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Negative absolute temperatures and Carnot cycles

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Abstract. Properties of a thermodynamic phase space, for which both positive and negative absolute temperatures have been defined, are discussed. The conclusions reached are applied to Carnot cycles and it is found to be impossible to operate such cycles when one of the heat reservoirs has an infinite temperature. It is shown also that such cycles may be run only in particular cases when the temperatures of the reservoirs are such that one is positive and the other negative.

1. Introduction

The notion of *reversibility* is not strictly necessary in all approaches to thermodynamics as is evidenced by the approach of Landsberg (1961). However, if used, the notion invariably presents a difficult problem of definition. One point where the idea of reversibility creeps into most texts is in the discussion of Carnot cycles. However, when a reversible engine is mentioned, it is usually taken to be an engine which describes its working cycle quasistatically. In common with Landsberg, the approach to be adopted here will avoid the term *reversible engine*. Instead, the forward and reverse cycles of a Carnot engine will be examined separately. One advantage of this approach becomes clear when two special cases are considered: (a) the case when the two heat reservoirs have absolute temperatures of opposite sign, and (b) the case when one of the reservoirs has an infinite temperature.

However, before discussing these two particular Carnot cycles in some detail, properties of a thermodynamic phase space, for which both positive and negative absolute temperatures have been defined, will be discussed briefly.

2. The phase space β

In the approach to thermodynamics using the analytical methods of Caratheodory, attention is soon confined to the set of points in thermodynamic phase space denoted by β—whether the Caratheodory axiom or the Kelvin statement of the second law is used as starting point (Landsberg 1956, Zemansky 1966). The set β is such that, between any two points of the set, an adiabatic change is physically realizable and no point that can be in the set is excluded. Also, it might be noted that every curve in a set β represents a quasistatic process.

As far as any discussion of the second law is concerned, the set of boundary points of β is excluded and attention is focused on the interior of the set—usually denoted by γ. By assuming the validity of either the Caratheodory axiom or the Kelvin form of the second law, together with the existence of adequate continuity conditions, it may be shown that all points in γ which are accessible from some given point P by quasistatic adiabatic processes lie on a single surface, and that P itself must lie on this surface (Landsberg 1964, Zemansky 1966). The argument may be repeated for different initial states P and γ is found to decompose into a family of non-intersecting surfaces; these are surfaces of constant entropy. Clearly, points lying in different level surfaces cannot be linked by quasistatic adiabatic processes. However, consider two points A and B which lie in different level surfaces. Although these points cannot be linked by quasistatic adiabatic processes, either A is accessible from B by a non-static adiabatic process or B is accessible from A by a non-static adiabatic process, but not both.

The sets of boundary points of β and γ are denoted by $F(\beta)$ and $F(\gamma)$ respectively. For any normal physical system, these two boundary sets would be expected to coincide. The assertion that a point lies in $F(\gamma)$ does not mean that that point necessarily belongs to β. A separate argument is required to decide which points of $F(\gamma)$ belong to β. The third law of thermodynamics makes an assertion as to which of the boundary points of a set γ may be regarded as being linked adiabatically with the rest of γ, and therefore are to be regarded as belonging to β. In general, all boundary points which do not correspond to states for which the absolute temperature is $T=\pm 0$ may be included in β. By this principle, states for which $T=\pm\infty$ must be regarded as belonging to β.

However, it is only for a set γ that the second law of thermodynamics asserts that the absolute temperature, T, is an integrating factor of $d'Q$, that is, it is only within the set γ that the equation

$$d'Q = T\,dS \tag{2.1}$$

holds. Within such a set, it may be possible to approach the hypersurface $T=\pm\infty$ as closely as desired but it cannot be reached in γ. It may be concluded that a set γ may not attain or cross the hypersurface $T=\pm\infty$; that is, points for which $T=\pm\infty$ are not accessible by quasistatic processes. However, points for which $T=\pm\infty$ do belong to the set β and, since they are also states of maximum entropy, they are accessible from other points of β by non-static adiabatic processes.

It has been shown (Landsberg 1961) that, for all systems having a finite number of energy levels, the set β possesses *two* sets γ. Also, the set β itself may have only isolated points, which lie in $F(\beta)$ and therefore outside γ, at $T=\pm\infty$. Hence, whenever positive and negative temperatures have been defined for a set β, which refers to a system having a finite number of energy levels, that set contains at least two *disconnected* sets γ. For such a case, the second law asserts the existence of an entropy S_1 and absolute temperature T_1 for the set γ_1 and also, entropy S_2 and absolute temperature T_2 for the set γ_2. As is usual, however, there is still an arbitrary element remaining in the definitions since equation (2.1) remains valid under the transformation $T\to cT$, $S\to c^{-1}S$. Therefore, when positive and negative temperatures have been defined for a set β, the absolute temperatures in the two sets will have opposite signs but the additive constants in the entropy may be chosen so that the entropies are positive in both γ_1 and γ_2. Also, since the two sets γ_1 and γ_2 are disconnected, it follows that points in one set cannot be linked to points in the other set by quasistatic adiabatic processes, although linkage by non-static adiabatic processes may be possible.

3. Carnot cycles

Following Landsberg (1961), a Carnot engine may be defined to be such that its working fluid possesses the following properties:

(i) in each cycle it passes through the same physical—equilibrium and non-equilibrium—states;

(ii) it consists of one and the same phase, and has a fixed mass, throughout the cycle;

(iii) it extracts a quantity of heat Q_1 from a large heat reservoir at temperature T_1 and delivers a quantity of heat Q_2 to a similar reservoir at temperature T_2, $(T_1 > T_2)$, during each cycle;

(iv) it exchanges no other heat with its surroundings and there are no other entropy changes in the engine.

The efficiency of such an engine may be shown to be given by

$$\eta \leqslant (T_1 - T_2)/T_1. \tag{3.1}$$

If the same engine was run in reverse so that the working fluid absorbed a quantity of heat Q_2 at temperature T_2 and rejected a quantity of heat Q_1 at temperature T_1, the efficiency would be

$$\eta_r \geqslant (T_1 - T_2)/T_1.$$

If both the forward and reverse cycles of the Carnot engine are performed quasistatically

$$\eta = (T_1 - T_2)/T_1 = \eta_r.$$

However, it is conceivable that, in a Carnot engine which may be reversed, both cycles are performed non-statically. In this case, the relation

$$\eta \leqslant (T_1 - T_2)/T_1 \leqslant \eta_r$$

holds.

The theory of Carnot cycles operating between two positive temperatures is well-known and is discussed fully in most textbooks on thermodynamics. The operation of Carnot cycles between two negative temperatures has also been examined in detail (Powles 1963). However, two further cases remain to be considered: (*a*) a Carnot cycle operating between temperatures of different sign, and (*b*) a Carnot cycle operating between two temperatures, one of which is finite and the other infinite.

3.1. *Case* (*a*)

Consider a Carnot engine operating between the temperatures T_1 and T_2, with $T_1 < 0$, $T_2 > 0$. Also, consider states P_1 and Q_1 at temperature T_1, states P_2 and Q_2 at temperature T_2. As has been shown, for such a case, the phase space β will contain two disconnected sets γ_1 and γ_2. States P_1 and Q_1 will belong to γ_1, states P_2 and Q_2 to γ_2. Again, states P_1 and P_2 will not be linked by quasistatic adiabatic processes—only non-static adiabatic linkage is possible. However, in general, if a non-static adiabatic change links two states, such a change would be accompanied by an entropy change and this would be a violation of one of the properties of Carnot cycles.

However, it is possible that, although belonging to disconnected sets γ_1 and γ_2, the states P_1 and P_2 could be states of equal entropy. In such a case, although the states would be linked by a non-static adiabatic process, there would be no accompanying entropy change.

A similar argument could be applied to the states Q_1 and Q_2 also. If the states P_1, P_2 and Q_1, Q_2 so defined were used, it would be possible to operate a Carnot engine, as defined, but due to the fact that non-static processes are involved, equation (3.1) would take the form

$$\eta < (T_1 - T_2)/T_1.$$

The possibility of operating such an engine would depend on the existence of non-static adiabatic processes linking states of equal entropy. Also, due to the nature of the processes involved, it would not follow automatically that such an engine could be run in reverse.

3.2. Case (b)

Due to the consideration of § 2, it is seen that states for which $T=\infty$ are only accessible from states at finite temperature by non-static adiabatic processes. Also, since states at infinite temperature are also states of maximum entropy, such processes would be accompanied by entropy changes. Again, states at finite temperature are not adiabatically accessible from states at infinite temperature;—the linkage is strictly one-way! Hence, it is not possible to operate a Carnot cycle between two temperatures, one of which is finite and the other infinite.

It is argued sometimes that such Carnot cycles are impossible in any case because the $T=\infty$ isotherm corresponds to an adiabatic of maximum entropy. However, states for which $T=\infty$ belong to the boundary of γ and the equation

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

only holds within the set γ. It has been shown (Dunning-Davies 1972) that the range of validity of this equation may be extended to include boundary points of γ. However, within the $T=\infty$ hypersurface, it is seen that, although the entropy remains constant, $d'Q$ may be non-zero. Hence, there is no obvious necessity for the $T=\infty$ hypersurface to be an adiabatic as well as an isotherm.

4. Conclusions

It should be possible, therefore, to operate a Carnot engine when the heat reservoirs are such that one has a positive absolute temperature and the other a negative absolute temperature. The operation would depend, however, on the existence of non-static adiabatic processes which link states of equal entropy. Since such processes appear to exist (Weinreich 1968), the operation of such an engine should be possible in theory. However, it is seen to be impossible to operate a Carnot engine when one of the reservoirs has an infinite absolute temperature.

One important fact to emerge from these considerations is that a Carnot cycle need not have quasi-static adiabatic components necessarily. Indeed, it appears that a useful Carnot cycle may be defined in which the changes of state between states of constant entropy can be effected by non-static means.

These conclusions, all based on existing laws of thermodynamics, seem to remove some of the 'anomalies' discussed recently by Tykodi (1975) and should remove also the need for introducing another 'principle' of thermodynamics such as he suggested.

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