Further Thoughts on Thermodynamics.

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Abstract.

Recently, attention has been drawn to a number of pieces written concerning classical thermodynamics in a biological setting. Several ideas have been put forward which are unusual for orthodox classical thermodynamics but, as they are supported by experiment, seem to offer suggestions for expanding the scope of that subject and even possibly helping make some aspects more amenable to students. The idea of introducing time into considerations is one such major notion which appears to lead to a new meaning of 'slow' processes in a classical thermodynamic setting and should be examined further because of the possible ramifications for the subject as a whole.

Introduction.

Recent readings of attempts to make classical thermodynamics more obviously applicable to situations totally outside its normally accepted field have awakened further thoughts relating to the basic structure of the subject. The specific field of study which was concerned in these readings was biology but, by direct implication, that would have to include medicine also. This led to an appreciation of the difficulties people in disciplines other than physics experience when attempting to apply results developed in physics to their own areas of interest and expertise. This can, and does, lead to a greater understanding of the problems others experience with one's own area of interest but also can, and does, lead to mistakes being made by them due to a lack of appreciation of some basic tenets of some areas. This is particularly true of thermodynamics and the unfortunate truth is that this is due, in part at least, to a lack of clarity of understanding of various relevant concepts by those in physics. As with many issues in thermodynamics, the fundamental problem often seems to be associated directly with the notion of entropy. This is something which caused confusion almost since the function was first introduced or, at least, since its interpretations in statistical mechanics and information theory entered into considerations. Up to that point, the idea of a change of entropy in classical thermodynamics had arisen out of the Second Law as something resulting from a change in heat. Heat and entropy in classical thermodynamics were, and remain, linked irrevocably. This was due to the fact that, up to this point, heat engines had been the main objects of interest and these were undoubtedly macroscopic entities. However, once attention veered away from these and the statistical idea of entropy was introduced from both statistical mechanics and information theory, the picture became less clear and much confusion seems to have arisen virtually from the date of this introduction. The reason for the introduction is quite clear and is, indeed, reasonable; many of the systems requiring discussion consist of huge numbers of particles and the only way to deal with them as far as past and present knowledge is concerned is through utilising statistical techniques. However, as discussed recently[1], it does seem that the accepted link-up between the expressions of classical thermodynamics and both statistical mechanics and information theory does seem somewhat contrived. Admittedly, the link-up, even if it has been contrived, has proved extremely successful in dealing with a wide range of scientific problems but, when biological processes begin to be involved, it becomes evident that the question must be investigated afresh. Any such investigation, though, must be carried out with no preconceived notions as to the outcome. It should be recognised also that physics itself could possibly benefit from such a reappraisal too since the whole topic of entropy, for example, is one which arouses confusion for so many at all levels of science.

The Laws of Thermodynamics.

Probably, the first and second laws of thermodynamics are by far the most important and far-reaching for many. Of course, the first law is really only a form of expressing conservation of energy but taking heat into account. As such, this law presents few difficulties and certainly is not a source of controversy. The same may not be said of the second law though. In its basic forms due to Kelvin and Clausius, or even that due to Carathéodory, few real problems arise immediately. The problems begin to arise when the question of entropy is introduced and when the notion of the second law being claimed to state that entropy never decreases. In conventional texts on thermodynamics[2], the function known as the entropy is introduced directly from the second law in one of the mentioned forms – usually the form due to Kelvin - and appears only when, mathematically, an integrating factor is deduced for the inexact differential representing a quantity of heat given to, or taken from, a system; that is,

$$dS = d'Q/T,$$

where $d'Q$ represents the quantity of heat, T the absolute temperature which is the mentioned integrating factor, and dS the total differential called the change in entropy. Immediately, it is seen that classical thermodynamics is concerned with changes in entropy, *not* with absolute values of the quantity. It is also obvious immediately that, if heat is added to a system, $d'Q$ is positive and so, dS is positive but, if heat is taken from a system, $d'Q$ is negative and so dS is negative as well. In other words, entropy may either increase or decrease depending on whether heat is added to a system or taken from that system.

This immediately raises one important problem since some often claim that the second law of thermodynamics may be stated in the form *the entropy always increases*. In fact, as Weaver[3] has commented, Eddington remarked that "The law that entropy always increases – the second law of thermodynamics – holds, I think, the supreme position among the laws of Nature". Obviously this supposed statement of the second law is incorrect but, unfortunately, it seems to have become accepted by many as a genuine form of that law. Whether this belief is purely due to Eddington's statement or not is immaterial, it is undeniable that the acceptance by many of this as a statement of the second law is not helpful in the development of the subject itself or to increasing use of thermodynamics in more and more areas of science. It might be noted also that this problem is seen clearly only when a return to fundamentals is made; that is, when considerations return to the original introduction of the concept of entropy via heat changes. Also, the notion of a sort of general entropy increase arises when consideration is restricted to so-called 'irreversible' processes. As has been noted previously[4], the whole idea of 'reversibility' can lead to difficulties and that is why Landsberg is so careful, when discussing cycles, to consider such cycles run in forward or reverse directions separately so that he is not faced with extra problems such as some which he enumerates.[2]

At this juncture it is possibly worth reflecting on some words written by Tatiana Ehrenfest-Afanassjewa in 1959 in the preface to the translation of the book she authored with her husband –*The Conceptual Foundations of the Statistical Approach in Mechanics*. She wrote:

At the time the article was written, most physicists were still under the spell of the derivation by Clausius of the second law of thermodynamics in the form of the existence of an integrating factor for the well-known expression for the quantity of heat ΔQ put into the system. In this derivation the irreversibility in time of all processes occurring in nature played an important role. Hence it seemed that the possibility of a reversal of the natural development (which according to the 'Wiederkehreinwand' of Zermelo *should occur after a sufficiently long time) threatened the validity of some of the most important results of thermodynamics. However, it became clear to me afterwards, that the existence of an integrating factor has to do only with the mathematical expression of $\Delta Q = dU + dA$ in terms of the differentials $dx_1, dx_2, ..., dx_n$ of the* ***equilibrium*** *parameters $x_1, x_2, ..., x_n$ and is completely independent of the direction in time of the development of the natural processes. As a result, the fact of the reversibility of the mechanical motion, which is inescapable in the kinetic interpretation of the laws of thermodynamics, lost some of its importance. Nevertheless, even today many physicists are still following Clausius, and for them the second law of thermodynamics is still identical with the statement that the entropy can only increase.*

There can be little doubt that this powerful statement from an acknowledged high-class theoretician is deserving of much wider publicity than it has received so far. There can be little doubt that she is casting grave doubt on the validity of the statement that the *'entropy can only increase'* as a statement of the second law of thermodynamics. Also, she is clearly drawing attention to the fact that the derivation of the mentioned integrating factor is involved only with the differentials of *equilibrium* parameters. This latter point is crucial and, as suggested to me by a colleague[5], might be interpreted as meaning that some thermodynamic results at least do not strictly apply to real systems as the examination of such systems is rarely concerned with purely equilibrium parameters. Of course, considering the undoubted success of so much thermodynamic theory in so many areas, this latter interpretation of the above quotation must be viewed with a degree of caution. Also, the details of the approach adopted by Landsberg and mentioned above should be born in mind. As with so many results in theoretical physics it is vital to remember *all* the assumptions made in their derivations and to adhere strictly to any restrictions imposed by such assumptions. Here in thermodynamics, the role of equilibrium states in so many basic derivations probably has real consequences when real systems come under consideration. On the other hand, it should be remembered also that the practical origin of much of this work was concerned with heat engines – actual physical heat engines – and, certainly in this context, the theory has had great success.

The Search for Clarity.

The above considerations might well be construed as indicating a need for more clarity of detail in the foundations of classical thermodynamics. If so, this also indicates a muddying of the waters at the amalgamation of ideas on classical thermodynamics with those of statistical mechanics and information theory. However, all three areas seem to be attempting to describe broadly similar systems and so it is not really unreasonable to accept that some sort of amalgamation should occur. Unfortunately, on reading his writings, it becomes clear that some, if not much, of the confusion in this area originates in the writings of Clausius[4]. This is unfortunate for several reasons but the fact that there is implied criticism of someone as eminent as Clausius is a major problem and evidence for this surely follows from the fact that the above quoted piece by Tatiana Ehrenfast-Afanassjewa has not achieved greater prominence, even though it appears in a well-regarded and widely consulted text.

It would seem that the search for clarity in this area is at least one of the motivations for the work of MacClare[6] when he set out to consider whether or not conventional chemical machines might be used in living organisms. Remembering that thermodynamics owes its origin to a need to understand and improve the operation of heat engines, it seems reasonable to suppose that, if and when applied in other areas, changes in detail might prove appropriate, even possibly necessary. As MacClare points out, due to their molecular nature, living systems pose unique thermodynamic problems, especially in relation to Maxwell's demon. By introducing time into the statement of the second law he claims to solve these problems. He also points out that this proposal, while clarifying certain logical anomalies in classical thermodynamics, makes no difference to it in practice. Of course, any discussion of Maxwell's demon is outside the realm of pure classical thermodynamics since it necessarily involves a statistical element. The proposed modified statement of the second law to which he refers, and which, by analogy with Kelvin's statement, is:

> *It is impossible to devise an engine, of any size whatever, which, acting in a cycle which takes a time τ, shall produce no effect other than the extraction of energies, which have equilibrated with each other in a time less than τ, from a reservoir at one temperature and the conversion of these energies into a form in which they would remain stored for longer than τ; either at a higher temperature or in a population-inversion.*

However, this statement creates more confusion in that it is more akin to Clausius's statement of the second law rather than Kelvin's. Having said that, this statement does contain references to the importance of cycles and to the absence of other effects. Unfortunately, MacClare proceeds to claim that the second law could be expressed very economically in the form:

> *Useful work is only done by a system when one form of stored energy is converted into another.*

This abbreviated form contains no mention of either cycles or absence of other effects and so must be regarded with suspicion at the very least. Strangely also, his definition of so-called *stored energy* renders it quite distinct from *thermal energy*, which seems a little strange given that thermodynamics is under discussion and, as mentioned already, that subject's entire raison d'être is linked with heat engines. Again, since there is no mention of work in MacClare's original more detailed original statement of the second law and since it is generalised from the Clausius statement of that law, it is difficult to see from where the abbreviated form, which is all to do with work, comes. It would seem that MacClare's restatement of the second law should have been more along the lines of:

> *It is impossible to devise an engine, of any size whatever, which, acting in a cycle which takes a time τ, shall produce no effect other than the extraction of energies, which have equilibrated with each other in a time less than τ, from a reservoir and the conversion of these energies completely into work.*

which is seen to be a direct modification of Kelvin's form but doesn't appear to offer an immediate link with the notion of *useful* work.

However, it should be noted that Ho[7], while appreciating much of MacClare's work, noting in particular the importance of his introduction of time, criticises his suggested new form of the second law – especially the abbreviated form. Her immediate objection is that the statement is simply incorrect and queries on what a motor car engine depends if not thermal energy? She feels him correct in stressing that useful work may be done by a molecular system through a direct transfer of stored energy without thermalization, pointing out that photosynthesis involves the non-thermal absorption of photon energy and non-thermal energy transfer is the rule in living processes. She feels MacClare's suggested restatement of the second law unnecessarily restrictive since thermal energy may be organised to do useful work in a cooperative system such as is the case of enzymes embedded in a non-equilibrium membrane. Again, as she points out also, thermalized energy from a small compartment is still stored energy within a larger compartment enclosing it. For this reason, Ho has proposed

> *Useful work may be done by molecules by a direct transfer of stored energy, and thermalized energy cannot be converted into stored energy in the same system*

as an alternative statement of the second law where the first part is the same as MacClare's and the second suggests a means of defining a system as the extent to which thermalized energies equilibrate in a characteristic time. However, once again this statement excludes all mention of cycles and of the absence of other effects. This is a vitally important point which simply cannot be ignored.

Useful Work.

As MacClare[6] makes quite clear, the notion of *useful work* is understood fairly easily. He illustrates the point by noting that work done against friction does not produce any useful effect, only heat, but working against a spring has the effect of storing energy which may be used later. He further points out that, even at the macroscopic level, distinguishing being doing work beneficially and wastefully is important but that that is not too difficult because it is easily seen if a process leads to a useful end effect or not. However, he asserts that it is necessary to consider the question in more detail if classical thermodynamics is to be applied at the molecular level in order to understand biological processes. Rather than redefining the whole concept of work, he resorts to introducing two new terms: - stored energy and useful work. However, as may be seen by considering comments in Moore's book[8], the second term is one which is already in use among practising engineers. The first term refers to energies which remain in a distribution other than that of Boltzmann for longer than some standard time but is not of concern here.

Moore is really concerned with quantities of energy actually available to do work. To this end, he introduces an availability function, Φ, defined by

$$\Phi = U + p_0 V - T_0 S$$

where U, S, V are properties of a closed system in an equilibrium initial state and T_0 and p_0 are the temperature and pressure of the surrounding environment. The decrease of this function in a process during which the system comes to equilibrium with its environment is

$$-\Delta\Phi = \Phi - \Phi_0 = (U + p_0V - T_0S) - (U_0 + p_0V_0 - T_0S_0).$$

He then considered the form of the first applicable to closed systems:

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

where the dash indicates an inexact differential as usual. Again as usual, $d'Q$ represents heat added to the system from a reservoir at temperature T_0, $d'W$ is the work done and dU the change in internal energy. From the second law it follows that

$$d'Q = TdS$$

if so-called reversible processes are considered.
Hence, in this case

$$d'W_{rev} = - dU + T_0dS$$

but it is normally assumed that, in general, $d'W \leq - dU + T_0dS$ with the equality sign referring to the reversible situation, although there are problems associated with the validity of this inequality as has been noted previously[4].
Moore points out that, during the process under consideration, some of the total work done is used to push back the boundary of the system, thus increasing the system's volume by dV while the resisting environment's pressure is p_0. It is the remainder of the work which is termed useful work and denoted by $d'W_{useful}$. Then

$$d'W = d'W_{useful} + p_0dV$$

that is

$$d'W_{useful} \leq - dU + T_0dS - p_0dV$$

Integrating this expression between its initial and final states leads to

$$W_{useful} \leq (U + p_0V - T_0S) - (U_0 + p_0V_0 - T_0S_0).$$

or

$$W_{useful} \leq -\Delta\Phi$$

where it must be stressed that a closed system is under consideration and that the whole notion of 'useful work' has been introduced via a quite specific example. It is also important to note any assumptions made here, particularly bearing in mind the dependence on the idea of reversible processes since the whole idea of reversibility can raise problems, as has been discussed elsewhere[4].

This abbreviated discussion of Moore's introduction of the notion of availability and useful work serves to illustrate the fact that the notion of 'useful work' is not new but has been very much in the minds of those who use thermodynamics in a practical context. Nevertheless, it is something which needs to be remembered particularly when attempting to extend results of classical thermodynamics to cover situations pertaining in the biological sciences. To this end at least, the work of MacClare is important and deserves to be noted, as has been acknowledged by Ho[7].

As mentioned above, an important consequence of MacClare's work arises from the explicit introduction of time. There seem to be two distinct ways of doing useful work; not just slowly as usually considered by conventional thermodynamic theory but also quickly. This, it seems, might be the most important outcome from this work to consider for thermodynamics as a whole. As far as the slow process is concerned, it should be viewed as one which occurs at the same rate as that taken to go to equilibrium or, alternatively, slow in comparison with the time required for exchanging energies to equilibrate or distribute themselves evenly throughout the entire system. As far as classical thermodynamics is concerned, such a process would be thought to be reversible and most efficient when it comes to producing a maximum amount of work. By introducing time into considerations, a so-called reversible thermodynamic process needs to be slow enough for all thermal-exchanging energies to be able to equilibrate; that is, slower than τ, which may, in reality, be a very short period of time. The processes involved might, however, be intrinsically fast. As is pointed out quite specifically by Ho[7], according to these considerations, most catalysis is a slow process when compared with the time for thermal equilibration. It is pointed out further that each enzyme molecule is a 'microdomain' isolated from its surroundings for the time of the catalytic reaction and so that reaction may be regarded as occurring at equilibrium provided the above condition is satisfied. It follows, therefore, that high efficiencies of energy conversion may still be achieved in thermodynamic processes which occur quite rapidly provided that equilibration is fast enough. This immediately represents a huge departure from normal thinking in classical thermodynamics but it is something which has powerful experimental back-up and so should be regarded seriously and possibly brought more to the fore in discussions of thermodynamics in all separate disciplines that topic pervades.

Concluding Comments.

It seems a great pity that the easily avoidable confusion concerning MacClare's clarification of the second law in the context of biological problems has been allowed to arise because MacClare appears to have raised some genuinely interesting points and introduced some fascinating new notions into thermodynamics. His stress on the need to identify *useful* work is one obvious example and possibly links with ideas on available and unavailable energy as discussed by Moore[8] and other mechanical engineers with an interest in thermodynamics[9], who also discuss the concept of useful work during the discussion of what they call the availability concept. Just as MacClare was approaching the overall problem from the viewpoint of a physiologist, so Moore's approach was motivated, at least in part, by his background in mechanical engineering. In both cases emphasis is placed on this notion of useful work; the backgrounds and basic approaches of the two may be somewhat different but the end result is the same and one which should probably be brought more to the fore in many traditional undergraduate and, indeed, postgraduate introductions to this important topic of thermodynamics. However, as far as classical thermodynamics in general is concerned, the fact that thermodynamic reasoning is seen to be applicable in situations where useful work may be done quickly and not just slowly seems to herald a major change in thermodynamic thought. No doubt this point is deserving of much more detailed consideration by the scientific body at large but the considerations sparked by MacClare and pushed even further by Ho are vitally important and may not be ignored. There is possibly little awareness of the work alluded to here in conventional thermodynamic circles but, while conventional classical thermodynamics is usually concerned with so-called quasi-static processes, particularly adiabatic ones, here the inclusion of such processes occurring in real time becomes a genuine possibility. Let it be hoped that this note has the effect, at least, of helping bring this work to the attention of a wider audience and, specifically, an audience stretching across all traditional scientific boundaries.

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