SOME THOUGHTS ON BASIC THERMODYNAMICS.

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Here attention returns to the fundamental starting point for classical thermodynamics – the notion of a heat engine working in a cycle. What follows is based exclusively on the lucid writings of Peter Guthrie Tait and much of the argument closely follows his original. However, this is used to illustrate how modern physics has tended to stray away from the basics of this crucially important topic of thermodynamics. Attention is drawn to the difference between such classical thermodynamics and statistical thermodynamics.

Introduction.

For many years now, much work on basic ideas in thermodynamics has concentrated on mathematically acceptable approaches. This follows Max Born's unhappiness with what he regarded as an engineering approach to the subject. There can be little doubt that the subject has benefitted from this more analytical approach but it has lost some physical insight too as is illustrated by the following:

It should never be forgotten that the subject thermodynamics originated with the study of heat engines which worked in cycles. All this started with Carnot whose work was clarified and extended by Clausius and Kelvin. Much of what follows here is recorded in Tait's book *Sketch of Thermodynamics*[1], which basically chronicled Kelvin's contributions to the subject. The starting point is the cyclically operating heat engine devised by Carnot. It is noted that, in the original engine, each stage may be operated in reverse and so the entire engine may be so operated also. It is shown that such an engine is the most efficient that can be produced. It follows immediately, therefore, that any engine which may not be operated in reverse must be less efficient than this ideal Carnot engine. This very straightforward point must be remembered for what follows.

Some fundamental ideas.

Following Tait, suppose an engine of finite range is composed of an infinite number of engines with infinitesimal range and let $q + dq$ and q be the amounts of heat absorbed and expelled at temperature t. Then, by the First Law, the work done is

$$Jdq$$

where J is the mechanical equivalent of heat. Although this quantity, J, rarely appears in modern literature on thermodynamics due to the widely accepted definitions of the units used throughout the subject, it is used here exactly as Tait himself used it[1]. It also helps recall the enormous contribution of Joule to the early formulation of thermodynamics since it was he who first determined an accurate value of the quantity experimentally. As an aside, it might be speculated that a return to the use of units so that this factor appeared once again might lead to students obtaining a better understanding of at least some aspects of the overall subject which is classical thermodynamics; after all, the fact that the existence of a mechanical equivalent of heat was recognised and its value determined was a vital point in the initial development of the subject as we know it today.

Again, by the Second Law, Tait shows quite clearly that the work done is given by

$$Jqdt/t.$$

also. Equating these two expressions leads to

$$dq/q = dt/t$$

which leads to

$$q/t = \text{const.}$$

Hence, for an engine where an amount of heat q is taken in at temperature t and an amount q_0 is given out at temperature t_0,

$$q/t = q_0/t_0.$$

Then the work done is

$$J(q - q_0) = Jq(t - t_0)/t.$$

As noted by Tait, whatever the temperature of a quantity, dq, of heat, the real dynamical value is Jdq. However, in practice, the work produced by an engine will be $J(1 - t_0/t)dq$. This may be written in the form

$$Jdq - Jt_0dq/t.$$

Hence, in any cyclic process whatever, if q_1 is the total heat taken in and q_0 that given out, the practical value of the work is

$$J(q_1 - q_0) - Jt_0 \int \frac{dq}{t}.$$

However, for a reversible cycle, the practical value is just $J(q_1 - q_0)$ by the first law and so, in this particular case, the value of the integral term is zero. In general, though, the integral term has a positive value because, in all non-reversible engines, the practical value for the work done is always less than this value of $J(q_1 - q_0)$, as was mentioned earlier. Of course, this is the origin of the notion that

$$\int \frac{dq}{t} \geq 0.$$

However, all this implies is that

$$dS \geq 0;$$

that is,

$$TdS = d'Q \geq 0.$$

It is important to note that this does *not* mean

$$TdS \geq d'Q;$$

in fact, it is difficult to see how this inequality follows from anything.
Also, it might be noted that the acceptable inequality

$$TdS = d'Q \geq 0,$$

does not violate the First Law but merely asserts that for an irreversible process

$$d'Q = dU - d'W \geq 0$$

and that raises no problems.

It is vitally important to note that all of the above discussion relates to cycles. The inequality derived refers quite specifically to the fact that, in all non-reversible engines, the practical value of the work done must be less than a specific value always and it is this demand that introduces the inequality. The question of the actual range of applicability of the said inequality remains. All the basics of classical thermodynamics are based on cycles so any result so derived cannot necessarily be valid for individual processes. This is precisely the main point here; the said inequality has been derived for a cycle *not* for an individual process and there is nothing in what has gone before to even suggest the inequality true for an individual process. Indeed, reference to the workings of a Carnot cycle shows that this cannot be the case for, in such a cycle, there is one leg in which the entropy increases but that is balanced by a leg in which the entropy decreases in order for the total entropy change in the cycle to be zero and ensure that, at the end of the cycle, everything is in exactly the same state as it was at the beginning of the cycle. Hence, a true cycle has been negotiated.

Again, all of the above discussion relates to classical macroscopic thermodynamics and *not* to statistical thermodynamics. Hence, the subject under discussion involves no indeterminacy whatsoever; classical thermodynamics must be – by its very nature – deterministic. Therefore, for example, talk of thermodynamic uncertainty relations must refer to statistical thermodynamics – to the subject *after* some statistical elements have been introduced, so that the subject is classical thermodynamics no longer. This point is brought out very clearly in appendix D of Baierlein's book *Atoms and Information Theory*[2], where he states that the conceptual bases of thermodynamics and statistical mechanics are "sufficiently different that one can expect only a close *correspondence* between the theoretical quantities, not a true equality or identity". He points out that, for example, the energy in thermodynamics has a definite value but, in statistical mechanics, that is simply not so – an expectation value would be calculated in that discipline and a root mean square estimate of the anticipated deviations could be found also. This, of course, links in extremely well with a comment at the bottom of page 84 of Elsasser's book *The Physical Foundation of Biology*[3], where he draws attention to "the efforts to get some profit out of the very rare statistical failures of the second law of thermodynamics". Such possible 'failures' can only exist if a statistical element is introduced into things but, in classical thermodynamics, that is simply not possible as it is – as stated above – a completely deterministic subject. Hence, *no* violations of the second law of thermodynamics are allowable as far as classical thermodynamics is concerned!

The deterministic nature of classical thermodynamics possibly leads to another relevant point re the subject as a whole and that refers to the nature of the function known as the entropy. Is it a state function or not? Some recent evidence would suggest it isn't, but other would seem to indicate the opposite.

From the First Law

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

which in certain special circumstances takes on the form

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

Also, in equation form, the Second Law may be written

$$d'Q = TdS.$$

Combining the two gives

$$TdS = dU + pdV$$
or
$$dS = \frac{1}{T}dU + \frac{p}{T}dV.$$

Mathematically, this is akin to regarding the function S as being dependent on two independent variables - U, the internal energy and V, the volume.

Now in any cyclic process where the end point is the same as the starting point, the internal energy will undergo no change and neither will the volume. Hence, the function denoted by S can undergo no change either. Hence, in this sense, in classical thermodynamics S must be a so-called function of state also. This may be regarded as a long winded argument to establish this fact since it might be deemed to follow immediately from the fact that the Second Law establishes $1/T$ as an integrating factor for the inexact differential $d'Q$ and, as such, the integral of the product of the two, indicated by the symbol dS, around a closed loop must equal zero, which is essentially what has just been illustrated. However, in statistical thermodynamics, because of the very nature of the subject, an element of uncertainty is introduced and so, theoretically, one can imagine a situation where such uncertainty in the value of S could lead to the end value in a cycle not being quite the same as the initial value. However, in traditional classical thermodynamics, no such possibility would seem allowable.

References.

1. P. G. Tait, 1877, *Sketch of Thermodynamics,*
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2. R. Baierlein, 1971, *Atoms and Information Theory,*
     W. H. Freeman & Co., San Francisco.

3. W. M. Elsasser, 1958, *The Physical Foundation of Biology,*
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