

TAIT, FORCE AND ENTROPY.

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Almost 150 years ago, Peter Guthrie Tait gave a lecture to a British Association meeting and took as his subject 'force'. His conclusions were both interesting and controversial but possibly offer a means to understanding better the notion of entropy as it appears in classical thermodynamics. This suggestion, however, applies to entropy – or, more accurately, entropy difference - as it appears in classical thermodynamics and not to the quantity with the same name which occurs in statistical mechanics and information theory.

Finally, there is included a brief examination of the plethora of recent claims to have identified violations of the Second Law of thermodynamics in nanosized systems. Doubt is cast on the validity of such claims.

Introduction.

When studying thermodynamics it is important, from the outset, to realise that the so-called 'common experiences' which form the basis of the subject are ones with which, in one way or another, everyone is familiar. Words such as 'hot' and 'cold' retain their everyday meanings; the idea of one body being 'hotter' than another is familiar to anyone who has inadvertently touched a heated towel rail; the idea of heat flowing from a body to a colder one is, again, a concept familiar to all who have wished to become warm after venturing out on a cold winter's day and have gained comfort from sitting close to a roaring fire. These simple experiences are at the heart of the subject and, when faced with a problem of understanding in thermodynamics, all would do well to remember these simple everyday occurrences with which they are familiar. Concepts such as temperature and pressure also retain their everyday meanings and this should be born in mind when meeting them in future thermodynamic discussions.

However, while thermodynamics *is* rooted in experiences which are familiar to all, some more advanced aspects of the subject place it among the most abstract branches of physics. Although rarely emphasized, this is an important point to note, since the main reason for it is that the basic theory contains results which, within broad limits, are independent of any particular system. This leads to the surprisingly wide range of applications for thermodynamic results: for example, as well as being of obvious use in physics and chemistry, parts of the theory apparently find application in biology, information theory, communications, and even the study of language; although it will be seen from what follows here that the inclusion of these latter applications might raise some non-trivial questions.

Anticipating what is to follow, it might be noted that the First Law of Thermodynamics concerns conservation of energy and may be stated as

**Energy is conserved when heat
is taken into account.**

The Second Law gives information concerning the way in which systems evolve. There are several statements of this particular law but the most important are those

dating from the very beginnings of thermodynamics as a subject in its own right; that due to Lord Kelvin is

**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 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.**

It is well-known that these two seemingly different forms of the law are, in fact, equivalent when positive absolute temperatures are involved so, in the vast majority of instances, either form may be used when making deductions. However, what is not so well-known apparently is that it is *these* two forms of the Second Law, with the possible addition of the more mathematical formulation due to Carathéodory, which form the basis of classical thermodynamics. It should be remembered that the manner in which the Carathéodory form is related to those of Kelvin and Clausius is well documented¹. Any other so-called forms of the Second Law are merely results deduced from one of these fundamental forms, usually under quite specific conditions. Basic classical thermodynamics is based, as Tait points out so graphically², on the ground breaking work of Carnot and, as such, is related directly to the operation of heat engines which had a cyclic series of operations. It is crucial when considering the Second Law in classical thermodynamics to recognise that it relates to some physical process being prohibited *in a cyclic process in the absence of other effects*. It is vital to note and remember these two conditions which are so important.

Again, it is probably the Second Law which causes more problems of understanding these days, - possibly because of its direct link to the introduction of the concept of thermodynamic entropy. However, historically, it was the First Law which easily proved the more difficult to establish - possibly due to the difficulty of understanding the precise nature of heat. In the 18th Century, heat was regarded as some sort of massless fluid, called caloric. It was thought that when one body is at a higher temperature than another and both are brought into thermal contact, caloric would flow from the hotter to the colder body until they came to equilibrium at the

same temperature. However, this theory had problems. For example, when a warm body is brought into contact with ice, caloric will flow from the warm body to the ice; but, although ice is converted into water, the temperature of the ice-water mixture remains unaltered. Also in the 18th Century, an alternative view developed according to which heat is associated with the motions or vibrations of the microscopic particles which make up matter. This theory - the so-called kinetic theory - associated heat with the kinetic energy of the motions of the microscopic constituents of matter.

Tait and Force.

To end his fascinating book *Recent Advances in Physical Science*, Tait³ included his lecture on Force which he delivered to the British Association in Glasgow in September 1876. He commented that, at the time, ‘even among the particularly well educated class who write for the higher literary and scientific Journals, there is widespread ignorance as to some of the most important elementary principles of Physics’. It was for this reason that he chose for the subject of that lecture ‘Force’, which he regarded as a ‘much abused and misunderstood term’. He proceeded to comment on the ongoing abuse of the word and ended by speculating that there is probably no such *thing* as force; that it is merely a convenient expression for a certain ‘rate’. The remainder of the lecture is devoted to showing the plausibility of this notion and he eventually draws on an expanded form of Newton’s Third Law of Motion, due to Newton himself, which states that:

‘If the action of an agent be measured by the product of its force into its velocity; and if, similarly the reaction of the resistance be measured by the velocities of its several parts into their several forces, whether these arise from friction, cohesion, weight, or acceleration;- action and reaction, in all combinations of machines, will be equal and opposite’.

The actions and reactions mentioned here and claimed to be equal and opposite are no longer simple forces but are the products of forces and corresponding velocities; that is, they are rates of doing work. Tait goes on to note that force appears to be a mere name and that it is the product of a force with the displacement of its point of contact which possesses a genuine objective existence. In other words, if a force F is displaced through a distance ds , it is the product $F.ds$ which has a real physical meaning, not the force F itself. This interesting interpretation has direct relevance to an ongoing problem in thermodynamics – the question of what is entropy?

Possible Consequences for Thermodynamics.

As mentioned already, in classical thermodynamics, it is customary and not unreasonable for all to feel they have some knowledge, even understanding, of many of the basic quantities that occur. Number of particles and volume have obvious immediate meanings; internal energy, pressure, heat and temperature are all quantities with which most have an acquaintance; the idea of heat flow and of the concepts ‘hot’ and ‘cold’ cause no concerns. All feel fairly comfortable when considering these. However, entropy is another matter. The introduction of this unfamiliar concept into the

framework of classical thermodynamics follows one of two routes, both of which rely on either the Kelvin or Clausius forms of the Second Law. Whether one follows the older introduction via a consideration of Carnot cycles or the more modern approach utilising the approach based on Carathéodory’s treatment, the end result is fundamentally the same. It is seen that the symbol representing an element of heat added to, or taken from, a system, $d'Q$, is mathematically a so-called inexact differential but the Second Law shows that an integrating factor exists which equals the absolute temperature T . Hence, the quotient $d'Q/T$ is an exact differential and is usually denoted by dS . It is this quantity S which is termed the thermodynamic entropy. The method of derivation confers some properties, such as additivity, on this quantity but, being a mathematical derivation, no physical meaning is attributed. However, by analogy with Tait’s notion about force, that it is only when multiplied by a distance, so that

$$F.ds = dW,$$

where dW represents an element of work, that the symbol, F , representing force has any real meaning, one might not unreasonably claim that the thermodynamic entropy, or, more accurately, the entropy difference, has an objective existence and, hence, physical meaning, only when its change is multiplied by the absolute temperature T to give

$$TdS = d'Q,$$

because here $d'Q$ has a definite physical interpretation as an element of heat.

Hence, the suggestion is that classical thermodynamic entropy has no separate physical meaning and may be interpreted physically only via this equation. It should be noted immediately also that, if heat is added to a system, the change in entropy is positive; if heat is taken from a system, the change is negative. It follows that it is incorrect to talk of entropy as being a quantity which can *never* decrease; such a statement, if ever true, may be true only under some quite specific conditions which would need to be stated whenever such a claim re entropy is made. It might be noted again that all these remarks refer to classical thermodynamic entropy and not to statistical mechanical or information theory entropies. When, or indeed if, these are ever equivalent is a separate issue but the above comments on the physical meaning of the classical thermodynamic entropy remain.

It is interesting also to note that these thoughts stress the importance of a heat change in the deduction of the entropy change. It is heat change and temperature which are the two variables here which possess an immediately recognisable physical interpretation. Without the presence of the heat change here, there would simply be no entropy change introduced. This then emphasises one major difference between the entropy of classical thermodynamics and *all other* so-called entropies – in classical thermodynamics, entropy change is irrevocably linked with a change of heat. Therefore, if such a heat change is not exhibited in other entropy expressions – even if they purport to refer to physical situations – these entropy expressions cannot, at least in general, be equivalent to thermodynamic entropy.

Again, in classical thermodynamics the introduction of the change in the quantity commonly referred to as entropy always follows from an amount of heat being

added to, or indeed subtracted from, a system. Considering the reasoning involved, it would seem reasonable to suppose this a one-way process; that is, it is not possible in classical thermodynamics for a change in heat in a system to be produced by a change in the quantity referred to as entropy. Of course, this immediately raises questions concerning Landauer's suggestion⁴ that erasure of information is a dissipative process and that a small quantity of heat must be produced when a classical bit of information is deleted. However, in view of what has gone before, one may wonder if Landauer was truly concerned with the entropy of classical thermodynamics when he formulated his suggestion.

More on the Physical Interpretation of Entropy.

In addition to what has been written earlier, the First Law of Thermodynamics may be considered in the form

$$dU = d'W + d'Q.$$

In this form, it is clear that the First Law shows that any energy change is, in general, composed of contributions of work and heat or, alternatively, as work and a quantity of energy not available for transformation into work. It is this second term which, as seen earlier, is shown to be equivalent to the product of absolute temperature and entropy change by the Second Law. Hence, it is easy to see how entropy can be viewed as the unavailable energy per degree. This interpretation does seem to come closer to assigning a genuine physical meaning to the function termed 'entropy' in classical thermodynamics. It might be noted that this is quite consistent with the notion of an adiabatic change in which there is no heat change. Crucially, though, this is an interpretation purely within the realm of classical thermodynamics; it is a quite definite quantity, not an average one, and certainly not one admitting fluctuations in its value. Hence, it might be stressed again that the entropies of statistical mechanics/statistical thermodynamics and of information theory are not being discussed here.

In connection with this latter point, it is worth noting the comments of Baierlein in appendix D of his book *Atoms and Information Theory*⁶ in which he makes it abundantly clear that. Although there is a close correspondence between quantities in classical thermodynamics and statistical mechanics/statistical thermodynamics, they are not identical. As he also points out, it is simply the case that 'for practical calculations, they are numerically equivalent'. In other words, numerical equivalence does not necessarily mean actual equivalence. Possibly it should be stressed again that the comments here concerning a physical meaning of the entropy relate specifically to classical thermodynamics. Finally on this particular point, it might be noted that Baierlein also makes some pertinent comments concerning the relation between the entropies of classical thermodynamics and information theory. Again he stresses numerical, but not conceptual, equivalence but he also goes on to note that 'the failure to preserve a distinction is often a stumbling block on the path to an appreciation of both.'

Possible Violations of the Second Law.

It seems that, almost from the moment the Second Law was enunciated, people have been seeking violations in order to prove it either completely wrong or, at least, of

limited applicability. All attempts have failed and the reason for this relates to the specific forms of the law quoted above – the forms due to Kelvin and Clausius. Both retain direct links with the original work which was based on heat engines operating in closed cycles. The attempts to discredit the Second Law have foundered because all have failed to obey both of those restrictive conditions – the violation which may be thought of as a quantity of heat being converted completely into work *or* a quantity of heat flowing from one temperature to another higher than itself must occur in a cyclic process *and* in the absence of other effects. However, more recently, attempts to claim violation of the Second Law have been following a different line⁵. The claims have related to the possibility of processes occurring for which an entropy decrease has been observed. It appears also that these possible violations have been observed in nanoscale systems and warnings have been voiced about some thermodynamic results at least breaking down when considering such systems. However, is this true?

At least since Newton's pioneering researches, there has been a tendency to extrapolate results determined in laboratories and on moderately sized systems to larger and larger situations. Newton himself came up with his idea of gravity as functioning here on the Earth and essentially extrapolated to cover events occurring in the solar system. Since those early days, his and other results have been used to consider events in the solar system but also even farther afield to the outer regions of the universe. This is possibly the only way forward as far as our present level of knowledge is concerned but it is a method not without risk since it is not obvious immediately why results valid at one dimensional level should continue to be valid for some much bigger entity. The same basic reasoning must hold true if one moves from laboratory dimensions to much smaller ones. Hence, when considering matters on the nanoscale, great care must be taken and it is not inconceivable that some familiar basic results will hold no longer. However, before discarding such results, their violation in these different situations must be absolutely certain. Such cannot be the case so far where the Second Law of Thermodynamics is concerned. This is because, so far, no-one has shown successfully a violation of either the Kelvin or Clausius forms of that law and those must remain at the foundation of the subject. As stated earlier, all other forms of the Second Law – with the exception of the Carathéodory form – are merely deductions from these two fundamental forms. Also, with none of the claimed violations has a closed cycle of operations been associated. This alone must raise grave queries for the validity of the claims but, unfortunately, today many seem to think the Second Law may be said to claim that the entropy can *never* decrease. This is surprising since it is obvious that when considering, for example, the operation of a Carnot cycle, it is clear that in one leg there is an entropy increase which is compensated by an entropy decrease in another leg so that the whole operation can be seen to be a complete closed cycle. In fact, a quick glance at the form of the equation derived directly from the Second Law

$$d'Q = TdS,$$

shows immediately that, as mentioned earlier, when a quantity of heat is removed from a system, there is an associated decrease in the entropy. The blanket claim that

entropy can never decrease is blatantly incorrect. Incidentally, it might also be remembered that it is generally accepted in classical thermodynamics that entropy tends to *decrease* to zero as the absolute temperature goes to zero⁷. It is, therefore, difficult to see from where these claims for violation of the Second Law come.

Conclusion.

Thermodynamics is a subject whose tentacles stretch into many fields these days but many students and practicing professionals are united in having little real understanding of what classical thermodynamic entropy really is physically. For many, its introduction is via a mathematical argument which results in a change in the quantity, subsequently termed entropy, being derived. It is often forgotten subsequently that only a change in the quantity is deduced, not an actual value for the quantity itself. This is an immediate difference with the quantities of the same name which occur in statistical mechanics and information theory. The question of whether these three entropies are equivalent must remain an open question, even though the supposition that they are seems to work in practice quite well. On the specific point of equivalence, though, it is useful to consider the argument put forward by Yockey in his book on information theory and molecular biology⁸. He concludes that there is no relation between what he refers to as the Maxwell-Boltzmann-Gibbs entropy of statistical mechanics and the Shannon entropy of communication systems since they do not refer to probability spaces that are isomorphic. To support this claim, he cites several articles in which it is shown that probability spaces are isomorphic if and only if they have the same entropy. Yockey undoubtedly advances a powerful case which is deserving of more widespread publicity. It should be mentioned though that not everyone agrees with this viewpoint. Ingarden⁹ has claimed that entropy is 'only one concept with various subtypes, only its applications are various, as is the case with probability and other mathematical and physical concepts'. Obviously some confusion exists but such is really associated with the positions of the ideas of probability and entropy in the discussion and this particular issue doesn't occur in classical thermodynamics but rather only in statistical thermodynamics which is a different, if related, subject. The argument due to Yockey simply indicates that the entropy of classical thermodynamics must be a quantity totally separate from the other entropies mentioned since these other entropies are irrevocably linked with probability distributions while that of classical thermodynamics is not linked with probability in any way but, rather, its change is linked with a heat change

This would seem, therefore, to provide an answer to the question, raised above, as to the equivalence of the three mentioned entropies.

Here concern has been simply with examining the position of the change in the quantity referred to as the entropy in classical thermodynamics by extending Tait's fascinating ideas on the nature of force. It would seem that this approach highlighting the physical meaning of the product TdS and indicating that the change in thermodynamic entropy, dS , has no direct physical meaning itself, may offer a way out of a difficulty which has faced so many for so long. However, it is seen also that this alternative approach raises questions of its own but these are really questions arising from earlier work and deductions from those earlier notions.

The final short section concerned with possible violations of the Second Law raises grave doubts, at least, over the validity of such claims and illustrates once again that great care must be taken over every small detail of the accurate statements of this law when considering anything associated with it.

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