Dialectical Thermodynamics' Solution to the Conceptual Imbroglio That Is the Reversible Path

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Abstract

According to the second law of thermodynamics, as currently understood, any given transit of a system along the reversible path proceeds with a total entropy change equal to zero. The fact that this condition is also the identifier of thermodynamic equilibrium, makes each and every point along the reversible path a state of equilibrium, and the reversible path, as expressed by a noted thermodynamic author, "a dense succession of equilibrium states". The difficulties with these notions are plural. The fact, for example, that systems need to be forced out of equilibrium via the expenditure of work, would make any spontaneous reversible process a consumer of work, this in opposition to common thermodynamic wisdom that makes spontaneous reversible processes the most efficient transformers of work-producing-potential into actual work. The solution to this and other related impasses is provided by Dialectical Thermodynamics via its previously proved notion assigning a negative entropy change to the energy upgrading process represented by the transformation of heat into work. The said solution is here exemplified with the ideal-gas phase isomerization of butane into isobutane.

Keywords

Thermodynamic Reversibility, Solution to Inconsistencies, Dialectical Thermodynamics

1. Dialectics

The tools of the dialectical method are embodied by a number of notions which are nothing more than generalizations about nature's behavior obtained through observation and rational interpretation. Among them we find the so-called three laws of dialectics, namely 1) The law of transformation of quantity into quality,

and vice-versa; 2) The law of the unity and interpenetration of opposites; and 3) The law of the negation of the negation.

The first one calls attention to the fact that "…in nature, in a manner exactly fixed for each individual case, qualitative changes can only occur by the quantitative addition or subtraction of matter or motion (energy)." [1]. This law finds exemplification in several instances such as the phase changes taking place, say on water, on reason for the addition or subtraction of heat; In the fact that "…the chemical properties of the elements are a periodic function of their atomic weights…and therefore, their quality is determined by the quantity of their atomic weight." [1]; In the generation of the paraffinic series where the addition of CH_2 to the previous one generates a qualitatively different compounds, thus methane becomes ethane, ethane becomes propane, etc., [1]; In per Back's pile of sand, etc.

The second one is, on its part, related to the fact that "…opposing and contradictory motions are the rule throughout the universe" [2]. As examples of this law, consider the following cases.

Regarding the expansion of the universe, Riess and Turner [3] state that:

Whether or not the expansion is slowing down or speeding up depends on a battle between two titans: the attractive gravitational pull of matter and the repulsive gravitational push of dark matter.

Von Bertalanffy [4] asserts, on his part, that:

…growth is the result of a continuous process of build-up and break down in an organism. An organism will grow as long as the anabolic build-up exceeds the catabolic break down; growth comes to a stand still if both processes have reached a steady state.

According to Forstner [5]:

Bohm saw in the wave-particle dualism the dialectic unity of opposing properties inspired by Friedrich Engel's philosophical writings on dialectical materialism. Which of the opposing forms of behavior (wave or particle) of an electron is realized, depends on the interaction with the environment.

Regarding the second law of dialectics, Levins and Lewontin [6] state that:

The appearance of opposing forces has given rise to the most debated and difficult, yet the most central concept in dialectical thought, the principle of contradiction… (namely) *Opposing forces lie at the base of the evolving physical and biological world*. (Italics are ours)

The message of the principle of the unity and interpenetration of the opposites (the second law of dialectics) finds succinct expression in the following quote attributed to Einstein by Gitlin [7]:

Truth comes "*zu zwein*" —by twos, in company, and *by* opposition.

The third law is, on its part, related to the fact that change, development, *i.e.*,

the transformation of something into something qualitatively different, implies a negation: The old condition becomes replaced, subsumed, negated by the new condition. It is no longer what it was, but what it has become. The third law finds exemplification in the replacement of the seed by the plant; the replacement of the egg by the chick, etc.

2. Dialectical Thermodynamics

2.1. Introduction

The presence of opposite or contradictory motions/processes at the core of the being and becoming of the universe has been expressed, with reference to the second law of thermodynamics, in the following manner:

In the words of M. Mitchell Waldrop [8]:

The universe started out from the formless miasma of the Big Bang. An ever since then it's being governed by an inexorable tendency toward disorder, dissolution, and decay, as described by the second law of thermodynamics. Yet the universe has also managed to bring forth structure on every scale: galaxies, planets, bacteria, plants, animals, and brains. How? Is the former cosmic compulsion for disorder matched by an equally powerful compulsion for order, structure, and organization? And if so, how can both processes be going on at once?

Teilhard de Chardin, on his part, asserts that [9]:

For a century and a half the science of physics, preoccupied with analytical researches, was dominated by the idea of the dissipation of energy and the disintegration of matter. Being now called upon by biology to consider the effects of synthesis, it is beginning to perceive that, parallel with the phenomenon of corpuscular disintegration, the Universe historically displays a second process as generalized and fundamental as the first: I mean that of the gradual concentration of its physico-chemical elements in nuclei of increasing complexity... The outflowing flow of Entropy equalled and offset by the rising tide of a Noogenesis!

Let me call the attention of the reader to the fact that both previous authors, M. Mitchell Waldrop, and Pierre Teilhard de Chardin, recognize that the being and becoming of the universe is determined by the interplay between two opposites: The tendency towards disorder, dissolution, decay, and disintegration; and the tendency—the compulsion, says the former author—towards order, structure, organization, and complexity. Let us also note that the second law of thermodynamics is only used by these authors regarding the former tendency, but not with regard to the latter.

This omission is not accidental. It can be traced to Planck's crusade directed at removing any anthropomorphism from physical theory with the intent to "reveal the absolute" in it [10].

2.2. Planck's Crusade against Anthropomorphism in Physical Theory

Planck had a profound knowledge of Clausius' work and of his results on the mechanical theory of heat. In his own words [11]:

> …I happened to come across the treatises of Rudolf Clausius, whose lucid style and enlightening clarity of reasoning made an enormous impression on me, and I became deeply absorbed in his articles, with an ever increasing enthusiasm. I appreciated specially his exact formulation of the two laws of thermodynamics…

The impression left by Clausius' work on Planck was enormous indeed. So much that Planck's doctoral dissertation at the University of Munich in 1879 was titled "On the Second Law of Mechanical Theory of Heat".

The present author has already stated and justified his conviction that Planck could not have been unaware of the logically at fault foundation of the thermodynamic analysis through which Clausius produced his law of increasing entropy [12], and that his work on thermodynamics, particularly his crusade against anthropomorphism, was directed at providing a "sound" foundation for Clausius' results.

The essential objective of this crusade of his was to remove any connection between entropy and work. To this end he advanced two arguments. In the first one, opposing the connection between the irreversibility of a process with the work lost in it, he declares the following [10]:

> Long ago Sadi Carnot recognized…that irreversible processes are less economical than reversible, or that in an irreversible process a certain opportunity to derive mechanical work from heat is lost. What then could have been simpler than the thought of making, quite in general, the measure of irreversibility of a process the quantity of mechanical work which is unavoidable lost in the process… This view…has persisted…up to the present day; but for the general case, however, it has shown itself fruitless, and in fact, misleading…the proposed method of expressing mathematically the irreversibility of a process does not in general effect its object, and at the same time we recognize the peculiar reason which prevents it doing so. The statement of the question is too anthropomorphic. It is primarily too much concerned with the needs of mankind, in that it refers directly to the acquirement of useful work. If one requires from nature a determinate answer, he must take a more general point of view, more disinterested, less economic… If…the distinction between reversible and irreversible processes is actually to have a lasting significance for all times, it must be essentially broadened and make independent of any reference to the capacities of mankind.

It was the entropy function the one through which such independence from "the capacities of mankind" was to be achieved. In other words, irreversibility

was to be solely, exclusively associated with entropy production. The actual argument advanced by Planck to discredit the connection between irreversibility and lost work [10] was of such a trivial nature, however, that it was ignored, disregarded by thermodynamics' authors, whom instead emphasize in their woks, as the following quotes attest, the existence of such a connection. In other words, the lost work in irreversible processes continued to be taken, Planck's admonishment notwithstanding, as the measure of irreversibility and its associated entropy production. A refutation to the said argument of Planck has been advanced by the present author [12].

Writing in 1904, Swinburne [13] states:

Energy…exists in many forms, such as potential, kinetic, electric, magnetic energy on one hand, and heat in the other. All of these except heat are interchangeable… All can be changed into heat; but heat can only be partially changed into the other forms… For simplicity…we may call the high-grade energy, such as potential, kinetic, electric, magnetic, &c., "work", and the low-grade "heat"… The term "dissipation of energy" is generally used to denote degradation of work into heat…the energy (however) is not dissipated, as it is not annihilated…it is degraded… The notion of degradation and of waste is here introduced…as a good way of getting at the significance of entropy.

From Pitzer & Brewer [14] we learn that:

If an amount of work δw is degraded to heat at temperature T, the increase in entropy is $dS_{irr} = \dfrac{\delta w}{T}$.

On this same matter, the noted author B. J. Kyle [15] states that:

Entropy's human scent can be traced to its derivation. Essential to both the conventional Carnot-cycle proof and the mathematically more elegant Caratheodory proof…is the concept of a reversible process. Seldom is this even an approximation of reality. It is a concept understandable only to economic man desiring to reap the most from his attempted taming of nature and cannot be considered scientifically objective. Yet, only in this context can an unambiguous interpretation of entropy be found: the total entropy change measures the lost work when a process falls short of this human-scented, value-laden standard. Something on which we have placed value has been lost.

From Weber & Meissner [16]:

The entropy change of the system plus surroundings may be viewed as a quantitative measure, or index, of the degradation of energy as work to energy as heat, as a consequence of irreversible elements in the process under study.

From Smith & Van Ness [17]

Actual processes are irreversible, and every irreversibility results in lost work. Thus, processes which produce work deliver less than the ideal, and processes which require work must be supplied with more than the ideal … The total entropy accompanying an actual process is a measure of the loss in capacity of the system and surroundings as a whole to do work. By combining this loss in work with the ideal, or reversible, work that could be obtained, it is possible to assign a thermodynamic efficiency to any process.

The fact that the connection between entropy production and degradation, dissipation, chaos, etc. has become firmly established in the thermodynamics of the second law, is what explains its use by Mitchell Waldrop and Teilhard de Chardin to refer to the chaos-related-tendency by them described in their previous quotes.

Having supposedly achieved this first objective of his, Planck continued his anti-anthropomorphic crusade by directing his attention to the elimination of any connection between entropy and *gained work*, that is, with whatever amount of work a spontaneous process could produce. This action, however, required of him the erasure of the boundaries between mechanics and thermodynamics, as through it he performed the extraordinary feat of transforming that mechanical body called the weight, in a weight-and-pulley mechanical reservoir, into a thermodynamic body.

Regarding the displacement of the weight in a weight-and-pulley mechanical reservoir attached to a work-exchanging thermodynamic process, he stated [18]:

Since the weights change only their position and not their internal state, no changes are left in them, since in general all purely mechanical processes are essentially reversible…

With a blatant disregard for the essential difference existing between mechanical and thermodynamic reversibility, the previous statement was incorporated into thermodynamics via the identification of the reversibility of mechanical bodies with their constant entropy evolution. What Planck' does with his previous statement is to extend to mechanical bodies the result previously obtained by Clausius about the constant total entropy evolution characterizing the reversible path. With Planck's previous dixit, the said weight became the embodiment of the thermodynamic process through which work is produced out of heat. This identification finds vivid exemplification in the following quote of Pitzer & Brewer [14]:

If a heat engine operates reversibly and passes through a whole number of complete cycles, so that it is in the same state as at the beginning, it will itself suffer no change of entropy. Hence all the entropy changes are in the rest of the system, and this must sum up to zero in a reversible process…if q_h is the heat taken from the hot reservoir at T_h and q_c is the heat given to the cold reservoir at T_c, then the increase in entropy of the hot reservoir is $-q_h/T_h$, and that of the cold reservoir is q_c/T_c. Equating the sum to zero,

$$-\frac{q_h}{T_h}+\frac{q_c}{T_c}=0 \quad \dots \textit{The work term does not appear in the\dots equation, since it}$$

involves no entropy… (Italics are ours)

The entropy balance performed by Bent [19] for an isothermal and reversible expansion of an ideal gas (σ) in contact with a thermostat (θ) and a mechanical reservoir of the weight (*Wt.*)-and-pulley kind, leads him to the following equation:

$$\Delta S_{total} = \Delta S_{\sigma} + \Delta S_{\theta} + \Delta S_{Wt.} = 0$$

About the previous equation, Bent forwards the following statement (Italics are ours).

We know, also, that the entropy of the weight does not change: $\Delta S_{Wt.}=0$.
Therefore:

$$\Delta S_{\sigma} + \Delta S_{\theta} = 0$$

Barrow's position on this issue [20] takes the following illuminating form (Italics are ours):

We are at liberty, you should recognize, *to ascribe any features to this new entropy function that we like*, the requirement being that we construct a function that is self-consistent and allows us to form a useful expression of the second law. In this vein we further specify that, for all processes
$dS_{mech\ res} = 0$.

If you think that the second law of thermodynamics, the so-called law of increasing entropy, is a fundamental law of nature, think again!

In Barrow's previous quote the term $dS_{mech\ res}$ has the same meaning as the term $\Delta S_{Wt.}$ has for Bent.

2.3. The Mechanical Reservoir Is Not Thermodynamic Body

The following argument will evince the incorrectness of Planck's transformation of a mechanical into a thermodynamic body. Said argument starts with the following quotes:

From Smith & Van Ness [17]:

The internal energy of a substance does not include any energy that it may possess as a result of its position or movement *as a whole*. Rather it refers to the energy of the molecules making up the substance. The molecules of any substance are believed to be in ceaseless motion and therefore to possess kinetic energy not only of translation but also in many cases of rotation and vibration… In addition to kinetic energy, the molecules of any substance possess potential energy resulting from the forces of attraction existing between them. On a submolecular scale there is energy associated with the electrons and nuclei of atoms and bond energy resulting from the forces which hold atoms together as molecules… The designation of this form of energy of a substance as *internal* distinguishes it from the potential and ki-

netic energy which the substance may possess because of its position or motion as a whole, and which can be thought of as *external* forms of energy. (Italics in the original)

The fact that no other kind of energy but potential energy can be exchanged by a mechanical body such as the weight in a weight and pulley mechanical reservoir implies that the *state* of any such body finds definition solely in terms of an *external* variable: its height. That no other variables, like the internal variables defining the internal state of thermodynamic bodies are at all involved in the definition of the state of the "Weight", nor in the description or quantification of the change it may experience when exchanging work, points out to the undefined nature of the internal state of these bodies, and if so, also to their non-thermodynamic nature.

It must be recognized that if it had any possibility of existence beyond the fictional realm, the so-called "entropy of the weight" was to be, necessarily, a function of the only state variable associated to such a body: its height, that is, $\Delta S_{Wt.} = f(h)$. Leaving aside the fact that as defined the only similarity existing between this entropy and that of Clausius is the symbol *S*, it can be immediately concluded that contrary to the claims of its supporters, it is not, it cannot remain constant for all changes of this body. Quite the contrary, being a function of the weight's height, we will find $\Delta S_{Wt.}$ changing in value alongside any change of said weight. Instead of the claimed $\Delta S_{Wt.} = 0$, what we got is that $\Delta S_{Wt.} \neq 0$.

Being 'height' the only state variable associated to this mechanical body, and in recognition of its inability to exchange energy in the form of heat —Callen [21] defines work reservoirs as "systems enclosed by adiabatic impermeable walls", we can write the change in Clausius' entropy for such a body in the following manner: $\Delta S_{Wt.} = \dfrac{Q}{} = \dfrac{0}{}$. This is as close as we can get to define the entropy change of Planck's weights. The undefined quotient written above will become defined when the temperature becomes a variable of state of these bodies.

The following quotes parallel our previous considerations:

From Garanin [22]:

(The) existence of the temperature as the new non-mechanical quantity that equilibrates in the case of systems in thermal equilibrium, is called the *zeroth law of thermodynamics*.

From Lavis [23]:

The characteristic feature of a thermodynamic, as distinct from a mechanical, system is the presence of at least one thermal variable.

From Jepps [24]:

While certain thermodynamic properties, such as the energy and pressure, find a natural place within the framework of mechanics, two of the thermodynamic quantities—temperature and entropy—do not.

From Sekerka [25]:

A price we pay to describe a macroscopic system is the introduction of the state variable, known as the temperature, that is related to statistical concepts and has no counterpart in simple mechanical systems… This second law will involve a new state variable, the entropy *S*, which like the temperature is entirely statistical in nature and has no mechanical counterpart.

The inevitable conclusion coming out of the previous considerations is that:

There is no such thing as the entropy of the weight.

The previous considerations also explain the irreducible difference existing between mechanical, and thermodynamical reversibility. Thus, while in the former reversibility involves the recuperation of an external variable, namely the weight's initial height, an event which finds, for the reason just stated, no description nor quantification in terms of entropy; in the latter it involves the recuperation of the initial internal state of the system as defined by given values of its thermodynamic state properties.

Attempting to make mechanical reversibility identical with thermodynamical reversibility is testament to the conceptual imbroglio residing at the core of Planck's position.

The following quote of Norton [26] is illustrative in this regard:

We would hope that no one would encourage the conflation of the two senses of reversibility. Unfortunately Planck (1897) does just this.

2.4. The Dialectical Position

In any spontaneous thermodynamic process evolving with work-production efficiency η, such that $0 < \eta < \eta_{max}$, were η_{max} stands for the maximum possible or limiting efficiency, we will find the coexistence of lost-work and gained-work. That is, some of the work-producing potential of the system will end up as work in a mechanical reservoir, and the rest wasted in the form of heat at the temperature of some heat reservoir. The increase in entropy associated to the lost-work finds quantification, as noted above by Lewis and Randall, via the quotient of the magnitude of the work lost in the operation, and the temperature of the heat reservoir in which this energy ends up in the form of heat.

The immediate question coming out of the previous statement is: What about gained work?

The "degradation" qualifier attached to the transformation of work into heat is, like anything else related to that form of energy we call work, anthropomorphic in nature, this in the sense that work is, for us humans, a more useful form of energy than heat. To get a sense of the meaning of this assertion, just compare what you can do with a torch, with that you can do with electricity.

Work is the vector of progress for us humans. It is what allows us to constructively interact with our surroundings. Neither the generation of knowledge, nor the organization of societies, or the creation of structure —of any kind, of any

size, from a simple tool to the most advanced computer; from unicellular to multicellular organisms, are possible without the concourse of work.

As far as mechanical work goes, it is its increased availability what has made possible the advancement, the progress of human kind.

The transformation of mechanical work into heat represents this way a detrimental occurrence for us humans; the opposite event represents, on its part, a beneficial occurrence.

With these antecedents in mind, it appears only natural to complement that known aphorism of J. B. Kyle [27], namely:

> Entropy reminds us that something we value has been lost —work

with the following:

> Negentropy reminds us that something we value has been gained —work

If a positive entropy change is produced every time the higher-quality energy form known as work is transformed into the low-quality energy form known as heat, shouldn't the opposite effect be assigned to the transformation of low-quality heat into higher-quality work? Should not then the total entropy change of work-producing processes be given by the algebraic sum of the oppositely signed entropy changes produced by work-degrading and work-upgrading? A positive amount for the former, and a negative one for the latter.

Just like you lose height when coming down a hill, you gain it when going up the hill; just like energy lose quality when transiting from work to heat, quality is gained when energy transits in the opposite direction. It is simply impossible to have one without the other. This elementary notion can be found in the writings of the original dialectician, Heraclitus, about 2500 years ago [28]:

> The way up is the way back

2.5. From the Entropy of the Weight Back to Clausius' Transformations

Two changes stood to attention at the conclusion of Planck's correction of Clausius' work on the second law: 1) The guiding concepts of Clausius' analysis, namely the entropy of the transformation from heat of one temperature to another, and the entropy of the transformation of heat into work, and vice-versa, were replaced in Planck's work by entropies of bodies. This transition was instrumental in the introduction of 'the entropy of weights'; and 2) The expressions of the second law in one and the other were correspondingly different. Thus, while Clausius [29] expressed that:

> The algebraic sum of all the transformations occurring in any alteration of condition whatever can only be positive, or as an extreme case, equal to nothing (Italics in the original)

Planck, on his part, expressed it in the following manner [18]:

> Every physical or chemical process in nature takes place in such a way as to

increase the sum of 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. (Italics in the original)

Clausius expressed the recognizable, measurable effects of processes in terms of transformations. Thus, for a reversible heat engine (refrigerator) he expressed:

Two transformations are produced, a transformation from heat into work (or vice versa) and a transformation of heat from a higher temperature to heat of a lower (or vice versa). The relation between these two transformations is therefore that which is to be expressed by the second Main Principle. [30]

While the entropy change for his transformation of heat from one temperature to another was composed of two terms, $(-Q/T_1) + (Q/T_2)$, one from each of the bodies involved in the heat exchange, a sum that goes to zero in the reversible case when $T_1 = T_2$, the entropy change for the transformation of heat into work was, on its part, composed only of a single term. The particularity of this transformation is that it is the result of the concerted action of a number of bodies, and as such it cannot be ascribed to any of them in particular. Take for example the isothermal and reversible expansion of an ideal gas. Following Clausius, the effects of this process find description in terms of a transformation of heat between two bodies of the same temperature, and the transformation of this heat into work. No transformation of heat into work could be possible, it should be clear, without the gas, once in possession of the heat to it transferred by the heat reservoir, expanding against a resisting piston, nor without the motion of the piston being transmitted to the work reservoir to end up in the form of an increase in height of its associated weight. No work is to come out if any of these concatenated changes, starting with the gas receiving heat from the heat reservoir, and ending in the raising of the weight, fails to take place. The entropy change of this transformation belongs to all these bodies in general, and not to one in particular. It is in this sense that the transformation of heat into work is a higher order transformation than that of a heat transfer. In what follows, this transformation is to be represented as: $\left[Q(T) \rightarrow W \right]$.

This seems the right place to give the reader a succinct explanation, using the ideal-gas isothermal and reversible expansion previously described by Bent [19], of how is it that Planck produced a zero total-entropy change for reversible processes. The fact that at the conclusion of this process three are the *bodies* left in a condition different to the one they initially had, means that the total entropy change should take the following form: $\Delta S_{total,rev} = \Delta S_{\sigma} + \Delta S_{\theta} + \Delta S_{Wt.}$ Being this a reversible process, the entropy changes of the gas $\Delta S_{\sigma} = Q/T$, and that of the heat bath $\Delta S_{\theta} = -Q/T$, combine to a total of zero. Being this so, the total entropy change reduces to $\Delta S_{total,rev} = \Delta S_{Wt.}$ The fact that in its condition of a purely mechanical body, the evolutions of the "weight" are reversible, and as

such at constant entropy, produced for Planck the desired result, namely $\Delta S_{total,rev} = 0$. For the irreversible version of this process, while $\Delta S_{Wt.}$ Continued to be zero, the summation of the entropy changes of the heat bath and the gas no longer added to zero. The reason being that the heat transfer between them could no longer be assumed to be taking place with these bodies at the same temperature. If so $\left(-Q/T_1\right)+\left(Q/T_2\right) > 0$, and consequently $\Delta S_{total,irr} > 0$.

The already evinced non-sensical position of assigning an entropy change to the mechanical body, forces us to replace such a notion with $\Delta S\left[Q(T) \to W\right]$, which as noted above, is the representation of the concatenation of reversible processes in which finds origin the transformation of heat into work. Still with the terminology of Bent, the correct expression for the total entropy change of the said reversible expansion is the one given below:

$$\Delta S_{total,rev} = \Delta S_{\sigma} + \Delta S_{\theta} + \Delta S\left[Q(T) \to W\right] \qquad (1)$$

When combined with the previously noted fact that in a reversible transfer of heat it is true that $\Delta S_{\sigma} + \Delta S_{\theta} = 0$, the previous equation reduces to:

$$\Delta S_{total,rev} = \Delta S\left[Q(T) \to W\right] \qquad (2)$$

The previous equation is testament to the fact that the validity of the law of increasing entropy, in the form it adopts for reversible processes, hinges on the value of the entropy change for the transformation of heat into work. The notion that reversible processes take place at constant total entropy, and with it the law of increasing entropy, will find themselves contradicted, negated, if $\Delta S\left[Q(T) \to W\right]$ turns out to be different from zero.

That this turned out to be the case stems from the proof advanced by the present author [31] to the effect that:

$$\Delta S\left[Q(T) \to W\right] = \frac{-Q}{T} = \frac{-W_{gained}}{T} \qquad (3)$$

where T is the temperature of the heat Q out of which the equivalent amount of work W is produced.

Negentropy's exclusive domain is represented by the universe of reversible spontaneous processes, as in it the negentropic contribution of transformation $\left[Q(T) \to W\right]$, in the amount given by Equation (3), finds no opposition on reason of the absence in these processes of any lost work. On the other hand, the exclusive domain of the law of increasing entropy is represented by all those universes characterized by the absence of transformation $\left[Q(T) \to W\right]$ [12]. For those spontaneous processes in which both, work gained, and work lost are present, that is, for those in which only a portion of their work producing potential ends up as mechanical work, with the rest being degraded to heat, the total entropy change is to come out of an equation of the form [12]:

$$\Delta S_{total} = \frac{W_{lost}}{T_c} - \frac{W_{gained}}{T_h} \qquad (4)$$

In the previous equation T_c is the temperature the cold reservoir or heat sink,

and T_h the temperature of the hot reservoir or heat source.

The previous equation is the thermodynamic version of the second law of dialectics, namely the law of the unity and interpretation of the opposites.

The negentropy associated to the generation of order through work, eliminated from thermodynamics by Planck's crusade against anthropomorphism via the reversibility of mechanical bodies, which translated into the constant entropy of the "weight", led Pitzer and Brewer (Lewis and Randall) [14] to declare "The work term does not appear in the…equation, since it involves no entropy…" With this action Planck not only provided Clausius results with what he must have considered a sound, foolproof foundation; he also negated to thermodynamics the capability to explain, and measure, the ordering, and structure forming capabilities of work. This is why neither Mitchell Waldrop nor Theilhard de Chardin use the second law when referring to the self-organizing nature of the universe.

Not only there was no opposition on the part of thermodynamicists then, nor there is today, to this non-sensical position; quite the contrary, one of his supporters, namely Eddington, felt himself entitled to prohibit us mortals of ever doubting the validity of the law of increasing entropy, or, what is the same thing in other words, of doubting the zero total-entropy change ascribed by Planck and followers to mechanical reservoirs.

From Eddington [32]:

The law that entropy increases holds, I think, the supreme position among the laws of Nature. If someone point out to you that your pet theory of the universe is in disagreement with Maxwell's equations —then so much the worse for Maxwell's equations. If it is found to be contradicted by observation —well, these experimentalists do bungle things sometimes. But if your pet theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

As Eddington quote evinces, the law of increasing entropy is unusual among scientific claims in that it appears to be the only one accompanied by the implicit caveats: 'do not dare to question it', 'do not try to find flaws in its structure', 'do not look for an alternative'; as well as with an openly expressed promise of punishment for disobeying said caveats: 'humiliation'. An unusual position this of Eddington, as one is given to think that doubts and questions are essential to science.

To the dogmatic and authoritarian position expressed above, we can always oppose the following statement by Feynman [33], a succinct expression of what science is all about:

I would rather have questions that can't be answered than answers that can't be questioned.

The following quote from Le Carré [34], dubbed by the present author as the

"Eddington effect", even if originally expressed in a different context, manages to appropriately describe, in my opinion, the common attitude of thermodynamicists regarding the questioning of the law of increasing entropy.

When a well packaged web of lies has been sold to the masses over generations, the truth will seem utterly preposterous, and its speaker a raving lunatic.

3. The Dialectics of Thermodynamically-Reversible Chemical Reactions

3.1. Antecedents

The bell-shaped, concave down graphs ($\Delta S_{total,irr} - vs. - \xi$) of the total entropy for thermodynamically-irreversible chemical reactions [35] [36] show that the condition of their universe, at each degree of advancement ξ along their evolving paths, is distinguishable from its condition at any other ξ. The previous statement finds the following mathematical representations:

$$S_{total}(\xi) - S_{total}(\xi - d\xi) > 0, \quad 0 < \xi \leq \xi_{eq}$$

$$S_{total}(\xi) - S_{total}(\xi + d\xi) > 0, \quad \xi_{eq} \leq \xi < 1$$

Or, equivalently:

$$\frac{d\Delta S_{total,irr}}{d\xi}(\xi) \neq 0, \quad \forall \xi \neq \xi_{eq}$$

$$\frac{d\Delta S_{total,irr}}{d\xi}(\xi_{eq}) = 0$$

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

The two initial equations show that $S_{total}(\xi_{eq})$ is larger than the value it acquires at any other ξ. In other words, it corresponds to the extremum, the maximum of the function, a fact also illustrated by the last one of the equations given immediately above.

For thermodynamically-reversible chemical reactions there is, however, no way of distinguishing the condition of their universe at one ξ and another, this on reason of the fact that for the law of increasing entropy the reversible path proceeds at constant total-entropy. The problem here is that a total-entropy of zero is also the thermodynamic condition of equilibrium. Being this so, the conclusion is inescapable: all the states along the reversible path of a chemical reaction are *chemical-equilibrium states*, which is precisely what currently accepted thermodynamic wisdom asserts:

A quasi-static process is thus defined in terms of a dense succession of equilibrium states [21]

For the meaning of 'quasi-static' let us go to Haase [37]:

Quasistatic equals reversible

The problem with this position is that it subsumes the preposterous notion,

one of many [26], that in the reversible path of chemical reactions there is one equilibrium state which is not like the other equilibrium states, yet not entropically distinguishable from any of them: *different, but at the same time not different*. This non-sense is indicative of a flaw in the current thermodynamic description of the reversible path. If reversible reactions reach, as do those irreversible, a chemical equilibrium condition, then this state should be entropically distinguishable from all other states along this path. How do we know, you may ask, that the reversible reaction actually reaches a state of chemical equilibrium? The answer is: because the minimum shown by its Gibbs energy function corresponds equally to the reversible and irreversible reactions. Here we face a dilemma. Either the constant total-entropy path prescribed by the law of increasing entropy for reversible reactions is correct, and contrary from what may be inferred from the minimum of their Gibbs energy graphs, no state of what we call chemical equilibrium actually exists for them; or the Gibbs energy criterion is correct, in which case the constant total-entropy path wouldn't be so.

While the constant total-entropy criterion for reversible reactions leads to an inescapable conceptual imbroglio; the one which based on the negentropic nature of the transformation of heat into work comes out of dialectical thermodynamics, provides, on the other hand, a rational picture for the state of chemical equilibrium of thermodynamically-reversible chemical reactions. This is the matter of the arguments that follow.

3.2. Thermodynamic Background

The following functional relation can be written for the Gibbs energy of a closed system represented here by a homogeneous mixture at temperature T, and pressure P, and constituted by n_i moles of each of its i components:

$$G = G(T, P, n_1, n_2, \cdots, n_i) \tag{5}$$

The total differential for the Gibbs energy of this mixture is given below:

$$dG = (\partial G/\partial T)_{P,n_i} dT + (\partial G/\partial P)_{T,n_i} dP + \sum_i (\partial G/\partial n_i)_{T,P,n_j} dn_i \tag{6}$$

The previous equation quantifies the total change experienced by the Gibbs function of the mixture on reason of changes in its temperature, pressure, and composition.

If the state of the mixture changes at constant temperature and pressure, then the previous equation reduces to:

$$dG = \sum_i (\partial G/\partial n_i)_{T,P,n_j} dn_i \tag{7}$$

The partial derivatives appearing on Equations (6) and (7), of capital importance in the thermodynamic theory of spontaneity, chemical, and phase equilibrium, are also represented in the following manner:

$$\mu_i = (\partial G/\partial n_i)_{P,T,n_j} \tag{8}$$

This intensive quantity μ_i, with units of energy/mole, is the chemical poten-

tial of species i in the mixture. As such, its value is dependent on the pressure, temperature, and composition of the said mixture. As defined by Equation (8), the chemical potential can also be described "…as the amount by which the capacity of the phase for doing work (other than work of expansion) is increased per mole of the substance added, for an infinitesimal addition at constant temperature and pressure" [38].

In terms of Equation (8), and for a mixture of two components, α, and β, Equation (7) adopts the following form:

$$dG = \mu_\alpha dn_\alpha + \mu_\beta dn_\beta \tag{9}$$

It was stated above that the chemical potentials defined by Equation (8) are functions of temperature, pressure, and composition. If so, we can expect these magnitudes to have the same value in two different amounts of mixture of the same components as long as the temperature, pressure, and composition are the same in one and the other. This characteristic of the Gibbs-centered chemical potentials provides us with the following avenue for the integration of the previous equation [39]: If by enlarging its size under conditions of constant temperature, pressure, and composition, an initially infinitesimal amount of the mixture represented by Equation (9) becomes finite, then μ_α and μ_β will remain constant along the transformation. Under these conditions, Equation (9) can be integrated as follows:

$$\int_0^G dG = \mu_\alpha \int_0^{n_\alpha} dn_\alpha + \mu_\beta \int_0^{n_\beta} dn_\beta \tag{10}$$

To produce:

$$G = n_\alpha \mu_\alpha + n_\beta \mu_\beta \tag{11}$$

In the previous equation G is the Gibbs energy of that mixture containing n_α moles of component α and n_β moles of component β, at temperature T, and pressure P.

Let us now assume that Equation (11) refers to the Gibbs energy of the reaction mixture produced at any given moment of the unfolding of the following spontaneous, thermodynamically-reversible, and stoichiometric reaction in the ideal-gas phase:

$$1\,\text{Butane}\,(1\,\text{bar}, 298.15\,\text{K}) = 1\,\text{Isobutane}\,(1\,\text{bar}, 298.15\,\text{K}) \tag{12}$$
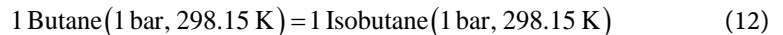
The connection between reaction (12) and Equation (11) finds concretion via the representation of butane as α, and isobutane as β.

The thermodynamic variable known indistinctively as the reaction coordinate, the degree of advancement, or extent of reaction ξ, is defined as follows [40]:

$$\xi = \frac{\Delta n}{v} \tag{13}$$

In it, Δn represents the change in number of moles of any one of the chemical species involved in the reaction at the point at which ξ is being evaluated, $0 \leq \xi \leq 1$, with v representing the respective stoichiometric coefficient, a negative number for reactants, and positive for products. For reaction (12), the pre-

vious equation takes the following form:

$$\xi = \frac{\Delta n}{\nu} = \frac{n_\alpha - 1}{-1} = \frac{n_\beta - 0}{1} \tag{14}$$

From which we obtain:

$$n_\alpha = 1 - \xi \text{ and } n_\beta = \xi \tag{15}$$

The fact that the total number of moles is constant and equal to one all along the course of the reaction ($n_\alpha + n_\beta = 1 - \xi + \xi = 1$), makes the number of moles previously written for α and β, numerically identical with their respective mole fractions, and also equal, given that the total pressure is constant and equal to one all along the reaction's course, to their respective partial pressures in the reaction mixture.

According to Denbigh [38], (Italics in the original):

…a gaseous mixture will be said to be perfect if the chemical potential of each of its components is given by the following relation, in which μ_i^o *is a function of temperature only*,

$$\mu_i = \mu_i^o + RT \ln P + RT \ln y_i$$

where P is the total gas pressure and y_i is the mole fraction of component i. Now, since μ_i^o is independent of composition it retains the same value when y_i is brought up to unity. It is thus…the value of the Gibbs free energy per mole of the gas i in its pure state at unit pressure… (The previous equation) can be put in more compact form by means of the *partial pressure* p_i:

$$\mu_i = \mu_i^o + RT \ln p_i$$

The substitution in Equation (11) of both, the previous equation, as well as the relations given in Equation (15), produce the following equation for the Gibbs energy of the reaction mixture of reaction (12) at any given degree of advancement ξ:

$$G = (1 - \xi)\left[\mu_\alpha^o + RT \ln(1 - \xi)\right] + \xi\left(\mu_\beta^o + RT \ln \xi\right) \tag{16}$$

Performance of the indicated operations, followed by rearrangement and simplification, transforms this equation into:

$$G = \mu_\alpha^o + \xi \Delta \mu^o + RT\left[(1 - \xi)\ln(1 - \xi) + \xi \ln \xi\right] \tag{17}$$

The previously noted identity between μ_i^o with the standard molar Gibbs energy of pure i at the temperature of the reaction, allows us to write:

$$G = G_\alpha^o + \xi \Delta G^o + RT\left[(1 - \xi)\ln(1 - \xi) + \xi \ln \xi\right] \tag{18}$$

Further combination of G with G_α^o allows us to express the previous equation in the following manner:

$$\Delta G = G - G_\alpha^o = \xi \Delta G^o + RT\left[(1 - \xi)\ln(1 - \xi) + \xi \ln \xi\right] \tag{19}$$

While G was the Gibbs energy of the mixture measured in reference to that of an infinitesimal amount of a mixture of identical composition, temperature, and

pressure; the previous equation quantifies the Gibbs energy of the mixture in reference to the standard Gibbs energy of 1 mole of butane at temperature T.

4. Analysis

If we were to write the total-entropy change for reaction (12) in accord with the dictates of the law of increasing entropy, we would have written:

$$\Delta S_{total,rev} = \Delta S_{sys} + \Delta S_{bath} + \Delta S(Wt.) \tag{20}$$

The previously evinced fallaciousness of the term $\Delta S(Wt.)$, combined with the recognition that the entropy change for the actual transformation of heat into work in thermodynamic processes, which we have represented as $\Delta S[Q(T) \to W]$, cannot be reduced to the contribution of a single body, explains the following equation for the total entropy change of reaction (12):

$$\Delta S_{total,rev} = \Delta S_{sys} + \Delta S_{bath} + \Delta S[Q(T) \to W] \tag{21}$$

As known, the first two terms of the right-hand side of the previous equation, that is the entropy changes for the reaction system (*sys*) and that for the heat bath (*bath*), add up to zero all along the reversible path of reaction (12). If so, then:

$$\Delta S_{total,rev} = \Delta S[Q(T) \to W] \tag{22}$$

As previously proved by dialectical thermodynamics, and as expressed by Equation (3), the entropy change associated to $[Q(T) \to W]$ turns out to be $\Delta S[Q(T) \to W] = -\dfrac{W}{T} < 0$, where W represents the work transferred by the reaction system to its mechanical reservoir, same that from now on will be designated as 'gained work'. The substitution of this value in Equation (22) leads us, in turn, to the following equation:

$$\Delta S_{tot,rev} = \frac{-W_{gained}}{T} = \frac{\Delta G}{T} < 0 \tag{23}$$

The term $\dfrac{\Delta G}{T}$ appears in the previous equation on reason of the identity existing between ΔG and $-W$.

Since:

$$dG = VdP - SdT - dW$$

then at constant temperature and pressure we will have:

$$dG = -dW$$

The reader should recall that on reason of its state function nature, the Gibbs energy change for the transit of reaction (12) from ξ_1 to ξ_2 is independent of the path. The difference being that while in the reversible path it represents the work transferred to a mechanical reservoir, in the irreversible path it represents the work-producing potential degraded by the system as heat into its heat reservoir. The negentropic effect of the work output of the reversible reaction is indicated by the negative sign attached to W_{gained} in Equation (23). This sign is what

distinguishes the previous equation from that corresponding to the irreversible reaction, *i.e.*,

$$\Delta S_{tot,irr} = \frac{W_{lost}}{T} = \frac{-\Delta G}{T} > 0 \qquad (24)$$

Equations (23) and (24) will be now combined in the following manner:

$$\Delta S_{total,rev}(\xi) = -\Delta S_{total,irr}(\xi) \qquad (25)$$

The previous equation embodies the fact that any one of the graphs $\Delta S_{total,rev} - vs. - \xi$, and $\Delta S_{total,irr} - vs. - \xi$ is the reflection of the other across the ξ axis. This means that the same equilibrium conversion, as well as the same equilibrium constant rules for one path and the other.

To give numerical substance to the previous results, we will start substituting Equation (19) in Equation (23). Performance of this action produces:

$$\Delta S_{tot,rev} = \frac{1}{T}\left\{\xi\Delta G^o + RT\left[(1-\xi)\ln(1-\xi) + \xi\ln\xi\right]\right\} \qquad (26)$$

The substitution in Equation (26) of $T = 298.15\,\text{K}$, $R = 8.314\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and of the standard Gibbs energy change for reaction (12), in the amount of $\Delta G^o = -3747.1\,\text{J}\cdot\text{mol}^{-1}$ [41], leads to:

$$\Delta S_{tot,rev} = -12.57\xi + 8.314\left[(1-\xi)\ln(1-\xi) + \xi\ln\xi\right]\text{J}\cdot\text{K}^{-1} \qquad (27)$$

Further substitution in Equation (27) of selected values of ξ, produces the results for $\Delta S_{tot,rev}$ given in Table 1.

The equation resulting from taking the first derivative of Equation (27) with respect to ξ is given below:

$$\frac{\text{d}\Delta S_{total,rev}}{\text{d}\xi} = -12.57 + 8.314\ln\frac{\xi}{1-\xi} \qquad (28)$$

On application of the equilibrium condition $\dfrac{\text{d}\Delta S_{total,rev}}{\text{d}\xi} = 0$, the previous equation becomes:

$$\ln K = \ln\left(\frac{\xi}{1-\xi}\right)_{eq} = \frac{12.57}{8.314} = 1.5119 \qquad (29)$$

The solution of the previous equation produces $K = 4.53$ for the constant of equilibrium, and $\xi_{eq} = 0.82$ for the equilibrium degree of advancement. This last value, in combination with Equation (15), leads us to the composition of the equilibrium reaction mixture: $n_{butane,eq} = 1 - 0.82 = 0.18\,\text{mol}$, and $n_{isobutane,eq} = 0.82\,\text{mol}$. These values are identical to those obtained for the irreversible path via the common following procedure:

$$K = \exp\left(\frac{-\Delta G^o}{RT}\right) = \exp\left(\frac{3747.1}{8.314 \times 298.15}\right) = 4.53$$

The second derivative of Equation (28) leads, in turn, to the following equation:

Table 1. The data displays the amount of gained work available in the mechanical reservoir for different values of the degree of advancement of reaction (12) along the thermodynamically-reversible path. This numbers correspond, for the same ξ, also to the amount of work lost along the irreversible path. The last row gives the values for the total-entropy change along the reversible path. The negatives of these numbers represent the corresponding total entropy changes along the irreversible path. ξ is in mol, and W in Joules.

ξ	0	0.2	0.4	0.6	0.82	0.9	1.0
$W_{gained} = W_{lost}$	0	1989.7	3168.4	3917.9	4244.3	4177.4	3747.1
$-\Delta S_{tot,rev}$	0	6.67	10.63	13.14	14.24	14.01	12.57

$$\frac{d^2 \Delta S_{total,rev}}{d^2 \xi} = \frac{8.314}{\xi(1-\xi)} \tag{30}$$

When evaluated at $\xi_{eq} = 0.82$, the second derivative turns out to be positive; an indication of the fact that $\Delta S_{total,rev}$ reaches a minimum at said ξ. The graphs for $\Delta S_{total,rev}$ and $\Delta S_{total,irr}$ versus ξ are shown in **Figure 1**. In it the bottom graph is the graphical representation in terms of total entropy, of the way dialectical thermodynamics conceives the evolution of a reversible chemical reaction. The path of decreasing entropy emerges on reason of the negentropic effect produced by the transformation of heat into work.

From the results of the application of the formalism of dialectical thermodynamics to reaction (12) we learn that:

1) Just like it was described above for the irreversible path, all points along the reversible path can be entropically discriminated from one another, that is:

$$S_{total}(\xi) - S_{total}(\xi - d\xi) < 0, \ \ 0 < \xi \leq \xi_{eq}$$

$$S_{total}(\xi) - S_{total}(\xi + d\xi) < 0, \ \ \xi_{eq} \leq \xi < 1$$

Or, equivalently:

$$\frac{d\Delta S_{total,rev}}{d\xi}(\xi) \neq 0, \ \ \forall \xi \neq \xi_{eq} \tag{31}$$

$$\frac{d\Delta S_{total,rev}}{d\xi}(\xi_{eq}) = 0 \tag{32}$$

$$\frac{d^2 \Delta S_{total,rev}}{d\xi^2}(\xi_{eq}) > 0 \tag{33}$$

2) That there is one and only one point fulfilling the thermodynamic condition of equilibrium given by Equation (32) negates the current thermodynamic definition of the reversible path as a "…dense succession of equilibrium states." [21]. In our construction the reaction system is not in equilibrium but infinitesimally away from it all along its reversible evolution towards its chemical equilibrium condition.

The fact that:

$$\frac{d\Delta S_{total,rev}}{d\xi}(\xi) \neq 0, \ \ \forall \xi \neq \xi_{eq}$$
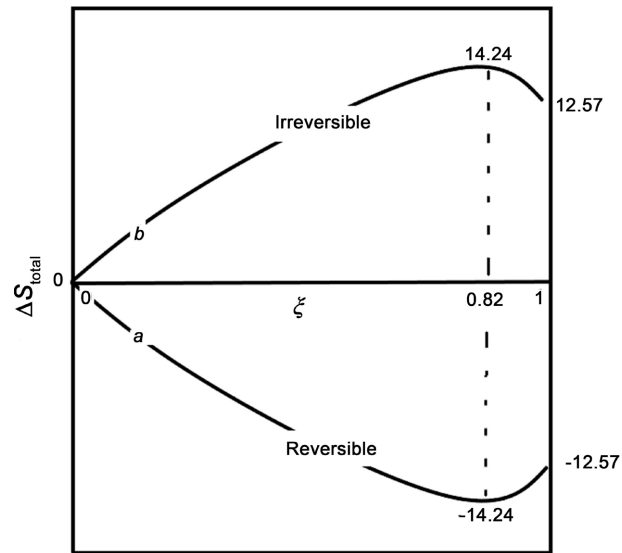
is proof of that.

Figure 1. The total entropy for the reversible, and irreversible paths of reaction (12) vs. ξ have been sketched above. Any one of them is the reflection of the other across the ξ axis. The entropy is in JK^{-1} and ξ in mol.

3) For Reiss [42] a reversible process is one which "…can be plotted in state space". In this regard, Schmidt [43] tells us that:

Reversible processes can be represented as lines in diagrams. For irreversible processes this cannot be done without certain reservations. When undergoing an irreversible process the working fluid is not in a uniform thermodynamic state and several different states appear simultaneously… The representation of irreversible changes as curves in diagrams is, however, unavoidable in practice, but it must be borne in mind that it is admissible only under the assumption that at every instant the irreversible process is imagined to be arrested and the momentary state of the working fluid made uniform by mixing.

This condition under which it is admissible to graph irreversible processes is called the "Postulate of Local Equilibrium" [40].

The following argument, dealing with the transit from a reversible to an irreversible universe via a work degrading step, explains how to construct the irreversible path without recourse to said postulate.

Let us start, however, providing an interpretation to some of the numbers of **Table 1**. Imagine the reversible reaction has taken place. The reaction system is at its chemical equilibrium condition where $\xi_{eq} = 0.82$, and the mechanical reservoir stores, as indicated by **Table 1**, an amount of work of magnitude $W_{gained} = 4244.3\,\text{J}$. Let us note that dividing this number by the temperature, $T = 298.15\,\text{K}$, produces, with the corresponding negative sign included, $\Delta S_{total,rev} = -14.24\,\text{J}\cdot\text{K}^{-1}$, which is the number quoted in **Figure 1** for the total entropy minimum at the state of chemical equilibrium reached along the revers-

ible path. This amount of work is the one that needs to be spent along the same path to force back the reaction system from its equilibrium to its initial condition, *i.e.*, from $(\xi_{eq} = 0.82) \rightarrow (\xi = 0)$. As also indicated by Table 1, a portion of it, in the amount of $4244.3 - 3747.1 = 497.2\,\text{J}$, suffices to push the equilibrium reaction system to complete conversion, in which case the amount of work available in the mechanical reservoir would reduce to 3747.1 J.

Let us now assume that the reversible reaction has transited from $(\xi = 0) \rightarrow (\xi = 0.2)$. At this point, the mechanical reservoir holds work in the amount of 1989.7 J, which makes the negentropy of the universe at this point, represented as *a* in Figure 1, equal to −6.67 JK⁻¹. The vast amount of time required for this change to take place is vast enough for the thermodynamic variables defining the state of the system, that is, the temperature, pressure, and concentration of this reaction mixture, to be uniform. Let us now, through a frictional process, say of the paddle-wheel kind used by Joule in 1845, frictionally degrade those 1989.7 J of work in the mechanical reservoir into an equivalent amount of heat that ends up in the heat bath. Let us recognize here that at difference of the transformation of heat into work, in which the whole of the bodies defining the universe of the process end up having a saying in it; the transformation of work into heat is a process which in taking place solely, exclusively between the work and heat reservoirs, does not involve in any way the reaction system, which like a true spectator, goes through it without experiencing any change in its condition, neither in its temperature, pressure, nor concentration. At the end of this work-degrading step the universe finds itself in point *b* of the irreversible path. Its irreversibility obeys to the fact that no work is available in the universe. The entropy of the universe at this point is given by 1989.7/298.15 = +6.67 JK⁻¹.

Before the work degrading step, the universe was negentropic in the amount of −6.67 JK⁻¹. Once this step is complete, it has become entropic in the amount of 6.67 JK⁻¹. The reversible to irreversible transformation of the universe corresponding to $\xi = 0.2$ involves this way a total entropy change of $\Delta S_{tot,rev \rightarrow irr} = \Delta S_{tot,b} - \Delta S_{tot,a} = 6.67 - (-6.67) = 13.34\,\text{J} \cdot \text{K}^{-1}$, which is the distance, in entropy units, between said points as represented in Figure 1.

The fact that the previous argument can be extended to any given point along the reversible curve, means that each of the reversible points generates a corresponding irreversible point via the frictional degradation of their associated work. The set of all these irreversible points define, this way, the irreversible curve. At no point in this procedure is necessary to take into account Schmidt's concerns about the undefinition of the state of the mixture, nor of its associated postulate of local equilibrium. The reaction mixture, with its state properties well defined and uniform, transits, unbeknownst to it, from being a part of a reversible universe to being a part of one irreversible, solely on virtue of the said work-degrading step.

The present author published a pair of papers making use of this work de-

grading step to link the constant total-entropy reversible path of the law of increasing entropy with the irreversible path [44] [45]. Let them be then superseded by the present work. Let me note, in passing, that the formalism of Dialectical Thermodynamics has allowed the construction of a model for the self-organizing phenomenon known as Rayleigh-Bénard convection whose first results are in agreement with experimental data [12] [46].

4) Once thermodynamically-irreversible reaction (12) reaches its chemical equilibrium condition, the only paths open to it, either in the direction of the reactants, or in the direction of higher conversions, are non-spontaneous, and work consuming. The fact that no work is in this universe available for this or any other purpose whatsoever, makes said transits, impossible. The impossibility of the reaction system to spontaneously leave the state of chemical equilibrium is what in the irreversible universe is represented by a total-entropy decreasing path. For reference, the just described spontaneous transit of the mixture away from its state of chemical equilibrium is equivalent to heat, *by itself,* passing from a colder into a hotter body.

Once reaction (12) reaches its chemical equilibrium condition along the reversible path, the only paths open, just like in the previous case, are non-spontaneous. The difference being that in the reversible universe there is enough work to produce either the full transit of the reaction from its chemical equilibrium condition to its initial state, or to complete conversion. Any of these two processes represent, in reference to the equilibrium condition, entropy increasing processes, this on reason of the fact that while the entropy changes of the system and the bath will continue to cancel one another, the amount of work/negentropy available in the mechanical reservoir, has diminished.

5) The recognition of the negentropic effect associated to the energy-upgrading process represented by the production of work out of heat not only unveils, as before done with heat engines [12], the dialectical nature of the field of chemical reactions, it also negates the currently accepted notion of the reversible path as a succession of equilibrium states. Instead, it asserts that along the reversible path there is only one equilibrium state: *the state of chemical equilibrium* in which the total-entropy reaches it minimum possible value.

Conflicts of Interest

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

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