to W\right]_{rev} + \Delta S_{total,PT}\left[W \to Q\left(T_c\right)\right]_{irr} \\
&= 0 + Q/T_c = Q/T_c
\end{aligned} \tag{32}$$

Instead of producing the correct total-entropy change for the irreversible transformation of Q, namely $-\left(Q/T_h\right) + \left(Q/T_c\right)$, the body of knowledge subsumed by the law of increasing entropy, as currently understood, assigns to this process the evidently incorrect total-entropy change of Q/T_c.

The formalism supporting the law of increasing entropy (*LIE)* requires the negation of the state function nature of the entropy, and with it of the whole of the thermodynamics of the second law, as the very same process, the irreversible transformation of Q taking place in Figure (c), is assigned two different total-entropy changes; the first one, given by Equation (28), in agreement with that known to correspond to an irreversible transformation of heat, namely $\Delta S_{total}\left[Q\left(T_h\right) \to Q\left(T_c\right)\right]_{irr} = -\left(Q/T_h\right) + \left(Q/T_c\right)$; the other one, given by Equation (32), $\Delta S_{total,PCT}\left[Q\left(T_h\right) \to Q\left(T_c\right)\right]_{irr} = Q/T_c$, in accord with the patently false notion that $\Delta S_{total,PT}\left[Q\left(T_h\right) \to W\right]_{rev} = 0$. It should be clear that the assignment to $\Delta S_{total}\left[Q\left(T_h\right) \to W\right]_{rev}$ of *any* value different from $-Q/T_h$ will lead to a similar conclusion *i.e.*, to an irreversible heat transfer with an entropy change different from the one it is known to be associated with. This fact evinces the inevitability of equation (29).

An interesting case revealing the absurd notions subsumed by Planck's second law is the one discussed in what follows.

Keeping in mind that as shown in **Figure 1(a)**, $Q = W$, let us then substitute, as allowed by the reversibility of engine (a), the Q in Equation (32) for $Q_h \dfrac{T_h - T_c}{T_h}$, where the temperatures-quotient stands for Carnot's efficiency. Performance of this operation produces the following result:

$$\Delta S_{total,PT}\left[Q\left(T_h\right) \to Q\left(T_c\right)\right]_{irr} = 0 + Q/T_c = Q_h \frac{T_h - T_c}{T_h T_c} = \left(Q_c + Q\right) \frac{T_h - T_c}{T_h T_c}$$

Note then that this result attributes the whole of the total-entropy change of process (c), which involves the irreversible transfer from the hot to the cold reservoir of both Q_c and Q, solely to the transfer of Q. If this were to be the case, we would be forced to conclude that the *irreversible* transfer of Q_c has taken place at *zero total-entropy*, in violation of that tenet of Planck's second law, whose conceptual frame underwrites this particular analysis, demanding a positive total-entropy change for all irreversible processes. This analysis constitutes, no more no less, a counterexample to the law of increasing entropy.

The previous arguments prove, in confirmation of that stated by Equation (12), that the energy-upgrading process represented by the transformation of heat into work is a negentropic process, and not as the fundamental tenet of Planck's version of the second law asserts, a constant total-entropy process.

7. The Non-Linear Universe of Thermodynamically-Reversible Chemical Reactions

The familiar concave down graphs ($\Delta S_{total,irr}$ *vs.* ξ) for the transit to equilibrium of thermodynamically-irreversible chemical reactions show that the condition of their universe, at each degree of advancement ξ, is distinguishable from its condition at any other ξ. The previous statement finds the following mathematical representations:

$$S_{total}\left(\xi\right)-S_{total}\left(\xi-\mathrm{d}\xi\right)>0,\ \ 0<\xi\le\xi_{eq} \tag{33}$$

or, equivalently:

$$\frac{\mathrm{d}\Delta S_{total,irr}}{\mathrm{d}\xi}\left(\xi\right)>0,\ \ 0<\xi<\xi_{eq} \tag{34}$$

With:

$$\frac{\mathrm{d}\Delta S_{total,irr}}{\mathrm{d}\xi}\left(\xi_{eq}\right)=0 \tag{35}$$

$$\frac{\mathrm{d}^2\Delta S_{total,rev}}{\mathrm{d}\xi^2}\left(\xi_{eq}\right)<0 \tag{36}$$

The two initial equations refer to the total-entropy increasing path along which the irreversible reaction system transits to its equilibrium condition. The third and fourth equations identify, on their part, the equilibrium condition as the maximum of the function $\Delta S_{total,irr}=f\left(\xi\right)$.

The confirmation via Equation (29) of that asserted by Equation (12), validates our previous interpretation of Equations (18) and (19) as reflections of one another across the ξ-axis. Being this so, and following the mathematical description of the irreversible path given by Equations (33)-(36), we can then describe the non-linear universe of thermodynamically-reversible reactions via the following set of equations:

$$S_{total}\left(\xi\right)-S_{total}\left(\xi-\mathrm{d}\xi\right)<0,\ \ 0<\xi\le\xi_{eq} \tag{37}$$

or, equivalently:

$$\frac{\mathrm{d}\Delta S_{total,rev}}{\mathrm{d}\xi}\left(\xi\right)<0,\ \ 0<\xi<\xi_{eq} \tag{38}$$

With:

$$\frac{\mathrm{d}\Delta S_{total,rev}}{\mathrm{d}\xi}\left(\xi_{eq}\right)=0 \tag{39}$$

$$\frac{\mathrm{d}^2\Delta S_{total,rev}}{\mathrm{d}\xi^2}\left(\xi_{eq}\right)>0 \tag{40}$$

Equations (37), and (38) make clear the fact that under Dialectical Thermodynamics the total-entropy path leading a reversible reaction to its state of equilibrium is no longer linear, as any state in it is total-entropy-wise distinguishable from any other. Equations (39) and (40) unambiguously define the state of chemical equilibrium of thermodynamically-reversible chemical reactions as that state at which the total-entropy reaches its minimum value.

8. Final Comment

At the core of the imbroglio of current thermodynamics about the reversible path, we find the previously detailed contradictory notions coming out of the total-entropy and Gibbs energy perspectives. Self-consistency is restored to this body of knowledge via the essential tenet of Dialectical Thermodynamics asserting a negative total-entropy change to the energy-upgrading process represented by the transformation of heat into work.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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