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Systematics of Carnot cycles at positive and negative Kelvin temperatures

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Abstract. The set of possible Carnot cycles involving positive and/or negative Kelvin temperatures is analysed in terms of graphs and of transported entropy and entropy production. The formulations of the second law of thermodynamics, allowing for the existence of negative Kelvin temperatures, proposed by Ramsey and by Landsberg are shown to be logically equivalent. Some properties of the limiting temperatures $T = +0$, $\pm\infty$, -0 are also investigated and a generalised third law is formulated.

1. Introduction

There have been many discussions about the thermodynamic behaviour of systems at negative Kelvin temperatures. One-heat-reservoir dissipative processes (entropy-producing processes) are permissible (Ramsey 1956, Schöpf 1962, Powles 1963) in the domains of both positive and negative Kelvin temperatures: a one-reservoir direct work-to-heat conversion is permissible in the domain of positive Kelvin temperatures, whereas a one-reservoir direct heat-to-work conversion is permissible in the domain of negative Kelvin temperatures. We consider here particularly two-reservoir processes (Carnot cycles) for all possible combinations of positive or negative temperatures.

In a previous paper by one of us (Landsberg 1977), a similar study of heat engines and heat pumps at negative and positive Kelvin temperatures was presented. An analogy between heat pumps at positive (negative) temperatures and heat engines at negative (positive) temperatures emerged. In the present paper, we re-examine these cycles from the point of view of transported entropy and entropy production.

We first introduce diagrams that summarise the results of Landsberg (1977) and of the present work in a qualitative and convenient manner. We then comment on the relation between Ramsey's and Landsberg's formulations of the second law and conclude with a discussion of the special properties of the temperatures $T = +0, \pm\infty, -0$.

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1.1. Carnot cycles

In a Carnot cycle, an engine undergoes two isothermal changes and two adiabatic changes. During each isothermal change the engine exchanges heat with a heat reservoir of fixed temperature. Let the two heat reservoirs have Kelvin temperatures T_h, T_c (positive or negative), with T_h being the temperature of the *hotter* reservoir, i.e. $1/T_h < 1/T_c$. Let the quantities of heat supplied to the engine per cycle be Q_h, Q_c, so that a negative value of Q means the engine rejects heat into the reservoir. Let W be the net work supplied to the engine per cycle, so that a negative value for W indicates a net gain of work potential in the surroundings, for example the raising of a weight in a gravitational field.

The first law of thermodynamics applied to one cycle of the engine gives, (note that our sign convention for W differs from that of Landsberg (1977))

$$0 = Q_h + Q_c + W. \tag{1.1}$$

Let the heat reservoirs at temperatures T_h, T_c function in such a way that the entropy change ΔS of each *reservoir* in one cycle is correctly given by the relations

$$\Delta S_h = -Q_h/T_h \qquad \Delta S_c = -Q_c/T_c. \tag{1.2}$$

The entropy change of the *working substance* itself is zero in one cycle and thus will not be discussed any further. The second law of thermodynamics implies that

$$\sigma \equiv \Delta S_h + \Delta S_c \geqslant 0, \tag{1.3}$$

where σ is the entropy produced (or generated) in the course of the cycle. Equation (1.3) is equivalent to the Clausius inequality

$$(Q_h/T_h) + (Q_c/T_c) \leqslant 0. \tag{1.4}$$

All results of this paper are derived from this theory. Our remarks for negative temperatures apply only to systems capable of achieving such temperatures, i.e. in general to systems which have an upper limit to the possible energy of their allowed states (Ramsey 1956).

We now proceed to investigate the various possible types of Carnot cycles.

2. Graphical catalogue of possible Carnot cycles

In a previous paper (Landsberg 1977) an analogy between heat pumps at positive (negative) Kelvin temperatures and heat engines at negative (positive) Kelvin temperatures was given. We present in figure 1 diagrams summarising these results. They enable us to see at a glance whether a proposed cycle violates the first or the second law of thermodynamics.

2.1. The graphs

(i) Two horizontal temperature axes and a vertical entropy axis are shown in each case. A *reservoir* is represented by a dark square along the temperature axis. Positive Kelvin temperature reservoirs are on the top temperature axis, negative Kelvin temperature reservoirs on the bottom axis. The dotted line can be thought of as the *engine* or *working substance*.

(ii) *Heat* is represented by a solid arrow originating or ending at a reservoir. The heat quantity is positive if the arrow points toward the engine, negative in the other case. The magnitude of the heat Q_h or Q_c is proportional to the length of the arrow.

(iii) *Entropy*. The sign of the entropy change of a reservoir is positive if the arrow points upward, negative if it points downward. The *magnitude* of the entropy change is proportional to the product of length and thickness of the arrow. Whether it is at positive or negative T, the thickness of an arrow is simply increased as one moves to the right of the diagram.

By use of these rules, the total entropy change in a given process can be calculated as the sum of the contributions of each reservoir and, to satisfy the second law, must be larger than or equal to zero. (The engine does not enter the calculation.)

(iv) *Work* is represented by a double arrow. The work quantity is positive if the double arrow points toward the engine, negative in the other case.

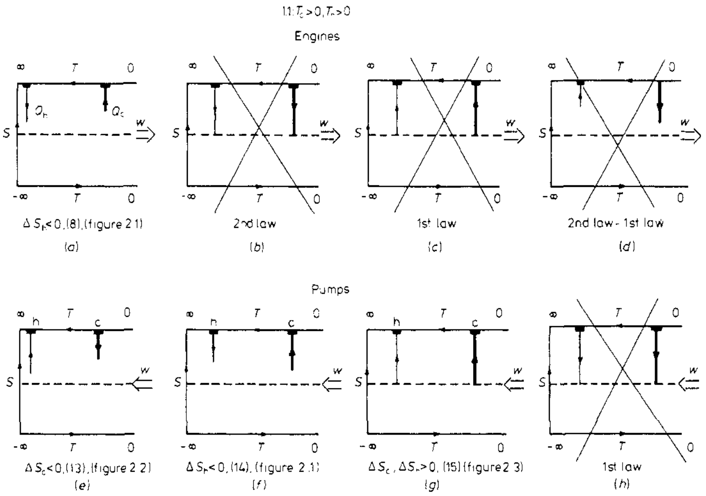

Figure 1.1.

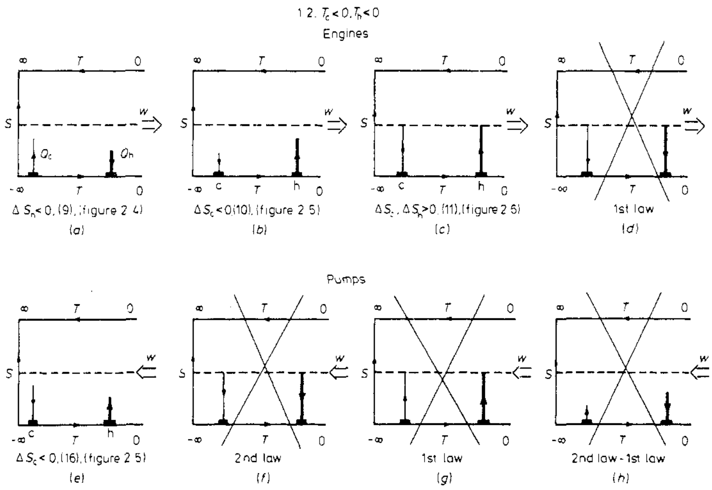

Figure 1.2.

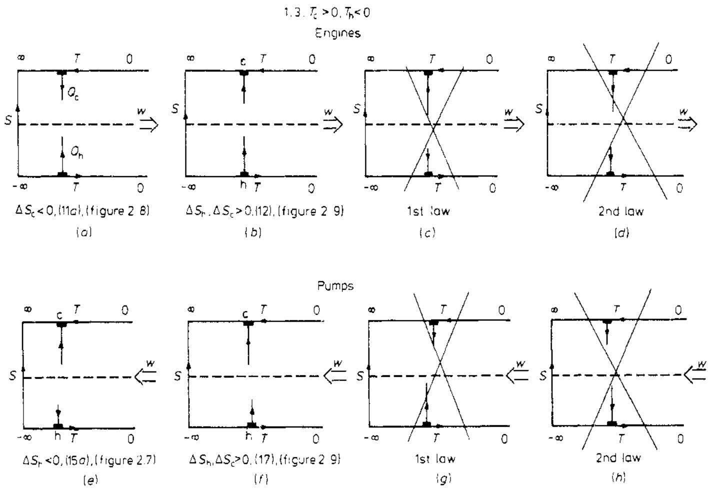

Figure 1.3.

Figure 1. Graphical catalogue of Carnot cycles. Forbidden cycles are crossed out and a caption indicates which law of thermodynamics they violate. When two laws of thermodynamics appear, it is meant that the cycle violates the second law if the first law is satisfied or vice versa. Below each of the twelve allowed cycles, we show, from left to right, some entropy changes of the reservoirs, the numbers corresponding to table 1 of Landsberg (1977) and the figure number for the T–S plane diagrams appearing in this paper. Other symbols are explained in § 2.

By the first law, the net amount of heat that goes into the engine must equal the net amount of work that comes out of it. Thus, for example, when the resultant of the vectorial sum of the lines representing heat points toward the engine, the double arrow comes out of the engine.

(v) *General.* Even though the diagrams are only qualitative, it is easy to eliminate cycles that are not thermodynamically allowed. They are represented by crossed out diagrams, and a subtitle indicates which law they violate. Sometimes these forbidden cycles can be drawn in various ways, some of which violate the first law but not the second and others which violate the second law but not the first.

When arrows go all the way between the reservoir and the dotted line, we mean that any one line can be longer than the other—the relative length is not fixed by any law of thermodynamics.

2.2. Comments

The pump–engine isomorphism of Landsberg (1977) can be easily seen from the diagrams. All pumps and engines can be put into one-to-one correspondence by transporting the heat arrows from the positive to the negative temperature axis, or vice versa, without changing their direction or magnitude. For example, if the arrows in figure 1.1(a) are transported from the positive to the negative temperature region without changing their direction or magnitude, we obtain figure 1.2(e).

For cycles linking reservoirs with Kelvin temperatures of opposite sign, the following points should be noted.

(i) The cycles in figures 1.3(a) and (e) can be realised in principle for a nuclear spin system by using adiabatic, non-quasistatic processes linking states of equal entropy but with Kelvin temperatures of opposite sign (Ramsey 1956, Schöpf 1962, Powles 1963, Purcell and Pound 1951, Abragam 1958, Bloembergen 1973) (and with $|T_c| = |T_h|$).

(ii) We could generalise diagrams (*a*) and (*e*) of figure 1.3 to reservoirs that do *not* necessarily have temperatures of equal magnitude even if of opposite sign. Such cycles could be realised by coupling the cycles of figures 1.3(*a*) and (*e*) to quasistatic Carnot cycles at positive or negative Kelvin temperatures.

(iii) The cycles of diagrams (*b*) and (*f*) of figure 1.3 are described by Dunning-Davies (1976). These cannot use the field-reversal trick (Ramsey 1956, Purcell and Pound 1951, Abragam 1958) of adiabatically linking states of equal entropy and oppositely signed Kelvin temperatures since the entropy of the *working substance* decreases during both isothermal parts of the cycle while it must add up to zero (as far as the working substance is concerned) over the whole cycle. Such cycles are thermodynamically allowed (they satisfy by construction the first and second laws of thermodynamics), but it is not known if they can be realised physically.

For each of the allowed cycles of figure 1, more conventional *T–S* plane diagrams are drawn in figures 2.1–2.9. (Note the $1/T$ temperature axis in these figures.)

We have not given special attention to trivial limiting cases such as, for example, $W = 0$. Such a cycle can be classified as a pump, an engine, or both. Limiting cases that overlap two categories can usually be found in either. This holds true for the rest of this paper.

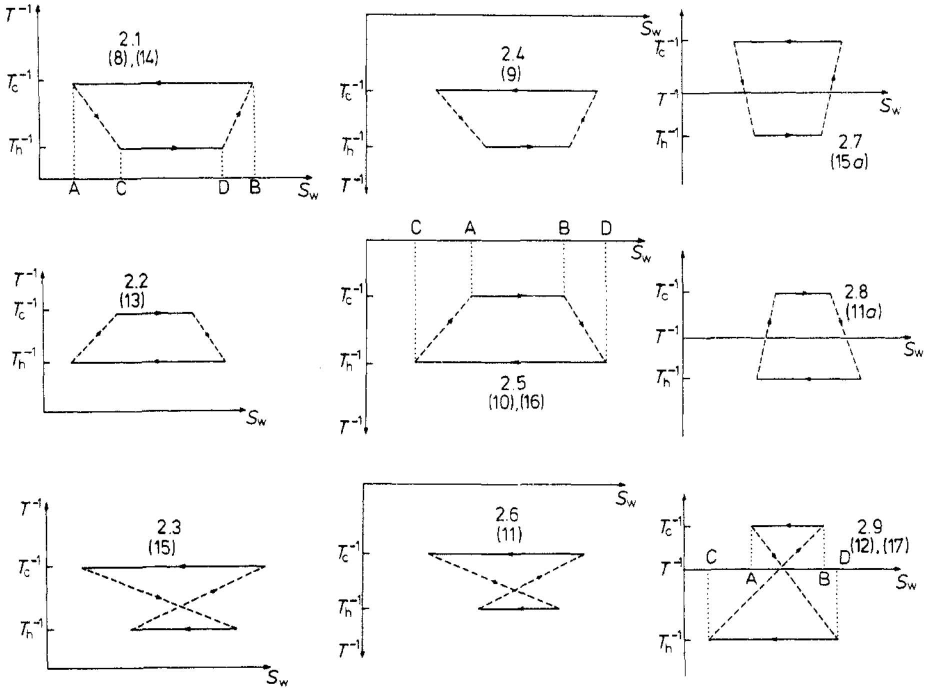

Figure 2. Carnot cycles in the $(T^{-1}–S)$ plane of the working *substance* (note subscript on S). Broken lines stand for parts of the cycle that are not necessarily quasistatic and thus may not be representable on a $(T^{-1}–S)$ diagram. The numbers in parenthesis refer to table 1 of Landsberg (1977). When two numbers appear in parenthesis for the same figure, the number to the left refers to the case where $|Q_c| < |Q_h|$ and the one to the right to the case $|Q_c| > |Q_h|$ corresponding to an increase of the segment AB relative to the segment CD.

3. Transported entropy, entropy production, and Carnot cycles

In eight of the twelve permitted cycles of figure 1, ΔS_h and ΔS_c are of opposite sign and we can regard them as implying an entropy transport between the reservoirs. The magnitude of the entropy actually transported from one reservoir to the other—when ΔS_h and ΔS_c are of opposite sign—is the lesser of $|\Delta S_c|$, $|\Delta S_h|$. In a quasistatic Carnot cycle between reservoirs with Kelvin temperatures of like sign—both positive or both negative—the entropy changes in the reservoirs are equal and opposite ($\Delta S_c + \Delta S_h = 0$, $|\Delta S \text{ (transported)}| = |\Delta S_h| = |\Delta S_c|$), and the work per cycle is directly related to the amount of entropy transported: $|W| = |\Delta S \text{ (transported)}|(T_h - T_c)$. We shall use the name *drop* cycle if $\Delta S_h < 0$ (figure 1.1(a) and (f), 1.2(a), 1.3(e)) and *lift* cycle if $\Delta S_c < 0$ (figures 1.1(e), 1.2(b) and (e), 1.3(a)). To the pump–engine analogy noted already (Landsberg 1977), one can therefore add a drop–lift analogy as shown in table 1. In the remaining four cycles of figure 1, the entropy of *both* reservoirs is increased and we may call them *roll* cycles (figures 1.1(g), 1.2(c) and 1.3(b) and (f)). In these cycles, entropy is 'rolled out' but not transported.

Table 1. Analogous pairs of cycles are placed in the same column. P stands for pump ($W > 0$), E for engine ($W < 0$). When no temperature inequality appears, the case $T_h < 0 < T_c$ is involved. For each cycle, both the figure number and the number corresponding to table 1 of Landsberg (1977) are indicated. Note that cycles appearing in the same column can be obtained from one another by transporting the heat arrows in figure 1 from the positive to the negative temperature axis, or vice versa, without changing their direction or magnitude.

Drop $\Delta S_h < 0$	Figure 1.1(a) (8) E; $T > 0$	Figure 1.2(a) (9) E; $T < 0$	Figure 1.1(f) (14) P; $T > 0$	Figure 1.3(a) (15a) P
Lift $\Delta S_c < 0$	Figure 1.2(e) (16) P; $T < 0$	Figure 1.1(e) (13) P; $T > 0$	Figure 1.2(b) (10) E; $T < 0$	Figure 1.3(c) (11a) E
Roll	Figure 1.2(c) (11) E; $T < 0$	Figure 1.3(b) (12) E		
Roll	Figure 1.1(g) (15) P; $T > 0$	Figure 1.3(f) (17) P		

Another pairing of cycles is possible. Given the signs of the Q's and the T's, it can be, in certain cases, just a question of the magnitudes of the heat exchanged with the reservoirs as to whether we have an engine or a pump. To discuss this, note that equations (1.1)–(1.3) imply

$$W = w_d + T_c\sigma = w_l + T_h\sigma \tag{3.1}$$

where

$$w_d = \Delta S_h(T_h - T_c) \qquad w_l = \Delta S_c(T_c - T_h). \tag{3.2}$$

The following definitions are also useful:

$$s_d = -w_d/T_c \qquad s_l = -w_l/T_h. \tag{3.3}$$

Now, consider the pair of drop cycles ($\Delta S_h < 0$), (figures 1.1(*a*) and (*f*)). The former is an engine and thus, as we can see from equations (3.1)–(3.3), satisfies $\sigma \leqslant s_l$ or, equivalently, $\sigma \leqslant s_d$. When $\sigma \geqslant s_l$ or, equivalently, $\sigma \geqslant s_d$, we obtain a pump as in figure 1.1(*f*).

Consider now the pair of lift cycles ($\Delta S_c < 0$) (figures 1.2(*b*) and (*e*)) in a similar way. The former is a pump and thus equations (3.1)–(3.3) reveal that $\sigma \leqslant s_l$ or $\sigma \leqslant s_d$. When $\sigma \geqslant s_l$ or $\sigma \geqslant s_d$, we obtain an engine as in figure 1.2(*e*).

Finally, the roll cycle figure 1.3(*b*) is an engine and thus satisfies $\sigma \geqslant s_l$ or $\sigma \leqslant s_d$ while the cycle figure 1.3(*f*) is a pump and thus satisfies $\sigma \leqslant s_l$ or $\sigma \geqslant s_d$.

Lastly, note that for cycles with $\sigma > 0$ the net effect of the cycle can be matched by other, suggestive processes. For example, the cycle of figure 1.1(*a*) with $\sigma > 0$ is equivalent to an entropy-conserving cycle of this type followed by a direct work-to-heat transformation into reservoir c. Similarly, the cycle of figure 1.2(*b*) is equivalent to heat conduction from h to c followed by direct heat-to-work transformation from h. Again, the cycle of figure 1.3(*e*) with $\sigma > 0$ is equivalent to an entropy-conserving cycle followed by a heat-to-work transformation from h, etc.

A number of studies have shown (Landsberg 1959, 1961, Tremblay 1976, Tykodi 1976) that the quasistatic versions of figures 1.3(*a*) and (*e*) are forbidden, but their non-quasistatic execution has not been disproved.

Table 2 summarises the properties of allowed cycles. Instead of the usual efficiency and coefficient of performance which can be found in Landsberg (1977), we define for drop cycles the *drop ratio*

$$R_d = -W/|Q_h| \tag{3.4}$$

and for lift cycles the *lift ratio*

$$R_l = W/|Q_c|. \tag{3.5}$$

Note that for figure 1.1(*a*), R_d reduces to the usual efficiency while for figure 1.2(*b*) R_l reduces to the inverse of the coefficient of performance. We note the identities which have been used to simplify the calculations for table 2:

$$R_d = (1 - T_c/T_h)Q_h/|Q_h| - T_c\sigma/|Q_h| \tag{3.6}$$

$$R_l = (T_h/T_c - 1)Q_c/|Q_c| + T_h\sigma/|Q_c|. \tag{3.7}$$

4. Second-law statements

The work of Ramsey (1956) showed that the usual Kelvin–Planck statement of the second law of thermodynamics had to be modified to allow for the existence of negative Kelvin temperatures. Ramsey's formulation of the second law is: 'It is impossible to construct an engine that will operate in a closed cycle and produce no effect other than (i) the extraction of heat from a positive-temperature reservoir with the *performance* of an equivalent amount of work, or (ii) the rejection of heat into a negative-temperature reservoir with the corresponding *work* being *done on* the engine.'

Table 2. Properties of each of the twelve allowed cycles. The definitions of the various symbols can be found in equations (1.1)–(1.3) and (3.1)–(3.7). We have also included some inequalities for the efficiency $\eta \equiv -W/(\text{all positive } Q)$ and the coefficient of performance $\text{CP} \equiv (\text{all negative } Q)/W$ defined by Landsberg (1977). Each cycle is identified by its figure number and by the number corresponding to table 1 of Landsberg (1977). See the last paragraph of § 2 for an additional remark.

	$T_h > T_c > 0$		$T_c < T_h < 0$		$T_h < 0 < T_c$	
Drop cycles $\Delta S_h < 0$	Figure 1.1(*a*) (8) $Q_h > 0 > Q_c$ $0 \leqslant \sigma \leqslant s_d$ $w_d \leqslant W \leqslant 0$ $0 \leqslant R_d \leqslant (T_h - T_c)/T_h < 1$ $\eta = R_d$	Figure 1.1(*f*) (14) $Q_h \geqslant 0 > Q_c$ $\sigma \geqslant s_d$ $W \geqslant 0$ $R_d \leqslant 0$ $1 \leqslant \text{CP} < \infty$	Figure 1.2(*a*) (9) $Q_c > 0 \geqslant Q_h$ $\sigma \geqslant 0$ $W \leqslant w_d \leqslant 0$ $R_d \geqslant (T_c - T_h)/T_h > 0$ $\eta = 1 + Q_h/Q_c < 1$		Figure 1.3(*e*) (15*a*) $Q_h \leqslant 0,\ Q_c \leqslant 0$ $\sigma \geqslant 0$ $0 \leqslant w_d \leqslant W$ $R_d \leqslant (T_c - T_h)/T_h < 0$ $\text{CP} = 1$	
Lift cycles $\Delta S_c < 0$	Figure 1.1(*e*) (13) $Q_c \geqslant 0 > Q_h$ $\sigma \geqslant 0$ $W \geqslant w_l \geqslant 0$ $R_l \geqslant (T_h - T_c)/T_c$ $\text{CP} \geqslant 1$		Figure 1.2(*e*) (16) $Q_h > 0 > Q_c$ $0 \leqslant \sigma \leqslant s_l$ $0 \leqslant W \leqslant w_l$ $0 \leqslant R_l \leqslant (T_c - T_h)/T_c < 1$ $\text{CP} = R_l^{-1}$	Figure 1.2(*b*) (10) $Q_h > 0 \geqslant Q_c$ $\sigma \geqslant s_l$ $W \leqslant 0$ $R_l \leqslant 0$ $0 < \eta \leqslant 1$	Figure 1.3(*a*) (11*a*) $Q_c \geqslant 0,\ Q_h > 0$ $\sigma \geqslant 0$ $W \leqslant w_l \leqslant 0$ $R_l \leqslant (T_h - T_c)/T_c < 0$ $\eta = 1$	
Roll cycles $\Delta S_h > 0$ $\Delta S_c > 0$	Figure 1.1(*g*) (15) $Q_h \leqslant 0,\ Q_c \leqslant 0$ $\sigma \geqslant 0$ $W \geqslant 0$ $\text{CP} = 1$		Figure 1.2(*c*) (11) $Q_h \geqslant 0,\ Q_c \geqslant 0$ $\sigma \geqslant 0$ $W \leqslant 0$ $\eta = 1$		Figure 1.3(*b*) (12) $Q_h > 0 \geqslant Q_c$ $\sigma \geqslant s_l$ $W \leqslant 0$ $0 < \eta \leqslant 1$	Figure 1.3(*f*) (17) $Q_h \geqslant 0 > Q_c$ $\sigma \geqslant s_d$ $W \geqslant 0$ $1 \leqslant \text{CP} < \infty$

Landsberg (1977) has suggested another formulation of the second law:

(i) Heat can be completely converted into work by a heat engine which takes a medium through a cyclic process if, and only if, the heat is withdrawn from a negative-temperature reservoir.

(ii) Work can be completely converted into heat by a heat pump which takes a medium through a cyclic process if, and only if, the rejection of heat takes place into a positive-temperature reservoir.

We can prove that these two formulations are logically equivalent.

If part (i) of Ramsey's formulation is wrong, then it is possible to construct an engine working in a closed cycle producing no effect other than the extraction of heat from a positive-temperature reservoir with the performance of an equivalent amount of work. This in turn implies that *part (i) of Landsberg's formulation is wrong.*

If part (i) of Landsberg's formulation is wrong, then there are two possibilities, (*a*) or (*b*):

(*a*) Heat can be converted into work by a heat engine taking a medium through a cyclic process if, and only if, the heat is withdrawn from a *positive*-temperature reservoir. This in turn implies that *part (i) of Ramsey's formulation* is wrong.

(*b*) Heat *cannot* be completely converted into work by a heat engine which takes a medium through a cyclic process if, and only if, the heat is withdrawn from a negative-temperature reservoir. This in turn implies that *part (i) of Ramsey's statement is wrong.*

The same procedure could be used for part (ii) of both statements. These results prove that the formulations of the second law by Ramsey (1956) and Landsberg (1977) are logically equivalent.

5. Properties of temperatures $T = \pm 0, \pm\infty$

We now justify the exclusion from the preceding considerations of reservoirs at any one of the temperatures $T_0 = +0, +\infty, -\infty, -0$. Recall that a thermodynamic phase of a system consists of a set of points β (representing equilibrium states) which are adiabatically linked with each other. The frontier of a set β may contain sets of points $\zeta(+0)$, $\zeta(+\infty)$, $\zeta(-\infty)$, $\zeta(-0)$ corresponding respectively to the temperatures $T_0 = +0$, $+\infty, -\infty, -0$. We ask which of a set of points (T_0) may be considered as belonging to β, and show that in each of the four cases the set $\beta \cap \zeta(T_0)$ is so poorly populated that no continuous curve can be drawn in it.

Proof. If such a curve could be drawn, a heat reservoir at a temperature $T_2 = T_0$ could be made into one of the reservoirs in an entropy-conserving Carnot cycle, where it would provide an isothermal process at T_0. This leads to the difficulty that the entropy conservation condition $Q_1/T_1 + Q_2/T_2 = 0$ cannot then be satisfied for $0 < |Q_1|, |Q_2|$; $|T_1| < \infty$. This can be seen by choosing the 'singular' reservoirs as follows:

$$
\begin{aligned}
T_1 &= T_h > 0 & T_2 &= +0\\
T_1 &= T_c > 0 & T_2 &= +\infty\\
T_1 &= T_h < 0 & T_2 &= -\infty\\
T_1 &= T_c < 0 & T_2 &= -0.
\end{aligned}
$$

Thus, if any equilibrium states at the singular temperatures T_0 belong to a set β at all, they can be only isolated states, lying on the boundary of β. The set γ consists of the internal points of a set β and our conclusion is in common with that of Landsberg (1959), Tremblay (1976) and Dunning–Davis (1976), i.e.

$$\gamma \cap \zeta(T_0) = 0 \qquad (T_0 = \pm 0, \pm\infty). \tag{5.1}$$

We have used only the *second law* in this argument (extending the reasoning of Landsberg (1961, p 98)). The singular nature of the four temperatures T_0 has, of course, been noted before (see e.g. the references cited including Tykodi 1975, 1978).

A more clear-cut sweep of this matter is required, and this shows the need for a *third law* of thermodynamics as regulating the status of boundary points in a thermodynamic phase space (Landsberg 1959). The unattainability of the temperatures $T_0 = \pm 0$ implies

$$\beta \cap \zeta(+0) = \beta \cap \zeta(-0) = 0, \tag{5.2}$$

which is stronger than (5.1) for $T_0 = \pm 0$. The adiabatic fast passage through $T_0 = \pm\infty$ shows that points representing states at *these* temperatures must be considered as part of the set β, though, as boundary points, they are not in γ. Thermal mixing experiments involving these temperatures have been performed by destroying the magnetisation of one of the spin systems by saturation (Purcell and Pound 1951, Abragam 1958, Bloembergen 1973). Hence systems exist such that

$$\beta \cap \zeta(\pm\infty) > 0, \tag{5.3}$$

i.e. irreversible processes exist that can reach $T = \pm\infty$ (Schöpf 1962, Powles 1963, Dunning–Davis 1976, Purcell and Pound 1951, Abragam 1958, Bloembergen 1973). This part of the third law is summarised as (a), below.

In an extension of Landsberg (1961, p 112), we now propose our form for the remaining part of the third law with a view to deducing results from it below: *Given a system A and a singular temperature T_0, the entropy is finite and differentiable near T_0 and converges to a unique value at T_0.*

Utilise first the finiteness and differentiability† part of this part of the third law. It implies with $\beta = 1/kT$ that $T(\partial S/\partial T)_V \to 0$ near $T = \pm 0$ and $-\beta(\partial S/\partial \beta)_V \to 0$ near $\beta = \pm 0$. Thus at all four points

$$C_V = T(\partial S/\partial T)_V = -\beta(\partial S/\partial \beta)_V \to 0 \qquad \text{as } T \to (\pm 0, \pm\infty). \tag{5.4}$$

This makes plausible, as we have already shown from the *second* law, that reservoirs at the temperatures T_0 cannot be expected: the smallest exchange of heat with such a reservoir must have a large effect on its temperature. If one also invokes statistical mechanics, following Tremblay (1976), one can go one step further. Since $T = \pm\infty$ implies equiprobability of all accessible states the entropy at these states must be maximal. Hence not only does (5.4) hold at these temperatures, but

$$\text{the } (S, \beta) \text{ curve has a maximum at } T = \pm\infty. \tag{5.5}$$

Next use the uniqueness of our third-law statement. This states that, given the system A and one of the singular temperatures T_0, the entropy $S(A, T_0)$ is unique, i.e. it cannot depend on other parameters x such as magnetic field, volume, etc. Thus all the

† Differentiability implies continuity, and not conversely (see, for example, Rudin 1964). Finiteness has to be stipulated separately since, for example, $S \sim T^{1/3}$ is allowed while $S \sim T^{-1/2}$ is forbidden near $T = 0$.

curves $S(A, x, T)$ converge to a single point $S(A, T_0)$. The conventional Nernst heat theorem deals with this convergence only at $T = +0$.

In summary, the two groups of singular temperatures $T = \pm 0$ and $T = \pm\infty$ *differ* in the following ways.

(*a*) States represented by points $\zeta(\pm 0)$ are not part of the appropriate set β, whereas states represented by points $\zeta(\pm\infty)$ are part of such sets (cf relations (5.2) and (5.3)). This remark should be regarded as the first part of the third law.

(*b*) States $\zeta(\pm 0)$ represent strictly least values, states $\zeta(\pm\infty)$ represent strictly maximal values of the entropy.

On the other hand they have the *common* third-law features.

(*c*) States represented by points $\zeta(T_0)$ are not in a set γ (cf relation (5.1)).

(*d*) $C_V \to 0$ as $T \to T_0$.

6. Summary

We produced a graphical catalogue (figure 1) of possible Carnot cycles involving both positive and negative Kelvin temperatures that matched the cases listed in Landsberg (1977). We then analysed each of the possible Carnot cycles in terms of transported entropy and entropy production, pointing out the analogies between lift cycles in one temperature domain and drop cycles in the other domain. We proved that two different-sounding generalisations of the Kelvin–Planck statement of the second law of thermodynamics are logically equivalent. Using a generalised third law, we also exhibited similarities and differences between the singular temperatures $T = +0$, $\pm\infty$, -0.

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