

A Cautionary Note on the Second Law of Thermodynamics.

Jeremy Dunning-Davies,
Departments of Mathematics and Physics (retired),
University of Hull,
Hull,
England.

and

Institute for Basic Research,
Palm Harbor, Florida, U.S.A.

j.dunning-davies@hull.ac.uk

Abstract.

Entropy and its physical meaning have been a problem in physics almost since the concept was introduced. Here questions are raised over the correctness of the idea that the Second Law of Thermodynamics may be expressed simply as ‘the entropy never decreases’.

Introduction.

The idea of entropy, or at least its change, first arose in classical thermodynamics via deductions made from the basic traditional forms of the Second Law. Either the Kelvin or Clausius form of that law was used to show mathematically that the quantity representing a change in heat, $d'Q$, an inexact differential, possessed an integrating factor which was the absolute temperature $1/T$. The product $d'Q/T$ was then a total differential denoted by dS , and referred to as a change in entropy. At a later stage, when it became desirable to consider the properties of systems, particularly gases with large numbers of particles, statistics were introduced and this led to the birth of statistical thermodynamics. Soon quantities in statistical thermodynamics were identified, not unreasonably, with quantities in classical thermodynamics but this identification seems to have been assumed valid, rather than actually proved valid. While all this was occurring, information theory was being developed separately but, in a classic book by Brillouin¹, an apparent link between statistical thermodynamics and information theory was established although this suggested link was hinted at by Shannon in his classic article of 1948². In all three areas, a function termed *entropy* appears but the question of whether or not these three are identical, or not, always seems to be being assumed, not proved.

Classical Thermodynamics.

In the usual approaches to classical thermodynamics, the First Law, *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.

The Second Law is then introduced into the discussion in one of its fundamental forms due to Kelvin or Clausius. In their modern wording, these are:-

Kelvin:

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

and

Clausius:

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 seen³, either of these forms, but usually that due to Kelvin, may then be used to show via a mathematical argument that the inexact differential $d'Q$ possesses an integrating factor which turns out to be the reciprocal of the absolute temperature, T . It is then customary to write

$$d'Q/T = dS$$

where dS simply represents the resulting exact differential. In the derivation, no direct physical interpretation is assigned to dS but, customarily, it is deemed to be the change in a quantity termed the entropy. However, here, *entropy* is simply the name given to the quantity

represented by the symbol S but it should be noted that, in classical thermodynamics, the change in this quantity is *irrevocably linked to a change in heat* experienced by the system under consideration.

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, as should be noted and remembered always.

If attention is restricted to systems for which the entropy is an extensive variable then the discussion is easily extended² to open systems and again considering the special case of compression of a fluid, this latter equation becomes

$$TdS = dU + pdV - \mu dN,$$

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

All of the preceding discussion is restricted to so-called quasi-static processes. If considerations are extended to include non-static processes, it may be shown that, for non-static adiabatic processes, the inequality

$$dS \geq 0$$

may be derived. If the entropy, S , is a state function, this inequality is a statement of the principle of increase of entropy. However, it is vitally important to realise that this result is *derived* from the basic form of the Second Law; it is *not* an actual statement of the Second Law. Obviously, there are occasions when the entropy of a system does decrease; for example, in a cyclic situation, such as a Carnot cycle, if the entropy increases in one section, there must a corresponding decrease in another to ensure a successful completion of the cycle. Also, from its actual derivation, it is immediately obvious that, if heat is added to a system, the entropy change is *positive* while, if heat is taken from a system, the entropy change is *negative*. Hence, at least as it stands with no stated limitations, claims that the principle of entropy increase is a statement of the Second Law^{1,4} are not accurate and could be misleading.

Comments.

As may be seen from a perusal of another, somewhat longer, article⁵, it is by no means certain that the entropy functions of classical thermodynamics, statistical thermodynamics and information theory are identical. It is true that they seem to be the same on occasions but their actual equivalence is not proven. Hence, great care should be exercised when assuming this. Again, it must be stressed that, as indicated above, the notion that the principle of increase of entropy is a statement of the Second Law of Thermodynamics is simply not true. It is this which has provoked the writing of this note because several recent articles⁶ have, in fact, assumed this to be so. It should always be remembered that the entire subject of classical thermodynamics is based on studies of heat engines and these engines worked in cycles as is evidenced by the accepted statements of the Second Law quoted here. Most of the theory involved relies on equilibrium properties of systems and so it is not certain that a thermodynamic entropy even exists in non-equilibrium situations. In fact, in such situations, much progress has relied on an assumed existence of such a function. Once again, it should

be stressed that great care should be exercised when using functions and procedures outside their original areas of definition.

References.

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5. Dunning-Davies, J., 2017, "The Second Law and Entropy Increase"
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6. e.g. see recent articles by George Rajna on the vixra site.