QUESTIONS RE THE CONCEPT OF ENTROPY.

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Key Words: entropy, thermodynamics, statistical mechanics, information theory, statistics.

Abstract.

The whole idea of entropy has caused, and continues to cause, problems of real understanding for all but especially for students. Here it is hoped to highlight some, but inevitably not all, of those problems and to provoke thought among interested parties towards producing clear and accurate solutions.

Introduction.

What is entropy? Surely this is one of the most common questions raised, especially by students meeting the concept for the first time but also one pondered extensively by many academics. Again, the associated question of to which entropy is reference being made arises also; is it thermodynamic entropy or statistical mechanical entropy, or information theory entropy or simply the entropy in statistics or are they all basically the same concept occurring in several seemingly different areas? Hence, there are so many questions surrounding this entity, it's little wonder it causes so many problems for so many, but especially students. The intention here is to try to highlight some of the many issues surrounding this problem which it seems is a potentially major one for science. Inevitably some issues regarded by several will be omitted, not because they're unimportant but because there are so many issues and so many different views. The hope is that drawing at least some of these problems into the public domain will provoke more to examine them and, hopefully, stimulate progress in achieving a better, clearer understanding of all the underlying issues.

For many these days the first port of call when requiring a piece of information is the internet and, when the search is for the history of the word *Entropy* the following is the entry for Wikipedia[1]:

"Entropy is a scientific concept, most commonly associated with states of disorder, randomness, or uncertainty. The term and the concept are used in diverse fields, from classical thermodynamics, where it was first recognized, to the microscopic description of nature in statistical physics, and to the principles of information theory. It has found far-ranging applications in chemistry and physics, in biological systems and their relation to life, in cosmology, economics, and information systems including the transmission of information in telecommunication.

Entropy is central to the second law of thermodynamics, which states that the entropy of an isolated system left to spontaneous evolution cannot decrease with time. As a result, isolated systems evolve toward thermodynamic equilibrium, where the entropy is highest. A consequence of the second law of thermodynamics is that certain processes are irreversible.

The thermodynamic concept was referred to by Scottish scientist and engineer William Rankine in 1850 with the names *thermodynamic function* and *heat-potential*. In 1865, German physicist Rudolf Clausius, one of the leading founders of the field of thermodynamics, defined it as the quotient of an infinitesimal amount of heat to the instantaneous temperature. He initially described it as *transformation-content*, in German *Verwandlungsinhalt*, and later coined the term *entropy* from a Greek word for *transformation*.

Austrian physicist Ludwig Boltzmann explained entropy as the measure of the number of possible microscopic arrangements or states of individual atoms and molecules of a system that comply with the macroscopic condition of the system. He thereby introduced the concept of statistical disorder and probability distributions into a new field of thermodynamics, called statistical mechanics, and found the link between the microscopic interactions, which fluctuate about an average configuration, to the macroscopically observable behaviour, in form of a simple logarithmic law, with a proportionality constant, the Boltzmann constant, which has become one of the defining universal constants for the modern International System of Units."

Undoubtedly, much that is contained in this extract is accepted as true but initially one must look carefully at all the content of the above and ask if it all truly accurate. This should lead immediately to a detailed examination of the origins of this problematical concept.

The Second Law and Entropy.

From the outset, it should be remembered that the founding fathers of thermodynamics were closely involved with the working of heat engines. The only place in the early development where cycles were not involved was in the observations of Rumford. Apart from that, people like Carnot derived their inspiration from the practical work of men like Watt and Trevithick who were concerned with improving the efficiency of heat engines for use in, amongst other places, the Cornish tin mines. Some of Carnot's inspiration came from a desire to help the French catch up with the British in this area of production of heat engines. Hence, cycles were a vitally important part of the beginnings of thermodynamics and the people who pushed it forward and began to give the topic a firm theoretical foundation – Lord Kelvin (William Thomson), Tait, Clausius – based their work on engines working in cycles. It should be noted that the two modern versions of the famous statements of the Second Law, that due to Kelvin :

It is impossible to transform an amount of heat completely into work in a cyclic process in the absence of other effects

and that due to Clausius:

It is impossible for heat to be transferred by a cyclic process from a body to one warmer than itself in the absence of other effects,

both stress the notion of cyclic processes as well as the absence of effects other than those specifically mentioned.

These are the forms of the Second Law used at the birth of thermodynamics as a subject in its own right and were deduced from experiment and observation with many of the ideas originating in engineering. It should be realized what an astounding achievement it was to establish so many highly abstract concepts via this approach based on such practical notions. However, this basis worried Max Born [2] to the extent that he discussed it with a mathematical colleague, Constantin Carathéodory and he, in turn, produced a more mathematical approach to the issue. The mathematical complexities of his approach meant that his work passed largely unnoticed until the work of such as Buchdahl, Landsberg, Turner and Zemansky made it far more accessible to scientists in general. Possibly the breakthrough article was a short letter by Landsberg [3] which allowed the above statement of the Second Law by Kelvin to be used alongside Carathéodory's more mathematical techniques. In classical thermodynamics, mathematically, any infinitesimal quantity of heat added to, or taken from, a system is denoted by an inexact differential, $d'Q$, but, using Carathéodory's methods, it may be shown that the Second Law shows that this inexact differential has an integrating factor which is the inverse of the absolute temperature. In other words, the Second Law of Thermodynamics implies that

$$dS = d'Q/T \qquad \text{(i)}$$

where dS represents a total differential but it is this which, in classical thermodynamics, is termed the change in what Clausius [4] originally called the *entropy*. Hence, crucially only changes in entropy are deduced and this change in entropy is quite specifically seen to be equal to a change in heat (either positive or negative) divided by the absolute temperature at which that change occurs. It is also vitally important to note that the derivation of the above relationship is totally dependent on the use of so-called quasistatic processes; that is, on idealised processes during which the system under consideration passes only through equilibrium states or, in other words, processes which consist exclusively of sequences of thermodynamics equilibrium states. Such processes do not occur in nature since a change from one equilibrium state to another is caused usually by outside interference with an existing equilibrium state. However, that interference may be made small so that the change from one equilibrium state to another may occur very slowly. It is in this way that approximations to quasistatic processes may be made in actual experiments. Processes which are not quasistatic are termed non-static [5]. It is important also to note that, as Lavenda [6] has put it so eloquently, one of Carathéodory's major achievements was 'the definition and proof of existence of the entropy solely in terms of mechanical variables such as pressure and volume'. Nevertheless, it must be remembered always that it is only *changes* in this function termed entropy that are defined, not the actual function itself. Hence, this might be seen to indicate some room for manoeuvre in the precise definition of entropy even in classical thermodynamics.

It is vitally important, as with any scientific theory, to note the assumptions made in deriving any theoretical result. In this case, as has been pointed out already, a crucial assumption here is the existence of the idealized idea of quasistatic processes and it is for that reason that care has been taken to highlight this and mention how such processes may be approximated to in actual experiments. Often, seemingly trivial mathematical assumptions are inadvertently forgotten or ignored and this can, and does, lead future mistakes [7]. It is also important to emphasize that all the above derivation does – even when followed through in detail [5] – is explain that, in classical thermodynamics, entropy is a quantity whose change equals a change in heat divided by the absolute temperature at which that change occurs and that is *all* it says in answer to the question 'What is entropy?

All the above is achieved via the use of quasistatic processes. The extension to cover non-static processes involves realizing that the methods introduced by Carathéodory result in the thermodynamic phase space being split up into level surfaces each of constant entropy. Hence, within each such surface, individual points may be connected by quasistatic (that is, reversible) adiabatic processes. This is not the case for points in different level surfaces. Points in different level surfaces may be connected by adiabatic processes but, if so, that process cannot be quasistatic; if the connection is quasistatic then it cannot be adiabatic. As has been shown previously [5], this leads to the conclusion that the entropy of a system in a given state cannot be decreased adiabatically for a thermodynamics in which the absolute temperature is positive and heat tends to flow from high to low absolute temperatures. This is just a statement of the principle of the increase of entropy of systems in adiabatic enclosures.

The usual argument then proceeds along the following lines – it is assumed that an increment of heat is transferred to a system by a more general process which is neither necessarily quasistatic nor adiabatic and it is said that the relation

$$TdS = d'Q$$

is replaced by the inequality

$$TdS \geq d'Q$$

where the inequality sign holds if the process is quasistatic. This basic inequality holds for any system undergoing any infinitesimal process provided the system does not exchange mass with its surroundings – that is, it is a closed system.

This extension of the basic result derived directly from the Second Law is accepted quite widely and has proved useful and seemingly correct in many applications. However, once again, care must be taken to note any extra assumptions made in its derivation. It must be wondered if the original definition of entropy may be extended to cover this generalization and also is it valid to generalize the result derived for adiabatic enclosures to far more general interactions? All of this may well be completely valid but, yet again, important issues are apparently glossed over and this can easily lead to confusion for both students and experienced academics alike. This whole problem, especially questions over a rigorous definition of entropy, readily spills over into irreversible thermodynamics.

Irreversible thermodynamics.

This extension of ideas to incorporate non-static processes indicates an introduction to the field of irreversible, or non-equilibrium, thermodynamics. This is an area which first appeared to be progressing usefully with the introduction of Onsager's reciprocal relations [8]. These produced a great flurry of activity with major contributions from de Groot [9] and Meixner [10[amongst others. However, there were other approaches advocated at the same time and these are all discussed carefully and extensively by Lavenda [6] whose analysis of the overall situation should be consulted. Slightly more recently though yet another approach to this area has been proposed by, amongst others, Jou, Casa-Vazquez and Lebon [11]. From the point of view of the basic topic under consideration here though, what all these approaches seem to have in common is a starting point of assuming the existence of an entropy function together with assumed properties for that function. It does appear that the entropy function is not defined specifically in these extensions of classical thermodynamics. Furthermore, later in life one of the originators of all this work, Meixner, expressed severe doubts of the existence of entropy in irreversible situations [12]. This situation raises a number of immediate questions surrounding the whole concept of entropy outside classical thermodynamics and all are seemingly quietly forgotten or ignored but would appear to be linked to the overall question of ‘What is entropy?’

Statistical Thermodynamics.

It might be remembered that, in the usual approaches to classical thermodynamics, the First Law which states that Energy is conserved when heat is taken into account, is often represented by the mathematical equation

$$d'Q = dU - d'W$$

where the three terms represent changes in heat, internal energy and work respectively. $d'Q$ and $d'W$ are not differentials of functions of state and the dashes indicate this and the fact that, mathematically, the first and third terms are inexact differentials.

It should be noted that the equation representing the combined form of the First and Second Laws is then:

$$TdS = dU - d'W.$$

Again, if the work done in compressing a fluid is being considered, this equation takes on the familiar form:

$$TdS = dU + pdV,$$

where p and V represent the pressure and volume as usual. Note though that this is not the general form of the equation representing the combined First and Second Laws; it refers to a quite specific set of circumstances.

If attention is restricted to systems for which the entropy is an extensive variable then the discussion is easily extended[2] to open systems and again considering the special case of compression of a fluid, this latter equation becomes

$$TdS = dU + pdV - \mu dN \qquad \text{(ii)}$$

where μ and N represent the chemical potential and number of particles respectively.

In statistical thermodynamics, there are various approaches to introducing the topic but all seem to rely on equation (ii) above to secure a link with the quantities of importance in classical thermodynamics. Hill [13[devotes an entire section to the association of thermodynamic variables with quantities of statistical mechanics. His approach is to consider the various ensembles separately, to associate immediately the internal energy of classical thermodynamics with the ensemble average of the internal energy. He then proceeds to evaluate the expression for the total derivative of this ensemble average in terms of the independent variables appropriate for the ensemble under consideration and then to compare the resulting equation with equation (i) above. In this way, he is able to identify the entropy, S, as

$$S = -k \sum plnp \qquad \text{(iii)}$$

where p represents the expression for the probability in the relevant ensemble. For example, this leads as far as the grand canonical ensemble is concerned to the identification

$$\frac{pV}{kT} = ln\Xi ,$$

where Ξ represents the grand partition function and, as usual, p represents the pressure, V the volume, k Boltzmann's constant, and T the absolute temperature. By noting further that, if F is the free energy

$$dF = -SdT - pdV + \mu dN,$$

where, additionally, μ represents the chemical potential and N the number of particles, then, once the expression for the pressure is known, those for the entropy, S, and number of particles, N, eventually follow from

$$S = V\left(\frac{\partial p}{\partial T}\right)_{V,\mu} \quad \text{and} \quad N = V\left(\frac{\partial p}{\partial \mu}\right)_{V,T}.$$

The relevant expression for the internal energy, U, then follows from

$$U = TS - pV + \mu N.$$

Hence, the expressions for all the important functions of classical thermodynamics follow by making use of well-known expressions from classical thermodynamics in what might appear to be a circular argument. However, an example of how this works in practice is provided by at least one examination of the thermodynamic properties of the ideal relativistic quantum gases [14]. Here it is clearly seen how expressions for functions such as the entropy are deduced.

In this approach of Hill, as in others in statistical mechanics/thermodynamics, there is no direct mention of any heat exchange at any point but it seems that, because equation (i) is assumed, success of sorts in linking classical thermodynamics with statistical mechanics/ thermodynamics is assured. In reality though, it seems the entropy of classical thermodynamics is assumed the same as that of statistical mechanics/thermodynamics. However, the nature of the above quoted expression (iii) for the entropy in statistical mechanics/thermodynamics bears no obvious resemblance to that of classical thermodynamics. In classical thermodynamics, as stated already, the entropy is linked irrevocably with the change of heat; here the expression above indicates that the entropy of statistical mechanics/thermodynamics is, first and foremost, linked to an undefined probability distribution. This is why the question of whether or not the two entropies are the same must arise, although Hill provides a good argument for thinking both are the same – no matter which ensemble is considered. However, it would seem to follow that this argument might follow for any distribution, whether it has direct physical significance or not and that is where the problem really arises, especially for students. Any change in thermodynamic entropy is irrevocably linked with a flow of heat. If there is no flow of heat in a system, what, therefore, is the meaning which may be attributed to an entropy function derived purely by manipulations of a statistical distribution?

It might also be noted that, as Richard Norman [15] has pointed out, Mayants [16] also follows the same route as Hill in that he too relies on the established equations of classical thermodynamics top justify the Boltzmann expression for the entropy. On the face of it there is little wrong with this but it is a point which must be acknowledged. He, Norman, also asserts that Mayants has argued/implied that entropy within statistical and classical formulations refer to the same quantity but his arguments contain subjective components and so can not be considered logically necessary. Hence we must distinguish clearly between the two ideas as the argument does not imply logical necessity. These again are comments deserving of careful scrutiny and consideration as a genuine search for meaning of entropy continues.

It should be noted that, although there are only two fundamental categories of thermodynamic theories which are covered by the classical approach outlined in the first section of this article and the statistical or probabilistic approach being discussed briefly here, there are several approaches to this second category. Another is beautifully outlined in the book by Lavenda [17]. Basically he derives all the accepted results via use of Gauss' principle and extensive use of error laws; error laws which are discussed in minute detail in Keynes' book on probability [18]. This rather elegant approach has much to commend it but, yet again, the link between probabilistic average values is made by assuming such – especially the entropy – are identical with the corresponding values in classical thermodynamics. Hence, the query raised in relation to the approach of Hill arises again and does so in all approaches to establishing a theory of statistical mechanics /thermodynamics.

However, it must always be born in mind that statistical mechanics/thermodynamics has proved to be an eminently successful branch of physics over many years. Nevertheless, the question of the actual equivalence of the entropy functions of classical and statistical thermodynamics remains a very real one and is one which should not be dismissed lightly. It is probably true to say, though, that this question has only arisen largely because of the rise in usefulness of information theory in both physics and, indeed, other branches of science such as biology and medicine.

Information Theory.

Possibly the best way to approach the introduction of the notion of entropy in information theory is to consider the way Shannon himself introduces the topic [19]. To do this, consider Shannon's own wording beginning on page 48 of the mentioned book:- he begins by pointing out that, up to that point in his presentation, a discrete information source has been represented by a Markov process. He then poses the question of whether or not it is possible to '*define a quantity which will measure, in some sense, how much information is "produced" by such a process, or better, at what rate information is produced*'.

He continues by considering a set of possible events whose probabilities of occurrence are p_1, $p_2, \ldots, p_n$. These probabilities are all that is known concerning which event will occur. The question than is whether or not a measure of how much "choice" is involved in the selection of the event or of how uncertain the outcome is may be found. If such a measure, say $H(p_1, p_2, \ldots, p_n)$, exists it is claimed that it is reasonable to require the following properties for it:

(i) H should be continuous in the p_i

(ii) If all the p_i are equal, $p_i = 1/n$, them H should be a monotonically increasing function of n.

(iii) If a choice be broken down into two successive choices, the original H should be the weighted sum of the individual values of H.

On the basis of these required properties, it is shown in appendix 2 (pages 116-8) of the quoted book that the only H satisfying these three assumptions is of the form:

$$S = -K \sum_{i=1}^{n} p_i log p_i \qquad \text{(iv)}$$

where K is a positive constant which merely amounts to a choice of a unit of measure. Shannon points out that expressions of this form '*play a central role in information theory as measures of information, choice and uncertainty*'. He also goes on to point out at this very stage in his discussion that 'the form of H will be recognised as that of entropy as defined in certain formulations of statistical mechanics where p_i is the probability of a system being in cell i of its phase space. Of course, in statistical mechanics/ thermodynamics, the constant K is the Boltzmann constant represented by k. Again at this point in his discussion, Shannon proceeds to say that '*we shall call*' expression (iii) above the entropy of the set of probabilities $p_1, \ldots, p_n$. He also says that , if x is a chance variable, we will write $H(x)$ for its entropy; thus x is not an argument of a function but a label for a number, to differentiate it from *H*(*y*) say, the entropy of the chance variable *y*.

It is quite clear from this abbreviated introduction to a basic formula of information theory that its introduction is purely mathematical and does not rely at all on any genuine physical input – certainly nothing remotely connected with notions of classical thermodynamics. Interestingly, the outline of this derivation also serves to emphasise that the same is basically true of the introduction of the entropy concept into statistical mechanics/thermodynamics. Also it seems the introduction of a link between the entropy functions of information theory and classical thermodynamics followed the route outlined in Brillouin's book [20] and that is that it was simply noted that the entropy expressions of information theory and statistical mechanics/thermodynamics had the same mathematical form and so were assumed to be the same. The link with classical thermodynamics then followed via the statistical mechanics link with that subject. However, in both Shannon's and Brillouin's introductions to the subject, the constant appearing, as in (iv) above is just a constant; it is not Boltzmann's constant *k* which appears from the outset in classical thermodynamics and does, of course, possess quite definite units = ergs/degree. Hence, when examining the origins of the three entropy functions, it quickly becomes apparent that as progression occurs from that for classical thermodynamics to statistical mechanics/thermodynamics to information theory, actual physical ideas play a gradually decreasing role and heat only appears in the first of these derivations. It is also important to remember that, in both statistical mechanics/thermodynamics and information theory, the entropy function often appears initially as a purely mathematical function, just as it does in mathematical statistics itself, with little immediate physical interpretation whereas, in classical thermodynamics it is irrevocably linked with heat exchange from the outset.

Again, it might reasonably be noted that, in 1961 [21], Landauer speculated that erasure of information is a dissipative process and, therefore, that a small quantity of heat is necessarily produced when a classical bit of information is deleted. However, in the cited discussion, when Landauer introduces the idea of heat being dissipated, he actually produces little justification for introducing the notion of heat into the discussion. One may only wonder if it arose purely because he assumed the entropies in information theory and classical thermodynamics were the same and, therefore, (i) above must hold in information theory as well. This specific point has been discussed in more detail already [22] and that reference should be consulted for completeness.

The above are all points which must come into consideration when examining the claim, implicit at least in some writings, that the entropy functions of classical thermodynamics, statistical mechanics/ thermodynamics, information theory and indeed in mathematical statistics are identical functions.

Other Reasons for Concern.

As has been noted previously [23], queries surrounding the Second Law of Thermodynamics and entropy have been raised before and have left some unanswered questions but it seems there are also some problems in areas such as biochemistry. A well known and oft used book on this subject is that by D, Voet, J. G. Voet & C. W. Pratt [24]. In this book – frequently used by undergraduate students - the Second Law of Thermodynamics is taken to be 'Entropy Tends to Increase' but it also claims that, according to this law, spontaneous processes are characterised by the conversion of order into disorder. Obviously, this has no obvious direct link with the basic ideas associated with the Second Law and entropy as rigorously derived in classical thermodynamics. Furthermore, it appears to claim that entropy given by the formula $S = k\log W$ so everything would appear to be based on Boltzmann's expression and so seems to be going on results in statistical mechanics/thermodynamics rather than Classical Thermodynamics and the original forma of the Second Law. Note also that there is no mention of limitations go with the statement 'Entropy Tends to Increase'! The results quoted obviously do not disagree with observation but the way the material is presented can lead to puzzlement and muddled understanding. However, it is also stated that 'In chemical and biological systems it is impractical, if not impossible, to determine the entropy of a system by counting all the equivalent arrangements of its components (W). However, there is an entirely equivalent expression for entropy that applies to the constant temperature conditions typical of biological systems; for a spontaneous process $\Delta S = q/T$. Thus, the entropy change in a process can be experimentally determined from measurements of heat.' The first question is 'What is q here?' Surely the reference should be a change of heat? Also, this so-called equivalent expression for a change in entropy actually refers to the original one from Classical Thermodynamics but are the two definitely the same? However, this use of the Second Law where change of entropy is definitely linked to a change in heat is correct; it's the link up with order/disorder and statistical ideas that causes problems. These link-ups may well be correct but is there a rigorous proof of that? This is the big question and is surely linked with the question first raised of 'What is Entropy?' Yet again though, this unintentionally careless wording can, and does, lead to confusion – this time specifically to students. It is yet another illustration of a topic which has caused confusion to many over the years and continues to do so. Negative energy is

Again, as pointed out by Richard Norman [15], it should be remembered that the basic physical component maintaining particulate stability, known as binding energy within modern physics, is represented by a negative quantity and so must be attributable to negative energy [26]. However, the concept of negative energy is not recognised in modern physics. This is yet another point to bear in mind when considering the equality, or otherwise, of the various concepts of entropy; contact with what is known about real physical systems must be maintained.

Conclusion.

In a very real sense there can be no conclusion written here to the above thoughts and speculations because what has been written actually poses a serious question which is still, after many years of its existence, awaiting a complete and clear answer; that question is 'What is entropy?'

Before continuing, it should be remembered that entropy has also been regarded in some circumstances as a measure of order or disorder in a system. This also poses questions concerning the meaning of entropy. Much of the confusion seems to have arisen because, following the introduction of the concept in classical thermodynamics, other meanings have been put forward, seemingly without serious questioning, and there appears to have been no attempt to show if, or how, all are connected into one overall concept. It is not the intention here to even attempt to answer this question. The purpose is purely to raise the question in the hope that people will look at it, realise it is a real, highly relevant question, and put their collective minds to providing an answer which will clear up the issue once and for all, as well as allowing future students a clearer understanding of what this area of science really means, especially as that area seems to be ever-growing with it now encompassing physics, chemistry, mathematical statistics, information theory, biochemistry and, therefore, medicine – to name those that come to mind immediately.

Again, as reminded by Richard Norman [15], the accurate use of language within science is vital as lives may be involved. Clearly language can be used to obscure vital truth within scientific discourse at great human cost. The student must keep closely in mind the fact that entropy within statistical formulations is dependent upon mathematics which does not necessarily have a physical foundation. Attention has been drawn to this problem concerning the accuracy of language in scientific discourse [25] and it is truly an issue of the greatest importance. Although it is an issue stretching through all layers of academia, it is possibly most important for the student embarking on a life in science and here clarity of language is of vital importance. Hence the purpose of this piece; the physical meaning of entropy causes immense confusion for students who often ponder the question 'What is entropy?' The more mathematically inclined face no such difficulty because, on its introduction in classical thermodynamics, it is simply viewed as an integrating factor and little attention need be given to its possible physical meaning, other than it's change is equal to a change in heat divided by the temperature at which that change occurs. However, that is frequently not enough of an explanation for the more physically minded. Any doubts thus aroused are then magnified by the appearance of the quantity in statistical mechanics and then further in information theory. When it further emerges that an entropy may be defined for any distribution – whether or not it has any physical significance – the confusion and doubt for the student becomes complete. This is a situation which should not be tolerated in science and so, once again, the question is posed "What is Entropy?"

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