

What is the Second Law of Thermodynamics?

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Abstract.

In this short note, attention is drawn to the fact that the Second Law of Thermodynamics specifically refers to cycles and certainly does *not* state that the entropy is, as some seem to think, a non-decreasing entity.

The original forms of the Second Law of Thermodynamics are due to Kelvin and Clausius and, in their modern wording, the Kelvin form is:

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

while that due to Clausius is:

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.

Although some minor variations in wording may be found in some texts, these are essentially the two forms of this law usually encountered and, as may be seen in most text books on thermodynamics, these statements are found to be equivalent for positive absolute temperatures [1,2]. The slight modification necessary to the Kelvin form to extend this equivalence to the case of negative absolute temperatures is of no concern here but may be found in various texts [3].

It is important to remember, however, that these two formulations of the law follow on from the pioneering work of Sadi Carnot [4]. The motivation for his work was the realisation that, by the 1820's, France was lagging behind Britain in various technological areas and nowhere was the disparity worse than in power technology. The area had become especially important at that time because of the widespread use of steam engines. For example, in Britain, such machines were being used extensively in the Cornish tin mines, both for pumping water out and for hauling men and loads of ore to the surface. Here the highly successful work of such engineers as Watt, Trevithick and Woolf was well-known and must have helped provide incentive for Carnot. In retrospect, it is easy to understand that Carnot adopted the so-called caloric theory in his work and he assumed caloric conserved in the cyclic operation of heat engines. He also postulated that the origin of the work done by a heat engine is the transfer of caloric from one body to a colder one. Crucially, he recognised that a heat engine works most efficiently if the transfer of heat occurs as part of a cyclic process. He also realised 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. His final achievement was to devise a cycle of operations, known as a Carnot cycle, as an

idealisation of the behaviour of any heat engine. His work was subsequently used and extended by such as Kelvin 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, thermodynamics as it is known today began to emerge. However, one crucial point in all this known history surrounding thermodynamics cannot be emphasised enough and that is that all Carnot's work was related to cycles and the two modern statements of the second law refer quite specifically to occurrences in cyclic processes. The oft-quoted claim that the second law states that entropy is non-decreasing is, at the very least, NOT a statement of the second law and in what sense, if any, the statement is true must remain open for discussion. In fact, it might be remembered that the notion of entropy didn't emerge until well after Carnot's lifetime; in fact, according to Münster [2], Clausius introduced the concept of entropy in 1854 and the actual term 'entropy' in 1865, while Carnot died in 1832!

However, this claim about entropy being a non-decreasing function obviously received a major boost in the earlier 1900's from the support of such eminent scientists as Eddington and Jeans if the book *God and the Astronomers* [5] is to be believed. This book was written by W. R. Inge, who was Dean of St. Paul's in London at the time. Dr. Inge was a Theologian/Philosopher and, from his writing, appears to have become interested in various areas of science, one of which was thermodynamics. If his writing is any guide, he was convinced that the Second Law of Thermodynamics was solely concerned with the non-decreasing property of the entropy. There is absolutely no mention of the need for cycles anywhere in any of his writing. To him, it would seem, cycles play no part in the second law!

It should be remembered from the outset that the whole concept of entropy is derived in thermodynamics via a mathematical manipulation which is reliant on one or other of the above-mentioned forms of the second law [3]. From a consideration of cyclic processes, it is shown that a change in heat at a given absolute temperature may be related to the change in another quantity subsequently called entropy. This relation is;

$$dS = d'Q/T$$

where S refers to entropy, Q to heat and T to absolute temperature. Mathematically, T is said to be the integrating factor for the inexact differential $d'Q$. It follows that dS is an exact differential and this fact is used extensively in the further development of thermodynamic theory. In truth, the dS appears initially simply as a representation of an exact differential which is equivalent physically to a change of heat divided by the absolute temperature which that change occurs; physically, it would seem, little more can be said about it. However, as far as this article is concerned, the important point to note is that the quantity $d'Q$ may represent either heat given to a body or heat removed from a body; in the first case it is usually regarded as a positive quantity and, in the second case, a negative quantity. Hence, from the very introduction of the concept into classical thermodynamics, the entropy change may be either positive or negative. It is, therefore, quite simply and obviously totally incorrect to claim that the Second Law of Thermodynamics states that the entropy is a non-decreasing quantity.

It might be noted that the deductions referred to in all the above have been made for so-called quasi-static processes. If non-static processes are considered, the work may be extended to show that the entropy change associated with a non-static adiabatic process is greater than the accompanying change in heat divided by the absolute temperature at which that change occurred; that is, for such a process

$$dS > dQ/T$$

However, to obtain this result, it is first assumed that a non-zero entropy change is associated with the original non-static adiabatic process [3]. Further, in order to generalise this inequality beyond just non-static adiabatic processes, it is further assumed that, if such a process as that envisaged here takes place, then the end-states of the process obey the stated inequality and so the inequality must hold for all types of non-static process between those two states, not just non-static adiabatic processes. It is this sort of reasoning which leads to the above inequality being accepted as a general rule for non-static processes and also indicates the origin of the claim that entropy never decreases. However, it is clear that, in order to obtain this inequality, assumptions have to be made and whether or not these are valid in the physical world as distinct from its mathematical representation must remain a real question. Nevertheless, whatever the answer to that particular query, it is absolutely clear that this inequality is at best a deduction from the Second Law of Thermodynamics but is certainly *not* a statement of it.

As for the assumed physical meaning of entropy, many of the explanations that have appeared over the years seem to rely on information from other fields such as statistical mechanics and information theory; for example, the idea that entropy is a measure of order in a system is clearly not a notion emanating from classical thermodynamics since, for a start, it has no link with heat flow. Whether or not the quantity referred to as entropy in these other fields is the same as that which occurs in classical thermodynamics is another serious question which is rarely, if ever, addressed but, in the area of classical thermodynamics – where, by classical thermodynamics, is meant the original thermodynamics of Carnot and his followers – the position must be exactly as outlined above and, in that context, the physical meaning of entropy is surely the one mentioned here and that is that entropy is defined by its change being equal to a change in heat divided by the absolute temperature at which that change occurs. Finally, as a relevant aside, it might be noted that, since the entropy of classical thermodynamics is irrevocably associated with a heat flow, it cannot sensibly be thought of as a property of a body and this again separates it from the entropies of statistical mechanics and information theory.

References.

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