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Heat engines and heat pumps at positive and negative absolute temperatures

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Abstract. Inequalities for efficiencies of heat engines and for the coefficients of performance of heat pumps are obtained for positive and negative absolute temperatures. There are strong analogies between heat engines at negative (positive) temperatures and heat pumps at positive (negative) temperatures. Minor improvements are shown to be desirable in the Kelvin–Planck formulation of the second law as amended for negative temperatures. The Clausius formulation is also discussed and the term *perpetuum mobile of a third kind* is proposed for a class of *realisable* physical situations.

1. Introduction

Although negative temperatures† are reasonably well understood (e.g. Ramsey 1956, Powles 1963), a systematic analysis of all possibilities is not available. This is supplied here in response to recent discussions by Tykodi (1975, 1976), Danielian (1976), Dunning-Davies (1976), Tremblay (1976) and White (1976). (That adiabatic surfaces connecting regions of opposite temperature sign do not exist (Tremblay 1976) has been known for some time (Landsberg 1959).)

It is shown on the basis of the principle of the increase of entropy (§ 2) by this systematic analysis that heat engines at positive (negative) temperatures have analogies with heat pumps at negative (positive) temperatures, and that this carries through to operations between temperatures of opposite sign (§ 3). Amendments to some second law formulations are suggested as a result of this study (§ 4). Various other minor corrections of earlier statements are implied in the present work; for example, negative efficiencies (Ramsey 1956, p 22) are here impossible because engines and pumps are clearly distinguished.

2. General theory

Two constant temperature reservoirs h and c, at temperatures T_h and T_c *deliver* quantities of heat Q_h, Q_c to a working medium during the isothermal parts of each cycle. These are separated by adiabatic changes of any kind. Negative Q implies that

† Temperatures will be understood to be absolute temperatures throughout.

Table 1. Main examples for § 2. $\eta=0$ is ruled out in (8), (10) and (12) since $W+l>0$ implies $(|Q_c|+l)/Q_h<1$. $\mathrm{CP}=\infty$ is ruled out in (14), (16) and (17) since similarly $(Q_h-l)/|Q_c|<1$. Entropy flow is h→c in (8), (9) and (14); it is c→h in (10), (13) and (16); it is indeterminate in other cases.

Assumptions \ Consequences	Relation (1)	Relation (2)	Relations (4), (5)	Heat engines: $W+l>0$	Heat pumps: $W+l<0$
$T_c, T_h>0$	$T_h\geqslant T_c$	$Q_h\leqslant\frac{T_h}{T_c}(-Q_c)$	$W+l\leqslant\left(1-\frac{T_c}{T_h}\right)Q_h$ $-(W+l)\geqslant\left(\frac{T_h}{T_c}-1\right)Q_c$	$Q_h\leqslant 0, 0\leqslant Q_c$ are ruled out by (4), (5) $Q_c<0<Q_h$ $0<\eta=\frac{W}{Q_h}=1-\frac{\lvert Q_c\rvert+l}{Q_h}\leqslant\frac{W}{W+l}\left(1-\frac{T_c}{T_h}\right)<1$ (8)	$Q_h<0\leqslant Q_c$ $1\leqslant\mathrm{CP}=\left\lvert\frac{Q_h}{W}\right\rvert=\left(1-\frac{Q_c-l}{\lvert Q_h\rvert}\right)^{-1}\leqslant\left\lvert\frac{W+l}{W}\right\rvert\frac{1}{1-(T_c/T_h)}$ (13) $Q_c<0\leqslant Q_h$ $1\leqslant\mathrm{CP}=\left\lvert\frac{Q_c}{W}\right\rvert=\left(1-\frac{Q_h-l}{\lvert Q_c\rvert}\right)^{-1}<\infty$ (14) $Q_c, Q_h\leqslant 0$; $Q_c+Q_h<0$ $0<\mathrm{CP}=\frac{\lvert Q_c+Q_h\rvert}{\lvert Q_c+Q_h\rvert+l}\leqslant 1$ (15)
$T_c, T_h<0$	$\lvert T_h\rvert\leqslant\lvert T_c\rvert$	$Q_h\geqslant\frac{T_h}{T_c}(-Q_c)$	$W+l\geqslant\left(\frac{T_c}{T_h}-1\right)(-Q_h)$ $W+l\geqslant\left(1-\frac{T_h}{T_c}\right)Q_c$	$Q_h\leqslant 0<Q_c$ $0<1-\frac{T_h}{T_c}-\frac{l}{Q_c}\leqslant 1-\frac{\lvert Q_h\rvert+l}{Q_c}=\frac{W}{Q_c}=\eta\leqslant 1-\frac{\lvert Q_h\rvert}{Q_c}$ (9) $Q_c\leqslant 0<Q_h$ $0<\eta=\frac{W}{Q_h}=1-\frac{\lvert Q_c\rvert+l}{Q_h}\leqslant 1-\frac{\lvert Q_c\rvert}{Q_h}\leqslant 1$ (10) $0\leqslant Q_c, Q_h$; $0<Q_c+Q_h$ $0<\eta=\frac{W}{Q_c+Q_h}=\frac{Q_c+Q_h-l}{Q_c+Q_h}\leqslant 1$ (11)	$Q_h\leqslant 0, Q_c\geqslant 0$ are ruled out by (4), (5) $Q_c<0<Q_h$ $1<\left\lvert\frac{W+l}{W}\right\rvert\frac{1}{1-(T_h/T_c)}\leqslant\left(1-\frac{Q_h-l}{\lvert Q_c\rvert}\right)^{-1}=\frac{Q_c}{W}=\mathrm{CP}\leqslant\left(1+\frac{Q_h}{\lvert Q_c\rvert}\right)^{-1}<\infty$ (16)

Table 1—continued

Consequences / Assumptions	Relation (1)	Relation (2)	Relations (4), (5)	Heat engines: $W+I>0$		Heat pumps: $W+I<0$	
$T_h<0<T_c$	Holds always	$Q_h \geqslant \frac{\lvert T_h\rvert}{T_c} Q_c$	$W+I \leqslant \left(1+\frac{T_c}{\lvert T_h\rvert}\right) Q_h$	$Q_h \leqslant 0$ is ruled out by (4)		$0 \leqslant Q_c$ is ruled out by (5)	
			$W+I \geqslant \left(\frac{\lvert T_h\rvert}{T_c}+1\right) Q_c$	$Q_c \leqslant 0 < Q_h$		$Q_c < 0 \leqslant Q_h$	
				$0<\eta=\frac{W}{Q_h}=1-\frac{\lvert Q_c\rvert+I}{Q_h} \leqslant 1-\frac{\lvert Q_c\rvert}{Q_h} \leqslant 1$	(12)	$1 \leqslant \left\lvert\frac{Q_c}{W}\right\rvert = \mathrm{CP} = \left(1-\frac{Q_h-I}{\lvert Q_c\rvert}\right)^{-1} < \infty$	(17)
				$0 \leqslant Q_c, Q_h$: (11) holds	(11*a*)	$Q_c, Q_h \leqslant 0$: (15) holds	(15*a*)

heat is given *to* a reservoir. The convention is made that h is 'hotter' than c in the sense $-1/T_h \geqslant -1/T_c$ so that

$$1/T_c - 1/T_h \geqslant 0. \tag{1}$$

As the medium recovers its initial state at the end of a cycle, the entropy increase per cycle (for the total system is isolated) arises from changes in the reservoirs and leads to

$$Q_h/T_h \leqslant -Q_c/T_c. \tag{2}$$

A heat leak between the reservoirs occurs if the heat lost by one reservoir is gained by the other: $Q_h + Q_c = 0$. Relation (2) then implies

$$(1/T_c - 1/T_h)Q_h \geqslant 0.$$

Using (1), it follows that $Q_h \geqslant 0$ and hence $Q_c \leqslant 0$. Thus spontaneous heat flow is from h to c for *all* signs of the temperature.

If l is the heat lost per cycle by such dissipative processes as heat leakage between the reservoirs, the work done by the medium per cycle is

$$W = Q_h + Q_c - l, \qquad (l \geqslant 0). \tag{3}$$

It will be assumed that l does not exceed numerically any of the other three terms in equation (3). In fact, to avoid algebraic complications, it will be assumed to be always small enough so that its presence does not change inequalities that would hold if $l = 0$. Using (2), one finds

$$(W + l)/T_c \leqslant (1/T_c - 1/T_h)Q_h \tag{4}$$

$$-(W + l)T_h \geqslant (1/T_c - 1/T_h)Q_c. \tag{5}$$

A heat *engine* is here defined by the condition $W + l > 0$. It has an efficiency

$$\eta \equiv W/(\text{all positive } Q) \qquad (W + l > 0). \tag{6}$$

If work has to be *supplied* to the medium to pump heat, one has a heat *pump*, which is defined here by $W + l < 0$. It has a coefficient of performance.

$$\text{CP} \equiv (\text{all negative } Q)/|W| \qquad (W + l < 0). \tag{7}$$

Both η and CP are decreased by a heat leak. But whereas $\eta \leqslant 1$, CP can exceed unity, as is demonstrated in any case below.

Heat pumps include refrigerators (r). The narrower definitions for $W + l < 0$

$$\phi_r \equiv \frac{Q_c}{|W|} \qquad (Q_c > 0), \tag{7a}$$

$$\text{CP}_{\text{hp}} \equiv \frac{|Q_h|}{|W|} \qquad (Q_h < 0) \tag{7b}$$

can of course be made, and lead for $Q_h < 0 < Q_c$ and $l = 0$ to

$$\text{CP}_{\text{hp}} - \phi_r = 1. \tag{7c}$$

Of the heat pump situations in table 1 none satisfy these narrower definitions except for (13), which satisfies both. We therefore do not pursue the distinctions (7*a*, *b*, *c*) here.

Note that the cycles need not be quasistatic. They are largely arbitrary, except that the working fluid must recover its initial state at the end of a cycle (Landsberg 1961).

3. Examples

The above theory is specialised in table 1. Some comments follow.

3.1. Heat engines at negative temperatures

In (9) entropy is lost by h, just as in the conventional positive temperature case, but heat flows *into* h. In (10) and (11), however, entropy is gained by h, and second law inequalities are not involved in these results. In all three cases the situation $\eta = 1$ can be approached in an *ideal cycle* (quasistatic and $l = 0$), since there is nothing against a choice of $Q_h = 0$ in (9) or $Q_c = 0$ in (10) and (11). In each case therefore the Kelvin–Planck statement of the second law (that heat cannot be subtracted from a reservoir and be completely converted into work without leaving changes elsewhere) must fail. This is known, for the case (9), but it applies also to the cases (10) and (11), as well as to (12) (see § 3.4 below).

There is no need to remove h physically in case (9). It is sufficient to allow the heat rejected into h, $|Q_h| \leq (T_h/T_c)Q_c$, to leak back into c after each cycle. The effect is that heat $Q_c - |Q_h|$ is withdrawn from c and fully converted into work, while h acts merely as a kind of catalyst. A numerical example is $T_h = -20$ K, $T_c = -40$ K, $Q_c = 70$ J, $Q_h = -30$ J, $W = 40$ J, with an entropy increase per cycle of $\frac{7}{4} - \frac{3}{2} = \frac{1}{4}$ J K^{-1}.

These findings seem to agree with White (1976), but not with the comments of Ramsey (1956, p 22) that $\eta < 0$, and Tykodi (1975) that the situation is 'canonical'.

3.2. Heat pumps at positive temperatures

The three cases arising under this heading have close analogies, not noted before, with the corresponding cases for heat *engines* at *negative* temperatures. All the work supplied can be converted into heat (CP = 1), as is expected from the possibility of using the work for irreversibly stirring a fluid. The second reservoir is not needed on thermodynamic grounds since $Q_c = 0$ in (13) and $Q_h = 0$ in (14) are possible. In fact after each cycle in the case (13) the heat withdrawn from c, $Q_c \leq (T_c/T_h)|Q_h|$, could be allowed to leak back to c. This would restore c to its original state and give it the status of a catalyst. A numerical example if $T_c = 20$ K, $T_h = 40$ K, $Q_c = 30$ J, $Q_h = -70$ J, $W = -40$ J, with an entropy increase per cycle of $\frac{7}{4} - \frac{3}{2} = \frac{1}{4}$ J K^{-1}.

3.3. Heat pumps at negative temperatures

There is in this (single) case again an analogy with heat *engines*, this time with the normal Carnot cycle.

3.4. Heat engines between temperatures of opposite sign

A thermodynamic phase space contains an open set of points γ within which entropy and absolute temperature can be defined, since each point has a neighbourhood which lies wholly within γ. The axis given by $1/T = 0$ does not lie within such a set (Landsberg 1959, 1961, Tremblay 1976), so that a cycle linking temperatures of opposite sign cannot be represented by a curve in phase space. It contains non-static adiabatic parts. Two possibilities of this type arise and are given in the table.

The condition for an *engine* is in case (12)

$$W = Q_h + Q_c - l = Q_h - |Q_c| - l > 0,$$

so that $(|Q_c| + l)/Q_h < 1$. This yields

$$\eta = 1 - \frac{|Q_c| + l}{Q_h} \leqslant 1. \tag{18}$$

If therefore η exceeds unity, then $|Q_c| + l > Q_h$ and $W < 0$. Thus the engine has turned into a pump according to the present definition; and for a pump one uses the CP rather than η.

The argument leading to (18) does not appeal to the second law. The second law constraint (4) states in the case (12)

$$\frac{W+l}{Q_h} \leqslant 1 + \frac{T_c}{|T_h|}.$$

It leads to (Dunning-Davies 1976)

$$\eta = \frac{W}{Q_h} \leqslant \frac{1 + T_c/|T_h|}{1 + l/W}. \tag{19}$$

This suggests that, for $l = 0$, η can exceed unity, but this occurs, as clear from (18), only if the engine turns into a pump. It may be thought that at least in the special case $l/W > T_c/|T_h|$, (19) may be useful since it then seems to be a stronger inequality than (18). However, this possibility will here be ignored since for convenience l is always regarded as small enough not to disturb inequalities which hold for $l = 0$. The second law provides therefore no constraints: the process is always compatible with it.

3.5. *Heat pumps between temperatures of opposite sign*

As in § 3.4, two cases are possible. The second law constraint for the lowest CP is now misleadingly low:

$$\text{CP} = \left|\frac{Q_c}{W}\right| \geqslant \left|\frac{W+l}{W}\right| \frac{1}{1 + |T_h|/T_c} = \frac{1 + l/|W|}{1 + |T_h|/T_c} \tag{20}$$

by (5). This suggests that for large enough $|T_h|/T_c$ the CP can lie arbitrarily close to zero. However, the condition for a *pump* is

$$|Q_c| > Q_h - l.$$

It follows that

$$\text{CP} = \frac{|Q_c|}{|Q_c| - (Q_h - l)} \geqslant 1 \tag{21}$$

so that the CP must be in excess of unity for small enough l. The thermodynamic inequality (20) is in this sense weaker than the condition for a *pump*.

3.6. *Infinite temperatures*

As the second reservoir can be dispensed with for engines utilising at least one negative-temperature reservoir, no new features are brought into play if reservoirs are effectively made unnecessary by allowing $T_h \to \infty$ or $T_c \to -\infty$. (We differ in this observation from some of the authors cited.) This is rather fortunate as the state $1/T = 0$ is on the boundary of sets γ (see § 3.4), and an entropy can be defined for it thermodynamically only by some limiting device (Landsberg 1961, § 16, Dunning-Davies 1972). The moot point whether or not processes using a reservoir having $1/T = 0$ are possible, and, if they are, whether or not they can be reversible is therefore eliminated from the present thermodynamic discussion. This seems reasonable since our conclusions should not depend on using one state rather than a closely neighbouring one.

4. Second law formulations

4.1. Engines

Given heat is absorbed from h in (8) ($Q_h > 0$), entropy is decreased and heat must be rejected ($Q_c < 0$) to increase the entropy. Hence $\eta < 1$, as required by the Kelvin–Planck statement. In (9) to (12), given that heat is withdrawn from a negative temperature reservoir its entropy is increased. The second law does not then require the other reservoir, so that heat can be completely converted into work in an ideal cycle ($l = 0$). One now needs to hypothesise $l > 0$ to stop such a complete conversion. This constraint *does* operate in the case of the non-static cycles needed in (12) and (11a), but it *does not* operate in (9) to (11) if the fiction of an isolated spin system is maintained. One is thus led to facing more squarely than heretofore the full conversion of heat into work, and to arrive at the following modified Kelvin–Planck statement (for engines):

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

It is in accordance with the ideas of the pioneers of thermodynamics to call an engine which converts heat from a negative-temperature reservoir completely into work a *perpetuum mobile of the third kind* (if it is of the second kind it uses a positive-temperature reservoir). Its usefulness is unfortunately limited by the fact that large and permanent negative-temperature reservoirs are not known. The above statement asserts the existence of the third kind and the non-existence of the second kind, of *perpetuum mobile*.

4.2. Heat pumps

Given that heat is rejected into a reservoir ($Q < 0$), its entropy is increased if its temperature is positive. The second law does not then require a second reservoir, and the whole of the work supplied can in principle be converted into this heat as noted in detail in connection with (13) in § 3. But it also applies to (14), (15), (17) and (15a).

If the rejection is into a negative-heat reservoir, its entropy is decreased and a second reservoir is needed, as seen in (16), which corresponds to the original Carnot case (8). Both cases were in fact picked up in Ramsey's modification of the Kelvin-Planck formulation: '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'. In fact (i) rules out $Q_c \geqslant 0$ in (8), and (ii) rules out $Q_h \leqslant 0$ in (16). This statement does not cover all cases. One has also to rule out under (i) the rejection of heat into a negative temperature reservoir ($Q_h \leqslant 0$) in (12), and under (ii) the extraction of heat from a positive temperature reservoir ($Q_c \geqslant 0$) in (17). This requires a reconstruction of Ramsey's statement, in such a way as to rule out the physical situations mentioned above, while at the same time *not* ruling out the cases $\eta = 1$ in (9), (10), (11), (11*a*), (12) and the cases CP = 1 in (13), (14), (15), (15*a*) and (17). Any such statement is bound to be rather complicated, and it seems preferable to replace it by the above rule of § 4.1. This applies to heat engines. The matching rule for pumps is:

> 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 to a positive-temperature reservoir.

4.3. Clausius statement

The Clausius statement of the second law may be formulated in various ways. (i) It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a cooler to a hotter body; or (ii) if heat is transferred from a body to one warmer than itself, then some interchange of heat and work occurs; or (iii) if heat is transferred from a body to one warmer than itself, then some mechanical work has to be used to heat a reservoir. Statement (i) is compatible with spontaneous heat flow from h to c, as 'other effects' are then needed to reverse this heat flow. Statement (ii) is compatible with this and also with (9) and (13). Statement (iii) holds for positive-temperature reservoirs only (cf (13)). For negative-temperature reservoirs the transfer from a cold to a hot reservoir is accompanied by the conversion of *heat into work* (cf (9)), and (iii) fails. Whether (i), (ii) or a corrected form of (iii) is used for the Clausius statement is of course a matter of taste.

Note added in proof. Dr C Gruber, Lausanne, has kindly drawn my attention to the following book: Stueckelberg E C G and Scheurer P B 1974 *Thermocinétique Phénoménologique Galiléenne* (Basel: Birkhäuser). On page 67ff a careful division between pumps and engines for positive and negative temperatures is also made.

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