On the Statistical Nature of the Second Law of Thermodynamics.

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Abstract.

It is intended here to consider the Second Law of Thermodynamics and various derivations made from it, especially the introduction of the quantity known as the entropy. The starting point will be the formulations of the law in classical thermodynamics. Attention will then move to so-called statistical thermodynamics to help illustrate the point that the Second Law of Classical Thermodynamics is certainly not statistical in nature

Introduction.

It does seem that, over the years, much has been written about the statistical nature of the Second Law of Thermodynamics but the starting point for any such discussion seems to have been the underlying assumption that the Second Law is, in fact, statistical in nature. However, is this so?

It is intended here to examine this important question afresh and, to start, a brief history of scientific events associated with the original establishment of the Second Law will be given before moving on to a brief consideration of concepts more readily associated with statistical thermodynamics. This should enable an attempt to be made to answer the stated question and put some other presently accepted ideas into perspective.

The Second Law in Classical Thermodynamics.

Historically, the origin of the Second Law of Thermodynamics is linked with the name of Sadi Carnot. He was born in 1796, the eldest son of Lazare Carnot who was best known for his political activities. Lazare Carnot was a member of the Directory after the French Revolution - having previously been, amongst other things, a member of the notorious Committee of Public Safety - and, later, during the Hundred Days in 1815, Napoleon's Minister of the Interior. However, throughout his political career, he managed to find time for intellectual pursuits. His big interest appears to have been mechanics and, although he did little original work, it is felt nowadays that his attempt to produce a general science of machines did influence his son.

Sadi Carnot himself was educated at the élite École Polytechnique and, after a period as a military engineer, devoted himself to research. His great work, with English title *Reflexions on the motive power of fire*, was published in 1824. In modern terminology, motive power is work and the book was concerned with the maximum efficiency of heat engines. By the 1820's, with the restoration of peace between Britain and France, it became apparent that the French lagged a long way behind the British in some technological areas and nowhere was the disparity worse than in power technology. At that time, this area had become particularly important because of the widespread use of steam engines - in Britain, such machines were used, for example, in the Cornish tin mines both for pumping out water and for hauling men and loads of ore to the surface. The work of such engineers as Watt, Trevithick and Woolf was well-known and must have helped provide some inspiration and incentive for Carnot.

Quite naturally, for the time, Carnot adopted the so-called caloric theory in his work. Basically, this theory regards heat as some sort of massless fluid. Carnot assumed caloric conserved in the cyclic operation of heat engines and postulated that the origin of the work done by a heat engine is the transfer of caloric from one body to a colder body; - this flow of caloric being regarded as analogous to the flow of fluid which, as in a waterwheel, produces work when falling down a potential gradient. Crucially, Carnot recognised that a heat engine works most efficiently if the transfer of heat occurs as part of a cyclic process and also, that the main factor in determining the amount of work which may be extracted from a heat engine is the temperature difference between the heat source and the sink into which the caloric flows. Both these points turn out to be independent of the actual model of the heat flow process. Finally, he devised a cycle of operations - now known as the **Carnot cycle** - as an idealisation of the behaviour of any heat engine.

From these essentially practical, engineering-linked considerations came much of what is now known as thermodynamics. Tragically, Carnot himself did not live to see any of the far-reaching consequences of his work;- dying from cholera at the early age of 36. However, his work was used and extended by, amongst others, Thomson and Clausius and, once the problem of reconciling Carnot's work, in which caloric is conserved, with Joule's work demonstrating the interconvertibility of heat and work had been resolved, modern thermodynamics began to emerge.

As mentioned earlier, the Second Law itself has been stated in various ways but probably the two most common forms are those due to Lord Kelvin (William Thomson) and Rudolf Clausius:

> **Kelvin:**
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> **It is impossible to transform an amount of heat completely into work in a cyclic process in the absence of other effects.**
>
> **Clausius:**
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> **It is impossible for heat to be transferred by a cyclic process from a body to one warmer than itself without producing other changes at the same time.**

As may be seen in most thermodynamics' text-books, these two statements of the Second Law are equivalent although, strictly speaking, they are only equivalent in the above form for the case of positive absolute temperatures. As has been shown, the Kelvin form of the Second Law has to be modified to take account of negative temperatures but that modified form is totally equivalent to the above Clausius form. It might be noted at this point that the idea of a machine which, in a cyclic process, converts an amount of heat *completely* into work has

been suggested. Such a machine, if permissible, would prove an extremely attractive proposition since it could be used to cool both the deserts and oceans and so provide a huge supply of energy for man's use. However, such a machine is prohibited by the Second Law, as is seen by glancing at the above statement of that law due to Kelvin. These machines, which are still sought by some people, are often called *perpetual motion machines of the second kind*; perpetual motions of the first kind being those which violate the First Law of Thermodynamics.

The above forms of the law are those used at the birth of thermodynamics as a subject in its own right. As mentioned already, the laws were deduced from experiment and observation, and many of the ideas were borrowed from engineering. The notions and experiences of the engineer were used to obtain the laws of heat transformation and it is a tremendous achievement that a theory with many highly abstract concepts should be established by this approach. It should be stressed at this point that the above are the two basic forms of the Second Law of Thermodynamics; other so-called forms of the law are deduced from these with the exception of the highly mathematical accessibility criterion proposed by Carathéodory. Here, though, attention will remain focussed on the two basic forms due to Kelvin and Clausius. It should always be remembered, though, when discussing these forms of the Second Law or when making deductions from them that, in both cases, reference is made to the impossibility of something happening *in a cyclic process in the absence of other effects*. These italicised words are crucially important and forgetting them often leads to incorrect deductions and conclusions. In fact, it is often these words which prove the incorrectness of many claimed examples of so-called perpetual motion machines of the second kind.

It is seen immediately that all the discussion leading to these two formulations has been macroscopic in nature; nowhere have any statistical considerations encroached on matters; nowhere has any mention of uncertainty or uncertainty principles raised its head. This is because, in classical thermodynamics, there are no statistical considerations encountered; there is no uncertainty involved at any stage. However, such is not the case in the seemingly closely related subject Statistical Thermodynamics which really grew out of a merging of classical thermodynamic ideas with those of statistical mechanics.

Before proceeding to discuss the related subject of statistical thermodynamics, it should be noted that one of the great achievements of classical thermodynamics was to derive the equation which represents this important Second Law mathematically. That equation is the one which introduces the concept of entropy into classical thermodynamics. The equation is, of course,

$$d'Q = TdS,$$

where $d'Q$ represents a quantity of heat, T is the absolute temperature introduced during the derivation of this equation and dS represents a change in a quantity termed the entropy. The details of this derivation are well-known and can be read up in any thermodynamics textbook. One crucial point to be noted at this point is that the introduction of the concept of entropy is irrevocably linked to a change in heat and the whole derivation has been via purely macroscopic considerations there with no mention anywhere of anything statistical.

Statistical Thermodynamics.

The emergence of statistical mechanics, quickly followed by statistical thermodynamics, occurred later in the nineteenth century and really started with Boltzmann's work and his definition of entropy, S, in that discipline via the now famous equation

$$S = k \ln W.$$

The great need was to be able to examine subjects consisting of huge numbers of individual particles, systems such as gases. Even for an ideal gas, this posed enormous problems because of the huge numbers of equations involved if the paths of individual particles were to be determined. The obvious answer to the problem lay in the application of statistical techniques and Boltzmann's famous equation helped in this task. Over the years, the use of various so-called ensembles arose, each one determined by the physical quantities assumed known and those which needed to be determined. The most popular for use are the micro-canonical ensemble (given variables being internal energy, number of particles and volume), the canonical ensemble (given variables being number of particles, volume and temperature) and the grand canonical ensemble (given variables being volume, temperature and chemical potential), although others, such as the pressure ensemble, exist and are used on occasions. In all cases, the introduction of statistical ideas and methods necessarily introduced an element of uncertainty into the model; an uncertainty characterised, at least in part, by the fact that only average values of the various physical quantities were derived and also by the presence of fluctuations in these average values. These are all well-known facts associated with statistical mechanical methods but it must be remembered that classical thermodynamics deals only with the actual values of these physical entities *not* average values.

Nevertheless, over the years, these statistical methods have been used with great success to describe various complex systems and to make deductions, which have proved valid, about them. Values of the various functions of classical thermodynamics have been found which are appropriate for the physical system under investigation but, frequently, these derivations have been made by utilising several well-known results, such as the Euler relation, of classical thermodynamics and this does raise the question of whether or not a circular argument has been used to justify the identification of quantities with their counterpart in classical thermodynamics. This must certainly be true of the quantity known in both areas as the *entropy*. This last remark follows because, in classical thermodynamics, any change in this function is irrevocably linked to a change in heat whereas, in statistical mechanics, the quantity is a purely statistical one with *no* necessary link to heat or changes in heat. Of course, this is a question which has been raised previously on several occasions and there seems, as yet, no real consensus of opinion on the outcome. It is, though, a very real and serious question which lies at the very heart of the foundations of the area of physics known as statistical mechanics. Again as has been pointed out before, it also raises the question of the link between classical thermodynamics and information theory because, once again, the real apparent link is via statistical thermodynamics; it is statistical thermodynamics which appears to have several formulae in common with information theory, *not* classical thermodynamics.

It has to be noted that it is in the subject statistical mechanics, or statistical thermodynamics, into which questions of uncertainty encroach. When one reads of thermodynamic uncertainty relations, for example, one is considering deductions made within statistical thermodynamics, *not* classical thermodynamics. The uncertainty involved is really a result of the use of the various statistical distributions involved in helping in the description

of genuine physical systems usually comprising large numbers of particles. It would seem the uncertainty involved is not associated with the actual system but rather with the methods used in an attempt to describe that system theoretically and make deductions about that system based on the model adopted. Such uncertainty has no place in classical thermodynamics. In a similar way, all arguments claiming the Second Law is only valid on average and, statistically speaking, violations could be found are totally dependent on a statistical approach to the subject. The uncertainty enters only because of the mathematical methods employed. No; the Second Law in classical thermodynamics does not admit violations; it is a law which, in its own strict context, is universally valid.

Some Closing Thoughts.

Ever since the Second Law of classical thermodynamics was introduced, attempts have been made to find violations. None has succeeded! Many claims have been made but not one has been valid. The basic reason for this failure in some cases is that people have not adhered to the precise details of the fundamental statements of the said law – those due to Kelvin and Clausius; many have foundered because the proposed machine either did not operate in a complete cycle and/or other effects which took place were ignored. The other category of claim involves recourse to the ideas and associated techniques of statistical thermodynamics and, once this step is made, the conclusions immediately become questionable, if not invalid, as far as classical thermodynamics and its all-embracing Second Law are concerned, since the use of statistical notions immediately introduces uncertainties into the discussion which are definitely not present in classical thermodynamics. Fundamentally, the Second Law of classical thermodynamics is not a statistical law and should never be viewed as such.

Over the years, more and more notions concerned with uncertainty in one form or another have entered into the practice of scientific investigation – whether it be through the realisation that man cannot measure anything with 100% accuracy or, when microscopic situations are being examined, through the uncertainty principles of quantum mechanics. However, it may well be asked if, in the first instance, it is purely man's inability to measure with complete accuracy and, in the second, it is due to the model devised by man to describe these microscopic systems. It is possible that all the problems of uncertainty are man-made and that all the systems themselves are exact with no room for uncertainty anywhere. However, although this may be an area ripe for further philosophical investigation, it cannot be doubted that classical thermodynamics is exact and harbours no uncertainties. This is probably another reason why the exact nature of the relationship between classical thermodynamics and statistical thermodynamics and information theory needs long and careful examination – not least, the question of whether or not the various entropies are equivalent must be resolved, although this seems a tricky question given that any change in the first is purely linked to a change in heat while the other two are definitely statistical in nature with no obvious direct link to heat. Overall, classical thermodynamics seems, in one sense, to stand alone and any possible violations of its laws must be viewed within the subject itself, rather than by incorporating seemingly appropriate statistical notions.