MISCONCEPTIONS CONCERNING NEGATIVE ABSOLUTE TEMPERATURES.

JEREMY DUNNING-DAVIES

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

j.dunning-davies@hull.ac.uk

The issue of negative absolute temperatures is addressed anew in the light of fairly recent publications in the scientific literature which have totally misrepresented the position of such temperatures on the accepted absolute temperature scale. In particular, claims have been advanced that such temperatures are in fact lower than positive absolute temperature in violation of the Third Law of Thermodynamics and incidentally in violation of all the work – both theoretical and experimental – of the original investigators of the phenomenon.

Introduction.

Recently, several pieces have appeared in the scientific literature concerning negative absolute temperatures and their place on the usually accepted temperature scale. Admittedly, the original article committed no errors but subsequent pieces commenting on the original article have blatantly referred to temperatures *below* absolute zero having been achieved, in violation of the Third Law of Thermodynamics. Examination of the original article shows that such violation was neither claimed nor achieved. However, the semi-popular scientific literature refuses to correct its mistake. Further, as will be discussed briefly also, the error is perpetuated in what is proving to be an extremely popular book on thermodynamics for students. This introduces an added dimension of worry for all interested in science progressing and certainly nor regressing.

Negative Absolute Temperatures.

Negative absolute temperatures were first considered in the early 1950's via the work – both experimental and theoretical – of Pound, Purcell and Ramsey. All their work is well documented and the detail may be found in the listed references[1-4]. Again, further confirmation of the ideas and results considered may be found in the writing of such as Landsberg[5], Powles[6] and Bazarov[7]. Negative absolute temperatures and Carnot cycles have also been discussed[8]. However, it is worth noting at least some of the background as an introduction to the topic as a whole. As is indicated in references[1-4], Pound, Purcell and Ramsey examined various properties of the nuclear spin systems in a pure LiF crystal for which the spin lattice relaxation times were as large as 5 minutes at room temperature while the spin-spin relaxation time was less than 10^{-5} seconds. Various experiments were performed with the nuclear spin systems of this crystal, including some with a spin system at negative absolute temperature. Possibly the most important point to emerge here is that these negative absolute temperatures were achieved in physical systems in the laboratory. Admittedly the systems concerned were hardly everyday ones but, nevertheless, they were genuine physical systems. Obviously, if such systems did not exist in nature, there would be little, or no, point in studying negative absolute temperatures.

The detailed theoretical basis for this early work did not appear, however, until Ramsey's article of 1956 when most of the details were made known, including modifications, where necessary, to the wording of the laws of thermodynamics. The Clausius form of the Second Law remained unchanged but the Kelvin form had to be modified to

In a cyclic process, in the absence of other effects, heat cannot be converted completely into work for states of positive absolute temperature and work cannot be converted completely into heat for states of negative absolute temperature.

Again, the unattainability form of the Third Law had to be modified to

It is impossible in a finite number of steps to reduce any system to the absolute zero of positive temperature (+0^{o}K) or to raise any system to the absolute zero of negative temperature (-0^{o}K).

Various aspects of, and approaches to, thermodynamics make it seem an extremely abstract subject. Nevertheless, it is a branch of physics with roots firmly embedded in physical reality and whose purpose is to help in the explanation of physical phenomena. Nowhere is this link with reality better revealed than in the everyday notions of "hotter" and "colder". Here the everyday linguistic meaning of the terms is used in the physical theory. As Weinreich[9] points out, when two systems are placed in contact via a diathermic wall, the one which gives up heat is called the hotter and that which absorbs heat is the colder. The property of being hotter or colder is found to be transitive and this may be used to order all states of systems so that any state will give up heat only to states which are in lower positions on the list. The property determining position on this list is temperature and the hotter state is said to possess the higher temperature.

Again, each thermodynamic system must be capable of coming to thermal equilibrium with another system; that is, it must possess the property of thermal stability. This means that, if two systems at different temperatures exchange heat, the result must be to reduce the temperature difference between them. It follows from the First Law that if, in a process during which no work is done, heat flows from a hotter to a cooler system, the internal energy of the cooler system will increase while that of the hotter system will decrease. These changes must correspond to a warming up of the cooler system and a cooling down of the hotter system. This in turn implies that the temperature of each system must be a monotonically increasing function of the internal energy; that is

$$\left(\frac{\partial T}{\partial U}\right)_{W=0} > 0, \qquad (1)$$

where T and U represent temperature and internal energy respectively and $W = 0$ means that no work is done during the process.

The entropy S of a system may be written as a function $S(U, X_1, X_2, \ldots)$ of the internal energy U and the deformation (or work) variables X_1, X_2,… Now, since

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{X_i} = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_{X_i} \qquad (2)$$

where X_i indicates that all the X_i are held constant for these partial differentiations, the above criterion for thermal stability[9] implies that the curve of S against U is concave. Hence, if a system is capable of achieving both positive and negative absolute temperatures, the equilibrium curve of S as a function of U will possess a maximum and, for values of the internal energy less than that for which the maximum occurs, the temperature, given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{X_i} \qquad (3)$$

is seen to be positive; while for those greater than that for which the maximum occurs, the absolute temperature has a higher internal energy than an equilibrium state of positive absolute temperature at the same value of the entropy and work variables. Hence, in order to preserve the property of absolute temperature being a monotonically increasing function of the internal energy, negative absolute temperatures must be higher than positive absolute temperatures.

This latter point was emphasised first by Ramsey[4] who pointed out that, due to the form of the entropy curve discussed above for systems which exhibit both positive and negative absolute temperatures, it follows that, in cooling from negative to positive absolute temperatures, such a system passes through infinite absolute temperature and *not* through absolute zero. He also drew attention to the fact that the negative temperature cooling curves produced experimentally by Purcell and Pound[3] support this view. It is important to note that, once again, theory is supported by experiment and, therefore, any discussion of negative absolute temperatures and consequences of their existence is relevant to physics.

Connection between the Clausius and Modified Kelvin Forms of the Second Law.

It might be wondered how the above affects the link between the two basic forms of the Second Law of Thermodynamics. As was first pointed out by Ramsey, it might be felt possible to violate the Clausius form by constructing an engine which would extract heat from a reservoir and convert it into work with no other effects. This work could then be converted into heat which would be transferred to a hotter reservoir. This would indeed violate the Clausius form. However, from the modified form of the Kelvin principle, it is seen that, at positive absolute temperatures, the first step in this process is impossible and, at negative absolute temperatures, the second step may not be achieved. Hence, if the modified Kelvin statement of the Second Law does not hold, the Clausius statement could be violated. Therefore, the Clausius statement does imply the modified Kelvin statement.

Now suppose the Clausius statement is false. In this case, an engine may be constructed which can transfer heat from one body to another warmer than itself without producing any other changes. Consider a process in which, at positive absolute temperatures, a quantity of heat is converted partly into work, the remainder having passed from the hot reservoir to a body at a lower temperature. The above Clausius violating engine could be used to return this amount of heat to the hotter reservoir. The combination of these two processes would result in a quantity of heat being converted, in a cyclic process, in the absence of other effects, completely into work in violation of the positive temperature part of the modified Kelvin statement of the Second Law. Hence, for positive absolute temperatures, the modified Kelvin principle implies the Clausius principle.

Now consider a process in which, at negative absolute temperatures, a quantity of work is converted partly into heat which is delivered to a hot reservoir. In this case, the Clausius violating engine could be used to transfer a further quantity of heat to this hot reservoir from a cooler one – a quantity such that the total amount of heat transferred to the hot reservoir is equal to the total work done. This combination of processes would result in a quantity of work being converted, in the cyclic process, in the absence of other effects, completely into heat in violation of the negative temperature part of the modified Kelvin statement of the Second Law. Hence, for negative absolute temperatures also the modified Kelvin principle implies the Clausius principle. The equivalence of the modified Kelvin principle and the Clausius principle may then be concluded.

Recent Developments.

Recently, an extremely interesting article concerned with negative absolute temperatures appeared in the journal *Science*, entitled 'Negative absolute temperature for motional degrees of freedom'[10]. This article made no untoward statements or claims. Indeed, this article contained an exceptionally lucid account of the physics with which the authors were concerned. However, it was followed by an article in the journal *Nature* purporting to explain the aforementioned article in detail for the interested layman. In this latter article

http://www.nature.com/news/quantum-gas-goes-below-absolute-zero-1.12146

the author, Zeeya Merali, stated that the authors of the *Science* article had succeeded in cooling a system to a temperature *below* absolute zero and even went by the title 'Quantum gas goes below absolute zero'. It should be noted from the outset that this was definitely *not* what was claimed in the said *Science* article. The article actually claimed to have achieved negative temperatures in a system but with the concept of negative temperatures being defined in accordance with the accepted principles of thermodynamics; that is, where negative temperatures are *higher* than positive temperatures. This point was explained very carefully in the opening section of the *Science* article; there was *no* mention of any system achieving a temperature *below* absolute zero

The important difference reported by the *Science* article is that earlier experimental work usually involved examining spin systems, whereas this latest work seems to involve more directly understood physical systems. It should be noted also that, as well as misrepresenting what the authors of the *Science* article wrote, the apparent claims by Zeeya Merali do not accord with accepted thermodynamics as has been shown quite clearly already. Hence, the importance of this present discussion. There are obviously people who claim to be scientists who do not understand this concept of negative absolute temperatures but write about them nevertheless. This situation has been compounded by the unfortunate remarks contained in a relatively new book by Atkins[11]. This is a well written book on thermodynamics which seems to have found favour, particularly among students. Finally, the issue has been raised yet again in the issue of *New Scientist* which came out on 22nd November 2014. This was in an article entitled 'Us versus the Universe' and, although the authors didn't explicitly refer to temperatures below absolute zero, they certainly wrote in such a way as to make readers consider such a happening. However, the journal itself published in quotation marks the statement that "A whole mirror-world of negative temperatures exists below absolute zero on the Kelvin scale". Nothing could be clearer than that scientifically incorrect statement. Obviously this is a dangerous state of affairs which this piece aims to address at least in part.

Concluding Thoughts.

Considering all the well-documented, unchallenged, pioneering work by Pound, Purcell and Ramsey and others dating back to 1951[1-8], it is disturbing to note these modern claims concerning negative absolute temperatures. It is possibly even more disturbing to realise that those actively promoting these incorrect notions are, in the main, not active scientists but usually what might be termed scientific journalists and, when their error is pointed out to them, they simply will not acknowledge it. This is certainly true as far as the journal *Nature* is concerned since, after a lengthy correspondence, the editor concerned felt he and the correspondent had to 'agree to disagree'. This seems a totally inappropriate way to end a supposedly scientific discussion. *New Scientist* didn't even have the courtesy to reply to the criticism of its statement. This should worry all scientists since journals such as those mentioned are influential with professional and layman alike. Hence, the misconceptions regarding negative absolute temperatures are being peddled as fact to those unable to distinguish between scientific fact and fiction. Many will just see this as the discovery of a violation of the Third Law of Thermodynamics and will question it no further. With the added problem of the comments in Atkins' book[11], must surface concerns about the correctness of the thermodynamic knowledge of many who will be the scientists of the future. No; potentially this question relating to negative absolute temperatures has far wider, serious ramifications for science and should raise concerns for all interested in science and its future.

References.

[1] Pound, R. V., 1951, Phys. Rev. **81,** 156

[2] Ramsey, N. F. and Pound, R. V., 1951, Phys. Rev. **81**, 278

[3] Purcell, E. M. and Pound, R. V., 1951, Phys. Rev. **81**, 279

[4] Ramsey, N. F., 1956, Phys. Rev. **103**, 20

[5] Landsberg, P. T., 1959, Phys. Rev. **115**, 518; 1961, *Thermodynamics with Quantum Statistical Illustrations*, (Interscience, New York)

[6] Powles, J. G., 1963, Contemp. Phys. **4**, 338

[7] Bazarov, I. P., 1964, *Thermodynamics,* (Pegamon Press, Oxford)

[8] Dunning-Davies, J., 1976, J. Math. A, **9** 605; 1978, Am. J. Phys. **46(5),** 583

[9] Weinreich,G., 1968, *Fundamental Thermodynamics*,(Addison-Wesley, Reading, MA.)

[10] Braun, S., et al., 2013, Science **339**, 52

[11] Atkins, P., 2010, *The Laws of Thermodynamics: A Very Short Introduction*, (Oxford U. P., Oxford)