OPEN ACCESS

1st International Electronic
Conference on Entropy and
Its Applications
3 - 21 November 2014

www.sciforum.net/conference/ecea-2

Conference Proceedings Paper – Entropy

Toward improved understanding of the physical meaning of entropy in classical thermodynamics

Ben Akih-Kumgeh

Department of Mechanical and Aerospace Engineering, Syracuse University, 263 Link Hall, Syracuse, NY 13244, USA; E-Mail: bakihkum@syr.edu

Published: 13 November 2015

Abstract: This year marks the 150th anniversary of the concept of entropy, introduced into thermodynamics by Rudolf Clausius. Despite its central role in the mathematical formulation of the Second Law and most of classical thermodynamics, its physical meaning continues to be elusive and confusing. This is particularly the case when one invokes the connection between the classical thermodynamics of a system and the statistical behavior of its constituent microscopic particles. This paper sketches Clausius approach to its definition and offers a modified mathematical definition that is still in the spirit of the derivation by Clausius. In the modified version, the differential of specific entropy appears as a non-dimensional energy term that captures the invigoration or reduction of microscopic motion upon addition or withdrawal of heat from the system. It is also argued that heat transfer is a better thermodynamic model process to illustrate the concept of entropy instead of the canonical heat engines and refrigerators that are not relevant to new areas of thermodynamics (e.g. thermodynamics of biological systems). In this light, it is emphasized that entropy changes, as invoked in the Second Law, are necessarily related to the non-equilibrium interactions of two or more systems that might have initially been in thermal equilibrium but at different temperatures. The overall direction of entropy increase indicates the direction of naturally occurring heat transfer processes in an isolated system of internally interacting (non-isolated) sub systems. We discuss the implication of the proposed modification on the interpretation of entropy in statistical thermodynamics as well as the formulation of the most common thermodynamic potentials.

Keywords: Entropy; heat transfer; heat engines; thermal non-equilibrium; Second Law

---

1. Introduction

In the first half of the 19th Century, von Mayer and Joule put forward the principle of conservation of energy, demonstrating that heat (internal energy) and work are inter-convertible and that the total energy of the universe is constant. The Second Law forbids the realization of perpetual motion machines and limits the effectiveness of heat engines and cold machines (heat pumps and refrigerators). Based on Carnot's theorems in the more analytical form developed by Clapeyron, Thomson and Clausius greatly advanced the theory of heat engines. Clausius eventually introduced the concept of entropy to represent the transformation or *Verwandlung* of heat into work and vice versa [1,2]. This year is the 150th anniversary of this entropy definition and it continues to be a challenging concept in thermodynamics. It is one of the challenges impeding the conceptual reconciliation of the microscopic view of matter offered by statistical thermodynamics with the macroscopic view of classical thermodynamics. In Clausius' work [2,3], the term emerges from his attempt to quantify the transformation of heat into mechanical work and mechanical work into heat. It should be noted that although the equality of work and heat was established in the First Law, the physical units were often not the same in thermodynamic analysis, so that a conversion factor was often needed in quantifying the mechanical equivalence of heat. Work was generally given in units of kilogram meters (kgm), from which in modern terms, the corresponding potential energy would be obtained as the product of the quantity in kilogram meter and the acceleration due to gravity. On the other hand, heat was often quantified in terms of the work-equivalence of heat, whereby 423.55 kgm of work were needed to raise the temperature of 1 kg of water by 1°C [2].

Confusion about the meaning of entropy is not a new problem in thermodynamics [4–6]. A few years after its definition, P.G. Tait suggested a redefinition of the term, such that entropy is the useful part of energy [7], and this was rather initially appealing to Maxwell [8]. Tait seemed to have pursued this line of thought in order to demonstrate that the entropy definition proposed by Clausius had initially been obtained by Thomson in the latter's earlier publications [7,9,10]. The widespread misconception about entropy continued into the 20th century with von Neumann allegedly advising Shannon to adopt the name entropy in his information theory, with the justification that " ... nobody really knows what entropy is, so in a debate, you will always have the advantage" (adapted from [6]).

Clausius' analysis focused on the interaction of a heat engine cycle with heat reservoirs and arrived at the cyclic integral, $\oint \frac{Q}{\tau}$, that equals zero for a reversible cycle. One of the critics of the foundations of Thermodynamics, Truesdell, attacks the rather circular definition of irreversible processes offered by Clausius as those processes which are not reversible [11]. One needs to understand irreversible processes in order understand reversible ones. Truesdell is looking for a mathematical expression for irreversible processes since he condemns thermodynamics as a subject with an unusually high ratio of words to mathematical equations. In modern thermodynamic textbooks, this difficulty is circumvented by defining reversible, internally reversible, and externally or fully reversible processes [12,13]. Uffink, in his criticism of the liberal extrapolation of the Second Law to the concept of the Arrow of Time, points out the problem with the opaque distinction between reversible and irreversible processes [6]. Difficulties in reducing classical thermodynamics to statistical thermodynamics [14–16], seem to also be related to differences in the physical meaning of entropy in these two fields. The need to clarify entropy continues to attract attention with a number of articles devoted to this topic.

Another area where problems arise owing to the current definition of entropy is in metrology, where entropy is used in defining the thermodynamic temperature scale [17]. Recommendations have been made to the international system of units to consider the change of temperature definition from a kelvin to the boltzmann constant, an energy parameter. The argument for this change is that precise temperature measurement based on the kelvin is still dependent on the equilibrium properties of some chosen material, whereas relating temperature to the more uuniversal constant, k_B, will make temperature measurement independent of the material, method of realization, and temperature range. Another area where the need to emphasize energy unit over the kelvin is in quantum metrology, where the authors argue that the necessary conditions of thermodynamic equilibrium and thermal contact are not made, thus making meaningless energy quantification through the kelvin [18,19]. These issues are related to entropy definition in the sense that entropy definition was seen as a basis for the realization of a thermodynamic temperature scale. In the pursuit, the implicit energy unit is lost and absolute temperature is exalted.

In its historical context, entropy is wedded to the concepts of heat engines and cold machines. It is also more important today than ever to clarify the physical meaning of this important property, since thermodynamics is increasingly used in the analysis of a wide range of problems that are very remote from heat engines, such as biological processes and quantum systems.

In this work, we offer a modified definition of entropy aimed at making clearer the physical meaning of this concept. We suggest that heat transfer between two systems initially at different temperatures is a better physical model for entropy explanation than the usual heat engines. From this perspective, entropy is therefore closely related to non-equilibrium thermodynamics: We start with two system at equilibrium but such that their temperatures are different; their interaction leads to the flow of heat down the temperature gradient. This, together with the heat sign convention, leads to the principle of entropy increase that is associated with the interaction of two systems initially at different temperatures. Alternatively the entropy increase principle is associated with the evolution of an isolated system from a prepared non-equilibrium state towards a new equilibrium state. We also show that further modification of the suggested entropy definition makes it possible to arrive at the proposition of the Third Law or Nernst Theorem, without the need for a separate law. The Third Law relates to the entropy difference associated with two temperatures close to zero. The actual value at absolute zero can be set by convention, similar to internal energy or enthalpy values at absolute zero.

We start by restating the definition of entropy and the related heat engine analysis. We then discuss some of the conceptual difficulties arising from this definition, especially in relation to entropy definition in statistical thermodynamics. This is followed by a presentation of our modification. We further assess the use of this modified definition in the analysis of model processes. We then discuss how the modified version of entropy aligns with statistical thermodynamics entropy and the Third Law.

2. Clausius approach to entropy definition

The kinetic theory, thermodynamic process relations, and the First Law were well established before Clausius's work on entropy.

The ideal gas provided a link between macroscopic and microscopic thermodynamics.

$$p = \frac{2}{3}\frac{N}{V}\left[\frac{1}{2}m\bar{v}^2\right] \tag{1}$$

$$p = \frac{NkT}{V} \tag{2}$$

$$\text{with } T = \frac{2}{3}\frac{\left[\frac{1}{2}m\bar{v}^2\right]}{k} \tag{3}$$

One could define $\epsilon = kT = 1/3m\bar{v}^2$ as an energy variable to obtain a gas law $p = \frac{N}{V}\epsilon$. More will be said about $\epsilon = kT$ later.

For an adiabatic process between two states 1 and 2, if constant specific heats and ideal gas behavior are assumed, then two of the three state variables, pressure, temperature, and specific volume may be related as:

$$pv^\gamma = const. \tag{4}$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^\gamma \tag{5}$$

The efficiency of a heat engine is generally given as

$$\eta = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} \tag{6}$$

For a four-process heat engine cycle with 2 adiabatic processes, heat is added during one process and rejected in a fourth. The heat exchange can be determined from the First Law, which for closed systems takes the form:

$$dU = \delta Q + \delta W = \delta Q - pdV \tag{7}$$

where U is the internal energy, δQ is the heat added, δW is work added, so that the internal energy of the system can increase on account of heat and/or work addition. For an ideal gas, internal energy is a function of temperature only and $dU = \frac{\partial U}{\partial T}dT = Nc_v(T)dT$ so that for an adiabatic process

$$Nc_v(T)dT = -pdV \; or \; c_v(T)dT = -pdv = -nkTdv \tag{8}$$

Isothermal heat exchange therefore implies that the internal energy stays constant and

$$\int \delta Q = \int pdV \tag{9}$$

For an isothermal process in which intermediate states can be assumed to be in quasi-equilibrium, pressure and volume are related as

$$pV = const \tag{10}$$

One can make use of the ideal gas law to express p in terms of v and T

$$pV = NkT = N\epsilon \tag{11}$$

The efficiency results

$$\eta = 1 - \frac{T_L}{T_H} \tag{12}$$

The point here is to emphasize that the true expression for the thermal efficiency, without simplifications, would be

$$\eta = 1 - \frac{NkT_L}{NkT_H} \tag{13}$$

And with our intensive energy variable, $\epsilon = kT$, this takes the form

$$\eta = 1 - \frac{\epsilon_L}{\epsilon_H} \tag{14}$$

Tait's contention that Clausius' entropy definition was a restatement of results previously obtained by Joule and Thomson seems to rest on the 1854 paper in which Joule and Thomson sum up their quest for an absolute temperature as "If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperatures of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of operations" [20,21]. This is equivalent to saying that $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$.

Clausius' path to entropy definition starts from the Carnot cycle and seems to be prompted by the fact that heat and work are interchangeable but don't have a common unit.

Transformations of work to heat and vice versa are such that the following relation holds,

$$W = Q \times f(T) \tag{15}$$

The equivalence value of the transformation of heat to work (Äquivalenzwert der Umwandlung von Wärme in die mechanische Arbeit) can be determined

$$N = \frac{Q}{\tau} \tag{16}$$

For a series of reversible heat engines in contact with many reservoirs, the equivalence value of all transformations can be determined from

$$N = -\sum \frac{\delta Q}{\tau} \tag{17}$$

For a very large number of reversible heat engines, the summation can be replaced by integration

$$N = -\int_1^n \frac{\delta Q}{\tau} \tag{18}$$

The term entropy is then introduced such that its differential corresponds the transformation

$$dS = \frac{\delta Q}{\tau} \tag{19}$$

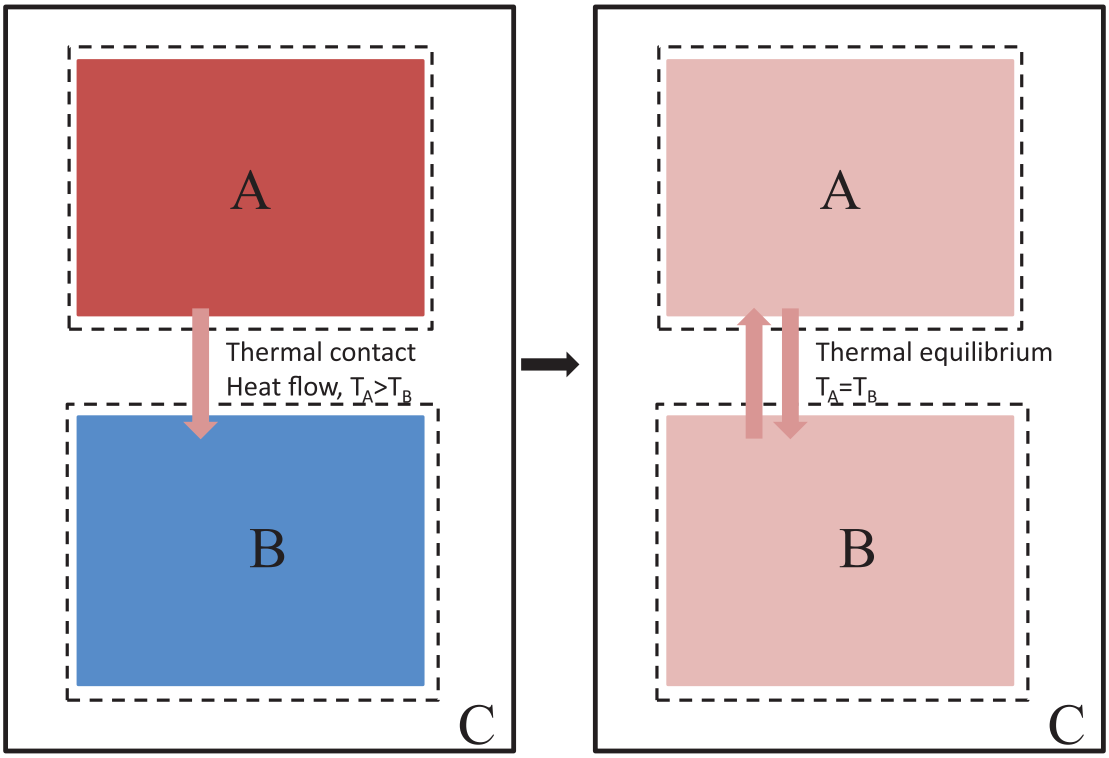
Clausius then seeks a suitable form for the function $f(T)$ and τ, with $f(T) = 1/\tau$. Drawing from previous derivation of the thermal efficiency of a Carnot heat engine using an ideal gas with constant specific heat, the equality $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$, is used to suggest that $\tau = T$. However, Clausius recognizes the potential for disagreement on this choice, given that the ideal gas uses many assumptions and a number of temperature functions could equally be acceptable [3].

One weakness with Clausius treatment is the focus on the reversible heat engine. It is often presented as the special feature of carnot heat engines that the efficiency does not depend on material properties. However, it can be shown that for heat engine cycles with two adiabats and heat addition at constant volume, temperature, or pressure, the thermal efficiency is $\eta = 1 - \frac{T_1}{T_2}$, where T_1 is the temperature at which the working medium loses contact with the heat sink and T_2 is the temperature at which the working medium establishes contact with the heat source. It happens that in the case of the Carnot heat engine, T_1 and T_2 are the minimum and maximum temperatures of the cycle. Analyzed without explicit focus on entropy changes of the reservoir, all these heat engines have no net entropy generation. The point here is that focusing on the cycles, and not the heat reservoirs or the walls of the engines, obscures the physical origin of entropy generation.

In theoretical analysis of heat engines, no attention is paid to the walls of the device but they tend to be sources of entropy generation through friction. It is therefore difficult to transfer analysis of heat engines to thermodynamic systems that are not concerned with work and heat interconversion. Heat transfer is a more appropriate model to illustrate the ideal that entropy generation is associated with the invigoration of microscopic motion.

1. We start with a simple heat transfer problem. Two systems, 1 and 2, are separately in thermal equilibrium but not in thermal equilibrium with each other, that is $T_1 \neq T_2$.

Figure 1. Heat transfer model: Non-equilibrium interaction of hitherto equilibrium systems, A and B, until both attain a new thermal equilibrium state. The entropy increase principle can only be invoked from the perspective of the *universe*, C.



2. We allow the systems to interact and seek a parameter whose sign will unambiguously indicate the natural tendency of heat to flow from hot to cold. In the conceptual language of Clausius, we consider the one losing heat to be transforming heat to mechanical work and the one gaining heat to transforming work to heat. That is microscopically, heat going to work is reducing chaos or randomness in motion to macroscopically ordered motion observable to us as work; conversely, work going to heat is transforming macroscopically ordered motion to random microscopic motion that is unavailable to directional motion.
3. A fundamental indicator of the natural tendency of this transformation is the specific entropy change. It is preferable that it takes the form of a non-dimensional energy parameter.

$$ds = \frac{\delta q}{kT} \tag{20}$$

where s is the specific entropy, q is the amount of heat added per unit particle of the system, k is the Boltzmann constant and T is the temperature. The convention is such that for heat added δq is positive, hence s increases.

We can introduce a microscopic energy variable, $\epsilon = kT$, termed the intensive energy of the system, with units of joule per particle. Alternatively, a derived unit named after Clausius can be adopted. This microscopic energy is basically the average kinetic energy of the particle without the 1/3 factor that accounts for the three translational degrees of freedom.

$$ds = \frac{\delta q}{\epsilon} \tag{21}$$

It is recognized that the designation of ϵ as intensive energy potentially conflicts with our current use of the term *specific internal energy*. This modification does not change existing thermodynamic relations but units are more aligned to highlight a physical meaning. The fundamental thermodynamic potential becomes $du = \epsilon ds + \Sigma F_i dx_i$ in specific terms and $dU = \epsilon dS + \Sigma F_i dX_i$ in units of energy, where $dS = Nds$.

4. In order to determine the sign of entropy associated with natural heat transfer from hot to colod, we consider heat transfer from hot body 1 to colder body 2. For simplicity, let both have same mass, m, and the same specific heat at constant volume, c_v. Let's further assume that no volume-change work occurs, so that all heat transfer results in changes in the internal energy of each system and $\delta q = du = c_v dT = c_v/k d\epsilon$. The final temperature, hence final intensive energy, attained by the two body can be determined from:

$$\int_{T_1}^{T_f} dU_1 + \int_{T_2}^{T_f} dU_2 = 0 \tag{22}$$

$$\int_{T_1}^{T_f} mc_v dT + \int_{T_2}^{T_f} mc_v dT = 0 \tag{23}$$

$$T_f = \frac{1}{2}\left(T_1 + T_2\right) \tag{24}$$

$$\text{so that}\, \epsilon_f = \frac{1}{2}\left(\epsilon_1 + \epsilon_2\right)\ \text{where}\, \epsilon = kT \tag{25}$$

We note here that $\epsilon_2 < \epsilon_f < \epsilon_1$ or $T_2 < T_f < T_1$, correspondingly.

The specific entropy change, Δs, associated with this heat transfer process can be determined from:

$$\int ds = \int_{\epsilon_1}^{\epsilon_f} ds_1 + \int_{\epsilon_2}^{\epsilon_f} ds_2 \tag{26}$$

$$\Delta s = \int_{\epsilon_1}^{\epsilon_f} \frac{\delta q}{\epsilon} + \int_{\epsilon_2}^{\epsilon_f} \frac{\delta q}{\epsilon} \tag{27}$$

$$\Delta s = \frac{c_v}{k} \int_{\epsilon_1}^{\epsilon_f} \frac{d\epsilon}{\epsilon} + \frac{c_v}{k} \int_{\epsilon_2}^{\epsilon_f} \frac{d\epsilon}{\epsilon} \tag{28}$$

$$\Delta s = \frac{c_v}{k} \ln\left(\frac{\epsilon_f}{\epsilon_1}\right) + \frac{c_v}{k} \ln\left(\frac{\epsilon_f}{\epsilon_2}\right) = \frac{c_v}{k} \ln\left(\frac{\epsilon_f^2}{\epsilon_1 \epsilon_2}\right) = \frac{c_v}{k} \ln\left(\frac{(\epsilon_1 + \epsilon_2)^2}{4\epsilon_1 \epsilon_2}\right) \tag{29}$$

The last expression in eqn. 30 can be rewritten as

$$\Delta s = \frac{c_v}{k} \ln\left(\frac{(\epsilon_1 - \epsilon_2)^2 + 4\epsilon_1 \epsilon_2}{4\epsilon_1 \epsilon_2}\right) \geq 0 \tag{30}$$

That is, two systems initially at different temperatures, such that 1 is hotter than 2, if allowed to interact by heat exchange will reach a new equilibrium state with a temperature intermediate between the initial body temperatures. The associated entropy change is always positive and the process is that of the non-equilibrium interaction of systems formerly in thermal equilibrium and seeking a new thermal equilibrium state. The heat transfer problem considered above imposed a direction by requiring that both systems achieve an equilibrium temperature; thus heat flows from the hotter to the colder until thermal equilibrium is attained. We found that this natural process is associated with an increase in entropy. Suppose we have two bodies, 1 and 2, of equal mass and heat capacity; but we are not told which of them is hotter, we seek to establish the condition that has to be fulfilled for the associated entropy change to be positive as they interact, going from states 1 to 1' and from 2 to 2'. Assuming that T_1 decreases by ΔT, then by virtue of energy conservation, T_2 increases by ΔT. Similarly, $\epsilon_1' = \epsilon_1 - \Delta\epsilon$ and $\epsilon_2' = \epsilon_2 + \Delta\epsilon$.

$$\Delta s = \frac{c_v}{k} \ln\left(\frac{\epsilon_1'}{\epsilon_1}\right) + \frac{c_v}{k} \ln\left(\frac{\epsilon_2'}{\epsilon_2}\right) \tag{31}$$

$$\Delta s = \frac{c_v}{k} \ln\left(\frac{\epsilon_1 - \Delta\epsilon}{\epsilon_1}\right) + \frac{c_v}{k} \ln\left(\frac{\epsilon_2 + \Delta\epsilon}{\epsilon_2}\right) \tag{32}$$

$$\Delta s = \frac{c_v}{k} \left[\ln\left(\frac{\epsilon_1 - \Delta\epsilon}{\epsilon_1}\right) + \ln\left(\frac{\epsilon_2 + \Delta\epsilon}{\epsilon_2}\right)\right] = \frac{c_v}{k} \left[\ln\left(\frac{\epsilon_1 - \Delta\epsilon}{\epsilon_1}\right)\left(\frac{\epsilon_2 + \Delta\epsilon}{\epsilon_2}\right)\right] \tag{33}$$

$$\Delta s = \frac{c_v}{k} \left[\ln\left(1 + \frac{\Delta\epsilon}{\epsilon_2} - \frac{\Delta\epsilon}{\epsilon_1} - \frac{(\Delta\epsilon)^2}{\epsilon_1 \epsilon_2}\right)\right] = \frac{c_v}{k} \left[\ln\left(1 + \frac{\epsilon_1 - \epsilon_2 - \Delta\epsilon}{\epsilon_1 \epsilon_2} \Delta\epsilon\right)\right] \tag{34}$$

From eqn. 34, two observations can be made. For natural heat transfer, that is, $\Delta s \geq 0$, it is necessary that $\epsilon_1 > \epsilon_2$, bearing in mind that it was assumed that body 1 transfers heat to body 2. If $\epsilon_1 - \epsilon_2 = \Delta\epsilon$, we are dealing with fluctuations around thermal equilibrium, so that $\Delta s = 0$.

2.1. The Third Law of thermodynamics

The Third Law of thermodynamics states that the change in entropy between two states approaches zero as both states approach the absolute zero temperature. However, in statistical thermodynamics entropy is evaluated at a given state. The question arises whether in this instance, statistical thermodynamics recovers the result of classical thermodynamics.

The Third Law, otherwise known as Nernst theorem grew out of investigations at low temperatures and the recognition that specific heats tend to zero as the absolute zero temperature is approached. The fact that the entropy change between two states close to absolute zero is zero does not arise directly from the current entropy definition. But we can explore whether it is possible to arrive at this result if we adopt the temperature function in Clausius equation, $f(\tau)$, to be $f(\tau) = \epsilon + \epsilon_0$, where ϵ_0 is microscopic or intensive energy at absolute zero for a given substance. If ϵ_0 is small but non-zero, this definition can render the Third Law of Thermodynamics (Nernst Theorem) unnecessary. That is, it follows that specific entropy differences tend to zero as $T \rightarrow 0K$. Assuming that we are cooling from ϵ_1 to ϵ_2, so that $(\epsilon_2 + \epsilon_0)$<$(\epsilon_1 + \epsilon_0)$ and $\epsilon_1 << \epsilon_0$

$$\Delta S = \int_{\epsilon_1}^{\epsilon_2} \frac{\delta Q}{\epsilon + \epsilon_0} \tag{35}$$

$$\Delta S = \int_{\epsilon_1}^{\epsilon_2} \frac{c_v/k d\epsilon}{\epsilon + \epsilon_0} \tag{36}$$

$$\Delta S = \frac{c_v}{k}\ln\left(\frac{\epsilon_2 + \epsilon_0}{\epsilon_1 + \epsilon_0}\right) \approx \frac{c_v}{k}\ln\left(\frac{\epsilon_0}{\epsilon_1 + \epsilon_0}\right) = 0 \tag{37}$$

$$\lim_{\epsilon_1,\epsilon_2 \rightarrow 0}(\Delta S) = \frac{c_v}{k}\ln\left(\frac{\epsilon_0}{\epsilon_1 + \epsilon_0}\right) = 0 \tag{38}$$

where we have assumed that $\epsilon_1 << \epsilon_0$ in the last equation. This does not eliminate the need to define an entropy value at absolute zero. The question is whether a law is needed for this, seeing that such definitions are used for enthalpies, internal energy, and other energies.

2.2. Connection to entropy in statistical mechanics

In his approach as presented in [22] (pp. 33 and 44 of 2014 Dover republication), Gibbs seeks a canonical distribution in phase, with the requirement that its probability be single-valued and for each phase it should neither be negative nor imaginary

$$\int_{phases}^{all} ... \int P dp_1 ... dq_n = 1 \tag{39}$$

The options, $P = const \times \epsilon$ and $P = const$, are considered impossible while the Boltzmann factor is taken as the simplest conceivable case that meets all requirement:

$$P = e^{\eta}; \text{ with } \eta = \frac{\psi - \epsilon}{\theta} \tag{40}$$

where η is the average probability index, ψ is a constant corresponding to the energy for which the probability is unity, and θ is called the modulus. The modulus is considered to play the role of temperature in classical thermodynamics. The subject is further developed to arrive at the differential of the average energy:

$$d\bar{\epsilon} = -\theta d\eta - \Sigma(A_i d\alpha_i) \tag{41}$$

which is then compared to the differential form of the Second Law, after ignoring the negative signs arising from the definition η:

$$d\epsilon = Td\eta + \Sigma(A_i d\alpha_i) \tag{42}$$

In this presentation, the average probability index, taken with its negative sign, is thought to correspond to entropy in classical thermodynamics. There are clearly conceptual issues with this approach that can be clarified by philosophers of physics but a striking point here is the difference in the dimensions of T and θ; the former being temperature and the latter, energy per unit of matter. One of the challenges in statistical mechanics is the axiomatic acceptance of prior results established in classical thermodynamics. The proposed modification would identify Gibbs modulus θ as analogous to $\epsilon = kT$, instead of T.

Entropy enters the statistical mechanics of Boltzmann through H-theorem. H is the sum of all values of the logarithm of the distribution function f corresponding to designated molecules in a volume element $d\omega$:

$$H = \int f ln f d\omega \tag{43}$$

$$S = -H = -\int f ln f d\omega \tag{44}$$

$$\text{alternatively } S = const.logW \tag{45}$$

$$W \propto f \tag{46}$$

Mathematically, H is the first moment of $logf$. Increase in H denotes an increase in mean $logf$ hence the notion that a system tends to the most probable state. The constant in eqn. 45 was introduced by Planck and named after Boltzmann. It has units in order to be consistent with classical thermodynamics. Since the modified entropy definition present specific entropy as a non-dimensional energy variable, the constant in eqn. 45 becomes unity and one interprets the increase in the number of ways upon addition of heat to the microcanonical ensemble to be similar to present notion of invigorating and increasing the average microscopic energy variable, ϵ.

3. Conclusions

This work contributes to improved understanding of entropy in classical thermodynamics by suggesting a modification to the central argument from which arises the entropy definition by Clausius. The proposed modification points to the fact that heat transferred to or from a system affects the internal energy of the system which is a macroscopic representation of the microscopic motion. It is also recognized that some residual energy is possible at absolute zero which is not properly represented by temperature. As the temperature approaches absolute zero, the entropy change between two states at low temperatures approach zero, in line with the Third Law of thermodynamics. It is shown that the modified definition of entropy preserves the entropy increases principle and direction of entropy change for heat transfer problems.

Acknowledgements

Support is acknowledged from the Syracuse University College of Engineering and Computer Science.

Author Contributions

The research problem is conceived, carried out, and reported by the author with appropriate acknowledgment of literature resources.

Conflicts of Interest

The author declares no conflict of interest. .

References

1. Clausius, R. Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie. *Annalen der Physik* **1865**, *201*, 353–400.
2. Clausius, R. *The mechanical theory of heat*; Macmillan and Company, 1879.
3. Clausius, R. Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie. *Annalen der Physik* **1854**, *169*, 481–506.
4. Wehrl, A. General properties of entropy. *Reviews of Modern Physics* **1978**, *50*, 221.
5. Wehrl, A. The many facets of entropy. *Reports on Mathematical Physics* **1991**, *30*, 119 – 129.
6. Uffink, J. Bluff your way in the second law of thermodynamics. *Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics* **2001**, *32*, 305–394.
7. Tait, P.G. *Sketch of thermodynamics*; D. Douglas, 1877.
8. Maxwell, J.C. *Theory of heat*; Longmans, Green and Co., London and New York, 1888.
9. Thomson, W. IX. On the Dynamical Theory of Heat. Part V. Thermo-electric Currents. *Transactions of the Royal Society of Edinburgh* **1857**, *21*, 123–171.
10. Thomson, W. 2. On a Universal Tendency in Nature to the Dissipation of Mechanical Energy. *Proceedings of the Royal Society of Edinburgh* **1857**, *3*, 139–142.
11. Truesdell, C.A. *The tragicomical history of thermodynamics, 1822-1854*; Springer New York, 1980.
12. YA, C.; Boles, M. Thermodynamics: An Engineering Approach, 2008.
13. Moran, M.J.; Shapiro, H.N.; Boettner, D.D.; Bailey, M.B. *Fundamentals of engineering thermodynamics*; John Wiley & Sons, 2010.
14. Sklar, L. The reduction (?) of thermodynamics to statistical mechanics. *Philosophical Studies* **1999**, *95*, 187–202.
15. Callender, C. Reducing thermodynamics to statistical mechanics: the case of entropy. *The Journal of Philosophy* **1999**, pp. 348–373.
16. Callender, C. Taking Thermodynamics Too Seriously. *Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics* **2001**, *32*, 539 – 553. The Conceptual Foundations of Statistical Physics.

17. Fischer, J.; Gerasimov, S.; Hill, K.; Machin, G.; Moldover, M.; Pitre, L.; Steur, P.; Stock, M.; Tamura, O.; Ugur, H.; others. Report to the CIPM on the implications of changing the definition of the base unit kelvin, 2007.
18. Nawrocki, W. Revising the SI: the joule to replace the kelvin as a base unit. *Metrology and Measurement Systems* **2006**, *13*, 171–181.
19. Nawrocki, W. The Quantum SI-Towards the New Systems of Units. *Metrology and Measurement Systems* **2010**, *17*, 139–150.
20. Joule, J.P.; Thomson, W. On the Thermal Effects of Fluids in Motion. Part II. *Philosophical Transactions of the Royal Society of London* **1854**, *144*, 321–364.
21. Chang, H. *Inventing temperature: Measurement and scientific progress*; Oxford University Press, 2004.
22. Gibbs, J.W. Elementary Principles in Statistical Mechanics (Scribner. *New York* **1902**.