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Sensible vs Nonsensible Work

Kent W. Mayhew
Independent Researcher, Ottawa, Ontario, Canada, Kent.Mayhew@Gmail.com

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Abstract

As a science structured around entropy, classical thermodynamics is filled with inconsistencies. Beyond its mathematical implications, entropy possesses no clear universal lucidity. Entropy's various interpretations tend to be application-dependent. Thermal entropy was devised in the 19th century by Clausius to enhance one's understanding of the relationship between energy and work. The accepted theory of work done by expanding systems has been strictly expressed in terms of that expanding system's parameters, which is non-sensible. A sensible second theorization of work will be discussed based on the facts that work is always external to the system performing that work and that an expanding system needs to lift the overlying atmosphere's mass. These two different mathematical interpretations of work will be discussed, along with the cataclysmic implications for accepted thermodynamics. Occam's razor points to sensible work, as presented herein.

Keywords: *Entropy, Exact differential, Non-Sensible Energy, Second Law, Work*

1 Introduction

Thermodynamics is not without its critics. Haddad [1] points out that" *no other discipline in mathematical science is riddled with so many logical and mathematical inconsistencies, differences in definitions, and ill-defined notation as classical thermodynamics* "Muschik [2] wrote, "*Why so many "Schools" of thermodynamics?*", which discusses the variations of interpretation held by different scientific groups. Sommerfield [3] said that. "*Thermodynamics is a funny subject. The first time you go through it, you do not understand it all. The second time you go through it, you think you understand it, except for one, or two points. And the third time you go through it, you don't know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore*".

Entropy is fundamental to our understanding of accepted classical thermodynamics. In 1865, Rudolf Clausius coined the term entropy claiming that entropy is energy divided by temperature. That claim was focused upon thermal entropy, meaning entropy as it applies to thermal processes. Since then, entropy's indulgence has grown, as it is now applied to many processes, universal and otherwise [4]. This paper is primarily concerned with work and Clausius's thermal entropy, what they mean and their implications to each other both.

To most, thermal entropy revolves around the 20th century notion that it signifies a system's disorder, i.e., entropy signifies the "*randomness of matter in incessant motion*"[5]. An early 21st century definition is, entropy is "*the dispersal of a system's molecular energy*" [6]. A more recent understanding belongs to Atkins [7] "*S is a measure of the quality of that energy; low entropy implies higher quality, while high entropy implies lower quality*". With so many different meanings no wonder why John von Neumann, told Claude Shannon (concerning information theory), "*You should call it entropy, for two reasons. In the first place, your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, no one really knows what entropy really is, so in a debate you will always have the advantage*" [8].

As a mathematical entity, entropy has been claimed to quantify the natural trend by systems toward lower energy states. This quantization towards disorder provided the sciences with a veritable sense of

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direction, hence one of entropy's accepted attributes is that is signifies the "*arrow of time*". Which coincides with Clausius' 1865 assertion that the "*entropy of the universe always increases*" [4], thus forming the basis of the second law of thermodynamics. Entropy's arrow of time association has been used to explain everything from the breaking of a porcelain cup to the irreversibile expansion of of our universe.

One cannot discuss entropy's association with the time's arrow without considering the second law. The second law states that for an adiabatic (completely isolated) system, a process is irreversible when the isothermal entropy change is greater than zero, i.e. $TdS > 0$.

Sir Arthur Stanley Eddington bravely stated: "*The law that entropy always increases holds, I think, the supreme position among the laws of Nature. If someone points 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 theory is found to be against the Second Law of Thermodynamics I can give you no hope; there is nothing for it to collapse in deepest humiliation*" [9]. Since no one knows what entropy actually means, it is a bold statement.

Early considerations of the second law include [10]; 1) Kelvin's statement concerning Second Law. "*There is no thermodynamic process whose sole effect is to transform heat extracted from a source at uniform temperature completely into work*". 2) Clausius' statement for the Second Law. "*There is no thermodynamic process whose sole effect is to extract a quantity of heat from a colder reservoir and deliver it to a hotter reservoir*".

Philosopher Jos Uffink wrote a treatise [11] that discusses many classical thermodynamics issues including a lack of consensus concerning the second law. This includes the setting up of a task force to study this in the late 19th-century (England) which attained no universal conclusions.

Uffink [11] provides numerous quotes of scientists, historians, mathematicians and others questioning the logistics of thermodynamics and the accepted second law. This includes Clifford Truesdell stating the cynical views of many: "*Clausius' verbal statement of the second law makes no sense [. . .]. All that remains is a Mosaic prohibition; a century of philosophies and journalists have acclaimed this commandment; a century of mathematicians have shuddered and averted their eyes from the unclean*". Uffink goes on to discuss the multifariousness of the second law, as well as numerous issues with accepted thermodynamics. He concludes that the second law has nothing to do with the arrow of time. Uffink and Harvey Brown [12] also pointed out that there is no theoretical evidence for the traditionally claimed notion that the path to equilibrium involves an entropy increase. This author has pointed out that the accepted second law is misguided [13], [14] and that irreversibility can in part be explained by other phenomena [13]-[17].

Consider the concept of isothermal entropy change and its application to our universe's expansion. At a symposium, when asked where does the work associated with an expanding universe go? Enrico Fermi suggested that it goes "*into the hands of god*" [18]. A traditional theorization of work is that work goes into the walls of an expanding system. This is a mathematical-based conjecture that applies to all walls, whether they are real or imaginary [19]. Seemingly, Fermi's answer was based on entropy change and work going into imaginary walls. Yet, Fermi's answer displays the reality that we simply do not know.

Work should always be considered external to the system that performs the work. This is to say that work goes through the system's walls, onto/into its surroundings, i.e., work is done onto/into something exterior of the expanding system and not into its walls [13]-[17]. Work into the walls versus work through the walls are two different interpretations. Interestingly, they share certain mathematical foundations yet they are governed by two distinctive mathematical explanations (DMEs) [20]. DMEs that result in different physics, ontic theories and philosophies.

In this paper it will be discussed that traditional misunderstanding concerning work, is the crux of the previously described issues. Although, it seems innocuous this confusion is the actual basis for a thermodynamic theoretical cataclysm. One that explains: • Haddad [1] noting that the science is filled with inconsistencies. • Muschik's [2] wonderment at so many schools • Sommerfield's [3] not understanding • Truesdell's [11] "*Clausius' verbal statement of the second law makes no sense*". • Uffink's [11] challenges to accepted thermodynamic reasoning. • Uffink and Brown's [12] realization that equilibrium's path does not require an entropy increase.

The above cataclysm has enabled the questionable association of isothermal entropy change with the accepted second law, hence the arrow of time. It will be argued that it all starts with accepted misunderstandings concerning work.

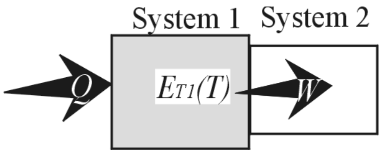

Figure 1: Shows System 1 doing work onto external System 2

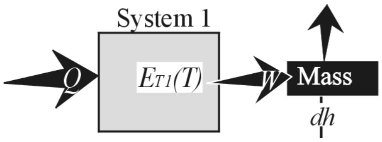

Figure 2: Shows System 1 lifting an exterior mass

2 The Basics of Work

The first law of thermodynamics is an expression for energy is always conserved. In the 19th century, James Joule showed that mechanical work and heat were inter-convertible. Thus, in terms of the thermal energy that goes into a system (Q), the energy change in that system (dE) and the work done (W) by that system, one can write:

$$Q = (E_f - E_i) + W \tag{1}$$

where the subscripts "f" and "i" respectively represent the final and initial states.

Fig.1 shows that the work done by System 1 onto arbitrary System 2, is exterior to System 1. Eq. 1 can be rewritten in differential form. That being:

$$dq_i = de_1 + dw_e \tag{2}$$

where the subscript "1" signifies System 1, "i" signifies into System 1, while the subscript "e" signifies that it is out of System 1, hence it is external to System 1.

Fig. 2 illustrates the most fundamental form of work, i.e., the lifting of a mass against the force of gravity ($\vec{g}$). The work required to lift the mass (M) by a height (dh) against Earth's gravitation field is:

$$dw_e = M\vec{g}dh \tag{3}$$

To calculate the total work as expressed in eq.1, one could integrate eq. 3. Thus:

$$W = \int dw_e = M\vec{g}\int dh \tag{4}$$

Since the work required to lift any mass against Earth's gravity is an exact differential, then one can equally write:

$$W = M\vec{g}dh = M\vec{g}(h_f - h_i) \tag{5}$$

Eq. 5 shows the work required to lift any mass, is a path-independent exact differential. Therefore, it only depends upon its final and initial heights. Note that, if the work was a path dependent inexact differential, then one would have to integrate work over its infinitesimal changes (dw), i.e., use a line integral.

Combining eq. 5 with eq. 2, one obtains:

$$dq_i = de_1 + M\vec{g}dh \tag{6}$$

Our atmosphere has mass therefore, an expanding System 1 (near Earth's surface) must displace the atmosphere's overlying mass. An expanding system will initially cause a short-lived localized pressure increase. The end result is an isobaric volume increase (PdV). This means that Earth's atmosphere undergoes an isobaric volume increase when any system expands near Earth's surface, i.e., the overlying atmosphere's mass is displaced upwardly against Earth's gravity. Mathematically speaking this is the same as lifting a column of the atmosphere that overlies the expanding volume.

In this case, the work required by expanding System 1 to upwardly lift the atmosphere's overlying mass (M_a) by some height (dh) is:

$$dq_i = de_1 + M_a\vec{g}dh \tag{7}$$

where the subscript ”a” signifies the Earth's atmosphere

The lifting of any mass results in its potential energy increase. Therefore, $M_a\vec{g}dh$ not only signifies the work done, it also represents the atmosphere's potential energy increase.

Let A be the area. Atmospheric pressure equals atmosphere's mass times gravity divided by area, i.e., $M_a\vec{g}/A$, and volume change equals area times elevation change, i.e., $dV = Adh$. Therefore:

$$M_a\vec{g}dh = (Pdv)_a \tag{8}$$

Clearly, $(PdV)_a$ represents an isobaric atmospheric volume increase that being work done onto the atmosphere.

Substituting eq. 8 into eq. 7 gives:

$$dq_i = de_1 + (Pdv)_a \tag{9}$$

The integration of eq. 9 will give the total energies involved, i.e.:

$$\int dq_i = \int de_1 + \int (Pdv)_a \tag{10}$$

As previously stated the lifting of any mass is a path-independent exact differential. Therefore, one can express System 1's work requirement in numerous ways, i.e.:

$$W_a = \int dw_a = \int (Pdv)_a = (PdV)_a = P_a(V_f - V_i)_a \tag{11}$$

Again, that work is external to expanding System 1. Therefore, one can increase the clarity by writing:

$$W_e = W_a = (PdV)_a = P_a(V_f - V_i)_a \tag{12}$$

If one accepts that both the total energy into expanding System 1 ($\int dq_i$) and System 1's total energy change ($\int de_1$) are also path-independent integrals. Then one can rewrite eq. 10 as follows:

$$dQ_i = Q_i = dE_1 + (PdV)_a \tag{13}$$

If the total energy change of System 1 only depends upon its temperature change, then it too is a path-independent exact differential, i.e., it only depends upon T_f versus T_i. In which case, eq. 13 has validity. Ditto if System 1's energy change is a potential energy change, e.g., a chemical reaction where $dE_1 = dU_1 = U_f - U_i$.

So that there is no misunderstanding, one could rewrite eq. 13 in terms of the atmosphere's potential energy increase, i.e. the overlying (column) atmosphere's mass, times gravity, times the change in atmosphere's elevation, i.e., $M_a\vec{g}dh$, as was done in eq. 7:

$$Q_i = dE_1 + M_a\vec{g}dh \tag{14}$$

Can the atmosphere's potential energy increase ever return to the expanded system? Imagine that a subsystem in the Earth's atmosphere collapses. Then any overlying atmospheric molecules will fall down towards the Earth's surface, thus attaining a kinetic energy increase [13]-[17],[26]. Kinetic energy of gas molecules is a form of thermal energy [13],[19],[21],[22]. Ultimately, this kinetic energy increase can be viewed as a thermal energy increase that quickly disperses throughout our atmosphere. Which is to say that the Earth's atmosphere behaves as a heat sink.

Therefore, an atmospheric potential energy increase cannot return to expanding System 1, if and when System 1 collapses. Hence, this is lost energy in so far as the expanded system is concerned. The realization that energy is lost has led to the concept of "*lost work*", as first discussed by Mayhew [13]-[17], [23]-25], and has been agreed upon by Hernandez [26],[27].

The above is no different than a man lifting a mass. The man exerts energy to lift the mass, as defined by eq. 5. The mass' potential energy increases. However, at no time does the energy exerted by the man, return to that man, i.e., that man's exerted energy has been lost.

Thus, the lost work (W_L) can be expressed as:

$$W_L = (PdV)_a \tag{15}$$

Inserting eq. 15 into eq. 13 one obtains:

$$Q_i = dE_1 + W_L \tag{16}$$

Those who choose to split hairs may argue that eq. 16 should be filled with differentials. However, it is written that way, for its theoretical understanding. Some may prefer eq. 16 being rewritten as follows:

$$Q_i = (E_f - E_i) + W_L \tag{17}$$

Equations 16 and 17 adhere to one ontic DMEs. They remain valid because the work involves the lifting of a mass. Whether that work is only on the overlying (column) atmosphere's mass, i.e., $[W_L = (PdV)_a]$, or the work includes the lifting of some other mass, such work is always an exact path-independent differential, thus giving eq. 16 and eq.17 equality.

If expanding System 1 lifts both the overlying (column) atmospheric mass and some other mass (M_o) then the first law equation becomes:

$$Q_i = dE_1 + W_L + W_o = dE_1 + (PdV)_a + M_o\vec{g}dh \tag{18}$$

To summarize, equations 11-17, all place an absolute understanding that work is done by an expanding system onto the overlying/surrounding atmosphere. That being exterior to the expanding system. Hence, that work is done through the system walls. Importantly, that work represents energy, that is forever lost by that expanding system.

Traditionally, eq. 9 has been written as follows:

$$dq = de + Pdv \tag{19}$$

Eq. 19 breeds ambiguity concerning what the parameters, q, e, $P$and v represent. Think of it this way. If dE is the change to System 1's total energy (i.e. the summation of all of System 1's microscopic energy changes), then PdV cannot also be part of System 1's energy.

Note that if work is done into walls, as certain math implies, then the walls must undergo a quantifiable energy change, e.g., a kinetic or potential energy change. This may be true for real walls with real mass undergoing real net forces. However, it is not true for theoretical walls that are deemed both massless and frictionless, or those that are considered imaginary. Furthermore, work through walls should be quantifiable to be considered real.

The point is that equations 13, 16 and 17 are all sensible. The same cannot be said of eq. 19. At least not until eq. 19 is provided with the necessary clarity.

All expanding systems near the Earth's surface must lift the overlying (column) atmosphere's mass and that the energy exerted in lifting that mass is "lost work". One now understands that processes involving expansion near the Earth's surface, are by their inherent nature, irreversible. Irreversibility will be discussed in Section 9.

3 Can Work Be Internal?

It has been incorrectly accepted that work can be done internally. Any notion of internal work being done by an expanding system is irrational. Importantly, a system's internal energy change (dE) is the summation

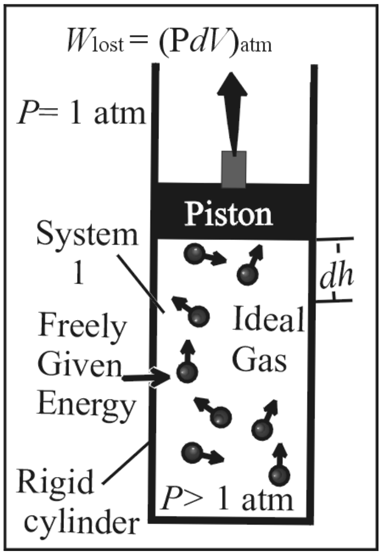

Figure 3: Shows System 1 undergoing free expansion

of all microscopic energy changes in that system. This inherently implies that the work is always external to that system.

One can view the above another way. It is problematic because work is defined in terms of the mechanical parameters (P, V) and not the thermal parameter (T), which is the parameter that generally determines a system's thermal energy. Of course, there can be other factors concerning a system's total energy such as chemical potential, or the energy associated with a tensile layer. Work is not like those other factors. Since it generally involves the movement of mass, it is best to describe it in terms external to the system that is powering it.

4 Free-Expansion

To better understand work, consider the quasi-static free expansion of System 1 near the Earth's surface. Furthermore, System 1 is a pressurized gas-filled piston-cylinder. There are two cases.

Case 1 the piston-cylinder is not insulated hence its quasi-static expansion can be an isothermal process. The reason; as the piston-cylinder expands, it must lift the overlying atmosphere's mass hence energy should be lost (eq. 15) by the expanding piston-cylinder, as illustrated in Fig. 3. However, as System 1 tries to cool, thermal energy freely enters System 1 from the surrounding atmosphere, through System 1's walls. Such energy can be deemed "freely given energy". Since the lost work equals the freely given energy, then System 1 remains isothermal.

Case 2 the piston-cylinder's walls are fully insulated. As the piston cylinder expands, it again does work, but this time lost work results in a temperature decrease of System 1.

5 Compression

Consider the compression of a gas. Does this constitute work onto that gas?

If System 1 is not insulated and it is quasi-statically compressed, then as happened in Case 1 for free expansion, this can be an isothermal process. Herein any thermal energy generated during compression, can freely escape through System 1's walls into the surrounding atmosphere, i.e., Earth's atmosphere behaves as a heat sink. Is the pressure increase, work done onto/into System 1?

If the gas remains isothermal, then there is no actual energy change to System 1. Accepting Joules experiment showing the equivalence of work and energy, then one could claim that no work was actually done onto/into System 1.

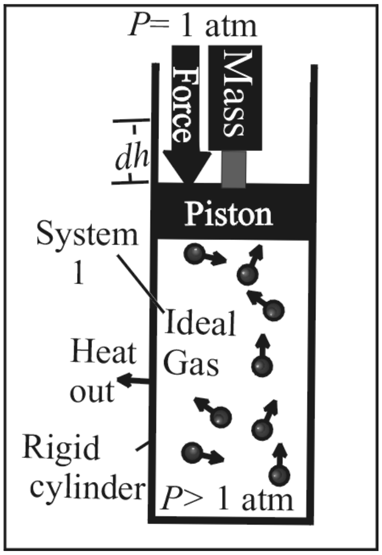

Figure 4: Shows System 1 compression by an external mass

However, the isothermal compression of System 1 has increased the potential of System 1 to do work. If the gas is ideal then the gas' potential to do work (W_p) increase is:

$$W_p = V_f dP_1 \tag{20}$$

Change to the potential to do work is not the same as actually doing work. Again ask, was work actually done onto/into System 1? One could argue it both ways dependent upon how they choose to separate one's understanding for actual work done and the potential to do work.

No matter the separation, in this case, the increase in the potential to do work was due to energy/work from a system/source that was external to System 1. For example, consider that the gas' compression occurred due to the placement of a mass on top of this piston cylinder, as is shown in Fig. 4. It was the external placement of that mass, which compressed the gas.

Consider that the compressed piston-cylinder is allowed to expand quasi-statically. Now System 1 actually does work. The work that is done by expanding System 1 is once more defined by eq. 15. Again, the quasi-static expanding gas does not cool because thermal energy is freely flows (freely-given energy) back into System 1.

Consider that the compression occurs in fully insulated System 1. As the gas is compressed its temperature increases. This temperature increase is due to increased friction between the gas molecules (a form of viscous dissipation). In this case, there is both a temperature increase, and an increase in the system's potential to do work.

If one is considering the work done by a system, then that work is always external to that system. Similarly, if one is considering a system's increase in its potential to do work, such increases are generally obtained due to an action external to that system. Note that an internal process, e.g., an exothermic chemical reaction, can lead to a temperature and/or pressure increase in a system, in which case any increase in potential to do work can be from an internal source.

6 The Acceptance of Non-Sensible Work in Eq. 19

Why has non-sensible work, hence eq. 19 been embraced?

Consider the process of boiling as shown in Fig. 5. One heats a liquid. When that liquid reaches its boiling point, liquid bonds break, and there is a mass transfer from the liquid to the vaporous state. This requires energy.

Importantly, the process is isothermal, therefore the only change to expanding System 1's energy, is its change in bonding potential, i.e., dU=dE. In which case, for boiling eq. 13 becomes:

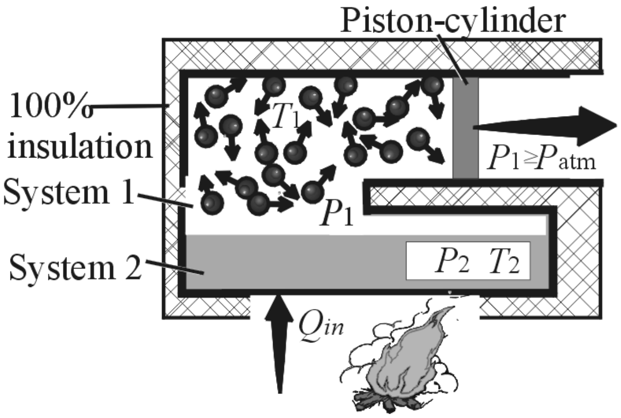

Figure 5: Shows an isothermal isobaric boiling process

$$Q_i = dU_1 + (PdV)_a \tag{21}$$

For isobaric mass transfer to occur, System 1 must expand. To physically expand, the pressure of expanding System 1 has to be greater than the pressure of the surrounding atmosphere. If the expansion is frictionless and does not involve the lifting of any mass, other than that of the overlying atmosphere, this pressure difference can be infinitesimal. In which case the System 1's pressure only need to be infinitesimally greater than that of the atmosphere. Therefore: $P_1 \approx P_a$.

Expanding System 1 can be viewed as a subsystem of the Earth's atmosphere. Hence one can write: $dV_1 = dV_a$. This applies to both open and closed systems. Therefore:

$$(PdV)_1 \approx (PdV)_a \tag{22}$$

Applying eq. 22 to eq. 21, one can write:

$$Q_i \approx dU_1 + (PdV)_1 \tag{23}$$

Eq. 23 forms the basis for the generally accepted equation for the latent heat of vaporization. However, expressing the work done in terms of System 1 remains non-sensible. The correct way (both theoretically and mathematically) is to write the latent heat of vaporization ($\text{Ł}_l \rightarrow g$) in terms of eq. 21. That being:

$$L_l \longrightarrow g = dU_1 + (PdV)_a \tag{24}$$

where "$l \longrightarrow g$" signifies vapourization i.e., from the liquid to gaseous state.

The latent heat of vaporization is another first law of thermodynamics equation based on latent heat (energy in) equaling the expanding System 1's energy (dU_1) change plus the work done [$(PdV)_a$]. Note that latent heat is an older term that has been replaced by the enthalpy of vaporization. Since Mayhew and Hernandez [26] have challenged the traditional interpretation of work hence the realities of both enthalpy and entropy, this author feels it is appropriate to return to the term latent heat.

Equations 21 through 24, all describe a process that is both isothermal (dT=0) and isobaric (dP=0). Furthermore, they all provide the correct calculated values when analyzing an experiment determining the latent heat of vaporization. However, eq. 21 and eq. 24 formulate a realistic DMEs based upon sensible work, while eq. 23 remains theoretically misguided.

Specifically, eq. 23 is the traditionally accepted DMEs. It is based on non-sensible work, hence facilitating non-sensible theorization that has become an over-complication. No wonder engineers have choose to call the enthalpy of vaporization non-sensible energy. Note that enthalpy change (dH) can be equated to the latent heat of vaporization [$L_l \longrightarrow g$].

Classical thermodynamics equations are founded upon hypotheses, which are claimed to be confirmed by experimentation. The fact that a given experimental result can be explained by more than one theory, each based upon differing DMEs, confounds accepted claims. Does one continue to blindly accept non-sensible work as the foundation for thermodynamics' accepted hypothesis? Or, should we reconsider classical thermodynamics in terms of sensible work? Sensible work represents a cataclysm to accepted classical thermodynamics. Even so, sensible work is the simplest understanding that possesses both clarity and reality.

The fact non-sensible eq. 23 and sensible eq. 24 are mathematically value-equivalent leads to the acknowledgment that two different interpretations of work, can be used to explain the same isobaric isothermal boiling process. This all reinforces the questioning of both entropy and enthalpy by this author and Hernandez [26].

If one considers the work done purely in terms of ambiguous PdV, then mathematically speaking both interpretations have similar simplicity. However, theorization requires clarity, therefore work as defined by eq. 5 and found in sensible equations 21, and 24 remains superior to the non-sensible work described in eq. 23. Importantly, the ambiguity that non-sensible eq. 23 creates has lent itself to convoluted confusion.

7 Clausius' Thermal Entropy: Convoluted Confusion?

Consider Clausius' entropy ($S = Q/T$). This enables isothermal entropy change (Tds) to adhere to the following mathematical guise:

$$Tds = dq \tag{25}$$

Thus, the first law eq. 19 can be rewritten as follows:

$$Tds = de + Pdv \tag{26}$$

At this point, one has three choices. 1): Leave eq. 26 as it is, that being an equation without clarity. 2): Adhere to the non-sensible notion that work can be expressed in terms of expanding System 1, thus write the following non-sensible equation:

$$(Tds)_1 = de_1 + (Pdv)_1 \tag{27}$$

Or, 3): Rewrite eq. 26 with a sensible understanding of work. That being, work is always done exterior to the system doing that work (e.g., expanding System 1). Thus write:

$$(Tds)_1 = de_1 + (Pdv)_a \tag{28}$$

Equations 26 through 28, all explain boiling in terms of Clausius' entropy change. A question becomes, is writing in terms of isothermal entropy change necessary? Since Tds lends itself to unnecessary over-complications, the answer becomes, it is not necessary. Boiling remains better explained in terms of eq. 24.

However, to fully appreciate the issues associated with isothermal entropy change and non-sensible work, assume that equations 26 through 28 have theoretical validity.

Other than boiling, it is hard to envision another process where a system expands both isobarically and isothermally. If isothermal, isobaric expansion is so process-limited, then equations 26 and 27 are not universally applicable, as traditionally claimed. Combined with the understanding that eq. 27 describes non-sensible work, leaves one to wonder if Clausius' thermal entropy has any real relevance. It is inarguable that Clausius's entropy has been applied to eq. 26 with its inference being non-sensible eq. 27.

It is inarguable that non-sensible eq. 27 enables natural logarithm functionality, something found throughout both thermodynamics and chemistry. Thus, reinforcing entropy's sense of correctness.

One must understand that natural logarithm function occurs for differential equations in the following form [26]:

$$dY/dX = kY \tag{29}$$

where X and Y are arbitrary variables, and k is an arbitrary constant. The corresponding solution is:

$$\Delta X = \int dx = \int dY/kY = [ln(Y_B/Y_A)]/k \tag{30}$$

"*Since natural logarithms represent the inverse of the exponential function, logarithms can also be found whenever an exponential term is present. Now, many phenomena involve the exponential term since it is closely related to the normal distribution, which is widely found in Nature, particularly when molecules are involved. Thus, exponential (and logarithmic) terms are quite commonly found in molecular processes. This is the case, for example, of the exponential term in Arrhenius-type reaction rate expressions*" [26].

Obviously, logarithm functionalities are used to describe natural processes, hence do not necessarily require the notion of entropy. [26] [28]

One can argue that isothermal entropy change is a grandiose mistake [13], [26] based upon misguided theories, starting with misunderstandings of work. Misunderstandings founded on the desire to explain first law style equations purely in terms of expanding System 1's parameters, i.e., non-sensible work. This misunderstanding founded in the process of boiling had its results treated as if they are universally applicable, when in fact they tend to be boiling-specific approximations.

Clausius' classical notion of entropy is based upon non-sensible work. If Clausius was thinking in terms of sensible work, he may have never devised entropy in the first place. This innocuous oversight helped create the convoluted confusion that has permeated thermodynamics and has gone unnoticed for far too long. A catastrophe that eventually became buried in statistical thermodynamics. No wonder entropy has a "*diversity of opinion among experts that is remarkable for a field that old*" [29].

Interestingly, Pictet's late 18th century, experiment shows that one cannot simply ignore the radiative thermal energy, which is associated with certain photons. This is not to say that statistical thermodynamics isn't a great approximation when describing the total energy of closed gaseous systems solely in terms of the molecule's kinematics. However, it is only an approximation because it ignores the energy associated with the thermal radiation that resides amongst the gas molecules. Since the energy associated with the gas molecule's kinematics tends to be significantly greater than that associated with a gaseous system's thermal radiation, the approximation has validity [13 pg 14], [30].

Arguably, both accepted classical and statistical thermodynamics are founded upon approximations that do not fully describe reality. Again, an approximation being valid does not guarantee that its math ensures correct theorization, i.e., a different empirically correct mathematical structure may better explain what is witnessed.

Consider the various definitions of thermal entropy, and what they may mean. Start, with entropy represents the "*randomness of molecules in incessant motion*" [5]. If one's focus is upon expanding gaseous System 1, thus ignoring the fact that System 1 must lift the overlying atmosphere's mass. Then as System 1 expands, its contents appear to become increasingly random. Interestingly, Ben-Naim has rightfully pointed out that randomness is in the eye of the beholder hence, it is not particularly scientific [31].

What about entropy representing the "*dispersal of a system's molecular energy*" [6]? Consider expanding System 1, its energy disperses as it expands. Certainly, the dispersal of energy corresponds a system's molecule's randomness.

What about entropy signifying "*a measure of the quality of that energy*"[7]. As expanding System 1's gases disperses then that gas's energy density decreases. Therefore, expanding System 1's potential to do work decreases.

Thermal entropy lacks universal lucidity, all because it is a mathematical structure without a grounded theoretical structure, i.e., it is a correlation between non-sensible work and energy, as described by eq. 26. Rationality does not require thermal entropy. Perspicuity in classical thermodynamics is found in equations 9, 13,14,16,17, 21 and/or 24.

8 Questioning The Second Law's Foundation

The second law of thermodynamics states that an adiabatic, isothermal entropy change, signifies an irreversible process. Therefore, irreversible processes are those where: [19]

$$Tds_1 > 0 \tag{31}$$

Certainly, if one questions the relevance of thermal entropy and its change, then the significance of isothermal entropy change (eq. 31), must also be questioned.

The second law is said to be valid for adiabatic processes. "*An adiabatic process is a type of thermodynamic process that occurs without transferring heat or mass between the thermodynamic system and its environment. Unlike an isothermal process, an adiabatic process transfers energy to the surroundings only as work.*" [32]

Consider that non-sensible eq. 26 (hence, eq. 27) has theoretical validity. If one substitutes eq. 27 into eq. 31, one obtains for an irreversible process:

$$de_1 + (Pdv)_1 > 0 \tag{32}$$

The non-sensible work in eq. 32 is not done onto its surroundings, as per the above definition for adiabatic processes.

Again, one may circumnavigate this issue by mathematically claiming that work is done into System 1's walls [19 pg 77]. Thus, mathematically speaking based upon eq. 32 adiabatic expansion here can occur on Earth's surface. One now enters the a logical abyss, as work done into the walls must be irrelevant as to whether the walls are real or imaginary. Repetition for emphasis, how work is done into imaginary walls remains mathematically plausible but logically speaking it is baffling.

Again, reality would be better described by eq. 28, where sensible work is done through expanding System 1's walls (real or imaginary), onto/into the surrounding overlying atmosphere, i.e.:

$$de_1 + (Pdv)_a > 0 \tag{33}$$

Not only is eq. 33 better aligned with the definition of an adiabatic process, it possesses a logic that non-sensible eq. 32 lacks. Importantly, eq.33 describes work that is real.

Furthermore, if a system's expansion is adiabatic then it cannot be heated. This eliminates boiling, the one process where eq. 22 holds thus eq. 27 holds any mathematical relevance.

What about the early considerations of the second law? Start with Kelvin's statement: "*There is no thermodynamic process whose sole effect is to transform heat extracted from a source at uniform temperature completely into work*". If by uniform temperature Kelvin means isothermal work, then boiling is the one isothermal process that does work. Does this mean that Kelvin's second law is limited to boiling?

Perhaps, Kelvin's real intention was for some isothermal system, which is not heated. Unfortunately, if expanding System 1 does work and is not heated, then System 1's temperature will either decrease (e.g., insulated free expansion) or, remain constant (quasi-static free expansion in a non-insulated vessel). For non-insulated quasi-static free expansion, heat enters (freely given energy) through the expanding system's walls. Therefore, although isothermal the process is not adiabatic.

Consider Clausius' Second Law statement: "*There is no thermodynamic process whose sole effect is to extract a quantity of heat from a colder reservoir and deliver it to a hotter reservoir*". Thermal equilibrium only involves the temperature equilibrium, i.e., the net flow of heat is always from hot to cold [13]. Arguably, Clausius was right, but for the wrong reasons, i.e., he was incorrectly thinking in terms of entropy change, rather then temperature change. No wonder Truesdell correctly stated that "*Clausius' verbal statement of the second law makes no sense*"[11].

Seemingly, Uffink and Brown [12] were correct in stating that there is no theoretical evidence for the traditionally claimed notion that the path to equilibrium involves an entropy increase. Then again, as a parameter without lucidity, entropy can be both nothing, and everything, at the same time. As von Neumann pointed out to Shannon, using entropy enables one to enter an argument that is impossible to lose.

It is of interest that others have questioned the second law. For example, Sabine Hossenfelder [33], questions the second law while accepting entropy. Based upon equations 25 through 28 the relevance of thermal entropy in classical thermodynamics, needs reconsideration.

Whether one questions both entropy change and its association with the second law, or just the second law, or just entropy change itself, this represents a cataclysm to thermodynamics.

Note that in some earlier writing [13], [14], that this author had incorrectly considered an adiabatic to be a completely isolated system, hence it exchanges neither energy, nor matter, nor work, with its surroundings.

9 Irreversibility

The reality is that all expanding systems near Earth's surface must lift our atmosphere's mass, hence increasing the overlying atmosphere's potential energy. This is the basis of lost work. Accordingly, all such expanding systems are fundamentally irreversible. This helps explain why the concept of irreversibility has been lost in classical thermodynamics.

Even without lost work, real processes tend to be irreversible. Movements of a mass often involve drag, that being friction with the atmosphere. There is also internal friction in machines. These two factors alone quell the notion of perpetual motion. Other factors cause a process to be irreversible such as electrical resistance, shock waves in fluids, inelastic deformation, magnetic hysteresis, mixing of substances, osmosis, flow of a viscous fluid along a solid surface, internal damping and mixing of similar substances at different temperatures.

Furthermore, the gathering of dispersed heat, followed by any attempt to control its direction of flow, remains illusional. That is unless there is some other input of resources/energy. Thus, the dispersal of heat by its very nature is irreversible.

Keep in mind that many devices are powered by processes that involve a system's expansion as part of their cycle, i.e., lost work means irreversible or if one prefers inefficiency. "*Useful processes/systems*" being systems that can move man and/or machine often involve expansion. This applies to most engines, e.g., steam, diesel and gas. Lost work both quantifies and explains why certain energy is lost, and where that energy goes.

However, there is another inherent inefficiency associated with an expanding gas. Only 2/3 of an expanding gas' energy can be used to perform work [13 pg 56], [34]. This is based on the flux of gases [13 pg 134], [19 pg 273]. Its essence can be witnessed by simply comparing the ideal gas law ($PV = NkT$) to the kinetic energy of a monatomic gas ($E_k = 3PV/2 = 3NkT/2$).

There is no need to cuddle the accepted second law to explain either irreversibility or the lacking of perpetual motion. That is unless one embraces non-sensible work [$(PdV)_Sys1$], hence, System 1's energy change and its non-sensible isothermal entropy change, as described by eq. 27.

Reality dictates that one should adhere to sensible work [$(PdV)_a$], thermal energy in, and System 1's energy change, as described by sensible equations 21 and 24. Therefore, irreversibility involves the gambit of previously described reasons.

10 Illusion of Reversibility

True reversibility in thermodynamics requires the return of all the energy originally expended by a system. One can have the situation, where a system mechanically returns to its initial state but fails to reattain all of its expended energy during expansion. Since the system has mechanically returned to its original state, one witnesses the illusion of reversibility. Reconsider boiling. Turn off the heat and the vapor, starts to condense. As heat vacates the system, the atmosphere's weight causes the expanded System 1 (piston-cylinder?) to contract back towards its original liquid state volume. Although the system mechanically returns to its original volume, all the expended energy has not been returned. Specifically, lost work is energy that is now part of the surrounding atmosphere, i.e., dispersed on our atmosphere.

Remember, as the overlying atmosphere's molecules fall downwards, their potential energy is converted into kinetic energy within the atmosphere. This energy is eventually dispersed throughout the atmosphere and is not returned to the contracting system.

Accordingly, the latent heat of condensation should be [13 pg 63], [26]:

$$L_g \longrightarrow l = -dU_1 \tag{34}$$

Why has the above not been realized? One can readily measure the latent heat of vaporization in a calorimeter. Unfortunately, one cannot similarly measure the latent heat of condensation. Therefore, due to the illusion of reversibility, we have been incorrectly instructed that the latent heat of condensation is equal magnitude but opposite to the latent heat vaporization. Reality is that condensation does not involve work as witnessed in eq. 34. This is part of the foundation of Loschmidt's Paradox (the 19th century reversibility paradox) [13 pg 63]. All the complicated arguments that this paradox has created, should now be questioned and possibly abandoned.

11 Implications

Both entropy and the second law are fundamentally mathematical contrivances [13], [35]. Whether their purpose is scientific or philosophical, they lack a solid theoretical foundation, at least from the perspective of classical thermodynamics. As such, one begins to understand how entropy and its change, can have so many application-dependent schools of thought [2]. Arguably, Uffink [11] was right to conclude that the arrow of time has nothing to do with the second law. If someone drops a fine china cup, it breaks thus, spreading over the kitchen floor. That cup has dispersed.

As for our expanding universe adhering to time's arrow. That arrow depends on neither entropy nor its change. It depends on the dispersal of matter versus the ever-pervasive attractive forces, e.g., gravitational attraction. Moreover, to claim that our expanding universe is doing work, is to claim knowledge concerning what surrounds our universe.

The reader is now faced with two choices:

1) Question entropy's epistemic knowledge, i.e., rewrite thermodynamics. 2) Keep entropy and believe that work is done by a system onto/into itself.

Hopefully, the realization that classical thermodynamics sheds its inconsistencies [1], becomes one theoretical school [2], and can now be understood [3], inspires others. Importantly, thermodynamics becomes a sensible science founded upon clarity [13].

Entropy has been used to calculate other phenomena such as free energies (both Gibbs and Helmholtz). This is based upon inserting *d(TS)* and/or $d(PV)$ into non-sensible eq. 26 and then performing the differential shuffle [13, pg 150]. It can be shown that other simpler explanations exist for such phenomena [13], [36]. Of course, there is always room for improvement, it just requires thought and courage.

This author is not alone in questioning entropy. Aguirre and Hernandez [37] questioned entropy's relevance. Although not discussed herein for the simplicity of argument, other relations whose derivation were based upon entropy change, can be explained in other terms. For example, the Clausius-Clapeyron equation [38, pg 171] and the relationship between isometric and isobaric heat capacities [13, pg 74], [26], [38, pg 74], [39] can all be explained in new, different terms.

12 Conclusions

One can be right for incorrect epistemic reasons. Therefore, one must continually question their indoctrination, even when their PET theory conforms to empirical findings. This applies to the accepted understanding of work. Specifically, classical thermodynamics has ventured down precarious paths of logic founded on non-sensible work.

Work fundamentally involves the movement of matter in a given direction, often against gravitational forces. In thermodynamics, work is defined in terms of the mechanical parameters (P, V). Our atmosphere has mass, hence its upward displacement by expanding systems requires work. Failure to recognize this fundamental form of work has allowed thermodynamics to embrace theorization that represents cumbersome over-complications.

Work that involves the elevation of any mass, including our atmosphere's, is path-independent hence, can be defined by simple exact differentials. Nowhere in classical thermodynamics is this reality properly addressed. The ramifications are profound. Not only does it challenge the accepted notions of work, it questions the very foundation of classical thermodynamics. This includes the validity of both Clausius's thermal entropy and the second law. To some, entropy will remain useful as a mathematical contrivance.

Importantly, work is always external to the system performing that work. As is the case when lifting any mass, the system (or person) performing the lift, loses energy, whilst increasing the mass's potential energy. Ultimately, for an expanding system lifting its overlying atmosphere's mass, the energy required to lift that mass is forever lost, by that expanded system. Such lost energy has been previously referred to as "*lost work*".

One must differentiate between the actual work that is done by a system, and that system's potential to do work. A system's potential to do work increases as its pressure increases above that of its surroundings, e.g., Earth's atmosphere. For a system's pressure to increase above atmospheric pressure (P_a), then an external device/source/system is often required to increase that pressure. Accordingly, an increase in a system's potential to do work often has an external component.

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It is of interest that in classical thermodynamics, it has been accepted to write the first law equation in terms of parameters without clarity. This innocuous act has enabled classical thermodynamics to incorrectly contemplate first law equations involving both a system's energy change and any work done by that system, strictly in terms of an expanding system's parameters. Again, work is external to that system, therefore it must be written as such, i.e., parameters that are external to the expanding system.

Writing work in terms of an expanding system's mechanical parameters is the act of thinking in terms of non-sensible work. Work must be sensible, e.g., the work required to lift a mass upwards against gravity. For the case of an expanding system lifting the mass of our atmosphere against Earth's gravitational forces, sensible work is defined in terms of the atmosphere's parameters, i.e., $(PdV)_a$. Such sensible work results in an atmospheric potential energy increase, i.e., $M_a \vec{g} dh$. Ultimately, this "*sensible work*" signifies energy that is lost by the expanding system into the surrounding atmosphere, i.e., "*lost work*".

The applicability of non-sensible work to expanding systems has been incorrectly believed to be backed by empirical experimental findings. Realize that in the process of boiling that expressing work in terms of the expanding system (nonsensible work) approximates expressing work in terms of the lifting the overlying atmosphere's mass (sensible work). This alone helps one to understand how this incorrect belief has gone unnoticed for over one and a half centuries. In other words, both sensible work and non-sensible work can be seemingly backed by the same empirical evidence.

Clausius's notion of thermal entropy is that it somehow signifying energy divided by temperature. Entropy is often related to the quality of energy, which has been based upon nonsensible work.

It should be pointed out that non-sensible work requires the traditionally accepted notion of path-dependent work. Conversely, sensible work involves path-independent work. Again, path-dependent work is non-sensible because it is calculated strictly in terms of the expanding system's parameters. The integration of non-sensible path-dependent work combined with Clausius's notion of entropy has created a theoretical catastrophe. A catastrophe founded in inherent ambiguity.

The above has resulted in a science full of inconsistencies. A science with too many schools. A science that is accepted, but never fully understood. A science that may just be an over-complication of reality. The implication may be that thermal entropy and/or its change (i.e., the second law) represent the biggest scientific gaffes ever.

Although, no experiment with alleged proof was found. Hopefully, this paper shows that our accepted understandings that formulate the basis of thermodynamics needs reconsideration.

It is of particular interest that the latent heat of condensation has traditionally been accepted to be equal in magnitude but opposite in sign to the latent heat of vaporization. This means that the work done in boiling (and/or vaporization) has been incorrectly considered to be reversible. As is the case for all expanding systems on Earth's surface, the work done is lost work. Therefore, the magnitude of the latent heat of vaporization must be greater than the magnitude of the latent heat of condensation. Accordingly, a plausible experimental proof concerning what has been discussed in this paper, could involve the actual measurement of the latent heat of condensation. This assumes that it can be done.

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